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I

ENVIRONMENTAL PROTECTION AND MONITORING

Characteristics of the Coagulate Obtained During the Process of Model Wastewater Treatment

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Abstract. **In the process of wastewater treatment by coagulation a large amount of sediment is being produced, which is the main drawback of this method. Therefore, the development of utilization or recirculation technology of the waste obtained, the research of the obtained by-products should be conducted. Within the scope of this work, the sediment, that is being formed during the coagulation of the model wastewater containing the wood originated pollutants, was studied. Using the aluminium-containing composition coagulant on a base of polyaluminium chloride, coagulates characterized by the low sludge volume index within 30 minutes (89 ml g^{-1}), and the optimal time of sedimentation is 20-30 minutes. The coagulate particles have an average size of 45.8 µm. The derived coagulate is composed primarily of carbon (27.9%), oxygen (49.4%) and aluminum (10.9%). Carbon, oxygen and hydrogen belong to an organic part of coagulate - the wood pollutants, which, in turn, has a high content of hemicellulose. It is concluded that the existing hemicellulose in the obtained coagulate is characterized by O-acetyl-4-O-methyl-D-glucuron-β-D-xylan with β-(1-4)-glucomannose.**

Keywords **– coagulation, model wastewater, coagulate, hemicellulose, lignin-containing substances.**

I INTRODUCTION

Latvia is one of the major plywood manufacturers in Eastern Europe. The hydrothermal wood treatment is one of the stages of plywood production, resulting in water pollution by components such as hemicellulose, lignin and wood extractive substances (HLES). The wastewater can cause considerable damage to the receiving waters if discharged untreated.

Several physico-chemical colour removal methods such as rapid sand filtration, membrane processes and adsorption have also been developed [1, 2]. However, the most acceptable technology of wastewater treatment within the framework of enterprise, applied presently, is based on the processes of coagulation. Chemical coagulation is a frequently applied process in primary purification of industrial wastewater. Coagulation is mainly induced by inorganic metal salts, such as aluminium sulphates and chlorides [3]. Research and practical applications have shown that coagulation will lower the pollution load and could generate an adequate water recovery [4, 5].

However, it should be noted that the most important drawback of the coagulation method is the large amount of the produced sludge that needs to be eliminated or used as a raw material for other technologies. The sludge produced during the physical-chemical treatment has arisen due to the amount of organic matter and total solids in suspension that have been removed, and the compounds, formed from the coagulant applied. Sewage sludge can be used as a fuel with a high calorific value [6], as a component of soil recovery [7], for the production of building [8] and sorbent materials [9, 10].

Based on the above, the goal of the present study was to describe HLES coagulate, which occurs due to the process of model wastewater coagulation by using new Al-composition coagulants.

II MATERIALS AND METHODS

The birch wood sawdust was used for the wood hydrothermal treatment. A hydrolysis was fulfilled in an alkaline water environment, at the water duty of 1/50, the temperature 90 °C and the duration was about 4 hours. The model wastewater was described by HLES content, COD, BOD_5 and its color [11, 12].

In order to find the wood pollutants coagulation pattern and to develop optimal conditions of wastewater treatment technologies, studies of the process of coagulation of model wastewater were completed using the aluminium-containing coagulants. The model wastewater coagulation process was performed using composite coagulant on PAC basis (COMPAC) [13] with dosage 100 mg L^{-1} at pH 6.0 and a room temperature.

The coagulation tests involved the rapid addition of the coagulant to the model wastewater followed by stirring at 100 rpm. After addition of coagulants, the model wastewater was stirred for a period of 1 min at 200 rpm and then it was followed by a further slow mixing of 2 min at 40 rpm. The formed flocs were allowed to settle for 120 min. In the process of sedimentation the volume with sludge occupying the 100 ml cylinder, was recorded every 30 minutes. The data received contributed in defining the sludge volume index (SVI). The sludge volume index is the volume in milliliters occupied by 1 g of a suspension after 30 min of settling. To determine the size of the coagulate particles the Laser Particle Sizer ANALYSETTE 22 NanoTec (Fritsch GmbH, Germany) with measuring range of 10 nm - 1 mm and Leica MZ 16 A stereomicroscope (Leica Microsystems (Switzerland) Ltd.) were used. The results are represented as a percent of complete sample volume, that is filled with particles with defined diameter and as a percent of mass content of defined particles fraction.

After 120 minutes of sedimentation, the system was filtered through a glass filter with a pore size of less than 16 µm. The filtered sludge was drained of for 24 hours at 103°C. The dried coagulates (HLES-Al) were quantatively and qualitatively characterized by scanning electron microscope (SEM) with energy dispersive X-ray analysis (EDX) (Mira/LMU Schottky, Inca Energy 350 Oxford Instruments), Fourier Transform Infrared (FT-IR) and Carbon Nuclear Magnetic Resonance (^{13}C-NMR) spectroscopy. For HLES-Al characterization FT-IR spectra was obtained on a FT-IR spectrophotometer (Perkin-Elmer Spectrum One) with KBr discs containing samples. ^{13}C-NMR spectra of HLES-Al was recorded on a Bruker 300MHz spectrometer from 150 mg of sample dissolved in 4% NaOD (1.0 mL). The NMR spectrum was acquired by applying a 90° pulse width, a 0.238 s acquisition time, a 2.0 s pulse delay, and $^{1}J_{C–H}$ of 145 Hz. In particular, 24 576 scans were used for the acquisition of ^{13}C-NMR spectra of coagulate.

III RESULTS AND DISCUSSION

In the coagulation process, the settling speed of the flocs formed is important since it would influence the overall cost and efficiency.

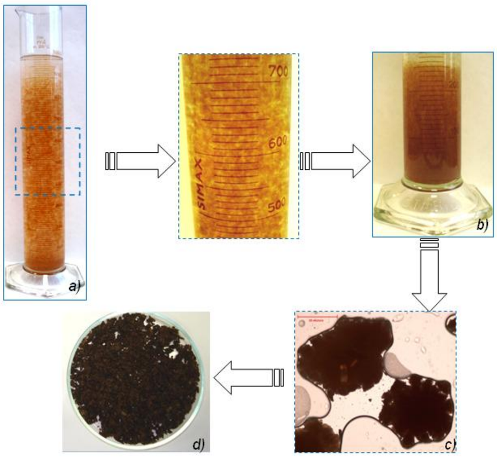

Fig. 1. HLES-Al coagulates formation process: a – beginning of sedimentation, b– coagulates developed, c – coagulates particles (Leica MZ 16 A stereomicroscope), d - dry coagulate

In order to evaluate this parameter, the settling time was recorded for the flocs formed in order to reach half of the solution's level. COMPAC exhibited excellent settling characteristics with majority of the flocs settled out in the initial 20-30 min of settling. The sludge volume index is 89 ml g^{-1}. A value less than 140 ml g^{-1} is considered a good settling sludge. Coagulate HLES-Al is characterized by high moisture - 98.2%.

The research of coagulates granulometric composition (Fig. 2) followed by the fact that the coagulate particles' sizes are ranging from 2 to 246 µm. Analyzing the data obtained, it can be concluded that 53% of the particles' size is between 40 and 100 µm, 22% of the particles - 16-40 µm and 25% of the particles have a size of 100 µm. By contrast, smaller particles (<16 µm) is 1%. The average particle size is equal to 45.8 mm.

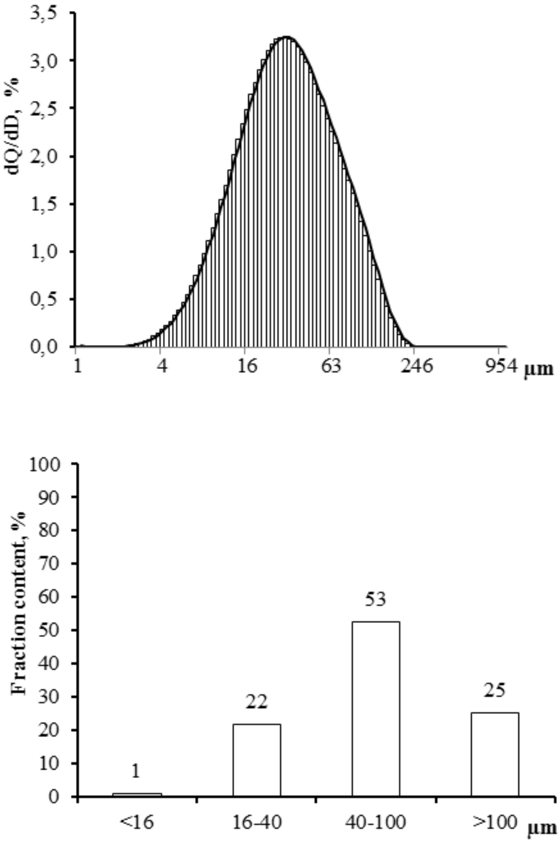

Fig. 2. Coagulate's granulometric composition

Coagulates elemental composition is shown in Table 2. The derived coagulate is composed primarily of carbon (27.9%), oxygen (49.4%). The aluminum, the metallic element that arised from the agent used for coagulation and sedimentation of the sludge, dominated among the inorganic elements of sludge.

TABLE I

COAGULATE ELEMENTAL COMPOSITION

C, %	O, %	H, %	N, %	Al, %	Na, %	Cl, %
27.9	49.4	4.3	0.3	10.9	4.1	3.1

Carbon, oxygen and hydrogen are referred to organic components of coagulate, namely, to the pollutants of wood origin the deposition of which is of aluminum-containing coagulant. The deposited pollutants of wood origin are characterized by a high content of hemicellulose (75-80%).

The structural characteristics of coagulates were studied by means of FT-IR and ^{13}C-NMR methods.

The FT-IR of coagulate are illustrated in Fig. 3.

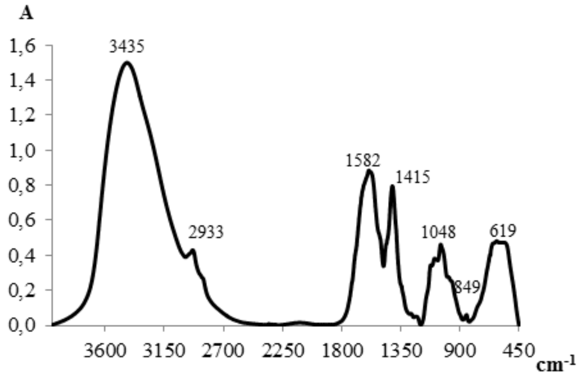

Fig. 3. FT-IR spectra of HLES-Al coagulate

A strong broad band at 3435 cm^{-1} was due to the stretching of hydroxyl groups, and the behaviour of these spectra in the 2934 cm^{-1} region shows the C–H stretch in methyl and methylene groups. Intensive peak at 1567 cm^{-1} characterise COO- skeletal vibrations in glucuronic acid. The wave number characteristic for typical xylan is 1046 cm^{-1} [14]. The adsorption at 1414 cm^{-1} are originated from aromatic skeletal vibrations in associated lignin [15].The absorbance at 849 cm^{-1} was attributed to β -glycosidic linkages between the sugars units. According to the coagulum FT-IR spectra the aluminum interaction with HLES occurs with HLES - Al coordination sites formation. Coordination takes place through HLES-OH and -COOH groups evidenced by the absorption band 619 cm^{-1} in the region characteristic of Al-O-link [16].

The ^{13}C-NMR spectra of coagulate are illustrated in Fig. 4.

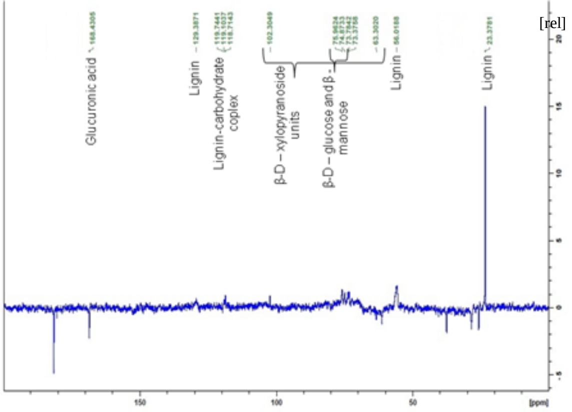

Fig. 4. ^{13}C-NMR spectra of HLES-Al coagulate

The signal at 23.3 ppm is most likely due to -CH$_3$ from acetyl groups in hemicelluloses and lignin [17]. The shift at 56.02 ppm is attributed to the presence of methoxyl groups of the aromatic rings of guaiacyl and syringyl units in lignin and methoxyl group of a 4-O-methyl-D-glucuronic acid residue in the xylan [18]. The peaks at 102.3, 75.9, 73.7, 73.3 and 63.3 ppm, which are attributed to C-1, C-4, C-3, C-2 and C-5 of β-D-xylopyranoside, respectively, confirmed the (1-4)-β-D-xylopyranoside linkage. The signals at 74.9 corresponds to C-3 of α-L-arabinofuranosyl residues linked to β-D-xylans [17]. However the signals at 74.9-75.9 ppm may be assigned to C-3 in β-glucose and C-5 in β-mannose [19]. The peaks at 118.7-119.7 ppm can be attributed to the presence of an ester bond between the carboxyl group of D-glucuronic acid and phenylpropan side chains of lignin. The signal at 129.4 ppm may be assigned to carbon atoms in the p-hydroxyphenyl units [15]. The chemical shifts at 168.4 ppm represents the C-6 of glucuronic acid residues [19]. The presence of quantities of associated lignin was identified by one weak signal at 182.0 ppm, which originates from the carbonyl group in associated lignin [20].

This finding demonstrated that involved in the Al-coagulate are composed, mainly, of O-acetil-4-O-metil-D-glucuron-β-D-xylan with the presence of small amounts of β-(1-4) linked glucomannose.

The derived HLES Al-coagulate may be considered as material, causing scientific and practical interest. Taking into account that the given coagulate is a waste of many tons, the question of its disposal or recycling is very topical.

IV CONCLUSION

Using the aluminium-containing composition coagulant based on polyaluminium chloride, coagulate is characterized by a low sludge volume index (89 ml g^{-1}). The optimal time of sedimentation is 20-30 minutes. The coagulate particles have an average size of 45.8 µm. The deposited pollutants of wood origin are characterized by a high content of hemicellulose (75-80%). It is concluded that the hemicelluloses in the HLES-Al coagulate are characterized by O-acetyl-4-O-methyl-D-glucuron-β-D-xylan and with β-(1-4)-glucomannose. The derived coagulate is composed primarily of carbon (27.9%), oxygen (49.4%) and aluminum (10.9%). Taking into account non-toxicity of hemicelluloses and the low aluminum content, the coagulate obtained is not seen as an intended one for disposal waste, but as a by-product, that can be used successfully in various industries.

V ACKNOWLEDGEMENT

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Comparing Two Models of Large-Scale White Sea Hydrodynamics and Thermal Dynamics

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***Abstract*. To calculate the water temperature of the White Sea we used two models of large-scale hydro- and thermal dynamics, maintained by the authors. Comparing two models, we show that the first one describes summer hydrophysical conditions better, while the second model is better for winter conditions. Now we are trying to improve and combine two models in order to describe the state of the Sea more accurately.**

***Keywords* – large-scale sea models, the White Sea.**

I INTRODUCTION

The White sea has some unique properties: tidal flows dominate; the sea is shallow and thus bathymetry is important; high density of available potential density and potential density; significant stratification. This makes the sea an interesting oceanological object [1]. Mathematical and computer modeling allows getting maximal amount of information from data, reduce costs, estimate quantities that are difficult or impossible to measure, make a forecast, estimate influence of different factor, and perform numerical experiment (which is possible when natural experiment is hardly possible).

Intensive development of computers in the recent decades significantly enforced the power of mathematical modeling. Beside ocean modeling and simulation [2], complex models of the White sea were developed. The book [1] reviews the White sea research, including numerical modeling and simulation. Nonlinear interaction of dynamical processes is very important in this sea; this implies need for complex hydrodynamical models of high resolution and demand efficient algorithms and high-performance computers. Dominating tidal flows facilitate modeling, making initial data less important.

II THE MODELS

In this paper we describe and compare two models of thermal and hydrodynamics of the White sea. The first model was developed by I.A. Neelov (see [1] and references therein), the second is the model of the Arctic ocean created by N.G. Iakovlev [3] in the Institute of Numerical Mathematics (Moscow) adapted to the White sea by the authors. Both models are based on primitive equations in spherical coordinates with free surface and the Boussinesq approximation. Vertical grid is inhomogenous and consists of 22 and 16 levels. Spatial steps of the models are 3' and 4' of latitude and 6' and 14' of longitude. Time steps are 10 min and 6 min, respectfully. Both models are climate models with seasonal components. Tide is described as oscillation of the sea level at the White sea-Barents sea liquid boundary. Atmospheric forcing (precipitation, clouds, air temperature, pressure, and humidity) are taken from the NCEP data [5] with linear interpolation both in space and time. Wind is either taken from the NCEP data or calculated via air pressure as quazi-geostrophical. Runoff of main rivers is taken into consideration: rivers are described as fresh water bays with given normal water velocity at the liquid boundary (calculated via mean yearly runoff with empirical month distribution) and monthly-mean temperature. The main difference between the models is the description of the sea ice, also some parametrizations, discretization, and details of calculation algorithms differ. Since 2012 both models are remotely available via Internet at the computer cluster of the Karelian Research Centre [6] in multiuser mode. The cluster consists of 10 nodes with two 4-core processors and a control node, the peak performance is 851 Gflops. The BOINC-based desktop grid is available. It is convenient for solving multiple poorly connected problems (e.g. estimating reaction of the sea to different model forcing).

III RESULTS AND DISCUSSION

Both models show almost the same behavior of water temperature. In. Fig. 1 there are monthly-mean water temperatures averaged over the sea surface for the two models. The second models gives higher surface temperature; though, general behavior is represented in the similar way. The lowest temperatures were in 1969 and 1978, the highest ones were in 1972 and 1989.

Fig. 2 and 3 compare distribution of surface temperature at some time (after 30 model years) for the two models.

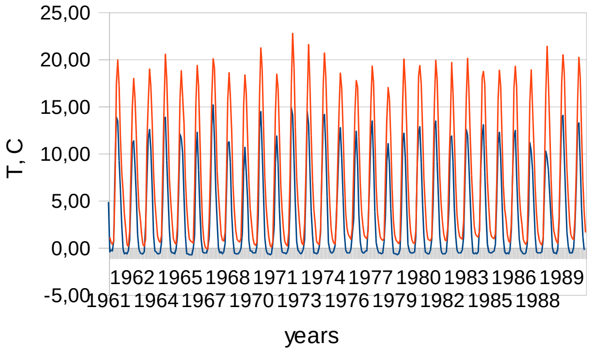

Fig. 1. Monthly-mean sea surface water temperature for the two models (higher peaks are for the first model, lower ones are for the second).

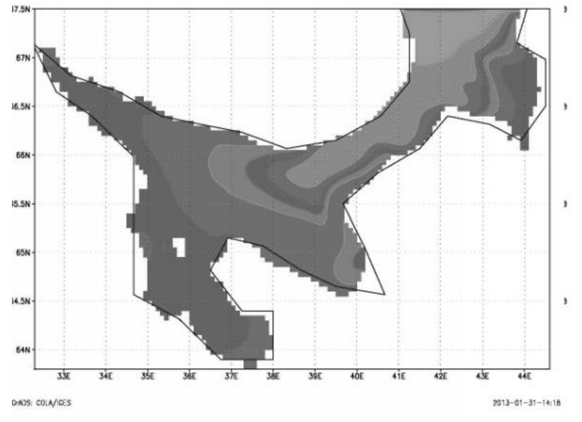

Fig. 2. Surface temperature distribution, 30 model years calculated, model 1.

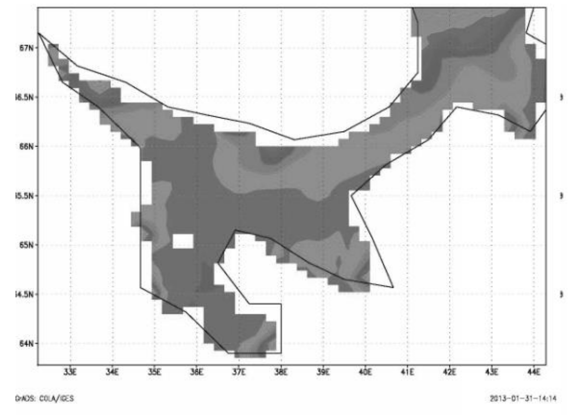

Fig. 3. Surface temperature distribution, 30 model years calculated, model 2.

Despite some difference, both models represent fronts in bays, the Kelvin wave, higher temperature of water in shallow bays. The same is true also for salinity; fig. 4 and 5 compare distribution of surface salinity for the two models. The Kelvin wave, and freshening effect of rivers are clearly represented.

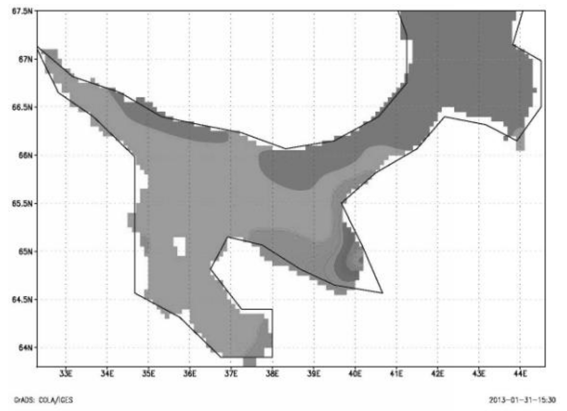

Fig. 4. Surface salinity distribution, 30 model years calculated, model 1.

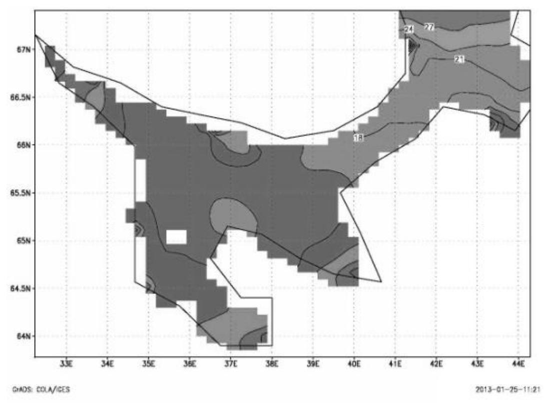

Fig. 5. Surface salinity distribution, 30 model years calculated, model 2.

The structure of vertical distribution of temperature and salinity also corresponds to observations: mixed layer near the surface, thermocline (or halocline), and almost constant temperature (or salinity) in deep places. Both models represent qualitative properties of other large-scale hydrodynamical fields: ice velocity, area, and compactness (although thicker, than real, ice appears in November and is out by July).

IV NUMERICAL EXPERIMENT

The strong side of climatic models is their ability to perform numerical experiments, including those that are hardly possible or absolutely impossible. As an example, let us consider the influence of air temperature on the sea system. In fig. 6 there are curve of time-dependent water temperature averaged over the sea surface. One can see that the influence is not drastic: the average temperature grows to 1,27^{o} during 60 years, while the increase of the maximal temperature is only 2^{o}. Minimal temperature does not change, because it is equal the melting temperature independent on the atmosphere. This conclusion is also justified by fig. 7-9 showing the surface temperature distribution similar to fig. 3 but after 30 years of real air temperature, warmer (+1^{o}) and colder (-1^{o}) atmosphere. The structure of the temperature field remains almost unchanged. Temperature change is about 1°C which is comparable to the change of the air temperature.

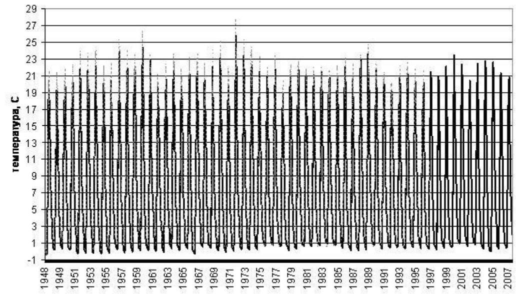

Fig. 6. Average surface water temperature for real atmospheric conditions and modified (+3oC added) air temperature.

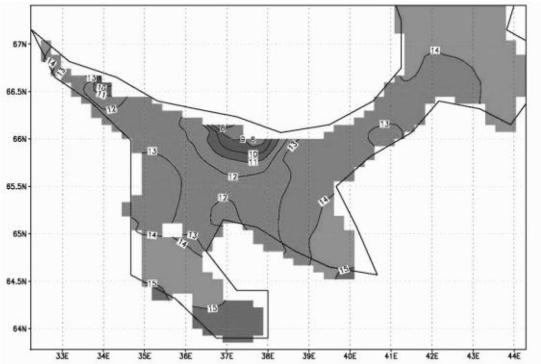

Fig. 7. Surface temperature distribution, 30 years of real atmospheric forcing (NCEP data).

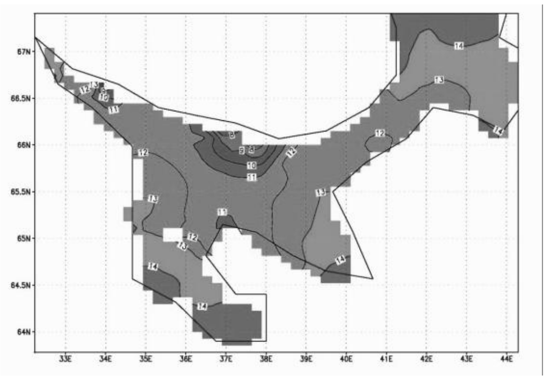

Fig. 8. Surface temperature distribution, 30 years of warmer (+1°) air.

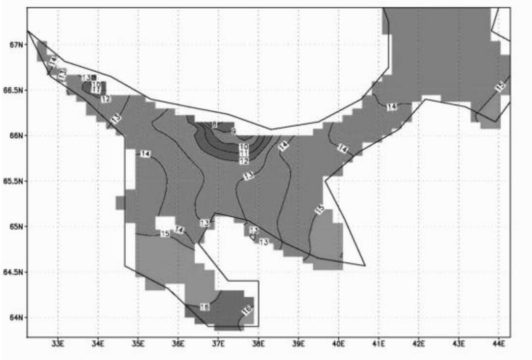

Fig. 9. Surface temperature distribution, 30 years of colder (-1°) air.

Similar influence is also at the salinity; fig. 10-12 show the surface salinity distribution for the same cases. Salinity even does not become higher or lower, just isohalines change slightly. General conclusion is that lower air temperature helps salinity to propagate from the Barents sea. Current velocity and ice distribution also react slightly on the air temperature change. Both models represent main circulations in the Basin and in bays and the Ekman spiral.

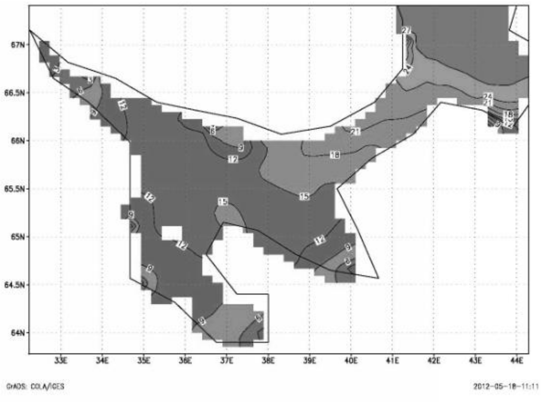

Fig. 10. Surface salinity distribution, 30 years of real atmospheric forcing (NCEP data).

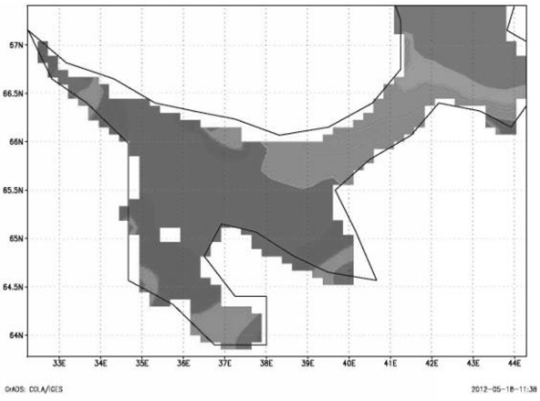

Fig. 11. Surface salinity distribution, 30 years of warmer (+1°) air.

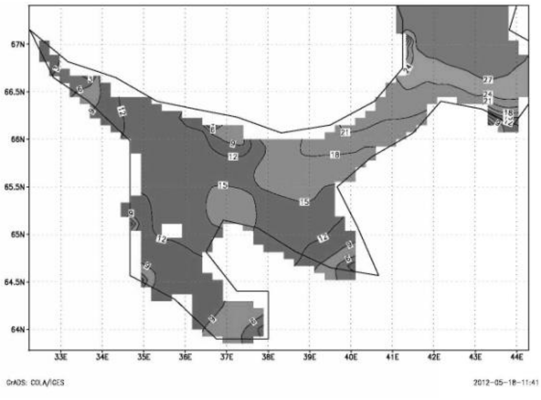

Fig. 12. Surface salinity distribution, 30 years of colder (-1°) air.

V CONCLUSION

Both models represent main qualitative properties of large-scale hydrodynamical and thermodynamical fields of the White sea. We currently are working on adjusting parameters in order to improve the quality of approximation of the measurements and the model data. The first models seems to give better results for the iceless parts of the year, while the second is better for the winter time. Beside parametrizations, there are other difficulties. Little is know about, for example, water temperature and salinity with respect to time, depth, and the point at the surface at the liquid boundary between two seas. These data serve as boundary conditions; we are planning to include part of the Barents sea into the domain in order to, firstly, use data measured there and, secondly, to reduce the influence of the boundary data on the sea. This is going to be useful also for ice dynamics, because ice gone out of the domain is lost and is does not come back in case when the current change its direction (while it must, and the situation is typical for the White sea with its strong induced tides). The general conclusion is that both models are useful tools for investigating large-scale dynamics of the White sea.

VI ACKNOWLEDGMENTS

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Ecological Quality Analysis of the Rezekne River after Zooplankton

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Abstract. **During seasonal studies 2012 (August/October), samples of zooplankton were collected and analyzed according standard method. Chemical quality of the Rezekne River's water investigated. Changes of quantitative and qualitative characteristics, saprobity index, species diversity (Shannon-Wiener index) and Renkonen index were employed for the analysis of zooplankton community structure in the Rezekne River. The Rezekne River saprobity varies from o – saprobity to β – mesosaprobity. The lowest ecological quality was determined in the leg of the Rezekne River in the territory of Rezekne city, which characterises with decrease in the total zooplankton abundance and species diversity according to Shannon - Wiener index, increase of saprobity.**

***Key words*: small river, saprobity, species biological diversity, Cladocera, Copepoda, Rotifera.**

I INTRODUCTION

The Rezekne River belongs to Daugava River basin. Daugava is a significant ecosystem for the environment of Latvia and its protection and long-term usage of resources is an important objective of Latvian environment in political system [1]. A number of authors have studied the ecological situation of the Rezekne River: Jastrežemskis, [2]; Meinerte, [3]; Benislavska, [4]; Strigajeva, [5]; Strucinska, [6]; Zute, [7] – in studies it has been concluded that river water's pollution is small or average. However, none of the studies has been carried out in the whole length of river, accordingly, there has not been an opportunity to assess the ecological situation of river in general. Previous studies were carried out either using only bioindication methods or chemical. Still it is not possible to gain information about the particular substance and its total impact on hydroecosystem only with the help of chemical methods. In addition, the number of chemical compounds, which pollutes environment, is so big that it is difficult to be controlled. [8]. For that reason findings gained as a result of biomonitoring supply much more extended and precise information about the impact of polluting substance on ecosystem.

A number of authors (e.g. Bothár [9]; Mulani *et al.* [10]; Gajbhiye & Abidi [11]) are indicating to the impact of wastewater on zooplankton. The indicative role of zooplankton in the studying of pollution processes is shown in some scientific studies. Potentiality of zooplankton as bio-indicator is very high because their growth and distribution are dependent on many abiotic (e.g., temperature, salinity, stratification, pollutants) and biotic parameters (e.g., food limitation, predation, competition) [12, 13, 14].

A great number of authors are drawing attention to possibilities of the use of zooplankton for assessing the river water quality (Bakaeva & Nikanorov, [8]; Vandish, [15]; Demenik, [16]; Kutikova, [17]; Krylov, [18], [19]; Mathivanan *et al.*, [20]; Vanjare, [21]; Mulani, [10]; Marneffe *et al.*, [22]; Whitton, [23]).

The aim of this study is to assess the ecological situation of the Rezekne River after zooplankton.

II MATERIALS AND METHODS

Sampling sites

Rezekne River basin occupies 2066 km^2 (with Malta), rising in Lake Razna, the second biggest lake in Latvia, flowing into the biggest lake in Latvia – Lake Lubans. The total length of the river is 116 km. The width of the Rezekne River on average varies from 6 – 20 m, the depth – 0.8 – 2.0 m. Annual average river run-off is 0.2 km^3, run-off is also regulated by locks of Kaunata Lake at the river's source. Speed flow in the river varies from 0.2 to 0.7 m/s. Average flow rate in the Rezekne River below Rezekne City is 5.5 m^3/s. In the upper part of river basin there is a significant mouth from lakes, but in lower part – from marshes. The Rezekne River's the biggest tributaries on the left bank are Reva (9 km), Geikinu stream (12 km), Vagaļu straem (8 km), Kovšupe (10 km), Rodupe (10km), Čečora (19 km), Malta (105 km), but on the right bank - Pārtava (10 km), Ancovas stream (5 km), Križutu ditch (12 km), Taudejāņi stream (13 km), Liužanka (26 km), Sūļupe (14 km) [6].

Sampling and analysis

During the expeditions to the following Rezekne River stretches Table 1 presents GPS coordinates of the Rezekne River sampling sites and dates from the outlet from Lake Razna to the mouth in Lake Lubans (21 sampling sites) in 30 August, 16 October, 2012, water samples and zooplankton were sampled at the banks.

TABLE I

TYPE SIZES, SPACES AND INTERVALS

No	Sampling sites	Sampling sites coordinates
1.	Rezekne River source from Lake Kaunata	56º19.57'N / 27º31.24'E
2.	Before Spruktu reservoir	56º22.35'N / 27º13.35'E
3.	After Spruktu reservoir at Stoļerova village	56º25.42'N / 27º32.16'E
4.	Before Spruževa village at cattle farm	56º29.5'N / 27º27.44'E
5.	Hydrological station in Griškani	56º30.42'N / 27º26.12'E
6.	Before Rezekne city in Griškani	56º31.3'N / 27º23.22'E
7.	Bridge Jupatovka	56º30.53'N / 27º21.40'E
8.	Bridge at the Bowling centre	56º30.49'N / 27º21.12'E
9.	Bridge at Rezekne Hospital	56º30.19'N / 27º30.37'E
10.	Pipe before castle mound – Krasta street	56º30.4'N / 27º20.12'E
11.	A small bridge at Rimi supermarket	56º30.7'N / 27º19.50'E
12.	Bridge at Concert Hall	56º30.14'N / 27º19.33'E
13.	Railway bridge on Viļānu Street	56º30.28'N / 27º19.4'E
14.	Railway bridge - Makarovka	56º31.21'N / 27º18.39'E
15.	Downstream of discharge of the Rezekne city treatment plant wastewater, Greivuļi	56º32.11'N / 27º17.15'E
16.	At Sakstagals village	56º32.55'N / 27º8.58'E
17.	At Uljanovs village	56º33.50'N / 27º3.57'E
18.	At Rikava village	56º37.55'N / 27º0.53'E
19.	Before Nagļi ponds	56º40.24'N / 27º0.21'E
20.	Malta River canal inflow into Rezekne River	56º43.41'N / 26º59.41'E
21.	Rezekne River inflow into Lubans Lake	56º46.33'N / 26º56.21'E

Samples gathering and analysis were carried out according to the standartmethods [24]. Samples of zooplankton were collected from the upper water layer till 0.5 - 1 m by filtering 100 l of river water with the 65 µm mesh-sized Apshtein plankton net. Collected samples were fixed in 4 % formalin.

Nikon Eclipse E200 light microscopes were used for the analysis of zooplankton; three subsamples (2 ml each) were examined at 100 – 400 x magnification. The aim of the qualitative study was to identify Rotifera, Cladocera, and Copepoda taxa. All taxa of zooplankton were identified using keys of Kutikova [17], Borutsky [25], Manuilova [26], Segers [27], Kotov *et al.* [28], Paidere [29].

Data processing and analysis

The calculation of zooplankton abundance 1 m^3 water was defined by formula (1):

$$N = \frac{a \times b \times 1000}{c \times d} \qquad (1)$$

where: N – number of individuals (1 m^3); a - average amount of individuals in three samples; b - capacity of sample (ml); c - capacity of examined sample (2 ml); d - capacity of filtered water (100 l).

Quantitative (abundance, biomass, number of taxa), qualitative characteristics (species composition) and species diversity (Shannon - Wiener index derivative N_1 according to the number of organisms) were employed for the analysis of zooplankton community structure in the Rezekne River.

Species diversity was calculated according to the Shannon - Wiener index, by formula (2) [30, 31]:

$$H' = \sum_{i=1}^{s} (p_i)(\log_2 p_i). \qquad (2)$$

where S – the number of species; p_i – the proportion of individuals of the i^{th} species to the total number of species.

The Shannon - Wiener index expressed in units of the number of species was used in these studies was calculated using formula (3) [32]:

$$N_1 = e^{H'}. \qquad (3)$$

where e = 2; H' – Shannon - Wiener function [30]; N_1 – number of equally common species that would produce the same diversity as H'.

Hill recommends using N_1 rather than H' because units (the number of species) are more clearly understandable to ecologists [33]. Therefore N_1 is used in the present research.

Saprobity index (S) was calculated by Sladechek’s method, using the created by P. Cimdiņš species - bioindicator catalogue for Latvia [35].

Hydrological data were obtained from the database of the company ‘Latvian Environment, Geology and Meteorology Centre’.

III RESULTS AND DISCUSSION

Conditionally, after anthropogenic load, the Rezekne River has been divided into 4 stretches:

I stretch – area not so much affected by anthropogenic activity – before and after Spruktu reservoir (from the 2nd till 3rd zooplankton sampling sites);

II stretch – territory of small villages – Sprūževa village, Griškani village (from 4th till 6th site);

III stretch – territory of Rezekne city (from 7th till 15th site);

IV stretch – behind the territory of Rezekne city - at Sakstagals village, at Rikava village, at Uljanovs village (from 16th till 20th site).

Generally, the zooplankton community of the Rezekne River was dominated by Rotifers, which due to their short generation time and their high reproductive rate dominate in rivers [36]. (Fig.1.,2.) The number of taxa changed from 1 to 12 in summer and 5 to 14 in autumn and species biological diversity according to the Shannon - Wiener index varied from 1.9 to 14.3 in summer and 2.8 to 12.6 in autumn.

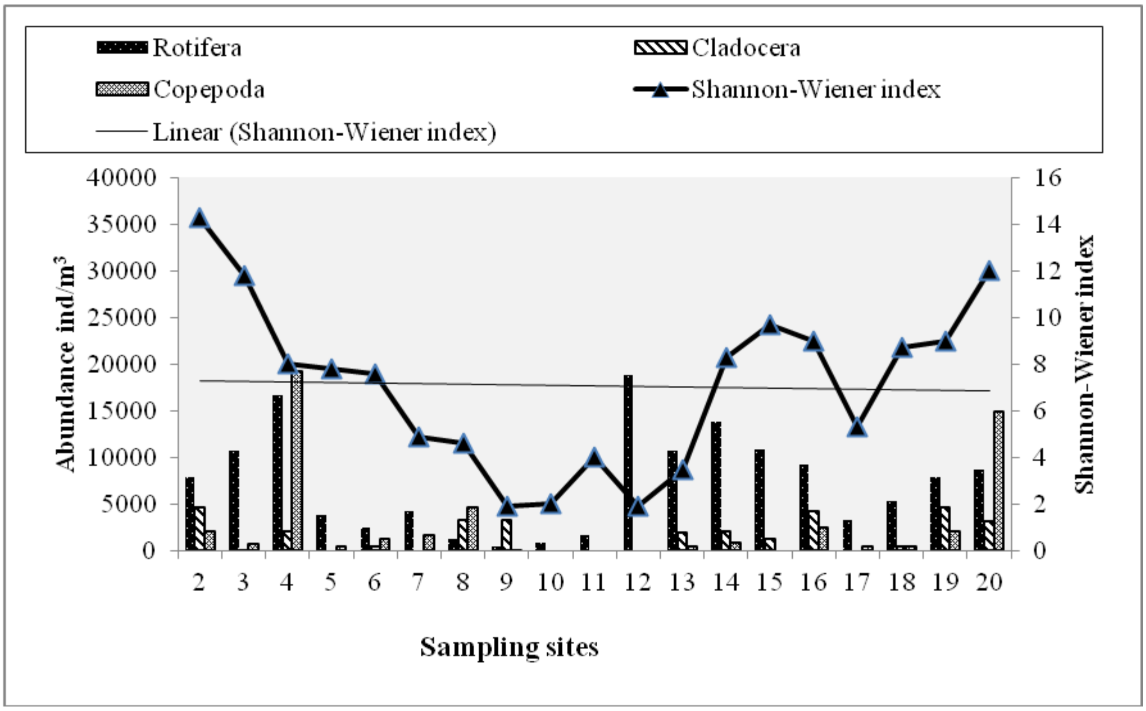

Fig. 1. Abundance of zooplankton taxonomic groups and Shannon – Wiener index in the Rezekne River during 29th and 30th August.

The biggest zooplankton species biological diversity according to the Shannon - Wiener index was determined at river source from Razna Lake and at the mouth of Lubans Lake, which is explained by the zooplankton inflow into the river from lakes, where the amount and diversity of zooplankton is bigger. Species biological diversity decreases in II river stretch, where many villages are situated alongshore. The fastest zooplankton species biological diversity and abundance decline is observed in III river stretch in the territory of Rezekne city, where the Shannon - Wiener index decreases till 1.9. Downstream of discharge of the Rezekne city treatment plant (WTP) wastewater into the Rezekne River species biological diversity of zooplankton does not decrease, which means that WTP is not the only and main source of Rezekne River pollution. Kononova points out that too big influx of biogenic substance in the river has a negative influence on zooplankton that expresses in decreasing of species diversity and increasing of Simpson index [37]. Also Kutikova points out that abundance of zooplankton and decreasing of species sensitive to pollution is an indicator for impact of untoward environmental factors [17]. During summer period, when water level is low (up to ~138,63 m.a.B.s.l.), negative impact of anthropogenic pollution on zooplankton (abundance and species biological diversity decline) is more marked than during autumn period when the water level is higher (up to ~139,07 m m.a.B.s.l.) and as a result higher level of pollution concentration dilution.

Assessing after organisms abundance and the Shannon - Wiener index the most polluted river stretch is from site Nr 5 to site Nr 11, after which the abundance of zooplankton noticeably increased mainly due to breeding of *Euchlanis dilatata* o-β, *Keratella Cochlearis* β, *Lecane Luna* β, *Chydorus sphaericus* β in large quantities. In that way in Rezekne River a β – mesosaprobity zone was formed, this is characterized by intensified growth of the abundance of zooplankton and decreased species biological diversity (Fig. 3.,4.).

The zooplankton abundance decreased mainly in Cladocera and Copepoda taxa. In river researches Rundle and Hildrew mention that in the division of zooplankton crustaceans water chemical content is one of the determinative factors [38].

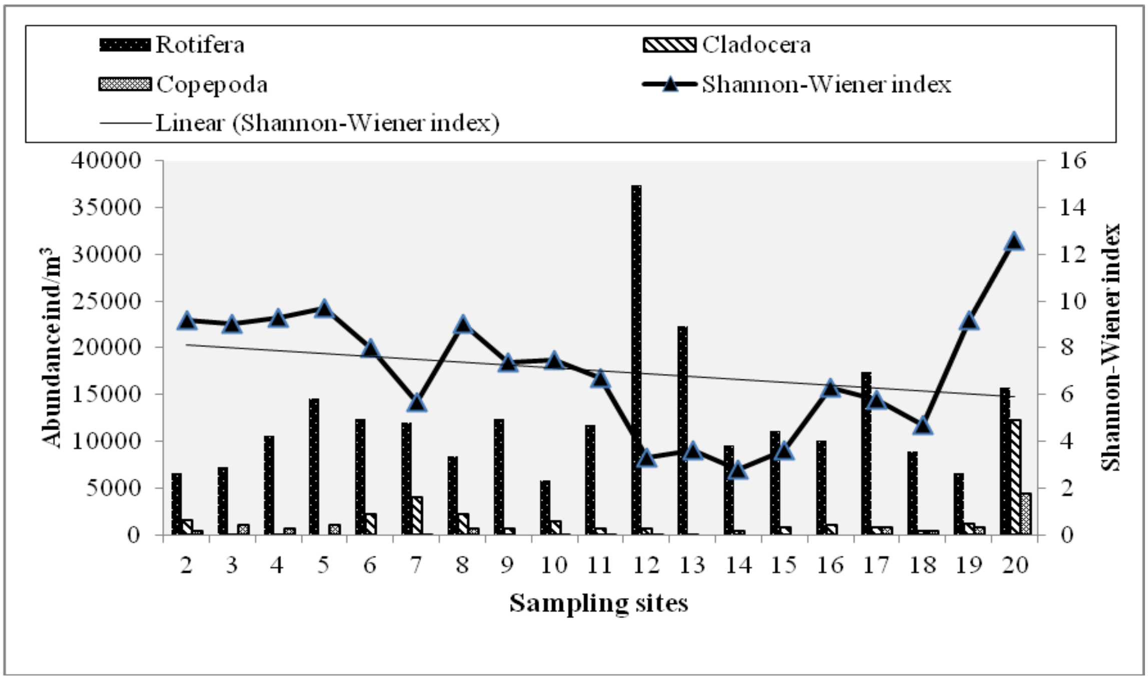

Fig. 2. Abundance of zooplankton taxonomic groups and Shannon – Wiener index in the Rezekne River during 16th October

Zooplankton abundance and numbers of taxa increased downstream from the territory of Rezekne city (Fig. 1.,2). Increase of zooplankton abundance and growth of biological diversity of species can be explained by the river self-purification processes, in this stretch of the river favourable wastewater dilution area is built up with richly developed bacteria plankton, which is very good feeding base for the development of zooplankton. A number of authors are also reporting the importance of zooplankton in effectiveness of self-purification process (Kutikova, [17]; Bakaeva and Nikonorov, [8]). In the whole length of the Rezekne River from the source till the mouth Shannon - Wiener index decreases, which points out to the negative impact of anthropogenic pollution on river zooplankton and ecosystem in general.

63% of the species found on the examined stretch of the Rezekne River were indicator species of saprobity, which is a sufficient amount to consider the river pollution level according to zooplankton. Kutikova indicates that it is difficult to consider the river saprobity if there are few indicator species of saprobity in the river [17].

In August and October 2012 saprobity changed from oligosaprobity (S=0.83), which describes clean or very slight pollution (water quality class I). In the I stretch of the Rezekne River to the β - mezosaprobity (S=1.80), which describes moderate pollution (water quality class II) behind Rezekne city WTP wastewater influx site (Figure 3.,4.), which means that also Rezekne city WTP is one of the important river pollution sources. Only in I stretch of the river dominate o-o-β oligosaprobity species, in other river stretches dominate β-α mezosaprobity species (Fig. 3.,4.).

In general saprobity increases in the whole length of the Rezekne River and β-α mezosaprobity species dominate (Fig. 3.,4.), which points out to river is not able to make self-purification and pollution flows into Lubans Lake. It has also been reported about insufficient river’s self-purification abilities in the Daugava River basin region management plan 2010 – 2015 [39].

Species biological diversity decreases and saprobity increases beginning with II river stretch, which means that this river stretch is already influenced by anthropogenic impact.

Decrease in zooplankton abundance III river stretch occurred not only on account of predominant species, but also on account of decreasing of oligosaprobes or even total extinction thereof, not a single oligosaprobity species was found (Figure 3). Only such species as *Euchlanis dilatata* o-β, *Keratella Cochlearis* β, *Lecane Luna* β, *Chydorus sphaericus* β, *Asplancha priodonta* β, *Pompholux sulcata* β, *Brachionus angularis* β–α, *Trichocerca cylindrica* α as well as Bdelloida increased in numbers. Ferdous and Muktadir [14] in their studies mention that species variation of these order deceased in polluted water. Some species were not found in some highly polluted area through these species have high tolerance level. Gulyas points out that species such as *Asplanchna priodonta, Brachionus angularis, B. calyciflorus, B. leydigi, B. quadridentatus, Euchlanis dilatata, Keratella cochlearis, K. quadrata, Polyarthra vulgaris* have all been recorded below the mouths of polluted tributaries [41]. The increasing of the pollution level causes decrease in numbers of the above predominant species, β and α-β saprobity species are developing [8].

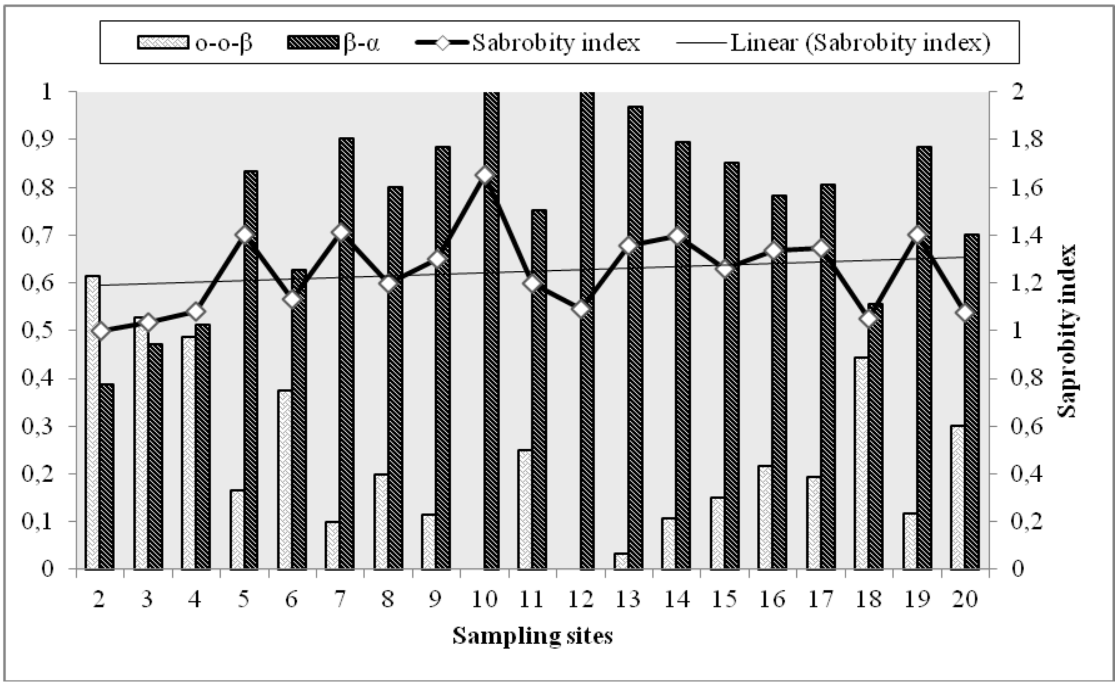

Fig. 3. Percentage distribution of the zooplankton abundance according to saprobity and saprobity index in the summers of August 2012.

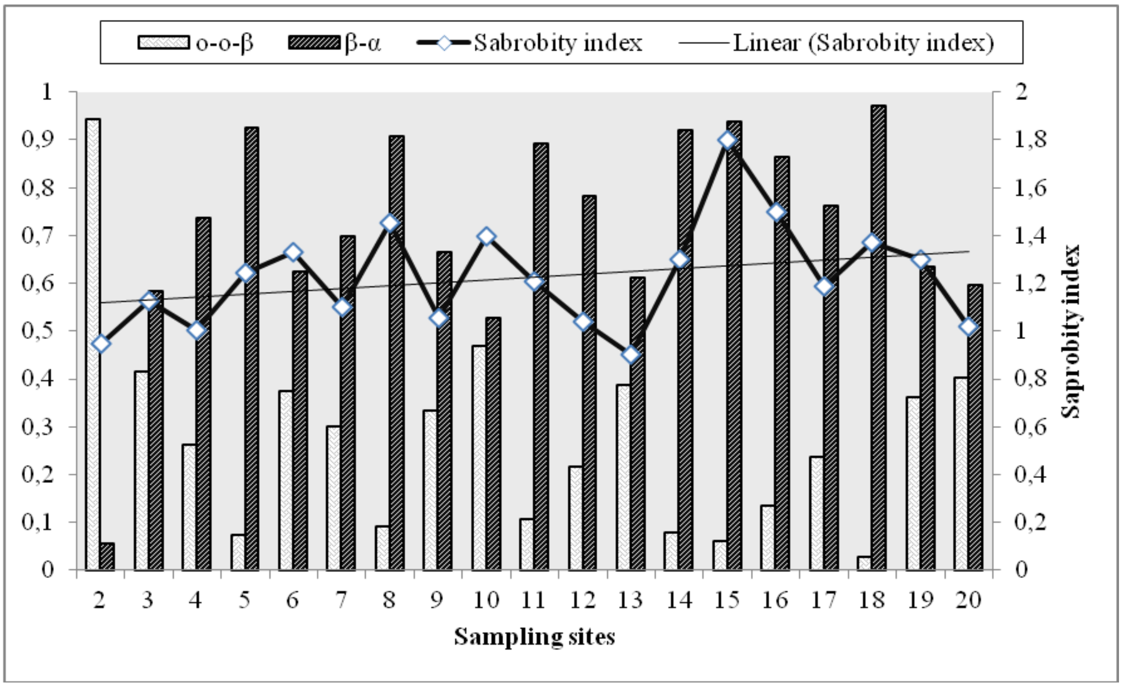

Fig. 4. Percentage distribution of the zooplankton abundance according to saprobity and saprobity index in the autumn of October 2012.

IV CONCLUSION

The Rezekne River saprobity varies from o – saprobity to β – mesosaprobity, which points out that river water is evaluated as slightly polluted to moderately polluted.

The lowest ecological quality has the river stretch in the territory of Rezekne city, which is characterised by decrease in the total zooplankton abundance and species diversity according to Shannon - Wiener index, increase of saprobity.

Rezekne city treatment plant is not the only source of the Rezekne River pollution; it is influenced by anthropogenic impact in the whole river length.

Saprobity increases from the Rezekne River source till the river mouth, in its turn biological diversity decreases, which points out to the river's inability self-purification and pollution flows into Lubans Lake.

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Effects of Temperature, Substrate Concentration and pH on the Polycyclic Aromatic Hydrocarbon Pyrene Biodegradation by *Arthrobacter* sp. NJ5 Strain

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***Abstract*. Polycyclic aromatic hydrocarbons (PAHs) are widely distributed in the environment and may persist for extended periods of time. PAHs are one of the most important classes of persistent organic contaminants. High molecular weight (HMW) PAHs (compounds containing four or more fused benzene rings) are generally recalcitrant to microbial attack. Until recently, only a few genera of bacteria have been isolated with the ability to utilize four-ring PAHs as sole carbon and energy sources. Because of the toxic, mutagenic, and carcinogenic characteristics of some, PAHs have been studied extensively by many scientists around the word. This paper presents research results, where 10 microbial strains belonging to genus *Arthrobacter* sp. and obtained from culture collection of JSC „Biocentras“ were tested for the best biodegradation of HMW PAH pyrene. Pyrene degradation experiments were conducted in liquid mineral medium. Pyrene concentration was 0.2 mg/mL at the beginning of degradation experiments. After 72 h incubation with ten *Arthrobacter* sp. strains, gas chromatography analysis revealed that highest pyrene degradation (19%) was reached by *Arthrobacter* sp. NJ5 strain. The effect of medium pH, pyrene concentration and temperature on the intensity of the degradation by the most active strain *Arthrobacter* NJ5 was investigated.**

***Keywords – Arthrobacter* sp., biodegradation, pyrene, polycyclic aromatic hydrocarbons, (PAHs).**

I INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) constitute a large and diverse class of organic compounds consisting of three or more fused aromatic rings in various structural configurations. The inertness, their low water solubility and strong lipophilic properties of these compounds lead to very high accumulation levels in the environment [1, 2]. They have been detected in air, soil, sediments, surface water, ground water and road runoff [3, 4, 5, 6]. Soil is the most important reservoir and reemission source of PAHs. Soil pollution with polycyclic aromatic hydrocarbons can have a bad influence on human health. Polycyclic aromatic hydrocarbons are resistant to degradation and can bio-accumulate through the food chain, so PAHs also may pose threat to human health over a long period [7]. These compounds enter the environment in many ways. PAHs and their derivatives are widespread products of incomplete combustion of organic materials arising, in part, from natural combustion such as forest, chemical fires and volcanic eruptions, but for the most part by human activities [8, 9, 10, 11, 12]. In recent decades the major sources of PAH pollution are industrial production, transportation, refuse burning, gasification and plastic waste incineration [13, 14, 15, 16].

Many PAHs are highly toxic, mutagenic, carcinogenic and teratogenic in nature; exposure to PAHs represents public health risks and raises environmental concerns [17, 18, 19, 20, 21, 22, 23, 24, 25, 26]. Numerous studies have indicated that one-, two- and three-ring compounds are acutely toxic, while higher molecular weight PAHs are considered to be geotoxic [4].

Because many PAHs are so toxic there is a big interest in understanding the physicochemical processes and microbial degradation reactions that affect the mobility and fate of these compounds in groundwater and soil sediment systems.

When dissolved in water or adsorbed on particulate matter, PAHs can undergo photodecomposition upon exposure to ultraviolet light from solar radiation. In the atmosphere PAHs can react with pollutants such as ozone, nitrogen oxides and sulfur dioxide, generating diones, nitro- and dinitro-PAHs and sulfonic acids, respectively. PAHs may also be degraded by some microorganisms [1, 27] (Fig.1).

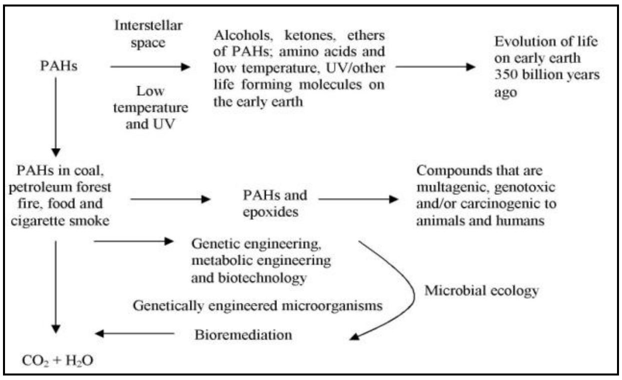

Fig. 1 Fate, toxicity and remediation of polycyclic aromatic hydrocarbons (PAHs) in environment [23]

Photodegradation is an important degradation pathway in aquatic systems for high molecular weight PAHs. Photooxidation can chemically transform PAHs and the resulting products may be more carcinogenic and toxic than the parent compounds.

Volatilization plays an important role in the removal of low molecular weight PAHs from aquatic systems.

Biodegradation using microorganisms is usually the preferred and major route of PAH removal from contaminated environment because of some inherent advantages such as its cost effectiveness, the safest and comparatively better cleanup [17].

PAHs are subject to biodegradation by various microorganisms such as bacteria, fungi, and certain algae that live in soils, in sediment substrate, or are suspended in the water column [4, 28].

Site contamination with complex mixtures of organic compounds such as creosote, petroleum, or their combinations results in the selection of a mixed population of microorganisms with improved abilities to tolerate and extract energy from the contaminants [20, 28]. Among bacteria *Xanthobacter, Serratia, Acitenobacter, Bacillus* [24], *Alcaligenes, Arthrobacter, Burkbolderia, Cychoclasticus, Pseudomonas* [29, 30], *Ralstonia, Nocardia, Rhodococcus, Sphinggomonas* [31], *Terrabacter, Mycobacterium* [32] and among fungi *Penicillium, Phanerochaete, Bjerkandera* [12] and *Trametes* are the frequently identified microorganisms involved in PAH bioremediation [28, 33, 34].

II MATERIALS AND METHODS

Polycyclic aromatic hydrocarbon

Pyrene($C_{16}H_{10}$) was obtained from Germany Merck-Schuchardt Co. with a purity >96%. Pyrene has 4 benzene rings; molecular weight is 202.26; the octanol–water partition coefficient ($\log K_{ow}$) is 4.88 [35].

Microorganisms

The following strains of hydrocarbon degrading bacteria belonging to genus *Arthrobacter* and obtained from culture collection of JSC „Biocentras“ were used: sp N3, NJ1, NJ5, NJ9, NJ6, Pr82, Mž811, Kl1, M1 and M2.

Media

Nutrient agar (Oxoid, Basingstone, UK) was used for plating microbial strains, and nutrient broth (Oxoid, Basingstone, UK) was used for the subculture and preculture of the strains. To investigate the ability of the strains to degrade pyrene, a mineral medium was used. The mineral medium had the following composition (g/L): 0.01 $(NH_4)_2HPO_4$; 0.2 NH_4Cl; 0.25 K_2HPO_4; 0.25 KH_2PO_4; 0.02 $MnSO_4$; 0.01 $(NH_4)_2Fe(SO_4)_2 * 6H_2O$; 0.01 $CaCl_2$ and 0.05 $(CH_3COO)_2Zn$.

Biodegradation of pyrene

The ability of the strains to degrade pyrene was investigated under sterile conditions in 250 mL flasks with 50 mL of mineral medium. Pyrene was used at a concentration of 0.2 mg/mL. Pyrene was entered into the nutrient medium as a 10 mg/mL pyrene/hexane solution. Hexane has been evaporated while intensive mixing and heating in the temperature of 75 °C temperature. Pyrene suspension in nutrient medium prepared with such method was used for experiments. Experimental flasks with 10% (v/v) of inoculum added and blank flasks were incubated in a rotary shaker at 30 °C and 200 rpm. The effect of medium pH, pyrene concentration and temperature on the intensity of the degradation by the most active strain was investigated under the same cultivation conditions.

Pyrene degradation dependency on medium pH was investigated at pH values of: 4; 5; 6; 7; 8 and 9.

Pyrene degradation dependency on temperature was evaluated at 5; 20; 25; 30; 35; 40 ^{o}C; and dependency on concentration was investigated with 0.1; 0.2; 0.3; 0.4; 0.6; 0.8 mg/mL of pyrene.

After 72 h incubation, pyrene was extracted with 20 mL of hexane from experimental and blank flasks.

GC analysis of pyrene

Samples were quantified with a GC system (GC-2010 Plus, Shimadzu, Japan) equipped with a flame-ionization detector and MXT-1 capillary column (Siltek treated stainless steel). Operation conditions were as follows: nitrogen was used as the carrier gas; the injector temperature and detector temperature were 330 and 350 ^{o}C, respectively; the column oven temperature was kept at 40 ^{o}C for 1 min and then raised to 320 ^{o}C at a rate of 10 ^{o}C min^{-1}.

Pyrene degradation intensity was calculated using the formula (1).

$$\text{Degradation intensity}(\%) = \frac{c_0 - c_x}{c_0} \times 100 \qquad (1)$$

c_0-pyrene concentration in blank flasks; c_x-pyrene concentration in experimental flasks.

III RESULTS AND DISCUSSION

Pyrene has been used as a model compound to study biodegradation of high molecular weight polycyclic aromatic hydrocarbons because it is one of the sixteen toxic, mutagenic and carcinogenic PAHs, that have been considered as priority pollutants by US Environmental Protection Agency [28, 36] (Fig. 2).

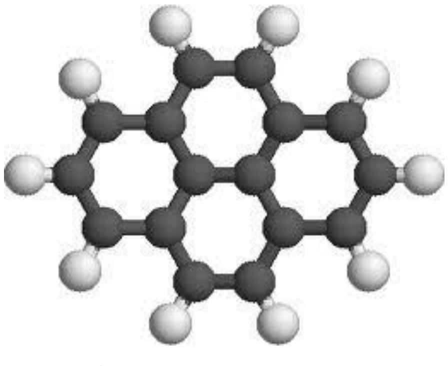

Fig.2 Structure of high molecular weight (HMW) polycyclic aromatic hydrocarbon pyrene ($C_{16}H_{10}$) [37]

After 72 h incubation with ten *Arthrobacter* strains in aerobic conditions in a rotary shaker, gas chromatography analysis revealed that the highest pyrene degradation was accomplished by *Arthrobacter* sp.NJ5 strain (Fig. 3), which was chosen for the later experiments.

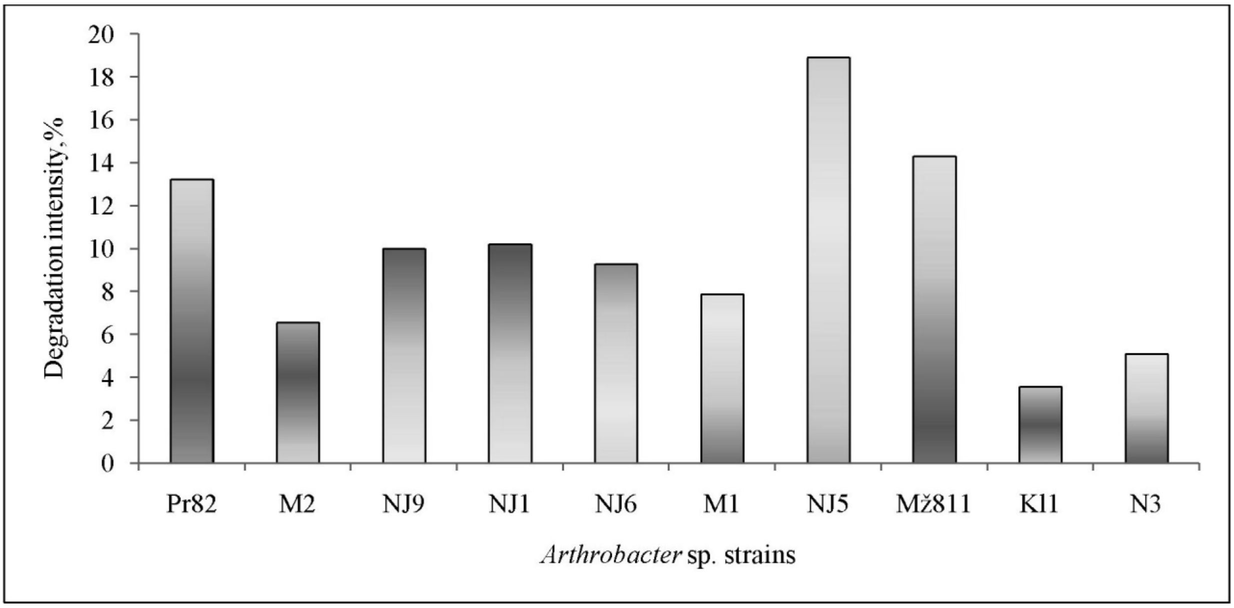

Fig.3 The effect of *Arthrobacter* sp. strains on pyrene biodegradation

Arthrobacter sp. NJ5 strain was isolated from clay contaminated with crude oil near Nefteyugansk in Russia.

The rate of degradation of hydrocarbons is mainly influenced by environmental limiting factors (salinity, nutrients, pH, temperature, oxygen) and therefore may not be due to the enzymatic capacities of the endogenous hydrocarbon degrading bacterial strain [38, 39].

The effect of initial medium pH, temperature and substrate concentration on pyrene degradation with *Arthrobacter* sp. NJ5 strain was investigated in this paper (Fig. 4; 5; 6). During the selection of an optimal medium pH, the maximum substrate degradation was achieved at pH 7 (Fig. 4).

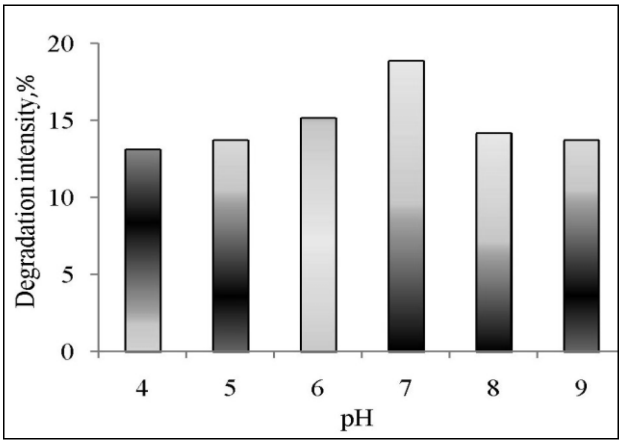

Fig. 4 Dependency of pyrene degradation by *Arthrobacter* sp. NJ5 strain on medium pH

After determining the dependency of degradation on medium pH, temperature regime was selected for the most efficient pollutant degradation. It was found that the rise in temperature from 5 to 35 ^{o}C promotes degradation of substrate and it is the highest at 35 ^{o}C, however, degradation level drops at a temperature range of 35-40 ^{o}C (Fig. 5).

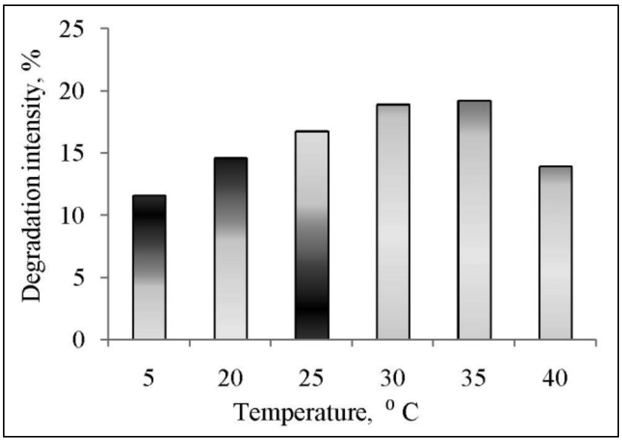

Fig. 5 Dependency of pyrene degradation by *Arthrobacter* sp. NJ5 strain on temperature

The effectiveness microbiological hydrocarbon degradation process is influenced by the substrate concentration as well, which can be inhibitory or even toxic to oil-oxidizing microorganisms [29, 40]. Therefore, the *Arthrobacter* sp. NJ5 strain oxidizing properties were tested against the polycyclic aromatic hydrocarbon substrate. Results revealed that, when substrate concentration in medium was increased from 0.1 to 0.4 mg/mL, substrate degradation level has risen, but higher concentrations (up to 0.8 mg/mL) slowed the intensity of degradation down. The best substrate degradation was observed when the initial pyrene concentration was 0.4 mg/mL (Fig. 6).

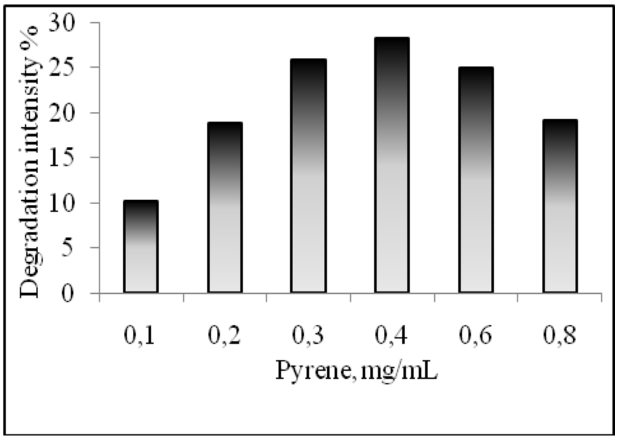

Fig. 6 Dependency of pyrene degradation by *Arthrobacter* sp. NJ5 strain on pyrene concentration

Results from previous experiment indicate that degradation of lower molecular weight polycyclic aromatic hydrocarbons is much easier. Experiments with antracene, where its concentration in the medium is 0.1 mg/mL, achieved 51.8 % degradation intensity of *Arthrobacter* sp. NJ5 within five hours [41]. Using the same concentration of pyrene, degradation intensity after 72 hours is only 10 %.

Gas chromatography analysis was carried out to investigate quantitative and qualitative changes of pyrene during biodegradation by the selected *Arthrobacter* sp. NJ5 strain (Fig. 7; Table 1). In biodegradation experiment initial concentration of pyrene and inoculate in mineral medium was 0.4 mg/mL and 10 %, respectively. Inoculated flasks were incubated at 35 °C and 200 rpm for 72 h. Control test was performed at the same conditions, except for the inoculate.

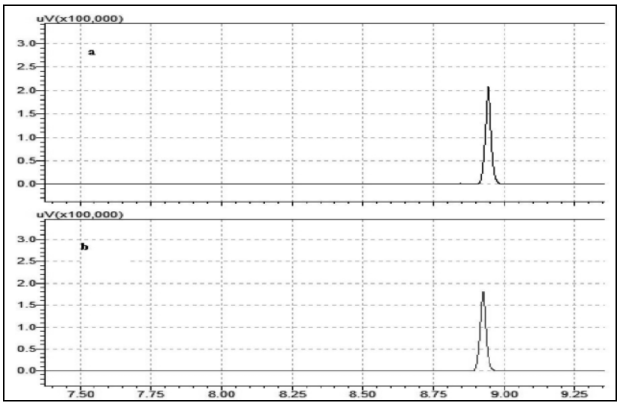

Fig. 7 Gas chromatograms of pyrene (a-control test; b-after biodegradation by *Arthrobacter* sp. NJ5 strain)

Gas chromatography data shows no qualitative structural changes of pyrene after biodegradation with *Arthrobacter* sp. NJ5 strain. According to lower pyrene peak plot it is considered that quantity of pyrene has changed during biodegradation.

TABLE 1.

QUANTITATIVE ANALYSIS OF PYRENE

No	Peak retention time	Peak area	Peak height	Concen-tration
a	8.907	321111.6	208099.0	0.24384
b	8.914	224021.1	104803.5	0.17609

IV CONCLUSION

Among all 10 *Arthrobacter* strains used for experiments, *Arthrobacter* sp. NJ5 showed the best results in polycyclic aromatic hydrocarbon pyrene degradation.

The highest intensity of pyrene degradation by *Arthrobacter* sp. NJ5 strain occurred at the intial medium pH value of 7.0.

Temperature range of 30-35 °C was found to be the most optimal for pyrene biodegradation by *Arthrobacter* sp. NJ5 strain.

The highest substrate degradation level with *Arthrobacter* sp. NJ5 was reached, when the initial pyrene concentration was 0.4 mg/mL, medium pH=7 and temperature 30 °C.

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Changes of Landscape Spatial Structure as a Result of Transformation of Land-Ownership

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***Abstract*. The aim of the research is to analyse the landscape structure changes from the end of the Soviet times in 1974–1986 until 2005 when market economy existed in Lithuania. The changes of landscape structure were observed in 100 sample areas (squares) each of them having 2.5 km^2 area and distributed in different landscape types. The changes in sample areas (squares) with determination of land cover structure transformations were observed using topographic photos and ortophoto images at a scale 1:10 000. More distinct manifestation of landscape re-naturalisation through land abandonment and conversion to forests, swamps and shrubs, also through transformation of arable land to meadows and pastures was the main direction of land cover changes. The opposite but lower scale conversion of forests, shrubs and other land use types to agrarian fields was also noticed. Acceleration of the conversion of landscape structure towards technogenisation through quick expansion of construction, recreational use and development of infrastructure was another important landscape structure conversion going on in the opposite direction of technogenisation. It manifested mainly as the change of agrarian fields, suburban gardens to built-up territories and as increase of percentage of other land use types related to them (ponds, streets and roads).**

***Keywords* – deforestation, land cover structure, land use, spontaneouos forestation.**

I INTRODUCTION

Development of Lithuanian landscape is very dynamic with periods of evolution and sudden changes. It is related to the changes of social, economical, political conditions, of abundant socio-economical reforms which left their mark in present landscape structure. Current Lithuanian landscape contains reflections of various past social-economic reforms recorded in landscape mosaics and land use structure. Especially sudden, as seen from our modern perspective, are the landscape structure changes that have taken place in Lithuania after regaining the Independence and after approving certain programmes of land restitution. The latter stimulated the fragmentation of owned land, bringing our country somewhat back to the interwar period, only with the traces of Soviet land management and signs of some new elements in our landscape.

Observation of landscape state in Lithuania has been done since 1999 as State monitoring [1]. However, the transformations observed by analyzing CORINE Land Cover which is intended to track the changes of large areas (scale 1:100 000) do not allow to reveal detailed fragmentation of landscape which is especially specific to such landscape types as lake areas, river valleys, morainic hills. The analysis of landscape structure changes in a more detailed scale (1:10 000) proposed by us enables to reveal not only the small changes of landscape mosaic, but also the changes of linear or point objects. The knowledge about them is especially important for purposeful forming of the directions of state landscape protection and management, for preparing of documents of different level territorial planning and for organising the activity for landscape forming and restoration.

II METHODS

The methodology of observation of landscape changes was described in detail during preparation of landscape monitoring program in previous article of the authors [2].

The changes of landscape were estimated in 100 sample areas each having 2.5 km^2 area (the length of the sides being 1581 m) which were distinguished in the main landscape types of Lithuania (Fig. 1) when analysing cartographic material at the scale 1:10000 (Soviet time aerial photographs of 1974-1986 and orto-photo views of 2005-2006) with the help of Arc/View 9.3 software. Thirty two land cover types were distinguished and their changes were observed during the above-mentioned period in each sample area. The statistical regularities of their distribution were determined for the whole territory of Lithuania. About 9000 plots with changes were distinguished which in total cover more than 4000 ha area.

The changes of land cover categories and the level of fragmentation were calculated and the main directions of landscape conversion were revealed. More detailed principle of evaluation of landscape structure changes has been discussed by the authors in another article [3].

III RESULTS AND DISCUSSION

After regaining the Independence, the fragmented small-scale land-ownership and land use structure was formed in Lithuania. Therefore it is normal that most of the changes are small: the average area of plot with changes is about 0.5 ha and plots less than 0.5 ha area comprise almost 80 % of total number of plots with changes (Table 1). Especially small changes are observed in landscape types with the greatest fragmentation: lake areas, river valleys, morain hills.

Total changes of land cover in distinguished sample areas during the study period comprise even 17.4 % indicating great transformations of landscape in Lithuania. It should be noted that the fragmentation of land cover significantly increased during the study period (Table 2). This fact is proven by the marked increase of the number of land use type units in the study territory (from 3127 to 4813) and by the respective decrease of the average area of land use plot (from 8 to 5.5 ha). The growth of landscape fragmentation is especially remarkable due to the increase of the shrubby areas and swamps both in the forested territories and in the agrarian fields, as well as due to growing extent of cuttings in the forested territories. The process of spontaneous forestation (conversion of arable land to shrubby meadows) is a characteristic phenomenon at the beginning of the period of the Independence it is manifested in the whole country, especially in those areas where according to other authors [4, 5] agriculture is weak due to poor soils.

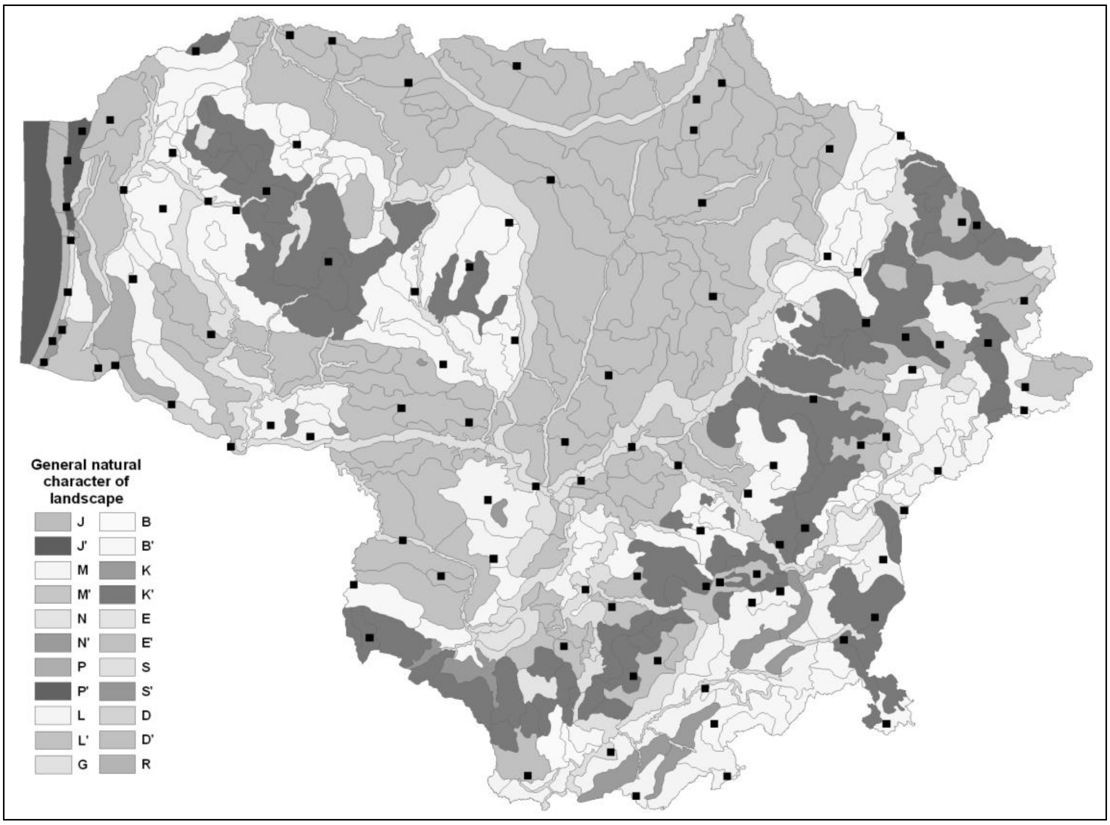

Fig. 1. Landscape sample areas (black ~~squares~~) in different natural landscape types of Lithuania (map according to [6]

Natural character types of landscape: J – marine landscape in the coastal zone (at a depth of < 20 m); J‘ – underwater plateaus and troughs; M – shallow lagoon (at a depth of < 2 m); M‘ – deep lagoon; N – smoothened spit; N‘ – rugged spit; P – lagoon coastal plain; P‘ – sandy coastal plain; L – continental sandy plains; L‘ – clayey plains; B – sandy downy plateaus; B‘ – clayey downy plateaus; G – morainic hills; K – sandy hills; K‘ – morainic hills; E – troughs with lakes; E‘ – lake terrains; S – valleys; S‘ – old valleys; D – delta valley; D‘ – delta; R – erosion washes.

TABLE 1.

STRUCTURE OF CHANGES ACCORDING TO THE SIZE OF AREAS

Area (ha) of plots with changes	Number of plots with changes	% from total number	Area (ha) of plots with changes	% from total area
less than 0.1 ha	3933	45.2	129.8	3.0
from 0.1 to 0.5 ha	2975	34.2	717.1	16.5
from 0.5 to 1 ha	813	9.3	570.5	13.1
from 1 to 5 ha	870	10.0	1798.8	41.3
from 5 to 10 ha	71	0.8	502.3	11.5
more than 10 ha	40	0.5	634.9	14.6
Total	8702	100.0	4353.3	100.0

TABLE 2.

Changes of land cover categories.

1 – at the end of the Soviet time (according to aerial photographs). 2 – in 2005-2006 (according to orto-photo views).

Land cover type (category))	Number of land use units			Area (ha) of land use type			% from total area		
	1	2	Change	1	2	Change	1	2	Change
Forests. swamps and schrubs	**1340**	**2094**	**754**	**8196.6**	**9110.7**	**914.2**	**32.79**	**36.45**	**3.66**
Forests	856	1001	145	7138.6	7441.6	303.0	28.56	29.77	1.21
Young forests	216	246	30	564.9	760.7	195.8	2.26	3.04	0.78
Forest cuttings	12	127	115	36.7	259.4	222.6	0.15	1.04	0.89
Schrubs	175	535	360	150.9	365.8	214.9	0.60	1.46	0.86
Swamps	81	185	104	305.5	283.3	-22.3	1.22	1.13	-0.09
Waters	**325**	**392**	**67**	**1145.0**	**1135.3**	**-9.8**	**4.58**	**4.54**	**-0.04**
Rivers	31	30	-1	313.8	307.4	-6.4	1.26	1.23	-0.03
Bars (in rivers)	10	16	6	33.2	3.5	-29.7	0.13	0.01	-0.12
Ditches and channels	2	9	7	3.1	9.2	6.1	0.01	0.04	0.02
Lakes	77	101	24	516.3	483.4	-32.8	2.07	1.93	-0.13
Ponds	195	226	31	48.9	102.9	54.0	0.20	0.41	0.22
Sea (and lagoon)	10	10	0	229.7	228.8	-0.9	0.92	0.92	0.00
Agrarian fields	**1021**	**1430**	**409**	**15054.8**	**13819.6**	**-1235.3**	**60.23**	**55.29**	**-4.94**
Arable land. meadows and pastures	501	725	224	14832.3	13128.0	-1704.2	59.34	52.52	-6.82
Schrubby meadows	0	309	309	0.0	519.2	519.2	0.00	2.08	2.08
Gardens	520	396	-124	222.6	172.3	-50.3	0.89	0.69	-0.20
Built-up territories	**305**	**756**	**451**	**308.5**	**690.9**	**382.4**	**1.23**	**2.76**	**1.53**
Urban built-up	21	43	22	46.5	114.2	67.7	0.19	0.46	0.27
Village built-up	179	365	186	77.2	206.2	129.0	0.31	0.82	0.52
Industrial built-up	25	88	63	86.4	112.2	25.7	0.35	0.45	0.10
Garden allotment built-up	54	220	166	87.7	211.2	123.5	0.35	0.85	0.49
Country-houses built-up	0	16	16	0.0	34.9	34.9	0.00	0.14	0.14
Stadiums. hippodromes. athletic fields	6	7	1	3.1	4.0	1.0	0.01	0.02	0.00
Cemeteries	20	17	-3	7.6	8.2	0.6	0.03	0.03	0.00
Exploitable territories	**53**	**25**	**-28**	**55.7**	**32.1**	**-23.7**	**0.22**	**0.13**	**-0.09**
Quarries	51	22	-29	18.0	18.9	0.9	0.07	0.08	0.00
Peatbogs	2	3	1	37.8	13.2	-24.6	0.15	0.05	-0.10
Infrastructure territories	**46**	**78**	**32**	**72.5**	**85.7**	**13.2**	**0.29**	**0.34**	**0.05**
Infrastructure networks	3	2	-1	7.9	2.8	-5.1	0.03	0.01	-0.02
Streets and roads	28	50	22	61.8	78.0	16.2	0.25	0.31	0.06
Embankments	1	1	0	0.6	0.4	-0.2	0.00	0.00	0.00
Docks	10	19	9	1.1	1.2	0.1	0.00	0.00	0.00
Landfills	4	6	2	1.2	3.3	2.1	0.00	0.01	0.01
Other categories	**37**	**38**	**1**	**157.7**	**116.6**	**-41.1**	**0.63**	**0.47**	**-0.16**
Sands	29	29	0	152.0	100.5	-51.5	0.61	0.40	-0.21
Stony land	2	2	0	2.3	0.2	-2.1	0.01	0.00	-0.01
Heritage objects	4	5	1	1.1	13.7	12.6	0.00	0.05	0.05
Foreign territory	2	2	0	2.2	2.2	0.0	0.01	0.01	0.00
Total	**3127**	**4813**	**1686**	**24995.6**	**24995.6**	**0.0**	**100.00**	**100.00**	**0.00**

TABLE 3.

MAIN CHANGES (TRANSFORMATIONS OF LAND COVER CATEGORIES)

Changes	Number of plots with change	% from total number	Area (ha) of plots with changes	% from total area
Renaturalisation. land abandonment and conversion to forests. swamps and schrubs				
Agrarian fields to forests and schrubs	2673	30.7	1328.7	30.5
Agrarian fields to schrubby meadowss	269	3.1	336.2	7.7
Agrarian fields to swamps	133	1.5	63.2	1.5
Scrubs and young forests to forests	247	2.8	256.6	5.9
Quarries and peatbogs to forests to forests and schrubs	36	0.4	41.3	0.9
Conversion to agrarian land				
Shrubs to agrarian fields	208	2.4	30.5	0.7
Forests to agrarian fields	1042	12.0	305.4	7.0
Swamps to agrarian fields	43	0.5	66.6	1.5
Gardens to agrarian fields	335	3.8	56.2	1.3
Build-up territories to agrarian fields	143	1.6	42.7	1.0
Expansion of construction. infrastructure and recreational use				
Agrarian fields to build-up territories	717	8.2	397.8	9.1
Gardens to build-up territories	224	2.6	42.8	1.0
Agrarian fields to gardens	261	3.0	53.1	1.2
Agrarian fields to ponds	166	1.9	55.8	1.3
Overgrowth of swamps and lakes				
Swamps to forests and shrubs	120	1.4	69.3	1.6
Lakes to forests. swamps and shrubs	82	0.9	37.6	0.9
Other more important changes				
Forests to young forests and shrubs	257	3.0	351.7	8.1
Forests to forest cuttings	127	1.5	240.2	5.5
Forests to shrubby meadows	147	1.7	151.3	3.5

Though increase of forested areas due to decrease of arable fields is observed also in other European countries [7, 8], it is usually associated with expansion of planted forests but not with forests which are naturally occupying an abandoned land. It is possible to state that the increase of land cover fragmentation was first of all predetermined by land reform which allowed formation of small land-ownership and the latter in turn lead to the land use fragmentation. Besides that, such processes as increase of built-up territories, expansion of recreational use in suburban territories, and forestation or spontaneous forestation of agrarian fields had and still have great influence on the growth of landscape fragmentation. Though presently the tendency of enlargement of farms can be noticed (first of all in fertile plains). This process is going on slowly and with difficulties because small landowners refuse to sell their land of agrarian use. Thus farmers are forced to rent the greater part of agrarian land. Manifestation of landscape re-naturalisation as a result of land abandonment and conversion to forests, swamps and shrubs, as well as, transformation of arable land to meadows and pastures are the main directions of land cover changes during the study period. According to some foreign authors [9, 10, 11, 12, 13], land abandonment and its spontaneous forestation is qualified as rather negative process, because of the loosing of land value from a cultural viewpoint and from ecological viewpoint, because of decrease of biodiversity during succession period. However, in Lithuania this process should be qualified positively, because it helps to restore the landscape stability in the sense of structure optimum after high landscape homogenisation experience in Soviet period.

Transformation of agrarian fields to forests and shrubs can be considered as the main axis of landscape structure conversion (it comprises more than 30 % according to number of plots with changes and covered area). Though at the same time the conversion of forests and shrubs and other land use types to agrarian fields was also going on. but it had significantly lower scale and comprised only about 20 % from total number of all plots with changes (the conversion of forests to agrarian fields was somewhat more distinct and made up 12 % of the total number of plots with changes) (Table 3). Therefore in total. the part of natural land use types (forests. shrubs and swamps) increased by 3.7% during the study period. meanwhile the part of agrarian fields decreased by 4.9 % respectively.

Quick expansion of construction, recreational use and infrastructure is another important landscape structure conversion which is opposite to the first one, because it goes towards technogenisation. It manifests mainly as the change of agrarian fields, suburban gardens to build-up territories resulting in the growth of the percentage of other land use types related to built-up territories (ponds, streets and roads). During the study period, the percentage of built-up territories increased more than twice (from 1.2 to 2.8 %).

It is possible to state that the processes of re-naturalisation were predetermined by the poor state in the villages and agrarian sector due to prolonged reform of agriculture, also by EU support for forestation of unproductive land. Very quick expansion of built-up areas began after Lithuania joined EU and the growth of large cities and employment of recreation areas, especially near lakes, rivers and seashore. intensified.

Increase of forestation of swamps and decrease of the lake areas due to implementation of melioration in Soviet times is also noticeable during the study period. Especially intensive forest cuttings (which increased 7 times and which are observed in sandy plains) can also be mentioned among other changes.

IV CONCLUSIONS

All traces of past social economical reforms are reflected in the present mosaic of Lithuanian landscape. but they are especially distinct when Soviet economy changed to market economy. Observation of landscape changes during the period from the end of the Soviet times to the middle of the second decade of the Independence using cartographic material of detailed scale (1:10000) enabled to determine the following main tendencies of landscape structure changes.

Significant increase of land cover fragmentation (mosaic) due to growth of the shrubby and swampy territories both in the forested territories and in the agrarian fields. The average area of land use plot decreased almost twice.

More distinct manifestation of landscape re-naturalisation through land abandonment and conversion to forests, swamps and shrubs, as well as through transformation of arable land to meadows and pastures. The conversion of forests, shrubs and other land use types to agrarian fields also takes place, but on markedly lower scale. Therefore in total the part of natural land use types (forests, shrubs and swamps) in land use structure increased by 3.7 % during the study period, meanwhile the part of agrarian fields decreased by 4.9 % respectively.

Acceleration of the conversion of landscape structure towards technogenisation through expansion of build-up territories, recreational use and expansion of road infrastructure. The part of built-up territories during the study period increased more than twice (from 1.2 to 2.8%). The extent of forest cuttings increased 7 times.

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Review of Creosote Pollution Toxicity and Possibilities of Bioremediation

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Abstract. **Creosote oil is a complex mixture of hydrocarbon compounds obtained from high temperature distillation of coal tar. It is used for over 100 years as a fungicide, insecticide, miticide, and sporicide to protect wood and is applied by pressure methods to wood products, primary utility poles and railroad ties. This treated wood is intended for exterior or outdoor uses only. Its commercial uses include railroad ties 70 %, utility poles 15-20 %, and other miscellaneous commercial uses 10-15 %. Composition of the creosote depends on the source and it has typically 85 % polycyclic aromatic hydrocarbons (PAHs), 10 % phenolic compounds, and 5 % heterocyclic. Between 20 and 40 % of the total weight of typical creosote can be attributed to the 16 PAHs defined as priority pollutants by the United States Environmental Protection Agency (EPA). The production of creosote in the European Union (EU) has been estimated to be approximately 60.000-100.000 t per year. The presence of the toxic PAHs and phenolic compounds make creosote treated wood harmful for the environment at the end of its service life and direct or indirect human exposure to creosote treated wood may cause carcinogenic affect to kidney, liver, bladder, eyes and skin. In this presentation we review creosote environmental pollution toxicity and possibilities of remediation**

Keywords **– creosote, PAH, pollution, remediation, toxicity.**

I INTRODUCTION

Wood-preserving industry uses more pesticides than any other industry worldwide. The one of major chemical employed for this purpose is creosote used in the wood treating industry for over 100 years. Wood treated with creosote is widely used, e.g., as poles for electric power or telephone lines and as railroad sleepers [1]. The production of creosote in the EU has been estimated to be approximately 60,000-100,000 t per year, preservation of railway uses 54 % of creosote. [2]. When properly used and disposed of, creosote does not appear to significantly threaten human health. However, misuse, accidental spillage, and improper disposal of creosote results in contaminated environments with serious potential health risk. Creosote contamination is generally associated with surface soils, waters in treatment lagoons or evaporation areas, and groundwater contaminated with leachate from the above sources [3]. Creosote oil is a complex mixture of hydrocarbon compounds obtained from high temperature distillation of coal tar. Coal tar creosote is composed of approximately 85 % polycyclic aromatic hydrocarbons (approx. 50 % two-ring, 39 % three-ring, 9 % four-ring and 2 % five-ring); 10 % phenolic compounds; and 5 % N-, S-, and O- heterocyclic [3-10]. Between 20 and 40 % of the total weight of typical creosote can be attributed to the 16 PAHs defined as priority pollutants by EPA and EU (Fig.1), many of the PAHs are recalcitrant compounds and have toxic properties.

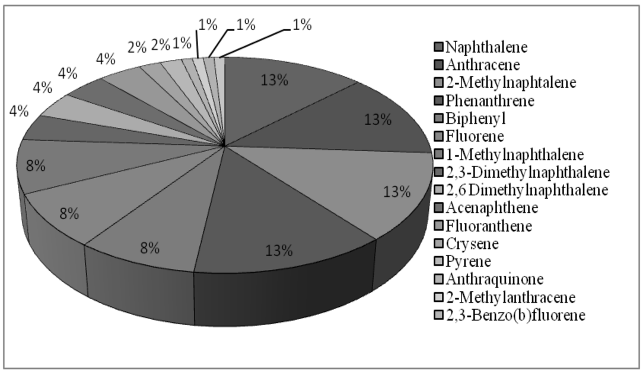

Fig.1. Predominant PAHs constituent in Creosote [3],[8],[11]

II CREOSOTE TOXICITY

Creosote's qualities as a wood preservative are excellent; however accidental spillage, improper disposal results in contaminated environments with serious potential health risks. Creosote compounds are commonly occurring industrial pollutants and are often found as co-contaminants in the environment. Most of creosote consisting compounds are known as carcinogenic, teratogenic, genotoxic and imunotoxic [8, 12-16]. The effects on human health will depend mainly on the length and route of exposure, the amount or concentration of creosote compounds.

Human exposure to creosote compounds occurs through 3 routes: respiratory tract, gastrointestinal tract and skin contact coming into direct contact with creosote and breathing in airborne creosote particles increase the chances for creosote exposure inside the body. Through the lungs and skin creosote will slowly pass into the bloodstream. Common external effects include rashes, either severe or mild, chemical burns around the eye area, sensitivity to light, eye damage and blistering or peeling skin. Internal damage can also occur from exposure to creosote from eating, drinking or breathing in the creosote chemicals [17]. Internal toxic damages can include unconsciousness, cancer, convulsions, mental impairment, kidney and liver problems and several other internal issues [18]. However, the industrialization of creosote has increased the amount of the chemical present in groundwater and soil. The creosote forms a tar-like substance in the water, where it takes many years to completely break down. One or two per cent of creosote used to treat wood ends up in the air [19]. Any plant or animal that is near the creosote in the water, air or soil absorbs the chemicals. Plants absorb less of the creosote than animals. The main danger of creosote exposure to the environment is then that the chemicals absorbed by the animals or plants move on to humans (Fig.2.).

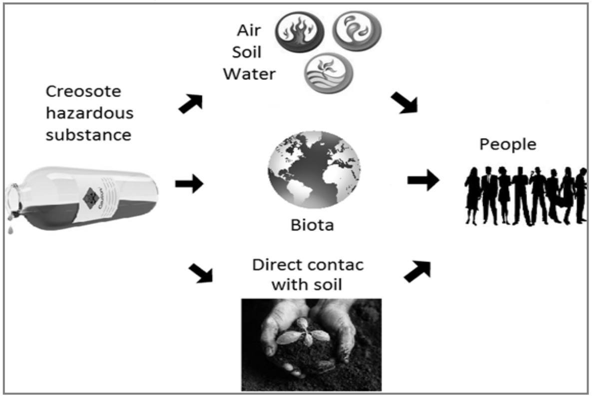

Fig. 2. Exposure pathways of creosote pollution.

III BIOREMEDIATION OF CREOSOTE

Biological degradation is the primary dissipation mechanism for the most of organic pollutants in the environment, however the activity of degrading microorganisms depends upon many factors, including contaminant uptake and bioavailability, concentration, toxicity, mobility access to other nutrients and activated enzymes [11]. The rate and extent of biodegradation of creosote in soils and sediments is affected by multiple factors, such as physico-chemical (physical/chemical properties of PAHs, phenols, heterocycles, organic content of soil, structure/particle size of soil, presence of contaminants), biological factors (characteristics of the microbial population: diversity, genetic/catabolic potential) and environmental factors (temperature, moisture, pH, sorption, degree of contamination).

Two-ringed PAH as naphthalene is broken down easily. The three-ring PAHs, such as acenaphtalene, fluorene, phenanthrene, anthracene and the four-ring PAHs such as fluoranthrene, pyrene, benzo(a)anthracene and crysene have been shown to be metabolized by microorganisms and degraded in creosote bioremediation although at slower rates as the molecular weight increases. However, the high-molecular weight five, six, seven ring PAHs, such as benzo(b)fluoranthene, indeno(1,2,3-cd)pyrene and coronene, have not been shown to significantly biodegrade even over long periods of time [7].

Because of its toxicity, creosote-treated wood does not degrade easily in the environment and requires special disposal methods. The detoxification of creosote treated wood has become more popular since this material has been classified as dangerous waste on the basis of the existing law dispositions (EU Directive 2001/90/CE).

It is generally accepted that creosote is a major wood preservative. Creosote-treated wood has commonly been used for railroad crossties and landscape facilities, as a result, creosote contamination of surface soils, segments, and groundwater is commonly observed in areas in which creosote-treated wood was used. The combustion of creosote treated wood is the main industrial treatment actually in use, however up to nowadays the great majority of bioremediation experiments concerned with creosote regards polluted soil, where different microorganisms are involved in the oxidation and subsequent mineralization of creosote components: soil bacteria or fungi, are described (Fig.3.).

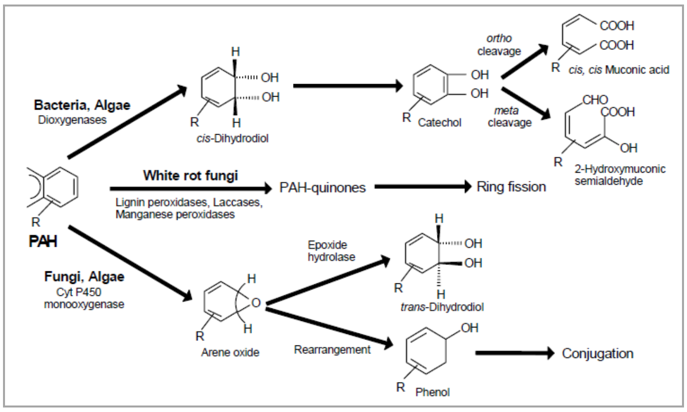

Fig. 3. Major pathways involved in the metabolism of polycyclic aromatic hydrocarbons by bacteria, fungi and algae [20].

There are a lot of articles related with bioremediation experiments concerned with creosote regards polluted soil, however, information related to wood impregnated with creosote bioremediation is not much compared to bioremediation of soil.

Creosote degradation by bacteria

Creosote is not easily degraded by microorganisms. Bacteria involved in degradation of creosote components (some PAHs, HACs, phenolic compounds) have been isolated and identified as belonging mostly to the genera *Pseudomonas* [21-24], *Spingomonas* [25], *Bacillus* [26] *and Mycobacterium* [27],[28]. Creosote biodegradation by bacteria strains limited the high- molecular-weight PAHs continued to be recalcitrant in treated soil [29]. Despite the removal of a majority of creosote contaminants from groundwater through biotreatment, only a slight decrease in toxicity and teratogenecity of biotreated groundwater was observed. Recent studies demonstrated that several treatments have been successful in reducing, for example, the total PAH concentration in contaminated soils, however increased the microbial mutagenicity of these soils [30]. Creosote compounds biodegradation by bacteria are used more frequently than biodegradation by fungi or removal with phytoremediation.

Degradation of creosote by fungi

The pollutants contained in the creosote-treated wood waste are also barriers to its use as landfill cover due to potential migration of contaminants into ground water. The life expectancies of creosote-treated railway ties depend on rail traffic, tie placement and environmental hazards. The service life of creosote-treated railway ties is from 30 to 50 years. Therefore, a proper disposal method should include an effective degradation of the pollutants in creosote treated wood waste. Positive results were obtained with fungi belonging to different genus are presented in Table 1 [31],[32]. High degradation was obtained with white-rot fungi *Phanaerochaete crysosporium* [33], *Pleurotus ostreatus* [34-36], *Cladosporium sp.* [31], *Polyporus* sp. [37], filamentous fungus *Fusarium sp.* (strain E0330) [38], ascomycetous fungus *Thermoascus aurantiacus* [43]. White-rot fungal species could be interesting for the treatment of wood waste because of their ability to degrade phenols and PAH and to grow on ligninocellulosic materials [39-41].

TABLE 1.

STUDIES ON CREOSOTE CONTAMINATED SOIL AND CREOSOTE TREATED WOOD BIOREMEDIATION BY FUNGI

Fungi	**Research findings**	**References**
Creosote-contaminated soil		
Pleurotus ostreatus, *Irpex lacteus*	Fungus degraded PAH with 4–6 aromatic rings more efficiently than the microbial community present initially in the soil. PAH removal was higher in *P. ostreatus* treatments than *in I. lacteus.* Indicates a potential for synergistic interaction between the fungus and actinobacteria in bioremediation.	[35]
Cladosporium, Fusarium, Penicillium, Aspergillus, Pleurotus	White-rot fungus belonging to the genus *Pleurotus* was better able to degrade creosote than other organisms studied, and that mixed fungal cultures more effectively degraded creosote than did pure cultures.	[31]
Phanerochaete sordida	Demonstrate the potential of lignin-degrading fungi in the solid-phase bioremediation of creosote-contaminated soils, but, the persistence of highly toxic PAHs containing > 5 rings represents a significant challenge which must be overcome before the technology can be considered a viable treatment option for creosote-contaminated sites.	[42]
Pleurotus ostreatus	*P. ostreatus* has an overall positive effect on the degradation of aged creosote in soil and that degradation is enhanced by increased temperature and pre-treatment.	[34]
Creosote-treated wood		
The fungal inoculums comprise at least one creosote-tolerant fungus (e.g, *Antrodia radiculosa, Neolentinus lepideus*, etc.)	Waste wood containing creosote is remediated or degraded by inoculating it with the fungal inoculums. The inoculums and waste wood are combined until an end product is achieved that is at least partially remediated or of a reduced volume.	[32]
Pleurotus ostreatus	Phenols are completely degraded. Some more dangerous compounds, such as methyl-PAH and 5–6 rings PAHs are generally well degraded. Almost complete degradation of creosote oil components, also confirmed by a significant reduction of ecotoxicity.	[41]
A total of 179 fungal isolates was recovered from 240 sampling points	There was a large difference in the fungal diversity between the surface and the inner area of crosstie wastes. *Heterobasidion annosum* and *Schizophyllum commune* showed very high resistance to PAHs, which indicates that these species may play a role in the degradation of PAHs.	[9]
Agrocybe, Armillaria, Auricularia, Daedalea, Pleurotus, Trametes	The most tolerant strain, *Pleurotus ostreatus* SMR 684, extracellular laccase and peroxidase specific activities were monitored during growth in the presence of creosote-treated wood.	[40]
Thermoascus aurantiacus	The inoculation of cellulolytic and thermophilic fungus *Thermoascus aurantiacus* did not accelerate the bioremediation process in degrading phenolic compounds and may have inhibited the metabolic activity of composting organisms.	[43]

Since the low bioavailability of PAHs by bacteria, the increased bioavailability of PAHs metabolites, produced by white rot fungi, can increase their mineralization by bacteria [44]. In contrast to bacteria, fungi generally do not utilize PAHs as sole carbon and energy source, but transform them comethabolically to detoxified metabolites. The degradation process in soil proceeds as a cooperation between white rot fungi (catalyse PAHs oxidation) and bacteria (mineralise PAHs with higher water solubility and oxidise metabolites of recalcitrant). In soil treated with *Pleurotus ostreatus*, where the soil bacteria were almost eliminated by the fungus, mineralization of PAHs was incomplete due to accumulation of intermediary metabolites that could not be oxidised by the fungus [45], but can be mineralised by bacteria.

Phytoremediation

Phytoremediation describes the treatment of environmental problems through the use of plants that mitigate the environmental problem without the need to excavate the contaminant material and dispose of it elsewhere. This cleaning method consists of mitigating pollutant concentrations in contaminated environment with plants able to accumulate, degrade, or eliminate various contaminants from media that contain them. There are several basic phytoremediation techniques: rizofiltration, phytoextraction, phytotransformation, phytostimulation, phytostabilization. The main advantages phytoremediation compared with other approaches are the preserve the natural structure and texture of the cleaned soil; it is low in cost and has potential to be rapid. One serious limitation is that many plant species are sensitive to contaminants [46].

The role of plants in remediation creosote and PAHs contaminations (which are the main part in creosote contaminants) presented in Table 2. PAHs can be degraded in the rhizosphere however may also interact with vegetation by accumulation in plant tissues or adsorption on root surface. Contaminant bioavailability and toxicity are critical factors in phytoremediation and bioavailability depends on lipophilicity and age, soil characteristics, such as pH, clay and organic matter content. The PAHs are widely distributed hydrophobic organic contaminants in soil usually exhibit low bioavailability to both microorganisms and plants due to their strong affinity to the soil matrix, especially to soil organic matter which limits the application of phytoremediation [11],[45],[47].

According the literature data there are selected number of plant species which have been found to be promising candidates for phytoremediation of such persistent pollutants as PAHs and could be used as an alternative technique to reduce creosote (PAHs) levels in soils [46-48] (Table 2). Plants provide root exudates with carbon, energy, nutrients, enzymes and sometimes oxygen to microbial populations in the rhizosphere. Root exudates of sugars, alcohols, and acids are annually from 10 to 20 % of plant photosynthesis [49] and provide sufficient amount of carbon and energy to support the large numbers of microbes. Root exudates are link between plants and microbes that causes the rhizosphere effect. This environmental cleaning method is effective, however evidence exists for the enhanced dissipation of PAHs in the rhizosphere when compared to nonrhizosphere soil [50-52].

TABLE 2.

STUDIES ON PHYTO-REMEDIATION WITH CREOSOTE (PAHS, PHENOLS) CONTAMINANTS IN SOIL

Common name of plant (Scientific name of plant)	Research findings	References
Alfalfa (*Medicago sativa* L.).	The residual concentrations of pyrene in the rhizosphere soil were lower than those in the non-rhizosphere soil.	[51]
	All vegetated treatments resulted in higher phytoremediation efficiency.	[53]
	Arbuscular mycorrhizal inoculation and addition of the surfactant consistently promoted phenanthrene dissipation in the soil	[54]
Alfalfa (*Medicago sativa L.*),tall fescue (*Festuca arundinacea Schreb.*).	Cropping promoted the dissipation of soil PAHs. Tall fescue gave greater removal of soil PAHs than alfalfa, intercropping was more effective than monoculture. Stimulates PAH degrading bacterial population.	[44]
Alfalfa (*Medicago sativa*), ryegrass (*Lolium perenne*).	Are potential plants for phytoremediation. The interactions among the consortia of plant root exudates, microorganisms, and amended compost in rhizosphere soils could facilitate bioavailability of pyrene and subsequently enhance its dissipation	[52]
Ryegrass (*Lolium perenne* L.).	Enhances dissipation or biotransformation of a large range of PAHs including 5 and 6-ring PAHs. The major part of PAHs dissipation in rhizosphere soil was due to biodegradation or biotransformation.	[50],[55]
Willows (*Salix Viminalis*).	Enhanced the degradation of all PAHs, most likely by the pronounced rhizosphere effect on the activity of active microorganisms, including PAH degraders.	[56]
Tall fescue (*Festuca arundinacea*), kentucky bluegrass (*Poa pratensis*), wild rye (*Elymus canadensis*).	Tall fescue is more suitable for use in phytoremediation. Plant growth promoting rhizobacteria were evaluated for plant growth promotion and protection of plants from contaminant toxicity.	[46]
Tall fescue (*Festuca arundinacea*), red fescue (*Festuca rubra*), ryegrass (*Lolium perenne*), red clover (*Trifolium pratense*), white clover (*Trifolium repens*).	In soils spiked with pure PAHs or coal tar the rate of loss of PAHs is much greater than in historically contaminated soils. There were clear differences in the losses of the PAHs depending on ring size amongst the 16 PAHs tested.	[57]
Bean (*Vicia faba*), corn (*Zea mays*), wheat (*Triticum aestivum*).	All vegetated treatments resulted in higher phytoremediation efficiency.	[58]
Vetch (*Vicia sativa L.*).	Vetch could tolerate and remove high phenol concentrations, avoiding serious phytotoxic effects. Thus, vetch could be considered an interesting tool in the field of phytoremediation.	[59]

Addition of surfactants has been explored in the cleanup of contaminated soils [60]; there are few reports of their application in phytoremediation, they found that the presence of the surfactant enhanced PAH degradation by a rhizosphere effect on the microbial activity and by increased bioavailability [54],[56].

IV CONCLUSION

Creosote, which is a common preservative used in wood treating processes, consists of different polycyclic aromatic, phenolic hydrocarbons and heterocyclic compounds. Because of their toxicity and their mutagenic and carcinogenic properties polycyclic aromatic hydrocarbons are classified as ubiquitous contaminants of highest concern in the environment. Toxic, environmental-persistent chemicals are resistant to degradation in the natural environment. Creosote contaminants do not degrade easily in the environment and require special disposal methods as there are not so many creosote-tolerant microorganisms, fungi and plant species.

Although many studies have been conducted to develop useful methods of bioremediation using microbes, fungi or plants, there is a limited number of species that can be used. Therefore, predictions of creosote dissipation from laboratory amended soil or treated creosote wood do not reflect the true situation in the field conditions. The further studies must be conducted to identify various species and fungal communities, microbial and plant species capable of bioremediation not only in lab conditions, but must show good results in field testing. Forthcoming studies should be the basis for the development of efficient technology, suitable for both in-situ and ex-situ processing of creosote-contaminated soil or large amounts of creosote-treated wood.

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The Flow Change of Mixed and Hazardous Waste at Utena Regional Landfill

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***Abstract*. While optimising the waste management, the Region waste management system – the system of regional waste management centres was created in Lithuania. Utena regional landfill is one of its elements. Since 2010 the waste flows were started to calculate by different fractions. Visually observing the waste disposal, it was noticed that the proportions of unsorted waste quantities flows were different in the districts, so it was decided that the custom random works of the mixed municipal waste content determination will be carried out in 2012 and 2013 four times a year, in different seasons. There is a possibility to dispose the sorted waste in Lithuania. Also, in all the municipalities there are Bulky and hazardous waste receiving and temporary storage sites, where the hazardous waste can be delivered. However, it was noticed that the sorting is insufficient – among the mixed municipal waste there are improper waste to be deposited, including the hazardous waste. The aim of the work is to analyze the change of the waste quantities at Utena regional landfill, distinguishing the quantities of the hazardous waste.**

***Keywords* – mixed waste, hazardous waste, waste landfill, waste sorting.**

I INTRODUCTION

Since 2008, while optimising the waste management, the Region waste management system – the system of regional waste management centres was created in Lithuania, 11 regional non-hazardous waste landfills are open, waste sorting is installed. In the waste sites next to the blocks of flats, the sorted waste containers for paper and cardboard, plastic and metal, glass are full. In 2006 – 2007, the condition of the waste deposition at that time was being analysed, the future situation was being forecasted, and the regional waste management plans were being created. The regional landfills started to operate in 2008 – 2009. Utena regional landfill started to operate in 2008.

It is important to analyze if the habits of the residents changed after the new opportunities arose, whether the waste quantities decrease as the population declines. Taking into account the fact that the hazardous waste must be collected and collected separately from other waste and must be not mixed with each others, except the cases if it is safer, it is important to determine the quantities of hazardous waste that are dropped off to the special sites and those that are dropped off with the mixed waste. In order to clarify these changes, one of the cleanest regions of Lithuania – Utena district – was chosen. Utena region waste management plan for 2008-2018 and Utena regional waste management centre reports of 2010 – 2012 were analyzed, and the flow change of the mixed and hazardous waste at Utena regional landfill was evaluated.

II UTENA REGIONAL WASTE MANAGEMENT CENTRE GENERAL REGION DESCRIPTION

Utena region, which is situated in the north-east of Lithuania, covers the regions of Anyksciai, Ignalina, Moletai, Utena and Zarasai and the municipalities of Visaginas, and its total area is 7201 km^2. It‘s the fifth region in Lithuania according to the size of the area. It makes about 11% of the total country‘s territory. It’s the land of the ravines, hills, lakes and forests. The district is rich with the underground water and sufficient quantities of explored underground drinking water. In the region of Utena there are existing sand, gravel and peat deposits. In the northern part there are wood resources. The forests cover 2228 km^2 or 31 % of the territory, and the waters cover 535 km^2 (7,4% of the total region territory). This region has the most of the lakes in Lithuania – 1002 lakes. Its landscapes are especially advantageous for the development of the recreation and tourism. The region of Utena has a relatively well-developed road network that connects the region with the other regions of the country and the neighboring countries. [7]

This information shows that the municipalities of Utena region should save its uniqueness and attractiveness to tourists and clean nature. One of the components of clean nature is a small quantity of waste that should be managed safely.

The biggest quantities of waste are formed in industry; domestic waste quantities are much smaller.

But in Lithuania the situation is opposite – here the quantity of the municipal waste is the biggest. The amount of waste depends on the industry development, the population change and the consumption growth. So, these major spheres, that form the biggest quantities of waste, are mostly represented by the industry branches which are particularly susceptible for materials and population. So, while calculating the outlook of the waste formation, three growth scenarios are used:

- slow growth scenario: the average annual consumption growth is 1 %;
- medium growth scenario: the average annual consumption growth is 3 %;

- high growth scenario: the average annual consumption growth is 5 %.

The main areas of activity in the region are: machine-building and metal-working, textile and knitwear industry, construction and woodworking, trade, transport, food and beverage production, rural tourism. [7]

So, in the economic activity of the county there should not be a lot of waste, especially, the waste that are deposited.

In the Republic of Lithuania the population censuses were in 2001 and in 2011. In 2006, the Department of Statistics calculated the data that is why the figures do not match the data given by the local neighborhoods. The population figures in Utena region, according to the data of the Department of Statistics and the municipalities in the region, are given in the Table 1.

TABLE 1.
THE POPULATION FIGURES OF UTENA REGION IN 2006. [7]

Municipality	Population (the data of the Department of Statistics)	Population (the data of the local neighborhoods)	Population in cities		Population in countries	
			Blocks of flats	Individual houses	Blocks of flats	Individual houses
Anyksciai district	32.637	33.185	5.730	8.948	971	17.536
Ignalina district	20.625	22.501	4.345	2.755	3.656	11.745
Moletai district	23.540	23.540	4.884	2.337	3.500	12.819
Utena district	48.376	44.444	28.588	5.302	1.600	8.954
Visaginas city	28.573	28.624	28.317	-	220	87
Zarasai district	20.991	20.700	5.261	3.452	2.361	9.626
Total in region	174.742	172.994	77.125	22.794	12.307	60.767

Utena region is one of the least urbanized regions in Lithuania. 55% of the district population lives in the cities. According to the data of the Department of Statistics of 2007, the biggest part of the population living in the rural areas is in the municipalities of Moletai and Ignalina. The majority of the population lives in the city only in Utena district (68 %) and in the municipality of Visaginas (99 %). The rural residential areas, having up to 10 residents, take the largest percentage in Utena district - 39%. [7]

TABLE 2.
THE POPULATION FIGURES OF UTENA REGION IN 2006 AND 2011. [1]

Municipality	Population in 2006.	Population in 2011.
Anyksciai district	32637	28668
Ignalina district	20625	18386
Moletai district	23540	20700
Utena district	48376	43275
Visaginas city	28573	22585
Zarasai district	20991	18390
Utena district	**174742**	**152004**

Table 2 and Figure 1 show the significant population decline in the district during the 5 year, especially in Visaginas city, Utena and Anyksciai districts. The population has decreased by nearly 23 thousand in Utena region.

Utena region is sparsely populated region in Lithuania, in 2006 the population density was 24,27 gyv./km^2. And in 2011 it was already decreased to 21,11 gyv./km^2.

The natural growth rate in Utena region is negative and is one of the lowest in all the region of the country. The population, comparing with the results of population census in 2011, has decreased in all the districts, mostly in Siauliai region - 18,5% and Utena region - 18,3 %. [2]

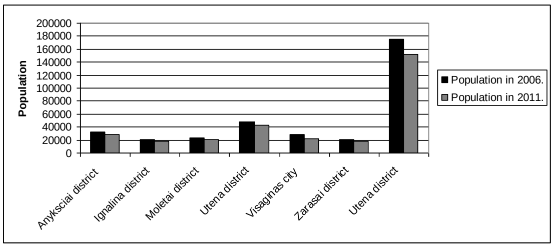

Fig. 1. The population figures of Utena region in 2006 and 2011. [1]

III WASTE MANAGEMENT SYSTEM IN UTENA DISTRICT

In Lithuania about 1,3 million tons of municipal waste were formed or 392 kilograms for one resident in 2006; in 2007 – 1,35 million tons of municipal waste (401 kilogram for one resident); in 2008 – about 1,4 million tons of municipal waste (408 kilograms for one resident); in 2009 – about 1,2 million tons of municipal waste (361 kilogram for one resident). In 2006 86% of collected municipal waste were eliminated in the landfills, in 2007 – 91,8%, in 2008 – 90,5%, in 2009 – 90,6%. It is obvious that the quantities of the collected waste slightly fluctuate every year, while the total amount of waste slightly increases. The same situation about the waste quantities is in Utena region. As the quantities of the waste were increasing, it was necessary to have the stricter waste management regulations; besides, it was demanded by EU law acts. In the Government of the Republic of Lithuania's resolution About The National Strategic Waste Management Plan Confirmation the shutdown of about 800 small landfills and the development of regional waste management system are foreseen. In Lithuania the waste are disposed in 11 regional non-hazardous waste landfills that meet the requirements of the environment protection and public health safety. The waste disposal in the landfills that do not meet the requirements of the environment protection and public health safety is stopped since 16 July, 2009. [5]

The waste landfill (storage) – is a waste disposal site where the waste are disposed of on ground or buried in the ground. The internal waste disposal sites are included here (i.e., the landfills where the formed waste are disposed by the waste producer in the place of its formation) but the sites, where the waste are stored in order to be prepared for the transportation to the other sites where they will be used and disposed, and the sites, where the waste are being stored temporally (up to one year) until they will be used or disposed, are not included. (Waste Management Act, article 2.15). [8]

So, the Region waste management systems were created in all the regions. While installing the waste management system in Utena district, the regional landfill was engineered by processing, extending and setting up Mockenai landfill (Utena district) according to all the environmental requirements. Mockenai landfill is being exploitable since 1986. The landfill area is 8,3 hectare, 7,6 hectare of that area is designated to dispose the waste, the rest of the area is used for the roads. At that moment, there were no surface water and filtrate collection systems, no treatment plants. While engineering the regional landfill, the accumulated waste, which in 2006 occupied 5,6 hectare area, were pushed together into the truncated pyramid-shaped mound, the old waste collection field was covered and re-cultivated. After joining the area of about 8 hectares to the existing territory, the regional landfill, meeting all the environmental requirements, was built in 2008. The landfill will be operated for about 20-25 years. The clamp of the regional landfill is planned to be set up in separate sections. The filtrate is collected by the drainage set up at the bottom of the clamp construction and led to the pumping station through which, together with the other contaminated wastewater of the landfill, will be passed to the treatment facilities of Utena city. It is planned to engineer the landfill gas collection system with the torch in the regional landfill. At the moment the torch is being used very rarely because methane, collected in the landfill, is sold to closed joint-stock company "Umaras". According to the fire norm requirements, fire tanks are engineered in the landfill. The special scales were installed to weigh the waste brought to the landfill. In the landfill territory, there is waste receiving site that is designated to collect the hazardous major, construction and household waste. There are also the temporary storage sites (one in each municipality), and two green waste composting sites: in the territory of Mockenai landfill, Utena district and in Karlai village (Visaginas municipality). [7]

There were only a few points in Lithuania where the waste was weighed until 2008. In the majority of the landfills the quantities of the waste were measured in cubic metres (m^3). In order to compare the amounts of waste from different regions, these quantities in cubic meters were converted to quantities in tons (according to the existing examples in the landfills, where the waste were weighed and measured in cubic metres), so they are not completely precise.

The recalculated statistical data on waste formation during 2005 and 2006 in Utena region were obtained from the regional municipalities. The provided data of 2010 – 2012 are precise – the waste were weighed and registered at Utena regional landfill but relatively small quantities of waste that were brought by the residents themselves are not evaluated. The total amount of the waste formed in the municipalities of Utena district is given in Table 3 and in Figure 2

TABLE 3.
THE AMOUNT OF THE WASTE FORMED IN THE MUNICIPALITIES OF UTENA DISTRICT DURING 2005, 2006 AND 2010 – 2012, IN TONS. [7] [8]

Year/ Municipality	Anyksciai district	Ignalina district	Moletai district	Utena district	Visaginas city	Zarasai district
2005	9119,00	4300,00	5534,00	23007,20	6507,70	5000,00
2006	9289,60	6297,60	5754,90	19989,90	6211,40	5500,00
2010	5444,3	3677,88	5711,98	16127,2	5486,73	3941,04
2011	5406,06	3247,18	5887,36	17115,7	5508,46	3685,5
2012	4345,3	3087,48	5059,48	30772,71	4940,52	3328,36

As it is obvious from the table and the picture, the total amount of the mixed waste has gradually decreased, except for Utena district. Besides, the tendencies in changes are different and uneven in different regions. Because the quantities of the waste are usually related to the population size and the industry development, so the provided data could partially correspond this tendency.

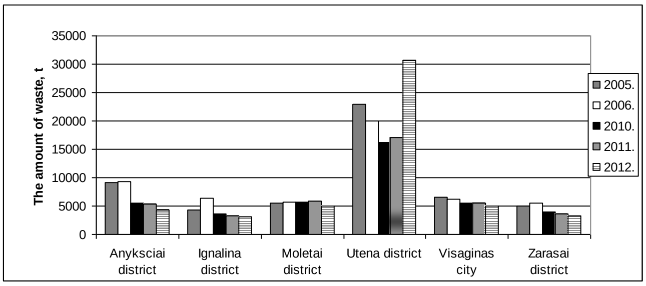

Figure 2. The amount of the waste formed in the municipalities of Utena district during 2005, 2006 and 2010 – 2012, in tons.

The growth of the waste quantity for one resident is obvious not only in the world but in Lithuania, too. After evaluating the growth of the sorted waste quantities, the opportunities to drop the waste off and be paid for it, Utena district is not regarded as exceptional.

42 018 tons of municipal waste were formed in Utena region in 2006, it is 240 kilograms for one resident a year, which is significantly less than the average in Lithuania because the annual waste amount for one resident in Lithuania is 392 kilograms. The quantity of the mixed municipal waste, which is collected from the regional companies and organisations, is included in this amount. The industrial waste, separately collected recyclables, the bulky waste, the packaging waste, the construction and demolition waste and the sewage sludge from the water treatment plants are not included in this amount. [7]

IV QUANTITIES OF HAZARDOUS WASTE

In Lithuanian industry section about 4,3 million tons of waste were formed in 2006, 111 thousand tons of which were hazardous waste. In 2007 about 4,4 million tons of waste were formed in industry section and about 105 thousand tons of them were hazardous waste, in 2008 there were 4,4 million tons of waste, 109 thousand tons of which were hazardous waste, in 2009 – 3,8 million tons of waste were formed and about 103 thousand tons of them were hazardous waste. The hazardous waste in Lithuania are managed by the hazardous waste management companies. In 2006, 34 companies used the hazardous waste, in 2007 – 23 companies, in 2008 – 19 companies, in 2009 – 18 companies. [5]

According to Waste Management Act, article 18, 1. the hazardous waste can not be diluted and mixed with other waste or materials during the processes of formation, sorting, storage, transportation, use, and disposal. 2. The hazardous waste can be mixed with other waste or materials only in the company of the hazardous waste use or disposal, if it is required by the hazardous wastes technical regulation. [8]

As the hazardous waste can not be disposed together with the mixed waste, the bulky and hazardous waste receiving and temporary storage sites were engineered in all the municipalities. Various waste are accumulated there: the bulky waste, waste containing asbestos, mixed construction and demolition waste, plastics, plastic packaging, textiles, paper and cardboard, glass packaging, glass, wood, metal, metal packaging, discarded electrical and electronic equipment, fluorescent lamps, oil filters, agrochemical waste, rubber waste, packages containing hazardous chemical substances, used oil, soil with hazardous chemicals, medicines, batteries and accumulators, discarded equipment containing chlorofluorocarbons, absorbents, cloths contaminated with chemicals and others. Figure 3 shows the total amounts of such waste that are accepted in the bulky and hazardous waste receiving and temporary storage sites in Utena region. [8]

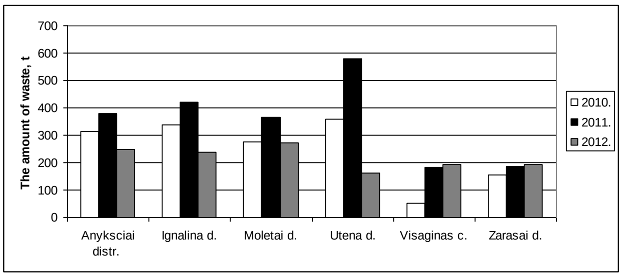

Fig. 3. Waste quantities in the bulky and hazardous waste receiving and temporary storage sites.

The picture shows, that the biggest quantities of the bulky, packaging and hazardous waste are in Utena city – the centre of industry and the district having the biggest population. There are visible signs of waste reduction in four sites in 2012, and there are two possible combined reasons for that – in these municipalities the information about the waste recycling importance was spread earlier and in a more intense way, and because the resident earlier did not know were to drop off the accumulated waste, they were dropped off in 2010 – 2011, while in 2012 only the newly formed waste were dropped off; as the society will become more conscious and the companies will install the new ISO systems, the quantities of such waste will gradually decrease in Lithuania, as well as in Visaginas city and the municipalities of Zarasai.

Because not all the waste accepted in the bulky and hazardous waste receiving and temporary storage sites are hazardous, it is important to identify the quantity of hazardous waste and to compare it with the total amount. Fig.4 shows the quantity of hazardous waste (tons) in Utena comparing with the total amount of waste and the quantity of non-hazardous waste accumulated in the bulky and hazardous waste receiving and temporary storage site in Utena.

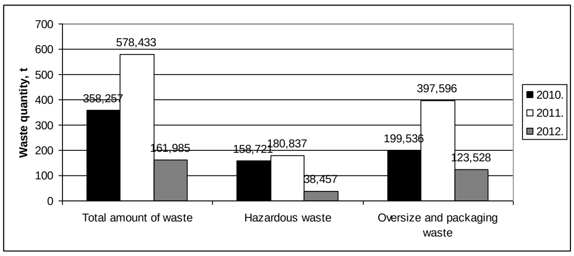

Fig. 4. Waste quantities in the bulky and hazardous waste receiving and temporary storage site in Utena.

It is visible that hazardous waste quantities are less comparing to the quantities of other waste accepted in the site and makes up significantly less than the half of the total amount of waste.

Table 4 shows the hazardous waste quantities, accepted in the bulky and hazardous waste receiving and temporary storage site in Utena regional waste management centre, which are grouped according to the waste lists approved in the replacement of the Environment Minister of the Republic of Lithuania December 30, 2003 No.722 decree About the Environment Minister of the Republic of Lithuania decree July 14, 1999 No.217 “about the approval of the waste management rules” [3] and in EU directive 2000/532/EC.[4].

As it is shown in the table, wide variety of hazardous waste are accepted and the quantities are very different – from very small to relatively big ones, and some kinds of the waste are dropped off not every year. Construction materials containing asbestos are distinctive in big quantities, the majority of these waste are made up by old asbestos slate.

TABLE 4.
THE HAZARDOUS WASTE QUANTITIES IN TONS IN THE BULKY AND HAZARDOUS WASTE RECEIVING AND TEMPORARY STORAGE SITE IN UTENA REGIONAL WASTE MANAGEMENT CENTRE [3] [4] [6]

Waste code	Waste title	2010 m.	2011 m.	2012 m.
02 01 08*	agrochemical waste containing dangerous substances	0,26	0	0
06 04 04*	wastes containing mercury	0	0,032	0
13 02 06*	syntheticengine, gear and lubricating oils	0,07	0	0
13 02 08*	other engine, gear and lubricating oils	0	0	0,08
13 05 07*	oily water from oil/water separators	6,174	5	0
15 02 02*	absorbents, filter materials (including oil filters not otherwise specified), wiping cloths, protective clothing contaminated by dangerous substances	0,04	0,03	0
15 01 10*	packaging containing residues of or contaminated by dangerous substances	0,006	0,01	0
15 01 11*	metallic packaging	0	0	0,017
16 01 07*	oil filters	0,018	0	0,017
17 05 03*	soil and stones containing dangerous substances	0,113	0	0
17 06 05*	construction materials containing asbestos	152,04	172,9	34,92
20 01 21*	fluorescent tubes and other mercury-containing waste	0	0,056	0,034
20 01 23*	discarded equipment containing chlorofluorocarbons	0	1,666	1,229
20 01 33*	batteries and accumulators, unsorted batteries and accumulator containing these batteries	0	0	0,023
20 01 35*	discarded electrical and electronic equipment	0	1,143	2,137

A large part of the rural residents changes their roofing receiving the support from the Lithuanian Rural Development program for 2007 – 2013 and the rules of publicity of the provided support, approved by the decree of the Agriculture Minister of the Republic of Lithuania April 26, 2007, No. 3D-191.

So, using the partial funding, while improving their living conditions, the residents increased the amount of hazardous waste.

IV HAZARDOUS WASTE ANALYSIS AMONG THE MIXED MUNICIPAL WASTE

According to the decree of the Environment Minister of the Republic of Lithuania, No.D1-661 31-08-2011 “About the content determination of the mixed municipal waste disposed at the regional landfills of non-hazardous waste and the approval of the assessment of procedure of the municipal biodegradable waste quantity in those landfills” at Utena regional non-hazardous waste landfill (address: Mockenai village, Utena parish, Utena district). The works of the determination of the mixed municipal waste content were carried out in spring, summer and autumn of 2012 and in winter of 2013, and they will be carried out in spring, summer and autumn (4 times a year), in order to find out the municipal waste content change, disposed in the landfill, during the different seasons. [6]

In order to determine the content of the mixed municipal waste in each municipality, random garbage trucks were chosen from Utena district, Anyksciai district, Ignalina district, Moletai district, Zarasai district and Visaginas municipalities. The carried out works were monitored by the representatives of Utena region environment protection department, Utena region municipalities and the administrators of the municipal waste management system established by the municipalities.

While carrying out January 2012 – 2013 analysis of the mixed waste, the waste amounts in tons were determined and calculated into per cents. It is surprising, that the conditions for waste sorting in Lithuania exist for several years now, but a large part of the mixed waste is made up of paper (1 – 12,14%), if the paper quantity up to 2% is acceptable, so the bigger quantities show that the people are not interested in sorting the easily sorted waste. The plastic waste, including packages, in the total amount of the mixed waste make up 1,47 – 18,33%. The metallic waste, including packages, in the total amount of the mixed waste make up 0,59 – 6,47%. The glass waste, including packages, make up 1,18 – 12,06%. A large quantity of these packages in the amount of the mixed waste can be justified because the packages have to be washed before sorting and that has some disadvantages, not all the packages can be thrown away to the containers but the existing amount of unsorted wastes is too big. A large amount, up to 15%, of food waste is very surprising. There is no tendency that more waste of some particular kind is thrown away in some particular district. It is difficult to notice such tendencies during a year from four random garbage trucks from the district. The observed amount of particular waste (e.g. plastics) during one season is the smallest while during the other season it is the biggest, although the waste were taken from the same municipality. [6]

While preparing the regional waste management systems in 2007, it was also important to evaluate the content of the municipal waste. It was important to determine whether it would be useful to sort the waste. Table 5 shows the content of the municipal waste (kg/resident/year) in 2007.

TABLE 5.
THE CONTENT OF THE MUNICIPAL WASTE (KG/RESIDENT/YEAR) 2007. [7]

Fraction	Amount, %
Plastics	9 %
Paper/cardboard	14 %
Glass	9 %
Metal	3 %
Textile	4 %
Biodegradable (kitchen and green) waste	42 %
Combined packaging	2 %
Construction and demolition waste	4 %
Hazardous waste	2 %
Other waste (leather, rubber, wood, and others)	11 %
Total	100 %

After comparing the information of 2007 and 2012, it is noticeable that although the conditions for waste sorting exist, yet the proportions of the waste quantities remain similar.

For the analysis of the hazardous waste it is important to evaluate the quantity of the hazardous waste in the total amount of the mixed wastes at Utena regional landfill.

In Lithuania people are regularly informed about the importance of the waste sorting, about the danger that is caused by the hazardous waste being deposited in landfill. The batteries can be left in the majority of the shopping centres for a few years. It is financially worth to drop off old accumulators and electrical household appliances that are bought at the branches of the companies collecting recyclables which are located in all the municipalities since 2012. The contests of electronic waste and batteries collection are organised at schools. The residents can bring such waste to the temporary storage sites for free. Yet, some of such waste are still being brought to the landfills of non-hazardous waste.

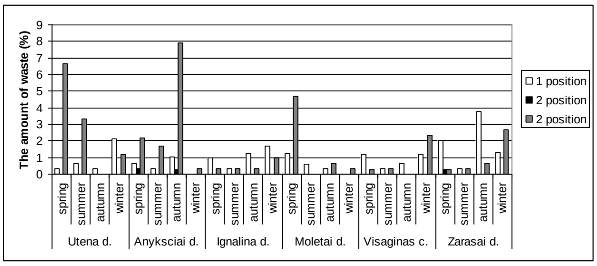

Fig. 5. The quantities of the hazardous waste among the mixed waste taken in at Utena Regional landfill.

For this analysis the most important thing is to evaluate the quantity of the hazardous waste among the mixed waste. During the analysis the hazardous waste were divided into 3 groups: 1) Electrical and electronic waste that were brought to the regional non-hazardous waste landfill at random, 2) Batteries and accumulators that were brought to the regional non-hazardous waste landfill at random, 3) Other hazardous waste that were brought to the regional non-hazardous waste landfill at random.

As it is shown in Picture 5, basically there are no batteries and accumulators or they make up less than 0,5%. The larger amounts are only of that hazardous waste, which the residents can not throw away to the containers or to drop off close to home. But even these amounts are not regular in the same district in all four times. So, the increase of the hazardous waste up to 8 % in one garbage truck could be regarded as a coincidence, rather than the rule of the district. But the amounts of the hazardous waste up to 3 % can already be regarded as a steady rate.

V CONCLUSIONS

The municipalities of Utena region should save its uniqueness, attractiveness to tourists and clean nature.

One of the components of clean nature (environment) is a small quantity of waste that should be managed safely. There should be not much waste formed because of the economic activities in the region. Especially those waste that are deposited.

The Region waste management systems were created in all the regions in Lithuania. The amount of waste depends on the industry development, the population change and the consumption growth. The total amount of the mixed waste has gradually decreased, except for Utena region. After comparing the information about the proportions of collected waste in 2007 and in 2012, it is noticeable that although the conditions for waste sorting exist, yet the proportions of the waste quantities remain similar.

The bulky and hazardous waste receiving and temporary storage sites are in all the municipalities. In Utena region, the biggest quantities of the bulky, packaging and hazardous waste are in Utena city – the centre of industry and the district having the biggest population. The quantities of the hazardous waste accepted in the region are much smaller than the quantities of other waste accepted in the site and make up significantly less than half of the total waste amount. A large variety of hazardous waste is accepted in the sites and their quantities are very different. The construction materials containing asbestos are distinctive in big quantities, the majority of these waste are made up by old asbestos slates.

Little quantities of the hazardous waste are still being brought to the mixed waste landfills. There are basically no batteries and accumulators or they make up less than 0,5%. The larger amounts are only of that hazardous waste, which the residents can not throw away to the containers or to drop off close to home.

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The System of Lithuanian Protected Territories from Environment Conservation Point of View

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***Abstract*. The article analyses the system of Lithuanian protected territories as well as their types form environment conservation point of view. The system of protected territories of LR includes the following types of areas: 6 state reserves, 1 biosphere reserve, 396 strict reserves, 5 national parks, 30 regional parks, 29 biosphere polygons and 3 recuperation plots. The system of protected territories, the order of establishment, management and the legal basics of protection of protected territories is determined by the law of protected areas of LR that was approved in 1993. The purpose of reserves is to preserve unique landscape complexes, their biota gene pool, to organize scientific research and observation, to promote natural and cultural values. The aims of the establishment of Lithuanian national and regional parks are not only to preserve naturally and culturally valuable landscape but also to support ethno cultural traditions of Lithuanian regions and to provide conditions for recreation. The purpose of strict reserves is to preserve the complexes of natural and cultural heritage or separate landscape elements, plant and animal species, to secure landscape diversity and ecological balance. Live and inanimate natural monuments are preserved naturally for scientific, cultural, educational and aesthetic needs. The purpose of biosphere polygons is to preserve bird species by assuring favorable conditions, to perform the monitoring of protected species, scientific research, etc. The aim of the recuperation plots is to restore natural resources. The system of Lithuanian legal acts allows applying such limitations that are necessary to preserve existing values in every protected territory.**

***Keywords*: protected natural territories, reserves, strict reserves, national and regional parks, natural monuments, biosphere polygons, recuperation plots.**

I INTRODUCTION

Due to the development of industry, transport, agriculture and other economic activities as well as the impact of urbanization country landscape is also undergoing significant changes; therefore, different protected territories have been established.

Environmental conservation traditions in Lithuania are very old. Sacred forests situated near the river Nevėžis were mentioned in Salyno pact in 1398. Since 1420 cuttings of old oaks were prohibited in Lithuania. The Wallach reform of 1557 identified the order of forest fellings, hunting, mushroom and berry picking. During the Soviet period (in 1959) the environment protection law of Lithuania SSR was passed. After the restoration of independence the law of protected territories of the Lithuanian Republic was passed in 1993 [2].

Exceptional character of protected territories as the object of used and protection is shown by the peculiarities of its protection regime that are determined by the specifics of their aim and functions. [3]. The aim of protected territories is complex: the territories are established in order to preserve not only natural, but also cultural-historical landscape and its objects. They should provide conditions for the organization of recreational, scientific research, environment observation activities.

Every country creates its unique system of protected territories. In this process Lithuania has chosen an integrated approach, i.e. integrated protection of natural and cultural heritage when both animate and inanimate natural values are preserved.

Big changes in the system of protected territories take place because of the obligations of Lithuania to the European Union to establish the network of protected territories „Natura 2000“by the year 2015.

The system of protected territories is not stagnant; the network is constantly reviewed and supplemented.

Aim: To analyze the structure, types and functions of the system of Lithuanian protected territories from the environment conservation point of view.

II MATERIALS AND METHODS

Work methods:

1. Analysis of scientific references.
2. Statistic data analysis.
3. Analysis of the use and legal protection regulation of protected territories.

Work object: The types of the Lithuanian protected areas: reserves, national and regional parks, strict reserves, biosphere polygons, recuperation plots.

III RESULTS

Protected territories are dry land and (or) water areas that have approved scientific, ecological, cultural and other value and where special protection and use regime has been established [1].

In Lithuania the system of protected territories has been started to be created in 1937 when following the initiative of T. Ivanauskas the Žuvintas reserve was established. Since 1960 quite a big number of strict reserves have been established. In 1974 the first Lithuanian national park has been founded. After the restoration of Lithuanian independence (in 1992) a lot of protected areas, especially regional parks have been established. Preservation of values is not possible without legal foundation that is why the legal base for protected territory system, its establishment, management and protection is defined by the law of protected areas of LR approved in Lithuania in 1993. The system of protected territories of LR includes the following types:

6 state reserves,
1 biosphere reserve,
396 strict reserves,
5 national parks,
30 regional parks,
29 biosphere polygons,
3 recuperation plots.

Lithuanian protected territories take up about 14 % of the country territory area [5]. The distribution of the types of protected territories according to the area is the following: regional parks – 44 %., biosphere polygon – 23 %., strict reserves– 15 %., national parks – 14 %., reserves – 2 % and recuperation plots – 0,1 %[1].

Reserves are protected areas established for the protection of extremely valuable natural or cultural territorial complexes as well as for scientific research, maintenance of natural flow of nature processes or the authenticity of cultural values, and the propagation of the protection of territorial complexes of natural and cultural heritage [5].

Reserves are divided into natural (for the preservation of extremely valuable natural landscape complexes) and cultural (for the preservation of extremely valuable cultural landscape complexes).

The characteristics of reserves are presented in Table 1.

TABLE 1

CHARACTERISTICS OF LITHUANIAN RESERVES (MARGELIENĖ, 2013)

Reserve	Category	Year of establishment	Area, ha	Environmental characteristics
Čepkeliai	Natural	1975	11212	It is the moor and forest complex of peculiar natural value which has not been damaged by human activity. The peat-moss swamps contain dwarf pines; Eurasian curlews, European Golden Plovers and wood sandpipers brood in open areas, cranberries grow their berries. Upland moor contains over 20 small lakes. In the Southern part the moor changes into the lowland moor, sedge wet meadows that give the origin to Musteika rivulet Katra rivulet flows along the Southern boundary of the reserve. There are a lot of rare species of plants, white-tailed eagles, ospreys, black storks, little eagles, Western capercaillies as well as black grouse brood here. It contains the largest population of cranes (up to 25 pairs), moose, wolves, and lynxes.
Kamanai	Natural	1979	3938	The biggest part of the reserve is occupied by a moor with numerous swamps and lakelets (up to 120). Several decades ago the moor was drained. This had a significant impact on it and the plants growing there. At the moment the reserve water regime has been restored, nature processes are naturalizing. The most impressive lakelets are Nimfėjai and Salų as well as Kamanų lake, the area of which is 6 ha. The moor is surrounded by mixed forests and shady spruce forests. A lot of rare species of plants are found in the reserve. Cypripedium calceolus are abundant here. European Golden Plovers, black storks, black grouse brood here. Wolves and lynxes live here.
Viešvilė	Natural	1991	3216	Reserve is composed of Artosios and Gličio moors with Buveinių and Gličio lakes, Viešvilės rivulet and impressive part of Karšuva forest. Only about15 km long Viešvilės rivulet outflows from boggy Buveinių lakelet and flows into the river Nemunas. The rivulet flows through moors, meadows and shadowy mixed forests. It is the home for trouts and otters. Away from the rivulet and the moor there are nice pine forests. European Golden Plovers, cranes brood in the reserve moors, little eagles, stock doves brood in the forests. There are wolves, moose, and lynxes.

Kernavė	Cultural	1989	199	Lithuania has the only archeological and historical museum-reserve in Kernavė. It was established in 1989 in Širvintai dist. Its area is 196,2 ha. Reserve was established close to the river Neris, in Pajauta valley. It has a complex of 5 mounds as well as the places that have a lot of archeological findings that are important for Lithuanian history. Kernavė was mentioned in written sources in 1279. Following archeological findings it was identified that the first inhabitants settled down in this place in IX–VIII centuries BC. In XII century Kernavė became the town, the centre of which was 4 mounds.. Altar mound contained duke estate, the others – protective castles. In the base of mounds the town was created with the quarters of craftsmen and merchants. After the Teutonic Order attacks in 1390 the town was abandoned; it was buried and preserved for future research by the silt of the river Neris.
Vilnius castles	Cultural	2002	360	State cultural reserve of Vilnius castles is the heart of Vilnius old town. Archeological values: Vilnius mound (A1961 K) – which is called Kreivuoju (Crooked) mound, Plikuoju (Naked) mound, the mound of Three Crosses (A1961 K1) together with low castles is also called Bekešo mound (A1961 K2), Gediminas grave mound (A1961 K3) and Stalo (Table) mound (A1961 K4). The area of the territory is 33,87 ha. Vilnius castle land (A1960) is called Gediminas castle mound, Upper castle, Lower castle. The area of the territory is 18,70 ha. Architectural values: the complex of Arch cathedral basilica, Lower and Upper castle and their remnants (G205 K). Building complex (G390 K): Palace, called Kirdiejų (G390 K1), Barboros Radvilaitės, Office (G390 K2), cart shed (G390 K3), fence (G390 K4). Other values: The monument of Three Crosses (D R1332), sculptural composition „Lithuanian ballad" (D V3557).
Dubrava	Reserve area	1994	120	The purpose is to preserve rare forest plantings, productive coniferous plantations and valuable plant communities. Very valuable natural high moor.
Žuvintas	Biosphere	2002	18493	Žuvintas biosphere reserve territory contains a lot of valuable biotypes. Active high moors, intermediate moors, low moors, high moor pine stands, wet black alder stands as well as eutrophic Žuvintas lake can be found in Žuvintas natural reserve. Žuvintas is the most famous because of birds. Since 1980 227 bird species were observed in Žuvintas biosphere reserve. 153 species have brooded here. 108 of mosses, 105 algae, 107 fungi and more than 600 species of higher plants are found here. About 2000 species of insects, 5 reptiles and 10 recorded, over 40 species of mammals were found. 22 species of fish are found in Žuvintas lake.

National parks are the territories protected by Lithuanian state with specific landscape, unique settlements, and cultural values [5]. Sightseeing tourism is promoted in national parks and the attempt to introduce visitors to natural and cultural values has been made. Human activity limited in these areas, it carefully combined with environmental conservation. Lithuania has five national parks: Aukštaitija, Žemaitija, Trakai historical, Dzūkija and Kuršių Nerija (fig 1.).

Fig. 1. Lithuanian national parks (www.lvmi.lt)

Characteristics of the Lithuanian national parks are presented in Table 2.

TABLE 2.

CHARACTERISTICS OF LITHUANIAN NATIONAL PARKS (MARGELIENĖ, 2013)

National park	Year of establishment	Area, ha	Conservation characteristics
Aukštaitija	1974	40570	120 lakes and 70 rivers are scattered among the woods and hills. Šilininkų ridge is situated here. 50 % of the territory is occupied by forests. Moors are concentrated in the hollows. 900 species of plants grow there; 60 of them are included into Lithuanian Red List (*Cypripedium calceolus*, *Liparis loeselii*, *Saxifraga hirculus*, etc.). About 200 bird species have been found in the park. Ažvinčių old forest and Minčios forest are of a special value.
Dzūkija	1991	55920	This is the biggest and the most forested national park in Lithuania. Two thirds of the territory is located in the sandy plain of the southeast of Lithuania. There are lots of rivers – Merkys, Ūla, Grūda etc. 50 lakes. Surroundings of Merkinė are especially spectacular. Almost all territory of the park is overgrown by forests. Lichen Scots pine and whortleberry pine forests dominate. 750 species of higher plants, 300 species of fungi, 40 species of mammals and 150 species of birds are found here.
Kuršių nerija	1991	26464	The aim is to preserve the grand ridge of Kuršių Nerija, old dunes near Juodkrantė, grey dunes in Agila-Naglis strip. The peak of the majority dunes is 60 m. This landscape is the youngest in Lithuania. The dry land occupies 50 % of park territory, the remaining part is the Baltic sea and Curonian Lagoon. About 70 % of dry land is occupied by forests dominated by pines. 1000 species of rare and interesting plants such as *Eryngium maritimum*, *Erica tetralix*, *Gypsophila paniculata*, etc. grow there. There is a huge variety of birds.
Trakai historical	1991	8200	This is the smallest national park. Almost half of the territory is overgrown by forests and 16 % of the park is occupied by water. Park territory is connected by the system of 30 lakes – Galvės, Skaisčio, Bernardinų etc. Coregonus albula live in the lakes. The castles of Trakai Island and Peninsula are situated there. There are a lot of black storks, Montagu's Harriers, Corncrakes and other species of birds. The highest place of the park is Nuobariškiai hill.
Žemaitija	1991	21720	Plateliai lakes and their surrounding natural complex is a very important part of the park. Forests occupy almost half of the park territory, spruce forests dominate. 26 lakes are located in the park. The biggest of them is Plateliai lake (1200 ha). The biggest river is Babrungas. 60 plant species included into Lithuanian Red List grow there. 180 species of birds, 50 species of mammals are discovered there. Rare insects such as clouded apollos, the Old World Swallowtails, the Large Coppers are found there. Different species of bats are found in the old park trees.

The purpose of establishing Lithuanian national and regional parks is not only to preserve naturally and culturally valuable andscape, but also to support Lithuanian regional ethno cultural traditions, to provide conditions for recreation [1].

Regional parks are protected territories that have been established to protect the landscape important from natural, cultural and recreational point of view as well as to regulate their recreational and economic use. Lithuania has 30 regional parks (one of them is historical), the area of which is 439842 ha. Regional parks were established in 1992. They are divided into four groups: sea and large water reservoirs (Kaunas reservoir), river valleys of different sizes (Dubysa, Venta, Nemunas loops, etc.), forested lakes and hills (Labanoras, Verkiai, Sartai et..) as well as plateaus and plains (Biržai, Tytuvėnai, Žagarė) [6].

TABLE 3.

CHARACTERISTICS OF LITHUANIAN REGIONAL PARKS (MARGELIENĖ, 2013)

Regional park	Area, ha	The most important park values
Anykščiai	16269	The park is famous for: The forest of Anykščiai, Puntukas stone, „Queen’s swamp“, etc.
Asveja	11589	Park focus – Asveja lake which is the longest in Lithuania
Aukštadvaris	15350	The standard of Lithuanian flora – Mergiškiai forest, where linden trees grow together with oak, maple and a mixture of hornbeam trees.
Biržai	14659	Unique landscape of Lithuanian sinkhole region.
Dieveniškiai historical	8747	Culturally valuable relics of old Baltic, Dzūkija and Aukštaitija ethno culture.
Dubysa	10571	Dubysa – one of the biggest and the most beautiful Lithuanian rivers.
Gražutė	29700	The landscape of Šventoji source full of lakes (70 lakes), rivers.
Kaunas reservoir	10221	This artificial water pond created by humans with impressive bank uncovering of 20-40 m.
Krekenava	11968	Protected river valleys of Nevėžis, Upytė, Liaudė, Vešėta and Linkava.
Kurtuvėnai	15090	90 % of the park is occupied by forests. About 100 Svilė sources of different size well up in Venta-Dubysa old valley.
Labanoras	55344	It is the biggest Lithuanian regional park in Lithuania. There are 260 lakes, Kanis, Snieginis and other moors.

Meteliai	17729	Hornbeams are preserved in Giraitė forest. There are big lakes: Dusia, Metelys and Obelija.
Nemunas delta	28870	It is a low flat plain, made from alluvial silt and lined by rivers and rivulets. It has Ventė cape, Kniaupas bay, Galzdonai islands, etc.
Nemunas loops	25171	Meandrous Nemunas valley with high, steep slopes, lined by rivulet valleys and washes. The biggest loops: Punia, Balbieriškis, Prienai and Birštonas.
Neris	10588	The landscape complex of the Northern edge of Dzūkija highland.
Pagramantis	14420	The landscape of the confluence valley of Akmena and Jūra rivers and forests
Seaside	5070	Unique formation – Dutch cap (ridge).
Panemuniai	11563	The towns of the park are famous because they are valuable from natural and cultural points of view.
Pavilniai	2153	The value of the landscape is determined by the relief marked by the differences up to 100 m. Ribiškis wash (hills) is especially unique.
Rambynas	4786	It is the smallest regional park in Lithuania. Its values: the landscape of Nemunas bends and Rambynas mound.
Salantai	13630	Natural heart of the park includes the valleys of Minija, Salantas, Bartuva and other rivers.
Sartai	12547	Sartai lake is the eighth lake in size in Lithuania; it has 7 islands. The line of the lake coast is 80 km.
Sirvėna	8735	Forests occupy 40 % of the territory. Mixed forests dominate. There are 30 lakes.
Tytuvėnai	10152	Unique heritage of the glacial period is Rūža or Velniakelis (Devil's Road), where a stone belt is extended for several kilometers.
Varniai	33800	The park contains a lot of mounds such as Medvėgalis, Šatrija, Sprūdė and others. The biggest lake is Lūkstas – over 1000 ha.
Veisėjai	12200	There are a lot of narrow and long lakes reminding about rivers.
Venta	10630	There are a lot of rivers, no lakes. The river Venta is abundant of fluvial fish – spined loach and European bitterling
Verkiai	2673	The adornment of the park is five green lakes situated among the hills overgrown by pine and spruce forests. Their underground waters are very carbonated.
Vištytis	10833	Vištytis lake. Mature broadleaf forests, oak forests with hornbeam and linden are especially valuable.
Žagarė	4784	The most valuable is the structure of Žagarė town.

Strict reserves are protected territories that have been established to protect scientifically and cognitively valuable natural and cultural places as well as their complexes and objects, for the preservation of landscape biological and genetic diversity unimposing economic activity [5]. The purpose of strict reserves is to preserve the complexes of natural and cultural heritage or separate landscape elements, species of plants and animals, to ascertain landscape diversity as well as ecological balance. In Lithuania the network of strict reserves has been started to form in 1960, and the last strict reserves were finished to be established in 1997. At the moment there are 396 strict reserves in Lithuania. Depending on protected values strict reserves can be of different kinds (table 4).

TABLE 4.

CHARACTERISTICS OF STRICT RESERVES (MARGELIENĖ, 2013)

Types of strict reserves	Number	Protected values
State strict reserves - 285		
Landscape	48	Landscape heritage objects of a special value
Geological	10	Deep earth structures, exposures, boulders and sinkholes
Geomorphologic	40	Variety of relief forms
Hydrographic	34	Structure of rivers, rivulets and lakes
Pedologic	11	Soil structure
Botanical	35	Types and communities of plants, fungi, biotopes
Botanical-zoological	29	Plant types and communities as well as types of animals
Zoological:		
teriologicalal	1	Bats
ornithological	10	Birds and their breeding - grounds
herpetological	3	European pond turtles
ichtiological	9	Fish and their resources
entomological	6	Extinct insects and their habitats
telmological	51	Moors
talasological	1	Valuable sea ecosystems
Municipality strict reserves - 111		

Biosphere polygons have been established for the observation of national and regional environment in the territories of special geo ecological importance.

They have been established in Lithuania since 2004 to 2006. There are 26 biosphere polygons; their total area is 188777 ha. According to their nature they can be complex or specialized (hydrologic, zoological, etc.). Their purpose is to preserve extinct bird species by assuring favourable conditions, to carry out the monitoring of protected species as well as scientific research, etc. [3]. The most valuable state protected objects of natural heritage are declared as natural monuments.

TABLE 5.

CHARACTERISTICS OF NATURAL MONUMENTS (MARGELIENĖ, 2013)

Types of natural monuments	Number
Stones	47
Exposures	22
Sinkholes	3
Botanical objects (oak woods, linden, ash woods, etc)	28
Geomorphologic objects (hills, dunes, etc.)	29
Hydrographic objects (lakes, peninsulas, islands, etc.)	13
Hydro geological objects (springs, sources)	19

Recuperation plots are protected areas for the protection, profusion and limited use of natural resources and their complexes emasculated by human activity. Their purpose is to restore natural resources; they are given the „Natura 2000“territory status which is the network of protected territories of European importance consisting of two directives (Habitations and Birds). Rich Lithuanian biological diversity is very important for ecological EU network „Natura 2000“(Western taiga habitation in Prienai forest, etc.) [6]. Regarding the peculiarities of natural resources protected natural plots of phyto resources (trees, berries, mushrooms, herbs), zoo resources (animal biotopes) and complex resources (recuperation moors as well as underground water ponds) have been established [3].

Some protected territories of Lithuania are important on international level. Čepkeliai, Kamanai and Viešvilė natural reserves as well as Žuvintas bio sphere reserve and the regional park of Nemunas delta were included into Convention on Wetlands, Ramsar, and the list of the wetland of international importance in 1993. Kuršių nerija, Trakai historical national park and Vilnius castle as well as Kernavė cultural reserve are included into the list of World heritage (UNESCO). Kuršių nerija national park, regional parks of Nemunas delta and the Seaside were included into the system of the Baltic Sea Protected Areas [2].

The system of Lithuanian legal acts allows applying such limitations that are necessary to preserve existing values in every protected territory (Table 6).

The activity of protected areas is coordinated by the state service of protected territories at the Ministry of Environment.

TABLE 6.

PROTECTION REGIME OF THE PROTECTED AREAS (MARGELIENĖ, 2013)

Protected territory type	Forbidden activity
Reserves	The change or damage to relief forms; the search and mining of minerals; construction of buildings, not related to the reserve activity; construction of roads, mains; use of chemicals or other types of environmental pollutants; change in hydrological regime; fishing and hunting; plant and animal introductions; any other activity that is considered harmful for the protected ecosystem.
Strict reserves	Commercial - economical, construction, recreational and other activity that is harmful to the environment; construction of industrial objects as well as stationary recreational institutions; exploitation of minerals; giving land to gardening communities, construction of individual summerhouses; land drainage; building or deepening of riverbeds; soil destruction; forestation of glades, natural meadows and pastures; hunting of protected species of animals, introduction of new animal species; use of pesticides.
Natural objects	Any activity that can damage natural values: to damage or to change relief; construction of mechanisms that are not related to the heritage exploitation or management, etc.
National and regional parks	Installation of new mining mineral quarries; expansion or construction of industrial as well as waste management enterprises; building new communications; construction of big bird, game and animal farms; establishment of new enterprises; damage or changes in relief; changes in hydrological and hydrographic regime; giving land to gardening communities, construction of individual summerhouses; damage to natural and cultural monuments, etc.
Biosphere polygons	Certain protection regime is introduced into protective zones. For example, in the protective zone of a sinkhole region it is forbidden to use the sinkholes for rain and water drainage, to dump rubbish and waste, to cover them with soil, to mine peat, etc.
Recuperation plots	Mineral mining and exploitation, the use of land, forests and water are restricted.

III CONCLUSIONS

The investigation of scientific and legal documents as well as data revealed that different types of protected areas have been established in Lithuania. They include: 6 state reserves, 1 biosphere reserve, 396 strict reserves, 5 national parks, 30 regional parks, 29 biosphere polygons and 3 recuperation plots. The protected territories occupy about 14 % of the total country territory area. While analyzing the types of protected areas their environmental characteristics that represent unique landscaping and biological diversity values that are clearly different from those of unprotected territories were presented. The investigation revealed that the sufficient number of territories has been established. The size of the territories is also adequate which is ensures their preservation. The territories are located evenly what allows for their expansion for visiting. After the identification of the forbidden activities of protected areas protection regime it is possible to say that some problems may be encountered when ensuring the identified protection and use regime. The problems include the undergoing land reform, the regulation of private interests' conflict as well as the lack of legal acts. The protected territories are gradually becoming the part of environmental conservation.

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Climate Change and Fluctuations in the Karelian-Kola Region

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***Abstract*. In this work we consider the regularities of changes of climate and assessed the potential impact of these changes on some of the characteristics of the hydrological regime and biota water bodies of the North of the European territory of Russia from temperate latitudes to the Arctic. Within the annual course, variation of monthly air temperature values is irregular for different seasons, with most intensive warming in January and March. In summer, variations in air temperature are multidirectional. Variations in the thermal regime led, in its turn, to later ice cover formation and earlier ice-breakup resulted in the longer ice-free period. Data analysis revealed variations in the course of precipitation of warm and cold periods. Under distinguished increase of precipitation sums, a total number of days with precipitation was revealed to be equal to or lower than its climatic norm. The total precipitation amount increase occurred due to increasing frequency of rainfalls of 10 mm and more. In winter, the snow cover height exceeded the climatic norm. As the increase of annual sums of precipitation is compensated by a rise of evapotranspiration, any trend in the total river inflow into Lake Onego is absent.**

***Keywords* – air temperature, linear trend, precipitation, climate change.**

I INTRODUCTION

Long-term data from weather observations suggest that the global climate system has been changing since the beginning of the 20th century. Patterns in the ongoing change in the late 20th – early 21st centuries appear the most interesting. Detailed analysis of the regional climatic characteristics and study of the way natural systems respond to climate change based on representative observations would contribute to climate change mitigation efforts. In this paper, the climate of the Karelian-Kola region is characterized with regard to latest observation data. Multiyear means of meteorological elements were computed through year 2010.

II MATERIALS AND METHODS

The climatic system can be studied by a variety of methods and at various angles, for instance, using statistical methods, long-term observations data, by studying the physical processes that shape the climate, or through modeling. Identification of climate change is a process meant to demonstrate that the climate fluctuations we observe are statistically unusual or statistically significant. Hence, the first task for any climate change study would be a statistical description of available long-term series of observations, first of all instrument-based observations.

The source data for this study were series of mean daily and mean monthly values of the main meteorological indices according to observations at the weather stations in Karelia and the Murmansk Region in 1951-2011.

III RESULTS AND DISCUSSION

Mean annual air temperature in the Murmansk Region had a gradient from 0°C on the Barents Sea and White Sea coasts through -2°C in the central part of the Kola Peninsula and to -3-4°C in mountainous areas. The long-term mean annual air temperature in Karelia ranged from 0°C in northern districts to + 2.6…+ 2.8°C in the south of the Republic. Normal annual air temperature means were the highest at Lake Ladoga (+3.0°C at the Sortavala weather station and +3.3°C at the Valaam WS). The overall trend of mean annual air temperature throughout the Karelian-Kola region over the 20th century and in the first decade of the 21st century has been upward. Yet, the mean annual air temperature has not been growing consistently throughout the century: a temperature rise continuing since the beginning of the century was superseded in the 1950s by a cooling, which was followed in the 1980s by a new wave of warming. In nearly all years since 1989, annual air temperature means have been higher than the climatic norm as computed for the 1961-1990 period.

Mean annual air temperature has been rising unevenly across the territory. The highest linear trend coefficients for the period of 1951-2010 in Karelia came from the weather stations in southern parts of the republic, along Lake Ladoga shore: Olonets WS $+0.34^0$C/10 yrs., Sortavala WS $+0.3^0$C/10 yrs. In the central parts of Karelia the upward trend in mean annual air temperature was not so explicit: $+0.26…+0.27^0$C/10 yrs. The mean annual air temperature linear trend coefficients describing warming in the northern districts of Karelia were the lowest: ca. + 0.2^0C/10 yrs. Thus, the rate of rise in mean annual air temperature in the region in question increases gradually from higher to lower latitudes.

In the Murmansk Region, the linear trend coefficients in the period of 1951-2010 were $+0.13^0$C/10 in Kandalaksha, $+0.17^0$C/10 in Krasnoshchelje and Murmansk, $+0.19^0$C/10 in

Lovozero, + 0.25^{0}C/10 in Nickel'. According to the Finnish Meteorological Institute, mean annual air temperature deviations observed in Finland in 1990-2010 were also only positive. They were 0.5-1.5^{o}C.

A characteristic feature of nonstationary processes, such as air temperature change, is a continuing change of the mean. Hence, the mean (norm) should be regarded as a function of time. Table 1 shows the climatic norms of mean annual air temperature in Karelia for two standard climatic periods: 1931-1960 and 1961-1990, and the 1991-2010 means at different weather stations. Analyzing the values one can see that there has been no or very little deviation from the climatic norms in the former two climatic periods, whereas the mean annual air temperatures averaged over the late 20th – early 21st century period were 0.9-1.2^{o}C higher than the norm.

TABLE 1.

MEAN ANNUAL AIR TEMPERATURE

Weather station	Averaging time		
	1931-1960	1961-1990	1991-2010
Kalevala	0.5	0.3	1.3
Reboly	1.2	1.1	2.1
Padany	1.4	1.6	2.4
Segezha	1.4	1.3	2.2
Medvezhjegorsk	1.5	1.5	2.5
Petrozavodsk	2.2	2.4	3.3
Pudozh	2.2	2.1	2.9
Sortavala	3.0	3.0	4.0
Olonets	2.5	2.7	3.9

Within a year, the following patterns can be discerned in the change of mean monthly air temperatures (1951-2010) in Karelia. Warming has been the most intensive in March (+0.5 …+0.6 ^{0}C/10 yrs.) and January (from +0.3^{0}C/10 yrs. in northern to +0.6^{0}C/10 yrs. in southern districts). The temperature rise in February has also been significant, 0.4^{0}C/10 years, throughout the republic. In the period from May to December, July and August excluded, warming has evenly covered the whole study region. The August trend in northern and central Karelia has been for a cooling.

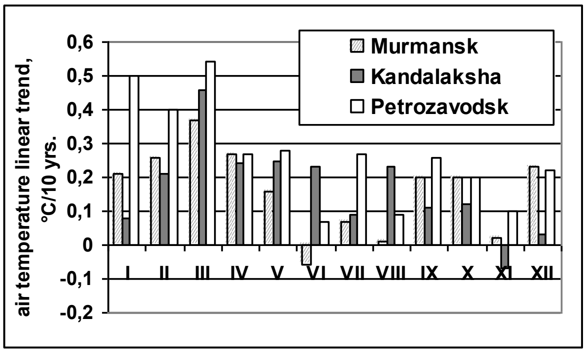

Fig.1. Coefficient of linear trend of air temperature (^{o}C/10 year) in the Karelian-Kola region, 1950-2010 y.

Similar trends have been observed in the Murmansk Region. The air temperature rise has been the most significant in March (+0.37…+0.54^{0}C/10 yrs.). For August, the mean monthly air temperature trend has also been negative. Also, negative linear trend coefficients have been obtained for the November air temperature series (Fig,1).

Changes in the temperature regime in the territory have caused a shift in the dates on which the climatic seasons begin and end. Computations show that the dates on which the air temperature steadied above or below 0, 5 and 10^{o}C in years 2000 - 2010 shifted relative to the multiyear means. The greatest deviation from the climatic norms is seen in the dates when the warm part of the year (above 0^{o}C) begins and ends. The cold period of the year began 5-23 days later than the long-term average date in Karelia, and 9-15 days later in the Murmansk Region. In years 2000-2010 the cold period ended 10-20 and 6-10 days earlier than the long-term average date in Karelia and the Kola Peninsula, respectively. With these deviations in the dates of the air temperature steady transition across 0^{o}C the duration of the warm period averaged over the stated time interval was 215- 225 days instead of the climatically normal 192-210 days in Karelia, and 180-200 days instead of 160-180 days in the Murmansk Region.

An essential meteorological element is precipitation. The estimates of change in precipitation volumes are however far less reliable than such estimates for the air temperature.

Average annual precipitation in Karelia, which belongs to the excessive precipitation zone, is 550-750 mm. Its volumes increase southwards. The distribution of precipitation is however much influenced by the orographic characteristics and the underlying surface, which distort the smooth precipitation trend. The precipitation distribution pattern in the Kola Peninsula is the following: the higher an area is positioned the greater the precipitation volumes there. Precipitation is the lowest (400—500 mm/a) in river valleys and flat areas. In areas with complex relief precipitation is distributed unevenly, amounting to 600—800 mm/a, and precipitation volumes on the tops of the highest mountain ranges (Khibiny and Lovozero tundras, Monche-tundra and Chuna-tundra) exceed 1000 mm/a. The air masses arriving from the mainland during the warm time of the year contain more moisture than in winter, and the precipitation volumes are therefore greater. Total precipitation in the summer months (July—August) is twice higher than that in the winter months (February—March) – a situation not typical of maritime climate.

Analyzing the deviations from the normal values of total annual precipitation (data averaged over the 1961-1990 period were considered the climatic norm) according to the measurements at weather stations in Karelia and the Murmansk Region one can draw the following conclusions. Before 1960, total measured annual precipitation had been much lower than the norm, the reason being measurement faults (Fig.2). Since 1960, the number of years with more precipitation than the norm has been nearly the same as the number of years with less than normal precipitation. Positive deviations from the norm have prevailed in total annual precipitation in the last decade.

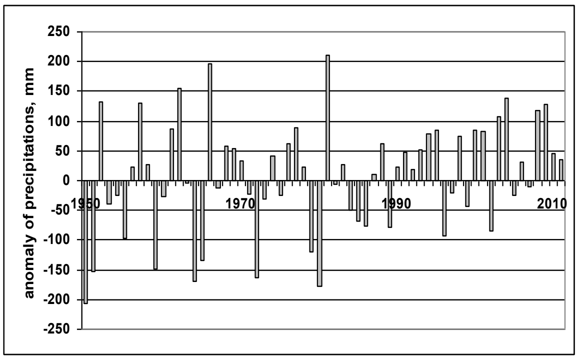

Fig.2. Anomaly of precipitations in Karelia (Petrozavodsk), 1950-2011 y.

In addition to the data about total precipitation, the annual number of days with precipitation can also provide important information. The total annual number of days with precipitation greater than 0.1 mm in Karelia is 193-212 days a year. Thus, precipitation occurs in the territory on more than a half of all days in a year. Comparing this information with averaged long-term data on the annual number of days with precipitation in the 1995-2010 period one can conclude the following. The amount of precipitation during this time period agreed with the norm or was 50-70 mm higher, whereas the total annual number of days with precipitation was mainly below the norm or at the normal level.

The total precipitation volume rose owing to the higher frequency of 10 mm and more of rainfall. Hence, rainfall in Karelia in 1995-2010 was more intensive than the long-term average, and the number of days with heavy rainfall exceeded the norm throughout the study region. More precipitation fell within fewer days.

A question of particular interest is how the snow cover regime may change in connection with the air temperature rise. Analysis of the data on the snow cover is based on the results of snow stake measurements in permanent sample plots. Data on the annual number of snow-covered days and snow depth (10-day averages) were taken into account. The snow cover duration in Karelia was 150-180 days on average. Persistent snow cover in the Murmansk Region usually forms in October, staying for an average of 220 days on the Khibiny and Chuna-tundra tops, and for 180 days in the rest of the territory. The average multiyear snow depth at the end of the winter is 70 cm in flat areas, and 40 cm on the Murman Coast, where snow is blown off by wind. The conclusion from comparing data from 1995-2008 observations in Karelia with the climatic norm is that the snow cover duration in the stated period was somewhat lower or in accord with the multiyear means. As regards 10-day means of the snow depth measured at permanent snow stakes, its values in 1995-2008 were higher than the climatic norm (Fig.3). The snow cover established in the 3rd ten days of October – 1st ten days of November, and its depth increased gradually to reach a maximum in the 1st-2nd ten days of March. By late April/early May the snow cover depth was no more than 1-6 cm.

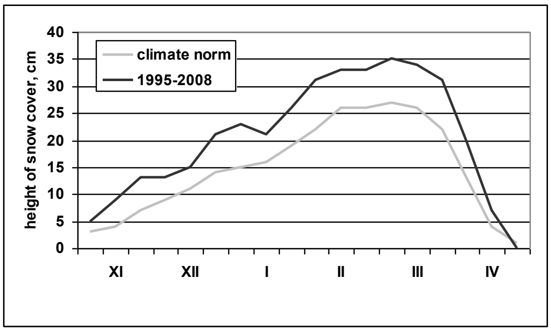

Fig.3. The average decade height of snow cover: climate norm and the average for 1995-2008 y. WS Petrozavodsk.

Under modern varying climatic conditions, evaluation of the water balance components for the river catchment areas is of timely importance. Analysis of variations and variability of the climatic and hydrological processes in the system Lake Onego – its watershed, which occupies a considerable part of Karelia and plays an important role in the socio-economical development of the region, is a strong prerequisite for successful definition of causes and scales of past and future changes in the water system.

Main features of variability and variations of climatic characteristics over and water balance components on the Lake Onego catchment area have been studied. For the period 1951-2010, the increase of annual air temperature, evapotranspiration, and precipitation sums is found to be pronounced. Significant variations in total river inflow are not detected. Intensity of the air temperature increase arises from high to lower latitudes.

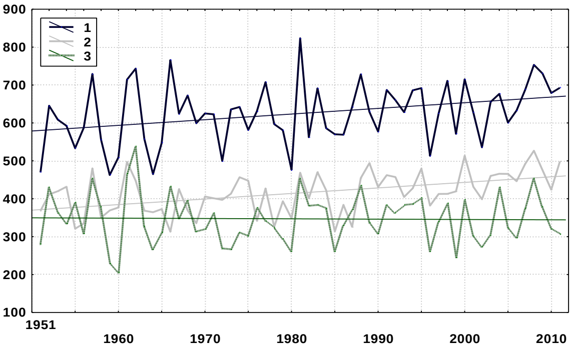

Fig.4. Annual sums of atmospheric precipitation (1), total evaporation from the catchment area (2), and annual depth of runoff from the Lake Onego watershed (3) in 1951-2011.

Within the annual course, variation of monthly air temperature values is irregular for different seasons, with most intensive warming in January and March. In summer, variations in air temperature are multidirectional. Variations in the thermal regime led, in its turn, to later ice cover formation and earlier ice-breakup resulted in the longer ice-free period (from 217 days in 1900`s to 227 days in 2000`s). During 2000-2011, water temperatures in Lake Onego were higher than its long-term value. Data analysis revealed variations in the course of precipitation of warm and cold periods. Under distinguished increase of precipitation sums, a total number of days with precipitation was revealed to be equal to or lower than its climatic norm. The total precipitation amount increase occurred due to increasing frequency of rainfalls of 10 mm and more. In winter, the snow cover height exceeded the climatic norm. As the increase of annual sums of precipitation (60-90 mm/60 years) is compensated by a rise of evapotranspiration (70-80 mm/60 years), any trend in the total river inflow into Lake Onego is absent (Fig. 4).

IV CONCLUSION

The study of the principal characteristics of the temperature regime in Karelia and the Murmansk Region in the second half of the 20th century and early 21st century using data from meteorological observations has brought about the following conclusions. Since 1989, mean annual air temperature has consistently been 1-2oC higher than the climatic norm. The rate of the mean annual air temperature rise showed a gradual upward trend from higher to lower latitudes. Warming has been the most intensive in the winter months. As the result, the onset dates of seasons shifted relative to the climatic norm. Analysis of changes in the precipitation volumes in the study region revealed an overall increase in total annual precipitation (50-150 mm/50 yrs.). In years 1995-2011, rainfall in Karelia and the Murmansk Region was more intensive than the long-term average, and the number of days with heavy rainfall was greater than the norm throughout the study area. More precipitation fell within fewer days. The above results indicate that the climatic indices of the study area fluctuate significantly.

A Review of Methods for Reduction of Polycyclic Aromatic Hydrocarbons from Waste Water and Flue Gases

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***Abstract*. This review describes methods which can be used for the reduction of the polycyclic aromatic hydrocarbon (PAH) emissions from wastewater and flue gases including principles of operation of the methods and studies of their effectiveness. There are discussed both methods, which nowadays are already used industrially, and their improvement opportunities as well as recent technological trends in this field. The methods have been classified into two main categories: flue gas treatment and wastewater treatment.**

Keywords **- polycyclic aromatic hydrocarbons, wastewater, flue gas, reduction.**

I INTRODUCTION

Polycyclic aromatic hydrocarbon compounds are class of complex organic compounds that contain two or more fused aromatic rings. These compounds are widely distributed in the environment and is one of the first atmospheric pollutants have been identified as potentially carcinogenic. Today they are recognized as highly carcinogenic and mutagenic compounds, and therefore part of them the U.S. Environment Protection Agency and the European Community regulated as priority pollutants [7].

Polycyclic aromatic hydrocarbons mainly are products of incomplete combustion and organic matter pyrolysis. They may originate from both natural and anthropogenic sources. A small portion of PAHs are released into the environment from natural sources such as forest and grassland fires or volcanic eruptions, but mainly they originate from human-made sources. Anthropogenic sources can be divided into two groups: pyrogenic and petrogenic. Pyrogenic PAHs are formed during combustion of fossil fuel and biomass (vehicle exhaust, waste incinerators, power plants), but petrogenic PAHs during combustion of crude oil and its products [8, 6, 52]. Nowadays there are different methods for treating flue gases and effluents to reduce emissions into the environment.

II MATERIALS AND METHODS

This article is a review of the scientific literature, therefore it was gathered and analyzed available information on the chosen topic. Based on it there was carried out an assessment of the performance of the currently used and potential methods and their inter-comparison.

III RESULTS AND DISCUSSION

Flue gas treatment

Polycyclic aromatic hydrocarbons due to their high volatility can be released in the environment not only in the particulate matter (PM) but also in the gas phase [7]. The PAH gas/solid partitioning is related to the liquid ambient temperature, vapour pressure, chemical composition, size and the surface area of the PM [8]. These characteristics combined with the PAHs volatile character determine the way in which they are emitted from a combustion process [6].

Partial elimination of PAHs can be achieved by capturing the particulate matter, which is carried out by conventional gas-cleaning systems such as cyclones, bag filters, scrubbers and electrostatic precipitators.

Cyclone separators

Cyclone separators are well known in the field of particle separation and collection from gas streams. Basically, a cyclone separator receives a gas stream and passes it through cylindrical conical housing thereby forming a vortex such that particles therein are separated from the gas stream and pass out a discharge outlet while the cleaned gas passes through a cleaned gas outlet. It is a centrifugal force created by the action of the vortex thus leaving the cleaned gas at the vortex center, where the cleaned gas continually flows outwardly through the clean gas outlet [52].

Bag filters

Bag filtration is one of the most reliable, efficient, and economic methods for removing particulate matter from gases. Bag filter provides a second filter stage for removing dust from air discharged from a cyclone or other primary separator. In the bag filter dust is filtered from the air, which is discharged through the filter walls. The filtered dust is conveyed along the bottom of the bag filter by an air conveyor and is recirculated back to the primary separator for removal thereat. Fabric or cloth filters in the form of tubular bags are generally used for gas filtration [43].

Wet scrubbers

In wet scrubber system an air stream containing the dust is wetted with water and impinged onto an impingement board which removes the major part of the dust as a mixture of dust and water. Wet scrubbers are used due to their high removal efficiency for coarse particles (1–2 μm in range), small onsite plot space, no problems at high temperatures [76, 5].

Electrostatic precipitators

Electrostatic precipitator having strong electrical field is generally used for the collection of particulate matter or dust. There are two general types of electrostatic precipitators, single-stage in which ionization and collection are combined, and two-stage in which the ionization is achieved in one zone and collection in other zone [44].

These types of air pollution control devices did not show high removal efficiencies for pollutants such as PAHs (Table 1). In two batch-type medical waste incinerators shared the same air-pollution control devices which were installed in series, including one electrostatic precipitator and one wet scrubber, were analyze the concentrations of 21 PAH species contained in the stack flue gas. The results showed that removal efficiencies of total PAHs by the air pollution control devices were only 15.2% and 15.4%. While the removal efficiencies of total PAHs in Taiwan joss paper furnace, which was equipped with a cyclone and a wet scrubber, was 42.5% and 11.7%, respectively. There were studied also emissions from batch hot mix asphalt (HMA) plants and PAH removal efficiencies associated with their installed air pollution control devices (cyclone and bag filter). The overall removal efficiency of the installed air pollution control devices on total PAHs and total Ba_{Peq} were 22.1% and 93.7%, respectively. This implies that the installed air pollution control devices have a very limited effect on the removal of total PAHs [77, 34, 78].

TABLE 1

PARTICLE-BOUND PAH REMOVAL EFFICIENCY OVER VARIOUS METHODS [34, 78, 77]

Method	**Substance**	**Removal efficiency, %**
Cyclone separator	Total PAHs	42.5
Cyclone separator + bag filter	Total PAHs	22.1
	Benzo[a]pyrene	93.7
Wet scrubber	Total PAHs	15.4
	Total PAHs	11.7
Electrostatic precipitator	Total PAHs	15.2

The gas-phase PAH emissions must be tackled by developing specific technologies, like those described below.

Catalytic oxidation

The metal (Mn, Co, Cu, Fe, and Ni) oxides or noble metals (Pt, Pd, Rh, and Au) supported catalysts have already been studied to destroy organic pollutants. Noble metals possess higher catalytic activity and selectivity for the oxidation of organic compounds at low temperature, but, because of their much higher cost, base metals have been more widely investigated for oxidation of organic compounds [78, 66, 59, 71, 19]. Most researchers used naphthalene as a probe molecule to develop efficient catalysts for PAHs destruction. These studies are mostly focused on naphthalene total combustion on different noble metal and some supported metal oxide catalysts, supported on γ-Al_2O_3. Among them, Pt/Al_2O_3 is recognized as one of the most active catalysts. The effects of support and other metal additives on Pt-based catalysts have also been considered for the improvement of naphthalene oxidation, such as SiO_2, SnO_2, TiO_2, CeO_2 and V_2O_5 [80, 42, 27, 81, 26]. There is also investigated an application of ozone in conjunction with Pt/Al_2O_3 catalysts, called ozonecatalytic oxidation (OZCO) process, to destruct gaseous naphthalene to enhance the performance of catalytic oxidation [53].

Active carbons

Active carbons are considered a promising technological solution for the PAH emission control due to their low price, high surface/weight ratio, easy handling and, usually, appropriate for regeneration in cycles [53, 1, 9]. The gas is generally passed through a bed of activated carbon where the molecules of the contaminants are transferred to the solid phase (adsorption process). It was shown that the main factors controlling the adsorption process are microporosity, mesoporosity and pore size distribution [1, 11, 13, 14, 12].

As it can be seen in Table 2, the removal efficiency of the catalytic process depends also on metal loading. Besides, improved PAH removal can be achieved using HNO_3 and NaOH as pretreatment solutions.

Electron beam technology

The electron beam flue gas treatment process is one of the most promising technologies in modern environmental protection. This is a dry-scrubbing process of simultaneous SO_2 and NO_x reduction, where no waste except the by-product is generated. The by-product is fully usable as a fertilizer. Also VOCs present in flue gas may be reduced in this process [3]. This makes it possible to suggest that the electron beam process applied to VOCs decomposition might be an effective and economically viable method.

However, several studies have shown that this technology produces modifications in the concentrations of organic compounds, in particular PAH. The total PAH concentration and PAH-based overall toxicity of flue gas decreased. While results, gained at EPS Kaweczyn, show that the concentration of PAHs of small aromatic rings (p3, except acenaphthylene) is reduced, while the concentration of PAHs of large aromatic rings (X4) is increased. But results from other research showed that after irradiation, the concentrations of higher-ringed PAHs decrease and less-ringed PAHs increase [2, 15, 4, 61]. In another study the observed reduction efficiency for total PAHs was 85% [60].

TABLE 2

GAS-PHASE PAH REMOVAL EFFICIENCY OVER VARIOUS METHODS [81, 19, 46, 60]

Method	Substance	Removal efficiency, %
Pd/Al$_2$O$_3$	Total PAHs	67.3-93.5
Rh/Al$_2$O$_3$	Total PAHs	80
Activated carbon fibers (ACFs)	Total PAHs	70
Pd/ACFs	Total PAHs	70.5-77.5
HNO$_3$–0,48% Pd/ACFs	Total PAHs	96.5
NaOH–0,52% Pd/ACFs	Total PAHs	86
0,53%Cu/ACFs	Total PAHs	80
1.63%Pt/ACFs	Total PAHs	95
Electron beam technology	Total PAHs	85

Wastewater treatment

Biological treatment

There are two main types of biological treatment:

- activated sludge treatment, and
- percolating filters (also referred to as trickling or biological filters).

Both types of biological treatment require subsequent sedimentation to remove suspended matter from the oxidized effluent (Table 3) [41].

Activated sludge treatment (AS)

A conventional activated sludge treatment facility consists of a primary clarifier, an aerobic biological treatment stage and a secondary clarifier. There may be also added such treatment steps as sand filtration for removing suspended solids, activated carbon filtration for removing dissolved matter and biological/chemical treatment for removing P and N.

In activated sludge treatment process is used oxygen and microorganisms to biologically oxidize organic pollutants. The produced sludge is partially recycled back to the aeration tank, which encourages rapid adsorption of pollutants in the incoming wastewater. The remaining waste sludge is removed for further treatment and ultimate disposal [69].

Depending on the mode of operation, the activated sludge treatment process may have up to four phases:

- clarification, by flocculation of suspended and colloidal matter;
- oxidation of carbonaceous matter;
- oxidation of nitrogenous matter;
- auto-digestion of the activated sludge [41].

In wastewater treatment plants, the majority of PAHs are typically bound to the sludge, thereby escaping aerobic treatment. Sorption to sludge particles is the main removal mechanism for PAHs (especially the heavier ones) during primary treatment, but during secondary treatment it is achieved by such processes as biodegradation or volatilization. Lower molecular weight PAHs (naphthalene, acenaphthene, phenanthrene, anthracene, and fluoranthene) during secondary treatment show losses for more than 40% [35, 25, 64, 69]. Overall removal of 16 EPA PAHs ranged from 83-98.3% [35, 63].

Some studies had demonstrated that concentrations of high molecular weight PAHs may increase during conventional wastewater treatment. Treatment plants had higher concentrations of HMW PAHs such as chrysene, pyrene, benzo(b)fluoranthene and benzo(k)fluoranthene than the incoming water. The largest increase was seen for pyrene [65].

As such pollutants as heavy metals and PAHs accumulate in the waste activated sludge it might not be possible to use it for farmland fertilization due to high levels of pollution.

Biological filters (BF)

Biological filters are generally used for removing organic pollutants from wastewater. The basic principle in a biofilter is biodegradation of pollutants by the micro-organisms attached onto the filter media. There are three main biological processes that can occur in biofilter: attachment of microorganism; growth of microorganism; decay and detachment of microorganisms. The success of a biofilter depends on the growth and maintenance of microorganisms (biomass) on the surface of filter media [24].

Membrane bioreactor (MBR)

Membrane bioreactors are reduced-size installations with low sludge production, which allow for the direct reuse of the treated water, as a complete elimination of microorganisms in the effluent and a high removal ratio for most abiotic contaminants are achieved [56]. The studies showed that the removal efficiency of PAHs by MBR is thought to be in the order of 80% (effluent concentration 0 – 0.01 µg/l) [36, 38].

Biofilm reactors

Wastewater treatment systems using biofilms that grow attached to a support media are an alternative to the widely used suspended growth activated sludge process. Different fixed growth biofilm reactors are commercially used for the treatment of municipal as well as industrial wastewater. The use of submerged fixed bed biofilm reactors (SFBBR) is advantageous for the pre-treatment of industrial wastewater, especially for wastewater with high organic loading or high content of compounds with low biodegradability [75].

The MBfR is based on membranes that deliver a gaseous substrate to a biofilm, while also serving as its substratum. The technology offers unique advantages to conventional biofilm treatment technologies and provides specialized treatment for a wide variety of reduced, oxidized, and organic compounds. After several decades of bench and pilot-scale research, the MBfR finally is reaching maturity. The development of the first commercial scale process, ARoNite^{TM}, is a significant milestone in MBfR development. If the process is successful, the same reactor configuration could be used to treat a wide range of water and wastewater contaminants. More basic and applied research on the life expectancy, cost, and reliability of the MBfR will allow the technology to provide a cost-effective, sustainable solution for water and wastewater treatment [45].

Biological aerated filtration (BAF)

Conventionally, BAF is submerged media wastewater treatment reactors that combine biological treatment and biomass separation by depth filtration. It adopts a granular media as the support for microbial biofilms that also provides the depth filtration action. The system does not require special maintenance operations and assures low management costs [48, 33].

Granular activated carbon-fluidized bed reactor (GAC-FBR)

GAC-FBR is an ex situ technology for the treatment of groundwater, wastewater and process water contaminated with hydrocarbons and other organic pollutants. It combines the advantages of biological and physical treatment in a single unit operation, by employing GAC as the solid support for biofilm growth in a fluidized-bed reactor. Aqueous waste streams containing organic contaminants such as benzene, toluene, ethylbenzene and xylenes (BTEX) and PAHs are treatable with this technology. Overall PAH removals of >99% were observed at high organic loading rates and a hydraulic retention time of about 6 min. Removal of 2- to 4-ring PAHs was found to be due primarily to biological oxidation and not to adsorption [39, 68]. However, it is worth noting that high concentrations of total organic carbon over 100 mg/l may need a denitrifying mode of operation. This would require large process volumes and the handling of nitric acid and/or nitrates [32].

Hypersol Macronet (MN200)

Searching for suitable sorbents for polycyclic aromatic hydrocarbons (PAHs) removal from aqueous solutions that solve many of the existing problems when using granulated-activated carbon, a new type of non-functionalized macroporous hyper cross-linked resin, Hypersol Macronet (MN200) had been evaluated. Due to the lack of precise information on the PAH sorption process by hyper-cross-linked resins, it is unlikely that a rigorous kinetic model can be developed. The Fick’s law (HDM) approach and the shell progressive model were used to fit some experimental data. As a first approximation both models can be used in the study of the PAH extraction processes by the hyper-cross-linked MN200 resin [22].

Sorption of six PAHs (acenaphthene, anthracene, fluoranthene, fluorine, naphthalene and pyrene) on activated carbon and the Macronet polymeric sorbent MN200 was investigated to determine the effectiveness of each sorbent for removal of pollutants from aqueous solution and their possible use as sorbent materials for groundwater. Activated carbon showed better sorption efficiency with maximum loadings of PAHs between 90 and 230 g/kg, while MN200 resin showed values of 25–160 g/kg [21].

TABLE 3

PAH REMOVAL EFFICIENCY USING DIFFERENT BIOLOGICAL WASTEWATER TREATMENT METHODS [35, 36, 38, 25, 63, 64, 69, 57, 68]

Method	Substance	Removal efficiency, %
Activated sludge treatment (secondary treatment)	naphthalene, acenaphthene, phenanthrene, anthracene, fluoranthene	>40
	Total PAHs	83-98.3
Membrane bioreactor	Total PAHs	~80
Biofilm reactors	Total PAHs	>99.7
Granular activated carbon-fluidized bed reactor	Total PAHs	>99

Chemical oxidation

Chemical oxidation modifies the structure of pollutants in wastewater to similar, but less harmful, compounds through the addition of an oxidizing agent (Table 4). During chemical oxidation, one or more electrons transfer from the oxidant to the targeted pollutant, causing its destruction [86].

Ozone Oxidation

Ozone (O_3) is a strong oxidant with an oxidation potential. O_3 reacts with organic contaminants through either direct reactions or through the formation of free radicals, including the hydroxyl radical (•OH). The •OH exposure (!•OH dt) can be determined through the use of para-chlorobenzoic acid (pCBA), an O_3-resistant probe compound which reacts selectively with •OH. Ozonation processes are particularly attractive because ozone can destroy hazardous organic contaminants [62, 58]. In studies indicated treatment efficiencies for ozonation of 50 – 90% for PAH (effluent concentrations 0 – 0.01 µg/L) [36, 38].

Ozone oxidation can be operated with UV irradiation. In this system up to three pathways of organic compound removal can develop: direct photolysis, direct ozonation and radical oxidation. The hydroxyl radicals result from the decomposition of ozone due to photolysis and a reaction with hydroxyl anion which produces hydroxyl radicals in subsequent reactions. The •OH radicals react without selectivity on numerous organic chemicals in water. The further reaction course is more complicated as primary products compete for ozone, hydroxyl radicals and UV radiation with the target compound. Organic molecules excited by UV radiation can react with oxygen and ozone. Additionally, intermediates can decompose giving radical species which can take part in the reaction. Oxygen, usually delivered to the reaction mixture with ozone, is also suspected of participation in the oxidation process [73].

The ozonation combined with UV radiation is an effective and quick method for selected PAHs removal from the aqueous environment. The highest rate of degradation is achieved in acidic solutions and the slowest in alkaline solutions. The process carried out in the presence of hydroxyl radical scavenger suggests that benzo(a)pyrene and chrysene decomposition follows the radical reaction to some extent, but for fluorene it is not so obvious. The comparison of the three methods of PAHs degradation using O_3, UV radiation and O_3/UV system permit to state that the combined process is the most effective [73].

A novel method for the degradation of PAH by ozonation, using a mixture of polar and nonpolar solvents, followed by bacterial biodegradation of the oxygenated intermediates was recently disclosed. The method involves dissolving ozone in a bipolar solvent which is contacted with the PAH compounds to solubilise them and to react them with the ozone. The bipolar solvent is then mixed with water to form separate non-polar and polar phases, and the polar phase is incubated with bacteria to biodegrade the oxygenated intermediates [67].

Ozone can also be combined with hydrogen peroxide. UV wavelengths of 200–280 nm lead to disassociation of H_2O_2, with mercury lamps emitting at 254 nm being the most commonly used. UV/H_2O_2 systems generate hydroxyl radicals which are highly powerful oxidizing species. Hydroxyl radicals can oxidize organic compounds producing organic radicals, which are highly reactive and can be further oxidized [70].

UV/H_2O_2 proved to be an effective treatment method for the degradation of phenanthrene and pyrene solubilized in perfluorinated surfactant solutions. The application of H_2O_2 dramatically enhanced the photolysis of the PAHs in both water and anionic surfactant solutions compared to direct photolysis. Surfactant solutions retarded the photolysis of phenanthrene and enhanced the photolysis rate of pyrene [82].

The oxidation of fluorene, phenanthrene, and acenaphthene in water was studied by applying UV radiation combined with H_2O_2. Disappearance rates of PAHs were found to be substantially increased with respect to those from UV radiation alone when the right conditions of H_2O_2 concentration and pH were established. The contribution of direct photolysis decreased with increasing H_2O_2 concentration and was the main way of degradation at acid pH (76% at pH 2 with 10^{-3} M H_2O_2 concentration, for fluorene oxidation). Both UV radiation and UV/H_2O_2 oxidation of PAHs yield numerous intermediate compounds, but most of these compounds disappear as the oxidation time is increased [28].

The study in which had been investigated treatment of fluorene, phenanthrene, and acenaphthene in water with ozone combined with hydrogen peroxide showed that the presence of H_2O_2 did not improve the oxidation rate of fluorene, phenanthrene, and acenaphthene in water compared to ozonation alone. Concentrations of H_2O_2 lower than 0.01 M did not yield significant variations of PAH degradation rate, and at higher H_2O_2 concentrations the process was inhibited, suggesting that direct reactions of ozone with PAHs are so important that the contribution of hydroxyl radical oxidation has no effect on the rate of PAH oxidation. It was concluded that, although ozone combined with UV radiation allows for the highest oxidation rates, the differences with respect to ozonation alone are so small that in a practical case it is likely that the cost associated with the use of UV radiation makes ozonation alone the more convenient technology to remove PAHs from water [29].

The process of photocatalytic oxidation is based on the production of electron–hole pairs by illumination with light of suitable energy, of a semiconductor powder dispersed in an aqueous medium, which subsequently react with adsorbed species of suitable redox potential. In the presence of air, adsorbed molecular oxygen accepts photogenerated electrons, while water molecules can react with photogenerated holes to produce hydroxyl radicals [49, 72].

Fluorene was used as a model PAH compound to compare the efficiency of six different oxidation methods: single ozonation (O_3), single adsorption (TiO_2), ozone photolysis (UVA/O_3), TiO_2 photocatalysis (TiO_2/UV_A), TiO_2 catalytic ozonation (TiO_2/O_3), and TiO_2 photocatalytic ozonation (TiO_2/UVA/O_3). At a fixed pH, the reactivity order for fluorene oxidation was $TiO_2/UVA/O_3 > UVA/O_3 > O_3 \approx TiO_2/O_3 \approx TiO_2/UVA > TiO_2$. The ozone photocatalytic process (TiO_2/UVA/O_3) showed the highest performance, while UV photolysis alone did not yield any fluorene removal. For ozone photocatalysis, total mineralization was achieved in less than 10 and 15 min at pH 5 and 2, respectively, and for ozone photolysis at pH 5. Approximately 50% mineralization was reached in photocatalytic oxidation and when ozone alone or combined with TiO_2 was applied [31].

Fenton oxidation

Fenton oxidation is widely accepted as efficient and environmental friendly process, the generation of sludge due to the flocculation of organic Fe(III) complexes and Fe(III) hydroxides at elevated pH values presents its disadvantage. However, introduction of ultrasound or ultraviolet irradiation in the systems lead to the enhancement of the Fenton oxidation, making it more competitive in terms of efficiency with other chemical oxidation methods (Table 4). Such processes are known as sono-Fenton and photo-Fenton process [37].

Fenton Oxidation is an advisable process for total degradation of PAHs such as, phenanthrene and acenaphthene in water within a few minutes, provided the reagent concentrations are optimized. At low concentrations, ferrous ion and hydrogen peroxide act as initiators of hydroxyl radicals, whereas at high concentrations they slow the oxidation rate. The best concentrations seem to be 10^{-3} M for hydrogen peroxide and 7 x 10^{-5} M for ferrous ion, and the pH of the water should be near 7 [30].

TABLE 4

PAH REMOVAL EFFICIENCY USING CHEMICAL OXIDATION METHODS [36, 38, 73, 16, 28, 50, 31]

Method	**Substance**	**Removal efficiency (%)**	**Reaction rate constant k, M^{-1} s^{-1}**
Ozonation	Total PAHs	50-90	
	benzo[a]pyrene		6.2×10^4
	fluorene		29
O_3/UV	benzo[a]pyrene		6.8×10^4
	chrysene		6.9×10^3
	fluorene		62
	Total PAHs	~100	
UV/H_2O_2	fluorene		9.9×10^9
	acenaphthene		8.8×10^9
	phenanthrene		13.4×10^9
Fe^{3+}/H_2O_2/UV	Total PAHs	>90	
TiO_2/UVA/O_3	fluorene	~50	

Biosorbents

Recently there has been increasing interest in PAH removal by biosorbents. There are already done some researches in this field using different kinds of materials such as:

- plant residues (ryegrass, alfalfa, tomato, potato, pumpkin, carrot and zucchini roots, cucumber, orange peel, bamboo leaf, pine needles and bark, tender and mature tea leaves, wood chip, cork waste) [85, 51, 17, 23, 84];
- algae (Botryococcus braunii, brown seaweed) [54, 55];
- white-rot fungi [18];
- modified biosorbents (aspen wood fiber, hydrolyzed wood fibers, brewed tender and mature tea leaves, acid hydrolysis of pine bark, fibric peat and surfactant modified fibric peat) [23, 84, 47, 78];
- nature organic matter (lignin, cellulose, collagen, cuticle of apple, grape, tomato, potato and mangrove) [54, 83].

Comparing all these sorbents and activated carbon by partition coefficient (Kd), which is an effective parameter to evaluate the sorption efficiency, shows that their removal efficiency for PAHs is more or less lower.

However, should not be forgotten the fact that raw plant materials are easily modified to enhance the sorption capability. Thus some of these natural adsorbents are potential alternatives of activated carbon in an innovative approach for the removal of this class of toxic compounds, and significantly reduce the regeneration costs of the process (Table 5) [85, 51, 17, 23, 84, 54, 55, 18, 47, 79, 83].

TABLE 5

PAH REMOVAL EFFICIENCY USING DIFFERENT BIOSORBENTS [17, 85, 84, 54, 55, 47, 79, 83]

Sorbent		**$\log K_d$**
Plant residues	Ryegrass root	3.44
	Wood chip	3.40
	Orange peel	3.47
	Bamboo leaf	3.57
	Pine needles	3.72
	Alfalfa root	3.37
	Tomato root	3.40
	Potato root	3.62
	Pumpkin root	3.62
	Carrot root	3.70
	Zucchini root	3.66
	Cucumber	3.52
	Ryegrass root	3.32
	Pine bark	3.53
	Tender tea leaves	3.52-3.54
	Mature tea leaves	3.77-4.05
Algae	Botryococcus braunii	4.13
	Brown seaweed	3.83
Fungi	White-rot fungi	3.83
Modified biosorbents	Aspen wood fiber	3.60-3.67
	Low-temperature hydrolyzed wood fibers	4.03-4.15
	High-temperature hydrolyzed wood fibers	4.63-4.75
	Brewed tender tea leaves	3.76-3.80
	Brewed mature tea leaves	3.95-4.20
	Acid hydrolysis of pine bark	4.23
	Fibric peat	4.11
	Surfactant modified fibric peat	4.42
Nature organic matter	Lignin	4.03
	Cellulose	2.98
	Collagen	4.47
	Cuticle of mangrove	4.21
	Cuticle of apple	4.73
	Cuticle of grape	4.54
	Cuticle of tomato	4.61
	Cuticle of potato	4.21

IV CONCLUSIONS

One of the most notable anthropogenic sources of PAH emissions are power plants, waste incineration plants and industrial enterprises, therefore it is important to minimize the emissions from them. Exists a wide variety of methods for PAH abatement, but a part of them are not developed specifically to treat them. They were originally created for abatement of other types of pollutants and are used for general treatment of wastewater or flue gases, however there is studied also the influence on PAH emissions.

Flue gas treatment methods, that are generally used for the collection of particulate matter or dust (cyclone separators, bag filters, wet scrubbers, electrostatic precipitators), showed rather low removal efficiency. For total PAHs it ranged only from 11.7 to 42.5%.

Much better results showed metals supported catalysts. The removal efficiency of them depending on metal-catalyst combination ranges from 67.3 to 96.5%.

In the wastewater treatment field very promising results shows recently developed technologies that are based on biofilms, but they are not yet widely used industrially because they still faces challenges, including biofilm management, the design of scalable reactor configurations, and the identification of cost-effective membranes.

The combination of ozone with UV radiation allows for the highest PAH degradation levels. However the high costs constitute a restriction on the use of this method.

All in all there is still being sought for the best PAH treatment methods that would be both efficient and cost-effective. None single emission control technology that is available nowadays, is not efficient enough, while the combination of technologies is recognized as the best approach.

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Impact of Microclimate and Indoor Plants on Air Ion Concentration

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Abstract **- Saturation of air ions is essentially important for all living beings, especially for human health. Existing sanitary norms provide that concentration of small ions has to be in range of 400 - 50000 ions cm^{-3} and unipolarity coefficient $0.4 \le K \le 1.0$. Many species of indoor plants emit organic volatile compounds and air ions, therefore they could be used for improving the quality of indoor air. The results show that ionization level of indoor air is significantly insufficient and selected species of indoor plants are not able to improve it. They serve rather as supplementary surfaces for ion absorption. Possible interaction between microclimate, ion concentration and indoor plants in different times of the day is analyzed.**

Keywords**: air ions, indoor plants, microclimate.**

I INTRODUCTION

Content of chemical substances or physical components are not the only factors characterizing quality of indoor air. Air is an environment where various types of physical fields concentrate and disperse. Many physical fields have an impact on the level of air ionization, giving energy necessary for air molecules to overcome the ionization barrier. Thus, the air becomes an environment that constantly contains certain amount of energy. In this case, it is necessary to talk about energetic saturation of air which inevitably affects living organisms. One of the most common descriptors of energetic saturation of the air is the level of air ionization, i.e. concentration of air ions in the air.

Atmospheric physics uses the term "air ions" to describe all airborne particles which have an electric charge and which assure electrical conductivity of air [1,2]. In a narrow sense, the term "air ions" means any airborne and charged particles whose size is from 0.36 to 79 nm and whose mobility is from 1.3 to 0.0042 cm^{2}V^{-1}s^{-1} (i.e., from unimolecular ion migrating in the air to aerosol particles whose upper size limit is not clearly defined). Usually, the upper limit of particles is considered to be 79 nm and mobility 0.00041 cm^{2}V^{-1}s^1. Charged particles within these limits are considered to be research objects of natural origin during air ion studies outdoors. To some extent, these limits are defined by sensitivity threshold of the air measuring device [3]. Nowadays, the most commonly used classification is based on physical structure of air ions [4]. Cluster ions contain only ionized and polarized gas molecules that form clusters, while the heaviest ions are aerosol ions which include not only ionized and polarized gas molecules but also atmospheric aerosol particles as ion condensation nuclei. Diameter of cluster ions is in range of 0.36 - 1.6 nm, and their mobility varies from 1.33 to 0.5 cm^{2}V^{-1}s^{-1}.

Air ions affect a wide range of wildlife from microorganisms, animals, plants, human beings to ecosystems and even global climate. Many studies show and characterize the impact of air ions on human beings and all other living organisms [5]. Oxygen and other ionized molecules of air components have stronger effect on human organism. Air ions may be healing or may harmfully affect human health. This effect depends on ion concentration in the air and on proportions of positive and negative ions [6]. These proportions are characterized by unipolarity coefficient

$$K = \frac{n^+}{n^-} \tag{1}$$

where n^+ and n^- mean concentration of positive and negative cluster ions.

The study carried out with primary school children in the U.S.A. shows that negative artificial air ionization in classrooms significantly increases physiological tolerance to stress factors thus reducing the impact of stress that manifests itself in nervous behavior of children, poor concentration skills and low educational attainments [7].

The content of positive and negative air ions in the air has a significant effect on physiological processes in human body, thus affecting the state of health, mental and physical performance, and well-being. In general, negative air ions have a positive impact on human health, whereas positive air ions are unfavourable [8].

In order to detect and evaluate the impact of air ions with various concentrations and different charge signs on human health, many experiments have been carried out on animals. For example, a therapy of negative air ions has helped to normalize physiological parameters of animal bodies even in conditions of prolonged stress. This fact opens up opportunities to use the therapy of air ions for treatment of human neuroses [9]. The therapy of negative air ions has contributed to faster wound healing of laboratory rats and to improve their health [10]. The therapy of air ions can be used to improve human health and well-being, to treat burning wounds, injuries, and other diseases [11]. It is important to know that negative air ions have a disinfecting effect as well and that they prevent development of dangerous bacteria [12,13]. Information on air ion concentration necessary for optimal human operational capacities obtained during scientific studies [14,15,16] are incorporated into national legislation of several countries. Studies on interaction between air ions and indoor air pollution with aerosols are described in numerous publications [17]. Air ionization technologies are widely used in purification of fine aerosols [18] and pathogenic bacteria [19] from indoor air.

On 16 June 2003, sanitary and epidemiological rules and regulations “Hygienic Requirements for the Air-Ion Level of Industrial and Public Facilities SanPin 2.2.4 1294-03” [35] *(Санитарно-эпидемиологические правила и нормативы "Гигиенические требования к аэроионному составу воздуха производственных и общественных помещений СанПин 2.2.4 1294-03"*)” entered into force in the Russian Federation.

This regulatory document sets requirements for air ion contents in facilities where a variety of reasons may cause decreased or increased concentration of air ions inappropriate for human organism. The lowest concentration limit of air ions appropriate for human well-being is 400 ions cm-3, while the highest appropriate ion concentration is 50000 m-3. Unipolarity coefficient must be $0.4 \leq K \leq 1.0$. In recent years, similar regulatory documents have been adopted in Ukraine and Belarus. However, neither the legislation of Latvia, nor regulatory documents of other EU’s countries control the levels of air ion concentration in work or living facilities.

Air ions and plants influence each other. Artificially controlled environment of air ions in greenhouses is experimentally used to harvest more vegetables [13] because ionized air particles contribute to a faster exchange of substances in plants [24]. However, numerous cases show that air ions in combination with strong anthropogenic atmospheric pollution can also enhance negative effects on plants. Air ions of different classes, products of radon gas decay and charged aerosol particles which are spread in the atmosphere are considered to be factors causing damages of tree foliage and trunk [21].

Most plants emit different types of volatile organic compounds (Bio VOCs) and even micro-amount of Bio VOCs have a great impact on formation processes of cluster ions [22]. This effect is reinforced when volatile compounds are emitted from the plant in ionic form, e.g., Bio VOCs emitted from the needles of conifers are ionized because of charges accumulated in the sharp tips of the needles. Ions of volatile compounds are very good condensation nuclei in the atmosphere that contribute to further formation of mist and clouds. Thus, coniferous forests can affect even the global climate [23]. To a certain extent, most of the plants are air ion generators. Intensity of such generation depends on the daily intensity cycle of metabolic process in these plants [20].

Houseplants improve the quality of indoor air. Some plants effectively clean the air from organic contaminants [26], while other plants reduce the amount of microorganismes in the air because of phytoncide effect. Plants produce oxygen and absorb carbon dioxide [25,27]. Many plants intensely humidify the air of the room. As elements of phyto design, houseplants have a positive impact on the psycho-emotional state of the occupants. As a consequence of people staying indoors, the indoor air is saturated with anthropogenic organic, microbial and aerosol pollution to a greater extent than the natural air. The indoor air contains less small oxygen ions than the natural air [28].

Plants are the source of negatively charged ions. Light-absorbing pigments in photo-organisms capture photons of certain colors and reflect other colors. The energy of a photon through a long chain of molecules is transferred to the reaction center, which splits water to produce high-energy electrons for biochemical reactions. The process of photosynthesis (especially the light phase) is directly related to the change in the difference of potentials on the thylakoid membranes of chloroplasts [30,31].

Negative ions promote synthesis and maintenance of vitamins in human organism and stimulate physiological processes. Normally, the human organism requires daily 13 milliards of negatively charged ions. Central heating and cooling equipment reduce the amount of negative ions in the air. Besides, synthetic fibers and carpets containing positive charges can easily absorb the negative ions. They are also absorbed by steel armature and wooden chipboard [29].

Phytoncides ionize the oxygen in the air, thus increasing its biological activity. Phytoncides improve the efficiency and profitability of cell energy. Phytoncides promote settling of dust particles, reduce the electric index of air pollution and neutralize microorganisms in the air [32].

In 1994, a conference "With plants against smog" was held in Frankfurt-am-Main. Participants of this conference discussed the issue of environmental degradation in the indoor spaces. The conclusion reached by the participants of the conference is as follows: a significant improvement in the indoor air quality can be achieved using plants for greening [33]. Such indoor plants as geraniums and begonias reduce the concentration of microorganisms in the ambient air by 43 %, cyperus - by 59 %, Chrysanthemum parviflorum - by 66% [34]. Tradescantia effectively absorbs gas pollutants, intensively emits oxygen and phytoncides [28]. Studies conducted by NASA, the purpose of which was to find ways to purify the air in the space capsules, have found that some of indoor plants can clean the air of many pollutants, including formaldehyde. Such plants are Spathiphyllum Wallisii, Syngonium Podophyllum, Dwarf banana plants (Musa), Scindapsus or Epipremnum (Scindapsus Aureus). Plants of three different types were found to perform the same function, but they are not so effective indoors due to their long and sharp tips of leaves. Such plants are: Aglaonema, Chlorophytum (Chlorophytum Elatum), Sansiveria (Sanseveria Trifasciata Laurentii) [27].

It would be perspective to develop technology for artificial greening that would ensure air ion concentration and microclimate conditions indoors optimal for human organism. In order to develop such technology, it is necessary to find out changes in air ion concentration depending on indoor plants and microclimate.**The aim of this research is to explore the impact of indoor plants and microclimate on air ion concentration in order to find opportunities to use plants for air quality improvement.**

II Materials and methods

In order to perform this study, several plants were selected which by their nature and taking into account the impact of external factors can affect the air ion concentration indoors. Therefore, plants with following characteristics were chosen: large area of leaves, leaves with a pointed tip and hair shaft; developed transpiration function (as a result of transpiration a lot of water is vaporized from plants), dust particle absorption, expressed phytoncide features.

A phyto-module was created (a complex of specially selected plants for environmental improvements) basing on the following plants: Chlorophytum - 2 pcs., Tradescantia - 2 pcs., Geranium (Pelargonium) - 2 pcs., Dracaena, Scindapsus Syngonium, Aglaonema, Spathiphyllum - 2 pcs., Sansevieria, Echinocactus Grusonii -1 pc. For characteristics of these plants see Table 1.

Fig. 1. Arrangement of measuring devices and plant group indoors

TABLE 1.

CHARACTERISTICS OF PLANTS [26]

Name / Number of plants in experiment (12 m^2, 36m^3)	Lightening requirements	Phytoncide features	Intensity of oxygen generation	Efficiency of air purification from gas admixtures (relative values) 0-10	Substances absorbed efficiently
Chlorophytum/2	Indirect, bright	*	**	7.8	Formaldehyde, carbon dioxide
Tradescantia/2	From partial shadow to sunny	**	**	7.8	Formaldehyde, carbon dioxide
Geranium /2	Indirect, bright	***	***	6.9	Formaldehyde,
Dracaena/1	From partial shadow to sunny	*	**	6	Formaldehyde, acetone
Scindapsus/1	Indirect, bright	-	*	6	Formaldehyde, benzene
Syngonium/1	Indirect, dissipated	*	**	7	Formaldehyde,
Aglaonema/1	Partial shadow	**	***	6.8	Benzene, toluene
Spathiphyllum/2	Bright, in spring dissipated	*	**	7.5	Formaldehyde, acetone, chloroethene, benzene
Sansevieria/1	Bright	*	*	6.8	Formaldehyde, acetone, chloroethene, benzene

*** high efficiency ** efficient * average efficiency - low efficiency

Air ion concentration was determined with a portable bipolar air ion counter "Sapfir-3м" (see Fig.1). It provides simultaneous measuring of positive and negative air ions with minimum resolution of 10 ions per 1 cm^3. The device measures air ion concentration in the air (mobility $k \geq 0.4$ $cm^2V^{-1}s^{-1}$) in the air. This mobility interval nearly corresponds to the class of cluster ions [4]. During the measurements, air ions, according to their polarities, are channelized to positive or negative aspiration collector in aspiration chamber and after coming into contact with this collector the ions are discharged. Afterwards, the charge is sent to amplifiers from which impulses are counted and displayed on the display. The charges of air ions are counted in the device, therefore if the ion has more than one charge, it is counted as several ions.

Indoor climate parameters were determined with a multimeter "Easy Sense Q". The systematic measurement error of this device for temperature is ± 0.3 ° C, whereas the error for relative humidity is ± 5%. The error for lighting is not specified, but its maximum measurable value is 1000 Lx. The total amount of radioactive α, β and γ radiation was measured in $\mu Sv \cdot h^{-1}$ with a portable device "Gamma-Scout" with systematic measurement error less then 5%. For all devices each measurement point is defined as the average value of 10 minutes.

The measurements were carried out in automatic mode: 24h without plants and 24h with plants that were placed in a room of 12 m2 and 36m3. The room has one window towards SW. The room is located on the first floor, it is closed and without forced ventilation. During the measurements, the heating was on. People were present in the room only 1 time a day for 30 min. to switch on the devices and to at just online mode for measuring. All daily measurements were repeated two times.

III RESULTS AND DISCUSSION

The experimental data (see Fig.2) show that the number of positive air ions in the given rooms is higher than the number of negative air ions: 15-25% (without houseplants) and 100-150% (with houseplants). Maximum / minimum concentration of positive air ions: 320cm-3/60 cm-3 (without houseplants) and 345cm-3/60cm-3 (with houseplants). Maximum/minimum concentration of negative air ions: 260cm-3/40 cm-3 (without houseplants) and 220 cm-3/40cm-3 (with houseplants). If there are no plants in the room, the concentration of positive and negative air ions is approximately two times higher in the night than during the day. If there are plants, the concentration of positive and negative ions is approximately two times lower in the night than during the day. These data suggest that, basing on the air ion concentration and unipolarity coefficient, the room used for the experiments is not recommended for human health (if not ventilated). The room has very low concentration of positive and negative air ions and inadequate unipolarity coefficient, because basing on the SanPin 2.2.4 1294-03 minimal admissible concentration of positive air ions is 400 cm-3, negative air ions 600 cm-3, admissible values of unipolarity coefficient ≤ 0.4 K <1.0.

During the day, the room temperature is increased and relative humidity is decreased because of the sunlight. The measured average ambient temperature in the room with plants is about 10C higher than in the room without plants. The average humidity is about 1% higher in the room with plants than in the room without plants (first measurement series) or the same as in the room without plants (second measurement series) (See Fig.2). It means that plants increase the air humidity (the water is evaporated through leaf pores).

Basing on the literature analysis and experimental research, the following factors influencing air ion concentration may be defined:

1) natural radiation splits neutral air molecules thus creating positive ions and electrons, therefore the number of positive and negative ions in the air is increased;

2) photo-ionization: as a result of lighting or other electromagnetic radiation, electrons are detached from neutral air molecules thus increasing the number of positive ions in the air; the higher the frequency of electromagnetic radiation (higher photon energy) and lower ionization energy of air molecules, the more free electrons and positive ions occur;

3) photo-effect: as a result of lighting or other electromagnetic radiation, free electrons are detached from surfaces, dust and aerosol particles; the higher the frequency of electromagnetic radiation, larger the surface area, more dust / aerosol particles and smaller electron's exit work for the surface material, the more free electrons are sent into the air; it increases the number of negative air ions; as a result of photo-effect the adsorbent surface (walls, furniture, curtains, plant leaves, human body, clothing, dust / aerosol particles, etc) is charged positively; it promotes the absorption of negative air ions but reduces the absorption of positive air ions (are repulsed away from the surface); the stronger is positive charge of the surface, the harder it is to knock out electrons from it;

4) organic compounds (phytoncides) emitted by plants into the air; a part of these compounds may have already been ionized during the process of emission from the plants; other compounds may be ionized as a result of natural radiation or light; this factor increases the concentration of positive and negative air ions; the speed of phytoncide emission depends on the process of metabolism in the plants which is largely determined by plant species, lighting and, possibly, by plant watering regime;

5) surface adsorption properties: the stronger is surface absorption of air ions, the lower is ion concentration in the air; it is possible that surface adsorption properties may be changed because of lightening (internal photo-effect activate surface of ion absorption: separate positively and negatively charged microscopic areas are created which promote air ion adsorption); absorption properties of different plant species are different;

6) surface area of ion adsorption: the larger surface area, the more ions are adsorbed; it decreases the amount of positive and negative ions in the air (if the photo-effect is not taken into account); if the photo-effect is taken into account, the enlargement of surface area increases the number of negative ions and free ions created by photo-effect; during the night (no photo effect) air ion absorption prevails, while during the day both photo-effect and air ion adsorption may prevail;

7) dustiness: the more dust particles in the air, the greater possibility for positive and negative ions to adsorb on the surfaces of these particles; the increase of concentration of dust particles decreases the amount of positive and negative air ions (ignoring the photo-effect); if the photo-effect is taken into account, the increase of dust particles increases the number of negative ions and free ions created by photo-effect; during the night (no photo effect) air ion absorption prevails, while during the day both photo-effect and air ion adsorption may prevail;

8) air humidity: the higher the humidity, the more aerosol particles in the air and greater possibility for positive and negative ions to adsorb on the surfaces of these particles; it decreases the amount of positive and negative ions (ignoring the photo-effect); if the photo-effect is taken into account, the increase of aerosol particles increases the number of negative ions and free ions created by photo-effect; during the night (no photo effect) air ion absorption prevails, while during the day both photo-effect and air ion adsorption may prevail; the presence of plants in the room increases the level of air humidity; air humidity might be influenced by plant watering regime;

9) temperature: the higher is the temperature, the easier it is to ionize neutral air molecules; it increases the number of positive and negative air ions; the rise of temperature reduces humidity; its impact on the amount of air ions may be seen in the description of factor No.8;

10)recombination of positive and negative air ions; the higher concentration and mobility of positive and negative air ions, the greater chance for ions to disappear by reciprocal recombination;

11)the Earth's electrical field and the convection air flow in the room promotes movement of air ions and their disappearance after contact with surfaces;

12)characteristics of surface absorbing the ions (e.g., the surface is smooth, rough, sharp), its shape and position (horizontal, vertical).

Air ion concentration is affected by all the above mentioned factors. In each specific case the impact of each factor on air ion formation process is different.

Unfortunately, it is not possible to give an unambiguous explanation of experimental results of the studies on factors influencing air ion concentration. For a complete understanding of the process, it is necessary to carry out experiments which explore the specific impact of each separate factor on the amount of air ions (studies of air ion concentration changes depending on one factor, excluding, as far as possible, all other factors). In order to predict air ion concentration changes over time, it is necessary to create a mathematical model that includes all the studied factors and their characteristics and where constants characterizing each factor are experimentally determined.

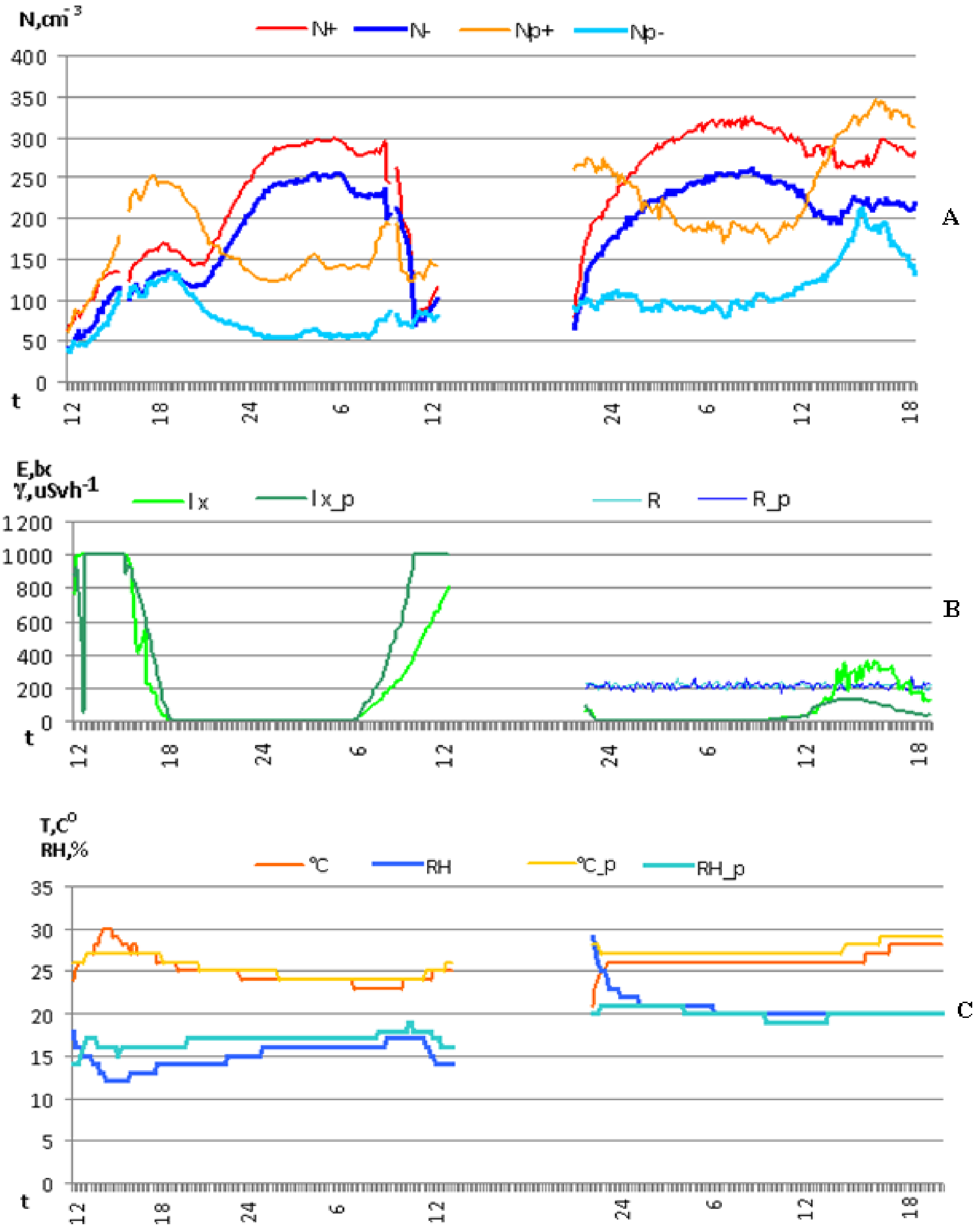

Fig. 2. Experimental results

A. Concentration of positive and negative air ions indoors; B. Measurements of lightening and radiation background indoors; C. Measurements of temperature and relative humidity indoors

In order to explain the experimental results to a first approximation (see Fig.2), the following simplifications are made:

1) as the natural radiation level (factor 1) fluctuates chaotically around the average value 215μSv•h-1 and the amplitude of these fluctuations is less than 10%, the level of radiation can be considered as constant; fluctuations of radioactive background do not affect daily changes of air ion concentration;

2) since the room is small and closed, the air convection flow is insignificant and dustiness (factor 7) is not changed;

3) temperature (factor 9), air humidity (factor 8), the Earth's electric field (factor 11) are approximately constant;

4) as the concentration of positive and negative air ions is low (maximum concentration of positive ions 345cm-1, negative ions 260cm-1), the recombination effect (factor 10) is insignificant;

5) the concentration of air ions is not significantly affected by characteristics of adsorptive surface or its shape and location (factor 12).

Thus, the experiments show that the established air ion concentration changes in this case are primarily affected by factors 2, 3, 4, 5 and 6. These factors are related to the changes of lighting, surface area, type (room with plants or room without plants) and absorbent characteristics.

It is necessary to explain the Fig. 2 showing daily process of concentration changes of positive and negative air ions in room with plants and in room without plants.

Plants used in the experiments are producers and absorbers of positive and negative air ions. During the night, the process of plant's metabolism and ion emission into the air slows down; during the night, the plants mainly adsorb air ions. Therefore, during the night a significant decrease in air ion concentration can be observed in the room with plants. During the day metabolic processes in plants are activated; plants emit positive and negative ions into the air and simultaneously adsorb these ions. During the day, electrons are knocked out from plant surfaces as a result of photo-effect. These electrons increase the amount of negative air ions. At the same time the plant surfaces are charged positively; it increases the adsorption of negative air ions and decreases the absorption of positive ones. As a result, during the day the room with plants has increased concentration of air ions (especially positive ones).

It is experimentally established that during the day the concentration of positive and negative air ions in the room with plants decreases (in comparison with night). It can be explained as follows: as a result of the lighting the surfaces absorbing air ions are activated; photons do not knock the electrons out of the surface but only disconnect them from the surface atoms creating free electrons (internal photo-effect); as in most cases the adsorbent surfaces are dielectrics, the free electrons resulting from such internal photo-effect do not flow away but create negatively charged and microscopic areas on these surfaces; the place from which the electron has been separated is positively charged; such positively and negatively charged microscopic areas on surfaces promote air ion adsorption; it also reduces air ion concentration during the day. During the night, the process of internal photo-effect is interrupted, therefore the charged surface areas gradually disappear and the adsorption process is decreased, while air ion concentration is increased (air ions are produced by natural radiation).

IV CONCLUSION

1. The authors of this research carried out experimental studies on total concentration changes of positive and negative air ions in a closed room ($12m^2$, $36m^3$). Level of natural radiation, light, temperature and relative air humidity in room with and without plants were measured as well. It was found that during the day air ion concentration is approximately two times increased if compared to the night (if there are plants in the room) (see Table 1). If micro-climatic conditions are almost the same in a room without plants, the changes in air ion concentration are opposite: during the day, air ion concentration is decreased, while during the night it is increased (by 20-100%).
2. Basing on the used information sources and experimental studies, 12 factors influencing air ion concentration were selected. In each specific case the role of each factor in the air ion formation process is different. For complete understanding of the process, it is necessary to carry out experiments to establish the role of each factor on the amount of air ions separately and to create a mathematical model including all selected factors. Such model would enable development of a methodology for anticipation of air ion concentrations and for optimization of indoor air quality with the help of houseplants.
3. Further experiments could be related to changes in air ion concentration depending on plant species, number, leaf shape, area and roughness, plant watering regime, lighting, temperature, air humidity, characteristics of surfaces located in the room. The aim of such studies would be to find the plants, their life conditions and to find the surface coatings in order to provide air ion concentration that would be optimal for human health indoors.

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Sustainable Thermal Insulation Biocomposites from Locally Available Hemp and Lime

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***Abstract. T*he key focus of the presented research is on sustainable thermal insulation biocomposites which can be made from locally available hemp and lime. The main gains of the use of such material are given, with emphasis on CO_2 reduction. In the first stage samples of an artificial hydraulic lime using three different limes and three hydraulic additives are created and tested, the one with the highest compressive strength (DL60 lime with 40% metakaolin addition) are chosen for further research. In the second stage three different density mixes with the chosen binder are created, optimal hemp/binder ratio is determined, as well as compressive strength and thermal conductivity. Results indicate that created mixtures have good potential as self-bearing thermal insulation material used in low-rise buildings.**

***Keywords* –hempcrete, hydraulic lime, low-carbon, sustainable materials.**

I INTRODUCTION

Sustainable building materials are one of the most topical subjects today in building material industry due to the growing concerns about anthropogenic factor impact on CO_2 levels in atmosphere and its correlation with global temperature rise [1]. Globally manufacture of building materials is responsible for about 10% of all CO_2 emissions [2], which is the same in Latvia [3].

In more indirect way building materials are responsible for another source of CO_2 emissions – from energy consumed for building heating and cooling in the cases when building is made out of inefficient materials with high thermal conductivity values. Heating energy losses are even larger then material manufacture industry – together with electricity and water heating it generates 36% of all CO_2 emissions in Latvia, 50% in UK [4], 45% Canada, 40% USA, and 20% in China [5].

Therefore, building material industry needs to give its solution to this problem. One of the ways to answer these challenges would be to perfect and promote the use of biocomposite materials. Along with other great properties, a lot less CO_2 is created in manufacture process of these materials, because one of the two main components of the composite is made from biological ingredients, which has sequestered CO_2 in the growing process. As to even more lower their carbon footprint, the binder usually used is low-carbon too – either lime or clay. And as these materials are considered sustainable, their thermal conductivity coefficient is low enough to be compatible with traditional building materials.

There are many different low carbon dioxide biocomposites, such as hemp-lime, hemp-clay [6], straw-clay [7]. One of biocomposites which is particularly interesting in Latvia, because it can be made using locally available resources, is hemp-lime self-bearing heat insulation material. Hemp shives and hydraulic lime are two main components of natural biocomposites. In Figure 1. biocomposite composition with three main CO_2 flows can be seen, which represent most significant carbon dioxide emission and absorption processes in biocomposite manufacture.

Hemp shives are inner part of hemp stalk, by chemical composition it is very similar to wood-pulp as it contains a lot of lignin. It is considered a by-product as the main purpose of hemp growing is obtainment of fiber and seeds. The chief market for hemp shives for now is their use as bedding material in horse stables, because of its outstanding moisture and smell absorption capabilities. It is due to this porous nature of hemp shives that it can be used as a filler in thermal insulating biocomposites, as it allows the material to have both great moisture regulating capabilities and low thermal conductivity.

Lime is an appropriate binder for biocomposites, because of its properties. First of all, it has a lot less embodied carbon in its manufacturing process as other binders, like concrete – for 1 ton of hydrated lime 337 kg of CO_2 are created, for concrete – 819 kg [8]. Secondly, when lime hardens, it reabsorbs carbon dioxide that was released in burning process from limestone, through carbonization. And third of all, its water vapor permeability makes it fully compatible with hemp shives, to create a material with good moisture regulating properties.

Hydraulic lime can be made by mixing air lime with hydraulic additives, to make it stronger and more appropriate as a self-bearing biocomposite binder. Most important properties of hydraulic additives are high amorphous SiO_2 amount and small particle size [walker]. Commonly used additives for lime are – silica fume [9], metakaolin [10], fly-ash [11], various ground glass [12] and brick [9].

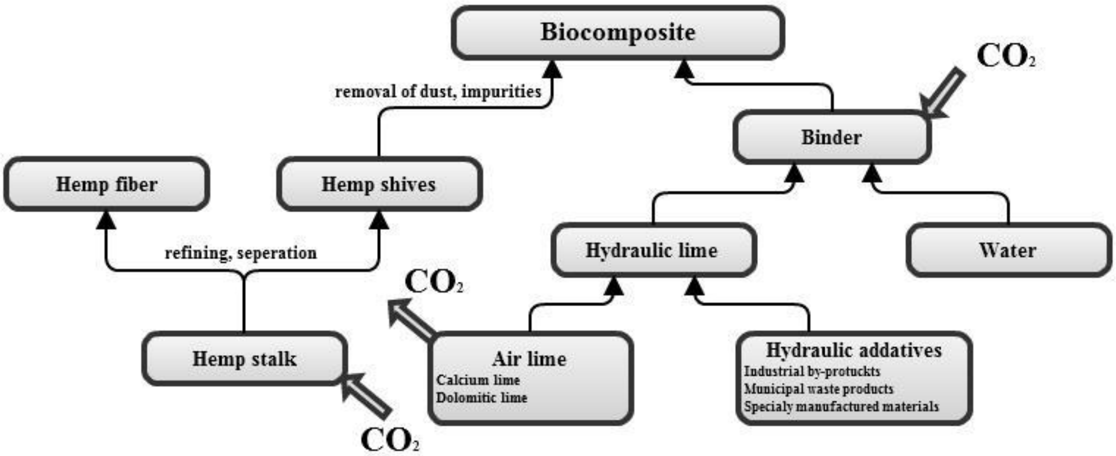

Fig. I. Composition of biocomposites with three main CO_2 flows

As for total CO_2 emitted by hemp-lime biocomposite, research shows that in fact this material absorbs, through growing of hemp stalk and carbonization of lime, more carbon dioxide than is emitted. Various researchers propose different amounts of CO_2 sequestered in full life cycle of material in 1 m^3 – 4 kg [13], 108 kg [4], 120 kg [14] – as they are using different calculation methods, but one thing is clear – biocomposite made of hemp-lime mix is carbon neutral or even negative.

The aim of this research first of all is to examine the effect of three hydraulic additives on compressive strength on various air limes, to compare it with previously known biocomposite binder strengths and to choose the most suitable for further research. Then it will be mixed with hemp shives to investigate thermal conductivity and compressive strength of heat insulating biocomposites made from locally available resources. Various binder proportions will be used to test the correlation between compressive strength, binder properties, density and thermal conductivity.

II MATERIALS AND METHODS

A. Material properties

To find out the effect of lime content on formation of hydraulic compounds, three different commercially available air limes were used, their composition is given in Table I.

TABLE I

PROPERTIES OF USED LIMES

Name	CaO+MgO content, %	Active lime, %	Bulk density, kg/m^3	Color
Hydrated lime CL90	≥ 90	≥ 80	627	white
Hydrated lime CL80	≥ 80	≥ 65	417	white
Quicklime DL60	≥ 60	X	807	grey

Three different pozzolanic additives were tested. First one - metakaolin which is obtained by burning kaolin clay at 800^0 C. Other two are ground crushed bricks from building demolition waste recycling – one with fireproof capabilities, the other – hollow loadbearing brick.

Hemp shives were obtained as by-product of hemp-fiber manufacture. Bulk density of used hemp shives is 97 kg/m^3. Particle size distribution of hemp material can be seen in Table II and in Figure 1.

B. Experimental methods

To test the ability of hydraulic additions to react with lime 160*40*40 prisms were made using oiled steel moulds. Mixing of specimens were done manually, water were added as necessary to ensure a constant plastic consistency of mortar, so no mechanical vibration tools were needed.

After casting in moulds, specimens were covered with polyethylene film, kept for 7 days, then demoulded, sprayed with water and again covered with film to ensure constant high relative humidity (95 ± 5 %), with was measured with hygrometer.

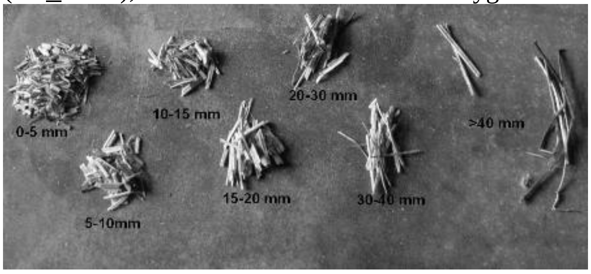

Fig. II. Hemp shive size

TABLE II

HEMP SHIVE GRANULOMETRY

Length, mm	0-5	5-10	10-15	15-20	20-30	30-40	>40
% of mass	27	15	14	19	13	8	4

Compressive strength of the samples was measured after 28 days of curing, tolerance of force determination ±1%. The binder with highest performance was selected for furtherer tests.

During the experiment 3 different compositions of biocomposites were made. To test the influence of material density on thermal conductivity and compressive strength, various binder proportions were tested.

Drum mixer were used to mix the samples. First of all hemp shives were put in the mixer with half of the necessary amount of water and mixed for 3 minutes. Then the binder was added, mixed for 2 minutes, and after all – the rest of the water. Preparation continued until the binder was evenly distributed, which took 3-4 minutes. The mixed compositions were cast in oiled steel moulds with dimensions of 100*100*100mm for compressive strength testing, and in 350*350mm water-proof plywood moulds for thermal conductivity testing. Material were cast in three layers, moderately tamping each layer, polyethylene film were placed on top to prohibit fast drying of the samples, then a steel plate with weight on top of it all for even compaction.

The film and weight were removed after 3 days, specimens were demoulded after 7 days of curing. Hardening conditions were 20±2^{0}C temperature and 55±10% relative humidity.

To assess material density, before tests specimens were weighted and their dimensions were measured.

Compressive tests were performed using universal testing machine Zwick Z100 (maximal applicable force – 100 kN). Pressure on specimens was applied in the same direction as compaction, by rate 10 mm/min, force – deformation diagram was recorded during the test. As biocomposites with relatively low compressive strength can exhibit relatively large deformations without noticeable breaking point, maximal compressive strength is measured at 10% deformation (in this case at 10 mm of absolute deformation).

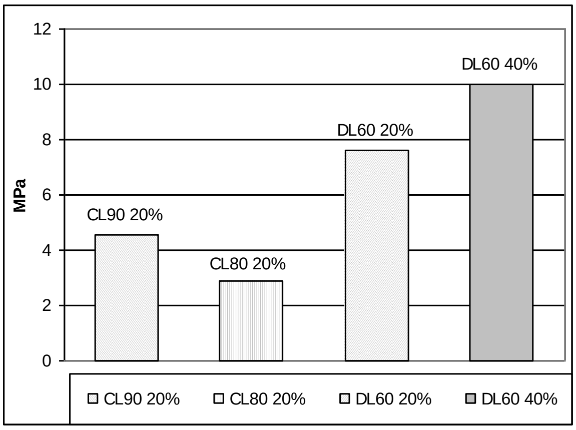

Fig. III. Compressive strength of various limes with metakaolin addition.

Thermal conductivity was determined using Fox 600 heat flow measuring device. Sample was fixed horizontally. During the test temperature of lower surface was +20^o C and 0^o C of upper surface (mean temperature +10^{o}C). Heat transmission coefficient was determined considering constant heat flow between two sides of sample.

III RESULTS AND DISCUSCTION

A. Composition of Lime binders

The testing of binders were done in two stages. During the first stage optimal amount of metakaolin were determined in combination with most suitable lime. During the second stage two different ground brick additions were examined to clarify their hydraulic properties.

TABLE III

ARTIFICIAL HYDRAULIC LIME MIXES

Sample name	Lime	Lime, g	Meta., g	Brick1, g	Brick2, g	Sand, g	Water, g	Hydraulic add., %
CL90 20%	CL90	240	60	0	0	600	266	20.0%
CL80 20%	CL80	240	60	0	0	600	300	20.0%
DL60 20%	DL60	240	60	0	0	600	200	20.0%
DL60 40%	DL60	180	120	0	0	600	200	40.0%
DL60	DL60	300	0	0	0	600	200	0.0%
DL60 +10% meta +10% brick1	DL60	240	30	30	0	600	200	20.0%
DL60 + 28.5% brick1	DL60	214.5	0	85.5	0	600	200	28.5%
DL60 +10% meta +10% brick2	DL60	240	30	0	30	600	200	20.0%
DL60 + 28.5% brick2	DL60	214.5	0	0	85.5	600	200	28.5%
CL90 + 20% brick1	CL90	240	0	60	0	600	300	20.0%
CL90 + 20% brick2	CL90	240	0	0	60	600	300	20.0%

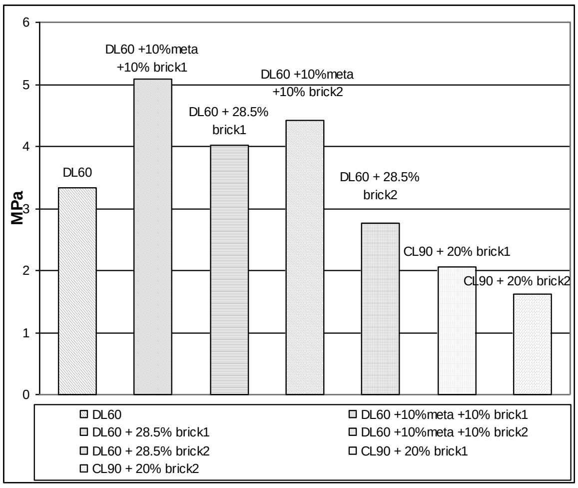

Fig. IV. Compressive strengths of binders with various additives.

Proportions of mix compositions are summarized in Table III.

Results of the first experimental stage are shown in Fig. 3. It shows that CL80 lime has the lowest ability to react with hydraulic additions, which is due to its lower amount of active $Ca(OH)_2$ [15]. Result of CL90 with 20% metakaolin shows good result (4.55 MPa) which is about the same as in similar researches [10]. The best result is generated by DL60 lime with 40% metakaolin addition – 9.98 MPa. The results of second experimental stage are summarized in Fig. 4. As shown, none of the compositions can match the best results of the first stage. It can be seen that both ground brick additives have little hydraulic activity, and works more as a microfiller. Of course it can be beneficial to supplement lime or some more active hydraulic additive not compromising the result, but in this particular research binder with the best compressive strength is needed, so for furtherer research DL60 lime with 40% metakaolin is chosen.

B. Producing Biocomposites

Three compositions of hemp shives and hydraulic lime binder (DL60 with metakaolin) were produced, mix proportions are summarized in Table IV. The most commonly applied hemp/lime proportion by weight was used in mix 2. – 0.38,[14], the other two are with lower and higher ratio, to test the effect of density on compressive strength and thermal conductivity.

As can be seen from Fig. 5, which is force-deformation diagram for compositions from Table IV – increasing the amount of hemp shives above 0.38 has a direct negative effect on compressive strength, as for lowering below 0.38 does not show any effect. This trend can also be seen in Table IV where applied force at 10% deformation is given. It can be explained that proportion of 0.38 is very optimal for this shive granulometry as binder can cover all shives, thus giving the required strength. Increasing the amount of shives creates spots with no binder, which leads to lower compressive strength, but increasing the amount of binder a little does not give notable strength rise, as area of contact zone between hemp shives does not significantly change. Of course, there is a proportion after which the compressive strength rises, but it also has its effect on thermal conductivity. If compared to other studies, then compressive strength of around 0.2 MPa for 330 kg/m^3 density samples is considered good and acceptable for using as thermal insulation material in low-rise buildings [16].

TABLE IV

BIOCOMPOSITE CHARECTARISTICS

Nr.	Hemp/ binder ratio	Density, kg/m3	Compressive strength, MPa	Thermal conductivity λ, W/m8k
1.	0.31	337	0.222	0.0867
2.	0.38	328	0.221	0.0757
3.	0.47	312	0.179	0.1010

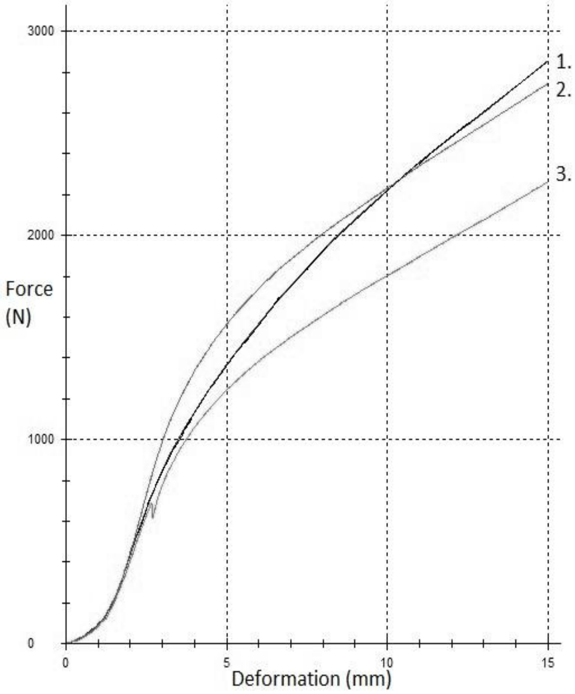

Fig. V. Force-deformation diagram of biocomposites

The results of thermal conductivity coefficient λ are also given in Table IV, and are compared to results of previous tests in Fig. 6. As can be seen from the figure, all three samples stand very close to exponential trendline, which means that all three mixes made are comparable to the ones tested before, whose results are considered as acceptable and usable in further development of thermal insulation biocomposites [16].

IV CONCLUSIONS

1. As the most suitable binder for biocomposites DL60 lime with 40% metakaolin addition was found, as it gave the highest compressive strength value.
2. CL90 lime showed lower results with metakaolin then DL60 lime, but it performed better than

CL80 lime, because of higher amount of active lime.

3. Ground brick showed little hydraulic activity, and could only be used to replace lime for cost saving, but could not increase compressive strength significantly enough to be used in further research.
4. The optimal hemp/binder ratio for this granulometry of shives is 0.38, as more shives decreases compressive strength, and less does not increase it noticeably.
5. The achieved result – hemp/lime biocomposite with compressive strength of about 0.2 MPa for 330 kg/m3 density is acceptable for use as self-bearing thermal insulation material in low-rise buildings.
6. The thermal conductivity coefficients that were achieved stand very close to the exponential trendline of results from previous studies, which means that they are compatible and usable.
7. The aim of this study was achieved as optimal natural binder composition was elaborated and sustainable thermal insulation biocomposites were created.

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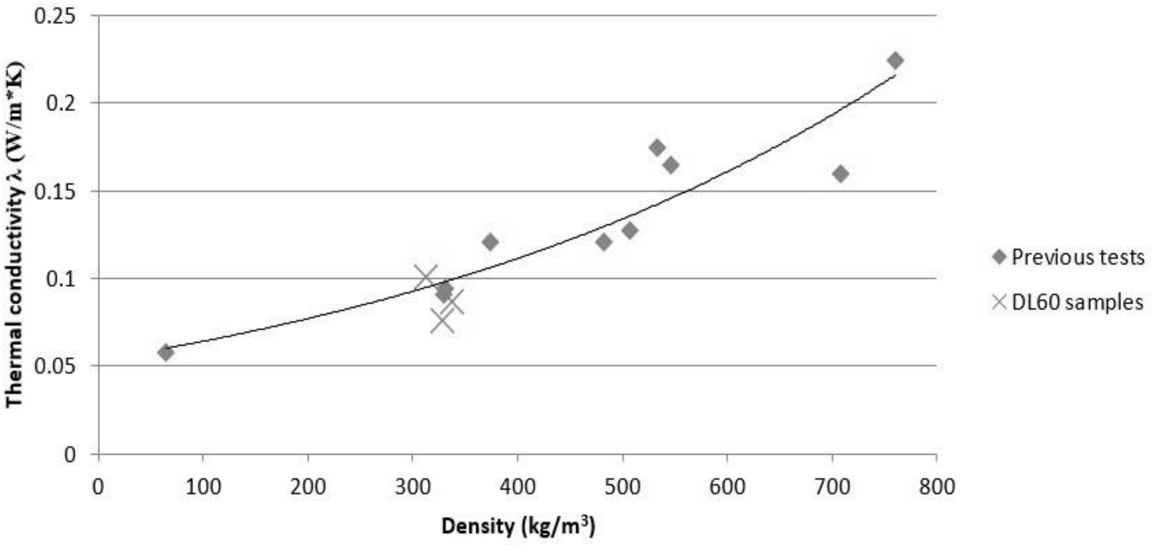

Fig. VI. Thermal conductivity correlation with density

Noise Level Measuring Options and Their Use in Technological Processes

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Abstract. **Working environment has changed in the last few years and work has become more intensive i.e. demand for maximum attention and concentration, workload adaptions with the mental and physical abilities of human, solvation of various organising issues. Risk factors of working environment can be found in every profession and may affect a large number of employees. One of the essential issues in wood processing is noise presence during machining, which is why noise level determination at the workbench during whole working day is important thing to do.**

Measuring devices of the noise level are with various technological abilities, from which one need to choose the most appropriate for the particular situation. Some of the devices are or may be equipped with data recorder, which allows to save measured data for subsequent computer assessment. The article analyses Latvian legislation concerning the noise level determination in the workplace as well as allowable limits. The article offers simplified means of the noise measurement and registration abilities.

Keywords **– noise recorders, noise measurements.**

I INTRODUCTION

Employees of various professions and from various fields in the whole world each day are succumbed to vital work environment risks. The work environment risk is possibility that the security or health of the employee may be damaged during the working process as well as the severity of the possible damage [1]. The working process risk includes draught, noise, vibration, dangerous substances etc. factors. In the wood processing especially expressed is noise presence during the machining. Noise as the working environment risk is essentially dangerous since it is not painful during the injury. It has lasting effect, which may be irreversible, which is why it is important to realize all the bad impact on the health of the employees as well as allowable noise exposure time according to noise exposure level.

The allowable noise level at the workplace is determined by the Cabinet Regulation No 66 “Labour Protection Requirements for employee protection against the noise risk at the workplace” [1] which mentions:

- The measurement and assessment of the noise risk;
- The assessment and reducing of the noise level;
- The use of personal protective equipment
- Health check of the employees
- The procedure of the noise measurement
- The allowable noise exposure time according to noise exposure level, which exceeds the threshold of the exposure level $L_{ex}8_h$=87dB(A).

The measurement and determination of the noise has been regulated by the Latvian State standards, where information can be found about:

• Calculation methods for the noise-induced hearing threshold of the expected permanent displacement, divided in threshold levels for adult target group that appeared during various noise level exposures LVS ISO 1999:2007 [2];

• Calculation of the noise level and exposure at the workplace, where noise has been determined by A and C levels, which means the usage or switching off the frequency filter. LVS EN ISO 9612:2009 [3];

• Testing methods of the basic noise emission to determine noise at the various wood processing working machines LVS ISO 7960:2005 [4];

• Determination of the noise emission pressure at the working machines at workplace or other specific places by using sound intensity. LVS EN ISO 11205:2010 [5].

Based on the State Labour Inspectorate`s first semi-annual report about approved occupational diseases that are connected with hearing, during 2011 has been detected 16 cases, but during 2012 first semi-final 11 cases [6].

Employer has to control the noise level at the workplace. It has to be done by verified equipment and it must create the working environment according to Ministry Regulation No 66 conditions [1]. To attract employers for purchase of the noise level measurement and registration devices, the article compares various noise level registrars and their capabilities. That means that employer personally may control the situation in processing plant and if necessary make all the working environment improvements.

II MATERIALS AND METHODS

Theoretical justification of noise

Noise is a risk factor of the working environment, which creates discomfort for employees. If human is continuously exposed to such noise effect that exceeds 80 dB(A) there is a chance that with time his/her hearing will worsen and hearing injury will appear.

Severity of the injury depends on noise level and exposure time, as well as sensitivity level of each person individually. Hearing injury is inner ear nerve cell damage. Hearing injury cannot be treated and usually it causes social isolation. Noise may cause not only hearing injury, but also stress, high blood pressure, fatigue, insomnia etc. It may stimulate exacerbation of other diseases and related absenteeism, accidents and increased number of errors [7]. A large number of employees who are employed in wood processing plants and furniture manufactories are exposed to such noise level that even hardens the communication of the workers. In lot of workplaces noise level exceeds 90 dB(A) and in some places even more.

The biggest noise level creates the mechanical processing of wood. They are fast moving and rotary cutting tools, which are shifting from one level into another, parts that are interfering with each other, pressured air from the pneumatic systems and noise from the ventilation system. Impulsive noise is also typical for this field when pressured air is discharging from various pneumatic tools or when massive objects are smashing together [7].

Two main characteristics of the noise are frequency that is measured in hertz (Hz) and intensity that is measured in decibels (dB(A)). Person`s organ of hearing perceives sound vibrations of 16…20000 Hz. Practical significance for sound is frequency zone, that corresponds to manufacturing conditions (40…10000 Hz) because it includes the most of the manufacturing noises [4]. A wide range of frequency zones determines *Equivalent* noise pressure level by using dB(A) measurements. According to Europe standards (ISO 1996/1) there is a specific terminology for determination of this measurement: A – weighted sound pressure level (L_{pA}) [8].

The noise may be theoretically divided into three groups: low-frequency noise, when frequency is lower than 300 Hz, average-frequency – 300…1000Hz and high-frequency when frequency is higher than 1000 Hz. The intensity of sound or volume has been determined in decibels (dB) that is logarithmic sound. Fact that the noise is dangerous can be determined by four factors: the intensity of sound or volume, frequency or tune, periodicity (how often in sounds) and duration (how long it sounds).

Level of the noise cannot exceed the noise exposure limit (87 dB(A)) or at the working place higher than (140 dB(A)) depending on the Ministry Regulation No 66. If the threshold of the noise exposure has been exceeded, all the necessary occupational health and safety measures must be done immediately and noise level must be reduced at least to its exposure threshold (87 dB(A)) [1].

Methodology of noise determination

The methodology of noise determination has been determined on 4th of February 2003 by Ministry Regulation No 66, 1 appendix [1]. Noise measurements are being done to determine the environmental noise level, as well as for noise effect determination on person and his/her hearing. During the noise determination, following conditions must be met.

- manufacturer`s technical documentation for noise measurement equipment, where information about noise level determination can be found. Even though noise level determination process is similar, various companies have various models therefore technological capabilities of the device are different;
- all the regulations of occupational health and safety that concerns the specific environment where noise level measurements will be done, must be observed;
- before the working day ensure, that calibration term for equipment, which will be used, has not expired, otherwise biased measurement results may appear;

Before the beginning of noise level measurements the following measures must be done;

- observe the intended measurement's place, if it will be in facility or outside, check all the organizing issues, for example, measurement time, accessibility of the object and other operations necessary for measurement`s preparation;
- check the microphone, accumulator and condition of device and make all the necessary measurement preferences;

During the noise level measurements, following conditions must be met;

- before and after each measurement, equipment preferences must be set and acoustic test of the microphone must be done;
- duration of the measurements is long enough to make all the necessary noise measurements and acquire sufficient amount of data;
- intermittent noise measurement time interval contains at least one full working cycle, characterised to noise source, but no less than 20 minutes;
- measurement duration, place and type is determined based on corresponding standard recommendations. During measurements, environmental conditions (side noise and direction of wind) and noise characteristical changes must be taken into consideration;

By choosing noise level measurement points, following conditions must be met:

- measurement points are determined based on applied measurement methodology recommendations to avoid measurement errors from other devices;
- in the place and territory of measurements at least three measurement points must be done;

When choosing measurement points, microphone should be placed at least 3,5 m from any reflective surface except for the earth`s surface. Microphone must be placed 1,2 m – 1,5 m above the earth.

If presence of employee is necessary or measurements are taken while employee is moving around, microphone must be placed 0,10 m – 0,01 m from employees ear, that receives most of the dB(A) – weighted sound exposure or equivalent uninterrupted dB(A) – weighted sound pressure level.

When choosing measuring points in facility, they must be at least 1m from the wall or other huge reflective surfaces e.g. 1,5 m large window and 1,2 m – 1,5 m above the floor. If the specific workplace does not have any specific indications, then the amount of measuring points (n) must be chosen by the following formula:

$$n = 4 \cdot \lg\left(\frac{V}{50} + 2\right) + 2,$$

where n — the amount of measurement points, rounded to the nearest integer;

V — volume of room, m^3

Measuring points near the noise source usually don`t place in the area, that is twice as big as its largest body.

In addition to aforementioned conditions, following demands must be complied:

- in accordance to aforementioned conditions microphone placement, measurement values, test bandwidth, measurement duration and other characteristic conditions;
- write down all the noise sources that is sounding during the measurement, their location, measurement equipment position, direction of microphone and distance till the noise source. Background noises are measured at the same measurement points as the investigation`s noise point;
- if undesirable side noises appears (non-characterised to investigating noise), measurements must be stopped as well if conditions for the measurements haven`t been met or measurement place selection`s underlying principles haven`t been complied.

Noise from machines and devices determines as time-weighted equivalent noise level L_{AeqT}, dB(A). Letter A behind dB indicates that measurement equipment is set for measuring in the scale A (all audible from 20 Hz to 20kHz).

The noise effect on person determines by allowable noise exposure`s performance value i.e. daily noise exposure level in the working environment during shift, $L_{EX,maiņā,}$ dB(A).

There are as follows noise exposure thresholds and exposure`s performance values:

- threshold of noise exposure: $L_{EX,maiņā}$ = 87 dB(A) and maximum threshold level during short-term performance L_{max} = 140 dB(A);
- the highest allowable noise exposure value, particularly in case when Personal hearing protection is not accessible: $L_{EX,maiņā}{}^{=}$ 85 dB(A)) and maximum threshold level during short-term performance L_{max} = 135 dB(A).

During noise level measurements at workplace, the Personal hearing protection impact is not taken into the consideration. Eveready’s noise exposure level $L_{EX,maiņā}$ determines by time, that employee needs to spend in noisy environment and by using mathematical calculations or computer software – calculator. If, during a working week in the specific workplace, the noise level significantly differs during day-time hours, employer is entitled to change noise level determination from every day’s noise exposure level to average weekly noise exposure level [9].

Noise measuring devices

For qualitative noise level determination a several measuring devices are necessary. Primarily, it is a noise level determination device. Sometimes these devices are equipped with display, where noise level can be seen during the measurements. Usually these devices work on batteries or accumulator and are not quite big, which means that they are easily movable. With such devices, measurements at workplace can be done comfortably but if data analysis is necessary, then additional noise pressure level reader and storage module are required. It may be built in measuring device or separately connected to noise registration device, if it has necessary output. The main task of the device is recording the level of noise changes. It is necessary to store data and analyse them later on the computer. Changes in the level of noise must be recorded with interval, which sometimes changes and gives a lot of data, which can be later analysed. With hand-writing such data cannot be written as fast. To set up and run noise pressure level reader and storage module, a computer with software that comes together with device is required.

A various devices may be used for noise recording: integral or broad frequency range sound level measuring devices (dB(A) scale) octave zone (individually separate frequencies) sound analysers, individual noise dosimeters, sound impact level indicators, devices for calibration of aforementioned equipment etc. There are also electronic measuring devices (multi-dosimeters) that combine several measuring functions.

A lot of companies are offering for purchasing sound level measuring devices, with the price range that is quite huge, ranging from a few tens of dollars (e.g. Triplett TSC-MC1 [10]) to several hundreds of dollars for one measuring device (e.g. SDL600 [11]) or even several thousands of dollars for one measuring system. The price of the device basically depends on its application possibilities:

- either its calibrated or not;
- either it can be connected to computer;
- either it has memory card;
- either it has a switchable range option;
- precision of measurements and acquired data amount per second;
- software for data processing etc.

Cheaper devices usually are for approximate noise level measurement at the specific moment, without an option for recording and analysing data later. Average priced devices can be connected to computer, which also allows to connect data storage device that makes it an intermediary between device and computer, for storage of a recorded data, e.g. HOBO U12 [12]. Data storage device can be connected to several other devices and save data, which can be later analysed on computer. In that way a cheaper device may be bought, without unnecessary purchase of memory cards and built in data storage devices. Measuring device, of course, must have output to connect it with data storage device. Expensive measuring devices have built-in data storage, which allows reading of registered data, when device is connected to computer. There are devices which save information on memory cards, which allow to copy data on computer. Particular software should also be taken into consideration, which allows process and send data, for example, to MS Excel software for graph, curve or other figure modelling. Expensive measuring devices may be connected to network, which allows to make a measuring system and look on noise level data at the making moment in the particular workplace e.g. NTi Audio XL2 [13]. Several measuring devices from each price category may be seen in table 1, which also shows comparison of characteristic parameters.

TABLE 1.
NOISE RECORDERS

Model	Triplett TSC-MC1	Eclipse MT-4018	AEMC CA832	General DSM403SD	Extech SDL600
Range, dB	40-130	30-120	30-130	30-130	30-130
Basic accuracy, dB	-	± 3.0	±1.5	± 2.0	±1.4
Weighting	-	-	A and C	A and C	A and C
Response Time, sec.	-	0.750	0.5	1.0	0.125
Datalogging	-	-	-	SD card	SD card
Analog Output	-	-	AC	-	AC
PC Interface	-	-	-	-	USB
Price (for 01.02.2013.)	$30.95	$89.95	$199	$355	$780

Table shows, that analogue output, that allows to connect data recorders, is available only at the average price range e.g. HOBO. With simpler devices it is possible to determine specific noise level at the particular measurement place, without a chance to save these data. A possible error chance also increases and on simplified devices such parameter is not shown at all. Table also shows, that technologically better devices may save several data in one second, but it should be noted, that data recording frequency effects memory, because the more data the more memory`s capacity is necessary. Some devices allow weighting frequency filter A or C. As table 1 shows, direct computer connection is available only for technologically better devices, which are equipped with USB connection. It also shows that such devices are very expensive and propose to choose cheaper devices that can be connected with computer.

Offer for noise level measurement devices is wide, so considering that particular situation is known, it is possible to choose the most efficient option for noise level measurement, recording or monitoring.

Example of the noise measurement.

For noise level measurements a noise level recording device “Sound level meter 93411” have been used, which provides short-term acoustic pressure level measurements and noise pressure reading and storing module “Hobo H08-004-02”, which allows to send acquired data to computer, where they can be easily processed (pic. 1)

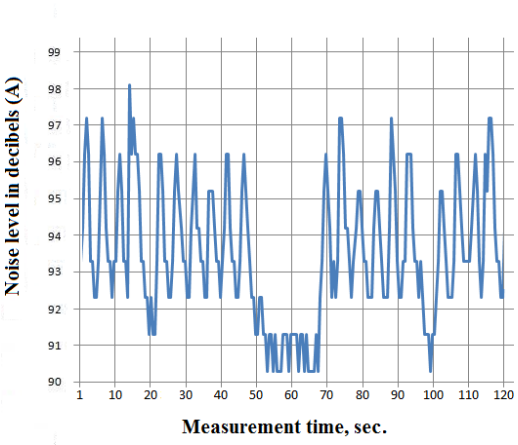
Pic. 1 Sound level meter and Hobo

Data recording must be according to work methodology, which provides information about data recorder`s placement, data recording time, period and beginning and finish of the recording. At the beginning of work, module must be connected to computer`s Com port. Specifically with Hobo software the necessary settings must be set. For example, about delayed start beginning time, record interval of the necessary data etc. When all the needed corrections have been made, module must be activated and record may begin

When data record has been finished, module must be connected to computer once again, to load information from module to computer`s software file. Loaded data on the computer appears in the form of table, which may be consulted, copied, printed and sent to different software e.g. MS Excel and process necessary parts of data.

III RESULTS AND DISCUSSION

Measured data may be stored in the workplace and offers results digitally, that allows us to save, forward and analyse them by using various software. For example, a diagram may be extracted, that shows noise level during the process (Pic. 2).



Pic. 2 Noise level at the workplace during wood processing

The given example shows noise level of the circular saw machine during wood processing, which is recorded in two minutes long interval. As it shows, this workplace mostly have 92,3 dB(A) to 96,2 dB(A) noise level. A peak noise of 98,1 dB(A) can also be seen, which is short and is not characteristic compering to all processing time. Graph also shows that in period between 50 to 70 seconds the level of noise significantly lower, which means that during this stretch work stopped and machine worked at idle. As seen in example, such noise level analysis gives insight about noise level at the workplace as well as its dynamics. It means that employer may control this noise level from an occupational health perspective and decide if additional improvements at company are really necessary, so that it would correspond to Ministry Regulation No 66 conditions [1]. The noise level data may be also used to keep an eye on other processes, like working machine`s workload. If continuous data recording has been made then later it may be evaluated in the form of diagram, sum up time, during which the working machine has worked at idle and how long at downtime. Such information would help to optimize processing work time. Noise level data gives an opportunity to control and manage technological processes.

To make possible control and management of the surface quality by applying noise level record, it is important to measure noise during inter-sharpening time of the cutting tool. It means that noise level measurements should be done right after change of new cutting tool and until the moment, when surface quality is not satisfactory. Noise level can be measured on an on-going base or cyclically. If during the processing time noise raises a bit, the main reason is worn off cutting toll which lead to worse surface quality. So under certain processing conditions it is possible to make provisions about surface quality according to noise level data. When the processing conditions are changing (e.g. type of wood, cutting depth or material supply rate) the level of noise will change but noise level increase connection during the processing will remain.

Publication may serve as a basis to choose appropriate noise level recording device for noise level data acquisition.

IV CONCLUSION

Companies are offering various noise level recorders with many different functions and possibilities.

Not every noise level recorder can save data for later analysis.

Noise level measurements play an important role in technical, technological, economical and social processes of wood manufacturing.

Noise level measurements at workplace give an opportunity to follow and assess changes in the working environment to take all the necessary actions to improve this environment and protect employees from undesirable noise effect.

Causes between noise level and quality of workpiece correlates, which may be affected by worn off cutting tool, work machine`s technical condition and other important issues related to manufacturing.

By improving (digitizing) the noise level`s measurement methodology, it would make possible to follow up not only the surface quality of the processing material and make judgements about the cutting toll`s worn off condition, but also develop the volume of cutting toll`s exchange cycle, track finished work and working machine`s workload, technical service maintenance and repair.

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Soil Contamination in One of Preschools Influenced by Metal Working Industry

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***Abstract.* The aim of research was to estimate the present impact of drill plant or other pollution sources on soil anomalies of the preschool area and to reveal the depth of penetration of pollutants. Soil samples from 9 cores in the territory of the preschool were taken from 5 depth intervals: 0-0.5 m, 0.5-1.0 m, 1.0-1.5 m, 1.5-2.0 m and 2.0-3.0 m. Total number of samples was 45. Each sample was sieved to <2 mm fraction, milled and homogenised with binder before pressing 2 pellets. All pressed pellets were analysed by energy-dispersive x-ray fluorescence for determination of the contents of harmful chemical elements As, Ba, Cr, Cu, Mo, Ni, Pb, Sn, V, Zn and major elements Al, Ca, K, Fe, Mg, Na, P, S. Si, Ti. Samples where maximum permitted concentrations of Mo, Pb, Sn are exceeded occur not only in the uppermost layers, but also in the deeper layers. The highest median contents of most harmful chemical elements, except V and As, are in the uppermost 0.0-0.5 m layer and decrease with depth until 2.0-3.0 m or 1.5-2.0 m. To eliminate the influence of soil clay content in different samples, normalisation of concentration coefficients by the median of Al, K and Ti concentration coefficients was used. The depth of penetration is largely influenced by lithological composition of soil and is much deeper in sandy soil without layers enriched in clay.**

***Keywords* – harmful chemical elements, metal working, preschools, soil contamination.**

I INTRODUCTION

Urban topsoil is inevitably polluted by harmful chemical elements [1, 2, 3, 4]. Children attending preschools are especially sensitive to this contamination [5]. Therefore the areas of preschools are important objects of urban geochemical investigations. In Lithuania they are carried out taking into account national hygienic norm for maximum permissible concentrations (MPC) of harmful chemical elements in soil [6]. Previous research of topsoil contamination in 49 preschool playgrounds located in 7 districts of Vilnius city has shown that 21 of them had moderately hazardous to hazardous levels of contamination and that Zn was the dominant soil contaminant, because the harmful chemical elements according to the number of areas where their MPC values were exceeded were arranged as follows: Zn(13)>Pb(5)>Ag(2)>Cu, Sn, Mo (1) [7]. The only area where MPC of Mo is exceeded is in Naujamiestis district. Previous investigations of Vilnius topsoil contamination by harmful chemical elements have shown that this district is one of the most heavily polluted [8]. The reason is that powerful metal-working, radio and electrical engineering plants operated in it in the 20th century. Drill plant was one of them which formed contrasting anomalies of Mo, Cr, Co, Cu, V, Ni, also Ba was its specific pollutant. Drill plant is still operating though production volume has decreased. One of the preschools of this district is located close to this plant.

The aim of this research was to estimate the present impact of drill plant or other pollution sources on soil anomalies of the preschool area and to reveal the depth of penetration of pollutants.

II MATERIALS AND METHODS

Soil samples from 9 cores in the territory of the preschool which is close to drill plant (Fig. 1) were taken from 5 depth intervals: 0-0.5 m, 0.5-1.0 m, 1.0-1.5 m, 1.5-2.0 m and 2.0-3.0 m. Total number of samples was 45.

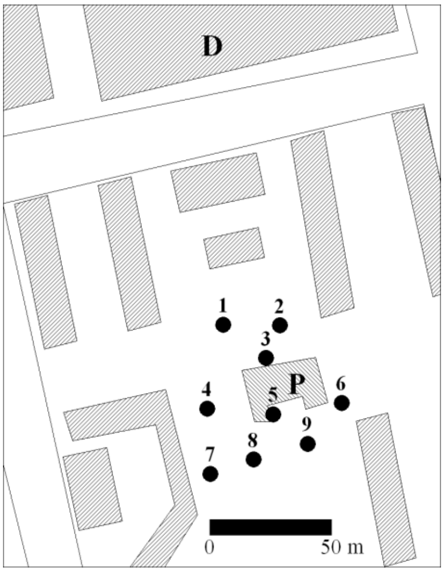

Fig. 1. Location of drill cores in preschool area. Note that P means preschool, D drill plant and black circle with the number above indicates location and number of core.

Each sample was sieved to <2 mm fraction, milled and homogenised with binder before pressing 2 pellets. All pellets were analysed by energy-dispersive x-ray fluorescence (Spectro XEPOS equipment with TurboQuant calibration method) for determination of the contents of harmful chemical elements As, Ba, Cr, Cu, Mo, Ni, Pb, Sn, V, Zn and major elements Al, Ca, K, Fe, Mg, Na, P, S. Si, Ti. The median value from two pressed pellets of each sample was calculated. The laboratory participates in International Soil-analytical Exchange (ISE) program of Wageningen Evaluating Programs for Analytical Laboratories (WEPAL) [9]. ISE samples were used for re-calibration of the element contents using linear, power and second order polynomial functions, for some elements the average from two re-calibrated values.

III RESULTS AND DISCUSSION

The contents of most harmful chemical elements, except Mo, Pb and Sn, do not exceed maximum permitted concentrations (MPC) for soil [6]. The samples where MPC values of Mo (5 ppm), Pb (100 ppm), Sn (10 ppm) are exceeded occur not only in the uppermost layers (Mo in core No 1, Sn in core No 5), but also in the deeper layers: at the depth 0.5-1.0 m in core No 7 (Sn) and core No 8 (Pb and Sn), at the depth 1.0-1.5 m of core No 9 (Sn) (Table 1).

TABLE 1.

THE CONTENTS OF CHEMICAL ELEMENTS (PPM) IN DEPTH INTERVALS OF CORES.

NOTE. THAT MAXIMUM CONTENT OF CHEMICAL ELEMENT IN EACH CORE IS IN BOLD AND MAXIMUM IN ALL CORES IS UNDERLINED.

No	H (m)	Zn	Pb	Cu	Sn	As	Mo	V	Cr	Mn	Ni	Ba	Al	K	Ti	Si
1	0.0-0.5	**156**	**50.2**	**18.6**	5.64	**5.94**	**5.75**	13.1	**26.8**	395	10.0	**290**	18615	12571	1099	303806
1	0.5-1.0	74.1	39.5	15.3	**9.44**	<3.0	1.18	12.7	17.2	**402**	7.2	251	18319	12725	1012	**390491**
1	1.0-1.5	48.1	18.3	10.0	6.26	4.14	0.70	18.0	16.7	366	8.2	276	25442	14729	1133	389035
1	1.5-2.0	29.3	11.6	7.2	<1.5	3.04	1.29	**35.9**	18.6	382	8.2	251	21235	13905	1027	325045
1	2.0-3.0	25.8	8.4	9.0	<1.5	<3.0	0.58	26.8	24.1	287	**11.9**	287	**30659**	**19736**	**1707**	336369
2	0.0-0.5	**47.8**	**18.0**	**9.2**	**7.06**	**3.10**	0.92	16.1	15.7	242	6.3	**277**	23380	15683	1208	417779
2	0.5-1.0	34.0	11.7	5.8	1.61	<3.0	0.68	5.9	13.6	234	5.4	251	25301	14814	1022	426738
2	1.0-1.5	19.3	8.9	4.6	<1.5	3.16	0.22	22.1	14.9	**412**	6.6	254	20946	13962	987	**445658**
2	1.5-2.0	18.7	8.6	4.7	2.46	<3.0	**1.08**	**29.7**	12.4	368	5.8	224	16746	12265	808	334550
2	2.0-3.0	24.3	9.4	8.3	1.74	3.04	0.39	19.3	**21.6**	284	**10.2**	270	**29416**	**19038**	**1536**	340417
3	0.0-0.5	33.6	17.6	11.9	1.94	<3.0	0.43	23.9	18.5	374	7.4	235	19468	12435	1134	**431559**
3	0.5-1.0	**39.6**	**22.5**	**18.2**	**5.57**	3.10	0.85	**24.2**	20.7	379	9.1	245	22456	13735	1250	394720
3	1.0-1.5	25.1	10.4	8.7	<1.5	3.23	**2.60**	18.8	24.5	**435**	9.6	231	23285	13400	1405	396312
3	1.5-2.0	28.2	10.4	9.5	<1.5	**5.14**	1.39	21.6	19.5	433	9.7	251	20846	12832	1368	381849
3	2.0-3.0	26.8	9.1	8.2	<1.5	<3.0	1.59	24.9	**26.1**	320	**12.3**	**303**	**34018**	**20520**	**1833**	311901
4	0.0-0.5	**66.9**	**39.0**	**17.6**	**7.00**	**3.96**	**1.21**	16.3	**21.8**	**339**	**10.5**	**293**	**25737**	16046	**1323**	369979
4	0.5-1.0	35.6	20.4	8.9	3.23	<3.0	1.05	**18.6**	11.5	314	6.4	286	21730	15614	1125	389081
4	1.0-1.5	17.2	14.8	5.6	2.27	<3.0	0.98	11.8	14.5	193	5.2	289	22009	**18243**	1103	427784
4	1.5-2.0	14.9	10.4	4.4	<1.5	<3.0	0.87	9.7	12.2	192	5.8	265	19557	16250	962	**441474**
4	2.0-3.0	17.2	9.0	4.4	<1.5	<3.0	1.21	14.9	13.6	258	6.2	254	18863	14030	827	416460
5	0.0-0.5	**71.7**	**51.8**	**28.5**	**12.8**	**3.47**	**1.37**	16.7	**18.4**	**256**	**7.6**	248	**19127**	14150	**929**	399541
5	0.5-1.0	32.7	31.0	15.2	6.01	<3.0	1.21	6.0	11.9	194	4.7	234	14738	11810	680	443247
5	1.0-1.5	7.3	7.2	2.6	3.30	<3.0	1.16	3.6	9.0	87	3.0	**282**	17853	**18323**	474	452389
5	1.5-2.0	14.5	6.0	5.6	<1.5	<3.0	0.77	**19.1**	9.0	168	4.1	199	12381	10271	751	457619
5	2.0-3.0	7.4	3.5	1.8	<1.5	<3.0	**1.37**	11.6	10.8	122	2.9	180	10545	9860	559	**471354**
6	0.0-0.5	**185**	**36.6**	**20.2**	**8.81**	**8.61**	**3.50**	21.2	21.3	329	10.0	250	20153	12793	1021	313584
6	0.5-1.0	73.1	28.8	15.7	3.49	6.00	1.56	**26.9**	**25.1**	469	**11.0**	241	**24747**	13832	1405	381440
6	1.0-1.5	44.2	16.7	9.7	2.33	4.02	1.45	18.3	21.6	469	9.0	**270**	23279	13201	1298	400678
6	1.5-2.0	28.5	12.1	8.5	2.40	<3.0	0.53	9.2	13.3	326	6.2	234	18341	12424	888	**431832**
6	2.0-3.0	38.6	12.8	9.1	<1.5	5.32	0.70	23.7	**25.1**	**481**	9.8	252	24229	**14950**	**1426**	327501
7	0.0-0.5	68.0	35.6	21.3	7.79	**8.35**	1.70	13.9	**19.1**	333	7.6	272	15083	11788	830	366659
7	0.5-1.0	**69.6**	**38.5**	**22.4**	**14.8**	3.66	1.13	**16.9**	14.4	**422**	**8.2**	**313**	19182	14655	1037	377802
7	1.0-1.5	11.7	7.8	3.6	2.59	<3.0	0.80	0.4	9.3	157	3.9	290	**19237**	**16841**	995	438927
7	1.5-2.0	8.7	5.9	3.5	3.11	<3.0	**2.04**	8.7	14.0	147	4.3	266	15164	15331	1083	**460029**
7	2.0-3.0	20.0	6.6	5.9	3.68	<3.0	0.95	16.6	16.0	308	5.9	192	15153	10719	**1465**	451661
8	0.0-0.5	120	42.2	17.6	4.25	**3.78**	**1.81**	25.0	18.9	**304**	**10.8**	269	**19006**	13576	1049	389581
8	0.5-1.0	154	60.6	**19.8**	12.5	3.60	1.42	13.7	**21.5**	303	7.5	**291**	18956	**13888**	1018	408364
8	1.0-1.5	**40.1**	**131**	12.4	**29.4**	<3.0	1.26	5.3	11.0	221	4.9	244	17225	13832	886	404453
8	1.5-2.0	22.5	15.6	6.0	6.38	<3.0	1.13	9.9	14.0	214	4.4	228	15920	12231	963	454526
8	2.0-3.0	14.3	6.7	4.2	1.81	<3.0	0.77	**20.1**	13.9	217	3.8	162	9209	8942	**1372**	**468398**
9	0.0-0.5	81.1	29.2	19.7	7.12	<3.0	**1.98**	11.2	**21.0**	276	**9.0**	**278**	**22082**	**14541**	**1096**	373890
9	0.5-1.0	92.2	63.9	19.6	12.4	**4.08**	1.05	14.1	15.8	277	7.2	247	18478	13434	999	397904
9	1.0-1.5	**95.3**	**71.7**	**33.1**	**104**	<3.0	1.13	**18.9**	15.7	**295**	6.9	265	16278	12730	981	408410
9	1.5-2.0	38.0	34.2	14.9	9.23	<3.0	1.08	7.3	9.9	243	4.5	234	15126	12111	758	430331
9	2.0-3.0	8.3	3.9	3.1	<1.5	<3.0	0.77	10.1	9.0	136	2.8	161	9506	8544	512	**465123**

Basing on previous investigations of drill plant, also its nearest surroundings [10], much higher contents of harmful chemical elements, especially siderophiles were expected. Most probably, there are several reasons. Possibly, the contamination level markedly decreases with distance from pollution source or lower production volume and environmental protection measures in drill plant result in rather satisfactory situation of the territory of preschool. Besides, it has been shown [11] that the contents of most harmful chemical elements earlier determined by OAES are higher than respective contents determined presently by EDXRF. According to the radio of respective medians the harmful chemical elements can be arranged as follows: V(2.48)>Ni(1.91)> Mo(1.75)> Zn(1.71)> Mn(1.70)> Cr(1.58)> Cu(1.56)> Pb(1.37)> Ba(1.01). The sequence shows that mainly the estimates of the contents of siderophiles by EDXRF equipment are significantly lower. This regularity can explain why large and contrasting anomalies of Mo are now hardly noticeable, except one sample in the uppermost layer of core No 1. However, the following facts confirm that the influence of drill plant still exists: 1) maximum contents of Mo and Cr are in surface layer of core No 1; 2) maximum content of V is in the 1.5-2.0 m layer of this core. Namely this core is the closest to drill plant and namely these elements are specific pollutants of this plant.

The highest median contents of most harmful chemical elements, except V and As, are in the uppermost 0.0-0.5 m layer and are as follows in ppm: 71.7 for Zn, 36.6 for Pb, 18.6 for Cu, 7.06 for Sn, 1.70 for Mo, 19.1 for Cr, 9.02 for Ni, 329 for Mn and 272 for Ba. For Zn, Pb, Cu, Sn, Mo they gradually decrease with depth until 2.0-3.0 m, for Cr, Ni, Mn, Ba only until 1.5-2.0 m depth where they are the lowest. On the other hand, the highest median contents of V (19.3 ppm) and As (4.18 ppm) are in the lowermost layer 2.0-3.0 m. However, increase of the content of harmful chemical elements can be related not only to anthropogenic activity, but also to natural reasons, first of all to increase of clay content in soil. It has been shown that major elements Al, K and Ti are good indicators of clay content in urban soil [12]. In some of the cores (No 1, No 2, No 3) the lowermost layer has the highest contents of Al, K, Ti, meanwhile in other cores (e.g. No 4, No 9), on the contrary, it has the lowest contents of these clay indicators. Unequal clay content is the first obstacle for precise estimation of contamination level. Another obstacle for the aim of this research is that the new background values based on EDXRF measurements are not yet estimated for different types of natural soil.

Quaternary sediments comprise soil parent rocks in Lithuania. Vilnius is located at the boundary between the sediments formed during penultimate glaciation (Medininkai) and sediments of the last glaciation. Great part of Vilnius soil was formed on sandy sediments. The preschool is located in the area which is at the boundary between marginal glaciofluvial sediments of Medininkai glaciation represented by various sand and glaciofluvial sediments of Baltija glaciation represented by fine sand [13]. Since the dominant sediments are sandy, their background values are supposed to be much lower than of sandy loamy or loamy soil as it was shown on the basis of OAES results [14]. Therefore the lower quartile values were chosen in this research as approximate estimate of background. First of all the concentration coefficients of chemical elements were calculated dividing their content in sample by respective background value. Then the median of Al, K and Ti concentration coefficients was calculated in each sample. This value serves as an estimate of sample enrichment in clay (EC). Aiming to obtain more precise estimate of contamination level, the enrichment factors of harmful chemical elements were calculated by dividing their concentration coefficients by respective enrichment in clay.

In most cores (except No 6, No 7) the maximum value of EC coincides with maximum value of Al/Si which is well known indicator of clay content. Pearson correlation coefficient between these variables is 0.921 and is significant ($p<0.001$) indicating that dividing by EC might give more precise estimation of contamination level. Enrichment factors (EF) exceeding 1.3 can be used as indicators of anthropogenic pollution [15]. Likewise, EC>1.3 values can be used as indicators of increased clay content.

There are obvious differences between the cores according to layers with maximum EC values: in cores No 1, No 2 and No 3 they are in the lowermost layer, in cores No 4, No 5, No 8 and No 9 in the uppermost, in cores No 6 and No 7 in the intermediate layers. The cores No 5, No 7, No 8 and No 9 are sandy, meanwhile in other cores the enriched in clay layers exist at different depth.

Overall maximum EF values of the greater part of harmful chemical elements are in the uppermost layers: of Mo and Cr they are in core No 1 which is the closest to drill plant indicating that the latter is pollution source of preschool, of Zn in core No 6 which is close to the street and might be influenced by traffic, of Ni in core No 8, of As and Ba in core No 7. However, overall maximum values of 5 other harmful chemical elements are in deeper horizons: either at the depth of 1.0-1.5 m or at the depth 1.5-2.0 m.

Approximate depth of penetration of pollutants can be estimated according to EF>1.3 values. In the closest to the drill plant core No 1 the maximum depth of penetration is 1.5-2.0 layer for V, Mn, Ni and Zn. All 4 upper layers are sandy, meanwhile the lowermost is enriched in clay and is probably waterproof. For Pb, Cu, Sn the depth of penetration is not so deep: only until 1.0-1.5 m. These elements are not specific pollutants of drill plant. Maximum values of most pollutants in core No 1 are in the uppermost layer or at 0.5-1.0 m depth, the only exception is V.

The lowermost layer of cores No 2 and No 3 is also mostly enriched in clay, so maximum depth of penetration also does not exceed 2 m. However, there are some differences between these cores. The uppermost layer of core No 2 is slightly enriched in clay, so only some of pollutants (V, Mo, Mn, Sn, partly Zn) penetrate deeper. On the contrary, in core No 3 the upper layer is sandy and the next two are slightly enriched in clay, so maximum EF values are usually not in the surface layer, but deeper.

In core No 4 the uppermost layer is mostly enriched in clay, also the third layer at 1.0-1.5 m depth is slightly enriched in clay. Therefore maximum depth of penetration does not exceed 1 m, besides, maximum EF values of most pollutants (except V) are in the uppermost layer.

In cores No 5, No 7, No 8 and No 9 there are no layers enriched in clay, so maximum penetration of pollutants is the deepest, for some of them until 2.0-3.0 m depth, despite the fact that the highest EC value is in the uppermost layer.

In core No 6 the uppermost layer is sandy and the layer 0.5-1.0 m is mostly enriched in clay. Therefore maximum EF values of pollutants, except Mn, are in the uppermost layer. Despite the fact that there are two deeper layers (1.0-1.5 m and 2.0-3.0 m) with EC>1.3 in this core, penetration of pollutants is deeper, the maximum depth of penetration for Zn, Cr, Mn is 2.0-3.0 m. Most probably, either the layers are not quite waterproof (other than 1.3 value should be selected for distinguishing layers enriched in clay), or the layers were disturbed by digging for installation of the service-pipes, or contamination origin is different: not from atmosphere and infiltration, but from underground pipelines or contamination from borer.

IV CONCLUSION

Samples where maximum permitted concentrations of Mo, Pb, Sn are exceeded occur not only in the uppermost layers, but also in the deeper layers. Whatever is the reason of pollution, the depth of penetration is largely influenced by lithological composition of soil and is much deeper in sandy soil without layers enriched in clay.

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The Mathematical Modeling of Metals Mass Transfer in Three Layer Peat Blocks

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***Abstract*. The mathematical model for calculation of concentration of metals for 3 layers peat blocks is developed due to solving the 3-D boundary-value problem in multilayered domain – averaging and finite difference methods are considered.**

As an example, mathematical models for calculation of Fe and Ca concentrations have been analyzed.

***Keywords*: averaging method, finite difference method, boundary conditions of third type, heavy metals, peat bog.**

I INTRODUCTION

Being based on the experimental data the mathematical model for calculation of concentration of metals in different points for different 3 layers (peat blocks) is developed.

An averaging [3] and finite difference method by solving the 3-D boundary-value problem with boundary conditions of the 3rd type in the N-layered domain of homogeneous materials with piece-wise diffusion coefficients, the concentrations functions in every layer and the fixed source function are in question.

The boundary-value problem herein deals with solving the elliptic type of second order for the partial differential equation with piece-wise diffusion coefficients in the N-layered domain.

Similarly, the results of a number of the previously modeled diffusion processes without mass transfer showed a comparatively good compatibility with the experimental data [1].

By using the averaging method with quadratic splines developed by A. Buikis [3], a finite-difference scheme was created. In its turn, it was used to reduce a 3-D boundary-value problem to a system of 2-D partial differential equations, which simplifies the task considerably.

II MATERIALS AND METHODS

1. A mathematical model

The process of diffusion the metal in the peats block is consider in 3-D parallelepiped

$$\Omega = \{(x, y, z): 0 \le x \le l,\ 0 \le y \le L,\ 0 \le z \le Z\}$$

The domain - consist of multilauer medium. We will consider the stationary 3-D problem of the linear diffusion theory for multilayered piece-wise homogenous materials of *N* layers in the form

$$\Omega_i = \{(x, y, z): x \in (0, l),\ y \in (0L),\ z \in (z_{i-1}, z_i)\},\ i = \overline{1, N}$$

where $H_i = z_i - z_{i-1}$ is the height of layer Ω_i, $z_0 = 0$, $z_N = Z$. We will find the distribution of concentrations $c_i = c_i(x, y, z)$ in every layer Ω_i at the point $(x, y, z) \in \Omega_i$ by solving the following partial differential equation (PDE):

$$D_{ix}\partial^2 c_i / \partial x^2 + D_{iy}\partial^2 c_i / \partial y^2 + D_{iz}\partial^2 c_i / \partial z^2 + f_i(x, y, z) = 0 \qquad (1.1)$$

where D_{ix}, D_{iy}, D_{iz} are constant diffusions coefficients, $c_i = c_i(x, y, z)$ - the concentrations functions in every layer, $f_i(x, y, z)$ - the fixed sours function. The values c_i and the flux functions $D_{iz}\partial c_i / \partial z$ must be continues on the contact lines between the layers $z = z_i$, $i = \overline{1, N-1}$:

$$c_i\big|_{z_i} = c_{i+1}\big|_{z_i},\ D_{iz}\partial c_i / \partial z\big|_{z_i} = D_{(i+1)z}\partial c_{i+1} / \partial z\big|_{z_i},\quad i = \overline{1, N-1} \qquad (1.2)$$

where $i = \overline{1, N-1}$.

We assume that the layered material is bounded above and below with the plane surfaces $z_0 = 0, z = Z$ with fixed boundary conditions in following form:

$$c_N(x, y, Z) = C_a(x, y) \qquad (1.3)$$

where $C_0(x, y)$, $C_a(x, y)$ are given concentration-functions, α is the mass transfer coefficient.

We have two forms of fixed boundary conditions in the x, y directions:

1) the periodical conditions by $x = 0,\ x = l$ in the form

$$c_i(0, y, z) = c_i(l, y, z),\ \partial c_i(0, y, z)/\partial x = \partial c_i(l, y, z)/\partial x$$
(1.4)

2) the symetrical conditions by $y = 0,\ y = L$

$$\partial c_i(x, 0, z)/\partial y = \partial c_i(x, L, z)/\partial y = 0 \text{ .(1.5)}$$

For solving the problem (1.1)-(1.5) we will consider conservative averaging (AV) and finite difference (FD) methods. These procedures allow to reduce the 3-D problem to some 2D boundary value problem for the system of partial differential equations with circular matrix in the x - directions.

2. The AV–method with quadratic splines

The equation of (1.1) is averaged along the heights H_i of layers Ω_i and quadratic integral splines along z coordinate in following form one used [2]:

$$c_i(x, y, z) = C_i(x, y) + m_i(x, y)(z - \bar{z}_i) + \\ + e_i(x, y)G_i\left((z - \bar{z}_i)^2 / H_i^2 - 1/12\right)$$

(2.1)

where $G_i = H_i / D_{iz}, \bar{z}_i = (z_{i-1} + z_i)/2$,
m_i, e_i, C_i are the unknown coefficients of the spline-function, $C_i(x, y) = H_i^{-1}\int_{z_{i-1}}^{z_i} c_i(x, y, z)dz$ are the average values of $c_i,\ i = \overline{1, N}$.

After averaging the system (1.1) along every layer Ω_i, we obtain system of N equations of 2-D PDE

$$D_{ix}\partial^2 C_i / \partial x^2 + D_{iy}\partial^2 C_i / \partial y^2 + 2H_i^{-1}e_i + F_i(x, y) = 0$$
(2.2)

where $F_i = H_i^{-1}\int_{z_{i-1}}^{z_i} f_i(x, y, z)dz$ are the average values of $f_i,\ i = \overline{1, N}$.

From boundary conditions (1.3) follows

$$\frac{6}{\alpha}(D_{1z}m_1 - e_1) + 3m_1H_1 = 6(C_1 - C_0) + e_1G_1 \quad ,$$
$$3m_NH_N = 6(C_a - C_N) - e_NG_N$$
(2.3)

From (1.2) follows

$$3m_i + e_iG_i = 6(C_{i+1} - C_i) - 3H_{i+1}m_{i+1} + e_{i+1}G_{i+1} \text{ ,}$$
$$D_{iz}m_i + e_i = D_{(i+1)z}m_{i+1} - e_{i+1}, \quad i = \overline{1, N-1} \text{ .}$$
(2.4)

From (2.1), (2.3), (2.4) we obtain following system of $N - 2$ algebraic equations for determining e_i

$$2e_{i-1}G_{i-1}(G_i + G_{i+1}) + e_i\left((G_i + 3G_{i-1})(G_i + G_{i+1}) + (G_i + 3G_{i+1})(G_i + G_{i-1})\right) + \\ + 2e_{i+1}G_{i+1}(G_i + G_{i-1}) = 6(C_{i+1} - C_i)(G_i + G_{i-1}) - 6(C_i - C_{i-1})(G_i + G_{i+1})$$
(2.5)

and for determining e_1, e_N

$$e_1\left(2G_1 + 4G_2 + \frac{2}{\alpha}\left(4 + \frac{6G_2}{G_1}\right)\right) + 2e_2\left(G_2 + \frac{2G_2}{\alpha G_1}\right) = 6(C_2 - C_1)\left(1 - \frac{2}{\alpha G_1}\right) \\ - 6(C_1 - C_0)\left(1 + \frac{G_2}{G_1}\right)$$
$$e_N(2G_N + 4G_{N-1}) + 2e_{N-1}G_{N-1} = -6(C_N - C_{N-1}) + \\ + 6(C_a - C_N)\left(1 + \frac{G_{N-1}}{G_N}\right)$$
(2.6)

In the case $N = 3$ (three layers) we have equations (2.6) and (2.5) for $i = 2$.
Then

$$e_i = e_{i,1}C_1 + e_{i,2}C_2 + e_{i,3}C_3 + e_{i,0} \text{ ,}$$

$$m_i = m_{i,1}C_1 + m_{i,2}C_2 + m_{i,3}C_3 + e_{i,0},\ i = 1; 2; 3 \text{ .}$$
(2.7)

From (2.2), (2.7) follows the system of three PDE

$$\begin{cases} D_{1x}\partial^2 C_1(x, y)/\partial x^2 + D_{1y}\partial^2 C_1(x, y)/\partial y^2 + \quad , \\ + 2H_1^{-1}e_1(x, y) + \widehat{F}_1(x, y) = 0 \\ D_{2x}\partial^2 C_2(x, y)/\partial x^2 + D_{2y}\partial^2 C_2(x, y)/\partial y^2 + \\ + 2H_2^{-1}e_2(x, y) + \widehat{F}_2(x, y) = 0 \\ D_{3x}\partial^2 C_3(x, y)/\partial x^2 + D_{3y}\partial^2 C_3(x, y)/\partial y^2 + \\ + 2H_3^{-1}e_3(x, y) + \widehat{F}_3(x, y) = 0 \end{cases}$$
(2.7)

where $\widehat{F}_i(x, y) = F_i(x, y) + 2H_1^{-1}e_{i,0},\ i = 1; 2; 3$.

3 The Finite Difference method

For solving 2-D problems a uniform grid $(N_x \times (N_y + 1))$ is considered:

$$\omega_h = \left\{ \begin{array}{l} (x_i, y_j),\ x_i = ih_x,\ y_j = (j-1)h_y,\ i = \overline{1, N_x}, \\ j = \overline{1, N_y + 1},\ N_x h_x = l,\ N_y h_y = L \end{array} \right\}$$

Subscripts (i, j) refer to x, y indices, the mesh spacing in the x_i, y_j directions are h_x and h_y. The PDEs (2.7) can be rewritten in following vector form:

$$D_x \partial^2 C / \partial x^2 + D_y \partial^2 C / \partial y^2 - AC + \widehat{F} = 0$$

(3.1)

where D_x, D_y are the 3-d order diagonal matrices with elements D_{1x}, D_{2x}, D_{3x} and D_{1y}, D_{2y}, D_{3y}, C is the 3 order vectors-column with elements C_1, C_2, C_3, $\widehat{F}$ is also the vectors-column with elements $\widehat{F}_1, \widehat{F}_2, \widehat{F}_3$, and matrix A is in following form:

$$A = -2 \begin{pmatrix} e_{1,1}/H_1 & e_{1,2}/H_1 & e_{1,3}/H_1 \\ e_{21}/H_2 & e_{22}/H_2 & e_{23}/H_3 \\ e_{3,1}/H_3 & e_{3,2}/H_3 & e_{3,3}/H_3 \end{pmatrix}.$$

The equation (3.1) with periodical conditions for vector function C in the uniform grid (x_i, y_j) is replaced by vector difference equations of second order approximation [4, 5].

They consist of vectors-columns and block-martices of order circulant symmetric matrixes.

The calculation of circulant matrix (matrix inversion and multiplication) can be carried out with MATLAB [2, 6]

The boundary conditions (1.5) are replaced by difference equations of first order approximation.

4 The numerical methods

The vectors-column W_j of vector difference equations is calculated by Thomas algorithm in the matrix form using MATLAB.

$$W_j = X_j W_{j+1} + Y_j = 0,\ j = N_y(-1)1$$

(4.1)

where X_j, Y_j are corresponding matrices and vectors, obtaining of following expressions

$$X_j = \left(CC_j - AA_j X_{j-1}\right)^{-1} BB_j \quad ,$$

$$Y_j = \left(CC_j - AA_j X_{j-1}\right)^{-1}\left(AA_j Y_j + F_j\right), \quad j = 2(1)N_y$$

(4.2)

Here $X_1 = E \quad Y_1 = 0 \quad W_{\widehat{N}+1} = \left(E - X_{\widehat{N}}\right)^{-1} Y_{\widehat{N}}$, $\left(\widehat{N} = N_y\right)$ where

$$E = \begin{pmatrix} [1,0,\ldots,0] & 0 & 0 \\ 0 & [1,0,\ldots,0] & 0 \\ 0 & 0 & [1,0,\ldots,0] \end{pmatrix}.$$

The inverse matrix of

$$A = \begin{bmatrix} A11 & A12 & A13 \\ A21 & A22 & A23 \\ A31 & A32 & A33 \end{bmatrix}$$

$B = A^{-1},\ (BA = AB = E)$ is in the form

$$B = \begin{bmatrix} B11 & B12 & B13 \\ B21 & B22 & B23 \\ B31 & B32 & B33 \end{bmatrix}$$

where B is obtained due to MATLAB [6].

5. Approbation of numerical algorithms

We consider following test for the approbation of the calculations:

$$f_1 = f_1 = f_1 = C_0 = 0,\ \alpha = 6D_{1z},\ \alpha = 600D_{1z},$$
$$C_a = C_{0a}\cos(\pi y / L)\sin(2\pi x / l),\ C_{0a} = 1.$$

The special solutions in the form $c_i(x, y, z) = g_i(z)\cos(\pi y / L)\sin(2\pi x / l),\ i = 1; 2; 3$ of the PDE (1.1) can be obtain from following boundary value problem for three ODE (for conditions (1.3, 1.4)):

$$g_1''(z) - a_1^2 g_1(z) = 0 \quad ,$$
$$D_{1z} g_1'(0) - \alpha\left(g_1(0) - C_0\right) = 0,$$

$$g_2''(z) - a_2^2 g_2(z) = 0,\ g_3''(z) - a_3^2 g_3(z) = 0,$$
$$g_3(Z) = C_{0a},\ g_1(H_1) = g_2(H_1),$$
$$D_{1z} g_1'(H_1) = D_{2z} g_2'(H_1),$$
$$g_2(L_1) = g_3(L_1),\ D_{2z} g_2'(L_1) = D_{3z} g_3'(L_1),$$

where $L_1 = H_1 + H_2$,

$$a_i = \pi \sqrt{\left(\frac{4D_{ix}}{l^2} + \frac{D_{iy}}{L^2}\right) / D_{iz}},\ i = 1; 2; 3.$$

Therefore the exact solution is

$$g_1(z) = P_1 \sinh(a_1 z) + P_0 \cosh(a_1 z),$$
$$g_2(z) = P_2 \sinh(a_2 z) + P_3 \cosh(a_2 z)$$
$$g_3(z) = P_4 \sinh(a_3 z) + P_5 \cosh(a_3 z),$$

where coefficients $P_i,\ i = \overline{0,5}$ are functions dependent of $a_i,\ i = \overline{1,3}$, D_{1z}, D_{2z}, D_{3z}, $\sinh(t), \cosh(t)$

(calculated for $t = a_1 H_1, a_2 H_1, a_2 L_1, a_3 L_1$),

$\tanh(t), \coth(t)$ (calculated for $t = a_2 H_1, a_3 L_1$).

The averaged values are

$$C_1 = H_1^{-1}\int_0^{H_1} g_1(z)dz = \frac{1}{a_1 H_1}\cdot$$

$$\left(P_1(\cosh(a_1 H_1) - 1) + P_0 \sinh(a_1 H_1)\right)$$

$$C_2 = H_2^{-1}\int_{H_1}^{L_1} g_2(z)dz = \frac{1}{a_2 H_2}$$

$$\begin{pmatrix} P_3(\sinh(a_2 L_1) - \sinh(a_2 H_1)) + \\ P_2(\cosh(a_2 L_1) - \cosh(a_2 H_1)) \end{pmatrix}$$

$$C_3 = H_3^{-1}\int_{L_1}^{Z} g_3(z)dz = \frac{1}{a_3 H_3}$$

$$\begin{pmatrix} P_5(\sinh(a_3 Z) - \sinh(a_3 L_1)) + \\ P_4(\cosh(a_3 Z) - \cosh(a_3 L_1)) \end{pmatrix}$$

We have following numerical results $H_1 = 1, H_2 = 1.5, H_3 = 0.5, Z = 3.0, C_0 = 0, C_{0a} = 1$ for maximal and minimal values of c_k in the plane $z = z_k, z_k = (k-1)h_z, k = \overline{1,12}$, $z_{13} = Z$, $z_5 = H_1$, $z_{11} = H_1 + H_2$, $h_z = 0.25$ by:

$D_{1z} = 10^{-3}$, $D_{2z} = 1.875 \cdot 10^{-3}$, $D_{3z} = 0.1333 \cdot 10^{-3}$, $\alpha = 600 D_{1z}$ and $\alpha = 6 D_{1z}$, $D_{1x} = D_{1y} = 3 \cdot 10^{-3}$, $D_{2x} = D_{2y} = 4 \cdot 10^{-4}$, $D_{3x} = D_{3y} = 5 \cdot 10^{-5}$

The numerical results by $N_x = N_y = 20, N_z = 12$ are given in the table 1 (c_{ap}, c_{an} are the approximate and analytical-exact values). We have following averaged (integral) values:

1) $\alpha = 600 D_{1z}$ - for C_{ap} : $C_1 = 0.0646$, $C_2 = 0.1894$, $C_3 = 0.6202$; for C_{an} : $C_1 = 0.0663$, $C_2 = 0.1931$, $C_3 = 0.6284$;

2) $\alpha = 6 D_{1z}$ - for C_{ap} : $C_1 = 0.1609$, $C_2 = 0.2545$, $C_3 = 0.6482$; for C_{an} : $C_1 = 0.1669$, $C_2 = 0.2617$, $C_3 = 0.6581$.

The numerical results for $N_x = N_y = 40$ are coincided with 3 decimal places.

TABLE 1.

THE ANALYTICAL AND NUMERICAL RESULTS FOR 3 LAYERS (MAX. AND MIN. VALUES ±)

z_k	$\alpha = 600$	$\alpha = 600$	$\alpha = 6$	$\alpha = 6$
	c_{ap}	c_{an}	c_{ap}	c_{an}
0.00	0.0020	0.0021	0.1206	0.1257
0.25	0.0328	0.0339	0.1395	0.1451
0.50	0.0642	0.0659	0.1599	0.1659
0.75	0.0963	0.0986	0.1820	0.1883
1.00	0.1292	0.1321	0.2057	0.2123
1.25	0.1476	0.1508	0.2196	0.2264
1.50	0.1671	0.1705	0.2350	0.2420
1.75	0.1877	0.1912	0.2521	0.2591
2.00	0.2096	0.2133	0.2709	0.2780
2.25	0.2331	0.2367	0.2917	0.2986
2.50	0.2578	0.2617	0.3142	0.3213
2.75	0.6189	0.6272	0.6469	0.6568

III RESULTS AND DISCUSSION

6. The numerical results

6.1. Determining of the difussion coefficients in the 1D case

In 1D case we have the boundary value problem of the following 3 ODEs

$c_1''(z) = 0$, $c_2''(z) = 0$, $c_3''(z) = 0$,

$D_{1z} c_1'(0) - \alpha(c_1(0) - C_0) = 0$, $c_3(Z) = C_{0a}$,

$c_1(H_1) = c_2(H_1)$, $D_{1z} c_1'(H_1) = D_{2z} c_2'(H_1)$,

$c_2(L_1) = c_3(L_1)$, $D_{2z} c_2'(L_1) = D_{3z} c_3'(L_1)$.

Using proportions $D_{1z} / D_{2z} = x_1$, $D_{1z} / D_{3z} = y_1$, $D_{1z} / \alpha = z_1$ z1 we have following solutions:

$c_1(z) = C_1 z + C_2$,

$c_2(z) = C_3 z + C_4$ $c_3(z) = C_5 z + C_6$, where $C_1 = \dfrac{C_{0a} - C_0}{H_1 + x_1 H_2 + y_1 H_3 + z_1}$,

$C_2 = C_0 + z_1 C_1$, $C_3 = x_1 C_1$,

$C_4 = C_{0a} - C_1 (L_1 x_1 + y_1 H_3)$, $C_5 = y_1 C_1$,

$C_6 = C_{0a} - C_1 y_1 Z$.

From experimentally obtained data $c_1(0) = C_{00}$, $c_1(H_1) = C_{01}$, $c_2(L_1) = C_{02}$, we can determin the relations

$$x_1 = \frac{H_1 (C_{02} - C_{01})}{H_2 (C_{01} - C_{00})},\ y_1 = \frac{H_1 (C_a - C_{02})}{H_3 (C_{01} - C_{00})},$$

$$z_1 = \frac{H_1 (C_{00} - C_0)}{(C_{01} - C_{00})}.$$

We consider the data for 2 metals in the peat blocks with $H_1 = 1, H_2 = 1.5, H_3 = 0.5$:

1) for Fe: $C_{0a} = 0.188$, $C_0 = 0$, $C_{00} = 0.66$, $C_{01} = 0.83$, $C_{02} = 1.50$ we get obtain $D_{2z} = 0.38 D_{1z}$, $D_{3z} = 0.22 D_{1z}$, $\alpha = 0.26 D_{1z}$,

2) for Ca: $C_{0a} = 4.63$, $C_0 = 0$, $C_{00} = 1.30$, $C_{01} = 1.90$, $C_{02} = 2.38$ we get obtain $D_{2z} = 1.875 D_{1z}$, $D_{3z} = 0.133 D_{1z}$, $\alpha = 0.46 D_{1z}$.

We obtain with MAPLE by $D_{1z} = 10^{-3}$ the figures (Fig. 1, 2) and the coefficients $C_1, C_2, C_3, C_4, C_5, C_6$ depending of C_{00}, C_{01}, C_{02}.

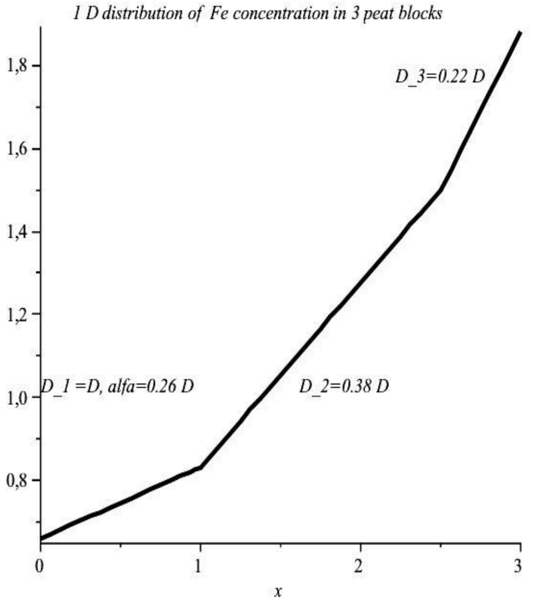

Fig. 1. Fe distribution and D_z

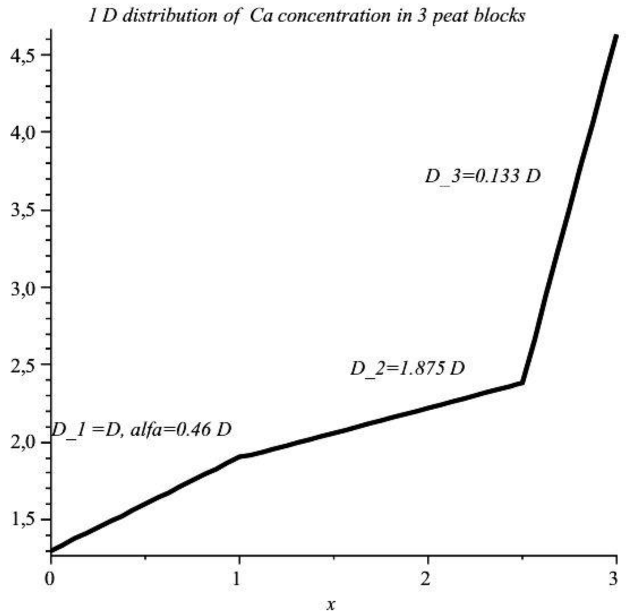

Fig. 2. Ca distribution and D_z

6.2. The calculation of concentration of metals in peat blocks

We consider the metals Fe and Ca concentration in the 3 layered peat blocks Ω with $L = l = 1m$ - dimensions of the block’s base, $H_1 = 1m$’ $H_2 = 1.5m$’ $H_3 = 0.5m$’ $L_1 = H_1 + H_2 = 2.5m$’ $Z = H_1 + H_2 + H_3 = 3m$ - heights of the layers.

On the top of the earth $(z = Z)$ we have the measured concentration $c\ \ mg/kg$ of metals in the following nine points in the (*x; y*) plane:

1) for Fe: *c*(01., 0.2) = 1.69; *c*(0.5, 0.2) = 1.83; *c*(0.9, 0.2) = 1.72; *c*(0.1, 0.5) = 1.70; *c*(0.5, 0.5) = 1.88; *c*(0.9, 0.5) = 1.71; *c*(0.1, 0.8) = 1.71; *c*(0.5, 0.8) = 1.82; *c*(0.9, 0.8) = 1.73,

2) for Ca:

c(0.1, 0.2) = 3.69; *c*(0.5, 0.2) = 4.43; *c*(0.9, 0.2) = 3.72; *c*(0.1, 0.5) = 4.00; *c*(0.5, 0.5) = 4.63; *c*(0.9, 0.5) = 4.11; *c*(0.1, 0.8) = 3.71; *c*(0.5, 0.8) = 4.50; *c*(0.9, 0.8) = 3.73.

This date are smoothing by 2D interpolation with MATLAB operator, using the spline function.

We have following diffusion coefficients in the layers:

1) for Fe: $(C_{00} = 0.66, C_{0a} = 1.88)$:

$D_{1z} = 10^{-3}$, $D_{2z} = 0.38 \cdot 10^{-3}$, $D_{3z} = 0.22 \cdot 10^{-3}$,

2) for Ca: $(C_{00} = 1.30, C_{0a} = 4.63)$:

$D_{1z} = 10^{-3}$, $D_{2z} = 1.875 \cdot 10^{-3}$, $D_{3z} = 0.1333 \cdot 10^{-3}$,

The diffusion coefficients in x, y directions are:

$D_{1x} = D_{1y} = 3 \cdot 10^{-4}$, $D_{2x} = D_{2y} = 4 \cdot 10^{-4}$, $D_{3x} = D_{3y} = 5 \cdot 10^{-5}$ .///

In the Fig. 3, Fig. 4 graphics of metals concentration c depending of vertical coordinate z by $x = l/2,\ y = L/2$ and in other points are given.

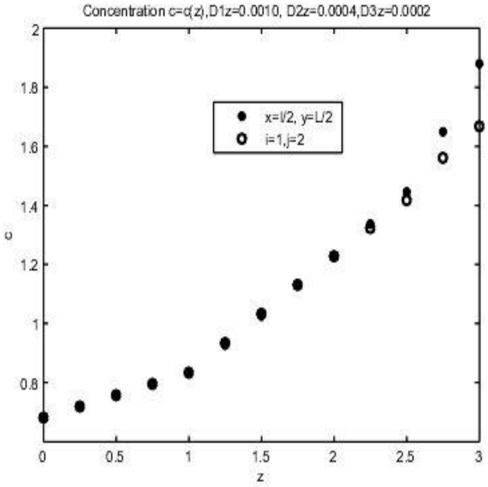

Fig. 3. Fe concentration *c* depending on z

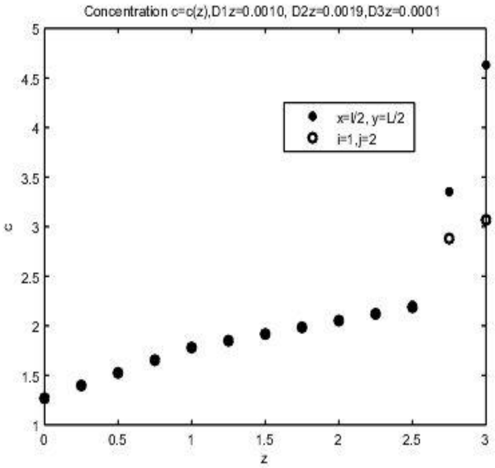

Fig. 4. Ca concentration *c* depending on z

The distribution of concentration c in the (x, y) plane is given: by $z = H_1$ (Fig. 5, 6.), $z = L_1 = H_1 + H_2$ (Fig. 7, 8.) $Z = H_1 + H_2 + H_3$ (Fig. 9, 10.).

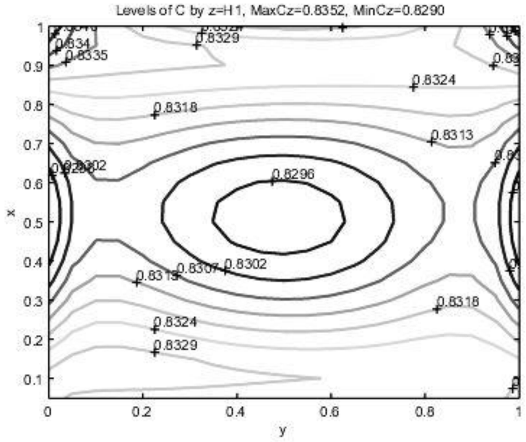

Fig. 5. Fe concentration *c* in the (x;y) plane by z=H1

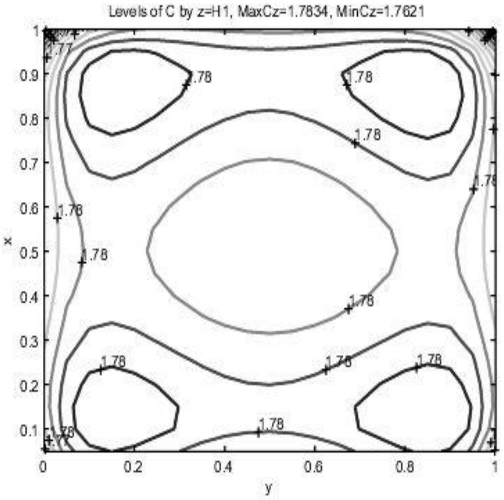

Fig.6. Ca concentration *c* in the (x;y) plane by z=H1

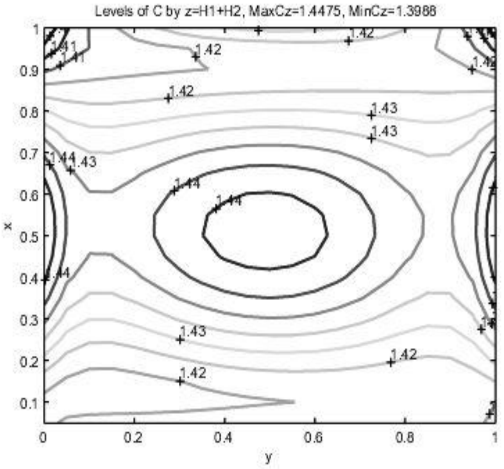

Fig. 7. Fe concentration *c* in the (x;y) plane by z=H1+H2

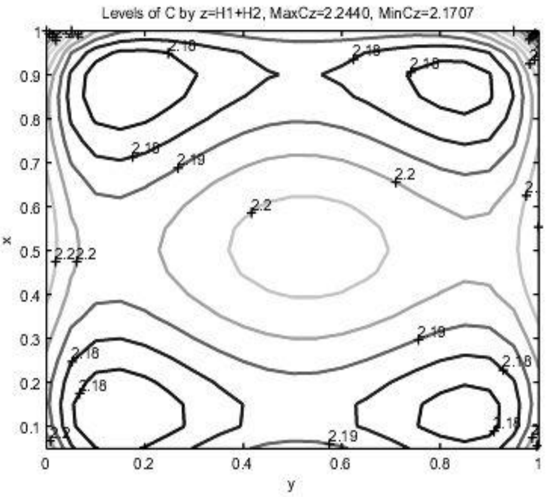

Fig. 8. Ca concentration *c* in the (x;y) plane by z=H1+H2

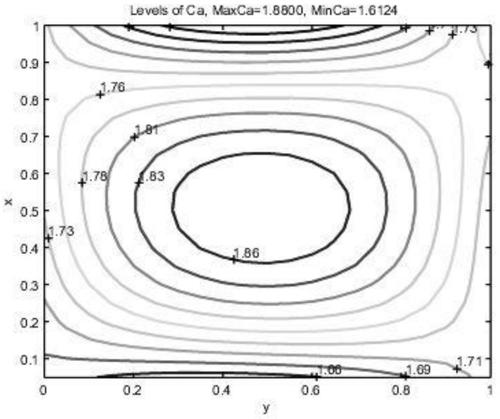

Fig. 9. Fe concentration *c* in the (x;y) plane by z=Z

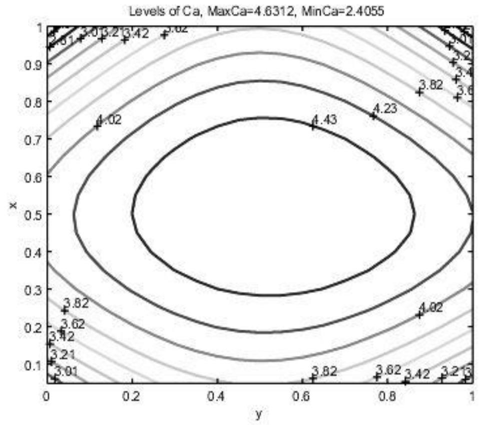

Fig. 10. Ca concentration *c* in the (x;y) plane by z=Z

The distribution of concentration c in the (z,x) plane by $y = L/2$ accordingly for Fe and Ca is given in Fig. 11, Fig. 12.

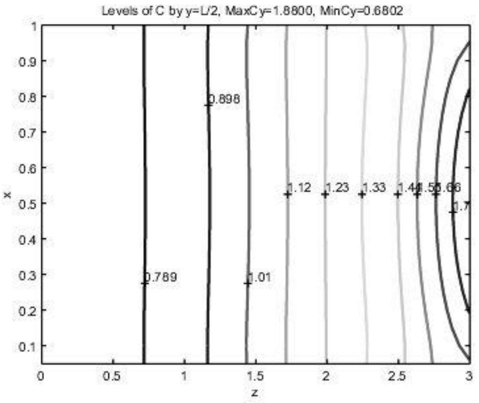

Fig. 11. Fe concentration *c* depending of vertical coordinate z by y=L/2

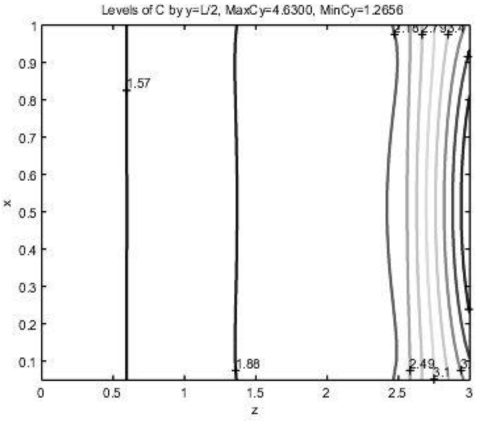

Fig. 12. Ca concentration *c* depending of vertical coordinate z by y=L/2

And the averaged values of concentration c in the second layer are given in Fig. 13, Fig. 14.

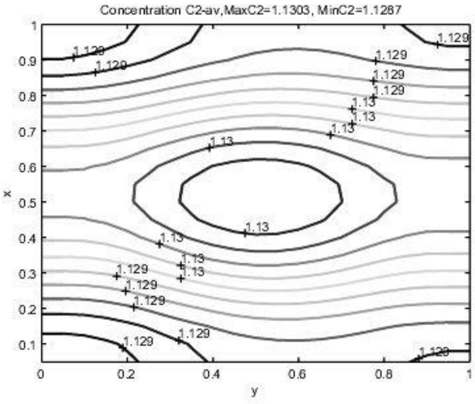

Fig. 13. Averaged values C2 in second layer for Fe concentration

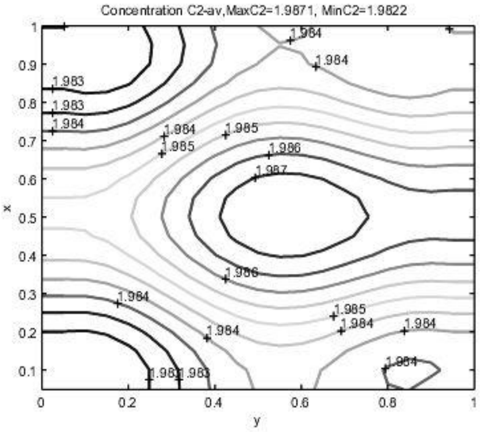

Fig. 14. Averaged values C2 in second layer for Ca concentration

IV CONCLUSION

The 3D diffusion problem in *N* layered domain described by a boundary value problem of the system of PDEs with piece-wise constant diffusion coefficients are approximate on the 2D boundary value problem of a system of *N* PDEs.

As opposed to the models analyzed previously [1,4], the newly established mathematical model envisages modeling mass transfer in N-layers, and the boundary conditions of the 3rd type included in the model enable the modeling of the substance flux through the boundary surface of the specified area in the direction of Earth's interior.

Test samples with an analytical solution (the indicator of transfer process) were developed and a numerical experiment was used to test and analyze the established method for three layers in comparison with the methods described previously.

The analytical and numerical results were coincided with 3 decimal places and it means that mathematical model have a practical application in real determination of trace elements concentrations.

The established mathematical model is applicable in studying transfer processes, where substance mass is transferred through boundary surfaces of the specified area, for instance, in a purification plant, purifying works etc.

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Investigations of Properties of Powdered Ferromagnetic Sorbents

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Abstract. **The paper examines possible application of certain disperse materials based on iron powders as ferromagnetic sorbents for collecting the oil products spilled on the water surface. Sorption ability is defined for the investigated ferromagnetic sorbents.**

Keywords – oil absorbent, oil spill collection, ferromagnetic absorbent, ecology.

I INTRODUCTION

The problem of water treatment from pollution by oil, oil products is becoming more and more topical. Accidents involving oil spills from large-capacity tankers and oil emission from bore wells at seas have begun to arise more often. Thus in April, 2010 there was accident on an oil platform of British Petroleum corporation. A large amount of oil was released into the Gulf of Mexico. The company spent huge numbers of forces and funds for cleaning of the Gulf, coast and compensation for pollution-made damages. In semi-closed water areas of harbours, in basins of the navigable rivers, the leakages of fuel, oils, unauthorized dumping of crude slop waters from passing and quayed ships are becoming material negative factors. Leakages of fuel from stationary capacities of oil depots, petrochemical productions, the large motor transportation enterprises, accidents on the oil pipelines are inevitably leading to pollution getting into soil, into underground waters, and with surface, thawed and storm water also into the river basins. Thus, the problem of elimination of pollution of the water surfaces with oil products is of a global nature and topical both for seas and oceans, as well as for streams and small rivers flowing inland of the continents.

There are various methods of water treatment from pollution by oil products [1]: mechanical, physical and chemical and biochemical one. Each group has its strengths and weaknesses, areas of concentration and total volume of pollution, in which these are the most effective. On a case-by-case basis it is necessary to apply complex and multistage technology of cleaning with a prevalence of one or other methods. However, papers [1,2] specify that only the use of sorbents allows to clear water from oil products to the highest degree of purity without introduction of secondary pollution.

Natural and artificial porous and other materials with the developed surface are applied as sorbents. They have to meet certain requirements: maximum available sorption capacity; buoyancy (in case of application by spraying over surface of the polluted water); wear resistance (in case of use in bulk filters), etc. There are data available about application of production waste of asbestos papers and cardboard as a sorbent for water purification from oil products [3]. Such sorbent allows performing its regeneration by thorough warming. There are widespread polymeric sorbents: granulated co-polymer of styrene and divinylbenzene [4], which can be regenerated by solvents; polyurethane foam [5], which regeneration is conducted by extraction. The sorbent on the basis of hydrofobized basalt fibers is easily regenerated by extraction and burning of the remainder oil products [6]. Woodchips and sawdust applied as a sorbent and placed in pervious woven covers [7] can be utilized by burning with output of energy. Shortcoming of this sorbent is its fast turgescence owing to absorption of water and the loss of buoyancy. The granulated activated charcoal is one of the most widespread sorbents of a wide range of atmospheric and water pollution, naturally is also used in water purification from oil products [1, 2, 8, 9]. However, the absorbent carbon is one of the most expensive sorbents owing to what it is used, as a rule, at supplementary treatment of potable water. All the above described sorbents have one more common shortcoming: complicated collecting from a water surface after implementation of the process of sorption, which is possible only by mechanical means – scrapers, sediment pumps, etc. from the increased concentration zone limited to boom obstructions.

Allocation of magnetic properties to sorbents can ensure substantial increase of efficiency of their use since an opportunity appears to introduce sorbents into the environment subject to decontamination in the form of a disperse phase at a controlled surface of interphase contact and to remove from the environment by means of a physical method [10-16].

Possibility to use disperse ferromagnetic sorbents for collecting oils and other oil products poured on a water surface and at the bottom of a water body, was reviewed in papers [17-18]. Iron powders, crushed particles of mill scale, etc. were used as initial materials. Ferromagnetic sorbents based on iron powders have perfectly recommended themselves when cleaning plumage of the birds getting into oil spills in water bodies [19-20]. Papers [21-22] are describing the "Nefteklin" sorbent used for collecting oil spills from the water surface. Fibrous organic substances, such as lignin, soybean seed coats, waste of agricultural and woodworking production, are used as raw materials to obtain the "Nefteklin" sorbent. The base is crushed, then processed in a disperser, separated from solution and dried. Then ferromagnetic particles are added. Shortcoming of this sorbent is its turgescence owing to absorption of water and the loss of buoyancy

The problems entailing utilization of slime collected by sorbents, realization of possibility of regeneration of sorbents are presenting interest. Three main methods of regeneration of sorbents and utilization of the oil products collected thereby are known [2]: chemical (processing by solvents); low-temperature (processing by water vapour) and thermal (desorption of high-boiling organic compounds by steam-gas mixes). The first method is comparatively expensive and toxic therefore it is barely used and only in the event of small volumes of pollution of water by oil products. The second method is effective for extraction of low-molecular organic compounds. The third, thermal method is the most widespread one and used on commercial scale. Treatment of sorbent with slime in this method is possible in drum furnaces, multi- hearth furnaces and in furnaces with a boiling layer. According to data from literature [2], losses of a sorbent at thermal regeneration do not exceed 10%, and sorption ability is restored at least 8-10 times and more.

Recently among processes of decomposition of organic compounds including slimes of oil products, polymeric waste, etc. increasing place is taken by pyrolysis – thermal decomposition without air access. As a result of pyrolysis less complicated particles, molecules of simple organic compounds and ashes are formed from molecules of organic waste; the products of pyrolysis can be used as raw materials for chemical productions and fuel. Pyrolysis is one of the most important industrial methods for obtaining raw materials for petrochemical synthesis. Target product of pyrolysis – a gas rich in unsaturated hydrocarbons: ethylene, propylene, butadiene. On the basis of these hydrocarbons, polymers are obtained for production of plastics, synthetic fibers, synthetic rubbers and other major products.

This paper is focused on the possibility of application of some powder ferromagnetic sorbents for collecting of spillages in water.

II MATERIALS AND METHODS

Powdery materials on the basis of iron were used as research materials, the majority from which are applied in production of constructional, tribotechnical and other materials. In particular we have selected iron powders of brands: ASC 100.29 – sprayed, used in production of constructional details by methods of powder metallurgy; MH 80.23 – reduced, spongy is used in production of self-lubricating sliding bearings; M20/80-19 with the lowered content of carbon and R-12 with lowered content of hydrogen, used in production of frictional products. All the powders are manufactured by Höganäs AB (Sweden). As well as the powder CMS represents waste from the filter in production of iron powders by the Höganäs AB (Certificate EN 10 204.3.1B), contains 94.1% of Fe, 0.6% of C.

Composite sorbent (CS) COMSOR developed jointly by the RTU and Rezekne Higher Education Institution was used as well. The technology of obtaining is described in the patent application under number P-12-205 dated 28.12.2012. Its characteristics – increased buoyancy and at the same time magnetic properties (Fig. 1, 2).

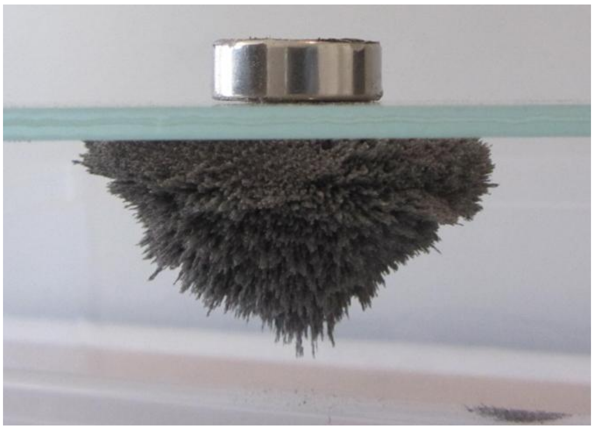

Fig. 1. CS retaining by a magnet

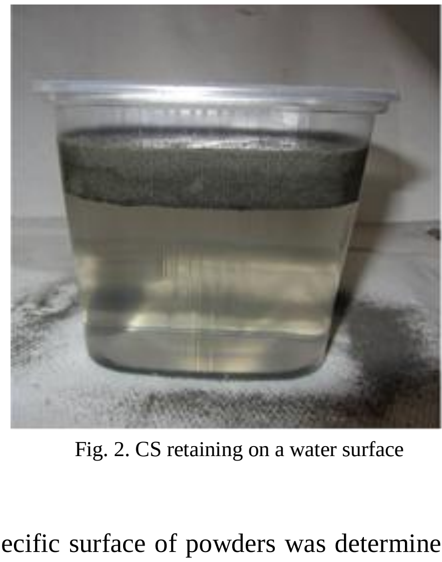

Fig. 2. CS retaining on a water surface

Specific surface of powders was determined on the SA 3100 analyzer made by "Beckman Coulter, Inc." company (USA). Morphology of the surface of particles was investigated on a MIRA scanning electronic microscope of high resolution made by “Tesla” company (Czech Republic). Bulk density, average size of particles and chemical composition of powders was taken from catalogues and accompanying documents of the manufacturers. For the analysis of sorption ability the TAD 17 transmission oil (GOST standard specification 23652-79) was used. The amount of the adsorbed oil was determined by weight of the previously weighed portion of a sorbent of each type after removal of a sorbent from the water surface on the MS 500 electronic scale with an accuracy of 0.1 g.

The methods of the experiment included stages as follows: filling in a non-magnetic container of tap water to a fixed height (not less than 30 mm; drawing on a water surface of transmission oil in the volume of 10 g; holding not less than 2 minutes for formation of a stable film on a surface; drawing of a portion of the powder subject to investigation weighing 50 g on a film by means of spraying; holding during not less than 2 minutes for ensuring full value of collecting oil by sorbent particles; removal of particles with oil by means of constant magnet wrapped up by a polymeric film; separation of the polymeric film with particles of a sorbent and oil from the magnet and carrying out further research - weighing for assessment of absorbing ability.

III RESULTS AND DISCUSSION

Some properties of iron-based powders are provided in the Table 1.

TABLE 1

PROPERTIES OF INVESTIGATED IRON-BASED POWDER MATERIALS

Brand	Manufacturer	Bulk density g/cm^3	Average size of particles, µm	Specific surface, m^2/g	Element content, weight %	
					Fe	C
M20/80-19	Höganäs AB, Sweden	1.56	250	0.159	92	0.23
ASC 100.29	Höganäs AB, Sweden	2.98	50	0.287	99.9	0.08
R12	Höganäs AB, Sweden	1.35	280	0.225	98	0.2
CMS	Höganäs AB, Sweden	2.6	20	0.315	94	0.6
Composite sorbent (COMSOR)	RTU	0.6-0.8	100	0.57	N/D	N/D

Figures 3-6 are presenting the morphology of surfaces of particles of the investigated samples of disperse sorbents based on the powders of iron and composite sorbent.

Images displaying the surface of particles (Fig. 2-5) demonstrate that the majority of the investigated particles of iron powder have a developed porous form, being characterized by presence of a system of micro- and macro-pores extending from the surface deep into the particle (Fig. 2, 4). Composite material particles mainly possess a regular spherical form, however the specific surface of a composite sorbent is significantly higher (Table 1) due to considerably smaller density of particles.

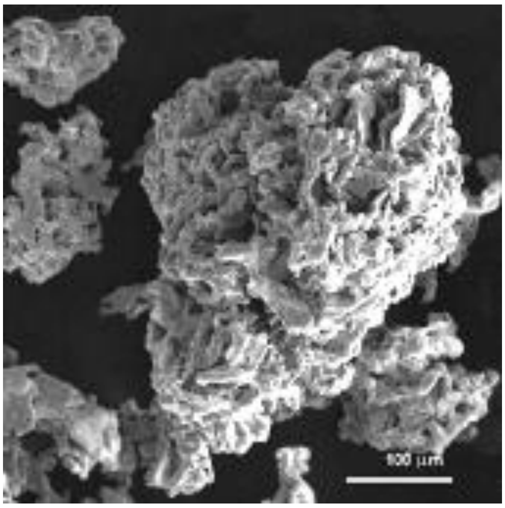

Fig.3. Morphology of the surface of particles of iron powder M20/80-19

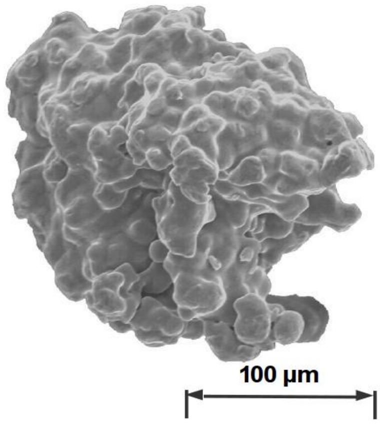

Fig. 4. Morphology of the surface of particles of iron powder ASC 100.29

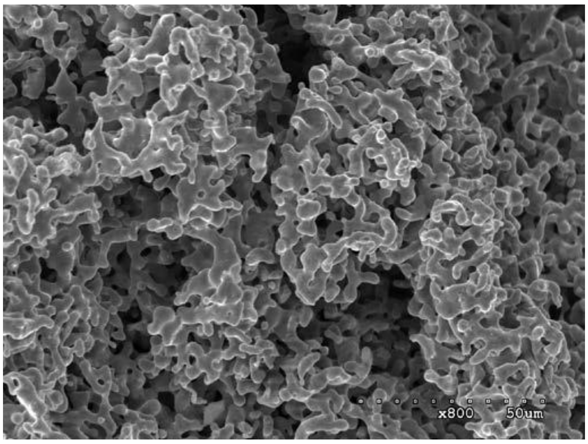

Fig.5. Morphology of the surface of particles of iron powder R12

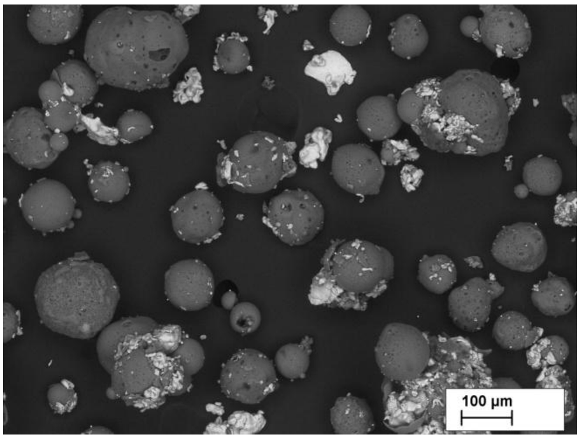

Fig. 6. Morphology of the surface of particles composite absorbent COMSOR

Results of research of the process of collecting oil from the water surface through using iron powder of the M20/80-19 brand are visually presented in Fig. 7, with use of COMSOR on Fig.8.


a


b


c


d

Fig. 7. Results of pilot studies of the process of collecting oil from a water surface using a powder M20/80-19: a) oil on a water surface: b) formation of the centres of coagulation; c) slime capture; d) slime evacuation


a b

c d

Fig. 8. Results of pilot studies of the process of collecting oil from the water surface using composite sorbent COMSOR: a) oil on the water surface: b) sorbent spreading over the oil film surface; c) slime capture; d) slime evacuation.

According to the experiment data it was established that at the expense of primary moistening of particles of the investigated powders, the capillarity and absorption phenomena, samples of sorbents based on iron powder can retain 10-22% (by weight) oils and up to 57% % (by weight) using CS (Fig.9).

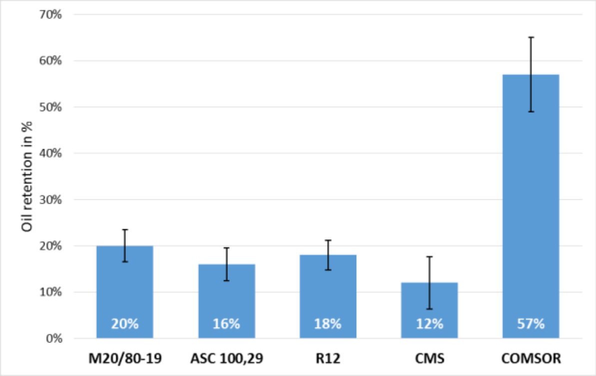

Fig. 9. Sorption ability of some iron-based powdered ferromagnetic sorbents on oil %

As apparent from Fig. 9, CS COMSOR possesses the greatest sorption ability that is explained by features of the morphology of surfaces of their particles (Fig. 6), as well by extended specific surface. Analyzing the sorbent activity, it is possible to affirm that oil and water are retained on the developed surface of iron powder for two reasons:

1. Due to the influence of moistening ability of the external developed surface of the powder particles;

2. Due to the expression of capillarity by the volume of spongy and porous particles (Fig. 2-4).

Thus, water is retained by internal pores of particles, and oil – by their entire external surface (Fig.11).

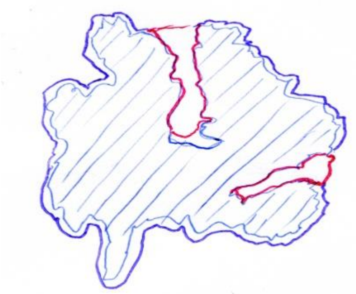

Fig. 11. Model of an iron powder particle MH 80.23, moistened by water (inside pores) and oil (a double contour over entire external surface of particles)

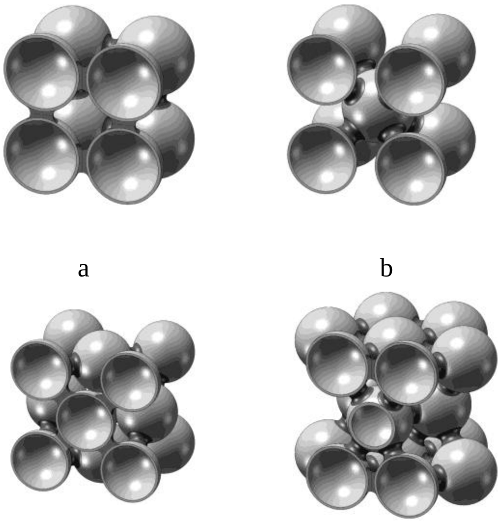

Fig 12. Simple topologies of spheres packaging: a) primitive cubic; b) body-centred cubic; c) face-centred cubic; d) hexagonal

A strong increase of oil absorption by the COMSOR absorbent can be explained by the following hypothesis. Spherical objects in ideal conditions can stack together in 4 main packaging types – shown in Fig. 12. Such formations may possess manifold channels between particles, which in case of positive wetting force, can be filled up with liquids.

The particles are kept together by liquid bridges at their contact points in the pendular state. This situation requires that the saturation is low enough to let discrete binary bridges exist between the solid surfaces. Such a lens-shaped ring of liquid causes adhesion due to the surface tension forces of the liquid/air interface and the hydrostatic suction pressure in the liquid bridge [24]. The capillary structure occurs when a granule is saturated. All the voids between the particles are filled with liquid and the surface liquid of the agglomerates is drawn back from the surface into the interior of the agglomerate. The particles are kept together in this configuration due to capillary suction at the liquid/air interface, which is now only at the agglomerate surface.

IV CONCLUSIONS

1. A research has confirmed that ferromagnetic iron-based powder materials may be used as sorbents for spilled oil products.

2. The highest sorption ability was demonstrated by the synthesised COMSOR absorbent, which can be explained by morphology of Hoganas M20/80 iron powder particles and its surface structure.

3. A sorption ability of the iron-based sorbents is proved by means of experimental setup. The following mean oil sorption characteristics (by weight a sorbent material) have been obtained: 22% (for iron-based powders), and 57% (for COMSOR absorbent).

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II

ENVIRONMENTAL TECHNOLOGIES AND AGRICULTURE

Extraction of Lignin from Hemp Shives

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Abstract. ***Industrial hemp contains 65-80% shives of the stalk and are composed of libriform fibres who are high lignin content. Steam explosion (SE) auto-hydrolysis is a simple treatment of biomass (agricultural waste, logging residues, etc.) by saturated only steam without any additional reagents, usually at pressures 32 atmospheres. This is the basic method how to produce lignin without any dash. Analogy if there is the most sever SE and more are destroyed hemp shives, the more lignin can extract. The aim is to definite the bulk volume, content of lignin in 'Belobrzesky' hemp variety depending on the SE treatment factor, doing extraction with H^2O and NaOH 0.4% and compare without going content of hemp shives lignin.***

Keywords – hemp shives, steam explosion, lignin, extraction.

I INTRODUCTION

All over the world there are not many substances that chemical structure is not know. We know the structure of cellulose other polysacharides, albumen. The chemical content of lignin is not fixed because it is highly variable structure, any extraction method of lignin of plants and wood, it gives deep changes in structure because the essential meaning of distribution method. The size Steam explosion (SE) fibre depends on the SE way of processing. If the way of processing is longer, it gives more smaller fibre particles [Zakis, 2008].

The extraction with water and alkaline off the mass off SE gives essential influence on the size and elasticity because hemicellulose has been washed out.

Extraction of lignes is made in two stages: dissolving the holocellulose in water leaving the insoluble cellulose and lignin in the residue further processed in alkali to dissolve lignin.

Lignin is one of the most abundant natural raw materials available on earth, second to cellulose by mass and even first by solar energy. Presently only about 2% of lignin contained in lignosulphonates from sulphite pulping [Gargulak and Lebo, 2000] is recovered in the craft process.

Lignin (Fig. 1) can be used as binder to plywood, fibreboards and particle boards. Lignin is also used as a component in coatings and foams. Lignin and its modification serve as dispersants, slow-release fertilizers, sorbents, carbon fibres, insecticides, and plant hormones. Commercial potential of many lignin derivatives showing good properties is still unclear. Lignin obtained by conventional technologies containing sulphur is often burned and used as a heat source. The SE lignin is sulphur-free and chemically reactive. During the SE treatment lignin coalescing in spheres of diameter to some micrometers on the surface of cellulose fibres promotes enzymatic attack on cellulose [Gravitis et al., 2010]. The aim of the study is to research extraction lignin from hemp shives, and study the effects of SE on the outcome of the lignin.

II MATERIALS AND METHODS

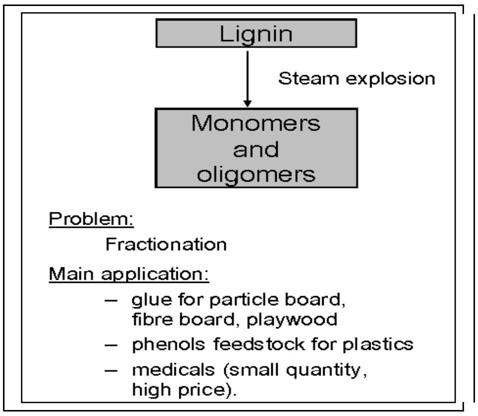

Fig. 1. Application of lignin from SE pulp [Gravitis, 1996].

The desintegration of hemp shives with steam explosion with the method of auto – hidrolysis are used with ‘Belobrzesky’ hemp variety that was grown in in Latvia. Hemp wood parts (shive) were obtained from the company "ZALERS" in Kraslava district, Latvia. In the shive fraction there still remains an average of 4-12% fibres [Andzs, 2010].

The SE samples depending on it pretreatment time could be defind as:

RUKK - industrial hemp dressing residues before treatment by steam explosion.

RUKK SE0.0 - industrial hemp dressing residues exploded immediately upon reaching the pressure of 3.2 Mp.

RUKK SE0.5 - industrial hemp dressing residues after SE treatment for 0.5 min.

RUKK SE1.0 - industrial hemp dressing residues after SE treatment for 1.0 min.

ROKK SE3.0 - industrial hemp dressing residues after SE treatment for 3.0 min.

Steam explosion (SE) is principally a rather simple process. The SE process shown schematically in Fig.2. The biomass is treated by saturated steam, usually at pressures up to 40 bars. The treatment time varies from some seconds to some minutes. After the treatment, within a split second, the biomass is decompressed (exploded) to the pressure of ambient atmosphere. Empirically, conditions of the steam explosion can be characterized by a single parameter comprising temperature and time – the severity parameter.

Empirically result of SEA is determined by severity parameter *Ro* expressed as:

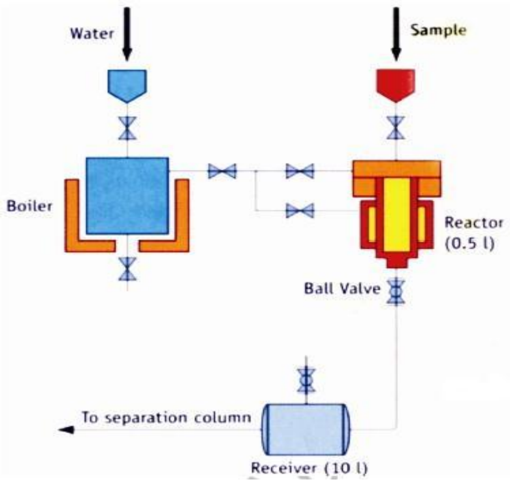

Fig. 2. Steam explosion unit [Gravitis et al. 2010].

$$\log Ro = t * \exp [(T- 100)/ 14.75]$$

Where duration of exposure to high pressure (*t*, minutes) and temperature (*T*, ^{0}C) express the SE severity against the base temperature *Tbase* = 100 ^{0}C. Similar SE results may be achieved with different combinations of *t* and T. However, there is a contribution from other factors such as moisture content of the sample, size of particles etc [Gravitis et al., 2008].

Hemp shives of the ‘Belobrzesky’ hemp variety containing 6 – 11% moisture after drying at room temperature were used for experimental treatment by steam explosion. Parameters used in the steam explosion treatment were selected on the basis of previous research experience of the Latvian State Institute of Wood chemistry, Laboratory of Eco-Efficient Conversion of Biomass (Table 1).

TABLE1

SE PARAMETERS

Parameter	Time, min.	T, 0C	Pressure, Mp.	log R0	Loss after SE, %
Reference Hemp shives	-	-	-	-	-
RUKK- 00	00	235	3.2	2.97	2.43
RUKK- 0.5	0.5		3.2	3.67	6.27
RUKK- 1.0	1.0		3.2	3.98	13.05
RUKK-3.0	3.0		3.2	4.45	19.99

Making the simple component fractionation of the pretreated material (all processes at room temperature), first, the soluble parts removed by adding water (1:4). Lignin is extracted from the residual by solving it in 0.4% solution of NaOH (1:4) wherefrom it is precipitated by adding hydrochloric acid to neutralize the solution. The precipitated ligneous mass is rinsed in water to remove the remnant of sodium chloride before filtration. After drying in air the filtrate turns into powder presented as steam-exploded lignin [Gravitis et al., 2010].

III RESULTS AND DISCUSSION

As seen from Figs. 3 and 4, the SE essentially affects the bulk density of hemp shives. The shorter processing time, the higher bulk volume of the processed substance. At small log R_0 the amount of extracted lignin is small.

Fig. 3. Hemp shives after SE.

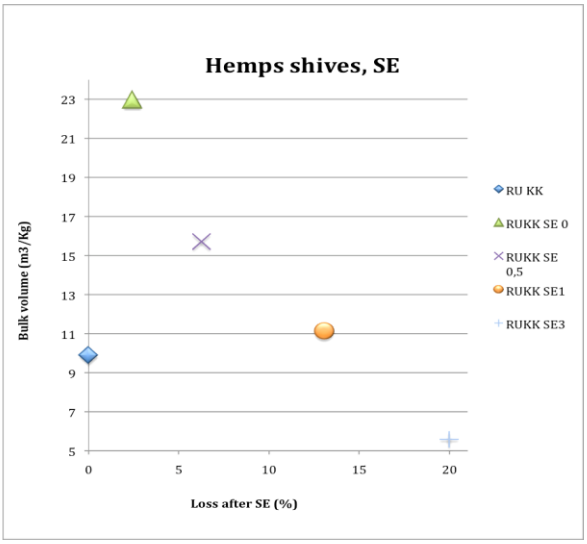

Fig. 4. Volume of loose steam exploded hemp dressing residues with relation to loss of massduring the treatment.

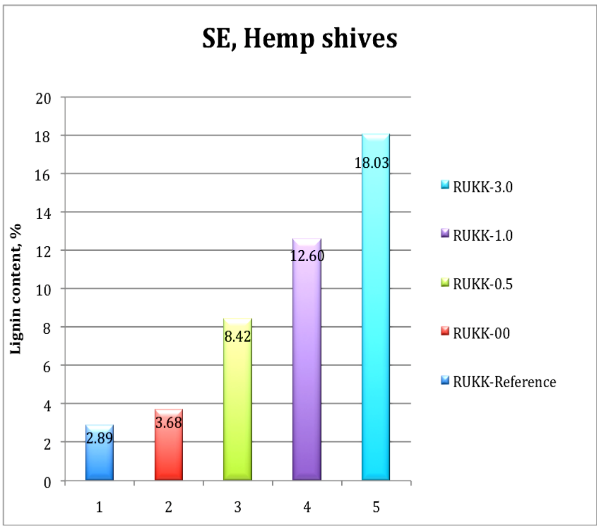

Fig. 5. Lignons extracted by alkali-solutions.

The first partial loss of the mass of hemp shives as indicated by weight loss and results of extraction after SE is due volatile sugars.

The amount of residual lignin in sample RUKK-3.0 treated at log R_0 = 4.45, points to complete collapse of the shives. The loss of mass is shown in Fig. 4, the extracted mass containing lignin – in Fig. 5. The SE results are affected by the moisture content of the material [Kaleine et al., 1990].

IV CONCLUSIONS

The resulting amount of Lignin is directly proportional to the SE conditions log R_0 the most important factor is the processing time. Mass loss and the resulting amount of lignin by steam explosion treatment is proportional to the severity factor. Among the samples RUKK-Reference and RUKK-00 a high bulk volume and should preferably be used as heat insulation material (Fig. 4).

V ACKNOWLEDGMENTS

Latvian State Institute of Wood chemistry, Laboratory of Eco-effective Conversion.

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Influence of Different Factors on Productivity of Reed Growths

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***Abstract*. The study shows results of research on reed productivity and on factors influencing this productivity. The research was performed during winter period from 2010 until 2012 in 23 natural and artificial water bodies of Latvia. The author of this study analyzed indexes of reed growth productivity and found regularities that statistically significantly (p<0,05) explain changes of reed productivity in water bodies depending on individual reed growing conditions in each water body.**

It is established that the productivity of reed growth depends on the amount of nutrients in the water of water body and that this productivity rises if the total concentration of nitrogen and phosphorus in the water is increased.

The reed productivity is lower in clearer water. This parameter may be used in order to evaluate the amount of extractable biomass. The coherence is characterized by statistically significant (p<0,05) regression equation.

***Keywords:* Common reed, reed yield, productivity of reed beds.**

I INTRODUCTION

Support for usage of renewable resources has become an important issue in the policy of European Union and in the rest of the world. [1]. Traditionally, wood is the most important type of biomass in Latvia [2], however lately it has become common to cultivate different energetic plants and to use them in energy production. One of the most suitable plants for energy extraction and saving is reed canarygrass (*Phalaris arundinacea L.*) [3,4,5] which is widely studied in the world and is suitable for energy extraction in the conditions of Latvia [6,7,8]. Besides, for energy extraction it is possible to use the biomass of hemp **(***Cannabis sativa* L) [9,10], flax *(Linum usitissimum L.)* [11,12], different grain and straw [13,14] and other plants. However, cultivation of energetic plants requires agricultural lands which conflicts with principles for sustainable development.

Another plant that could be used for energy extraction in Latvia is reed (*phragmites australis (Cav.) Trin. ex Steud.*) growing in lakes and pisciculture farms. In many literature sources from all over the world, reed is characterized as invasive and unwanted species that spreads rapidly, reduces biological diversity in water bodies [15,16,17] and creates emission of gases CH_4 and CO_2 in the atmosphere thus stimulating greenhouse effect [18,19]. Therefore, reed harvesting would be useful for solution of the aforesaid problems as well.

Biomass output or productivity is one of the most important factors characterizing suitability of plants for bioenergy production. [20]. Parameters of reed growths (length of stalks, dimensions of leafs, density, diameter, etc.) vary depending on climate zone [21]. Reeds offer 40–60 t*ha^{-1} of green matter or 7,5–13,0 t*ha^{-1} of dry matter [6]. Foreign literature sources show that the productivity of reed growth may reach even 30 t*ha^{-1} of dry matter by cutting it in winter period. [22]. In reed growths that are used for sewage treatment in Estonia, dry matter of reed varies from 3 to 17,6 t*ha^{-1} [23]. These wide variations of reed productivity in different international studies indicate that the productivity depends on reed location.

In order to ensure sustainable use of reed for bioenergy production in Latvia, it is necessary to study the distribution of reed growths, available volumes and principles for sustainable use. One of the main parameters that characterize the suitability of each reed growth for energy production is productivity. Hitherto, no studies on productivity of reed growths have been made in Latvia.

The aim of this study is to define the productivity of reed growths in the water bodies of Latvia and to explore factors influencing this productivity, to find regression equations that could assist in evaluation of reed growth productivity in Latvia’s water bodies where no research on reed growth has been made.

II MATERIALS AND METHODS

Studies on reed productivity were performed in 23 natural and artificial water bodies of Latvia. Studies were performed in areas that are potentially important for reed production in Latgale region - in Lubana lake, Kvapanu ponds, Idenas ponds, Raznas lake, Cirmas lake, L. Ludzas lake, Rusonas lake, Feimanu lake, Cirisa lake, Lukna lake and Sivera lake studies were made in spring of 2010, 2011 and 2012. In Papes lake studies were carried out in string of 2012, while in lakes of Birzkalna, Carmanis, Ilzas Geranimovas, Balvu, Ismeru, Aluksnes, Gaidulu, Adamovas, Zolvu, Zosnas and Nirzas studies were performed in spring of 2013. All studies were performed in March because this period is characterized by the thickest ice surface that allows mechanized reed harvesting, therefore the obtained data can be practically used for calculation of reed productivity.

For reed studies, in each water body four reed growths were selected which correspond visually by their characteristic parameters to the average level of the given water body. Two sampling plots were studied in every growth. In each of these plots, obtainable amount of biomass was defined. In every year of these studies (in lakes where the studies were carried out within three year period), the sampling plots were created in the same reed growths thus allowing to compare parameter changes over the years.

Method of direct measurement was used to determine the amount of dry matter (M_{dry}) that can be obtained in 1 m^2 of reed growth in lakes and pisciculture farms. Calculations include the part of reeds that is located above the ice in winter period. Reed mowing and sample weighting was performed in eight sampling plots (two sampling plots of four different growths) in each of the studied lakes. Surface of each sampling plot was 25 m^2. The plots were selected in places corresponding to the average thickness of the overgrowth. The thickness of the overgrowth was defined by surveying reed growth. The amount of obtained biomass was defined using indexes of natural moisture content. Reed mowing was performed using a scythe by mowing reeds above the ice surface (Fig. 1).

Fig. 1. Sampling plot for determination of reed biomass in Lubanas lake, winter 2010.

The mowed reeds were collected and weighted. Moisture content of the reed biomass was determined basing on standard method CEN / TS 14774-2. The amount of biomass obtained in the sampling plot was converted to t of dry matter * ha-1. For analysis, values of dry matter obtained from one plot unit were used.

In order to determine importance of influence of various factors on productivity of reed growths, the author used values of dry matter obtained within three years in the six largest lakes of Latgale region that are important for reed extraction: Lubanas lake, Kvapanu and Idenas ponds, Rusonas lake, Razna Lake and Sivera lake. For this determination, the method of three-factor dispersion analysis was used [24]. The water body, the year of extraction and the location in each individual water body were analyzed as the main influencing factors. The factor of water body is a complex index that characterizes each specific water body and includes growing conditions of individual reeds in the given water body. The year of extraction characterizes the influence of climatic conditions, while the location of extraction shows variations of reed productivity in one water body.

It was established that individual growing conditions in each water body have the most important influence on reed productivity. In order to evaluate the parameters affecting reed productivity, regression and correlation between average reed productivity and individual conditions in lakes, were analyzed. For this analysis, the author used studies on productivity in 23 water bodies of Latvia. Average values of the following indexes obtained in the last ten years were analyzed as characteristic parameters of each water body: transparency basing on Secchi disk, total concentration of nitrogen, total concentration of phosphorus in the water and electrical conductivity. These indexes were defined using information available in Lake Database of Latvia [25].

III RESULTS AND DISCUSSION

Results of the studies show that average amount of dry matter of reed obtainable in the six major water bodies in the region of Latgale (Lubanas lake, Kvapanu ponds, Idenas ponds, Rusonas, lake Razna lake, Sivera lake) varies from 4.2 to 7.7 t * ha^{-1}. The output of dry matter of reed is similar to the crops of reed canarygrass plantation which varies from 4 to 10 t * ha^{-1} [6.26]. Dry matter of reed in reed growths that are used for sewage treatment in Estonia varies from 3 to 17.6 t * ha^{-1} [23]. In our study, differences between the studied reeds growths were less pronounced (Fig. 2).

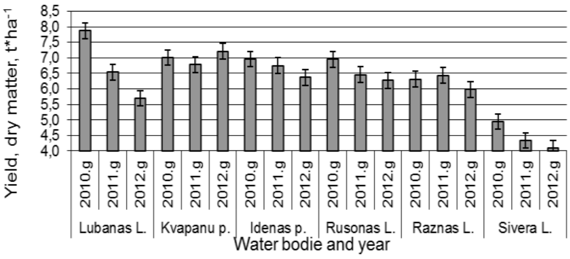

Fig. 2. Average obtainable amount of dry matter of reed in water bodies of Latgale region, 2010-2012.

Significant differences were established in reed productivity over the years in Lubanas lake. As shown in Figure 2, such differences were not established in other lakes. Therefore, it can be concluded, that climatic conditions are not the main factors creating these changes. The main influencing factors are individual growing conditions in Lubanas lake.

Previous studies show that for nutrition reed growths use N and P compounds located in coastal waters. [27]. N is the main element that stimulates reed growing, whereas the influence of P is much smaller, therefore the content of N in read biomass is more pronounced than the content of P [29.30]. Thus it can be assumed that the amount of nutrients in natural waters is one of the main factors affecting reed productivity.

Basing on monitoring data, reduction of water pollution and quality improvement in Lubanas lake during the years of studies can be seen. In summer 2009, the average total concentration of nitrogen was 1.765 mg * l^{-1}, the total concentration of phosphorus was 0.099 mg * l^{-1}, water transparency basing on Secchi disk was 0.6 m. In summer 2011, the concentration of nitrogen was 0.9 mg * l^{-1}, the total concentration of phosphorus was 0.065 mg * l^{-1} and water transparency basing on Secchi disk was 0.83 m [31]. These data indicate that reed productivity is directly dependent on the amount of nutrients available in growing process.

The three-factor dispersion analysis of the results of productivity studies over three years in six water bodies (Lubanas lake, Kvapanu ponds, Idenas ponds, Rusonas lake, Razna lake, Sivera lake) shows that the key factor that affects productivity of reed growths is the water body with its inherent reed growing conditions. The proportion of this influence is high, i.e. 66.34%, which indicates that the major differences in reed productivity are caused by different lakes. The influence of the factor of the year of mowing is much lower, i.e. 8.23%. The factor of the place of extraction within on lake has the lowest proportion of influence, i.e. 0.66%. The influence of all factors is significant (p <0.05) (Table 1).

TABLE 1

PROPORTION OF INFLUENCE OF THE WATER BODY, THE YEAR OF MOWING AND THE PLACE OF EXTRACTION ON THE AMOUNT OF OBTAINABLE DRY MATTER OF REED, H, %

Factor	Ffact.	F0,05	η, %
Water body (A)	499.23	2.34	64,31*
Year of mowing (B)	154.89	3.13	8,41*
Place of extraction (C)	8.26	2.73	0,69*
Interaction (A×B)	27.91	1.97	8,77*
Interaction (A×C)	14.23	1.81	5,83*
Interaction (B×C)	16.79	2.23	2,77*
Interaction (A×B×C)	8.92	1.62	7,28*
Unstudied factors	-	-	1,92

* Influence of studied factors is significant, 95% of credibility ($F_{fact} > F_{0,05}$).

The results show great importance of the factor of water body on the amount of obtainable reed biomass which is related to the growing conditions of reed in each specific water body.

In order to find out the growing conditions of reed that affect productivity, the author analyzed regression and correlation between average indexes of reed productivity in 20 water bodies of Latvia and parameters characterizing amount of nutrients and the total pollution level in water bodies. Influence of the following parameters on indexes of reed productivity was analyzed: the total concentration of nitrogen and phosphorus in the water, transparency basing on Secchi disk and electrical conductivity. The author used average values of the total concentration of nitrogen and phosphorus in the water, transparency basing on Secchi disk and electrical conductivity in each water body in last ten years. These values were defined basing on monitoring data available in Lake Database of Latvia [25] (Table 2).

In order to define interconnection between reed productivity and factors influencing this productivity, correlation analysis of parameters was made.

In order to find regularity changing reed productivity if factorial features change, one-factor linear regression analysis was made.

The author found significant (P<0,05), average positive correlation (r=0,51, n=20) between obtainable dry matter and total concentration of phosphorus in the water of the studied lakes (Fig 3). This fact indicates that reed productivity is higher if the total concentration of phosphorus in water bodies rises.

The coherence is characterized by statistically significant (P<0,05) regression equation (1st equation), however its coefficient of determination is relatively low (R^2=0,27).

$$M_{dry} = 27{,}69 P_{total} + 3{,}33 \qquad (1)$$

Where: M_{dry} – Yield, dry matter (t*ha^{-1});

P_{total} – Average total concentration of phosphorus in the water of water bodies (mg*l^{-1}).

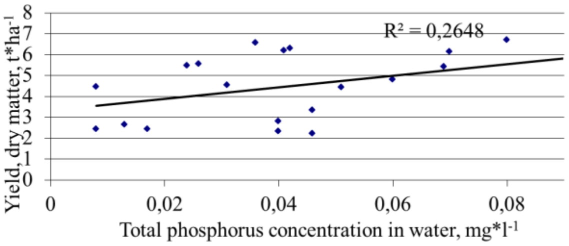

Fig. 3. Obtainable amount of dry matter in dependence on total concentration of phosphorus in water.

TABLE 2

INDEXES CHARACTERIZING REED PRODUCTIVITY AND GROWING CONDITIONS USED FOR CORRELATION ANALYSIS

Npk.	Ezers	Mdry,t*ha-1	Hsecchi, m	P total, mg*l-1	N total, mg*l-1	El, µs
1	Lubanas L.	6,69	0,4	0,08	1,94	335
2	Feimanu L.	4,8	1,3	0,06	1,21	246
3	Sīvera L.	4,46	3,1	0,008	0,9	217
4	Rusonas L.	6,56	0,95	0,036	1,18	269
5	Cirisa L.	4,41	0,9	0,051	1,44	293
6	Cirmas L.	5,55	1	0,026	1,47	300
7	Luknas L.	6,19	1,8	0,041	0,83	290
8	L.Ludzas L.	6,65	0,38	0,142	2,22	346
9	Birzkalna L.	6,29	0,48	0,042	1,21	242
10	Carmaņa L.	2,43	2,1	0,017	0,94	278
11	Ilzas Geranimovas L.	2,65	3,9	0,013	0,44	321
12	Balvu L.	6,12	0,55	0,07	1,63	227
13	Ismeru L.	3,33	1,21	0,046	0,79	300
14	Aluksnes L.	2,79	2,46	0,04	0,67	212
15	Gaidulu L.	2,22	2,95	0,046	0,35	303
16	Adamovas L.	5,42	1,03	0,069	0,82	282
17	Papes L.	5,46	1,7	0,024	1,14	287
18	Zolvu L.	4,54	1,2	0,031	1,53	261
19	Nirzas L.	2,32	2,73	0,04	0,49	267
20	Zosnas L.	2,42	3,5	0,008	0,62	288

Obtainable amount of biomass directly depends on the total concentration of nitrogen in the water of water bodies. The author found significant ($P<0,05$), average positive correlation ($r=0,76$, $n=20$) between obtainable dry matter and total concentration of nitrogen in the water of the studied lakes (Fig. 4). This fact indicates that reed productivity is higher if the concentration of nitrogen in water bodies rises. Such tendency has been noticed in other studies as well. [28,29,30].

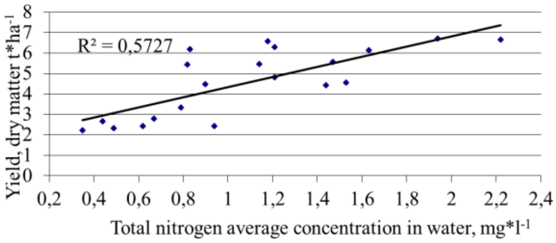

Fig.4. Obtainable amount of dry matter in dependence on total concentration of nitrogen in water.

The coherence is characterized by statistically significant ($P<0,05$) regression equation (2nd equation), its coefficient of determination is relatively high ($R2=0,57$).

$$M_{dry} = 2,48 N_{total} + 1,86 \qquad (2)$$

Where: M_{dry} – Yield, dry matter ($t*ha^{-1}$);

N_{total} – Average total concentration of nitrogen in the water of water body ($mg*l^{-1}$).

Both total concentration of nitrogen and total concentration of phosphorus in natural water promote productivity of reed growths. However, there is multicollinearity between both of these features therefore it is not possible to define summary influence of both of these features on reed productivity by using multifactorial regression analysis. One of factors characterizing the total intensity of eutrophication process in water bodies is water transparency basing on Secchi disk. If level of water pollution and intensity of eutrophication processes increases, water transparency is reduced. The author found significant ($P<0,05$), average negative correlation ($r=-0,79$, $n=20$) between obtainable dry matter and average indexes of transparency basing on Secchi disk in the studied lakes (Fig 5). This fact indicates that reed productivity is lower if water transparency basing on Secchi disk increases.

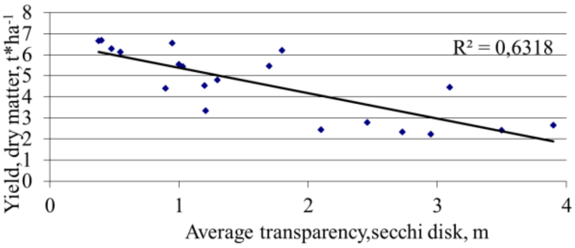

Fig 5. Obtainable amount of dry matter in dependence on water transparency basing on Secchi disk.

The coherence is characterized by statistically significant (P<0,05) regression equation (3rd equation), its coefficient of determination is relatively high (R^2=0,63).

$$M_{dry} = -1{,}2H_{secchi} + 6{,}59 \tag{3}$$

Where, M_{dry} – Yield, dry matter (t*ha^{-1});
H_{secchi} – Average transparency, Secchi disk (m).

No significant correlation was found between reed productivity and average values of electrical conductivity in water bodies.

Among all studied parameters, the most significant correlation was established between obtainable amount of dry matter and water transparency basing on Secchi disk. The given regression equation may be used to forecast average values of obtainable dry matter in places where biomass productivity has not been studied.

IV CONCLUSIONS

Reed productivity considerably (p<0,05) changes depending on water body, year of extraction and place of extraction within one water body.

The most significant differences were established in studies of reed parameters made in different lakes. The factor of water body had the largest proportion of influence on obtainable amount of biomass.

Reed productivity depends on the amount of nutrients in the water of water bodies. The productivity is higher if the total concentration of nitrogen and phosphorus in water is increased.

Reed productivity is lower if water transparency basing on Secchi disk in water bodies increases. This parameter may be used to evaluate the obtainable amount of biomass. The coherence is characterized by significant (p<0,05) regression equation.

V ACKNOWLEDGEMENTS

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Steam Explosion Impact to Technical Hemp Fiber Diameter

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Abstract. **Microfibers and nanofibers from natural products have high mechanical properties. For this reason researchers pay particular attention to the natural fibers and to the method how they are obtained. In the research samples with different treatments (alkaline pretreatment, steam explosion and water extraction) were investigated to evaluate treatment influence on fiber diameters. Fractionation does not provide actual results of fibers diameter as thinner fibers agglomerate to each other and around thicker fibers and cannot be sieved. Fiber diameter measurement with an optical microscope shows that pretreatment and treatment reduced the thickest fiber percentage and increase the number of fine particles. Dew-retted hemp gives 16% of thicker fibers and only 39% fibers with a diameters less than 63µm. 50% of alkaline pretreated and steam explosion treated fibers diameters are less than 63µm and only 8% of diameters fall in range 160-630µm.**

Keywords **– natural fiber, fiber diameter, steam explosion, alkaline pretreatment.**

I INTRODUCTION

In recent years researchers and manufacturers try to replace man-made fibers, such as glass and carbon fibers, with natural fibers. Now they are used to strengthen the materials and as a fillers to make environmentally friendly products.

The natural cellulose-based fibers have several advantages. They are low cost renewable resource with low density, high specific strength and stiffness, high sound absorption capacity and non-abrasive nature [1, 2]. As microfibers and nanofibers from natural products have high mechanical properties researchers pay particular attention to the natural fibers, trying to combine them with polymers in composites and nano-composites [3] for usage in automotive industry, as geotextiles, in medicine and elsewhere. The appeal of natural fiber products should primarily be its quality.

Microfibers are defined as fibers of cellulose of 0.1-1µm in diameter, with a corresponding minimum length in range 5-50µm, and nanofibrils if at least their one-dimension is at the nanometer scale (1-100nm) [4].

The lignocellulosic fibers are made up of cellulose microfibrils bonded together by lignin and hemicellulose matrix. Physical properties of natural fibers are basically influenced by the chemical structure such as cellulose content, degree of polymerization, orientation and crystallinity, which are affected by conditions during growth of plants as well as extraction methods used [2, 4].

Micro and nanofibers can be obtained by chemical, mechanical or chemico-mechanical methods. The main problem is in the way how to obtain micro and nanoscale natural fibers. It is important to clarify which of them has potential and which technologies produce low yields and are not environment friendly or energy efficient.

The main objective of this study is to investigate the alkaline pretreatment, steam explosion treatment and water extraction impact on technical hemp fibers geometric parameters. The main aim are to determine types of diameter distributions and find out which fraction has the highest share (modal fraction) depending on applied treatments and evaluate their influence on further processing.

II MATERIALS AND METHODS

C. Hemp

Hemp (Cannabis sativa L.) is an annual herbaceous plant from the hemp family (Cannabaceae). Technical hemp plants in Latvian weather conditions in 114-117 days can grow from 1,77 (local variety) to 2,7 m (industrial variety Bialobrzeskie) high with the stem yield 1120-1140g/m2 depending from variety and with 22% to 24% fibers yield [5].

Hemp fibers from hemp varieties grown in Latvia contain about 65-68 % cellulose, 20-22 % hemicelluloses, 6-8 % lignin and 1,4-1,6 % pectin, 0,8-1,25 % fats & waxes [6].

As experimental objects fibers from dew-retted hemp grown on trial fields of Latgalian Agricultural Science Centre at vegetation periods of 2011 and 2012 are used.

D. Alkaline pretreatment

The 4 wt% sodium hydroxide was used for one hour at 80 degrees as alkaline pretreatment to partially extract lignin, pectin and hemicelluloses, and separate the fiber bundles [7, 8].

E. Steam explosion treatment

One of techniques that can open the hidden nanostructures is the steam explosion auto-hydrolysis. The process of which includes fast impregnation of the plant material with saturated steam in a closed reactor. The treatment proceeds at moderate temperature and pressure for a desired period of time (from some seconds to some minutes). After that the substance is decompressed within parts of a second [9]. The steam explosion process gives clean fibers with rough surfaces and increased crystallinity index [10]. Hemp fibers in the experiment were treated with 16 bar pressure for 1 minute. Water extraction was used to separate fibers from dissolved lignin.

F. Experiment parameters

In this research dew-retted hemp fibers of Latvian local genotype Purini grown in Agricultural Science Centre of Latgale were used. Fibers were cleaned from impurities and shives and cut into 2 mm long pieces.

TABLE I

Sample	Dew-retted	Alkaline pretreatment	Steam explosion
1.	+	-	-
2.	+	4 wt% NaOH	-
3.	+	4 wt% NaOH	16bar 1min

EXPERIMENT PARAMETERS

Three samples with different treatment were examined (table1):

1 - dew-retted hemp fibers without treatment;

2 - dew-retted hemp fibers with alkaline (4%NaOH) pretreatment followed by water extraction;

3 - dew-retted hemp fibers with alkaline (4%NaOH) pretreatment, steam explosion (16 bar, 1 minute), water extraction.

Dried fibers of all three variants were fractionated through sieves with meshes of three sizes (630µm, 160µm and 63µm).

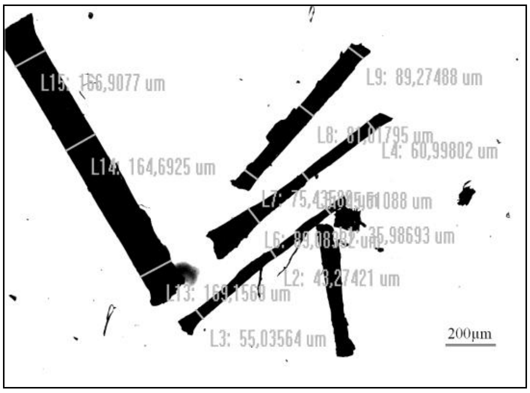

Fig.1. Fibers optical microscope measurements

Fiber diameters of each sample where measured with the optical microscope under amplification 2,5 times. From each sample 100 fibers were measured, each hemp fiber was measured in 3 places - in both ends and in middle (Fig.1.).

III RESULTS AND DISCUSSION

G. Fiber diameter ratio determination by sieving and weighing method

To determine fraction’s share after fractionation through a sieves each fraction was weighted.

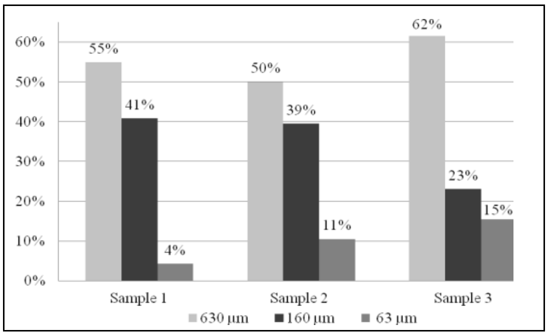

Fig.1. Weight percentage after fractionation

Graphs of Fig.1 shows that modal width percentage in each of three groups exceed 50 % and show the highest value 62% for variant with NaOH pretreatment and the following steam explosion treatment, as well increase group of finest fibers with the diameters less than 63 µm from 4% to 15 %. In spite of noteworthy growth of the finest fibers diameter group with using alkaline pretreatment and steam explosion treatment, it is still too low for further processing.

Cumulative percentage of fibers with diameters 160µm and less for all three variants are high enough (45%; 50% and 39 %) and these fibers are subjected to the further treatment

Fig.2. Dew-retted alkaline pretreated, steam explosion treated fiber agglomeration

There is a large amount of fiber that did not sieve, this is because fiber agglomeration. Fig.2. shows that thinner fibers agglomerate to each other and around thicker fiber.

In order to obtain a homogeneous mass of fibers it is useful to fractionate fiber before pretreatment and treatment, because thinner fibers agglomerate more than thicker.

H. Fiber diameters ratio determination by optical microscope

Dew-retted fiber diameters distribution graph (Fig.3) show clear expressed asymmetry and 39 % of tested fibers diameters fall in modal range 22- 98 µm.

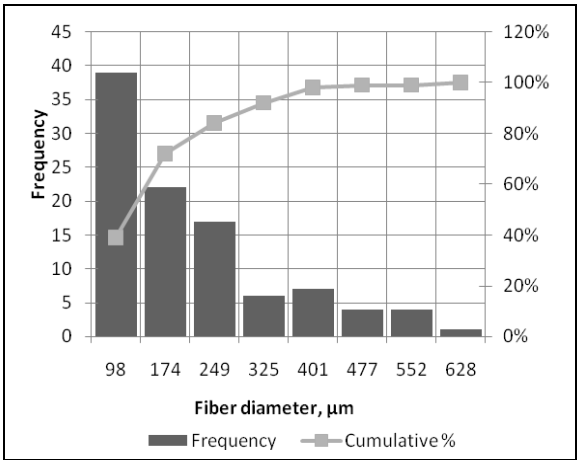

Fig.3. Dew-retted Purini hemp fiber diameters distribution

Diameters of 70% fibers not exceed 174µm. No one diameter find larger than meshes of chosen sieve. The average diameter (175, 67 µm) fall into the second interval as distribution has a long right hand tail.

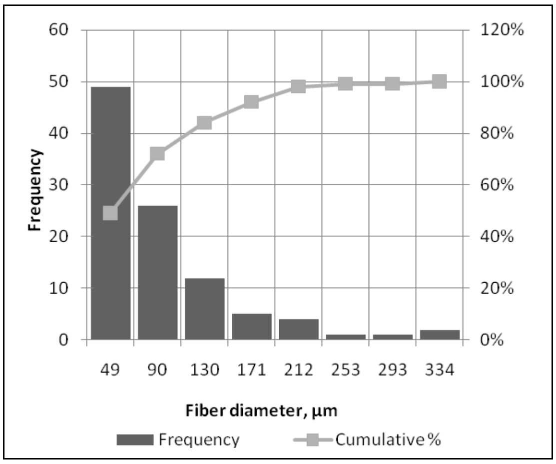

Fig.4. Diameters distribution of the dew-retted Purini hemp fibers with alkaline pretreatment and water extraction

After alkaline pretreatment and water extraction modal interval covers range from 8.268µm to 49 µm and includes 50 % diameters of measured fibers as well diameters of 82 % fibers not exceed 130 µm witnessed about substantial treatment influence on separation level of fibers complexes (Fig. 4).. Average fibers diameter 64,69 µm is 2.64 times less than that of dew-retted fibers.

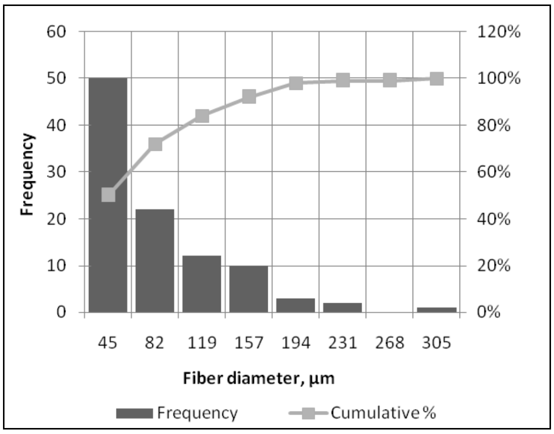

Fig.5. Dew-retted Purini hemp fiber diameters distribution after alkaline (4%NaOH) pretreatment, steam explosion 16 bar, 1 minute, water extraction

Graph of Fig 5 shows that optional treatment by mild steam explosion moves distribution to the direction of smaller diameters to compare with the distribution of sample2. Modal interval corresponds to the diameters range 5,098-45µm and includes 50% of measured fibers diameters, more then 72% of diameters do not exceed 82 µm. Only 8% of fibers show diameters exceeding 157µm. Average fiber size 64,690µm.

TABLE II

Sample	Fiber diameter, %		
	160µm - 630µm	63µm - 160µm	≤ 63µm
1.	16%	45%	39%
2.	8%	43%	49%
3.	2%	48%	50%

THE PERCENTAGE OF FIBER DIAMETER

Table II shows that in result of alkaline pretreatment and steam explosion treatment the share of fine particles increases, the share of thick fibers decrease substantially.

IV CONCLUSION

After 4 wt% sodium hydroxide pretreatment substantially increases hemp fine fibers share, decreases modal diameters range, increases from 40% to 50% fibers share with diameters fall in modal range and decreases share of thick fibers bundles.

Optional steam explosion treatment following alkaline pretreatment does not change very much two larger distribution groups impact, but decrease substantially share of thick fiber bundles.

Comparison of alkaline treatment influence on hemp technical fibers decomposition with the steam explosion treatment with different treatment severities as parallel methods could be investigated in future

For further experiments to avoid fiber agglomeration before any treatment full fractionalization is necessary.

Further investigations are needed to compare fibers after various steam explosion treatment conditions to determine which of them gives the best result of fiber defibrillation.

V ACKNOWLEDGMENTS

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Investigation of Changes of Stinging Nettle's (*Urtica dioica* L.) Crop Density

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***Abstract*. Recently all countries are looking for the renewable resources. Stinging nettle (Urtica dioica L.) is a perennial plant owning many valuable properties, including yielding natural fibres. Fiber nettle is a cultivated form of the wild nettle. The aim of the research was to investigate changes of productivity of stinging nettle's crop established at different crop densities. Main criterion discussed in the article is the number of the stems per measuring unit (i.e., crop density). The investigation was carried out at the Upytė Research Station of LRCAF in 2008-2012. The crop of different implantation density was established: 60x60 and 60x100 cm. The results of our investigation show that in the first cropping year stinging nettle produced 25-43 stems per plant. Plants from the crop of 2nd year, 60x60, were grosser, more productive than that of the 1st year crop. Plants of the 1st year crop, 60x100, had more stems per plant than that of 1st year crop, 60x60, but amount of stems per ha^1 was higher in the crop of 1st year crop, 60x60. The inundation early in 2010 led to the decrease of plant density of stinging nettle's crop. Crop density in the spring was lower than that in the autumn. The greatest increase of amount of stems per plant was found in the plots of lower implantation density (60 x 100 cm). It could be that the optimal crop density (112-136 plants m^{-2}) was already achieved in the crop of 4th and 5th cropping year, and it will not increase any more in more matured crop in following years. Further investigation would be intrigued**

***Keywords* – crop density, number of stems, stinging nettle, *Urtica dioica* L.**

I INTRODUCTION

Recently the one of main global tasks to survive for the mankind is looking for the renewable resources. We should look around us to decide what can be used with the highest value instead of losing it worthless.

The kingdom of plants is very rich in their appliance. One of such interesting plants is a stinging nettle (*Urtica diocia* L.) which use is very multipurpose [1].

Fiber nettle is a cultivated form of the wild stinging nettle. German researcher Bredemann used many nettle provenances in over 30 years of breeding (1918-1950), from which the most efficient clones were chosen for further development. His criteria for breeding were: frost-tolerance, good growth (long and not ramified, straight and stable stalks, many leaves and strong tillering) and high fiber content [2]. So developed fibre clones have been first selected in 1959 [3]. By the way of selection fiber content was increased from about 5 % in wild nettle plants to up to 17-18 % of stalk dry matter in the cultivated species [2].

Clone varieties dating back to Bredemann are still maintained at research institutions in Germany. After 40 years the plants Bredemann bred during that period (30 clones) have been started to being cultivated again at the Institute of Applied Botany, Hamburg, FRG between 1992 and 1995 [4].

Recently stinging nettle (*Urtica diocia* L.) is currently the subject of scientific interest and development in the some countries through Europe: Germany, Austria, Italy, Finland, UK, the Netherlands, and of course, in Lithuania. This plant is a promising candidate for sustainable production of natural fibre, particularly in Germany and central Europe [5]. Investigations in those countries showed that the nettle's dry stalks matter can vary from 2.3 to 9.7 t ha^{-1} [6]. The fiber yields (fiber yield = fiber content x dry matter yield) ranged from 335 to 411 kg ha^{-1} in second growing year and from 743 to 1016 kg ha^{-1} in third growing year [2]. When growing clones of high productivity (Austrian or German clones of stinging nettle), the yield between 6-8 t ha^{-1} of dry matter of straw with a raw fibre content of up to 25 % (1.5-2.0 t ha^{-1}) could be produced [7].

Investigation of stinging nettle in Italy in 2006-2007 showed that clones of German origin survived well, produced stalks the height of which was 1.71 m, diameter – 5.2 mm. Stalks dry matter in average was 1542 g m^{-2}, i.e. 15.4 t ha^{-1} [8].

First results of the investigation of stinging nettle in Lithuania also gave promising results [1], [9].

Stinging nettle is a perennial plant, but how long it can be productive needs to be investigated. Some author report that the economic life of stinging nettle cultivation is about 6 years, and productive years range from the second to sixth, with a maximum at the third and fourth year [10]. Some other sources report that 4 years is the economic limit of growing fibre nettle in the same place while by the other authors the period of 10-15 years or even without limit is mentioned [6].

The researchers report that fiber yield of stinging nettle increases with plant density [6].

The aim of our research was to investigate changes of productivity of stinging nettle's crop established at different implantation densities as well as of different crop age (the number of growing (harvesting) years).

II MATERIALS AND METHODS

The investigation was carried out at the Upytė Research Station of the Lithuanian Research Centre for Agriculture and Forest. Research was started in 2008 and in still running.

Soil of growing field for stinging nettle was kept free from weeds by the way of soil cultivation. In the autumn it was fertilised by manure and ploughed. In the spring it was cultivated and prepared for plant transportation.

The establishment of the first variant (crop at density 60 (between the plants in the row) x 60 (inter-row spacing) cm) was done in May of 2008. Plants were irrigated, full care of plants was carried out (dead plants were replaced by alive ones, cultivation of inter-row spaces was carried out manually, observations on plant development and growing were conducted). None of pesticides (mineral fertilisers, herbicides, insecticides, fungicides or dessicants) were used for growing of stinging nettle.

In the autumn of 2008, the first yield of stinging nettle was already harvested and evaluated.

In 2009, the 2nd and 3rd variants were founded – the crop of 60 x 60 and 60x100 cm, respectively. In this way the crop of different implantation density was established: 60 x 60 and 60 x 100 cm. Therefore, in 2009 the biometrical indices of the 2nd year crop (established in 2008) and 1st year crop (established in 2009) as well as of different crop density (60 x 60 and 60 x 100 cm) of first year crop have been investigated. Similar observations were carried out in the following years also.

In 2008 and 2009, in the established crop before harvesting all stems of stinging nettle plants (9 plants at crop density of 60 x 60 cm and 6 plants from the plots where crop density is 60 x 100) in the area of 4 m^2 (2 x 2 m) (in tree replications) were cut (leaving the stubble of 15 cm for sprouting of the plant) for the evaluation. Then the data were re-calculated for 1 m^{-2}, 1 ha^{-1}, for 1 plant.

In 2010, 2011 and 2012 all stems of stinging nettle in the area of 4 m^2 (2 x 2 m) (in tree replications) were cut as the inter-rows already could not be visible because of increased density of the crop. In 2010, some inter-row space still could be noted in the crop at density of 60 x 60 cm.

For statistical data evaluation the statistical software developed in the Lithuanian Institute of Agriculture was used [11].

In 2008 the weather conditions (Tables 1 and 2) were favorable for the naturalization of transferred stinging nettle plants (sufficient amount of precipitation on I and II ten-day periods of May). Later on (III ten-day period of May and I of June) the luck of precipitation occurred, and stinging nettle was irrigated manually. The second part of June was rainy. Meteorological conditions were favorable for growing of stinging nettle. Stinging nettle from 1st year crop was harvested on 3rd of September.

In 2009 the beginning of the vegetation of stinging nettle was observed on the III ten-day period of April. For the establishment of different density crop weather was selected to be rainy and overcast (beginning of May), transferred stinging nettle also was irrigated manually. Later on (on I and II ten-day period of May) the luck of precipitation occurred. June and July had sufficient rainfall for stinging nettle. Plants were thriving well and flowering for a long time. Stinging nettle was harvested on 15th of August.

In 2010, the first green shoots have been found on the 3rd of April, but the weather was still cool. The inundation on the part of stinging nettle's crop was recorded at the end of March, and it has negative influence on the crop, detectable even few years later – the amount of stinging nettle's shoots decreased; the weeds occupied free place. Stinging nettle was harvested on 30th of August.

TABLE 1.

MEAN WEATHER TEMPERATURE AND PRECIPITATION DURING STINGING NETTLE'S GROWING SEASON

UPYTĖ, 2008-2012

Month	Ten-day period	Mean weather temperature, ºC					
		2008	2009	2010	2011	2012	Long-term average
May	I	8.5	12.1	12.6	11.2	12.1	11.0
	II	11.8	15.3	15.6	12.6	12.1	12.6
	III	13.4	17.6	15.1	14.9	15.1	13.5
	Aver./total	11.2	15.0	14.4	12.9	13.1	12.4
June	I	17.0	16.3	18.4	16.5	12.9	14.4
	II	15.0	17.3	15.9	18.7	16.5	15.3
	III	15.4	21.3	17.8	19.6	15.3	16.2
	Aver./total	15.8	18.3	17.4	18.3	14.9	15.3
July	I	16.8	21.9	21.3	22.6	21.1	17.2
	II	17.9	20.5	24.5	22.6	16.0	18.0
	III	17.4	18.5	23.9	21.3	20.1	18.0
	Aver./total	17.4	20.3	23.2	22.2	19.1	17.7

August	I	17.1	17.6	23.9	16.7	18.1	17.2
	II	19.9	17.6	23.3	18.2	16.5	16.1
	III	16.1	15.8	15.3	17.0	15.0	15.0
	Aver./total	17.7	17.0	20.9	17.3	16.5	16.1
September	I	16.9	16.6	12.5	14.1	14.1	-
	II	8.3	14.0	11.3	12.6	13.9	-
	III	10.7	15.0	14.7	13.6	11.7	-
	Aver./total	12.0	15.2	12.8	13.4	13.2	-
October	I	8.1	7.1	12.6	11.0	9.7	-
	II	9.9	2.8	4.5	6.0	8.6	-
	III	7.9	5.4	8.3	5.8	3.5	-
	Aver./total	8.6	5.1	8.5	7.5	7.2	-

TABLE 2.

Amount of precipitation during stinging nettle’s growing season

Upytė, 2008-2012

Month	Ten-day period	Rainfall, mm					
		2008	2009	2010	2011	2012	Long-term average
May	I	16.1	10.0	25.0	1.0	12.5	16.0
	II	12.5	2.1	18.0	19.0	27.0	16.0
	III	0.1	10.5	20.5	7.0	39.0	18.0
	Aver./total	28.7	22.6	63.5	27.0	78.5	50.0
June	I	0.0	57.0	11.0	11.0	36.5	22.0
	II	32.0	21.0	49.5	15.0	13.5	23.0
	III	56.0	7.5	21.0	13.5	41.5	24.0
	Aver./total	88.0	85.5	81.5	39.5	91.5	69.0
July	I	9.5	37.5	28.0	37.0	33.0	25.0
	II	41.0	55.0	17.0	28.0	49.0	25.0
	III	15.5	30.0	72.0	69.5	30.0	26.0
	Aver./total	66.0	122.5	117.0	134.5	112.0	76.0
August	I	47.5	0.0	11.0	29.5	44.0	28.0
	II	44.5	28.5	30.5	36.5	10.5	29.0
	III	21.1	45.0	27.0	29.0	28.0	28.0
	Aver./total	113.1	73.5	68.5	95.0	82.5	85.0
September	I	4.5	17.0	8.0	21.0	14.0	-
	II	5.0	21.0	20.0	28.0	29.0	-
	III	2.0	10.0	27.0	1.0	1.0	-
	Aver./total	11.5	48.0	55.0	50.0	44.5	-
October	I	10.3	38.0	0.0	5.0	31.0	-
	II	44.6	36.0	10.0	11.0	15.0	-
	III	31.5	12.0	18.0	2.0	12.0	-
	Aver./total	86.4	86.0	28.0	18.0	58.0	-

In 2011 already in the middle of March small (0.5 cm) violet shouts of stinging nettle have been noticed after the snow has melted. Nevertheless, meteorological conditions still were not suitable for growing. In the beginning of April, the shouts of stinging nettle were already 3 cm in height; the vegetation started early. Stinging nettle was thriving well; it was harvested on 12th of September.

The spring in 2012 came late. In the beginning of May stinging nettle started to grow. Despite the quite great amount of precipitation, the plants were not very luxury. Stinging nettle was harvested on 4th of September.

III RESULTS AND DISCUSSION

The biometrical indices of stinging nettle's crop in 2008 and 2009 were evaluated only at harvesting time, because in the spring there were only few stems (plants) in measuring unit (9 plants per 4 m^{-2} (i.e., 2.25 stems per 1 m^{-2}) in the plots at crop density 60 x 60 cm, and 6 plants per 4 m^{-2} (i.e., 1.5 stems per 1 m^{-2}) in the plots at crop density 60 x 100 cm).

In 2008, in the crop of the 1st year, crop density 60 x 60 cm, the amount of stems per 1 plant varied from 15 to 79, but the average was close to 43 stems per plant (Table 3). Amount of stems in 1 m^2 was close to 100, i.e., it increased from 2.25 to 96.3 units 1 m^{-2}, or 1 plant produced more than 40 stems.

TABLE 3.

THE BIOMETRICAL INDICES OF THE 1ST YEAR STINGING NETTLE CROP (ESTABLISHED IN 2008), 60 X 60 CM (ABBREVIATION OF THE TREATMENT – 1ST YEAR, 60X60) AT HARVESTING

UPYTĖ, 2008

The biometrical indices	Mean
Amount of stems (number 1 m^{-2})	*96.3*
Amount of stems (number per plant)	*42.8*
Amount of stems (number ha^{-1})	963 333

In the last rows of the presented tables we can see what huge amount of stems could be produced in 1 ha.

In 2009 in the crop of the 2nd year, 60x60, plants were grosser than that of the 1st year crop. The amount of stems (number per plant) varied from 12 to 68. The highest significant averaged amount of stems (42.9 units per plant) was found to be in the crop of 2nd year, 60x60 (Table 4). Plants of the 1st year crop, 60x100, had more stems per plant (32.9) than that of 1st year crop, 60x60 (25.4), but the differences between treatments were not significant. Nevertheless, amount of stems (number ha^{-1}) was significantly higher in the crop of 2nd year, 60x60, and significantly lower in the crop of 1st year, 60x100. In 2009 the stems of stinging nettle were less branched than that in 2008.

In 2009, in the crop of the 2nd year, 60x60 the number of stems per plant was very similar to that in 2008, i.e., 1 plant in the second year did not produce any more new stems.

In 2009 the amount of stems per plant was lower than that in 2008. In the 1st year crop 1 plant produced close to 33 stems at lower density (60 x 100) (while in 2008 it was close to 43 stems per plant) and close to 25 stems at higher density (60 x60). Crop density in the nettle trials in Italy was found to be much higher – it was close to 132 stems m^{-2} of 2nd cultivation year (implantation density was 50x75 cm) [12].

TABLE 4.

THE BIOMETRICAL INDICES OF STINGING NETTLE CROP AT HARVESTING

UPYTĖ, 2009

The biometrical indices	2dn year, 60x60**	1st year, 60x60**	1st year, 60x100**	Mean
Amount of stems (number 1 m^{-2})	96.6*	57.2	44.8*	66.17
(LSD$_{05}$ 17.23)				
Amount of stems (number per plant)	42.9	25.4	32.9	33.7
(LSD$_{05}$ 9.19)				
Amount of stems (number ha^{-1})	965 833*	571 667	493 333*	676 944
(LSD$_{05}$ 179 361)				

* – significant at 0.05 probability level;

** – the 2dn year stinging nettle crop (established in 2008), 60 x 60 cm (abbreviation of the treatment – 2dn year, 60x60); the 1st year crop (established in 2009), 60 x 60 cm (abbreviation of the treatment – 1st year, 60x60); the 1st year crop (established in 2009), 60 x 100 cm (abbreviation of the treatment – 1st year, 60x100).

Since 2010 we started calculating the crop density also in spring (in May). As some part of the stinging nettle suffered from the inundation early in 2010, the results show decrease of crop density when compare to that in the autumn, 2009 (Tables 5 and 4). The differences between variants in crop density and amount of stems per plant were significant.

TABLE 5.

THE BIOMETRICAL INDICES OF STINGING NETTLE CROP IN SPRING

UPYTĖ, 2010

The biometrical indices	3rd year, 60x60**	2dn year, 60x60**	2nd year, 60x100**	Mean
Amount of stems (number 1 m^{-2})	57.9	45.4	23.7	42.33
(LSD$_{05}$ 4.47)				
Amount of stems (number per plant)	25.7*	20.2	15.8*	20.57
(LSD$_{05}$ 2.12)				
Amount of stems (number ha^{-1})	579 167*	454 167	236 667*	423 333
(LSD$_{05}$ 44 744.9)				

* – significant at 0.05 probability level;

** – the 3rd year stinging nettle crop (established in 2008), 60 x 60 cm (abbreviation of the treatment – 3rd year, 60x60); the 2nd year crop (established in 2009), 60 x 60 cm (abbreviation of the treatment – 2nd year, 60x60); the 2nd year crop (established in 2009), 60 x 100 cm (abbreviation of the treatment – 2nd year, 60x100).

During growing season in 2010, amount of stems per plant have increased, but the differences between variants were not significant (Table 6). The greatest increase was found in the plots of lower implantation density (60 x 100 cm) – from 16 to 37 stems per plant per growing season. In the plots with implantation density 60 x 60 cm, increase of stem amount per plant was rather similar – 13.9-16.0 stems per plant per growing season, and was not depending on crop maturity (3rd or 2dn cropping year). In the trials of Hartl and Vogl, in the third cultivation year the amount of stems per plot (implantation density was 60 x 100 cm) was doubled when compared with those from the second cultivation year [2].

TABLE 6.

THE BIOMETRICAL INDICES OF STINGING NETTLE CROP AT HARVESTING

UPYTĖ, 2010

The biometrical indices	3rd year, 60x60**	2dn year, 60x60**	2nd year, 60x100**	Mean
Amount of stems (number 1 m^{-2}) (LSD$_{05}$ 27.90)	89.1	81.5	55.4	75.33
Amount of stems (number per plant) (LSD$_{05}$ 13.65)	39.6	36.2	36.9	37.59
Amount of stems (number ha^{-1}) (LSD$_{05}$ 279 026.1)	890 833	815 000	554 167	753 333

** – the 3rd year stinging nettle crop (established in 2008), 60 x 60 cm (abbreviation of the treatment – 3rd year, 60x60); the 2nd year crop (established in 2009), 60 x 60 cm (abbreviation of the treatment – 2nd year, 60x60); the 2nd year crop (established in 2009), 60 x 100 cm (abbreviation of the treatment – 2nd year, 60x100).

In the spring, 2011, crop density was again lower than that in the autumn 2010, but rather similar to that in the spring, 2010. In the spring, 2011, the amount of stems per plant was rather similar in all treatments (20.5-25.7), nevertheless, the amount of stems per 1 m^2 was higher in mature crop (4th year, 60x60) than that in younger crop (3rd year, 60x60), and higher in the plots of the crop of higher implantation density (60 x 60 cm) than that in the plots of lower implantation density (60 x 100 cm) (Table 7). The differences between treatments were not significant.

TABLE 7.

THE BIOMETRICAL INDICES OF STINGING NETTLE CROP IN SPRING

UPYTĖ, 2011

THE BIOMETRICAL INDICES	4TH YEAR, 60X60**	3RD YEAR, 60X60**	3RD YEAR, 60X100**	MEAN
AMOUNT OF STEMS (NUMBER 1 M^{-2}) (LSD$_{05}$ 11.40)	56.3	46.1	38.6	46.97
AMOUNT OF STEMS (NUMBER PER PLANT) (LSD$_{05}$ 5.44)	25.0	20.5	25.7	23.73
AMOUNT OF STEMS (NUMBER HA^{-1}) (LSD$_{05}$ 114 035.87)	562 500	460 833	385 833	469 722

** – the 4th year stinging nettle crop (established in 2008), 60 x 60 cm (abbreviation of the treatment – 4th year, 60x60); the 3rd year crop (established in 2009), 60 x 60 cm (abbreviation of the treatment – 3rd year, 60x60); the 3rd year crop (established in 2009), 60 x 100 cm (abbreviation of the treatment – 3rd year, 60x100).

Growing season in 2011 was favourable for stinging nettle – crop density increased more than twice. The differences between variants were not significant, but crop density was over 100 stems per 1m^2 (Table 8). When compared older and younger crop (60 x 60 cm), matured crop showed better results. When compared different implantation density crop (60 x 60 cm and 60 x 100 cm), the lower implantation density crop showed better results. The amount of stems per 1 plant was significantly higher in the plots of lower implantation density crop (60 x 100 cm) – even 82.2 stems per 1 plant.

TABLE 8.

THE BIOMETRICAL INDICES OF STINGING NETTLE CROP AT HARVESTING

UPYTĖ, 2011

The biometrical indices	4th year, 60x60**	3rd year, 60x60**	3rd year, 60x100**	Mean
Amount of stems (number 1 m^{-2}) (LSD$_{05}$ 40.12)	121.8	106.7	123.3	117.28
Amount of stems (number per plant) (LSD$_{05}$ 20.06)	54.2	47.4	82.2*	61.26
Amount of stems (number ha^{-1}) (LSD$_{05}$ 401225.20)	1 218 333	1 066 667	1 233 333	1 172 778

* – significant at 0.05 probability level;

** – the 4th year stinging nettle crop (established in 2008), 60 x 60 cm (abbreviation of the treatment – 4th year, 60x60); the 3rd year crop (established in 2009), 60 x 60 cm (abbreviation of the treatment – 3rd year, 60x60); the 3rd year crop (established in 2009), 60 x 100 cm (abbreviation of the treatment – 3rd year, 60x100).

In the spring, 2012, crop density again was lower than that in the autumn, 2011, but it was much more higher than that in the spring 2011 in the plots of different implantation density crop (60 x 60 cm and 60 x 100 cm) (Table 9). The amount of stems per 1 plant in the beginning of vegetation was significantly higher in the plots of lower implantation density crop (60 x100 cm).

TABLE 9.

THE BIOMETRICAL INDICES OF STINGING NETTLE CROP IN SPRING

UPYTĖ, 2012

The biometrical indices	5th year, 60x60**	4th year, 60x60**	4th year, 60x100**	Mean
Amount of stems (number 1 m^{-2}) (LSD$_{05}$ 29.03)	57.9	83.7	90.6	77.39
Amount of stems (number per plant) (LSD$_{05}$ 17.90)	25.7	37.2	60.4*	41.10
Amount of stems (number ha^{-1}) (LSD$_{05}$ 1 161 281.8)	579 167	836 667	905 833	773 889

* – significant at 0.05 probability level;

** – the 5th year stinging nettle crop (established in 2008), 60 x 60 cm (abbreviation of the treatment – 5th year, 60x60); the 4th year crop (established in 2009), 60 x 60 cm (abbreviation of the treatment – 4th year, 60x60); the 4th year crop (established in 2009), 60 x 100 cm (abbreviation of the treatment – 4th year, 60x100).

Crop density at harvesting in 2012 was rather similar to that in 2011 at harvesting. It could be that the optimal crop density is already achieved, and it will not increase any more in more matured crop in following years. Crop density was approximately the same in more matured and younger crop, 60 x60 cm (112-115 plants m^{-2}), and higher – in the plots of lower implantation density crop (60 x 100 cm) – even 136.4 stems per 1 m^2. Crop density during growing season in 2012 has increased, but not as great as it was in 2011. In 2012 as well as in 2011, the highest amount of stems per 1 plant was significantly higher in the plots of lower implantation density crop (60 x 100 cm) – even 90.9 stems per 1 plant.

TABLE 10.
THE BIOMETRICAL INDICES OF STINGING NETTLE CROP AT HARVESTING
UPYTĖ, 2012

The biometrical indices	5th year, 60x60**	4th year, 60x60**	4th year, 60x100**	Mean
Amount of stems (number 1 m^{-2}) (LSD_{05} 54.38)	114.7	112.2	136.4	121.08
Amount of stems (number per plant) (LSD_{05} 29.00)	51.0	49.9	90.9	63.92
Amount of stems (number ha^{-1}) (LSD_{05} 153333.3)	1 146 667	1 121 667	1 364 167	1 210 833

** – the 5th year stinging nettle crop (established in 2008), 60 x 60 cm (abbreviation of the treatment – 5th year, 60x60); the 4th year crop (established in 2009), 60 x 60 cm (abbreviation of the treatment – 4th year, 60x60); the 4th year crop (established in 2009), 60 x 100 cm (abbreviation of the treatment – 4th year, 60x100). (established in 2009), 60 x 100 cm (abbreviation of the treatment – 3rd year, 60x100).

IV CONCLUSION

In the first cropping year stinging nettle produced 25-43 stems per plant.

Plants from the crop of 2nd year, 60x60, were grosser, more productive than that of the 1st year crop.

Plants of the 1st year crop, 60x100, had more stems per plant than that of 1st year crop, 60x60, but amount of stems per ha^1 was higher in the crop of 1st year crop, 60x60.

The inundation early in 2010 led to the decrease of crop density of stinging nettle's crop.

Crop density in the spring was lower than that in the autumn.

The greatest increase of amount of stems per plant was found in the plots of lower implantation density (60 x 100 cm).

It could be that the optimal crop density (112-136 plants m^{-2}) was already achieved in the crop of 4th and 5th cropping year, and it will not increase any more in older crop in following years. Further investigation would be intrigued

V ACKNOWLEDGMENTS

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Belt Feeder for Biomass Mixing

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Abstract. **Level of agricultural productivity has been increased and also increased land area not utilized for food production. This area can be used for growing energy crops, including grasses. In addition, there are non-agricultural lands in Latvia suitable only for growing energy crops like Reed canary grass etc. Reed canary grass growing for energy needs could be an additional source of income for Latvian farmers, whom have harvesting technique for hay, for example dairy farming. It could be also a local heat energy source if wood in farm area is not available. Pelletizing or briquetting of dried herbaceous biomass has several advantages such as increasing energy density, improving storability and reducing handling and transport costs, but remains, of the fuel quality negatively affecting things, such as high ash and chlorine content (wheat straw 0.1 – 2.3%). Therefore, to reduce ash content and corrosion of heat transfer surfaces suggestible to make blends with others biomass where those parameters are lower. Briquettes of herbaceous biomass blends with peat are denser, durabler and take less energy for briquetting and pelleting. A new mixing method in this article is described. Experiments of biomass feeding in mixing process with belt feeder were done. The throughput of the belt feeder is increasing nearly linearly at feeder belt velocity from 0.18 to 0.89 m·s^{-1}. The specific throughput of belt feeder was evaluated for Reed canary grass. Noticeable influence of the belt velocity on the specific throughput of belt feeder was not found.**

Keywords **– mixer, feeder, Reed canary grass.**

I INTRODUCTION

Biofuels and especially – herbaceous biomass, contain more alkali metals (mainly potassium and sodium) than coal and peat. Alkali metals lower the ash melting point and upon reaction with chlorine, also contained in biomass, have a strong corrosive effect on heat exchangers [1]. Strategies for minimizing deposition problems include co-firing biofuels with “cleaner” fuels. Suitable “clean” fuels include certain types of coal or peat, which contain large amounts of inert species such as silica or alumina in their ash. By blending peat with chips or herbaceous biomass also sulphur content of the fuel is increased, sulphates are formed instead of chlorides, and the risk of corrosion is avoided [2].

Components of mixtures have to be in the required proportion and homogeneous mixed to provide good quality (density, durability, and burning properties) of briquettes or pellets. Usually in mixing process at least two feeders and mixer have been involved. If for bulk material feeding two belt feeders are used, blends from two components can be achieved by merging flows without additional mixing [3]. This type of inflow mixing showed good results. The standard deviation of the component field ratio was 6% that is an acceptable result for biomass mixtures [3].

To achieve better results it is necessary additional mixing but it requires for additional technique unit. The task of the research was to design biomass mixer without additional expensive components. Therefore the mixer showed in Fig. 1 was designed. This mixer is recommended for mixing different kinds of bulk materials (Patent Nr. LV14603 B). Mixer consists of two belt feeders with special knobby belts. Feeders are placed above each other in determined height and belts are moving with appropriate speeds to ensure additional mixing of two components in space between conveyor belts (Fig. 2).

Fig. 1. Bulk material mixer (Patent Nr. LV14603 B)

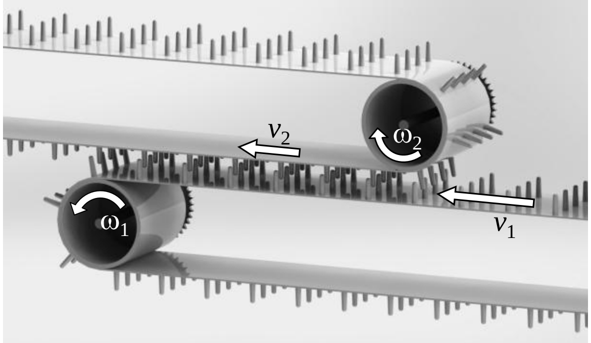


Fig. 2. Working principle of mixer

Mixing process is essentially influenced by quality of the continuous feed. The objective is to feed set quantities of material per unit of time in an uninterrupted product flow. Feeding can be performed volumetrically by feeder equipment which draws material by volume or gravimetrically by controlled feeding using weight or mass as the control value. Gravimetric feeding offers greater accuracy even over periods of hours or days (long term constancy) and is also suited to the feeding of materials with fluctuating bulk density or flow properties, such as cohesive powders and liquid additives with a variable viscosity.

Gravimetric feeding also enables the actual metered volume to be reported back for the purposes of recording, taking printouts and storing, as well as data transference to the process control, information management and alarm systems [4].

By feeding volumetrically it is important that the flow pattern be such that the whole outlet of the feed hopper is fully active. This is of fundamental importance in the case of mass-flow hoppers [5]. In a mixer design presented in this paper (Fig. 1) feed hoppers outlet is fully active. In this case respect of this rule is very important because of poor flowability of the chopped biomass. Mixer should have to have possibility to change proportion of blended components therefore feeder throughput characteristic is important to calculate parameters and to adjust feeders. In this paper the volumetric throughput of a belt feeder by feeding Reed canary grass was stated.

II MATERIAL AND METHODS

Estimation of the volumetric throughput of a belt feeder was carried out in experimental equipment (Fig.3). It consists of belt feeder, bin for chopped biomass with changeable gate opening and hydraulic motor for driving feeder.

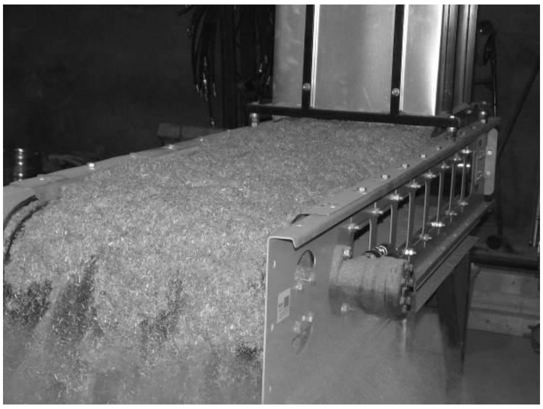


Fig. 3. Experimental equipment

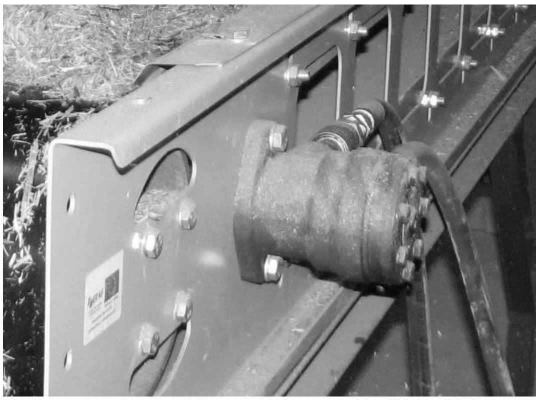


Fig. 4. Hydraulic drive of feeder

Rotation frequency of feeder was changed by hydraulic motor (Fig. 4). The angular velocity of feeder was measured with inductive sensor and impulse counter MP5W-4N (Fig. 5). Feeder bin was filled with determined weight chopped Reed canary grass biomass. Time was set during bin emptying.

Fig. 5. Inductive sensor and impulse counter

Experiments were carried out with chopped Reed canary grass. There were two experiment sets with different particle size distribution of chopped biomass (Fig. 6 – coarse chopped and Fig. 7 – fine chopped). Moisture content of Reed canary grass was ~22%.

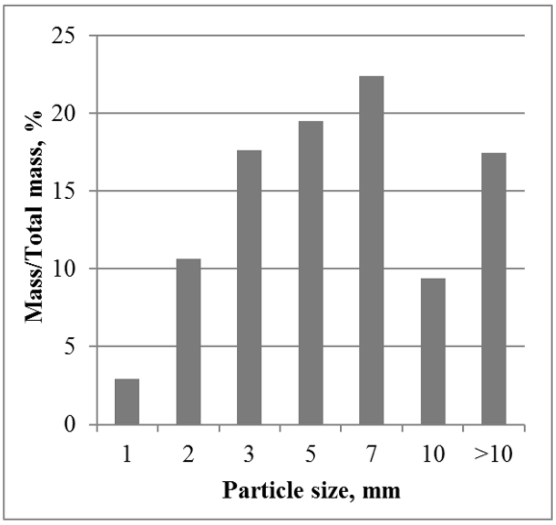


Fig. 6. Particle size distribution of chopped material for first experimental set – coarse chopped

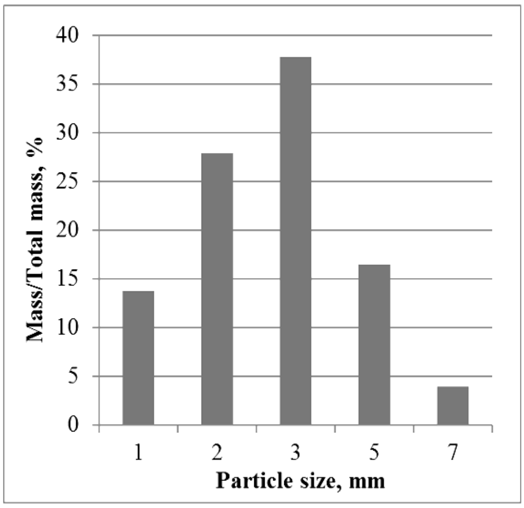


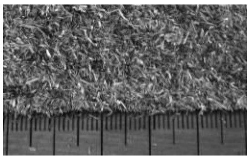
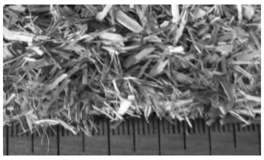
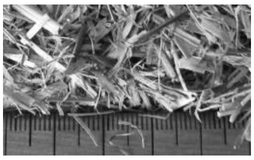
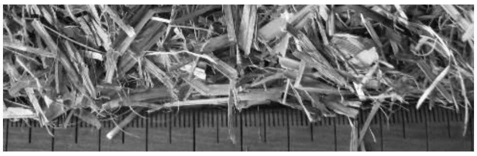
Fig. 7. Particle size distribution of chopped material for second experimental set– fine chopped

In the first experiment set coarse chopped biomass was used. Sieve analyze showed that there are more than 15% particles that didn't pass through sieve with holes diameter 10mm. Visual estimation (Table 1) of particles let us state that particles of chopped stalk are thin and long. Particles passed through sieve holes with diameter 3mm could be in average 5-10 mm but in some cases up to 30mm long.

In the second experiment set fine chopped particles was used there were just 4% of particles which didn't passed through sieve with 5 mm holes.

TABLE I

SIEVE AND PARTICLES SIZE

Sieve holes diameter 1mm	Sieve holes diameter 2mm
	
Sieve holes diameter 3mm	Sieve holes diameter 5mm
	
Sieve holes diameter 7mm	
	
Sieve holes diameter 10mm	
	
Particles above sieve with holes diameter 10mm	
	

III RESULTS AND DISCUSSION

Experiments were carried out to establish parameters of belt feeder by feeding Reed canary grass. The throughput of the belt feeder is increasing nearly linearly at feeder belt velocity from 0.18 to 0.89 m·s^{-1}. The throughput with rough chopped particles and bin gates opening 20 mm grows from 0.02 to 0.11 kg·s^{-1} (Fig. 8) but for fine from 0.08 to 0.33 kg·s^{-1} (Fig. 9). The feed intensity is influenced by particles size, particles orientation and other bulk properties. Bulk density of fine chopped particles is higher and also throughput is higher. There are some other factors that influences feeder throughput. Coarse chopped Reed canary grass is a material with poor flowability. In Fig. 12 is showed that material is pulled out from the bin with V design profile belt. As a result is discontinuous flow. Even at large opening 75 mm the flowabilty of material is still poor. Moreover, the material itself makes jam (Fig. 13) decreasing opening and feeder throughput. After some time jams collapses and creates blowouts (Fig. 14) therefore material flow stability brakes down.

Belt feeder throughput increases to 1.8 kg·s^{-1} at belt velocity 0.89 m·s^{-1} and opening 75 mm (Reed canary grass fine chopped) (Fig. 10).

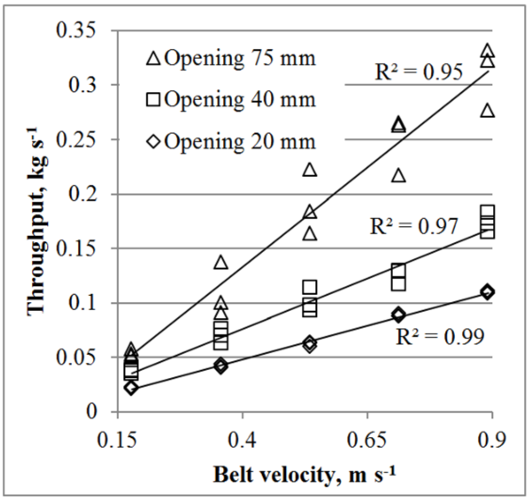


Fig. 8. Feeder throughput with coarse chopped Reed canary grass

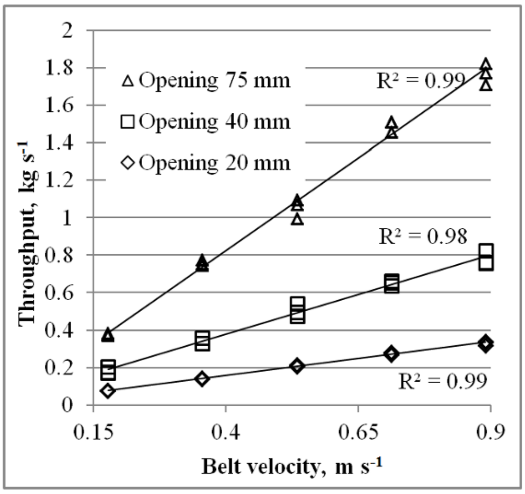


Fig. 9. Feeder throughput with fine chopped Reed canary grass

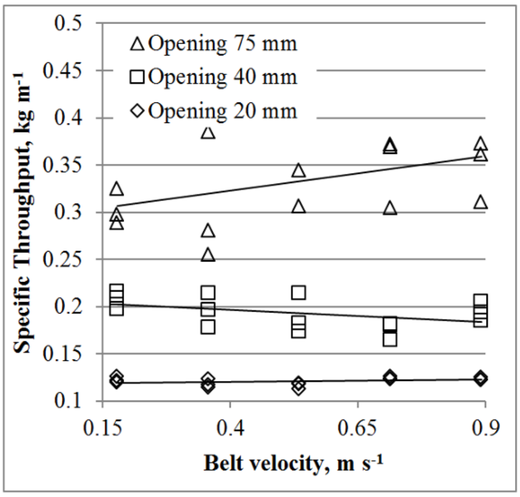


Fig. 10. Specific throughput of the belt feeder with coarse chopped Reed canary grass

The specific throughput of belt feeder shows that there is no noticeable influence of belt velocity on it by feeding coarse chopped particles (Fig. 10). The specific throughput at opening 20, 40 and 75 mm respectively is 0.12±0.002, 0.19±0.009, 0.33± 0.025 kg·m^{-1} (Confidence Level 95.0%).

The specific throughput of finer particles by the same belt speed is higher (Fig. 11) because of the density of material and steady flow (Fig. 3). The specific throughput at opening 20, 40 and 75 mm respectively is 0.39±0.011, 0.94±0.041, 2.06± 0.047 kg·m^{-1} (Confidence Level 95.0%).

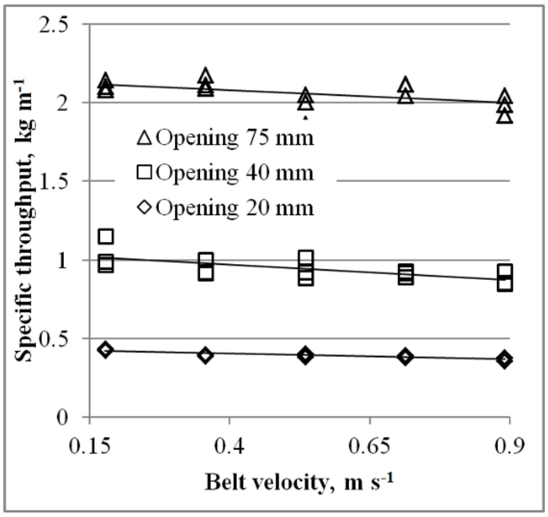


Fig. 11. Specific throughput of belt feeder for second set of experiment

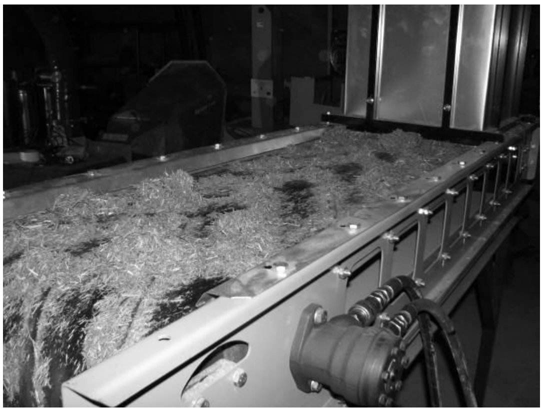


Fig. 12. Discontinuous flow

Fig. 13. Jam of chopped biomass

Belt feeder application for fine chopped Reed canary grass is acceptable. Necessary to continue experiments of feeder equipped with special knobby belts showed in Fig. 2.

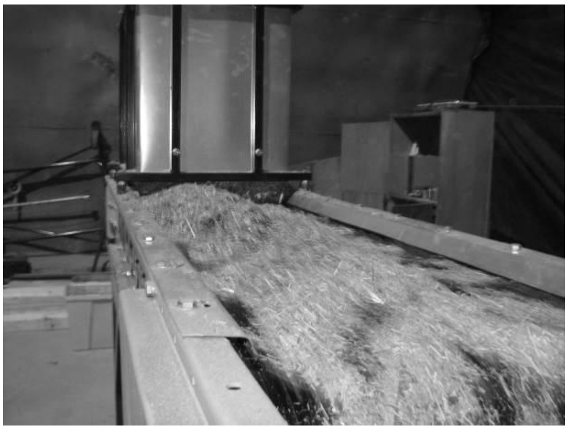


Fig. 14. Blow-out

IV Conclusions

1. The throughput of the belt feeder is increasing nearly linearly at feeder belt velocity from 0.18 to 0.89 m·s^{-1} and it grows from 0.02 to 0.11 kg·s^{-1} (opening 20 mm, rough chopped biomass).

2. Belt feeder throughput increases to 1.8 kg·s^{-1} at belt velocity 0.89 m·s^{-1} and opening 75 mm (Reed canary grass fine chopped).

3. Belt feeder application for fine chopped Reed canary grass is acceptable. Necessary to continue experiments of feeder equipped with special knobby belts

V ACKNOWLEDGMENTS

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Nr. 2010/0306/2DP/2.1.1.1.0/10/APIA/VIAA/128.

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Improvement of Technologies for Mining Waste Management

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***Abstract*. Mining waste reduction methods include all mining processes beginning from resource distribution until final products in the plant. For comparing and testing possibilities of mine waste reduction, a cooperation project has been set up aiming to create a transnational network with regional networks. The activities carried out on the regional and transnational level will secure better access to knowledge, state-of-the-art technologies and good practice. The study addresses all the waste management challenges and opportunities facing the Baltic Sea Region mining industry, which should be understood as extending to all forms of extraction of natural non-renewable resources.**

In addition to the main mineral resource, oil shale, there are sufficient reserves of limestone and dolostone, peat, sand, gravel and clay. Phosphorite and granite are considered as occurrences in today's economic situation, in spite of the fact that phosphorite has been extracted for 70 years in the past. All previous mining activities have produced mining waste, e.g. the total volume of waste rock from Estonian oil shale mining is more than 76 million m3 and covers about 790 ha [31][32][33][34]. From an environmental point of view Estonia is in good position, not having acidic reactions and having neutralising alkaline limestone present in all mining areas. Thanks to this, reclamation is easily done with the help of the same mining equipment. Water is purified in settling ponds and does not require additional chemical treatment. For underground mining, the main concern is the stability of the room and pillar mining area [35][37].

Similar problems are found in Sweden and Finland. In Sweden, there are several old deposits from shale mining, the largest one (Kvarntorp) contains some 40 million m3 of crushed processed black shales and contains several metals of potential value.

***Keywords* – mining, waste management, pilot unit, Baltic Sea Region, oil shale, sand, gravel, waste heap.**

I INTRODUCTION

Mining waste management issues have to take consideration in all mining sites. The main aim of mining waste management is to use Best Available Technology (BAT) in production line, giving minimal waste and best products. How to use old waste heaps as raw material is also a problem. A possible solution is to test different mining waste reduction methods and choose the most practical technology for the site [9][12].

In Estonia, two types of mining waste are currently produced: waste rock from oil shale separation and limestone mining fines (grain size 0-4 mm) from crushing and screening. In addition, previously deposited phosphate rock flotation sand and uranium ore processing waste are being handled. Estonia has 48 mining waste objects [11]. Some of them are limestone fines, but most are oil shale fines.

Mining waste is located and measured in amounts and substances: 1) waste rock dumps are located in huge amounts near the areas of abandoned mines; 2) mining waste contains very often metal elements, including a mix of rare earth metals; 3) the total amount mining and mineral processing wastes stored on the waste facilities.

The aim of this study is locate mining waste heaps and analyze mining waste reduction methods and find solutions to use mining waste as product in different mineral resources.

II METHODS

Mining waste reduction methods include all mining processes beginning from resource distribution until final yield in the plant. For comparing and testing possibilities of mine waste reduction the study addresses all the waste management challenges and opportunities facing the Baltic Sea Region (BSR) mining industry, which should be understood as extending to all forms of extraction of natural non-renewable resources.

The majority of all excavated materials are used in civil, industrial and road building, renewing of road network and railways alone needs many million cubic meters of building stone, gravel, sand and other materials [30].

The Estonian Road Administration put into practice in the spring 2012 the directive regulating mineral resources used in the determination of roadworks. This directive restricts greatly the amount of suitable mineral resources, because filtration coefficient requirements not being fulfilled. In case the quality of a natural resource does not meet the requirements, one option is to use a variety of enrichment to improve the quality. Many quarries, where mining permit is issued, intended for use in road construction, drop out of the competition, because the natural quality and the processed quality are not as required.

To answer the question why there is a lot of waste production in limestone and dolostone reserves, it is important to know about limestone and dolostone production methods, its standard and specifications. In order to better understand the current situation as a whole, it is necessary to describe the existing standards, which are used by the Estonian Road Administration for technical requirements and specifications definition in road construction projects. According to the decree of the head of the Estonian Road Administration no. 95 17.04.2006 "The requirement for acceptance of construction and repair of public roads" construction material for road pavement must meet strict requirements, which are listed below in Table 1[2].

As it can be seen in Table 1, the fine particle content for limestone aggregates is 2 %, which increases waste content in production line up to 40 %. It is quite necessary to get the crusher alignment installed and optimized for given characteristics of the deposit. For instance, many manufactures work according to the following processing system: first there is a jaw crusher complex, secondly a crusher is processing the overall fractions, which are forwarded from the screen. To achieve the highest quality of aggregate, the material should be lead to an additional cone crusher. It helps to reduce the weak grain content, but the number of the waste material rises up to 40 % [3]. Consequently, higher quality rank for limestone and dolostone aggregates means larger waste content in production line.

TABLE I

THE AGGREGATES QUALITY SPECIFICATIONS [1]

Sample	Class I	Class II	Class III	Class IV	Norms
Abrasive resistance upon the Nordic test	≤ 10	≤14	PN	PN	EVS-EN 1097-9
Frost-resistance -upon direct freezing	≤2	≤2	≤4	≤4	EVS-EN 1367-2
Crushing strength upon the Los Angeles test	≤20	≤20	≤30	≤35	EVS-EN 1097-2
Fine particle content	≤1	≤1/≤2	≤2/≤3	≤3/≤4	EVS-EN 933-1
Grain shape by the plateness factor	≤10	≤20	≤25	≤35	EVS-EN 933-3
Radioactivity			shows that generate natural radioactivity not more than 85 Bq / kg	Estonian Radiation Law	EVS EN 1744-1 p.15.1

A. Production of material from mining waste appropriate for construction industries (aggregate for structural concrete).

Therefore, construction of a mobile unit for sieving, crushing and screening of material has been chosen. The mobile unit can be transported to different locations of waste dumps. Alternatives to Portland cement and other standard aggregates are being sought.

Mining related waste is mainly solid waste from separation and processing, operating solid waste from overburden removal and drifting, liquid waste from dewatering, processing and washing processes. Origin of mining waste is separation waste form heavy media separation (HMS), processing waste, crushing and screening waste [14] [16] [36].

The main usage of solid mining waste is material for filling, construction and cementing [35]. The principal direction of developing mining technology is filling the mined area [23][24]. This provides control over majority of environmental effects. Filling the workings decreases the loss of resources and land subsidence, and at the same time provides usage for stockpiling. Filling the spoils of a surface mine decreases dewatering; harmless waste can be used for filling surface mines and in this manner offer new building ground [22] [25][26] [27] [28][34] [38].

B. A pilot plant to develop business opportunities for SMEs by extracting valuable and/or hazardous metals etc. from mining and metal processing waste.

The pilot unit includes: (1) Crushing and milling (2) Leaching (3) Recovery of elements from solution. There is a possible innovation related to treating old tailings and slags through leaching with different aqueous media, which has not been performed before. Transnational relevance as metal recovery from waste is not usual in BSR.

The objective is to test recycling of mine waste with a view to future commercial potential [14]. A mobile module will be constructed, transportable to sites where waste is processed. The main element is dry grinding and classification of the material according to the grain size. Simultaneous analysis is required to control the promotion of classification procedure. A novelty is that produced material combined with other components can be used as an adsorbent in waste water purification [12].

An investment objective is to prepare aggregate for waste from mineral treatment plant and useful minerals enrichment plant. Aggregate from fine-grained waste will be produced using an agglomeration process. Installation will include screamer, crusher, mixer, and measurement devices (to control physical and chemical properties). The installation will allow to test various types of coal processing waste, and other mineral processing waste (sandstone/mudstone/claystone mixed waste from gravity washers in heavy liquids). The product will be crushed aggregates mix 4(5)-31.5 mm, useful in mining, building and road construction.

III RESULTS

In total, 48 different waste heaps or production loss heaps have been defined in Estonia (Fig. 1, Fig. 2) [11]. For each heap, many characteristics are defined to describe its situation. The main characteristics are: heap location, time period of mining, mined mineral resources, type of heap, geometry of heap (height, area, volume), administrator, description of material, category of waste heap according to the directive.

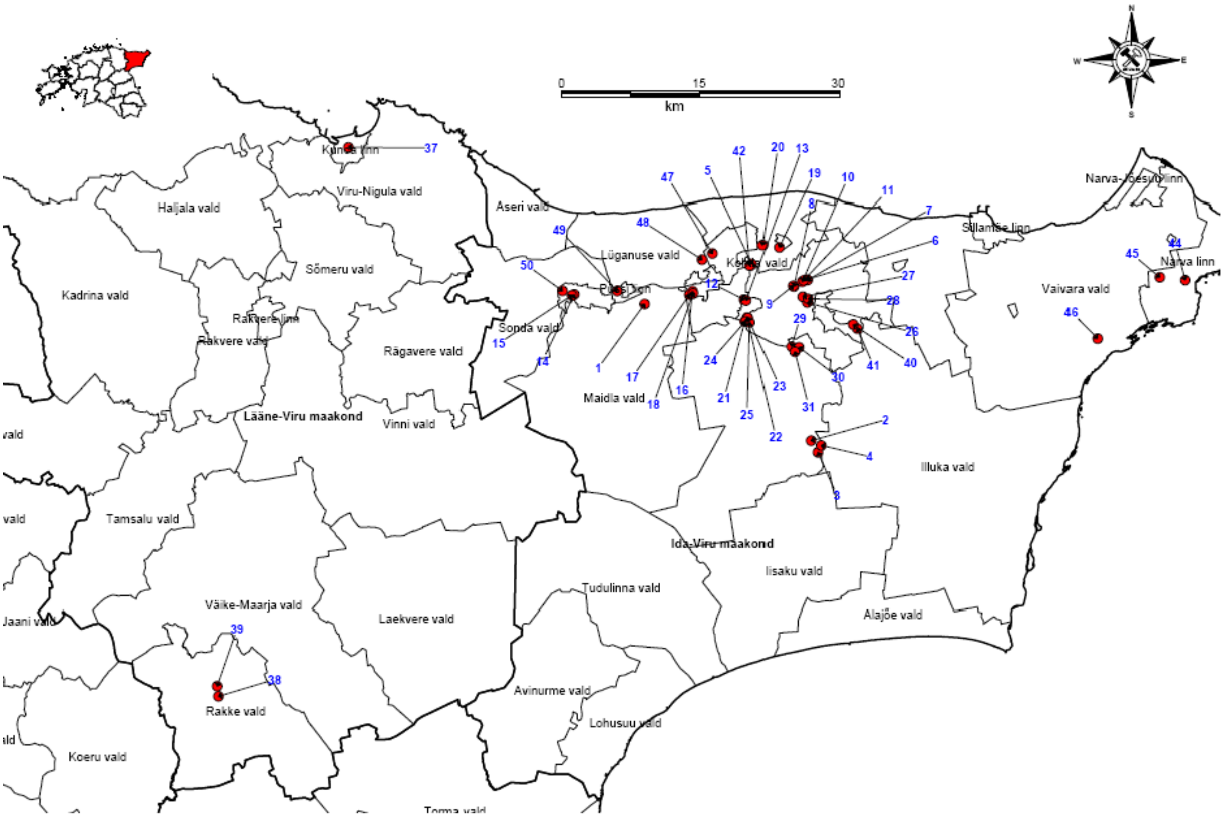

Fig. 1 Mining waste objects – East Estonia

Fig. 2 Mining waste objects – North Estonia

Oil shale utilisation losses reach 70% in some cases [21][29][39]. These are closely related to legislation, backfilling and waste rock usage [30][31]. Much smaller sections include production of oil, electricity and chemicals which are the focus of most of research and development today. Current urgent topics for investigating, testing and developing of oil shale mining are backfilling, mechanical extracting of shale, fine separation, selective separation and optimised drilling and blasting [4][5][6][7][8][10][13][15].

First small scale tests with dry crushing have been carried out at several sites with oil shale, run of mine (Fig. 3) and waste rock in addition to sand and gravel crushing [12]. The material has been evaluated and initial results received.

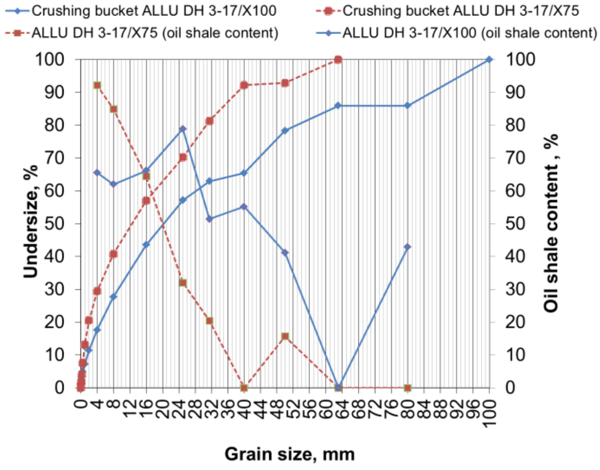

Fig. 3 Oil shale selective crushing test results with ALLU crushing buckets

IV Discussion

To avoid open quarries, where the material not suitable for using in building, we must know the quality at particular locations. The compositions of sand and gravel deposits in the Harju County have been analysed. Thus it is possible to determine precisely enough usability exploration, as well as areas where it is possible to find new gravel, sand or complex deposits.

All 27 presently operating gravel and sand pits may be divided to groups considering their position to glaciation stadial, distance from ice margin and genesis. In the central part of the county, between the Pandivere and Palivere Stadial zones, glacial sediment forms four groups of deposits oriented in the direction of ice margin, NE 45-75º, during the deglaciation here [17][18] [19][20].

Sediments near the Pandivere Stadial ice margin contain more gravel and clay than fluvioglacial sandy deposits. These positions are Voose (Kuressaare) and Punamäe deposits (Fig. 5). Next deposits is characterized by variation of gravel part 20-45% and decreasing of clay content up to 3-6% in the Vahelaane and Kose-Risti open pits. In the Vahelaane open pit it was possible to observe, how older bedded fluvioglacial sands are deformed into folds, their upper part subsequently eroded and covered by new layers of gravel and sand (Fig. 4).

Fig. 4 Folded sand in the lower part is deformed into folds, the later part of the sequence is eroded and covered by horizontal gravel and sand layers. The Vahelaane open pit.

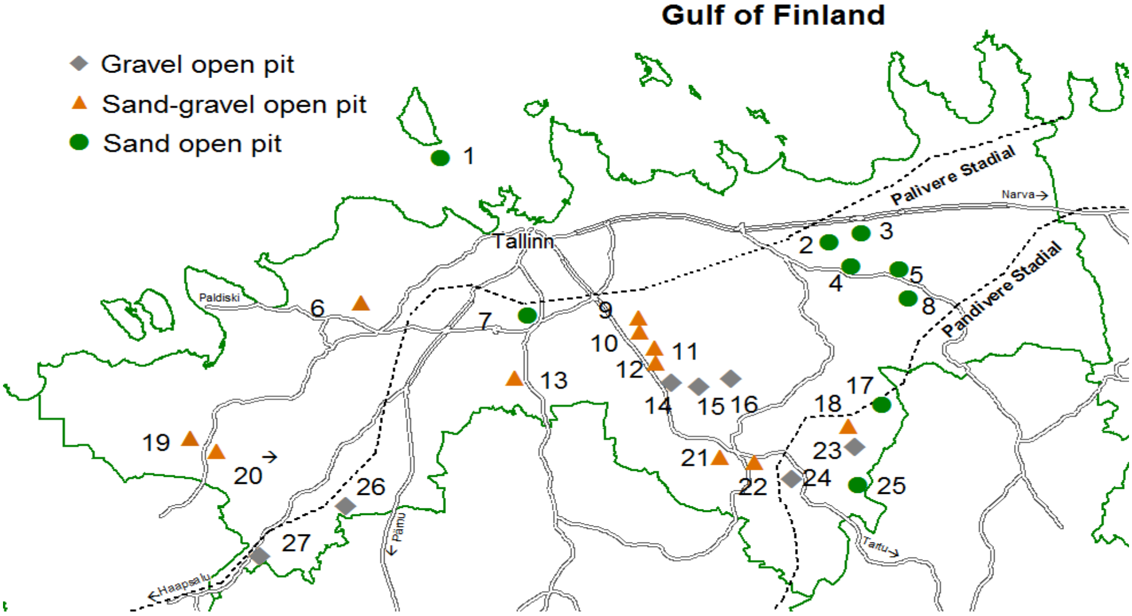

Fig. 5 Working gravel, sand-gravel and sand open pits of the Harjumaa County in 2013.

1- Naissaare, 2-Huntaugu, 3-Kuusalu, 4- Soodla, 5- Raudoja, 6- Karjaküla, 7- Tallinn-Saku, 8- Poolvahe, 9- Seli, 10- Suuresöödi, 11- Suuresta, 12- Vaidasoo, 13- Kõrnumäe, 14- Piuga, 15- Nõmme, 16- Pihuvere, 17- Vetla, 18- Vahelaane, 19- Tatramäe, 20- Audevälja, 21- Kose-Risti, 22- Sõmeru, 23- Voose(Kurissaare), 24- Punamäe, 25-Kiruvere, 26- Mustu, 27- Kalda.

V SUMMARY

Mining waste management issues have to take consideration in all mining sites. The main aim of mining waste management is to use Best Available Technology (BAT) in production line, giving minimal waste and best products. It is also a problem how to use old waste heaps as raw material. A possible solution is to test different mining waste reduction methods and choose the most practical technology for the site.

Mining waste reduction methods include all mining processes beginning from resource distribution until final products in the plant. For comparing and testing possibilities of mine waste reduction the study addresses all the waste management challenges and opportunities facing the Baltic Sea Region mining industry, which should be understood as extending to all forms of extraction of natural non-renewable resources.

To answer the question why there is a large amount of waste production in mining limestone and dolostone reserves it is important to know about limestone and dolostone production methods, its standards and specifications. In order to better understand the current situation as a whole, it is necessary to describe the existing standards used by the Estonian Road Administration for technical requirements and specifications definition in road construction projects.

To avoid opening quarries, where material is not suitable for building, we must have overall knowledge on quality at each location.

Futures research will focus on using environmental friendly mining methods in all areas of mineral resource mining. For better mining waste management different pilot units have been designed in order to determine how to use old waste heaps as new raw material.

VI ACKNOWLEDGMENT

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Thixotropic Properties of Latvian Illite Containing Clays

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Abstract. **Thixotropic properties of Latvian Devonian and Quaternary clays were studied. Dynamic viscosity of the water clay suspensions were measured with a rotating viscometer. Influence of concentration, pH and modifiers on the thixotropic clay properties was analyzed. It was found that Latvian clays have thixotropic properties. Stability of clay suspensions is described with the thixotropy hysteresis loop. Increasing the speed of the viscometer rotation, dynamic viscosity of the clay suspension decreases. It was found that the solid phase concentration and mineralogical composition make an impact on the thixotropy of clays. Decreasing the solid phase concentration in the clay suspensions from 50% to 25%, dynamic viscosity decreases proportionally to the solid phase concentration.**

It was found that modifying clay suspensions with carboxymethyl cellulose (0,1g) increases concentration of structure forming. In the same time, modifying of clay suspensions with calcified soda (0,1g) decreases the structure forming concentration. Dependence of pH value from the solid phase concentration slightly decreases with the clay phase concentration increasing in the suspension.

Key words. Thixotropy, viscosity, clay, suspension, solid phase.

I INTRODUCTION

Studying thixotropic properties could clear the way to a perspective and vital chance to use Latvian clays in the powdered compositions which are used as sorbents for collection of leaked oil and oil products from water aquatoriums or like components of drilling solutions. Thanks to thixotropy, clays can be used even in medicine or cosmetics that nowadays are trying to create innovative products from natural materials. Thixotropic properties of Latvian clays are not yet completely investigated. Thixotropy is the phenomenon of the fluid which shows a reversible structural transition (i.e., gel–sol–gel conversion) due to the time-dependent changes in the viscosity induced by temperature, pH or other components without any changes in the volume of the system [1-3]. According to the IUPAC terminology, thixotropy is defined as the continuous decrease of viscosity with time, when flow is applied to a sample that has been previously at rest and the subsequent recovery of viscosity in time when the flow is discontinued. There are three essential elements of the thixotropy definition used nowadays: it is based on viscosity; it implies a time-dependent decrease of the viscosity induced by flow; the effect is reversible when the flow is decreased or arrested [2].

In other words, thixotropy is a term to describe an isothermal system in which the apparent viscosity decreases under shear stress, followed by a gradual recovery when the stress is removed [1]. Systems that correspond to a definition of thixotropy, have various rheological parameters. Quantitative determination of thixotropy is a sophisticated process, since measuring of rheological functions is complicated. Since the system is heterogenic, it is often not easy to take measurements, because particles may sink or stick to the walls. Under the impact of microstructure variation, other physical, optical and dielectric properties may also change. There are many methods of thixotropy determination, but the most suitable way for the measurement of thixotropy is to describe the material response in shear stress due to an inflicted deformation or a shear rate [1-3]. Thixotropic properties depend on microstructure of the system, ability of particles to form agglomerates of various sizes under impact of mutual interaction. Also, thixotropy is impacted by concentration, particle sizes, system pH value, temperature, presence of anions and cations, sample concentration and other factors. If the solid phase contains polar particles, then structure forming in suspension occurs also at comparatively low concentrations, for example, a smectyte concentration of 1% is sufficient to demonstrate thixotropic properties, for smectyte clays form three-dimensional ("card-house") structure and suspension can coagulate. Apparent viscosity increases exponentially with the clay concentration. If a suspension contains a high solid phase concentration, and the particles sedimentate, then the structure is not forming. [4-6].

Thixotropy is a very widely spread phenomenon in various fields of industry and natural systems. Industry applications involve mineral and metal processing, manufacturing of foods, pharmaceuticals, cosmetics. We see it every day when we use products like tooth paste, shampoo, lotion, coatings, dyes, gels and tints [7-8]. By modifying natural Latvian clays, one may achieve desired surface and thixotropy properties, that give possibility to use them for processing waste waters or vegetable oils or in many other industries. [9].

In the present research, the typical hysteresis loop rheology test method was employed to evaluate thixotropy of various Latvian illite containing clays. Influence of concentration, pH and modifiers on the thixotropic clay properties was analyzed.

II MATERIALS AND METHODS

Research objects and preparation for thixotropic experiments

Objects of this research are Latvia originated Devonian (Pavāri, Planči, Skaņkalne) and quaternary (Ceplīši, Prometejs, Ugāle) deposits of illite clays.

Granulometric composition of the analyzed samples was determined using the particle size analyzer "Analyzette 22 NanoTech"(Fritch, Germany). Mineralogical composition of clay samples was analyzed by X-ray powder diffraction (XRD) (X'Pert Pro, Philips, The Netherlands). Description of the researched clay samples is given in Table 1 and Fig.1.

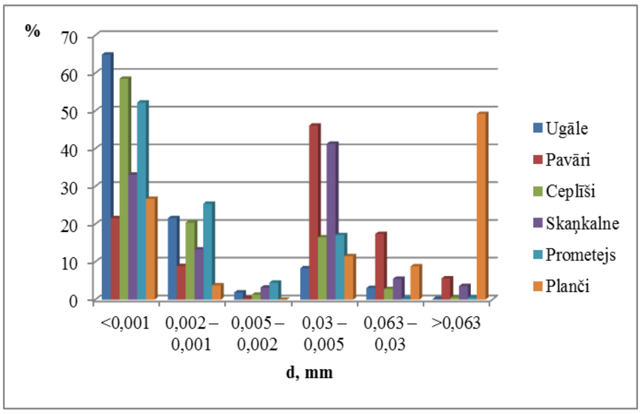

Fig.1. Granulometric composition of the analyzed clay samples.

1.TABLE

MINERALOGICAL COMPOSITION OF ANALYZED LATVIAN CLAY SAMPLES

Mineral content %	Clay sample			
	Pavāri	Prometejs	Skaņkalne	Ugāle
quartz	53,89	12,65	42,59	9,92
illite	34,54	42,98	37,16	36,46
kaolinite	3,94	2,93	9,53	1,89
goethite	-	2,64	4,79	1,02
orthoclase	-	17,01	5,94	5,38
albite	7,64	-	-	5,51
chlorite	-	4,61	-	13,9
calcite	-	8,39	-	7,97
dolomite	-	8,17	-	4,48
muscovite	-	0,22	-	-
haematite	-	0,4	-	-

Determining volume of humidity in the analyzed clay samples

In order to determine clay sample humidity composition, a sample of 1 g mass is placed in a porcelain pot which was previously dried at 105˚C temperature up to a constant weight. The clay sample containing pot is dried at 110˚C temperature up to a constant weight. The obtained results are summarized in Table 2.

Humidity volume (W%) is calculated using the following equation:

$$W\% = \frac{(m_1 - m_2)}{m} \cdot 100 \qquad (1)$$

where m_1 – clay mass with the pot before drying, g;
m_2 – clay mass with the pot after drying, g;
m – clay mass, g.

. TABLE 2

VOLUME OF HUMIDITY OF LATVIAN CLAY SAMPLES

Clay deposit	Period	Layer thickness of taken samples (m)	Humidity %
Ceplīši	Quaternary	2,2 – 3,0	24,0
Pavāri	Devonian	1,8 – 2,3	16,6
Planči	Devonian	1,5 – 2,2	19,9
Prometejs	Quaternary	1,5 – 2,0	20,1
Skaņkalne	Devonian	2,0 -3,0	19,0
Ugāle	Quaternary	1,5 – 3,0	31,0

Clay suspensions were prepared from the studied clay samples which are mechanically cleared from additions, crashed in a pestle, dispersed and swollen in a distilled H_2O for 1 month. Swollen clays in suspension form are sieved and dried in 105°C temperature, by that obtaining a fine clay-aleirite fraction with particle size < 63 μm.

Dry samples, 250 g each, were crushed in a mortar, added to 250 g of distilled water and the prepared 50% clay suspensions were matured for 1 months in order to ensure replicability and invariability.

Density measurements

10 ml of suspension sample was weighted on the analytical scales and its density was calculated using the following equation:

$$\rho_s = \frac{m_s}{V_s} \qquad (2)$$

where ρ_s – solution density, g/ml;
m_s – fluid mass, g;
V_s – fluid volume, ml.

Viscosity measurements

For viscosity measurements rotational viscometer Fungilab EXPR 300002 (Spain) was used. For measuring viscosity, sample suspension in a 600 ml glass is taken. 5 minutes before measuring suspensions were mechanically activated, mixed with a mechanical mixer, in order to increase clay sample dispersity and ability to respond. One of the viscosity measuring spindles is chosen. Suspension density value is inserted, required time and regime of measurements is set – rotation speed gradual variation interval (RAMP) which may vary in the range from 0.01-200 rotations per minute or multistep program with set speeds of spindle rotation.

Thixotropy measurements

The hysteresis loop rheology test method was employed to evaluate thixotropy of various Latvian illite containing clays.

Viscosity measurements are taken using a rotation viscosimeter MULTISTEP program. Measurement points are set in an available thixotropy interval, increasing in the beginning (until the chosen maximum) and then the reducing rotation speed sequence. Obtained dynamic viscosity data is processed, calculating the angular speed:

$$\omega = 2\pi / 60 \cdot N , \qquad (3)$$

where ω – angular velocity of spindle, rad/sec;
N – spindle RPM.

For calculating shear stress and shear rate formula (4) and (5) were used:

$$\dot{\gamma} = \frac{2\omega R_C^2 R_b^2}{R_b\, 2(R_C^2 - R_b^2)} , \qquad (4)$$

where $\dot{\gamma}$ - shear rate, sec^{-1};
ω – angular velocity of spindle, rad/sec;
R_c – radius of container, cm ;
R_b – radius of spindle, cm.

$$\tau_w = \frac{M}{2\pi R_b^2 L} , \qquad (5)$$

kur τ_w - shear stress, dyn/cm^2
M – Torque acting on surface of spindle, N·m (instrument reading);
R_c – radius of container, cm;
R_b – radius of spindle, cm;
L – effective spindle side length, cm

III RESULTS AND DISCUSSION

Viscosity of clay suspensions

Figure 2 shows variation of dynamic viscosity depending in the sample's solid phase concentration mass share w%, at rotation speed 10 rpm. Viscosities of clay sample suspensions significantly differ in between. It can be explained by their different composition and construction. It can be observed that the Planči deposit samples demonstrate the highest viscosity, followed by Ugāle and Prometejs deposit samples since the samples not only contain clay minerals, but also aleirite fractions, viscosity may also be impacted by dolomite contained in the samples. All the samples demonstrate reduction of viscosity with reduction of solid phase, which can be explained by quartz contained in the samples, which quickly sinks in the diluted suspensions and does not form any structures.

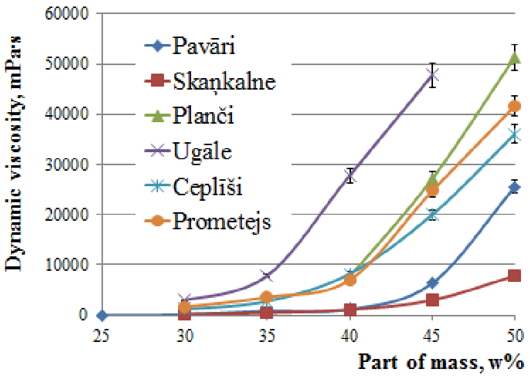

Fig.2. Dynamic viscosity of clay suspensions depending on solid phase concentration

Thixotropy of clay suspensions

In order to determine if a material has any thixotropic properties, viscosity is measured using multistep program. The data obtained was processed and shear rate and shear stress were calculated using formulas (4) and (5). The results were showed on figures, plotting shear rate on the abscissa and shear stress on the ordinate. If a hysteresis loop is formed, it shows a thixotropy. If no hysteresis loop is formed, it means that this material has no thixotropic properties.

Almost all the analyzed samples have thixotropic properties with only solid phase concentration varies where they are more pronounced. Comparing thixotropic properties of all the samples with a similar concentration as it is shown on figure 3, it is characteristic to all the samples. More distinct thixotropic properties at 30% solid phase concentration are demonstrated by samples from Ceplīši and Prometejs deposits. Hysteresis loops do not correspond to a theoretical shape, but since the suspensions also contain aleirite which makes their structure uneven, and other clay minerals, these hysteresis loops are considered as proof of thixotropy. Analyzing each of the samples separately, in a certain interval, hysteresis loops are closer to the expected shape.

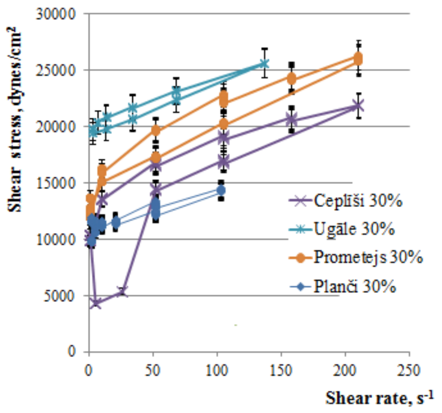

Fig.3. Hysteresis loops of 30% clay-water suspensions

With solid phase concentration changing in the suspension, thixotropic properties change as well. In the much diluted suspensions, particle sedimentation is observed and their mutual attracting powers are not so distinct. In the concentrated suspensions, gaps between particles are too small and it causes particle repulsion. (see Fig.4).

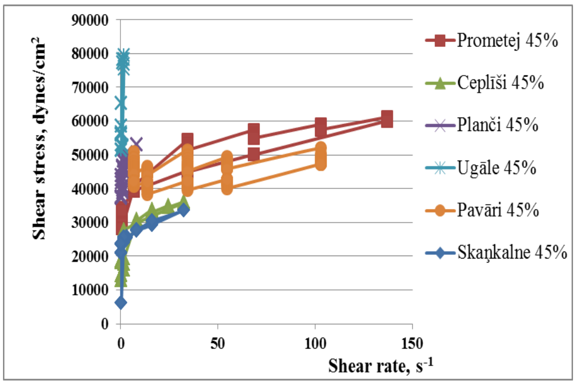

Fig.4. Hysteresis loops of 45% clay-water suspensions

As the Fig. 4 shows, thixotropic properties of a 45% suspension differ from those of 30% suspension. A high content of solid phase gives a possibility that non-polar particles might sedimentate in the lowest part of measuring cylinder.

pH influence on clay thixotropy

The analyzed clay suspensions have various compositions and properties. They are also different by pH value and electric conductivity. The output values of pH and electric conductivity values of the 50% suspension are shown in Table 3.

TABLE 3

PHYSICAL PROPERTIES OF THE ANALYZED CLAY SUSPENSIONS

Sample	pH	E_o, mV	T, ˚C	ρ, g/ml
Ceplīši 50%	7,34	-47,2	21,6	1,458
Skaņkalne 50%	4,79	100,7	23,4	1,485
Pavāri 50%	5,2	40,9	21,5	1,421
Planči 50%	6,65	-9,2	22,4	1,479
Prometejs 50%	7,14	-38,7	21,8	1,246
Ugāle 50%	7,19	-47,1	23,2	1,436

With changing the solid phase concentration, clay suspension physical properties also change. At every sample these changes are different, however a general tendency is observed that with solid phase concentration reduction, the pH value increases and the density decreases (see Table 4). With solid phase concentration change, clay suspension physical properties are also changed. These changes are different at every sample, however a general trend is observed – with solid phase concentration reduction, pH value increases and density is reduced (see Table 4). It therefore impacts viscosity and thixotropy, for with density reduction, dynamic suspension viscosity decreases as well.

TABLE 4

PHYSICAL SAMPLE PROPERTIES DEPENDING ON CLAY MASS SHARE COMPOSITION

Physical properties of the sample	Clay mass share, %				
	50%	45%	40%	35%	30%
Skaņkalne, pH	4,79	4,88	4,85	4,98	4,92
Skaņkalne, ρ, g/ml	1,49	1,42	1,36	1,35	1,33
Pavāri, pH	5,20	5,95	6,10	6,38	6,40
Pavāri, ρ, g/ml	1,42	1,41	1,41	1,40	1,26
Ugāle, pH	7,19	7,30	7,37	7,52	7,66
Ugāle, ρ, g/ml	1,44	1,42	1,39	1,30	1,28
Planči, pH	6,65	6,19	6,52	6,13	6,39
Planči, ρ, g/ml	1,48	1,48	1,48	1,39	1,27

Modifier impact on clay – water suspensions stability and thixotropy

Modifiers – sodium carbonate (Na_2CO_3) and carboxymethyl cellulose sodium chloride (KMC) – impact both physical properties of the suspension and viscosity and thixotropy. 0.1 g of additives for 200 ml of suspension were added to 30% of Skaņkalne, Planči and Ugāle deposit samples. A general trend is observed at all the samples – after processing with soda-ash, viscosity reduces and the structure forming concentration lowers. It is explained by the contents of carbonates in the samples that react with the soda and sedimentate as $CaCO_3$. With adding KMC, viscosity increases, suspension becomes more stable and structure forming concentration increases. Comparison of dynamic viscosity of the non-modified and modified samples is demonstrated on Figure 5.

Adding modifiers impact clay thixotropic properties and change suspension structure. Adding the Na_2CO_3 negatively impacts the thixotropy, hysteresis loops are not formed or gaps between them are very small. Adding KMC improves the thixotropic properties, hysteresis loop is formed with a wider area, and thixotropic properties are demonstrated after a short period of time – when the suspension is no longer mechanically influenced, it quickly restores its viscosity (see Fig.6).

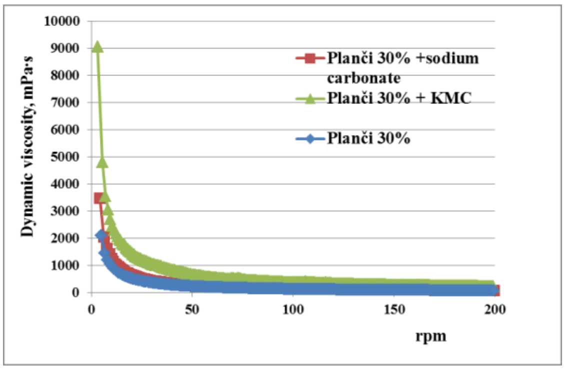

Fig.5. Dynamic viscosity of Planči deposit clay water suspension depending on added modifier

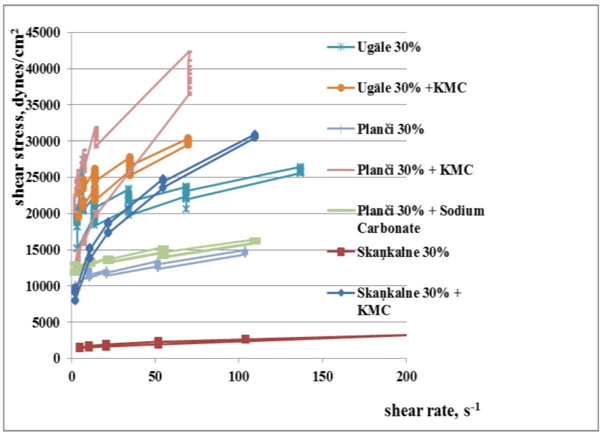

Fig.6. Thixotropy of Latvian clays depending on added modifier

Fig.6.shows how adding KMC stabilizes the clay suspension; hysteresis loop is significantly wider than the hysteresis loop of a non-modified clay suspension.

IV CONCLUSIONS

It was found that Latvian clays have thixotropic properties.

Clay suspension stability is described by the thixotropy hysteresis loop.

Increasing the speed of the viscometer rotation, dynamic viscosity of the clay suspension decreases.

Solid phase concentration and mineralogical composition make an influence on the thixotropy.

Decreasing the solid phase concentration in the suspensions from 50% to 25%, dynamic viscosity decreases proportionally to the solid phase concentration.

It was found that modifying of clay suspensions with carboxymethyl cellulose (0,1g) increases concentration of structure forming. In the same time, modifying of clay suspensions with the sodium carbonate (0,1g) lowers the structure forming concentration.

Dependence of pH value from the solid phase concentration slightly decreases with the clay phase concentration increasing in the suspension.

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Effect of Lignosilicon on the Content and Antioxidant Activity of the Polyphenols of Buckwheat *Fagopyrum esculentum* Moench

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***Abstract*. Lignin preparations, introduced into soil jointly with buckwheat *Fagopyrum esculentum* Moench, variety ’Aiva’ (cultivated throughout Latvia) seeds during the sowing in quantities of 20 kg ha^{-1} and 40 kg ha^{-1}, exerted a favourable effect on the ned in alcohol extracts from the biomass of different morphological parts of buckwheat, were represented mainly by rutin. The content of rutin in the ethanol extracts from the biomass of flowers with bract reached the maximum values in the phase of accomplishing blooming – beginning of fruit formation to be 2.74% in terms of dry mass (exceeding the rutin content development of plants and the synthesis of flavonoids in flowers with bract. Flavonoids, determin the control by 65%) in the variant with 40 kg ha^{-1} of Lignosilicon. Lignin preparations favoured the increase in the radical scavenging capacity of the alcohol extracts of the biomass of flowers with bract of buckwheat, as well as grain and hulls. The increment of the buckwheat grain crop, in comparison with the control on the background of 40 kg ha^{-1} of lignin, was 12%, and that on the background of 20 kg ha^{-1} and 40 kg/ha of Lignosilicon 10% and 15%, respectively.**

***Keywords* - buckwheat, lignin, Lignosilicon, flavonoids, rutin, antioxidant activity, crop.**

I INTRODUCTION

Systematic studies on the effect of silicious lignins (Lignosilicon) on the growth and development of different agricultural plants are under way at the Latvian State Institute of Wood Chemistry. Lignosilicon, applied as fertilizers and growth activators in cultivating cereals (oats, wheat, rye, maize) [1-3], legumes /*Leguminosae*/ leguminous plants (red clover) [4, 5] and *Solanaceae* plants (tomato, potato) [6, 7] exerted a favourable effect on the development of plants, on the enhancement of their productivity and the qualitative characteristics of agricultural products. The results of the studies, performed jointly with the LLU Research Institute of Agricultury (Skriveri, Latvia) with plants of buckwheat, variety “Aiva” have demonstrated a favourable effect of Lignosilicon (LSi), introduced into soil (10 kg ha^{-1} and 20 kg ha^{-1}) simultaneously with the sowing of seeds, on the activation of the development of the aboveground and root system of plants, on the grain crop and the yield of straw [8].

Buckwheat is a cereal belonging to the *Polygonaceae* family. The fatherland of buckwheat is believed to be Northern India. At present, interest in both wild tartary buckwheat *Fagopyrum tataricum*, cultivated in countries of South-Eastern Asia (China, India), and Central and Southern Italy, and common buckwheat *Fagopyrum esculentum* has grown [9-11]. Thanks to the activities of the International Buckwheat Research Association (IBRA), tartary and common buckwheat have become the object of versatile research [9].

Big work is under way in countries of South-Eastern Asia (China, India) on selecting tartaric buckwheat, and obtaining food products and physiologically active substances from different morphological parts of the plant [10, 11]. The world’s leaders of the production of common buckwheat at the beginning of the XXI century are Russia, China and Ukraine. In Western Europe, the leader is France, where relatively small areas are sown, but the highest crops are obtained – 3.5 t ha^{-1}. The buckwheat grain crops worldwide, except in France, are not high and on average range from 0.8 t ha^{-1} to 1.2 t ha^{-1} [12]. According to the data of FAOSTAT (Food and Agriculture Organisation of the united Nations), the sown area of buckwheat was 2.5 million ha in 2008 [12]. In Latvia the sown area under buckwheat in 2009-2011 was 1% from all spring crops and in 2011 buckwheat occupied 9.5 thousand ha. The average yield of buckwheat grain in Latvia was 0.48 tha^{-1}, 0.56 t ha^{-1} and 1.0 t ha^{-1} in 2009, 2010 and 2011, respectively **[**13**]**. The reason for the low crops of buckwheat are the biological peculiarities of the culture **[**12-15**]** which is very sensitive to weather conditions, long and disunited periods of flowering and maturing and the weak homeostasis of grain formation. Buckwheat has a complex of unique properties useful for the life and health of humans [10-12, 14] incl. mineral elements (phosphorus, calcium, kalium, iron, zink, copper) and vitamins (P, B_1, B_2, B_C, PP). Buckwheat grain, has an unique amino acid composition of protein in comparison with other grain cultures. Interest in buckwheat as a medicinal plant rich an antioxidant rutin is growing [10-12, 14-21] owing to its pronounced capillary strengthening, hepaprotective, nootropic [22], anti-diabetic, anti-cancer and anti-mutagenic action [10]. For obtaining rutin-containing preparations, the flowers with bract, leaves and pericarp of buckwheat seeds are used. The highest content of rutin in inflorescences and leaves in the stage of accomplishing blooming – beginning of fruit formation is observed [17, 22]. According to the technical documentation of different countries the plant biomass can be considered as raw material for pharmacy if rutin content is not less than 2.5% (Russian Federation) [22], and more that 3% (in France) [23]. The rutin content in various morphological parts of the buckwheat plant is influenced by numerous factors such as environmental conditions, lighting intensity, moisture supply, etc. [10, 14, 16]. For the European region, urgent is the search for the pathways of the activation of the development of common buckwheat plants, the enhancement of the crop capacity and quality, the increase in the content of antioxidants, firstly flavonoids (incl. rutin) of this valuable culture. One of the ways is the use of plant growth and development activators [24-27]. This was demonstrated in microfield conditions at pre-sowing treatment of seeds and spraying of the plants. Among the exogenous growth regulators were tested: Emistin (a product of the metabolism of the symbiotic fungus *Acremonium lichenicla,* isolated from ginseng), epibrassinolide (an analogue of phytohormones – brassinosteroids), Ecost (a composition on the basis of high-disperse silica with microelements) [24], Circon (a mixture of hydroxycinnamic acids, isolated from purple coneflower *Echinacea purpurea*), Corvitol (active – acetylene alcohol) [25], the preparation on the basis of the strain of the bacteria *Halobacterium salinarum* (the active substance – a fragment of the retinal's molecule), ethanol extract of the seaweed *L.Cichorioides* was tested [27]. The pre-sowing treatment of buckwheat seeds with an ethanol extract of seaweed under conditions of the microfield experiment activated the growth of the plant seedlings and the rutin content (from 1.8% to 2.2%) in the green mass of the plants of buckwheat *Fagopyrum esculentum Moench.*

The objective of the study was to evaluate the effect of lignin (L) and Lignosilicon (LSi), synthesised on its basis, introduced into soil jointly with seeds during the sowing of buckwheat *Fagopyrum esculentum* Moench, variety "Aiva", on the content and antioxidant activity of polyphenols in 3 morphological parts of the plant: in the biomass of the flower with bract, in grain and in hulls.

II MATERIALS AND METHODS

Culture - buckwheat *Fagopyrum esculentum* Moench, variety 'Aiva', cultivated throughout Latvia. This is the only variety registered in this country. Duration of the vegetation period from the instant of emerging seedlings to technical maturity: 67-73 days. Seeds sowing rate: 70 kg ha^{-1}. Average yield of grain of this variety in conditions of Latvia is: 2 t ha^{-1}, potential crop capacity can achieve 3 t ha^{-1}.

Lignin products: L – hydrolysis lignin with the content of Klason lignin of 72%. LSi – Lignosilicon – a product with a silicon content of 5%, synthesized on the basis of hydrolysis lignin.

Lignin preparations were introduced into soil jointly with seeds during the sowing with the rates of 20 kg ha^{-1} and 40 kg ha^{-1}.

Microfield experiment with buckwheat was started on 2 June, 2011 in experimental plots of the Research Institute of Agriculture (Skriveri, Latvia) after 2 years of red clover cultivation. Soil – sod-podzolic (humus content 2.1%), granulometric composition – loam, pH KCL 6.0, content of plant available nutrients P_2O_5, 106 mg kg^{-1}, K_2O – 141 mg kg^{-1}. Additional amount of macro- and micro- nutrition elements did not used.

4 variants of experiments were established in triplicate. The area of one experimental plot was 45 m^2.

Sowing of seeds was performed using a seedling machine "Hege". Before sowing, the seeds were mixed with lignin products. The crop was harvested by a "Wintersteiger" combine.

During the vegetation process (in 28 and 60 days after the sowing), phenological observations of the plants were performed. The plant length, the number of side branches, inter-nodes and inflorescences, and the mass of the above ground part and roots were determined. For measuring the length and thickness of the 1st inter-node, an Electronic Digital Caliper was used.

Samples of the biomass of flowers with bract for determining substances of phenolic nature therein were taken in the bloom phase (48 days after the sowing) and in the phase of accomplishing blooming – beginning of fruit formation (60 days after the sowing) in triplication.

The total polyphenol content in the ethanol extracts from the raw biomass of flowers was determined by the Gallic Acid Equivalence method (GAE) using the Folin-Ciocalteu phenol reagent (FCR). The FCR assay relies on the transfer of electrons in alkaline medium from phenolic compounds to phosphomolybdic-phosphotungstic acid complexes (reducing them to molybdenum blue), which are determined spectroscopically at 765 nm. This assay was performed in 15 mL test-tubes and assessed in an UV/VIS Spectrometer *Lambda 25* (PerkinElmer Instruments).

To evaluate the summary antioxidant activity the DPPH• (2,2-diphenyl-1-picrylhydrazyl) radical scavenging assay described in [28] was used. 0.03 mL of a sample solution in methanol/ethanol (with a known mass concentration of the dry matter of the extract) was mixed for 15 min with 3.0 mL of a $1*10^{-4}$ mol L^{-1} DPPH• methanol solution, and then the absorbance at 517 nm of the mixture was immediately measured using a Perkin Elmer Lambda 25 UV/VIS spectrometer. The inhibition percentage (IP) of the radical species was calculated as follows:

$$IP = \frac{(A_B - A_A)}{A_B} \times 100\% \qquad (1)$$

where A_B is absorbance in blank probe (antioxidant was omitted) and A_A is absorbance in the sample after 15 min. Using different concentrations of extracts, the dependence of the IP values on the antioxidant concentration was established and used for the calculation of IC_{50} (the concentration of the tested sample required for a 50% inhibition of radical species). To calculate the IC_{50} values, the linear regression analysis was made, using SPSS Statistics 17.0 (level of significance 0.05). According to the definition, higher antioxidant activity results in lower value of IC_{50}.

HPLC analysis [29] was performed with HPLC Agilent Technologies 1100 Series coupled with an UV diode-array detector. The separation of the analytes was done with a column Zorbax Extend - C18, 4.6 x 250 mm, 5µm. Two eluents were used: water with 0.1% formic acid (v/v), 5% methanol (v/v) (A) and methanol (B). The elution conditions were 0-5 min 30% B; 5-25 min from 30% B to 70% B; 25-29 min 100% B; 29-30 min from 100% B to 30% B. The operating conditions were: column temperature 30 °C; injection volume 10µL. The components were detected by absorbance at 355 nm. The flavonoids calibration curves were made by diluting flavonoid solutions with methanol to give the concentration of the standard in the range of 10-100 mg/L. The curves were plotted from chromatograms as a peak area *vs.* the concentration of the standard. The concentrations of rutin, quercetin and quercitrin were calculated from their standards (Sigma Aldrich, HPLC purity ≥ 94%).

Weather conditions of the vegetation period of 2011 were favourable for the development of buckwheat plants [30]. The seeds were sown into the soil, supplied well with moisture; mean temperature in June, July, August and September was 17.8 ^{o}C, 20.2 ^{o}C, 16.9 ^{o}C and 12.8 ^{o}C, respectively. The moisture supply of soil, except for the end of August – beginning of September, was favourable. Because of the rains in the 3rd decade of August and the 1st and 2nd decades of September, the crop was harvested with a 10-15-day delay (29.09.2012). Grain losses due to its fall, especially in the variant with Lignosilicon, are possible.

III RESULTS AND DISCUSSION

Visual differences in the development of plants growing on the background of lignin products began to manifest themselves in the phase of bud formation: in 28-30 days after sowing when blooming has not yet began (Fig.1). The plants were developed best on the background of 40 kg ha^{-1} of LSi. The green mass of the above ground part of the plants in the variant with LSi 40 kg ha^{-1} in 28 and 60 days (the phase of blooming – beginning of fruit formation) after the sowing exceeded the values of the green mass in the control by 40% and 37%, respectively. In the variant with LSi 20 kg ha^{-1} increase in green mass in comparison with the control is significantly lower, namely, by 13% and 8%, respectively (Table 1). On the background of lignin, the plants were also developed better than in the control variant, but worse than on the background of LSi. The number of flower clusters in plants in the bud phase in variants: L, LSi - 20 kg ha^{-1} was on the level of control, and in the variant with LSi - 40 kg ha^{-1}, it exceeded the value in the control by 24%. The number of the flower clusters in plants in the variant with LSi 40 kg ha^{-1} in the phase of blooming – beginning of fruit formation was also the highest and exceeded the value in the control by 38%. In comparison with the control in other variants, in the variant with LSi 40 kg ha^{-1}, a greater number of bolls/fruits has formed. The least number of bolls/fruits has formed in the control variant and the variant L. The development of plants on the background of LSi 40 kg ha^{-1} was distinguished for better parameters during the whole vegetation period, incl. the phase of fruit formation.

Fig.1. Effect of lignin product on the development of plants of common buckwheat *Fagopyrum esculentum* Moench, variety 'Aiva' in 28 days after the sowing – bud phase. From the left to the right, plants from the variants: control, L – 40 kg ha^{-1}, LSi – 40 kg ha^{-1}. 10 plants are represented in each variant.

TABLE 1

EFFECT OF LIGNIN PRODUCTS ON THE CHANGE IN BIOMETRIC PARAMETERS OF PLANTS OF COMMON BUCKWHEAT *FAGOPYRUM ESCULENTUM* MOENCH, VARIETY 'AIVA' MICROFIELD EXPERIMENT, 2011

Variant	Rate of lignin products, kg ha^{-1}	Plant length, cm	Thickness of the first inter-node, mm	Length of the first inter-node, cm	Number of inter-nodes	Number of branches	Number of inflorescences	Green mass of the plant above ground part, g
28 days after the sowing (30.06.2011)								
Control		30.4	5.3	4.4	5.2	3.5	3.3	14.3
LSi	20	36.8	5.3	4.9	5.0	3.6	3.7	16.2
LSi	40	37.4	5.5	4.9	5.6	3.8	4.1	17.7
L	40	37.2	5.4	4.6	5.7	3.7	3.8	14.8
$RS_{0.05}$		*2.82*	*0.63*	*0.64*	*0.40*	*0.79*	*1.00*	*2.30*
60 days after the sowing (02.08.2011)								
Control		112.4	6.4	4.5	10.3	3.7	16.0	35.7
LSi	20	113.3	6.7	5.4	10.5	3.7	19.2	38.5
LSi	40	113.8	7.0	5.5	10.6	3.8	22.0	48.7
L	40	114.0	6.9	4.7	10.2	3.8	20.0	46.3
$RS_{0.05}$		*8.66*	*0.60*	*0.74*	*0.79*	*0.67*	*5.41*	*11.58*

Analysis of the ethanol extracts of the biomass of flowers with bract in the bloom phase (48 days after the sowing, more than 50% of plants bloom) and in the phase of blooming – beginning of fruit formation (60 days after the sowing) of plants has shown that the lignin products favoured the increase of the polyphenols content therein (Table 2). The most considerable distinctions are detected in the phase of blooming – beginning of fruit formation of plants. Against the background of L(40 kgha^{-1}) and LSi (20 kgha^{-1} and 40 kgha^{-1}), the content of polyphenols in the ethanol extracts of flowers with bract exceeded their content in the control by 50% and 70-73%, respectively. The content of flavonoids reached the maximum values in the phase of blooming – beginning of fruit formation. The rutin content in variants with L (40 kg ha^{-1}) and LSi (40 kg ha^{-1}) exceeded the control values by 25% and 65%, respectively the quercetrin content – by 30% and 55%, respectively. The results obtained showed that rutin was the predominant component of the flavonoid fraction in all buckwheat samples (Fig.2.)

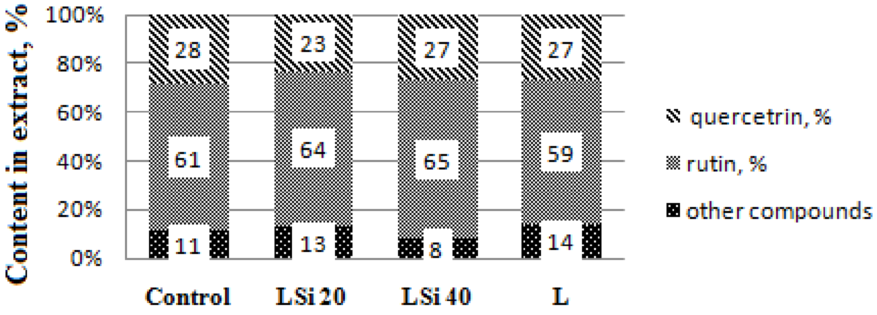

Fig. 2. Effect of lignin products on the content of flavonoids in the ethanol extract of the biomass of buckwheat flowers with bract, selected in the phase of blooming – beginning of fruit formation of the plants.

The rutin and quercetrin content in the extracts was more than 85%. Buckwheat extracts, except the identified flavonoids, containig small amounts other compounds, which absorb at 355 nm. In summary, the best results are obtained with LSi in the rate of 40 kg ha^{-1}, because in this case the content of rutin, quercetrin and quercetin in the ethanol extracts was the highest.

Alcohol extracts of the biomass of flowers with bract of the buckwheat cultivated on the background of the lignin products demonstrated a higher radical scavenging capacity in the test with DPPH•, in comparison with the control. The radical scavenging capacity of the alcohol extracts of the biomass of flowers with bract was higher in the biomass, selected in the bloom phase of the plants and declined in the sample of the biomass of flowers with bract, selected in the phase of accomplishing blooming – beginning of fruit formation (Table 2) in spite of increase in flavonoids content in extracts and decline of total polyphenol content. Considerable distinctions in the indices of radical scavenging capacity in variants were observed for the extracts from flowers with bract, selected in the phase of accomplishing blooming – beginning of fruit formation. Radical scavenging capacity for the extracts from variants L (40 kg ha^{-1}) and LSi (40 kg ha^{-1}) exceeded this index in the control by 40%, and that in the variant LSi (20 kg ha^{-1}) by 16% (Table 2).

TABLE 2

EFFECT OF LIGNIN PRODUCTS ON THE RADICAL SCAVENGING ACTIVITY DETECTED BY DPPH• AND CONTENT OF POLYPHENOLS IN ETHANOL EXTRACTS OF FLOWERS OF COMMON BUCKWHEAT PLANT

Variant	Rate of lignin products, kg ha^{-1}	Content of total polyphenols, GAE g per 100 g*	Content of flavonoids, %*			IC $_{50}$, mgL^{-1} **
			Rutin	Quercetrin	Quercetin	
48 days after the sowing		**Bloom phase**				
Control	0	7.02±0.10	0.93	0.40	0.010	15.4
LSi	20	7.00±0.10	0.97	0.43	0.010	14.2
LSi	40	7.50 ±0.15	1.07	0.47	0.011	13.6
L	40	7.23±0.20	0.71	0.27	0.007	13.5
60 days after sowing		**Phase of blooming – beginning of fruit formation**				
Control	0	2.60±0.10	1.66	0.70	0.015	27.3
LSi	20	4.5±0.10	2.55	0.82	0.029	23.0
LSi	**40**	**4.40±0.10**	**2.74**	**1.10**	**0.022**	**16.4**
L	40	3.90±0.15	2.07	0.90	0.030	16.2

* in terms of the oven dry sample of the biomass of flowers with bract

** the concentration of the tested sample required for a 50% inhibition of radical species.

It have to be pay attention that non-modified lignin applied at the same rate as LSi gave similar results. This fact allow to suggest the dominant role of phenyl propanoid structures in the effect observed.

Lignin preparations favoured the increase in the indices of the antioxidant activity of the alcohol extracts of the biomass of flowers with bract of buckwheat (Tabl. 2), as well as grain and hulls (Tabl.4). No correlation between the radical scavenging capacity and the rutin content and the total content of polyphenols was found, as mentioned in [18].

The conditions of the vegetation period of 2011 were favourable for cultivating buckwheat, which ensured a good development of the plants and a high crop (Table 3) that achieved the potential value pointed for this buckwheat variety (3.0 t ha^{-1}). Because of the unfavourable weather conditions (rains), the crop was harvested with a 10-15-day delay, and a part of the fruits fell off, that decreased the waiting yield.

TABLE 3

EFFECT OF LIGNIN PRODUCTS ON THE CROP CAPACITY OF BUCKWHEAT

Variant	Rate of lignin products, kg ha^{-1}	Crop, t ha^{-1}	Crop, % against control	Mass of 1000 grains, g
Control	0	3.00	100	26.2
LSi	20	3.31	110	26.6
LSi	40	3.45	115	26.7
L	40	3.36	112	26.7

TABLE 4

EFFECT OF LIGNIN PRODUCTS (40 KG HA^{-1}), INTRODUCED IN SOIL BEFORE THE SOWING OF SEEDS ON THE ANTIOXIDANT ACTIVITY AND CONTENT OF POLYPHENOLS IN METHANOL EXTRACTS OF THE FRUITS AND HULLS

Variant	Rate of lignin products, kg ha^{-1}	Content of total polyphenols, GAE g per 100 g*	Rutin, mg/100 g*	IC $_{50}$, mgL^{-1} **
Hulls				
Control	0	0.52±0.01	14.0	14.4
LSi	40	0.53±0.01	13.0	13.5
L	40	0.49±0.01	13.0	10.3
Grain				
Control	0	0.32±0.01	3.0	90.7
LSi	40	0.33±0.01	3.3	68.3
L	40	0.33±0.01	3.2	67.3

* in terms of the oven dry sample of biomass

** the concentration of the tested sample required for a 50% inhibition of radical species

Methanol extracts of the flour from the hulls and grain of buckwheat in comparison with those from flowers with bract, contained a small amount of polyphenols. Content of rutin was higher in the hulls, tah have shown a higher radical scavenging capacity (Table 3). Content of rutin in hulls extracts was 13.0-14.0 mg/100 g of dry mass, and in grain extracts only 3.0-3.3 mg/100 g of dry mass (Table 4). The results obtained have shown that in favourable vegetation conditions the quality parameters of buckwheat grain, including the content of rutin and polyphenols, can be comparable with this ones achieved in the regions with warm climate. The content of rutin in methanol extracts from the hulls and grain of buckwheat *Fagopyrum esculentum Moench French, variety* „La Harpe" was 5.2 mg/100 g dry mass and 2.3 mg/100 g dry mass, respectively [18]. The grain of the buckwheat cultivated in high-mountain areas in warm climate regions of Italy (1200 m above the sea level) the rutin content ranged from 5 to 58 mg/100 g of dry mass in the grain of common buckwheat of different varieties, cultivated in 2009 was docucmented [10]. Despite the absolute values of crop indicies obtained were lower than above mentioned in principle flowers with bract can be used as raw materials for rutin production.

IV CONCLUSIONS

Lignin preparations, introduced into soil jointly with buckwheat seeds during the sowing in quantities of 20 kg ha^{-1} and 40 kg ha^{-1}, exerted a favourable effect on the development of plants and the synthesis of flavonoids in flowers with bract.

Flavonoids are represented mainly by rutin and quercetrin. The content of rutin in ethanol extracts from the biomass of flowers with bract, selected in the phase of accomplishing blooming – beginning of fruit formation, was 59%-65%, and that of quercetrin 23%-28% from the total sum of components in the extract.

The rutin content in the biomass of flowers with bract in the phase of accomplishing blooming – beginning of fruit formation in the variant with 40 kg ha^{-1} of Lignosilicon exceeded that in the control variant by 65% to be 2.74 % in terms of dry mass. The raw material with such content of rutin can be used as an industrial raw material for obtaining rutin-containing pharmaceutical preparations.

Lignin preparations favoured the increase in the indices of the antioxidant activity of the alcohol extracts of the biomass of flowers with bract of buckwheat, as well as grain and hulls.

The increment of the buckwheat grain crop, in comparison with the control on the background of 20 kg ha^{-1} and 40 kg ha^{-1} of Lignosilicon and 40 kg ha^{-1} of lignin, was 10%, 15% and 12%, respectively.

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Oil Additive Testing Equipment

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Abstract. **Automobile industry annually is to reduce harmful emissions into the environment. Anti-friction oil additives in automotive internal combustion engines is one way fight against friction losses which result from fuel economy, which in turn reduces the amount of harmful emissions vehicle exhaust. Assessment of the effectiveness of oil additives need to tribologycal properties for further analysis. For the purpose of this research is carried out in a variety of major friction equipment design studies, evaluating their properties and create an experimental facility with the assistance possible to evaluate changes in oil additives on friction over the existing components and their mutual friction.**

Keywords **– oil additives test, friction surfaces, engine oil, internal combustion engine.**

I INTRODUCTION

World's automobile industry each year are brought ecological requirements for the automotive internal combustion engine harmful emissions, as one of the ways fight against frictional energy losses combustion engine with a friction loss in engine oil by adding a special anti-friction additives, which can reduce friction losses combustion engine component friction pairs, the reduction of fuel consumption and the internal combustion engine the harmful emissions. In relation to this problem is the need for effective oil additive test. To make this possible is designed device (Fig. 1), which provides for sliding friction pairs working of a closer working conditions of an internal combustion engine, the ongoing process of identifying friction pairs.

Fig.1 Oil additive testing machine

Thus be simulated in any of the internal combustion engine sliding friction pairs working conditions of the engine oil through oiling material and anti-friction motor oil with additives, observing the differences with and without anti-friction additives one oil brand. In this way it is possible to determine the oil additive on the friction surfaces without the use of the internal combustion engine, excluding the risks of possible adverse effects of oil additives on the friction surface Simulating the internal combustion engine friction pair working conditions, use of friction pairs in the samples according to materials that are used in internal combustion engines, and can be technologically processed in accordance with the following models: make material compliance, heat treatment, machining, surface hardness, surface roughness. During the experiment, the friction pair ensures a proxy for the ongoing conditions of internal combustion engine, by providing relevant: the contact pressure between the sliding speed, oil temperature. In experimental work, it is planted, and controlled the following specification, oil temperature, friction elements reciprocal downforce, the friction force changes over time (recorded in a computer), the rotating disk rotation speed, the oil supply.

II MATERIALS AND METHODS

Lubricating substance and additives research and testing

In this time there is no generally accepted quantitative indicators that characterize lubricating substances by retarding the wear and anti-friction properties. For this reason, the most common tests are carried out over a given lubricating substances in the benchmark. The benchmark can be chosen for any lubricating substance that is sufficiently tested in practice, and which, by its use and properties are close to the test substance. However, if the oil additive testing, the first test oil without additives, and then added.

Lubricating substance testing has been performed in several successive steps, as listed below.

1. Random testing - short sample tests on the friction devices using the new benchmark and lubricating substances under laboratory conditions.
2. Stand landfill testing - testing simulating long-term mode of operation, the process of making a real mechanical assemblies and machine lubrication of the test substance. Trials take place on billboards in laboratory or field site and road conditions strictly regulated trial modes.

3. Operational testing - testing of long-term continuous real machine lubrication process, which is the final stage of the testing process for monitoring the lubricating substance material, which has passed all previous tests.

New lubricating substances in the development process is mandatory for all three stages of the trial. In most of the lubricants tested by consumers, it is limited only to the first (random) experimental stage. When lubricating materials testing laboratory should be targeted in order to defined their subsequent properties:

- friction coefficients that are related to sliding speed
- specific pressure and temperature;
- maximum load of to blocking in;
- friction pair ability to operate after the grease exclusion, etc.

Lubricant additive material is to try their using different pairs of different structural materials such as steel steel, steel, bronze, etc.

Lubricating oil additives and material testing general features

In laboratory studies concerning wear resistance of materials, following the aim of shortening the duration of testing, researchers often increases specific pressure and slip speed compared to what is observed in real rubbing node conditions. In these trials, accelerate wear resistance of the material can be determined within a few hours, or even minutes. However, as is indicated in V. Kuznetsov's work [1], accelerated testing over the results may also be wrong. This is due to the fact that the abrasion resistance of the material very strongly influenced by friction surface temperature, but the temperature on the basis of theoretical and experimental research in motion is proportional to the pressure and speed. It follows that the acceleration of the wear process, that is, an accelerated test method is related to the temperature of the friction surfaces, which significantly affects the wear. If the temperature on wear process should be equal for all metals, there is a basis for extrapolation to normal operating conditions.

Lubricating oil additives and materials testing equipment principal operation

To determine the antifrictional characteristics, is available in a lot of equipment, machinery and apparatus. Also, almost every researcher has constructed his own personal, or even multiple machines, which are sometimes quite complex. The literature describes a large amount of friction and device for lubricating materials research laboratory. Trial, samples of some of the described equipment and devices contact point or linear. For example, a four-ball friction machine (see Figure 2.) Oil is tested pyramid, which is composed of four spheres, where the three lower ball rigidly attached cup which is poured into the test oil, but the upper ball rotates vertical center shaft. Here is a spot by three pins. Hardened steel ball acts on the same analogy.

Fig.2. Four-ball test subassemblies principal block diagram

Timken device, which is a common oiling material tests, the test item is selected reel - rolltype conical bearing outer ring and a plane - rectangular model (see Fig.3).

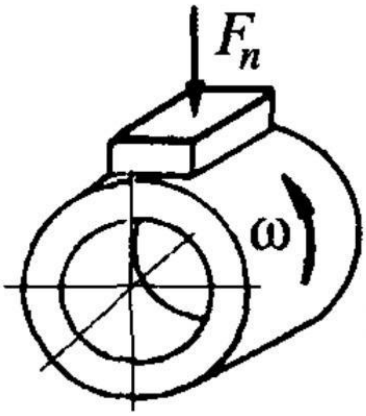


Fig.3 Timken test methods principal scheme

Testing occurs gradually increasing the load on the methodology I = f (P), where I - is the depreciation feet limit, in this case it is a rectangle. One test lasts for 10 minutes. Oil on the appropriate areas of contact load. Timken plant components is linear initial contact. Described friction devices not tested lubricants which implements random transfer of friction, as they tested the samples is a point, or linear contact. As previously described, lubricants, performing random transmission friction, can lead to friction surfaces dissipative structures with certain properties. Overlapping metal grease containing copper, tin, or a combination, greatly reduces friction wear surfaces where there is realized dissipative structure, the lower the wear more than a step.

Dissipative structures can be realized in bronze steel friction pairs, applying lubricant that does not contain copper compounds, but a film of selectively lysed bronze. Dissipative structures distribution surface occurs when there is a specific type of diffusion process, which determines the sample dissolution, lubricants ligands, as well as high deformed surface activation friction. Intensive vacancy formation resulting from dissolving, dislocation changes the direction of motion and speed.

Moving toward the surface, they get there by creating an area where the atoms are free links. In these areas happen chemical reaction between lubricants and active ligand atoms and have a complex connection. Not all alloys are able to create dissipative structures, and for the distribution of alloys which capable produce it, is used in rolling sheaf X-Ray method.

A complex combination of lubricating compositions basis and does lubrication performance as adsorbable surfactant. Partly decomposition friction zone, it re-creates the ligands and metal ions. Inside it there is a limited transformation cycle of grease, this is different from tribodestruction and oxidation processes that occur in limited and unlimited grease friction cases. The described process can be a point or linear contact cases. It is necessary to contact the plane, where the metabolism oiling between the environment and the friction surfaces.

Following on from the above, that the friction device with punctate or linear contact model (four-ball device, Timken equipment, etc.) are irrelevant lubricant testing, which implements random transmission friction. The lubricants testing must be done to such friction equipment, specimens of friction contact with the planes, which is the length and width.

So here it is necessary to note that the academician V. Kuznetsov based on the number of machines tested The analysis has concluded [1] that a simple equipment consisting of a rotating disk, and pressed it to the facility, which is equipped with a friction force measurement device has made a series of very valuable principally important result. No other equipment science has not delivered as certain results, and, in his view, machine designers going the wrong way because of complicated machinery design, complicating the process of wear phenomena.

This device has the advantage that it enables:

1) a wide range of frequency and change the rotation of the load;

2) to measure the friction force, the calculation of the coefficient of friction;

3) to study the dry friction and friction, using lubricants;

4) to study the friction force, rubbing against abrasive wear, or where the metal rubbing against metal;

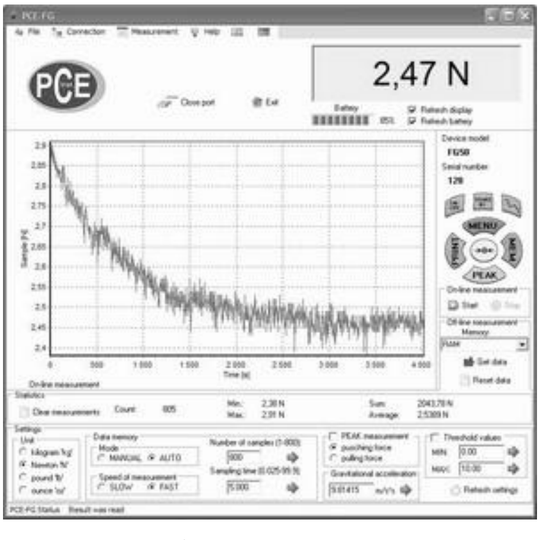
5) carry out testing of different temperature regimes;

6) to determine the surface temperature of an object scrubbing;

7) The determination of the specific wear, turn the volume or mass with respect to the original.

III RESULTS AND DISCUSSION

For the experiment to be correct and able to judge the oil additive effect on the internal combustion engine friction pairs are properly prepared samples of the materials and the friction pairs used in the automotive internal combustion engine parts suitable materials, for example. pair of crankshaft - plain bearing, uses a rotating disk of material Steel45 (Gost) that the technology worked, produced material sample is tempered obtaining material surface hardness of HRC 51, then surface is sanded obtaining roughness corresponding class 9a roughness (Ra = 0.31... 0.25) [2]. Rotating disk friction pair puts the model in plain bearings suitable material (aluminum or babbit). Components installed on the device providing a degree of interdependence such pressure 5kg/cm^2. Following injection into the oil reservoir 1l, oil is heated to the requisite temperature, which indicates the most similar experiments at 90 ° C [3] [4]. Oil temperature is maintained by a thermostat which is connected to the heating element, the temperature changes is maintained at the set temperature value.



2,47 N

Device model: FG50

Serial number: 128

Count: 805

Min.: 2,38 N

Max.: 2,91 N

Sum: 2043,78 N

Average: 2,5389 N

Unit: ○ kilogram 'kg' ● Newton 'N' ○ pound 'lb' ○ ounce 'oz'

Mode: ○ MANUAL ● AUTO

Speed of measurement: ○ SLOW ● FAST

Number of samples (1-800): 800

Sampling time (0.025-99.9): 5.000

☐ PEAK measurement: ● pushing force ○ pulling force

Gravitational acceleration: 9.81415 m/s²

☐ Threshold values: MIN 0.00 MAX 10.00

PCE-FG Status: Result was read

Fig.4. Dynamometer software screenshot

Once the oil is heated on the circulation pump, which provides oil circulation and the supply of fresh oil on the friction surfaces. Are further connected to the dynamometer and the electric motor is switched on, (motor power of 1.5kW nominal 1500RPM). Motor speed can be set with frequency converter and can set the engine speed steady 100-2000RPM within which the disc is rotated. Dynamometer the electronic recording of the friction force on the computer (Fig. 4) with an accuracy of 0.01N range of 0.01-50N, with the ability to record data records with a 1-800 time interval between entries in the 0.1-99.9 seconds.

Equipment description of intervention

The electric motor 2 screwed on facilities housing 1. On electric motor 2 axis 3 is a shift 4 for rotary disc 5 strengthening. At rotating disk 5 with the pendulum 6 is pressed against the test material sample 7, which from the reservoir 8 with the help of pump 9 through a delivery tube 17 is supplied with oil on the 10. Sample 7 downforce disc 5 provides a pendulum 6, which is attached to the pendulum axis 11 and is moving from the linear bearing 12. The pendulum axle end 11 mounted counterweight 13, which provides a certain downforce drive the fifth. The oil temperature to ensure the reservoir 8 mounted heating element 14 and the oil temperature control temperature sensor 15. Friction torque is measured on the dynamometer 16, which is forcing the pendulum 6.

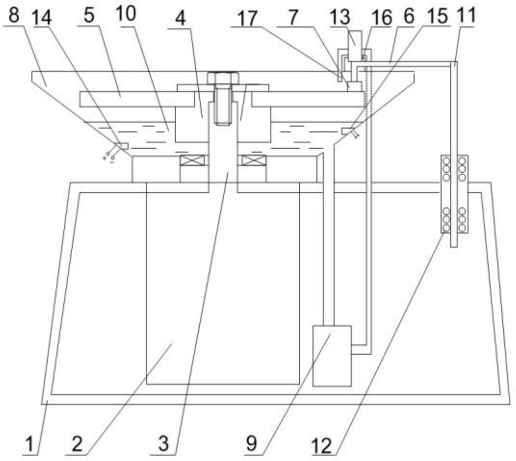


Fig.5. Oil additives tester scheme

IV CONCLUSION

The above-described oil additive test equipment can be an effective additive for oil test sliding friction pairs, which possible to put a variety of materials samples. Facility possible set the several constant parameters, which are zooms in the working conditions similar to existing internal combustion engines. Computer program recorded friction force changes easily processed the data on computer. With the help of such devices in a reasonably short time possible to determine the oil additive on the friction pair justify the the labor-intensive process where oil additive should be used in the engine, which also excludes the risk of damaging the engine if the oil additive negative effect on the friction surface, for example promotes reinforce wear of the friction surfaces.

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Using Anther Culture Method for Flax Breeding Intensification

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Abstract. **Flax breeding is a long and complicated process based on hybridization and following selection of the best plants. Because of possible occasional cross-pollination the development of genetically stable homozygous lines could last more than 15 years. For more rapid creating of initial material for flax breeding anther culture methods for producing doubled haploid (DH) lines could be used successfully. The goal of this study was to develop the best anther culture protocol for producing DH lines from hybrids included in Latvian flax breeding programme and to do preliminary field evaluation of obtained DH lines. F_4 hybrids were used in the experiment. Method, most applicable for establishing of DH from anther cultures, was elaborated; 13 DH lines were obtained during the experiment. Such agronomic important traits, as vegetation period, total plant height, number of seed vessels, number of seeds in a seed vessel, 1000 seeds weight, oil and bast fibre content were evaluated for obtained DH lines. Several accessions showed high 1000 seeds weight, number of seeds in a seed vessel, good oil and bast fibre content. It was concluded that anther culture method is of value of using as an adjunct to classical methods of flax breeding.**

Keywords **– agronomical traits, anther culture, doubled haploid lines, flax**

I INTRODUCTION

Flax (*Linum ustatissum* L.) is one of the oldest cultivated plants in temperate regions. Flax is growing both as the oil and fiber crop. Seeds of oil flax recently became important constituent for many industrial applications, such as pharmacy, medicine, food production *etc.* and have high prospective for use in Latvia. Development of methods of obtaining flax varieties suitable for regional agriculture and industrial particularities is of high importance.

Flax is a self-pollinating plant with about 5-10% cross-fertilization [1], [2]. Therefore, breeders mainly use pedigree selection, bulk breeding or progeny methods to develop new breeding lines and varieties [1], [3]. Major breeding objectives of Latvia flax breeding are creating early or mid-early ripening varieties with the improved yield (seed or fibre) and oil content, high fibre quality, resistance to lodging and diseases [4].

Traditional breeding methods are time consuming and take at least more than 15 years, therefore there is high demand for the use of alternative methods, such as producing homozygous doubled haploid (DH) lines [2], [3], [5], [6] which give a possibility speed up the breeding for several years [7]. Currently, anther culture is the most successful method for producing DH lines of flax [8], [9], [10].

Importance of different factors of success of establishment of anther culture and following development of plants-regenerants is known; most critical are genotype and growing conditions of donor plants, stage of microspore development, composition of the culture medium and temperature during the culture induction period [1], [11], [12].

The goal of this study was to develop the best anther culture protocol to producing DH lines from hybrids included in Latvian flax breeding programme and preliminary field evaluation of obtained DH lines.

II MATERIALS AND METHODS

Donor plants growing

Hybrids of F_4 generation of both oil and fibre flax (Table 1) were used for DH obtaining. Two different growing seasons of donor plants were applied: spring (sowing in March, buds collection during May-June) and summer (sowing in July, buds collection during August-September).

TABLE 1
FLAX F_4 HYBRIDS USED FOR ANTHER CULTURE ESTBLISHMENT

Hybrids	Hybrid combination
Fibre flax	
N1-1	W196/Baltučai
N3-1	Rigaer LIN 748-82/W-196
N4-7	Rigaer LIN 748-82/Nynke
N5-5	Tverca/Nynke
Oil flax	
E37/2	Ceies/Norlin
E37/49	Ceies/Norlin
E38	Krupnosemjanij/Mikael

The donor plants were grown in a greenhouse with a temperature 24-28 ºC in daytime and 15-18 ºC during night time. All plants were grown in mixture of soil and peat (2:1) in 20 cm diameter pots, in each pot 30 plants were sowed.

Buds collection and sterilization

Buds were collected at the middle of late uninucleate stage of microspores. Buds were sterilized by 50% solution of commercial bleach (4% of hypochlorite content) for 20 min and rinsed three times by sterile, deionized water. The developmental stage of microspores was determined by squashing in the acetic carmine on a glass slide [13].

For establishment of anther culture buds with length 5-7 mm, width 1.5-3 mm, length of anther 1-2 mm, were collected. The length and width of buds were measured before sterilization, the length of anthers after it placing on induction medium was determined.

Three fibre flax hybrids (N1-1, N3-1, N4-7) (Table 1) were used to determine better buds and anthers size for anther culture establish. Correlation coefficients among size of buds or anthers and embryogenesis capacity were calculated by MS Excel.

Cultivation on induction mediums

Three oil flax hybrids (E37/2, E37/49 and E38) (table 1) were used to estimate influence of different anther culture induction mediums. For this purpose two different medium were used: Nichterlein (NC) induction medium [2] with 6% sucrose, 0.4% agarose, pH 5.5; modified NLN82 medium [3] with 3% sucrose, 0.4% agarose, pH 5.8. For fibre flax hybrids anther culture establish NLN82 medium were used. Petri dishes with anthers at 26 ºC in the darkness were cultured.

Four fibre flax hybrids (N1-1, N3-1, N4-7, N5-5) (Table 1) were used for evolution of influence of cold stress. For this purpose 50% of anthers cultures were cultivated at +4 °C for 24 hours. After cold treatment all cultures were cultivated at 26 ºC in the darkness.

Cultivation on regeneration mediums

Embryos obtained from two oil flax hybrids (E37/2 and E37/4) (Table 1) were used to estimate influence of different regeneration mediums on embryo regeneration capacity. All embryos witch formed generative calli were transferred on two different regeneration mediums: NC regeneration medium with 3% maltose, 0.8% gelrite, pH 5.8 [2], [12] and MS/B5 medium (MS medium mineral salts [14], B5 medium vitamins [15] with 3% sucrose, 0.6% plant agar, supplemented by 1 mg/l BAP, pH 5.8. Obtained embryos of other hybrids were cultivated only on MS/B5 medium with 3% sucrose, 0.6% plant agar, supplemented by 1 mg/l BAP, pH 5.8 [16].

Cultures were grown in light conditions (24 ºC, 16h/8h of day/night, light intensity 3000 lx). The diameter of calli was determined after three weeks of cultivation on regeneration medium. Every four weeks calli were transferred onto fresh medium.

Obtaining of plants- regenerants

Shoots from different calli were transferred onto MS/B5 medium with 0.01 mg/l BAP and 0.001 mg/l NAA from shoot elongation and rooting. Rooted plantlets were potted into autoclave-sterilised soil and incubated at 20 °C. First days plantlets were covered with glass jars to maintain high humidity. The seeds of each regenerated plant were collected separately.

Field evaluation

DH lines were preliminary evaluated in field trials at the Agricultural Science Centre of Latgale. DH lines were sowed in plots (3 lines per plot). Between plots the long straw variety of oats were sowed to prevent the DH lines cross-fertilization. Colour of flower and agricultural important traits, such as flax total plant height, technical plant height, number of seed vessels, number of seeds in a seed vessel, 1000 seeds weight, oil and bast fibre content were recorded.

III RESULTS AND DISCUSSION

Influence of donor plants growing seasons on embryogenesis

It was found that donor cultivation season has an influence on embryogenesis (Fig. 1). On average anther cultures established in spring (anthers were collected and transferred into *in vitro* in May) have higher embryogenesis (2-13 embryos on 100 anthers). Embryogenesis level of anthers, harvested from the summer-grown donor plants, was 1-6 embryos on 100 anthers. Similar results were published earlier elsewhere [17]: number of microspore-derived plants was significantly higher from anthers collected during January-July, than from those collected during August-December.

In our experiment not only seasonal influence on embryo formation was visible, but also genotype and growing season interaction on embryos development was observed. Thus, for instance, for the hybrid N3-1 embryogenesis level of spring harvested anthers was 13%, but for anthers harvested in summer – only 2%. In the opposite, for the hybrid N1-1 embryogenesis level of spring harvested anthers was lower (2%), than for summer harvested (6%) of anthers (Fig. 1).

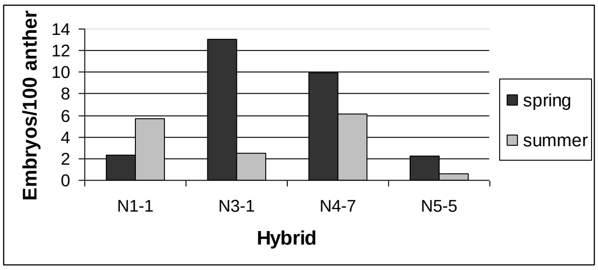

Fig. 1. Embryos formation from anthers depending of the season of donor plants growing.

Buds and anthers size influence of embryo formation

It was found that the most suitable buds length for highest embryogenesis ranged from 5-6 mm for all genotypes used (Table 2). Hybrids N1-1 and N4-7 showed relatively high embryogenesis with 7 mm long buds. Buds of width 3 mm were not suitable for anther culture establishment: anthers obtained from these buds did not form any embryos. Embryogenesis was better for anthers, which were derived from the buds smaller in width (1.5-2.5 mm).

TABLE 2

ANTHER EMBRYOGENESIS DEPENDING OF BUDS AND ANTHER SIZE

	Hybrids		
	N1-1	N3-1	N4-7
Length of buds (mm)	Embryos/100 anthers		
5.0	11.3	6.7	11.8
5.5	-	6.7	-
6.0	2.3	3.3	5.9
6.5	-	0	-
7.0	3.3	0.7	3.9
Width of buds (mm)			
1.5	-	-	13.3
2.0	7.0	3.5	6.4
2.5	4.0	2.5	5.7
3.0	0	0	0
Length of anther (mm)			
1.0	21.4	-	0
1.5	3.8	2.8	12.6
2.0	5.1	3.3	3.5
2.5	-	-	0

Anthers ranged from 1.5 till 2 mm were formed embryos for all genotypes. Embryogenesis from anthers with length 1 mm was observed only for the hybrid N1-1. No embryos were form from 2.5 mm anthers.

TABLE 3

CORRELATION COEFFICIENTS AMONG NUMBER OF EMBRYOS AND BUD/ANTHER SIZE FOR DIFFERENT FLAX HYBRIDS

	Hybrids		
	N1-1	N3-1	N4-7
Length of buds / number of embries	-0.156**	-0.110*	-0.138**
Width of buds / number of embries	-0.091	-0.080	-0.128*
Length of anthers / number of embries	-0.181***	0.023	-0.217***

$* \ p \leq 0.05$; $* * \ p \leq 0.01$; $*** \ p \leq 0.001$

Correlation coefficients among bud or anther size and embryogenesis and (Table 3) were statistically significant but very small. It could be explained by clear nonlinear relationship of the parameters of the interest.

Influence of cold stress on embryogenesis

Effect of the cold stress was not pronounced and varied depending from the genotype (Fig. 2): embryogenesis level for hybrids N1-1 and N3-1 was increased, but for hybrids N4-7 and N5-5, in the opposite, decreased. The influence of cold treatment was observed by several authors [10], [18], [19]. Mostly used cold stress temperatures ranged from +4 °C till +8 °C. All of authors mentioned influence of genotype and duration of the treatment on embryogenesis level.

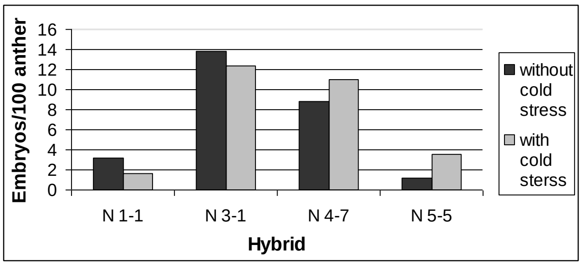

Fig. 2. Embryos formation from anthers depending of cold stress

Influence of induction medium on embryogenesis

Induction medium NLN82 was found as the most appropriate: anthers placed on this medium developed from 5 (E38) till 11 (E37/2) embryos on 100 anthers (Fig. 3). Embryogenesis on the NC induction medium ranged 3-4 embryos on 100 anthers. The genotype influences were observed: even genetically close hybrids E37/2 and E37/49, which derived from the same crossing combination, had different embryogenesis capacity on the medium NLN82, at the same time embryogenesis capacity of those hybrids on the NC induction medium was similar (Fig. 3).

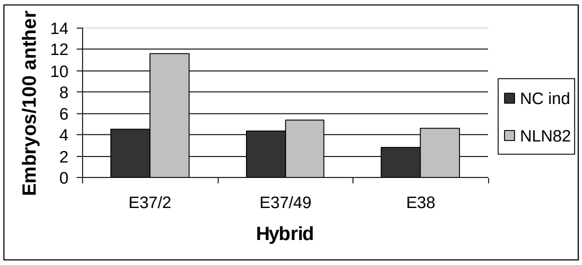

Fig. 3. Embryos formation from anther depending of induction medium

In continuation of the experiment with other hybrids the medium NLN82 was used as the induction medium. All obtained plants-regenerants were produced from calli, which had been grown on this induction medium.

Influence of regeneration medium on calli regeneration capacity

Development of the calli on regeneration medium is illustrated in Fig. 4. Better growth of calli was observed on the regeneration medium MS/B5 with BAP. The influence of genotype on calli growth on this medium was not observed.

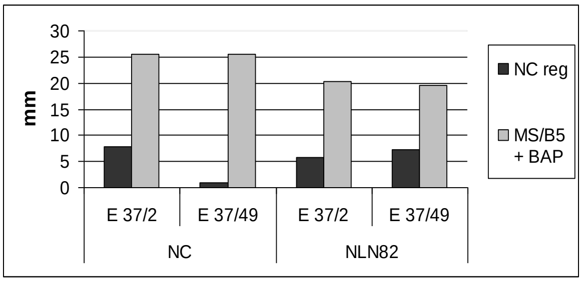

Fig. 4. Calli diameter (mm) after four weeks of cultivation on the regeneration medium.

Calli cultivated on NC induction medium had grown less intensive. As appeared later, plants-regenerants were obtained only from calli grown on the induction medium NLN82, not depending of regeneration media (data not presented). It shows that for obtaining plants-regenerants important is not only composition of the regeneration medium, but even more crucial is the selection of used embryo induction medium.

Field evaluation

Several DH lines were tested in field trial to determine exhibition of some agronomical and biologically important traits. Vegetation period for all lines was 99 days. None of the lines showed presence of any flax diseases. Manifestation of other traits is presented in the Table 4.

All lines showed a relatively low total plant and technical height, but had a high content of bast fibre. Six DH lines had bast fibre content higher than 35% and only fibre content of the single line was lower than 30%. It means that straws of DH lines are suitable for industrial processing for short flax fibre.

Number of seed vessels of tested DH lines was rather small, just 5 lines were with a seed vessels number of 10 or higher. Possible, it can be explained by particular growing conditions in this experiment, as flax plants were grown between rows of oats. However, number of seeds in a seed vessel, what is genotypically more determined, for all lines was above eight. A good indicator for the potential yield quality is the weight of 1000 seeds, which exceeded 5 g, for 9 DH lines it was higher even more than 6 g. Since absence of sufficient quantity of seeds oil content could not be determined for all samples, therefore it was measured for 8 lines only, for all of them it varied 43-45%, which is a good value.

IV CONCLUSION

The influence of different factors on embryo induction, development and plant-regenerants formation were found. Higher embryogenesis was observed when anthers were harvested from plants grown in the spring. Higher embryogenesis was observed on anther culture, which was derived from the buds in particular size: length - 5-6 mm, width - 1.5-2.5 mm. Cold treatment effect on anther culture was dependent on the used genotype. Better for embryogenesis and plant-regenerants obtaining was NLN82 induction medium. Better calli regeneration capacity was observed on the regeneration medium MS/B5 with BAP (1mg/l), and calli shoot formation was observed on this medium as well. Plants-regenerants were obtained when for embryo induction NLN82 medium and regeneration medium MS/B5 with BAP was used. Some DH lines were found with rather high baste fibre and oil content. All DH lines had a high weight of 1000 seeds. It means that obtained flax DH lines are suitable for further selection process of oilseed flax, for obtaining oil flax varieties with short fibre. Elaborated flax anther culture protocol is suitable for obtaining of DH lines to speed up the Latvian flax breeding program.

TABLE 4

FIELD CHARACTERISATION OF THE FLAX DH LINES

DH line	Plant height, cm		Bast fibre content, %	Number of seed vessels	Number of seed in seed vessel	1000 seeds weight, g	Oil content, %	Colour of flower
	Total	Technical						
ALE1	44.1	26.5	34.7	10.1	9.1	6.70	45.0	Blue
ALE2	42.8	24.8	20.9	9.9	8.8	5.99	43.2	White
ALE3	40.9	23.0	30.1	10.6	8.9	6.03	44.3	Blue
ALE4	28.4	17.2	32.4	5.4	8.4	6.72	-	White
ALE5	45.7	28.2	32.7	10.1	8.7	5.63	43.2	White
ALE6	28.2	17.4	34.9	6.0	8.6	6.84	-	White
ALE7	33.3	18.7	34.2	6.0	8.6	5.80	-	White
ALE8	39.0	22.6	34.8	9.2	9.0	6.85	43.7	White
ALE9	41.0	22.8	37.8	10.8	8.9	6.57	44.6	Blue
ALE10	40.8	22.4	35.5	10.0	8.6	6.51	44.4	Blue
ALE11	32.3	19.2	33.3	8.0	8.6	6.24	43.1	White
ALE12	38.2	23.4	34.7	7.4	8.1	5.31	-	White
ALE13	35.1	20.6	33.3	5.0	8.5	6.54	-	White

V ACKNOWLEDGMENTS

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Harmonization of Piece-by-Piece Measurement Methods of Roundwood Approved by Latvian Standard LVS 82:2003 “Apaļo kokmateriālu uzmērīšana”

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***Abstract*. This paper analyses the volume differences of mixed pine and spruce roundwood loads and logs (roundwood assortiments) devided in to sample clusters according to the species, diameter, lenght and stem/log surface shape, stem zones and measured by the methods approved by standard LV 82:2003 „Apaļo kokmateriālu uzmērīšana”. The volumes of roundwood loads/logs determined by these methods were compared with the most precisious determination of the volume by Measuring Diameter in Short Intervals and the Top and Butt Diameter Measurement method.**

The volume of mixed pine and spruce round timber load determined by Measuring Diameter in Short Intervals using harvester measurement system is 2.44% higher than the volume determined by manual comparative the Top and Butt Diameter Measurement method. The volume deviation is in the range of accepted 3% measuring accuracy.

The volumes of roundwood assortiments from neiloid zone of spruce stems determined according to the Mid Diameter Measurement method are 3.96% lower than the volumes determined by careful manual the Top and Butt Diameter Measurement method. The volume deviation surpass the acceptable measuring 3% accuracy.

The volumes of roundwood assortiments from paraboloid zone of spruce and pine stems determined according to the Mid Diameter Measurement method are lower than the volumes determined by the Top and Butt Diameter Measurement method. The deviation is in the range of acceptable 3% measuring accuracy.

This paper gives recommendations for adjusting the application area of different measurement methods for achieving the volume deviation in the range of accepted measuring accuracy.

***Keywords*: roundwood, piece-by-piece measurement method, volume.**

I INTRODUCTION

Different volume value results are often the reason of doubts about its accuracy and reflecting also relationships between suppliers and processors of wood. The term „true volume” of roundwood is equally actual for both sites.

Every determination of log volume based on the calculation of the volume of geometrical bodies (cyllinder, truncated neiloid, truncated paraboloid) represents only approximation to reality but not its expression. The logs are an irregular body the form and volume of which can be determined by manual or automatical measurement methods or with each other only approximately. The roundwood volume can be calculated using a logical cubic formula and a value achieved by this way represents only ”comercial” volume of roundwood. But it is not the same as „true volume” of roundwood. Cubic metre of roundwood measured by the national standard in one country may be different if measured by the national standard of another country.

Some national and subregion roundwood measuring standards treat the log as a cylinder with a diameter of the small end of the log; assume the log forms as a cylinder with the diameter that exists in the middle of the log lenght; or use assumed taper rates to establish diameters other than the small- end of the log; assume the log form is a cylinder with the diameter that exists in the middle of the log lenght; or use assumed taper rates to establish diameters other than the small-end. Some national standarts (Finland, Ireland, UK Hardwood) calculate the over bark volume.

All of these differences can lead to variation in roundwood volume (fig. 1) [3] The figure shows veneer log volumes calculated using thirteen different roundwood measurement standarts[3; 2; 10; 6; 11; 12; 7; 16; 19]. The veneer log size parameters used for volume calculation are following: actual lenght (5.02m); top diameter (232/227mm); middle diameter (253/255mm); butt diameter (278/281mm).

The difference between measuring results by using different national and subregion roundwood measuring standards reaches 40%.

It is known that many of the countries (Finland, Sweden and United States) are going to atjust their national roundwood measuring standard volume to a „true volume” for accuracy, comparability and harmonization of the measurement methods [3].

According to the results of investigation [17] the rate of decline of roundwood volume achieved according to national standard of each country compared with the volume of logs determined by the most precisious determination of the volume by Measuring Diameter in Short Intervals (intervals as cylinders of a length of 10 cm and diameter given in mm) varies from (-) 5.5% (German Rahmenvereinbarung fur die Werksvermessung von Stammholz, logs of medium diameters) to (-) 9%

(Austrian O-Norm L 1021, mid diameter value given in whole cm). Procedures, which give lover deviations are following: (EN 1309-2) from (-) 1.5 to (+) 3%, ONORM L 1021, mm version from (-) 0.7 to (+) 3%, or the ČSN 480050 Standard 480050-1 from (+) 0.3 to (+) 0.8%.

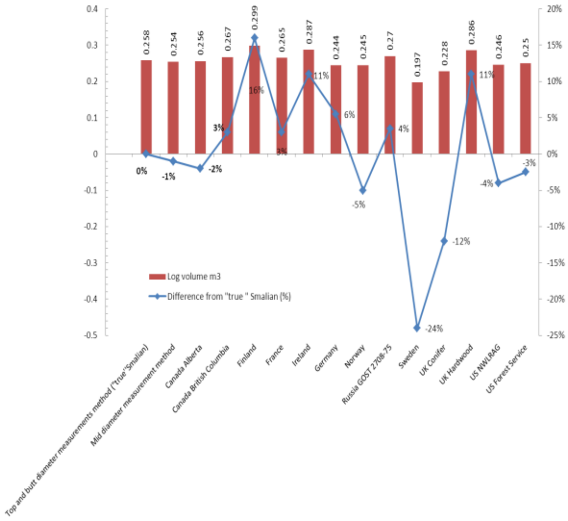


Fig. 1. Veneer log volume comparison between national roundwood measuring standards, where:

NWLRAG – Northwest Log Rules Advisory Group; GOST 2708-75 standard for domestically consumed roundwood in the Russion Federation; UK Conifer- top diameter method, UK Hardwood-mid diameter method

The same problems related to measuring accuracy exist also in Latvia.

The figure 2 shows spruce log (from neiloid zone of stem) volumes calculated using four different measuring methods approved by standard LVS82:2003 [1]. The volume deviation between the measuring results reaches 5%.

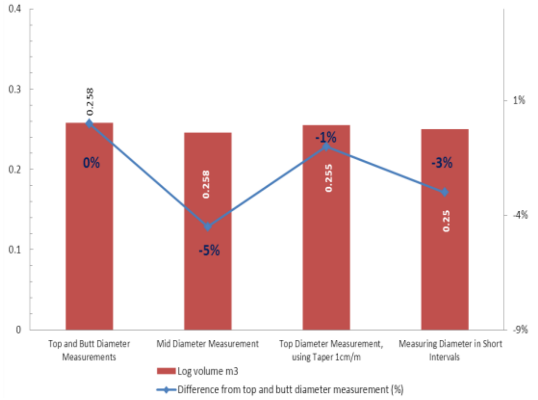


Fig.2. Spruce log volumes calculated using four measuring methods approved by standard LVS 82:2003

When using the measuring methods approved by the standard LVS 82:2003 the term „true volume" of roundwood remain actual for suppliers and processors of wood. The permitted roundwood volume deviation from the actual volume according to standard requirements, using piece-by-piece measurement method, is 3%. In practise, because of some factors it is impossible to carry out this requirement. The factors are following:

A. Stem/ log surface shape

The tree stem/log is a body, the form which is mostly compared to trunckated cone, paraboloid, neiloid or cylinder. The real form does not correspond to any regular geometric body, which is affected by considerable individual diversity given by tree position in the stand, various taper, sweep, flattening, root swelling, buttress and cracks.

According to requirements of standard LVS 82:2003 for automatical piece - by - piece measurement, it is not necessary to identify the log shapes. The piece - by- piece measurement method, approved by standard LVS 82:2003, is used for all frustums of the geometric figure they resemble. Because of simplification of the log surface shape and ignorance of the geometric figure of log the acceptable deviations (+/-) 3% usually are exceeded. The satisfactory results are obtained only for the wide average of the large number of logs but not for particular logs.

B. Stem zone

When the log shape is not a paraboloid the errors given by determination of the volume according to the Mid Diameter Measurement are proportional to log length and the square of the difference between the two diameters, i.e. the longer the log and the greater the taper, the greater is the error. Errors in the volume estimate increase rapidly when the interval between measurements is greater than 5m.

For conic or neiloidic frusta, determination of the volume according to the Mid Diameter Measurement or determination of the volume according to the Top and Butt Diameter Measurements under and over estimate volume respectively. The method undervalues the volume of butt logs while top logs are overvalued [20; 13; 14; 12; 15; 13; 14].

C. The technical parameters of automatical measurement equipment

In Latvia forest sector there are no legislative norm that would determine the requirements for technical parameters of scanning devices, methods of processing the measured data and methods of calculating the logs volume.

The volume of the logs determined by the 2D system are 0,4-0,5% higher than the volume determined by manual comparative measurement. The deviation is in the range of accepted measuring accuracy. The log volume determined by the 3D system are 2.5-5.5% lower than by manual measurement.

The measurement values are affected also by the way of filtration of taken data. Through various types of filtration applied at the same taken data on logs even about 2% deviations are achieved [8].

D. The technical parameters of harvester measurement equipment

Different calculation methods are used in harvesters for estimation butt end diameter values from the first measured values. Butt end values are creating using either linear or non linear functions or diameter coefficient tables. Different harvester models start diameter measuring at different heights of stem. Tests in Latvia have shown that the butt diameters of neiloid zone of stem are not predicted well enough, expecially for spruce species. Because of that the diameters are often underestimated and as the result - the volumes of logs are underestimated [8; 9; 4].

E. Bark thickness and condition according to actual bark type

Because of the different methodology in estimation of the bark thickness in harvesting process and in roundwood processing, the different volume values are obtained. Bark thickness and condition represents the separate problem at the measurement of roundwood [7; 21; 1].

It is impossible to eliminate the differences of measurement results even theoretically. Through the practicable procedure of measurement it is possible to achieve the volume deviation only in the range of accepted measuring accuracy.

For harmonization of the measurement methods approved by standard LVS 82:2003 the adequate tasks have been handled:

To calculate the volumes of mixed spruce and pine rounwood loads and logs devided in to sample clusters according to species, diameter, stem/log surface shape, stem zone and measured by the methods (1; 2; 3; 4.2) (fig. 7) approved by standard LV 82:2003 „Apaļo kokmateriālu uzmērīšana”.

To compare the calculated volume values with the results of the most precisious measurement methods by Measuring Diameter in Short Intervals and the Top and Butt Diameter Measurements. To investigate the reasons of the volume deviations.

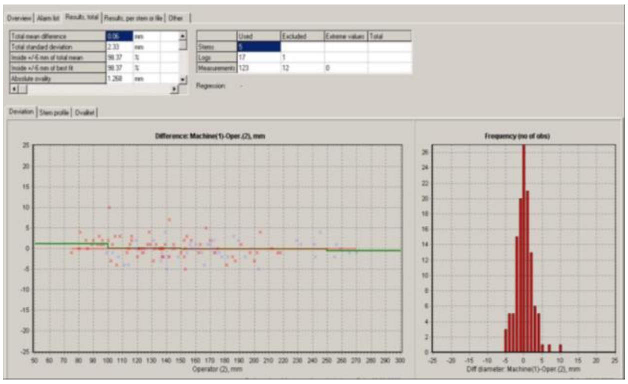
3. To give the recommendations for achieving the volume deviation in the range of accepted measuring accuracy in each technological stage of roundwood processing.

II MATERIALS AND METHODS

To achieve the aim of the research, three objectives were stated:

1. To control the measurement accuracy of the manual and automatical measuring devices (calliper, girthing tape to measure circumference, log measuring ruler, automatic device etc.) according to requirements of standard LVS 82:2003 and the technical requirements for automatical and harvester measuring systems.
2. To control the estimated thickness of the bark at the point of measuring.
3. To control the algorithm of the volume calculation in each technological stage of roundwood processing.

All calibrated measuring devices ensured measuring accuracy appropriate to requirements of standard LVS 82:2003 and the technical requirements for automatical and harvester measuring systems (fig.3; 4; 5; table1). The length was determined with an accuracy 1cm for manual and automatical measurement devices and 3cm for harvester measuring devices; the diameter was determined with an accuracy 1 mm for manual and automatical measurement devices and 3mm for harvester measuring devices.

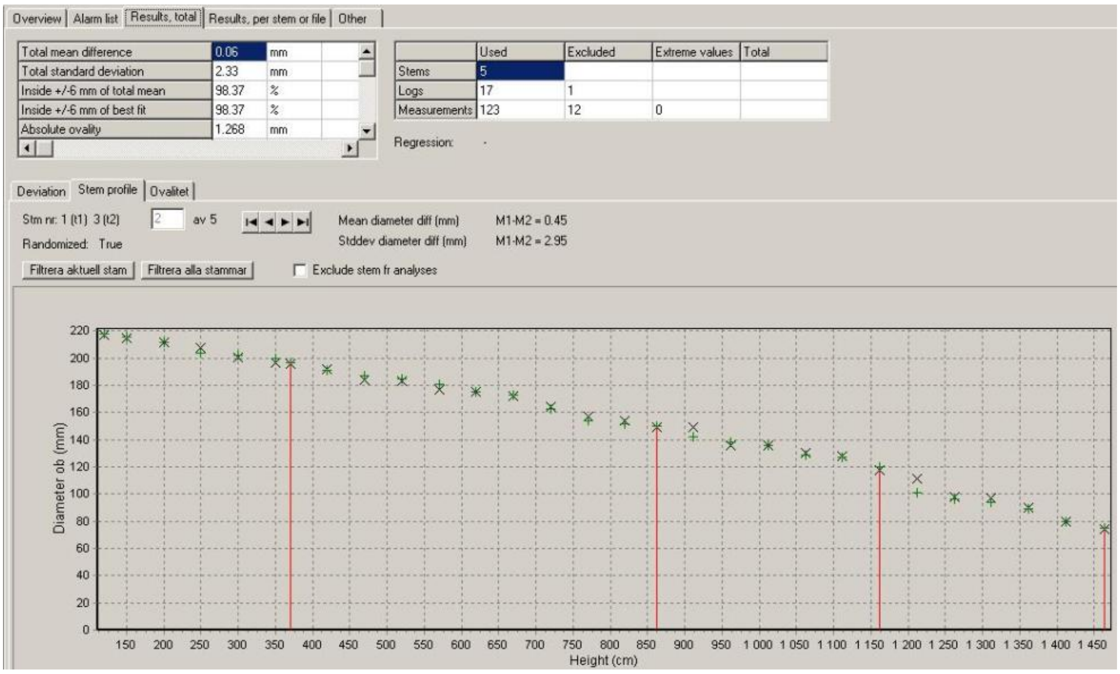


Total mean difference	0.06	mm
Total standard deviation	2.33	mm
Inside +/-6 mm of total mean	98.37	%
Inside +/-6 mm of best fit	98.37	%
Absolute ovality	1.268	mm

	Used	Excluded	Extreme values	Total
Stems	5			
Logs	17	1		
Measurements	123	12	0	

Regression: -

Fig.3. The example of control of the harvester measuring system, where: Stem – 5 control stems; Measurements-123 diameter measurements; Logs- 17 round wood assortiments; Standard deviation- 2.33mm diameter standard deviation



Total mean difference	0.06	mm
Total standard deviation	2.33	mm
Inside +/-6 mm of total mean	98.37	%
Inside +/-6 mm of best fit	98.37	%
Absolute ovality	1.268	mm

	Used	Excluded	Extreme values	Total
Stems	5			
Logs	17	1		
Measurements	123	12	0	

Regression: -

Stm nr: 1 (t1) 3 (t2) 2 av 5

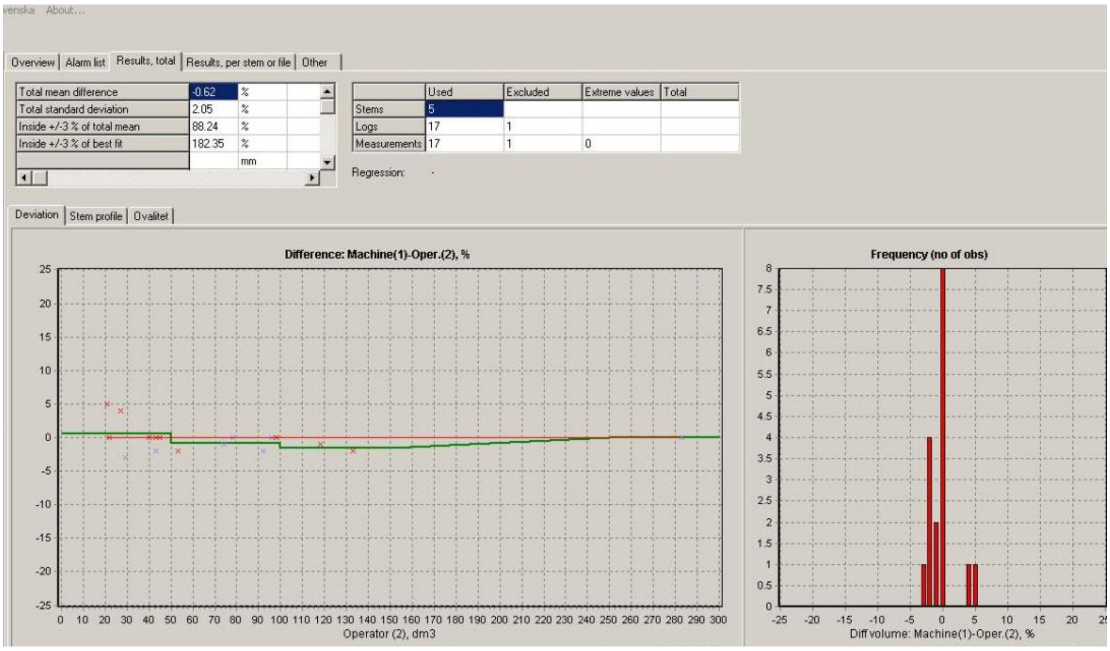
Randomized: True

Mean diameter diff (mm) M1-M2 = 0.45

Stddev diameter diff (mm) M1-M2 = 2.95

☐ Exclude stem fr analyses

Fig.4. The example of control of the harvester measuring system, where MI- measuring data from harvester measuring system; M2- manual measuring results; Stddev-2.95mm diameter standard deviation



Total mean difference	-0.62	%
Total standard deviation	2.05	%
Inside +/-3 % of total mean	88.24	%
Inside +/-3 % of best fit	182.35	%
		mm

	Used	Excluded	Extreme values	Total
Stems	5			
Logs	17	1		
Measurements	17	1	0	

Regression: -

Fig.5. The example of control of the harvester measuring system towards roundwood volume calculation, where volume standard deviation is 2.03%

TABLE 1.

THE EXAMPLE OF CONTROL OF THE AUTOMATICAL MEASURING SYSTEM

Measurement Nr	Etalon Nr /Etalon diameter (mm)						
	51011630	51011730	51011830	51011630	51011730	51011830	
	110.3	200.7	315.5	110.3	200.7	315.5	
1	110.6	200.4	315.0	0.3	-0.3	-0.5	
2	111.1	200.1	314.7	0.8	-0.6	-0.8	
3	111.1	200.1	314.9	0.8	-0.6	-0.6	
4	110.8	200.3	315.0	0.5	-0.4	-0.5	
5	111.4	200.0	314.5	1.1	-0.7	-1.0	
6	110.9	200.0	314.8	0.6	-0.7	-0.7	
7	110.9	200.0	314.8	0.6	-0.7	-0.7	
8	111.1	200.1	314.7	0.8	-0.6	-0.8	
9	110.9	199.8	314.6	0.6	-0.9	-0.9	Accepted (mm)
10	111.0	199.8	314.2	0.7	-0.9	-1.3	
			Average:	0.7	-0.6	-0.8	+/-1
			Standard deviation	0.2	0.18	0.23	
			Maximal positive:	1.1	-0.3	-0.5	+2
			Maximal negative :	0.3	-0.9	-1.3	-2

To achieve the objective, the analitical and experimental investigations, based on different measuring methods (fig. 7), have been performed for spruce and pine logs volume calculation. The logs were devided in to sample clusters according to the top diameters, stem/log surface shape and stem zone which was used for cut-to-lenght logging (fig. 6).

The calculations of deviations betweeen automatical and manual comparative measurement methods were made respectively.

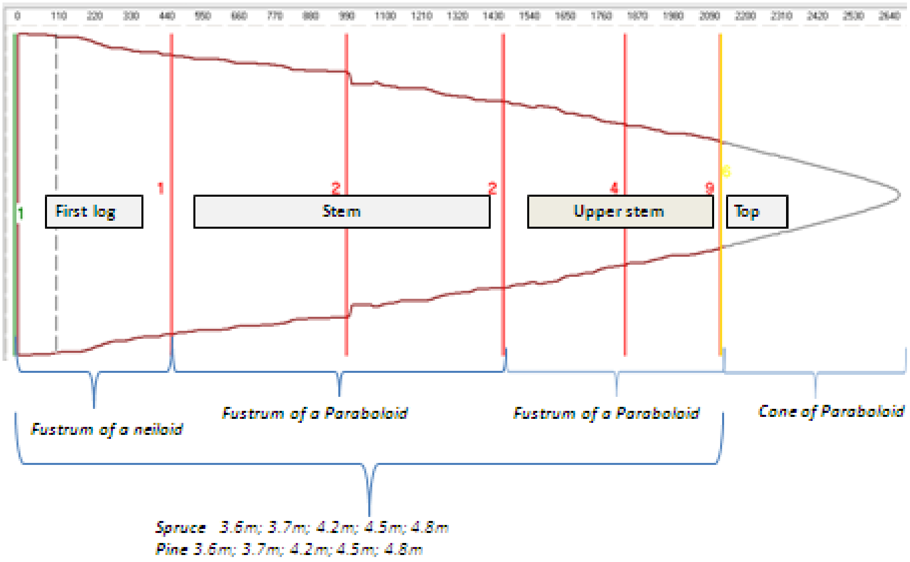
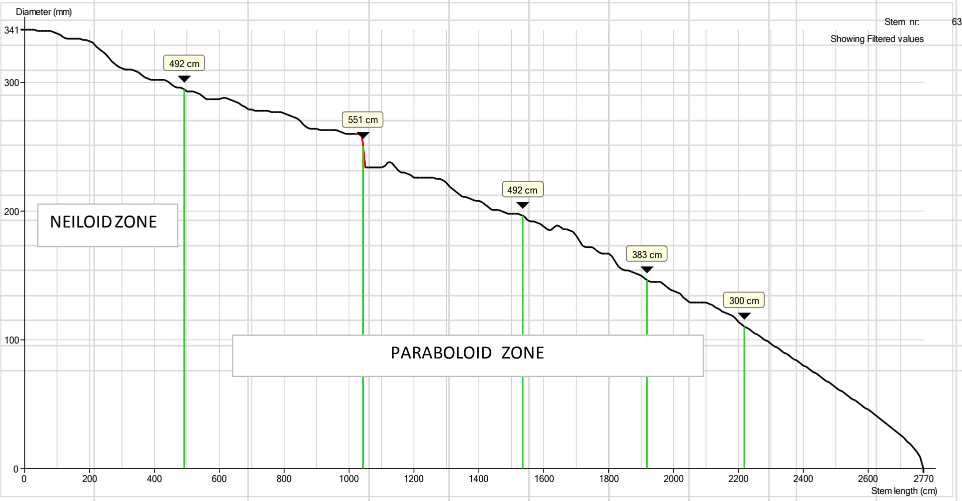


Fig.6. Specification of roundwood assortiments from different stem zone



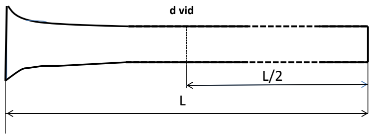
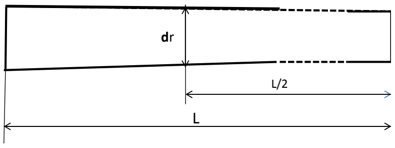
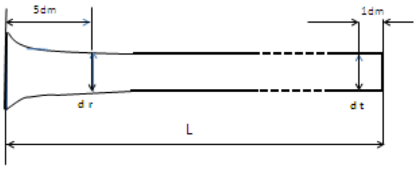
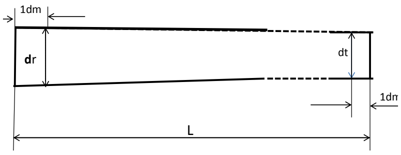
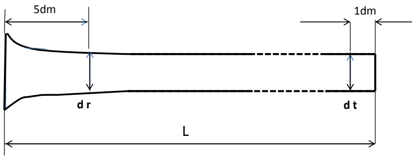
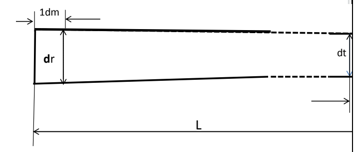
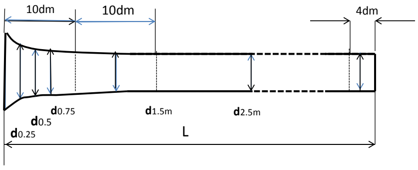
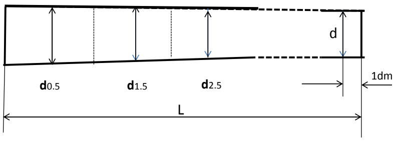
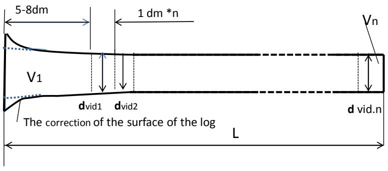
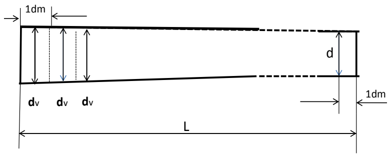
Method	**Determination of the Volume**	**The formula**	**Measurement method for neiloid zone logs**	**Measurement method for paraboloid zone logs**
1	According to the Mid Diameter Measurement	$$V_v = \frac{\pi \times d_v^{\,2} \times l}{4 \times 10000}$$		
2	According to the Top Diameter Measurement, Using Taper	$$V_t = \frac{\pi \times \left[d_t^{\,2} + (d_t + s \times l)^2\right] \times l}{4 \times 2 \times 10000}$$ $$s = \frac{d_r - d_t}{l}$$		
3	According to the Top and Butt Diameter Measurements	$$V_{tr} = \frac{\pi \times \left(d_t^{\,2} + d_r^{\,2}\right) \times l}{4 \times 2 \times 10000}$$		
4.1.	By Measuring Diameter in Short Intervals using electronic 3D systems	$$V_s = \frac{\pi \times \left(d_t \times d_t + d_t \times d_r + d_r \times d_r\right) \times l}{120000}$$		
4.2.	By Measuring Diameter in Short Intervals using harvester measurement systems	$$V = V1 + \left(\frac{\pi \times d_{v1}^{\,2} \times 1}{4 \times 10000}\right) + \left(\frac{\pi \times d_{v2}^{\,2} \times 1}{4 \times 10000}\right) + Vr$$		

Fig.7. Methods of measurement approved by standard LVS 82:2003

III RESULTS AND DISCUSSION

The volume values of mixed pine and spruce roundwood assortiments from different zone of stems were calculated according to the measuring methods approved by standard LVS 82:2003. The results were compared with the volume values calculated according to the Top and Butt Diameter Measurements**.**

For volume estimation the different measuring methods were applied (fig. 8) by using manual measuring equipment, harvester measuring system (harvester T1386LH; measuring equipment TimbermaticH 1.13.14.; caliper version: SKALMAN 5.16) and automatical measuring system (3D scanner SAWCO POS A181).

The volumes of roundwood assortiments measured on bark were estimated without bark by using the sequential formulas (1; 2.).

For spruce roundwood assortiments the double bark thickness at the point of measuring were determined:

$$B=3{,}08+0{,}0404Xd \qquad (1)$$

where: D – diameter of roundwood assortiment, mm.

For pine roundwood assortiments the double bark thickness at the point of measuring were determined:

$$Bv = 1{,}97+0{,}0354 \times D \quad (2)$$

where: D – diameter of roundwood assortiment, mm.

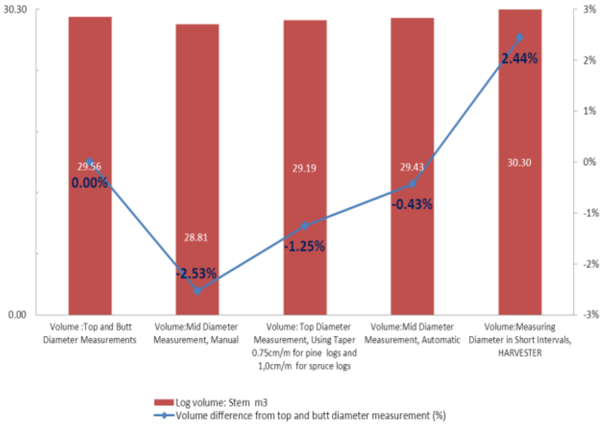


Fig.8. Roundwood load volume comparison using measuring methods approved by standard LVS 82:2003, where the taper values for pine assortiments (14-17.9cm; 18-27.9cm)-0,75cm/m; for spruce assortiments (14-17.9cm; 18-27.9cm)-1.0cm/m

The results of measuring are sequential:

The volume of roundwood assortiments determined according to the Mid Diameter Measurement method was 2.53% lower than the volume determined by the Top and Butt Diameter Measurement method.

The volume of roundwood assortiments determined according to the Top Diameter Measurement method, using Taper was 1.25% lower than the volume determined by the Top and Butt Diameter Measurement method.

The volume of roundwood assortiments determined according by Measuring Diameter in Short Intervals was 2.44% higher than the volume determined by the Top and Butt Diameter Measurement method.

The volume of roundwood assortiments determined according to the Mid Diameter Measurement method was 4.97% lower than the volume determined by Measuring Diameter in Short Intervals.

The volume of roundwood assortiments determined according to the Top Diameter Measurement method, using Taper was 3.69% lower than the volume determined by Measuring Diameter in Short Intervals.

For the volume estimation of debarked pine roundwood assortiments according to stem/ log surface shape the sample cluster was prepared. The log surface were trunckated paraboloid. The volume of sample cluster was estimated by automatical measuring system Sick Optik Electronic 5000079. The volume of the roundwood assortiments arranged in to diameter groups were calculated automatically according to the algorithm approved by the measuring methods (1; 3) (fig. 7). The results are given (fig. 9).

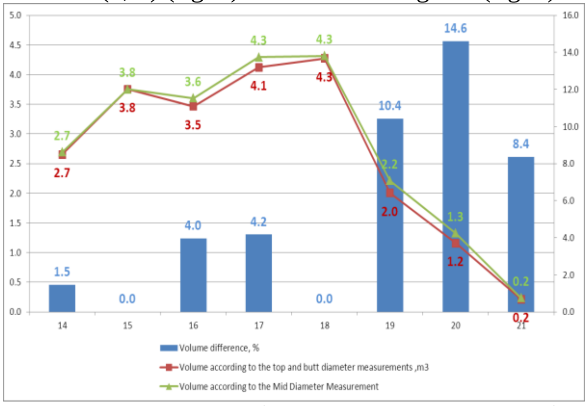


Fig.9. The volume results of pine roundwood assortiments from paraboloid zone of stems, devided in to diameter groups and estimated according to the Mid Diameter Measuring method and the Top and Butt Diameter Measuring method

The roundwood volume values from paraboloid zone of stems estimated according to the measuring method (1; 3) (fig. 7) are given (fig. 10)

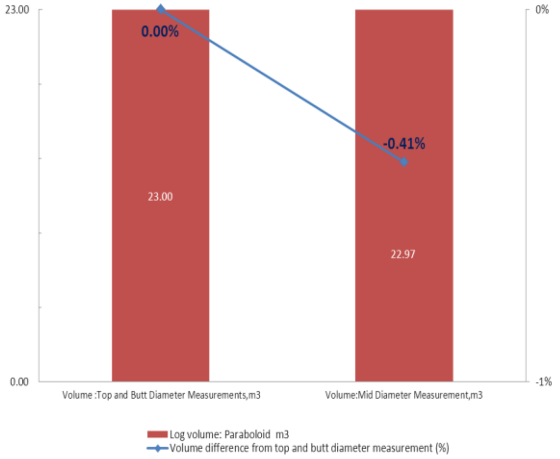


Fig.10. The roundwood volume values from paraboloid zone of stems estimated according to the Top and Butt Measuring method and the Mid Diameter Measuring method

a. The results of measuring are sequential:

The volume of debarked pine logs from paraboloid zone of stems in all diameter groups determined according to the Mid Diameter Measurement method was 0.41% lower than the volume determined by the Top and Butt Diameter Measurement method.

For the volume estimation of spruce roundwood assortiments according to stem/log surface shape the sample clusters were prepared. The log surface were trunckated neiloid and trunckated paraboloid. The spruce roundwood assortiments were devided in to sample clusters according to log surface shape. The volume of sample clusters were estimated by automatical measuring system Rema Control 9000 according to the algorithm of the measuring method 1(fig. 7). The volume of the roundwood assortiments were calculated also according to the algorithm of the measuring method (3) (fig. 7). The top diameter values of logs for volume calculation were taken from automatical measuring system Rema Control 9000 and the butt diameter parameters were measured manually.

The volume results are given (fig. 11; 12; 13)

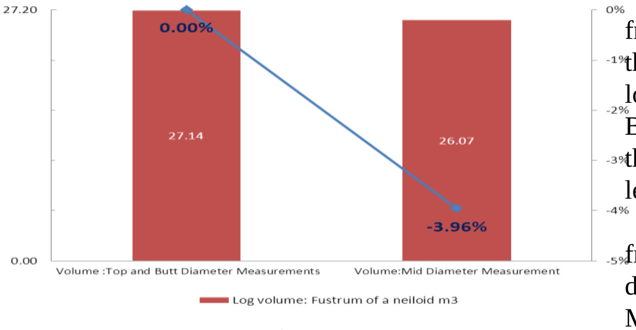


Fig. 11. The volume results of spruce roundwood assortiments from neiloid zone of stems measured by the Top and Butt Measuring method and the Mid Diameter Measuring method

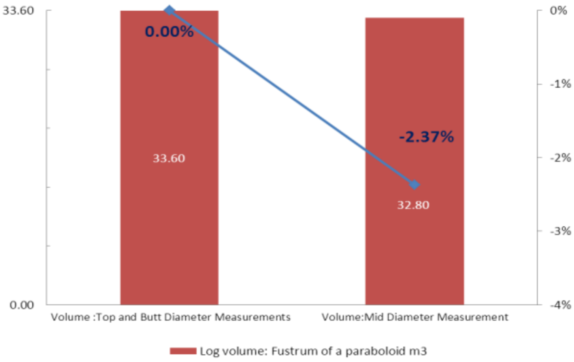


Fig. 12. The volume results of spruce roundwood assortiments from paraboloid zone of stems measured by the Top and Butt Measuring method and the Mid Diameter Measuring method

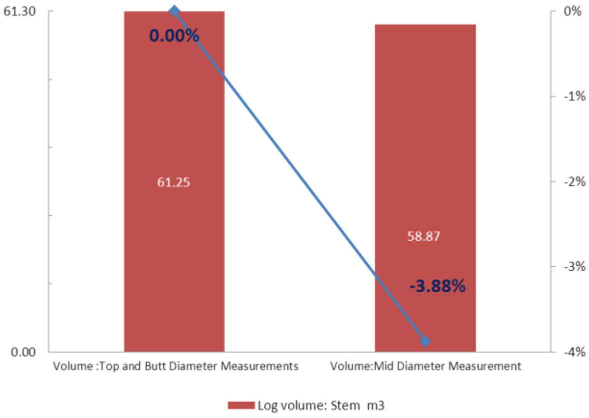


Fig. 13. The volume results of spruce roundwood assortiments from all parts of stems measured by the Top and Butt Measuring method and the Mid Diameter Measuring method

b. The results of measuring are sequential:

It is impossible to reach accurate volume results using determination of the volume according to the Mid Diameter Measurement for spruce logs from neiloid zone of stems.

The volume of spruce roundwood assortiments from neiloid zone of stems determined according to the Mid Diameter Measurement method was 3.96% lower than the volume determined by the Top and Butt Diameter Measurement method. The greater are the differences in diametre between the log ends the less reliable will be the volume values.

The volume of spruce roundwood assortiments from paraboloid zone of stems (measured under bark) determined according to the Mid Diameter Measurement method was 2.37% lower than the volume determined by the Top and Butt Diameter Measurement method.

The volume of spruce stems determined according to the Mid Diameter Measurement method was 3.88% lower than the volume determined by the Top and Butt Diameter Measurement method.

IV CONCLUSION

Determination of the volume according to the Mid Diameter Measuring is an accurate method for pine roundwood assortiments, but for spruce assortiments approach the form of truncated neiloids the results are unaccurate compared to the most precisious determination of the volume according to the Top and Butt diameter measuring.

To increase the accuracy of volume values, to decline of commercial profability by using different measurement methods and to remove differences originating among particular procedures of measurements, it is proposed to base manual measuring on determination of the volume according to to the Top and Butt Diameter Measuring method, but automatic measuring on determination of the volume according to to the Top and Butt Diameter measuring or Measuring Diameter in Short Intervals.

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Changes of Photosynthesis-Related Parameters and Productivity of Spring Oilseed Rape under Different Nitrogen and Sulphur Fertilizers Supply

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Abstract. **Fertilization with essential mineral elements is important to get high quality yield results. The lack of necessary mineral elements in soil can affect oilseed rape plant physiological functions, photosynthesis and plant productivity. Oilseed rape plants have high requirements for nitrogen and as oil crop – for sulphur. The aim of the investigation was to explain changes of chlorophyll *a* fluorescence parameters in spring oilseed rape leaves and yield changes under nitrogen and sulphur supply. During laboratory experiments changes of chlorophyll *a* fluorescence parameters and during field experiments changes of yield parameters under different nitrogen and sulphur supply were observed. Laboratory and field experiments showed that sulphur fertilizer rate 18 kg ha^{-1} is the most effective sulphur dose for spring oilseed rape, when nitrogen 55 kg ha^{-1} is added, because its presence has positive effect on photosynthetic reactions. There was found out in laboratory experiments that chlorophyll *a* fluorescence parameters F_v/F_m and PI can be used to describe sulphur and nitrogen mineral element supply efficacy on spring oilseed rape. There was observed in the field experiment that oilseed rape yield increases significantly (from +0.34 t ha^{-1} to +0.64 t ha^{-1}) under optimal ($S_{18}N_{55}$) nutrient supply, but lack of sulphur leads to significant yield losses. To avoid excessive fertilizer usage, its negative impact on plant physiology and yield losses, we consider that sulphur: nitrogen = 1:3 as additional fertilizer is optimal for spring oilseed rape plants.**

***Keywords – Brassica napus*, chlorophyll, fluorescence, nitrogen and sulphur top-dressing, yield.**

I INTRODUCTION

Oilseed rape (*Brassica napus* L.) is one of the most important sources of vegetable oil in the world and widely grown as main oil crop in Europe [1] – [4]. The total area of oilseed rape grown in Latvia has increased almost 7 times during the past 10 years (2002: 18.4 thousand ha; 2011: 121.3 thousand ha) (data from Central Statistical Bureau of Latvia). Oilseed rape growers in Latvia usually prefer winter oilseed rape varieties, but due to different weather conditions across Latvia in some regions, especially Eastern Latvia, it is possible to grow only spring oilseed rape [5]. The area of spring oilseed rape was 63.6% of the total oilseed rape area in Latvia in 2011 (data from Central Statistical Bureau of Latvia). Compared to other European countries the average spring oilseed rape yields in Latvia are relatively low.

Request for high seed yield increased rapidly, accordingly with increasing number of opportunities for use of oilseed rape. Fertilization with essential mineral elements is important to gain high quality yield. New oilseed rape varieties can produce high seed yields, but it is important to ensure proper growing conditions, including complex and balanced mineral fertilisation during growing season. Oilseed rape requires a higher amount of nutrients as compared to cereals [6], [7]. Nitrogen is limiting element for plant growth, because it is an integral component not only of chlorophyll but also of amino acids, proteins, nucleotides, chromosomes, genes, ribosomes and is also a constituent of all enzymes [7], [8]. Sulphur is also an important mineral element for oilseed rape development [9], [10]. Several studies have established positive interaction between sulphur and nitrogen [11] – [13]. Sulphur fertilizer improves nitrogen use efficiency [12] and is involved in the synthesis of chlorophyll and it is in the sulphur-containing amino acid [14] and enzyme content [15]. The deficiency of necessary mineral elements as well as too high element amounts in soil has negative impact on oilseed rape physiological functions, photosynthesis and plant productivity [16].

Rapeseed contains 40 – 46% of oil [2], [6], [15], [17] and 43 – 48% of protein [2]. Oil content of seeds can be affected by many factors, such as variety, crop management and fertilisation [2]. Several research confirmed essential role of mineral fertilizers on rapeseed oil quality [2], [7], [11], [18] – [20].

Chlorophyll content and photosynthetic activity in plant leaves are main parameters describing plant physiological conditions [21], [22] and mineral nutrition of plants [23] – [25]. Young plant leaves which have reached optimum size and development stage are the best indicators for mineral nutrient content in oilseed rape plants, especially for deficiency of elements [26]. Non-destructive methods of plant analysis have become more popular in plant biology [22], [27]. Chlorophyll *a* fluorescence has been widely used to measure the stress level of plants induced by many factors [21], [28] – [30].

However, there is a lack of information about the effect of supplementary sulphur and nitrogen on physiological processes in plants, such as photosynthesis as a yield forming factor under Latvian climatic and agroecological conditions. Therefore, the aim of the research was to explain changes of chlorophyll *a* fluorescence parameters in spring oilseed rape leaves and yield changes under nitrogen and sulphur supply.

II MATERIALS AND METHODS

Laboratory experiments

Laboratory experiments were carried out at University of Latvia, Faculty of Biology in 2011.

Spring oilseed rape variety 'Forte' was used in studies under laboratory conditions. Seeds were sown on January 19 in plastic containers (five seeds per container), filled with mineral-enriched peat substrate KANO (pH_{KCl} 5.5 – 7.0, nitrogen content 180 mg L^{-1}, K_2O content 400 mg L^{-1}, P_2O_5 content 245 mg L^{-1}). Containers were placed in a growth chamber, at 15 h photoperiod, 22 ± 2°C and illuminated with luminescent lamps with photon flux density of 200 µmol m^{-2} s^{-1}.

Five different trial treatments were included in the study: 1) untreated – S_0N_0, 2) $S_{18}N_{15}$, 3) $S_{18}N_{55}$, 4) $S_{36}N_{55}$, and 5) S_0N_{55} (Table 1). Ammonium sulphate ($(NH_4)_2SO_4$; nitrogen content 21%, sulphur content 24%) was used as a sulphur (S) fertilizer source in the experiments at rates 18 and 36 kg ha^{-1}. Ammonium nitrate (NH_4NO_3; nitrogen content 34.4%) was used as an additional nitrogen (N) fertilizer source in experiments. Treatment 5 (S_0N_{55}) with nitrogen rate 55 kg ha^{-1} was included in experiment to observe pure nitrogen effect on the physiological processes in spring oilseed rape plants.

Fertilizer treatment was performed on February 10 when plants had reached 3 – 4 leaf stage. For fertilisation a 10 % $(NH_4)_2SO_4$ and NH_4NO_3 solutions in distilled water were used. Each experimental pot received 50 mL of mineral fertilizer solutions at calculated dose-rates and 50 mL of distilled water were applied on the untreated pots.

Measurement of chlorophyll *a* fluorescence was performed four times: on February 24 (14 days after fertilizer were applied – DAF), on March 3 (21 DAF), on March 10 (28 DAF) and on March 17 (35 DAF). Chlorophyll *a* fluorescence was measured using a Handy PEA (Plant Efficiency Analyzer) portable fluorescence measurement system (Hansatech Instruments, UK).

Young plant leaves were chosen for analysis. Dark adaptation was performed with special leaf clips for 25 min before measurement. Twenty measurements per treatment were performed. The data were analyzed by appropriate software.

TABLE 1

SCHEME OF EXPERIMENT

Treatments	Top-dressing rate, kg ha^{-1}	Top-dressing rate per 1 pot, mL	Top-dressing rate per 1 plot (30 m^2), g
1. Untreated	-	-	-
2. $S_{18}N_{15}$ $[(NH_4)_2SO_4]$	75.0	0.75	225.0
3. $S_{18}N_{55}$ $[(NH_4)_2SO_4]$ + $[NH_4NO_3]$	75.0 + 116.0	0.75 + 1.16	225.0 + 348.0
4. $S_{36}N_{55}$ $[(NH_4)_2SO_4]$ + $[NH_4NO_3]$	150.0 + 67.0	1.50 + 0.67	450.0 + 201.0
5. S_0N_{55} $[NH_4NO_3]$	160.0	1.60	480.0

Field experiments

Field trials were established in Priekuli municipality in 2010 and in Talsi municipality in 2011 on the farmer's field in spring oilseed rape. In the field trials the treatments were arranged within a randomized complete block design with four replicates. Plot size was 30 m^2. In both years conventional soil tillage was employed according to recommendations for spring oilseed rape. Plant protection products were applied to the whole trial as necessary.

In 2010 the soil type was sod podzolic loamy sand and in the field had pH_{KCl} 5.3, an organic content of 46 g kg^{-1} and a previous crop was annual ryegrass and clover mix. Spring oilseed rape variety 'Forte' was seeded on April 30 at seeding rate 4.5 kg ha^{-1}. At sowing the trial area was fertilized with mineral fertilizer (N_4:P_{15}:K_{31}) 250 kg ha^{-1}.

In 2011 the soil type was sod-podzolic loam and in the field had pH_{KCl} 5.5, an organic content of 26 g kg^{-1} and a previous crop was spring barley. Spring oilseed rape variety 'Perfekt' was seeded on May 5 at seeding rate 5.0 kg ha^{-1}. Before sowing the trial area was fertilized with mineral fertilizer (N_{16}:$P_{16}K_{16}$) 330 kg ha^{-1}.

Field trial treatments were the same, used in laboratory experiments. Sulphur and nitrogen top-dressings according to trial scheme (Table 1) were broadcasted on the field on June 19 (in 2010) and on June 8 (in 2011).

The total seed yield from each plot was harvested by trial combine "Sampo 130" on August 17 (in 2010) and "Wintersteiger Delta" on September 6 (in 2011). Yield was recalculated to t ha^{-1} and given at 100% purity and 8% moisture content.

Data on meteorological conditions were obtained from Priekuli (in 2010) and Stende (in 2011) HMS. The growing season in 2010 was unusually warm and air temperatures exceeded long-term norm during the season: 0.3 – 5.3°C above the norm. Overall amount of precipitation per month was satisfactory and favourable for spring oilseed rape development during the beginning of growing season, but was only 51.6% of norm during the period of seed development in July. The weather during the growing season in 2011 continued to be warmer than long term averages (0.3 – 2.9°C above the norm). During the beginning of the growing season (April, May) amount of precipitation was only 67.9 – 74.2% of norm. There was sufficient amount of precipitation during June, July and August to provide very good conditions for reproductive organ formation and seed development of spring oilseed rape.

The oil content (%) of spring oilseed rape seeds was determined in Latvia University of Agriculture Institute of Agrobiotehnology, Grain and Seed Research Laboratory using Grain Analyzer INFRATEC 1241 (FOSS Analytical, Sweden) using a special device for oil content determination.

Data analysis was performed using *MS Excel* and the statistical package *GenStat for Windows* 15th edition.

III RESULTS AND DISCUSSION

Laboratory experiments

Chlorophyll *a* fluorescence parameters F_v/F_m and PI were used to describe additional sulphur and nitrogen fertilizer effect on photosynthesis of spring oilseed rape plants.

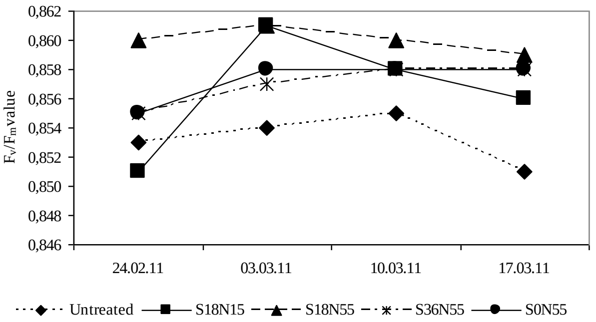

Fig. 1. Effect of sulphur and nitrogen fertilizer on F_v/F_m of spring oilseed rape plants under laboratory conditions

Parameter F_v/F_m is widely used to detect plant stress and is directly correlated to the photochemical efficiency of the photosystem II for which values of 0.83 correspond to high efficiency [31]. In our experiment F_v/F_m values exceeded 0.83 in all treatments (Fig. 1). The highest F_v/F_m values during whole time of experiment were detected to the plants with optimum sulphur and nitrogen fertilizer supply ($S_{18}N_{55}$). It indicates that fertilizer at the optimum rates has positive effect on light dependent reactions of photosynthesis. Lower F_v/F_m values were detected to the $S_{36}N_{55}$ and S_0N_{55} plants, compared to $S_{18}N_{15}$ and $S_{18}N_{55}$ plants. In comparison with all treatments, untreated plants had very low photosynthetic activity. Results indicate that mineral element deficiency (S_0N_{55}) or too high rates ($S_{36}N_{55}$) can lead to decrease of photosynthetic efficiency. The results of present study agree with those of Verhoeven and his co-workers [32] who reported that F_v/F_m value in spinach plants decreases under conditions of nitrogen deficiency.

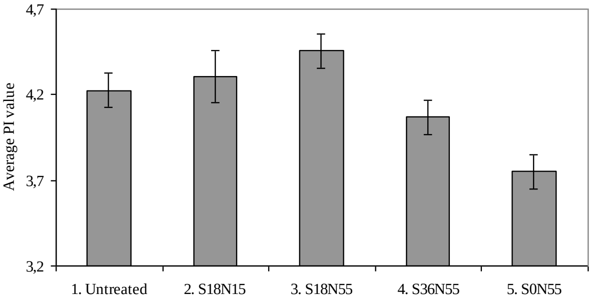

Fig. 2. Effect of sulphur and nitrogen fertilizer on PI of spring oilseed rape plants under laboratory conditions

The Performance Index (PI) is suggested to be one of the most valuable fluorescence parameters describing vitality of the plant [33]. Additional sulphur and nitrogen fertilizer at optimum rate ($S_{18}N_{55}$) significantly increased spring oilseed rape plant vitality (Fig. 2). Sulphur deficiency (S_0N_{55}) as well as sulphur double dose ($S_{36}N_{55}$) had led to significant plant vitality decrease compared to control plants and plants fertilized with 18 kg sulphur ha^{-1}, which only approves significant role of sulphur and nitrogen ratio in plant growth [12].

Field experiments

Yield of spring oilseed rape varied between experimental years in spite of the fact that both spring oilseed rape varieties used in experiment were highly productive.

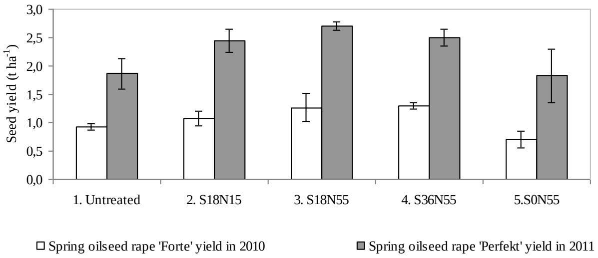

Fig. 3. The effect of sulphur and nitrogen fertilizer on spring oilseed rape seed yield

The average spring oilseed rape yield (Fig. 3) in the control plots was very low (0.9 – 1.9 t ha^{-1}), especially in 2010, when oilseed rape seed development was strongly affected by meteorological conditions. Researchers in Iran concluded that seed yield decreases can be associated with the water stress during rapeseed reproductive growth stages [34]. Seed yield increased with an increase of sulphur fertilizer rate from 0 to 36 kg ha^{-1}. In both years significantly higher spring oilseed rape seed yield was produced in the plots where sulphur 18 and 36 kg ha^{-1} and nitrogen 55 kg ha^{-1} fertilizer was applied compared to untreated. It is obvious that there is a relationship between nitrogen and sulphur rates and their impact on seed yield. A significant impact of increasing sulphur fertilizer rates on the oilseed rape seed yield was recorded in earlier studies [10], [12].

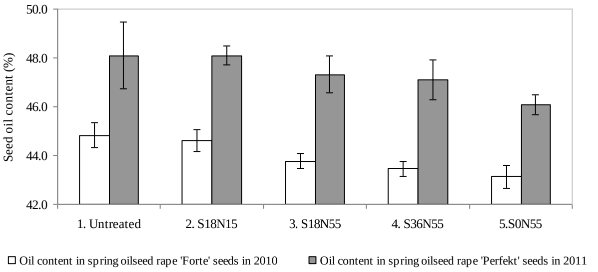

Fig. 4. The effect of sulphur and nitrogen fertilizer on the oil content in spring oilseed rape seeds

One of the most important quality factors of oilseed rape is oil content. The average oil content in the spring oilseed rape ‘Forte’ seeds was 43 – 45% and in spring oilseed rape ‘Perfekt’ seeds: 43 – 48% (Fig. 4). Oil content was highest in the untreated plot oilseed rape plant seeds and decreased with the increasing sulphur and nitrogen fertilizer rates. Negative correlation between oil content and nitrogen fertilizer rate has been reported previously [7], [15], [17]. It is strongly related with protein content in oilseed rape seeds, which increases with the increasing nitrogen rate [7] and has negative impact on oil content in seeds [1].

IV CONCLUSIONS

Chlorophyll *a* fluorescence parameters F_v/F_m and PI can be used to describe sulphur and nitrogen mineral element supply efficacy on spring oilseed rape to predict possible yield results.

High seed yields of good quality can be expected when an optimum concentration and good balance of additional sulphur and nitrogen are used. Sulphur and nitrogen fertilization in relation 1:3 should be considered not only as a fertilizer increasing biological spring oilseed rape yield, but improving the quality of plant product and reducing the unnecessary distribution of fertilizer in the environment.

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Investigation of Biomass Ash Properties for Their Utilization Assesment

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***Abstract*. Ash is a mineral waste group, which quantity increases on a global scale and now it has achieved hundreds of millions of tons, and as they are an integral part of the any solid fuel, including biomass the production rate will continue. At the same time ash, due to their nature and composition is a unique material that can be valuable technogenic resource.**

The paper studies the wood ash physical properties (density, porosity, specific free surface) composition and the metal adsorption ability. It was found that wood ash contains a significant percentage of metals in the mobile phase, which dissolve in the water and thus are able to spread into the surrounding soil. The study established a high adsorption activity of ash (95-99%) to the metals. It was found that the adsorption capacity of the ash is possible to increase with the activation of the ash particle surfaces and changing the pore structure.

***Keywords* - biomass ashes, specific free surface, adsorption capacity, physical properties of ashes.**

I INTRODUCTION

Fuel contains the inorganic mineral components which after fuel combustion form ash. The quantity, composition, structure and properti of ash depend primarily on the fuel type and composition. Gaseous fuels practically does not have ash, fuel oil gives very little ash (depending on the type of fuel,for example, diesel – 0.01%, oil- 0.15-0.3%), soli fuel has the highest ash content fluctuation rang. The highest ash percentage have solid fossil fuels. A coal contain ash ranging from 2 to 50%, lignite -8-48%, oil shale -50-72% [1,2]. Peat, which is located in the buffer zone between fossil fuels and biomass, has ash from even 1%(high peat bogs -2-4%) to 20% (low peat bogs 6-18%)[3,4]. As a result, the world eergy sector as well as all other sectors that use fuels formed large quantity of mineral waste – ash and disposal and managing of this volume is problem which solving has recently become acute. Thus, the Russian Federation is produced Thus, the Russian Federation is produced over $28{,}10^6$tons of ash per year. Siberian Federal District have collected 300.10^6 tons of unused ash.Statistical data. show that only the fly ash content in the world grows up 180.10^6 tons per year [5].The use of Biomass - (wood, energy plants, straw, reeds) for heat production gives a much lower ash outcome- from 0.5 to 12% depending on the types of plants and their growth conditions (wood-0,3-1,0%, straw - 4.5 to 11.3%) [6]. Thus, the transition to renewable energy sources - biomass seriously reduces the weight of the ash forming, but not solve the problem as a whole.For example, Finland in energy-use fuel - wood and peat annually produces 6.10^5 tons of ash, but in general, the pulp and paper industry and other companies which use wood as fuel, this amount constitutes $1{,}02.10^6$ tons of ash per year. The same situation in Sweden - 8.10^5 tons of wood ash per year. In the US. annually is produced approximately 3.10^6 tons wood ash, in the China – 20.10^5 t per year [7]. In the Latvia putting out timber volume consumed for heat generation and industrial technology and taking into account the average wood ash content around 3% the annual production of ash is not less than 30000 tons. Consequently, the optimal utilization of ash is an essential to the Latvian conditions also, especially in view of the national and the EU's energy development strategy relating to the transition to renewable energy sources, including biomass. It is necessary to note that the solid organic waste for energy production gives the additional increase in the amount of ash. Also, from an environmental point of view and rational exploiting of resources it is important to find the optimal methods to utilize ash as technogenic resource [8].

Their composition, structure and properties are very diverse, and their use is therefore associated with the ash parameter studies[9,10,16,21,29].Ash utilization problems in the world are widely studied, the technology is put into practice. The main directions of ash application at the moment may be divided into 4 groups : agriculture, construction and building, production of materials, water purifying. These directions are summarized in the table below (Table 1).

TABLE 1

ASH APPLICATION AREAS

Agriculture[7,24,25,26]	Construction[12,15,17,20,23]	Material production[11,12,13,14,15]	Water treatment[18,19,32]
1.Mineral fertilizers for soil improvement 2.Composting component 3.Litter 4.Sludge pasteurization	1.Binder 2. Fiber cement 3. Aerated cellular concrete 4. Bricks 5. Asphalt filler 6. Road construction stabilization	1. Polyethylene filler 2.Zeolite 3.Synthetic lightweight aggregates 4.Rubber filler 5.Phosphate ceramics 6.Inorganic fiber 7. Vitrocrystalline materials 8. Ceramicrete	1.Adsorbent 2.Electrocoagulation optimization 3.Neutralization 4. Extraction

TABLE 2

ELEMENT CONTENT IN ASH

Chemical element	Content in wood ashes, C_{mas}%	Content in coalashes,C_{mas}, %
Ca	15 (2,5-33)	18 (7-33)
K	2,6 (0,1-13)	1,6 (3-4)
Mg	1,6 (0,5-3,2)	1,2 (1-2)
Mn	0,4 (0-1,3)	1,2 (0,3-1,3)
P	0,5 (0,1-1,4)	0,9 (0,3-1,4)
Na	0,2 (0-0,54)	0,3 (0,2-0,5)
N	0,15(0,02-0,8)	
Fe	2 (1,6-2,45)	

TABLE 3

ASH CHEMICAL COMPOSITION IN TERMS OF OXIDES

Oxides	Contents in wood ashes,C_{mas},%	Content in coal ashes,C_{mas},%
SiO_2	20-60	40-70
Al_2O_3	0,1-12	14-35
Fe_2O_3	1,5-5,3	2-20
Fe_3O_4	-	2-14
MgO	0,3-5	1-10
Na_2O	0, 1-0,8	0,1-5
CaO	0,8-43	0,5-30
K_2O	1-1,8	0,5-3

TABLE 4

THE METAL CONTENT IN ASH

Metal	Content in wood ashes,mg/kg	content in coal ashes, mg/kg
Fe	5000-6000	7000-160000
Zn	350-620	
Cu	87,8-127	
Cr	54-133	2-1100
Pb	20-27	4-230
Cd	3,5-4,9	3-7

It can be seen that in the solid fossil fuel ash composition prevail silicon, aluminum, iron, while the biomass ash composition is characterized mainly with calcium, potassium, magnesium. Wood ashes observed significantly lower content of heavy metals [8,9,22].

The specific direction of the ash application depends on the ash composition and structure. Thus, the ash being used in the production of adsorbents options determine the porosity, pore shape, size and structure, the specific free surface area, adsorption ability and capacity. The paper presents results of wood ash physico-chemical studies

II MATERIALS AND METHODS

Object of research - wood ash, collected from firewood, consisting mainly of pine, birch wood mixture burned in private home furnaces. Ashes were dried to constant weight in a drying oven at a temperature of 115-120^{0}C and screened out through a sieve with a mesh width of 0.5 mm.

Weed out ash color was light gray with small black particles of unburned coal impurities.Experimentally determined ash characteristics:

1. Friable weight - by the direct weighing of the volume of ash, poured into a beaker. Mass of the samples were 20-40g.
2. Mineral mass density–with pycnometer method. Mass of samples were 2-3g.
3. Specific free surface - with methylene blue adsorption method, which is based on the Langmuir adsorption theory equation, which defines the relationship between adsorbed on the surface quantity of molecules mononuclear layer and the amount of the surface.The surface area of the adsorbent surface S_f, which holds the adsorbed molecules

$$S_f=V\cdot N\cdot CA_m/m\cdot M$$

Where:
V- volume of solution use for titration, ml,
C-concentration of the solution
N-Avogardo's number
A_m –square,which occupies one molecule of the substance adsorbed on the adsorbent surface
M-adsorbable substances molecular weight
m- ash sample mass

In an experiment using methylen blue
$M = 319.9$ g, $Am = 106 \cdot 10^{-20}$, m^2,$C = 0.03$ g / l,
$N=6.023.10^{-23}$.

The sample of the ash (about 1 mg) was poured in 25 ml of water, then added the sulfuric acid - 5n concentration, mixed and then the suspension was titrated with 0.3% methylene blue according to the standard method [27].Specific surface area calculations were performed according to the formula

$$S_f=5.98\cdot10^3 V/m, m^2/g.$$

4. Loss on heating η - by the direct weighing method. Samples (m_0 = 5 g) were heated in a muffle furnace at a temperature of 850-900 ^{0}C 2 hours, and then weighed(m_1): $\eta=m_0/m_1$

5. One of the most important characteristics of the ash is quantity and composition of soluble components in the ash[28]. The study determined experimentally ash component solubility changes depending on the time of contacting with water. Ash samples - 6 portions each of the 10 g were tipped onto 6 glasses with distilled water 200 ml and suspension was stirred in flocculation device "Armfield" 10, 20, 30, 40, 60, 90 minutes at a temperature of 20^{0}C at a speed of 150 RPM. Solutions were filtered, and then were measured: optical density, electrical conductivity, pH, phosphate, nitrate and nitrite contents.

Having regard to soil contamination with heavy metals profound impact on the quality of the environment and ecosystems in all filtrates were determined concentration of heavy metals - the moving soluble phase, which is able to migrate into the soil. Analyzes were performed with a Perkin Elmer atomic absorption spectrometer firm AAnalyst200.

In the ash samples after their flltration and drying was determined specific free surface.

In order to analyze the potential use of ash as adsorbents for wastewater treatment for all ash samples was determined adsorption capacity. For this purpose, the experimental solution was made with six metal ion content.In distilled water were dissolved 0.02 to 0.06 g salts ($CuSO_4$, $FeSO_4$, $MnSO_4$, $CrCl_3$, $PbSO_4$, $CoSO_4$) so that the metal ions in solution should be between 2.5 and 4.5mg/l.

Adsorption ability was investigated as follows:In 7 flasks were poured 200 ml of experimental solution, and 5 g of the ash samples. The flasks were placed on a rotary shaker for 1 hour. After the shaking solution was filtered and in the filtrate was determined the concentration of remaining metal by Perkin Elmer atomic absorption spectrometer AAnalyst200. Were calculated the absolute amount of adsorbed metal m_{ad}, solution concentration change ΔC, solution treatment of metals degree η and the relative adsorption capacity of 1 gram of ash A_n.

III EXPERIMENTAL RESULTS

The investigated wood ash mechanical and physical properties are summarized in the Table 5.

TABLE 5

MECHANICAL PROPERTIES OF WOOD ASH

NR	PROPERTIES	RANGE	AVERAGE
1	FRIABLE WEIGHT , G/CM^3	0,50-0,59	0,53
2	MINERAL MASS DENSITY P_0,G/CM^3	1,74-1,87	1,82
3	POROSITY IN LOOSE PHASE P,%	68- 72,3	70,8
4	LOSS ON HEATING H, %	6,9-7,8	7,75
5	SPECIFIC FREE SURFACE S_F,M^2/G	2,2-2,4	2,25

Specific free surface of filtered ash after extraction of soluble substances is shown in the table 6.

TABLE 6

Rinse time,min	10	20	30	40	90	Sinte-red	Heated in water
Specific free surface S_f(m^2/g)	2,9	2,3	2,4	2,9	2,2	2,2	9,6

In the table 7 are results of the filtered ash adsorption efficiency to metals as changes of their concentration in the experimental solution after adsorption.

Adsorption rates were calculated as the concentrations ratio ΔC / C.Table 8 summarizes the ash extract physico-chemical properties and Table 9 – metal content of wood ash extracts depending on extraction time.

TABLE 7

ASH ADSORPTION EFFICIENCY (CONCENTRATION C, MG / L) TO METALS DEPENDENCE OF MIXING TIME.

Metal	Experimental solution (C_0)	10min	20min	30min	40min	90min	C_{avg}	Adsorption rate,%
Cu	2,84	0,12	0,14	0,12	0,14	0,13	0,13	95,4
Co	2,62	0,0	0,01	0,0	0,006	0,0	0,003	99,9
Cr	3,52	0,04	0,06	0,05	0,05	0,04	0,048	98,6
Mn	3,87	0,01	0,016	0,013	0,02	0,006	0,013	99,6
Fe	4,48	0,0	0,03	0,0	0,03	0,0	0,012	99,7
Pb	2,37	0,007	0,035	0,17	0,02	0,01	0,018	99,2

TABLE 8

THE PHYSICOCHEMICAL PROPERTIES OF ASH EXTRACT

Properties	Extract after the mixing, min						Heated in water, 60 min
	10	20	30	40	60	90	0,646
Optical density A,% ,λ=350nm	0,176	0,104	0,097	0,140	0,099	0,083	
λ=760nm	0,019	0,003	0,006	0,019	0,006	0,04	0,015
Electrical conductivity σ,mS	3,1	3,0	3,0	3,1	3,0	3,2	7,7
pH	9,9	9,9	9,5	9,6	9,6	9,6	9,9
Nitrates, mg/l	3,6	2,5	3,2	2,4	2,6	5,9	-
Nitrites, mg/l	0,15	0,34	0,25	0,18	0,20	0,32	-
Phosphates , mg/l	1,9	1,4	1,4	1,9	1,0	1,2	-

TABLE 9

THE METAL CONTENT IN THE WOOD ASH EXTRACT

Mixing	Cu		Co		Cr		Mn		Fe		Pb	
time, min	C, mg/l	C', mg/kg ash	C, mg/l	C', mg/kg ash	C, mg/l	C', mg/kg ash	C, mg/l	C', mg/kg ash	C mg/l	C', mg/kg ash	C, mg/l	C', mg/kg ash
10	0,077	1,54	0,032	0,65	0,223	4,46	0,012	0,24	0,058	1,16	0,018	0,37
20	0,072	1,44	0,033	0,66	0,256	5,13	0,007	0,14	0,007	0,14	0,018	0,36
30	0,113	2,27	0,053	1,06	0,259	5,17	0,018	0,37	0,003	0,06	0,018	0,36
40	0,096	1,92	0,046	0,92	0,368	7,36	0,025	0,49	0,00	0,00	0,021	0,41

IV DISCUSSION

From the literature data the properties of biomass ash are quite different, which means that each type of biomass, depending on the composition, growth conditions and possible burning regimes may have extensive property variation.

At the same time our experimental data show that the investigated wood ash density, friable weight, loss on ignition is possible properties within a fluctuation band: density range 1.7 to 1.9 g/cm^3 is also characterized by wood and other biomass ash.

Wood ash particles after screening were analyzed visually under a microscope and compared to paper and reed ash obtained in analogous burning conditions (Fig.1).

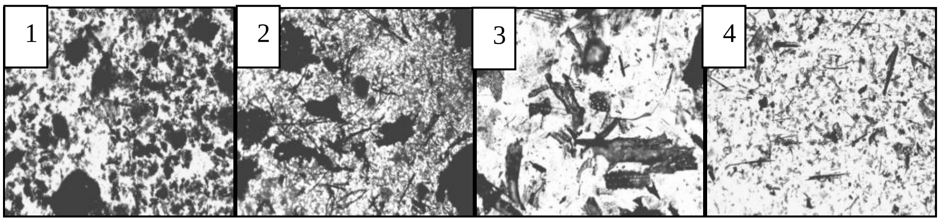

Figure1. Biomass ash under a microscope:1 - wood ash, 2- reed ash,3-paper ash, 4 - reed ash heated at 900 0C

The images show significant differences in the structure of the ash. Wood ash particles have finer shape close to spherical, stick together in clusters.Reed ashes contain the unburned plant cells, the paper ash has more fibrous particles structure. It can be concluded that wood ash must have larger specific free surface, which determines the activity of contact with other substances to be higher.The measured wood ash free surface S_f average 2.4 m$^{2/}$gis characterized by the ash of biomass and other fuels, for example the fly ash of coal and lignite ash have S_f between 2.01 to 5.4 m^2/g Typically, the ash specific free surface is independent of the flushing time of 10-90 min range (table 6). This means that washing itself without temperature changes practically does not change the pore structure.

Exposure to biomass ash activation can achieve much higher specific free surface values. Thus, as shown in the study [30], rice husk ash additional processing increases the specific surface of 119 m^2/g. Also, in our experiments ash samples, which were treated in hot water at 90^0C increased the specific surface area of up to 9.6 m^2 / g (see the table 6). Typically, the only heating without the presence of water up to 900 ^{0}C show that specific surface area remained at 2.2 m^2 / g range.

As already mentioned the soluble component content in ash in many cases determines their using potential areas and restrictions.

This is especially important for heavy metal migration ability in soil from ash. A dangerous situation is possible not only when the ashes are used for improvement of soil, but also in emergency situations. In Greece performed studies of mobile metal ions from the ashes spread of forest fires and their impact on soil and ground water quality [31,32]

Given that in the Latvia quite extensively are burned in spring last year's litter, this question arises in our environment also.

Therefore, in our investigation in ash extracts were determined concentrations of heavy metals

Experiments showed that in the water from ashes were extracted copper, cobalt, chromium, manganese, iron and lead. (Fig.2, Fig.3, Fig 4.) In solutions were did not found nickel and cadmium.

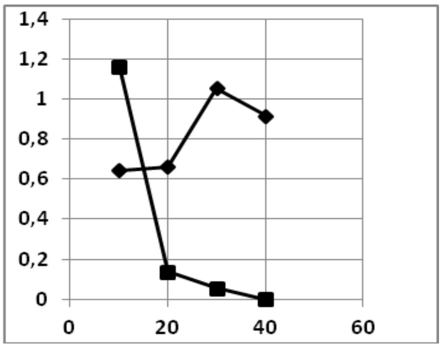

Figure 2. Cobalt and iron concentration C in the water changes depending on the ash flushing time t.

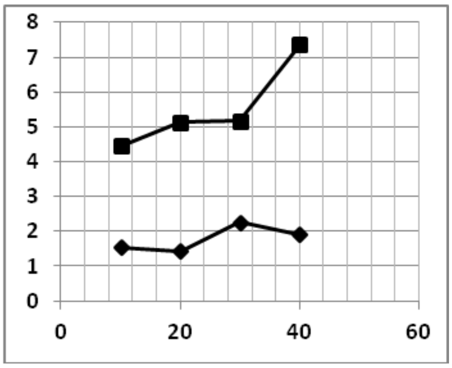

Figure 3. Chromium and copper concentration C in the water changes depending on the ash flushing time t.

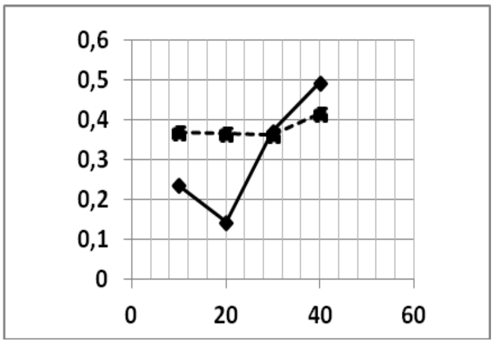

Figure4. Lead and manganese concentration C in the water changes depending on the ash flushing time t.

In filtrate, where the ashes were heated in at 90 ^{0}C, turned out to be significantly higher dissolved metal concentrations.

Thus, the copper concentration in the solution increased 1.27 times, the cobalt -1.73, chromium - 1.27, manganese-1.16, Iron-2.69 lead -1.9 times compared to the maximum concentration of extract at a temperature of 20^0C (Fig.5).

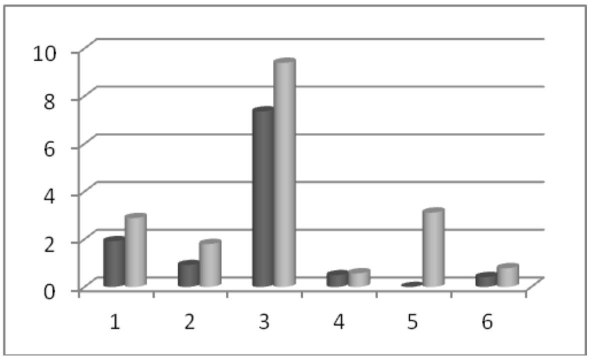

Figure 5. Metal concentration changes in water after heating to 90^0C in water compared with rinsing at T = 20^0C. 1 - copper, cobalt 2-3,4-chromium-manganese, 5 - iron, 6 – lead

In these circumstances the nickel (C = 0.06 mg / l) was found in solution also.

Substantial increasing all the dissolved elements concentrations in the hot water is also confirmed by the solution conductivity enlarging (2 times) and the optical density of high-frequency light wave range (3.7times) increasing.

In ash extracts were found phosphates, nitrates $NaNO_3$and nitrites $NaNO_2$.Nitrate concentration greater than nitrite concentrations between 13 and 24 times (see table 8.). Typically, the mixing time did not affect significantly the concentrations of the substance, and did not change the pH of the solution (9.7), the specific electrical conductivity (3 mS) and optical density. Ash adsorption capacity were investigated in all ash samples after washing - as a result of the ash were removed soluble components

Solution after the ash adsorption (table 9.) show that from the solution were adsorbed all metals. Extract metals constitute 95.4 to 99.9 percent. Parallel experiment showed that the ash flushing for at least 90 min did not give a significant change in the ash adsorption ability.

But the ashes, which were previously subjected to heating at a temperature of 900^0C per hour adsorption capacity increased with respect to all metals (Fig. 6).

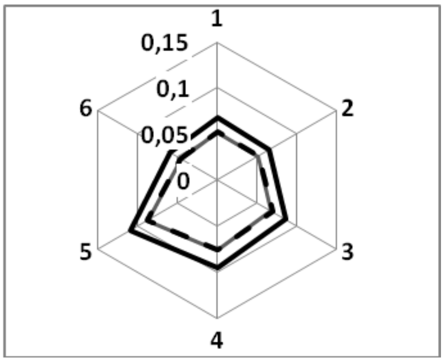

Figure 6. Ash adsorption capacity (mg / g) changes after heating at 900^0C (solid line) compared with rinsing at T = 20^0C (dotted line). 1 - copper, 2-cobalt,3 –chromium,4-manganese, 5 - iron, 6 – lead

The obtained experimental data were converted to ash adsorption capacity β - the adsorbed amount of metal per gram mass of ash.

Since on the ash surface in our case absorb all metals was calculated integral ash adsorption capacity for all six metals, which amounted to an average of 0.367 g of metal per 1 kilogram of ash (Fig7).

Note that the metal concentration in solution were relatively low and the total amount of adsorbed metal on ash did not reach maximum saturation. This means that the results

of adsorbent capacity are conditional, but they strongly characterize wood ash as perspective adsorbent.

Apart from the initial concentration of the elements in the experimental solution each metal adsorption capacity β ratio to the metal λ

$\lambda = \beta / C_M = 0{,}185$

This means that the degree of adsorption within the limits of the carried experiment data is constant and independent of the initial metal concentration

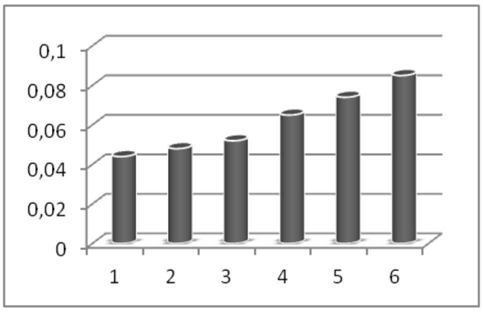

Figure 7. The average mass of the adsorbed metal by wood ash, mg / kg. 1 -lead,2-cobalt, 3-copper, 4-chromium, 5-manganese, 6-iron.

As was shown, ash specific free surface is relatively small in comparison with the specially designed adsorbent specific surface area. This means that despite the high adsorption capacity of the ash capacity is low. There is a need to continue research into the ash to increase the specific free surface and form a specific pore structure of the space optimally suitable physico-chemical adsorption smoothly

V CONCLUSIONS

Researched wood ash mechanical and physical properties specific free surface, metal content of wood ash in extracts, ash adsorption capacity in connection with metals.

It was found that wood ash density is in the range of 1.74 to 1.87 g/cm^3, porosity 68-72% in loose phase. It is concluded that even at relatively low - 2.2 -2.4 m^2 / g specific surface free of ash adsorption capacity to metals (Cu, Co, Cr, Mn, Fe, Pb) is quite high. In the experimental solution after adsorption metal concentrations decreased by 95-99%.

Part of metals in ash are in the soluble in water compounds. After stirring ash in water during10-90 min in the extracts were identified metals in concentrations comprised between 0,02 mg / l (Mn) up to 0.36 mg/l (Cr). Mixing time did not significantly increase concentrations of metals. The iron concentration in the extract even decreased to 0 after 90 minutes mixing time, which means that the iron changed in insoluble compounds. Cadmium and nickel were not found in the ash extracts. However, after heating the ash in water at 90^0C gives a significant increase in metal ion solutions - an average of 1.2 to 2.7 times. In addition, in the solution appears nickel.

This means that each kilogram of ash can give in the groundwater up to 2 mg Cu, 7 mg Cr, 1 mg Fe, less than 1mg - Pb, Mn, Co.

Experiments have shown that the ash specific free surface can be increased under pre-preparation, using physical effects to change the spatial pore structure and activate the particle surface adsorption capacity, such as when exposed to hot water.

It can be concluded that the ash is a perspective raw material for production adsorbents and their use have positive effect not only in the traditional farming areas, but is perspective in wastewater treatment technologies as well.

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Mining under Kalina and Selisoo Bogs

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***Abstract*. Continuous developing of Estonian power engineering on the basis of oil shale requires ever taking into use of new exploration fields. When the reserve of Estonia mine is depleted, mining of the exploration field of Seli has to be started. But that field is located under the Selisoo bog which is defined as a region of the Natura 2000 network and is planned become a nature preserve. Conservationists are interested for what extent oil shale mining under the Selisoo bog and in its immediate nearness will spoil the natural water regime of the bog. To clear up the environmental impact are carried through several investigations in the Selisoo bog. As a result of modeling is proposed a perceptible lowering of water table in peat layer.**

At the same time we have a positive experience on mining under bogs and water bodies, some kilometers to the north from the Selisoo bog. In Viru mine situated under the Kalina bog there is oil shale mining practically finished for today, but the Kalina bog exists as before, also the Lake Kalina in this bog.

The aim of this research is to compare the geological and hydrogeological parameters of the Selisoo and Kalina bogs, clearing up the essential factors owing to which the mining in district of the Selisoo bog could exert a larger influence on environment than under the Kalina bog. In this paper are some measures for diminishing of the environmental impact brought on.

***Keywords* – underground mining, bog, water level, precipitations, water-resistance.**

I INTRODUCTION

Observable Selisoo bog lies in Northeastern Estonia in oil shale area beside of working Estonia mine. About 10 km to the north is located the lake Kalina surrounded by a bog of the same name (Fig. 1). Under that bog the reserve is depleted already. In the Estonia mine mining activities are approaching the bog Selisoo to the west. But Selisoo is defined as a region of the Natura 2000 network**Error! Reference source not found.** and it is planned become a nature preserve [4][4]. The aim of intended nature preserve is to protect different birds and valuable natural habitats – humus alimentary lakes and lakelets, bogs and bog forests.

Therefore all measures to prevent or reduce to a minimum changes in the natural state of Selisoo need to be carefully considered. Above all it is essential that the present water conditions will not be spoiled and biotope of that place will remain.

The reserves of Seli exploration field are validated in 01.04.1998. Only in first block the productivity is over 35 GJ/m^2 what meets the requirements of proved resource. The area of proved reserve is 1964.20 ha. 248 ha of planned nature preserve remains above the Estonia mine.

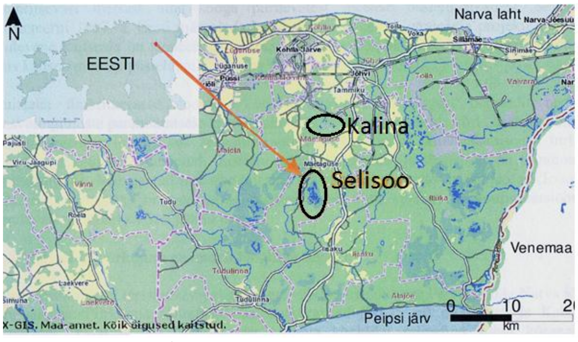

Fig. 1. Location of Kalina and Selisoo bogs [2].

II GEOLOGICAL CONDITIONS

For preservation of peatlands and water bodies in mined areas is essential the good water-resistance of sediments. In table I there is presented two geological cross-sections of observation wells in comparison [6][6]. The geology of sediments is investigated also just on shore of the Lake Kalina (borehole 1 in fig. 8) [7][7], where the thickness of little-decomposed peat was measured 1.72 m. Under peat was found 0.45 m of lake mud (gyttja) and 2.1 m clay with gravel and pebbles, containing 1 – 6 cm thick bands of sand. Sandy loam is laying in southern part of Lake Kalina, elsewhere is fine sand [7].

TABLE I
GEOLOGICAL CROSS-SECTIONS

Kalina			Selisoo		
85 0.5 km in the southeastern of the lake			233 0.8 km in the western of Selisoo		
Geol. index	Description of layer	Thick-ness, m	Geol. index	Description of layer	Thick-ness, m
QIV	Peat	3	gQIII	Sandy loam	4.5
lgQIII	Varigrained sand	1.5	O2-3nb	Fissured dolostone	9.6
O2jh-kl	Fissured dolostone	25	O2rk	Fissured dolostone	9.2
O2id	Compact limestone	7.87	O2on	Clayey limestone	3.3
O2kk	Dolostone	0.01	O2kl	Limestone	8.05
O2kk	argilliit	0.62	O2jh	Clayey limestone	10.45
O2kk	Dolomitic limestone	6.86	O2id	Clayey limestone	7.9
O2kk	Oil shale	5.53	O2kk	Oil shale	13.7
	Depth of oil shale	44.86		Depth of oil shale	53

The Quaternary cover under the Selisoo bog is 1 – 7 m thick; it is the thickest in the west of the bog above the esker of Mäetaguse and the thinnest in the northern part of bog [2].

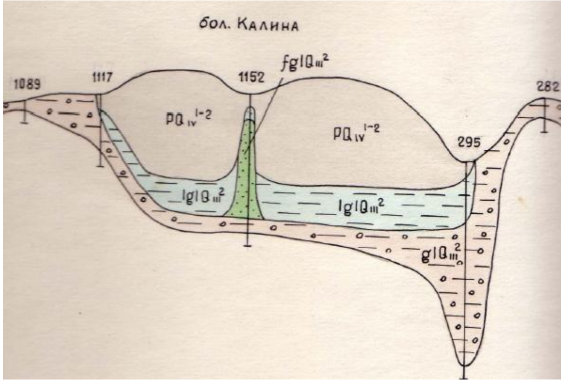

Fig. 2. Profile of Kalina bog, Quaternary deposits [13][13].

On the ground of figures 2 and 3 the both bogs are lying on a layer of silt, under what is till. Under Selisoo the silt contains 30% of pelite and 15% clay particle, which are not remarked under Kalina bog. A mound bounding the southeastern part of Selisoo is lying simply on bedrock and consists almost of pure sand, is dangerous because of large water permeability. By presence of gradient the ground water of Qaternary can move horizontally along more sandy layers in the direction of relief downfall [2].

A. Jointing

Fissured regions and crush belts are essentially facilitating the moving of water in rocks. About 5 km to the northeast from Selisoo is 50 km long and 0.5 – 2 km wide Ahtme crush belt and in the southeast 30 km long and 2 – 5 km wide Viivikonna crush belt [9]. The dislocation of Ahtme is about 800 m from Lake Kalina. The jointing belts of bedrock ranging along Mäetaguse and Metsküla eskers which width is about 150 m remain to the north from Selisoo [10]. In Viru mine the drainage of roof rocks has been largely influenced by an extensive karst belt ranging 420 m to the west of Lake Kalina along an entry on a scale of 250 m [12].

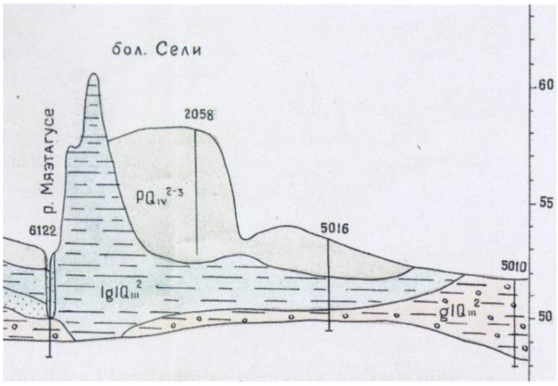

Fig. 3. Profile of Selisoo, Quaternary deposits [13].

III HYDROGEOLOGY

The Ordovician aquifer system immediately under the Quaternary deposits is formed by varying layers of limestone and dolomite. As a rule their hydraulic conductivities are irregular areally and also in profile. Joint belts spreading laterally are mostly 1 – 2 m thick [30][30]. Jointing and karst decrease with depth. The filtration rate of upper 20 m is 10 – 50 m/d, in depth of 20 – 50 m mostly 5 – 8 m/d and in depth of 50 – 100 m only 1 – 2 m/d [11][8]. Water flows downwards along vertical joints. The drain from workings neighboring karst forms 20 – 25% of whole drain [28]. In case of rare occurrence of joints we can consider filtration rate of limestones 1*10^{-3} m/d.

Nabala-Rakvere aquifer is separated from Keila-Kukruse aquifer by Oandu local aquitard consisting of clayey limestones and marl [14] (Fig. 4).

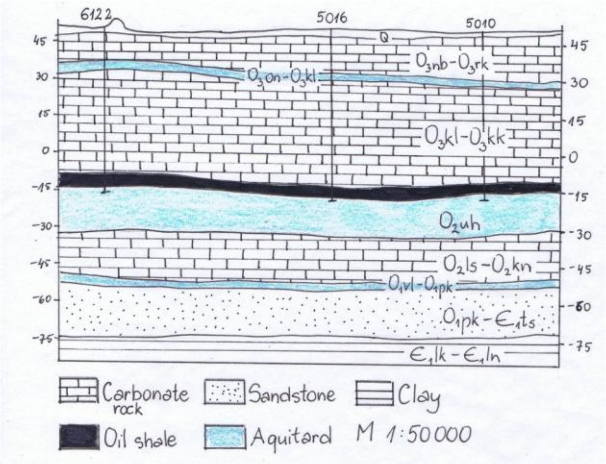

Fig. 4. Profile of Selisoo , bedrock.

Nabala-Rakvere aquifer is absent under Kalina bog. There are existing Keila-Jõhvi and Idavere-Kukruse aquifers separated from each other with bands of metabentonites [15] Local aquitard in upper part of Idavere stage can consist up to 11 metabentonite bands with thickness of 1 – 5 cm [16]. Relatively water-resistant interlayers are found also in aquifers. Practice shows that in limestone above mine is water and there is possible to ground also wells [2]. It is possible, if from sides flows enough water and at the same time vertical drain is small.

IV HYDROLOGY OF PEAT LANDS

In mires there are natural conditions for gathering and preservation of water. Both Kalina and Selisoo bog have under peat layers a mineral bottom of concave shape what has caused formation of wetland. The water of peat deposit has free surface, its depth of bedding is 0.2–0.5 m from ground in natural conditions and 1.0–1.5 m in dewatered areas. The range of water table changes yearly 0.2–0.5 m [8]. Fens feed on ground water, bogs on precipitations.

B. Kalina Bog

The area of Kalina bog is 2819 ha, from which peat extraction area covers 1239 ha [17]. Peat is produced from year 1963 to 1991. The area of abandoned peat extraction area is 107.50 ha at present [3]. The table of surface water was in October 2006 in average 1 m [3] in drainage ditches below ground surface. In autumn 2011the water table reached ground surface (Fig. 5).

Little-decomposed peat of abandoned peat extraction area has the medium thickness 0.9 m and the medium decomposition rate 17 %, well decomposed peat accordingly 1.0 m and 26 % [17]. The layer of lake mud is found on 23.8 ha in surroundings of Lake Kalina. Its thickness is about 0.5 m. Under the influence of draining in the middle part of mire the bog with stunted pines is replaced with pine bog. In places there is found hollows and treeless bog. In the northeastern part of mire water table has lowered owing to oil shale mining [8].

Fig. 5. Abandoned peat extraction field in Kalina bog (photo of J. Olikainen 2011).

C. Selisoo Bog

The area is located on slope of Jõhvi upland what is favoring the pouring of water towards the mire. The esker of Mäetaguse bounding the mire from west and on southeastern boundary located bank are hindering the runoff of water and are very essential from the standpoint of development of mire [2].

The area of bog is 2051 ha, from what eutrophic mire covers 734 ha, mesotrophic mire 359 ha and mire 958 ha [4][24]. It is typical mire with a convex surface and very rich of bog-pools. Fen is located mostly in the northern part of the mire [8], transition bog in the eastern part.

People have influenced Selisoo by drainage ditches grounded in years 1950. – 1970. Whole mire of Selisoo is bordered with ditches and fen and transition bog are practically dewatered in the whole extent [2]. In marginal areas of Selisoo the water table is in average 1 m from ground surface [5].

At present, the state of Selisoo is near to the natural. Resting upon observation of this autumn wood drainage ditches are grown over with peat moss in extent of 70% and therefore the water runoff in ditches is minimal or absent at all. Also, the former small peat harvesting fields are grown over. The water table is at a depth of 0.1 – 0.2 m in the whole area of abandoned peat fields what has created optimal conditions for regeneration of peat [25][25].

The maximum thickness of peat is 6.5 m in the mire, mesotrophical and fen peat at the outskirts is 1.0 m thick in average [8]. Filtration rates of peat of Selisoo are measured in two peat profiles $0.1 – 1*10^{-4}$ m/d [5]. In the north and middle part there is a sporadic deposit of lake mud (gyttja) which serves as a moderate aquitard [11].

In spring the largest[8] runoff was in the northern part of Selisoo and the smallest in the western part [2]. In fall runoff from the southern part exceeded the runoff from the northern part quite essentially. We can say that discharge in southern ditches is more influenced by precipitation than in northern ditches. Northern ditches gather their water rather from forest and get supplement also from groundwater what adds the stability to discharge**Error! Reference source not found.**.

D. Precipitations

The increase of amount of precipitation induces the rise of water level and herewith larger vaporization and runoff [18]. In years rich of water the surface of bog can rise 10 – 15 cm [19]. The arching of bog surface betters runoff and stops its further rise. By deep water level the runoff practically is absent. In the time of drought water level sinks the less the deeper it is. The preservation of bogs through the millenniums, as in the time of favorable as unfavorable climate periods give evidence of reliability of these natural systems. In case of sufficient amount of moisture peat mosses are accumulators of water consisting water over 90 % of their mass. As in Estonia the amount of precipitations exceeds vaporization the mires areas would expand also nowadays. For preventing it there are digged border ditches in mires [18][18].

We have about 650 – 750 mm precipitations yearly in Estonia and 470 – 480 mm vaporization. 250 – 270 mm flows away by rivers. In clayey areas the existence of plentiful nutrient salts prevents the expanding of bogs. The best conditions for formation of bogs are in areas where on clays lying sand layer prevents and unifies runoff of water. The evaporation ability of bogs is 20 – 25 mm yearly smaller than in fens.

The natural moisture content of well decomposed peat can be 500 % and for weakly decomposed peat 3000 % [20][20]. A rise or fall in water level of 10 mm is equivalent to a water gain or loss of 1 mm [21].

Evaporation measurements showed that the average summer daily evaporation above mire vegetation was about 1.5 mm. It is about 3 times less than from a mineral soil with non-limiting soil moisture content [21].

In periods abounding on water a part of hollows will form to pools [18]. In waterless climate periods a part of pool have begun to grow over. The water permeability of bog was in depth of 1.5 m 10 times and in depth of 1.0 3.3 times smaller than in depth of 0.5 m [22][22]. Only the first 10 cm of peat are able to drain off big amounts of water accompanied with rainfalls.

E. Water Conductivity of Peat

The higher is the degree of decomposition the smaller is its water conductivity. It depends also on compressibility and type of peat. In case of equal degree of decomposition the permeability of bog peats is 35 times smaller than fen peats [23]. In saturated peat difficulties between horizontal and vertical water conductivity are usually small. The results of water conductivity experiments showed that the main part of water exchange is taking place in extent of 1.5 m of upper part of peat.

F. Mines Influence

In natural conditions the range of yearly water level is up to 2 m, in spoiled conditions 8 m and yet more [1]. Very great amount of snow melting water reaches from ground surface by means of shafts, technical bore holes and karst joints right into mine [6]. About 90 – 96% of mine water comes via roofs. The coefficients of storage are dependently of season 3.2 – 63.2 m^3/t in lower northern mines and 2.6 – 7 m^3/t in deeper southern mines [15].

In figure 6 are represented hydroisohypses of upper Nabala-Rakvere aquifer before oil shale mining. The natural water level is the highest on Ahtme uplift and lowers in the direction of Lake Peipus. In figure 7 are represented hydroisohypses of same area when Ahtme, Viru and Estonia mines were working already. The water level of Nabala-Rakvere aquifer has lowered about 10 m, Keila-Kukruse 20 – 25 m and Lasnamä-Kunda 35 m. During 6 years the water table has raised in closed Ahtme mine 21.5 m.

The bale up of mine water influences above all the aquifer lying immediately on exploitation seam and the aquifer lying about 15 m deeper from it. In consequence of mining the pressure level of Ordovician–Cambrian water complex has also lowered about 20 m [14].

In the district of the Estonia mine, the radius of drawdown cone is 6 – 7 m, at the same time in Nabala-Rakvere aquifer only 1 km. The radius of drawdown cone in Lasnamäe-Kunda aquifer is 25 km [2].

Several groundwater observation wells (Fig. 9; 10) show that the water tables in Nabala-Rakvere aquifer remained stable in observing wells of Sõrumäe and Metsküla. In wells 5500 and 5504 located in the Estonia mining district the free surface of Nabala-Rakvere aquifer has lowered from year 1972 to1986 accordingly 10 and 7 m. In wells of Kalina water table has also lowered about 10 m.

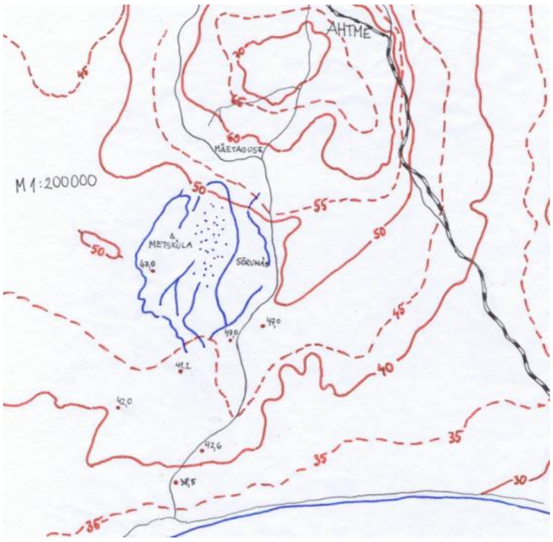

Fig. 6. The hydroisohypses of Nabala-Rakvere aquifer in 1961 [13].

Fig. 7. Hydroisohypses in year 1987 [26]. Green line – Nabala-Rakvere aquifer, blue line – Keila-Kukruse aquifer, red line – Lasnamäe-Kunda aquifer.

G. Investigations in surroundings of Lake Kalina

Research (05.1982-04.1985 a.) ascertained that water levels in Keila-Jõhvi and Keila-Idavere aquifers were lowered in comparison with static level 10 and 20 m [12]. Consequently the detachment of Quaternary aquifer from bedrock's aquifer was 10 – 25 m. Lake water can infiltrate to bedrock through the Quaternary deposits. Clear signs of leaking of mire or lake water into mine are heightened moisture, smell of hydrogen sulphide, heightened oxidation and content of NH4+ion, what was observed in entries opening the karst zone about a half kilometer away from the lake. Runoff was found as from horizontal as vertical joints and under the anchors. Discharges of runoff were 0.04 – 0.14 m^3 per hour. Measuring of lake water levels since May 1982 till August 1983 showed that the volume of lake (40000 m^3) practically didn't change. It was in 1969 the same.

Observations began again in March-April 1995 when mining operations were approached to the lake at the distance of 70 – 80 m [7]. During 11 years water level of the lake had risen 20 – 30 cm, water level of Keila-Kukruse aquifer remained practically changeless and water level of Idavere-Kukruse lowered 15 m.

In space of time 03.95 – 07.96 when excavating took place directly under the lake, only seasonal fluctuations of water tables were ascertained.

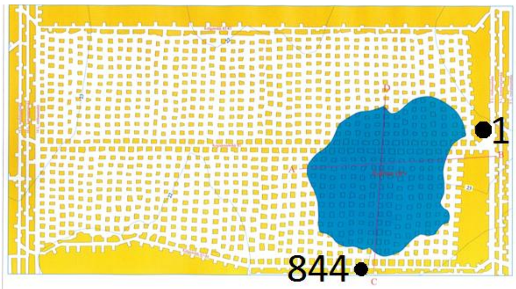

Fig. 8. Lake Kalina and the pillars in underground area.

When about a quarter of area under lake was excavated, an observation was carried through at 05.12.95 in the mine. The roof under lake was practically dry except some few moist places. Water appearance was noticed in the anomalous fissured part of an entry. From a passing energy borehole nr 844 (Fig. 8) located 35 m in the southwest of the lake the water was flowing in 4 trickles with total discharge of 0.2 l/s.

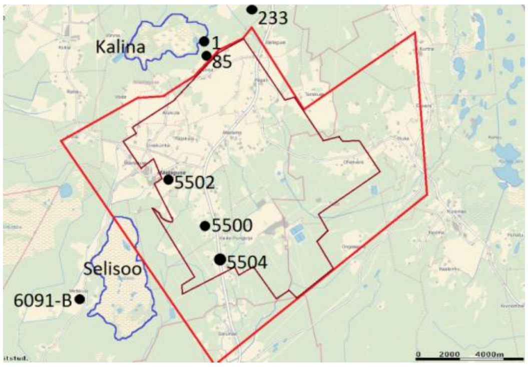

Fig. 9. The claim and depleted area of Estonia mine. Observation wells.

V RESULTS

The influence of mining on mires water regime depends on horizontal and vertical water conductivity of limestone of the region. In surroundings of Selisoo upper Nabala-Rakvere aquifer ought to have been preserved by Oandu aquitard which water conductivity is very small - 10^{-5} m/d [30]. According to other data water conductivity of this aquitard is 0.0003 – 0.0004 m/d [2]. Nobody has specially determined water conductivities of bedrock limestone for this research.

Existing data are very different. It is not possible to determine equable water conductivity for a layer because it varies areally and also in profile.

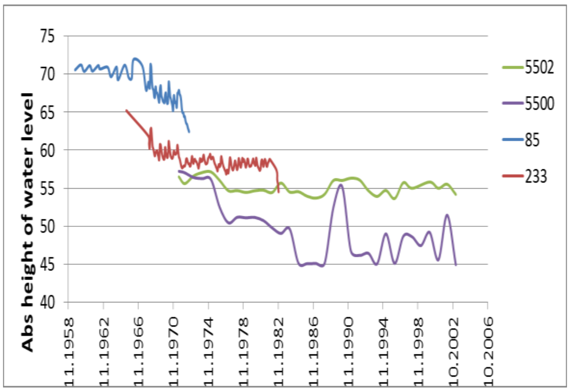

Fig. 10. Water levels in observation wells.

On the ground of data of observation wells the water table in the area of Estonia mine has lowered in upper aquifer up to 10 m. Similarly water level has lowered also in Kalina (figure).

Quaternary sediments are also not absolutely impermeable. The medial filtration rate in Selisoo is 0.39 m/d, whereas filtration rate of silt was $1*10^{-3}$ m/d and of sediments with higher clay containing $2*10^{-4}$ m/d [2]. In Kalina bog the medial filtration rate of Quaternary sediments was 1.4 m/d. Medial thickness of peat was 4.5 m in Selisoo and only 2.5 m in Kalina bog. The degree of decomposition of Kalina peat is a little higher [8]. In sum we can say that these bogs are similar by their geological conditions.

In 2012 hydrogeological modeling was carried through on an area of 16×27 km what covers Ratva bog, Selisoo and Estonia mine [5][5]. In the model there was used following filtration rates (table II). Water conductivities of carbonate rocks were partly determinated by means of fitting into working model.

TABLE II

FILTRATION RATES

Layer	Thickness, m	Vertical filtration rate, m/d	Horizontal filtration rate, m/d
Peat	1	0.01	0.1
Peat	up to 3.4	0.001	0.03
Peat	up to 2.2	0.0002	0.0007
Mineral soil		0.001 – 0.0005	
Nabala-Rakvere	25	0.005	40
Oandu	2.5 – 3.5	0.0003 – 0.0004	
Keila-Kukruse	45	0.01	1.2 - 7

For checking the trustworthiness of the model, calculated water tables were compared with levels measured in observation wells. If the difference was below 2 m, the result was considered good. In consequence of modeling was found out that in case of widening of Estonia mine under Selisoo water level in peat layer would lower more than 2 m, above all in southern part. Therefore an aquitard of clay or peat with water conductivity not higher than $1*10^{-5}$ m/d was considered an essential assumption. But netoinfiltration 200 mm yearly will also preserve the water level in conditions of maximal mining [5].

Also department of mining of TUT has made calculations about water level lowering in Selisoo [29]. On the ground of these results the water level in Selisoo would not lower during first 4 years after beginning of mining. Only the runoff by ditches will decrease. The depression cone ought to shape up within about 14 years. After this time the water table in bog has lowered by 70 cm.

VI CONCLUSIONS

The investigations have shown that an absolute water-resistance in case of underground mining is not possible to gain. In Estonian oil shale area the water-resistance of Quaternary and peat deposits is more essential than water-resistance of limestone. Lake Kalina is isolated from bedrock in addition to mineral sediments with a layer of gyttja up to 0.5 m thick. The filtration rate is predictably in size of $1*10^{-5}$ m/d [2]. Nevertheless nobody has determined exactly the water conductivity of that material. It is known that the layer of gyttja does not extend under the whole Kalina bog [3][17].

As regards the model there is considered the time factor not at all what makes the result quite questionable. Unfortunately whatever calculations about so large and variable geological massif are inexact. Better is to take into consideration practical experiences. Lake Kalina and the bog are preserved in spite of total underground mining (figure). Although the water level in border ditches is low, in bog there is found enough free water (Fig. 5). On the ground of investigations of year 1995 it is known that water was flowing into working 0.2 l/s. It makes 6307 m^3 yearly, as a result of which the lake had to be after 6 years practically empty. It is not happened owing to reliability of bogs in our climate where precipitations exceed vaporization. It is possible to increase the netoinfiltration in place of runoff.

Consequently the mining under Selisoo is possible without spoiling the water regime in bog in substance. It is needful to prevent peat water decrease by building dams before draining ditches. Water table fluctuations need to be followed and runoff in ditches measured. When building of ventilation roads and boring holes it is necessary to use only constructions isolating groundwater layers. Electricity and other communications have to be taken into mine underground. It is needful to avoid fissured and karstified zones at establishing of workings.

VII ACKNOWLEDGMENTS

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Paste Fills Technology in Condition of Estonian Oil Shale Mine

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Abstract. **Oil shale mining and processing industry in Estonia produce a wide assortment of waste could be considered as available fill materials. Waste rock which is not usable in civil engineering and road building may be used for backfilling underground mines. Paste fills technology, which has several benefits, requires careful selection of oil shale waste rock aggregates and other carbonate stones. The laboratory tests and theoretical investigations were made for determination the applicability of limestone and dolostone aggregates as backfill material. It enables to determine the feasible parameters of aggregates from oil shale mining waste rock. Analysis showed that limestone aggregates of Estonian oil shale mines suit best for backfill technology in conditions.**

Keywords – **oil shale industry, backfill technology, paste fill, fill materials, limestone and dolostone aggregate, geometrical parameters of aggregates.**

I INTRODUCTION

The oil shale industry of Estonia provides a significant contribution to the country's economy, but causes a large number of different problems [15][16]. Oil shale is used as a fuel for producing energy and shale oil [10][20][16]. The mining sector faces challenges to increase the output of mines and at the same time to minimize the environmental impact of mining [16]. Limestone and dolostone companies, where material is excavated by blasting and crushing technology, are in need of fillers distribution also.

Underground oil shale mining is performed by using a room-and-pillar method with blasting [11][16][17][18]. It is cheap, highly productive and easily mechanized. Unfortunately, if the depth of excavation is over 60 m (mine Estonia) the loss in pillars increases up to 40% [19]. On the other hand, there are problems of use or bury the waste in landfill due to large amount of neutral (limestone) and hazardous (ash) waste generated by oil shale industry [9] [12]. A complex approach is needed for solving the above mentioned problems. Backfill technology would have a significant impact on the mining practice in Estonian oil shale industry [8] [9][14][18][35] .

Backfilling in mining operations is in wide use in all over the world. Nowadays attention has been focused on the use of combustion and mining by-products as filling materials. Separation of limestone from the raw oil shale generates large amount of waste, which proportion is approximately 40%.

Waste rock which is not usable in civil engineering and road building may be used for backfilling already mined areas [29].

In modern backfill technologies paste fills are preferred [4]. It requires careful selection of fill materials, including limestone aggregates. Past fills method has several benefits, most of them are crucial for the usefulness of backfill technology. On the same time there is lack in data characterizing the above mentioned waste filling materials. The choice of a proper backfill material is essential in the control of fill costs and backfill properties after placement. The main aim of these investigations was to determine the applicability of waste rock aggregates as backfill material in condition of Estonian oil shale mines.

II GEOLOGICAL SITUATION

The Estonian oil shale deposit is located in the north-eastern part of the country. The oil shale bed has a form of a flat bed slightly inclined (2 – 3 m per km) southward. The commercial oil shale bed and its immediate roof consist of oil shale and limestone seams [15][26]. The main roof consists of carbonate rocks of varying thickness. Characteristics of the individual oil shale and limestone seams are rather different. The strength of the rocks increases southward. The underground mining works are going at deepness 35-65 m, but at the southern border of deposit mining deepness will grow up to 120-130 m, notable increases overburden and its pressure to pillars [8][11][16]. The thickness of commercial oil shale seam is about 2.8 m. The waste rock separated from run of mine, which proportion is approximately 40%, is suitable for production of construction and backfill material [13].

Limestone companies are mostly located in Harjumaa County. It is in the northwestern Estonia, on the southern shore of the Finnish Gulf, about 80km to south from Helsinki, Finland. Geologically this area belongs to the southern slope of the Fennoscandian shield, where the Precambrian Early Proterozoic crystalline rocks of age 2.0-1.3Ga are covered by sequence of the Ediacaran and Paleozoic sedimentary rocks with age between 600Ma and 359Ma in Estonia [2]. In the Harjumaa County there are being registered 16 carbonate stone deposits, four of them:

Vasalemma, Harku, Nabala, and Väo are listed as deposits of all-country importance [21].

III BACKFILL TECHNOLOGY

In Estonian oil shale industry a wide assortment of fill materials is available [6][7]. The whole processing of oil shale from mining up to energy and oil generates large amount of different waste:

Separation of limestone from the raw oil shale generates large amounts of waste, which consists in 82...94 % of limestone and 6...18 % of oil shale residues. These are stockpiled in form of cones (55 m height) and total area of these piles is about 3.5 km2. Limestone production is about 6.5 Mt per year.

1. The Estonian Thermal Power Plants use two different oil shale combustion technologies: pulverized firing (PF) and circulating fluidized bed combustion (CFBC) technology. The compositional and morphological variation between PF and CFBC ashes [3] are principally controlled by firing temperature differences between combustion technologies, and by grain size difference of oil shale fuel. From the point of chemistry ash from oil shale combustion is very similar to cement (with exception in alkalinity) and there is no significant difference between the potential environmental impacts from the side of oil shale ash. About 4 km2 of the landfill are occupied with ash ponds. Annual production is about 5 Mt. The determination of different ashes parameters demands supplementary investigations and is under construction.
2. In modern backfill technologies paste fills are preferred [4][5]. It requires carefully selected grain-size distribution of solid particles and is able to flow without sedimentation in pipes by low water content (10...30 %). In this case backfill slurry has several benefits:

Mixtures are able to set with lower or without presence of additional binders.

Shorter binding times and better mechanical properties.

Drainage and processing of bleed water eliminated.

Consequently, at a first approximation the limestone aggregates properties determine the behavior of backfill. Oil shale waste rock (limestone) is produced during extraction as reject material from separation plant and material from crushing and sizing operations in aggregate production. It became clear that production of aggregate produces large amount of non-commercial aggregate [13].

IV GEOMETRICAL PARAMETERS OF AGGREGATES

The porosity of fill material consists of the void spaces between solid fragments. If the fragments are solid spheres of equal diameters the cubic and rhombohedral pacing is possible (see Fig. 1) [1].

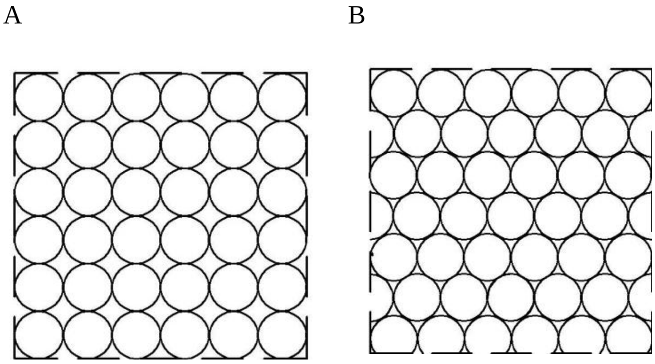

Fig. 1. Packing of the solid fragments [1], A – cubic packing; B – rhombohedal packing

These two configurations represent the extremes of porosity for arrangements of equidimensional sphere with each sphere touching all neighboring spheres. The porosity of well-rounded backfill materials, which have been sorted so that they are all about the same size, is independent of the particle size and falls in the range of about 25.95% to 47.65%, depending upon the packing [1]. If a backfill contains a mixture of grain sizes, the porosity will be lowered. In this case the smaller particles can fill the void spaces between the larger ones. The wider the range of grain sizes, the lower the resulting porosity.

In addition to grain-size sorting, the porosity of material is affected by the shape of the grains [1]. Well-rounded grains may be almost perfect spheres, but many grains are very irregular. Sphere-shaped grains will pack more tightly and have less porosity than particles of other shapes. The orientation of the particles, if they are not spheres, also influence porosity.

This phenomenon determines the bearing capacity of backfill/pillar. Conformation of getting theoretical result demands supplementary investigations of in situ conditions.

A. Uniformity Coefficient

The uniformity coefficient of a material is a measure of how well or poorly sorted it is. It is presented by following formula[1]:

$$C_u = d_{60} / d_{10} \tag{1}$$

where C_u – uniformity coefficient; d_{60} – grain size that is 60% finer by weight; d_{10} – the grain size that is 10% finer by weight.

A sample with a uniformity coefficient less than 4 is well sorted, if it is more than 6 it is poorly sorted [1].

The grain-size distribution curve and uniformity coefficients for aggregate sizes 4/16, 16/32 and 32/63 mm have been determined. Fig. 2 demonstrates the grain-size distribution curve for aggregate size 16/32 mm, mine Estonia.

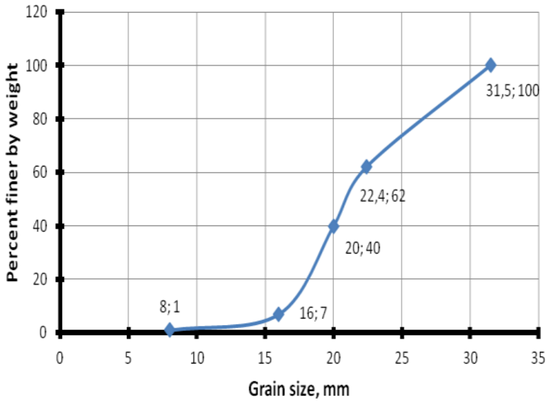

Fig. 2. Grain-size distribution curve. Aggregate size 16/32 mm, mine Estonia

Investigation showed that uniformity coefficient for all aggregate sizes is less than 4. For limestone and dolostone uniformity coefficient is less than 3. Consequently, the above mentioned aggregates are well sorted and they satisfy the paste fills requirement.

B. Shape of the Coarse Aggregate

Flakiness Index is the percentage by weight of particles in it, whose least dimension is less than 0.6 of its mean dimension. Flaky particles may have adverse effect on concrete mix. For instance, flaky particles tend to lower the workability of concrete mix which may impair the long-term durability. The results of flakiness index investigation in Estonian oil shale mines and open casts are presented in Table 5.

TABLE 5

FLAKINESS INDEX OF WASTE ROCK AGGREGATE

Aggregate size, mm	Flakiness index Fl (average), %			
	Mine Estonia	Open cast Aidu	Tondi-Väo limestone deposit	Kareda dolostone deposit
4/16	9	6	11	5*
16/32	6	3	7	4
32/63	4	2	10	10

*produced and tested aggregate 8/16 mm

Investigation showed that the flakiness index depends on aggregate size for limestone aggregates of Estonian oil shale mines. If the aggregate size increases, the flakiness index decreases. In general, the flakiness index of produced aggregates does not exceed 35% and that depends on type of crushers and number of crushing stages [12]. If the flakiness index is less than 50% the negative influence on the strength parameters of backfill is negligible.

V AGGREGATE PARAMETERS FOR BACKFILLING

A complex method, including laboratory tests and theoretical investigations, were made for determination of the applicability of limestone aggregates as backfill material. The results of investigations are presented in Table 6.

TABLE 6

OIL SHALE WASTE ROCK (AGGREGATES) PARAMETERS

Parameter	Measured values	Recommended values
Porosity of fill material, %	40 - 50	26 -48
Uniformity coefficient	1 - 2	<4, well sorted
Flakiness index, %	2 - 11	<35

In conclusion, it is visible that the aggregates from oil shale mining waste rock can be used as a material for backfilling the underground mined area. As long as Estonian oil shale mines are located near to the backfill required areas, other aggregates of limestone and dolostone not suitable because of the location.

VI RESULTS

In Estonian oil shale industry a wide assortment of fill materials is available. In modern backfill technologies paste fills are preferred. It required careful selection of limestone aggregates as a component part in fill mixture and is able to flow without sedimentation in pipes by low water content. The general parameters for paste fills technology are porosity, uniformity coefficient and shape of coarse aggregate. Getting results based on large amount of theoretical investigations and of in situ experiments.

Porosity of fill material determines the amount of power plant ash in mixture. Theoretically it is between 26 and 48% depending on packing of the solid fragments. In real conditions, the fill material contains a mixture of different grain sizes and shapes. Investigation of in situ conditions showed that it is in range of 40 – 50%, which guarantees optimum amount of ash in mixture.

Strength parameters of backfill are determined by uniformity coefficient of aggregates. It is calculated, using grain-size distribution curve. Investigation showed that uniformity coefficient is less than 4. Consequently, all the aggregates are well sorted.

Shape of coarse aggregate influences on long term durability of mixture and it is presented by flakiness index. Laboratory tests showed that flakiness index for all aggregate sizes is up to 11. If the flakiness index is less than 35%, the negative influence on the strength parameters of backfill is negligible.

Analysis showed that limestone aggregates suit best for backfill technology in conditions of Estonian oil shale mines. Usable investigation methods and getting results are applicable for different aggregates as a component part in fill mixture.

VII ACKNOWLEDGEMENTS

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Evaluation of Biomass Briquetting Mechanism

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***Abstract*. The main task of this investigation is evaluation of patented (LV 14604 B) biomass briquetting mechanism. Theoretical relationship between necessary drive force and resistance force during pressing in die was determined.**

Briquettes from grinded common reed (*Phragmites Australis*) or common reed – peat mixture were produced with designed experimental briquetting press. Density of common reed briquettes depending on the size of particles was stated. Density of briquettes obtained during compacting was from 826.3±16.4 to 934.5±35.1 kg m^{-3}. The minimum of density 826.3±16.4 kg m^{-3} had briquettes with particles from 6 mm grinding screen, but maximum density 934.5±35.1 kg m^{-3} had briquettes, when particles from 1.5 mm grinding screen had been used. Compositions of reed particles with peat allow obtaining briquettes density > 1000 kg m^{-3} if peat proportion in mixture is 30%.

Results of theoretical and experimental investigation show that the designed pressing mechanism can be recommended for mobile biomass briquetter design.

***Keywords* – briquetting mechanisms, common reed briquetting.**

I INTRODUCTION

Firewood, agricultural straws, and energy crops are the most prominent biomass energy sources. In Latvia, approximately 14.6% [1] of unfarmed agricultural land can be used for herbaceous energy crop growing.

Herbaceous energy crops would be the main basis for solid biofuel production in agricultural ecosystem in future.

Herbaceous energy crops – reed canary grass (*Phalaris arundinacea*) and hemp (*Cannabis sativa*) are grown in recent years. Beside that there is possibility to utilize for bioenergy production natural biomass of common reeds overgrowing shorelines of Latvian more than 2000 lakes.

The major limitation of using biomass for energy purposes is it low bulk density, typically ranging from 80 to 150 kg m^{-3} for straw material. Therefore compacting of biomass is important process for effective handling, transport and storage of this fuel material. Low bulk density also makes difficulties in feeding the fuel into the boiler and reduces burning efficiencies.

Peat can be used as additive for manufacturing of solid biofuel, because it improves density, durability of stalk material briquettes (pellets) and avoid corrosion of boilers. More than 230 million tons of peat is available for biofuel production in Latvia.

The aim of this paper is theoretical and experimental evaluation of patented (LV 14604 B) briquetting mechanism. Typical compacting equipment’s are classified into the following categories based on their working principles: piston press, screw press, roller press and pelletizer. In this investigation is presented piston press with rhomb mechanism drive.

The presented rhomb mechanism can be used where overcome of large resistance with a small driving force is necessary.

II MATERIALS AND METHODS

Relationship between necessary drive force and resistance force during pressing in die was expressed using virtual work theory [2]. Scheme of rhomb mechanism is shown in Fig. 1.

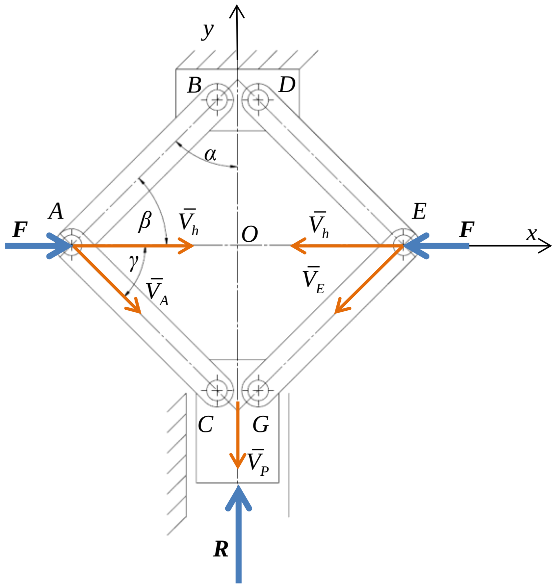

Fig. 1. Scheme of briquetting mechanism

Notes: *AB*, *DE*, *EG*, *AC* – links of mechanism; α – angle between mechanism link and y-axis; *β* – angle between mechanism link and *x*-axis; *γ* – angle between velocity vectors $\bar{V}_A$ and $\bar{V}_h$; $\bar{V}_A$ – velocity vector of point *A*; $\bar{V}_E$ – velocity vector of point *E*; $\bar{V}_h$ – velocity vector of hydraulic cylinder displacement; $\bar{V}_P$ – velocity vector of mechanism piston; *F* – drive force; *R* – reaction force in pressing die.

For reaction force *R* calculation power equation can be used

$$F\,\bar{V}_h = R\,\bar{V}_P . \qquad (1)$$

Mathematical relationship between velocity vectors is

$$\bar{V}_h = \bar{V}_A \cos\gamma + \bar{V}_E \sin\gamma; \tag{2}$$

$$\bar{V}_P = 2\bar{V}_A \sin\gamma = 2\bar{V}_E \sin\gamma. \tag{3}$$

From equation (3) expressed $\bar{V}_A$ and $\bar{V}_E$

$$\bar{V}_A = \frac{\bar{V}_P}{2\sin\gamma}; \; \bar{V}_E = \frac{\bar{V}_P}{2\sin\gamma}. \tag{4}$$

Replacing $\bar{V}_A$ and $\bar{V}_E$ in equation (2)

$$\bar{V}_h = \frac{\cos\gamma\, \bar{V}_P}{2\sin\gamma} + \frac{\cos\gamma\, \bar{V}_P}{2\sin\gamma} = \frac{\bar{V}_P}{\tan\gamma}. \tag{5}$$

From equation (1) unknown reaction force in briquetting die

$$R = \frac{F\, \bar{V}_h}{\bar{V}_P} = \frac{F\, \bar{V}_P}{\bar{V}_P\, \tan\gamma} = \frac{F}{\tan\gamma}. \tag{6}$$

Experimental briquetting press is shown in Fig. 2.

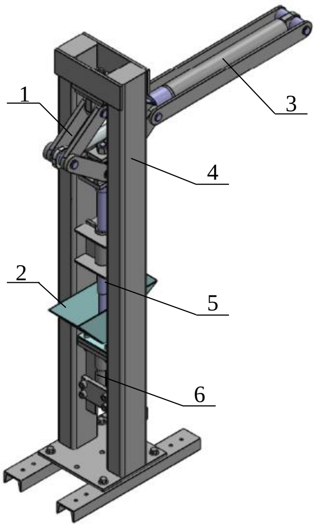

Fig. 2. Briquetting press
Notes: 1 – pressing mechanism; 2 – container; 3 – hydraulic cylinder; 4 – frame; 5 – pressing piston; 6 – pressing die.

Pressing mechanism (1) links size are 200 mm. Pressing die diameter 25 mm. Piston stroke 175 mm. With experimental briquetting press briquettes were made continuously in conical die. For pressing mechanism drive hydraulic cylinder with piston diameter 60 mm was used.

During briquetting experiments hydraulic pressure was measured with calibrated pressure sensor. For data collection was used *Pico Data Logger* and computer.

For briquetting experiments grinded common reeds was used. Grinding of common reed was realized with hammer mill using four different screen opening sizes 1.5, 6, 12 and 20 mm.

With aim to increase the density and mechanical durability of briquettes, common reed and peat mixtures was used. Peat proportion in mixture was 15, 30 and 50%.

Moisture of experimental material was less than 10%. The moisture content was determined according the standard BS EN 14774-2:2009, where oven drying of the samples was carried out at 105±2 ºC [3].

The briquettes with different density had been obtained as result. Briquette density was determined from the ratio of the mass to the volume of the briquette. The weight of briquette was measured on electronic scales Sartorius GM312 with division 0.01 g and size of briquettes was measured with sliding calipers (division 0.1 mm).

European countries have standards (ŌNORM 7135, SS 18 71 20 and DIN 5173 [4, 5] concerned with properties of wood pellets and briquettes. Demand of mentioned biofuel density is > 1000 kg m^{-3} in standards. For lower quality biomass solid fuel permissible density is > 900 kg m^{-3}.

Results of briquetting experiments were evaluated on bases of mentioned standards.

III RESULTS AND DISCUSSION

During briquetting experiments hydraulic pressure was measured with calibrated pressure sensor. Example of briquetting pressure dependence on time is shown in Fig. 3.

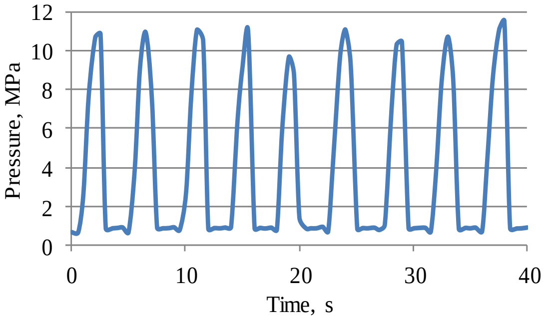

Fig. 3. Briquetting pressure diagram

The maximal pressure values for all types of pressing material were recorded from briquetting pressure diagrams. Average values of maximal pressure are shown in Table 1.

Expressions in Table 1: S, 1.5; S, 6; S, 12; S, 20 – common reed particles from grinding screen opening sizes 1.5, 6, 12 and 20 mm accordingly. P15, P30 and P50 – peat additive proportion 15%, 30% and 50% accordingly.

Average maximal pressure values in rhomb mechanism drive cylinder from 9.14 MPa to 10.82 MPa show dependence on particle size and characteristics of briquetting material.

TABLE 1

MAXIMAL PRESSURE AVERAGE VALUES

	Type of pressing material						
	S, 1.5	S, 6	S, 12	S, 20	S6 P15	S6 P30	S6 P50
Average maximal pressure, MPa	10.82	9.86	9.74	9.06	10.29	10.10	9.14
Force from hydraulic cylinder, N	16992	15474	15297	14225	16160	15849	14356

For pressing mechanism theoretical evaluation measured maximal pressure was converted to force of hydraulic cylinder. Calculated pressing forces R, corresponding to maximal drive force *F* = 15 kN, using equation (6) are shown in Fig. 4.

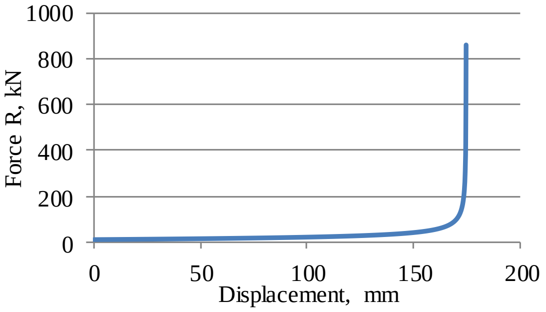

Fig. 4. Pressing mechanism force – displacement characteristic

The presented pressing mechanism piston force – displacement characteristics are nonlinear curves with two quasilinear parts. Calculated results show that designed pressing mechanism is able develop much bigger pressing force *R* (800 kN) comparing with drive force *F* (15 kN).

The briquettes from four common reed particle groups were produced using designed briquetting press with rhomb mechanism. For particle group's characterization four different screen opening sizes 1.5, 6, 12 and 20 mm of hammer mill was used. Experimentally obtained density results are shown in Fig. 5 depending on grinding screen opening sizes of particles. Density is the most important parameter in briquetting. The higher the density, the higher is the energy volume ratio.

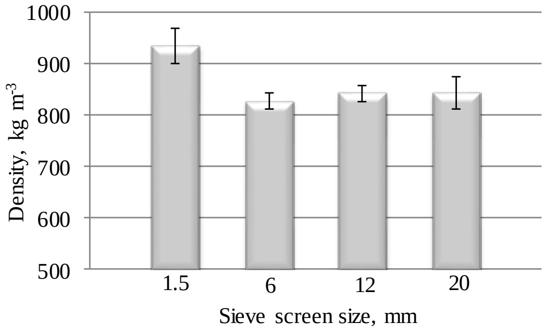

Fig. 5. Common reed briquettes average density

Average density of experimental briquettes was 934.5±35.1 kg m^{-3} (screen opening size 1.5 mm), 826.3±16.4 kg m^{-3} (screen opening size 6 mm), 841.5±16.5 kg m^{-3} (screen opening size 12 mm), 842.2±31.9 kg m^{-3} (screen opening size 20 mm). The briquettes of common reed particles from grinding screen opening size 1.5 mm let obtain density > 900 kg m^{-3}, recommended in EU standards for wood briquettes. The density non-linear change depending on particle size can be explained by particle orientation in die with diameter 25 mm.

Common reed particles with one size group (screen opening size 6 mm) were used for composition with different proportion of peat (15, 30 and 50%). Briquettes density and mechanical durability can be improved with peat additive in densification. Fig. 6 shows peat proportion influence on common reeds briquette density.

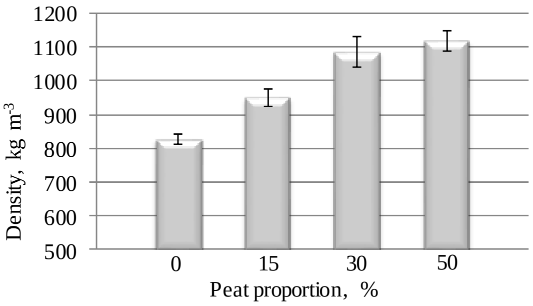

Fig. 6. Common reed – peat mixture briquettes average density

Fig. 6 shows that the briquettes average density increase from 826.3±16.4 to 1118.2±30.9 kg m^{-3} if peat proportion in mixture increases up to 50%. The density of common reed particles and peat mixture briquettes larger than 900 kg m^{-3} has been obtained then peat proportion is > 15% in composition.

In Fig. 7 and Fig. 8 are shown a photo of produced common reed briquettes.

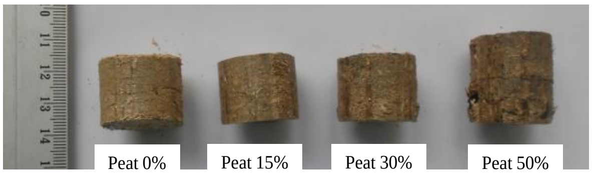

Fig. 7. Common reed briquettes

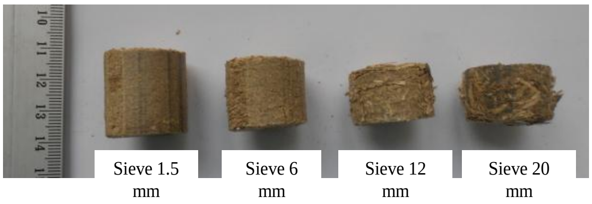

Fig. 8. Common reed and peat mixture briquettes

Notes: Common reed particles from grinding screen opening size 6 mm.

These experimental briquettes with diameter 25 mm can be classified also as pellets and used appropriately for heating.

The designed rhomb pressing mechanism can be recommended for biomass briquetting with drive from tractor hydraulic system with pressure < 20 MPa in rural conditions.

IV CONCLUSION

Average maximal pressure values in rhomb mechanism drive cylinder from 9.14 MPa to 10.82 MPa show dependence on particle size and characteristics of briquetting material.

The presented pressing mechanism piston force – displacement characteristics are nonlinear curves with two quasilinear parts. Calculated results show that designed pressing mechanism is able develop much bigger pressing force R (800 kN) comparing with drive force F (15 kN).

Average density of experimental briquettes was 934.5±35.1 kg m^{-3} (screen opening size 1.5 mm), 826.3±16.4 kg m^{-3} (screen opening size 6 mm), 841.5±16.5 kg m^{-3} (screen opening size 12 mm), 842.2±31.9 kg m^{-3} (screen opening size 20 mm). The density non-linear change depending on particle size can be explained by particle orientation in die with diameter 25 mm.

The briquettes of common reed particles from grinding screen opening size 1.5 mm let obtain density > 900 kg m^{-3}, recommended in EU standards for wood briquettes.

The briquettes average density increase from 826.3±16.4 to 1118.2±30.9 kg m^{-3} if peat proportion in mixture increases up to 50%. The density of common reed particles and peat mixture briquettes larger than 900 kg m^{-3} has been obtained then peat proportion is > 15% in composition.

The designed rhomb pressing mechanism can be recommended for biomass briquetting with drive from tractor hydraulic system with pressure < 20 MPa in rural conditions.

V ACKNOWLEDGMENTS

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Wood Biomass from the Model Wastewater and Its Fractionation

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Abstract. **The production of veneer in Latvia and many countries of East Europe is accomplished by the hydrothermal treatment of hardwood in special water basins. As a result, formed effluents contain wood-originated pollutants, which are responsible for the enhanced chemical oxygen demand and the intensive colour of the wastewater. Keeping in mind the volume of the polluted effluents formed annually at the Latvian plywood plants, it is very important to extract qualitatively and quantitatively the formed biomass from the effluent. The choose of an effective method of the waste biomass extraction depends on chemical characterisation of the effluent. In this work, for imitating woodworking wastewater, birch sawdust was hydrothermally treated in mild alkaline conditions at 90^{o}C. The yield of the solid biomass did not exceed 7% and contained, mainly, hemicelluloses in the polysaccharide form and lignin. The applied instrumental analysis (FTIR-, UV-, Raman spectroscopy) testify the dominant content of hemicelluloses in the obtained biomass.** The f**ractionation of the biomass was performed using concentrated sulphuric acid and ethanol. As the obtained results have shown, the content of lignin, hemicelluloses and water-soluble degraded wood products in the solid biomass corresponded to the following mass ratio: 1.2 /6.7 /1.0, respectively.**

Keywords – **biomass, hemicelluloses, hydrothermal treatment, fractionation, lignin, wastewater.**

I INTRODUCTION

Biomass pre-treatment, directed to the destruction of the lignocellulosic matrix, occupies a leading position in lignocellulosic biorefinery for obtaining biofuels and chemicals from cellulose, hemicelluloses and lignin [1-3]. The production of veneer in Latvia and many countries of East Europe is accomplished by the hydrothermal treatment of hardwood in special water basins for 16-18 h at a temperature lower than 100^{o}C and a normal pressure [4]. Depending on the conditions of the hydrothermal treatment, a different yield of wood hydrolysis products occurs due to the hydrolysis of the lignocellulosic matrix [5]. As a result, the formed effluents are polluted with lignin, hemicelluloses, extractives and degraded products from these wood substances, which are responsible for the enhanced chemical oxygen demand and the intensive colour of the wastewater. The chemical indexes of the effluents depend on many factors, namely, the wood species, temperature, pH, etc. Keeping in mind the volume of the polluted effluents formed annually and the zero waste policy for rational use of bioresources, it is very important to extract qualitatively and quantitatively the formed biomass from the effluents for more rational its utilisation than the dilution with pure water to maximum allowable concentrations and then to discharge to natural water basins. It is known that sewage sludge can be used successfully for soil improvement [6], and for producing building materials [7] and sorbents [8]. Evidently, the proper selection of methods for effective extracting of wood biomass from the wood processing effluent is based on its chemical composition and, mainly, on the content of lignin and hemicelluloses.

The aim of the study was to assess the content of lignin- and hemicelluloses-containing fractions in the model solution imitating wastewater of veneer production.

II MATERIALS AND METHODS

Hydrothermal treatment of 60 g of sawdust (< 1.00 mm) was performed with 0.04% NaOH solution at the hydromodulus 1/50 (mass ratio of the oven dry sawdust to water) and a temperature of 90°C for 4 h, using a 5 l three-neck flask equipped with a return condenser, a thermometer and a stirrer. After hydrolysis, the cooled hydrolysate was separated from the treated sawdust by filtration, and the obtained biomass was dried to a constant mass, at first, at room temperature and then in an oven at 40^{o}C. The treated sawdust was washed with distilled water to remove the adsorbed hydrolysed degraded products and dried to a constant mass, at first, at 60^{o}C and then in an oven at 105^{o}C. The characteristics of the treated sawdust and the obtained hydrolysate are represented by their average arithmetic values.

The elemental composition of the sawdust and was determined with the Elementar Analysensysteme GmbH (Germany). Inorganic matter (ash) was found according to Obolenskaya and co-authors [9]. The composition of birch sawdust - lignin, hemicelluloses, cellulose and extractives, before and after hydrolysis, was determined according to analytical chemical procedures. The content of lignin and cellulose was determined by Klason and Kürschner methods, respectively. The content of hemicelluloses was determined as a difference between the content of holocellulose found by treatment with sodium chlorite and glacial acetic acid and cellulose. The content of extractives represented the sum of the content of the wood substances dissolved in acetone, using a Soxlet extractor, and in boiled water (100°C) during 3 h [9]. The found content of cellulose, lignin, hemicelluloses and extractives in the birch wood residue was the following: 40.3%, 25.2%, 29.2% and 3.9%, respectively. Biomass component composition was identified by Fourier Transform Infrared (FTIR), Ultraviolet-Visible (UV) and FT Raman spectroscopy. For FTIR- and UV-spectroscopy, a spectrophotometer (Perkin-Elmer Spectrum One, USA) with KBr tablets and a UV-VIS Spectrometer Genesys™ 10 (Thermo, USA)[18] were employed.

Due to the high fluorescence, for obtaining the spectral characteristics of the biomass, a Multiram FT Raman spectrometer by Bruker with laser power of 125 mW was used.

Monosugars in the hemicelluloses fraction were determined by a high performance liquid chromatography (HPLC) using a liquid chromatograph (LC) SHIMADZU LC-20A (Shimadzu, Tokyo, Japan) with a refraction index detector. HPLC grade acetonitrile (Sigma-Aldrich, Germany) and water (distillated and deionised) were used for the HPLC analysis. Xylose, arabinose, rhamnose, mannose, glucose and galactose were reference standards. The column configuration was an Alltech Platinum Amino column (100Ǻ 5u, 250x4.6 mm) with a Platinum Amino (NH_2) guard column (5u, 7.5x4.6 mm). The flow rate was 1.5 ml/min and the separation was performed at 35°C. The mobile phase consisted of a degassed filtered mixture of acetonitrile and water (80:20 %v/v). For measuring, a 1.0% biomass water solution in 0.01M NaOH was prepared and filtered through a 0.45 μm membrane filter before injection, filed in 1.5 ml bottles with caps and placed in an auto-injector. All samples where tested three times.

Z potential of the hydrolysate was measured with Malvern Nanosizer SZ (UK). Indexes of COD and colour for the obtained hydrolysate were determined according to ISO 6060:1989 [10] and ISO 7887:1994 [11].

III RESULTS AND DISCUSSION

As shown in Table 1, the obtained hydrolysate was characterised by a moderate alkaline pH value, a low concentration of dry matter, representing the sum of wood degraded products passing to the hydrolysate, a moderate value of chemical oxygen demand (COD) and a pronounced colour associated with the presence of lignin and lignin-like substances in the hydrolysate .

TABLE 1.
PARAMETERS OF THE OBTAINED HYDROLYZATE

Sample	pH	Dry solids, $g\ l^{-1}$	Density, $kg\ m^{-3}$	COD, $mg\ O\ l^{-1}$	Colour, $mg\ Pt\ l^{-1}$
Hydrolyzate	9.02	1400	0.998	1285	746

The average yield of the solid biomass from the hydrolysate was 7.1±0.2% relative to the initial sawdust mass. The yield calculated from the sawdust mass loss was a little higher than that of the dried biomass, which may be associated with a partial adsorption of the formed degraded wood products at the sawdust surface. The defined elemental composition of the dried biomass was the following: 37.75% C; 4.78% H; 56.69% O; 0.30% N; 0.14% S, 0.34% of inorganic matter. A SEM image (Fig. 1) characterised the obtained lignocellulosic biomass as an amorphous one without pronounced morphological features.

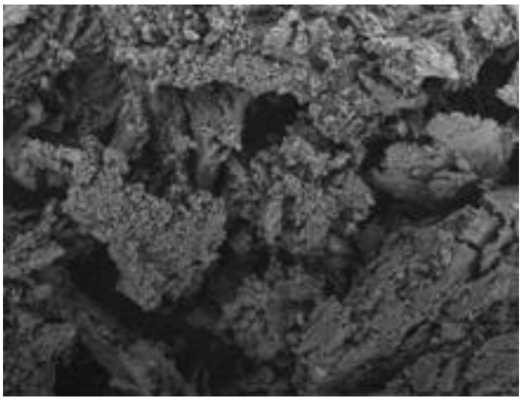

Fig.1. SEM image of the biomass.

The biomass had an enhanced ratio O/C close to 1.5±0.1 that indicated the presence of a great amount of oxygen–containing groups including hydroxyl, carbonyl and carboxyl groups in the hydrolysed wood products. The zeta potential value of the hydrolysate close to - 30 mv testified the high content of these groups in the biomass. With decreasing pH to 2.0, the Z potential value of the hydrolysate fell to -10 mv, reflecting the decrease in the ionisation degree of the hydroxyl and carboxyl groups in lignin and hemicelluloses fragments.

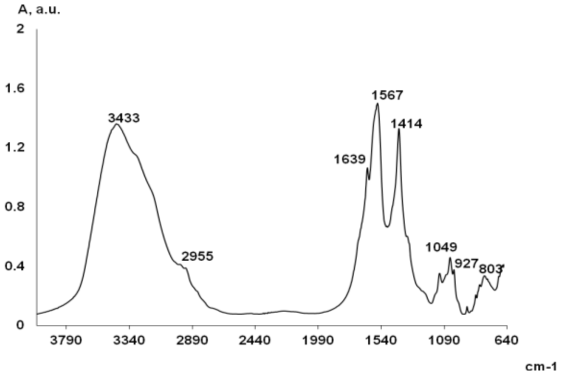

Fig.2. FT-IR spectrum of the biomass.

For fuller characterisation of the chemical composition of the biomass, the FT-IR, UV and FT Raman spectroscopy were applied. The interpretation of the obtained results was based on the literature data concerning the studies of lignin and hemicelluloses by the methods [12-14]. According to the FT-IR spectrum of the biomass (Fig. 2), the strong broad band at 3433 cm^{-1} is attributed to both aromatic and aliphatic hydroxyl groups. The band at 2955 cm^{-1} is caused by C–H stretch vibrations in the methoxyl, methyl and methylene groups present in the aromatic and saccharide structures of the hydrolysed products. The narrow bands at 1639 cm^{-1} and 1567 cm^{-1} may be assigned to the presence of ketones, carbonyls and ester groups in the biomass lignin and hemicelluloses. At the same time, in the spectrum, the pronounced bands corresponding to the aromatic skeletal vibrations of lignin structures, namely, 1600 cm^{-1} and 1505 cm^{-1} [15] are absent. The presence of lignin structures in the biomass is testified by the absorbance at 1414 cm^{-1}, assigned to skeletal vibrations and C=O group stretching in the syringyl and guaiacyl aromatic rings. The CH_2 deformation vibrations appear at 1351 cm^{-1} and may be caused by both lignin and hemicelluloses structures. The bands in the region of 1115–803 cm^{-1} are typical for hemicelluloses. This region contains C-C ring vibrations, overlapped with the stretching vibrations of C-OH side groups and the C-O-C glucosidic band vibrations. The band at 1115 cm^{-1} may be caused by the presence of pectin. The band at 1047 cm^{-1} is attributed to the C-O-C stretching in glucosidic linkages, which is typical for xylan. The small bands at 927 cm^{-1} and 803 cm^{-1} are characteristic of the β-glucosidic bonds between the sugars units.

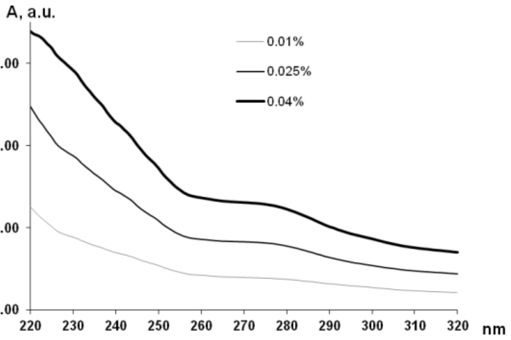

Fig. 3. UV spectra of the biomass water solutions at pH 9.0.

Fig. 3 shows UV-spectra of 0.01-0.04% solutions of the biomass with pH 9.0. The obtained spectra testify the presence of aromatic fragments in the biomass, namely, the absorption at 280 nm is typical for lignin. At the same time, the relatively low value of the calculated extinction coefficient (3.89 l g^{-1}cm^{-1}) at this band indicates the dominant content of the non-aromatic structure in the dried biomass.

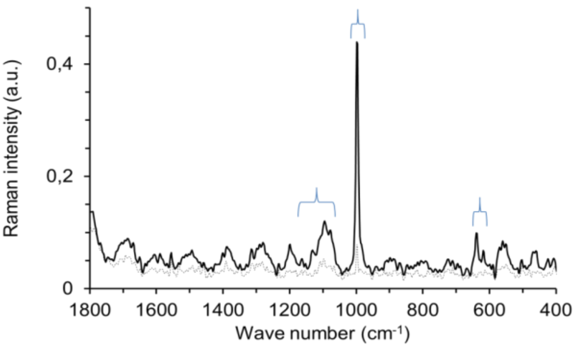

Fig. 4. FT Raman spectrum of the biomass.

This suggestion confirms the obtained FT Raman spectrum of the lignocellulosic biomass presented in Fig. 4. According to the known assignment of the vibration bands in FT Raman lignocellulosic materials [16], the strong pronounced bands observed in the interval of 1200-1000 cm^{-1} may be assigned to C-C an C-O stretching vibrations in hemicelluloses. At the same time, less manifested and weaker bands in the interval of 550-630 cm^{-1} may testify the presence of aromatic structures of lignin in the obtained biomass.

To fractionate the lignocellulosic biomass and calculate the content of lignin and hemicelluloses therein, the precipitation of the hydrolysate with concentrated sulphuric acid, with the following treatment of the formed filtrate with ethanol, according to Liu and co-authors [17] was employed. The scheme of the applied fractionation is given in Fig. 5. For the fractionation, the biomass dried at room temperature was dissolved in 0.1M NaOH for obtaining 50 ml of a 35% biomass solution. The concentrated hydrolysate was, at first, acidified with 20% sulphuric acid to a pH of 2.0 at room temperature with the following filtration and centrifugation of the obtained suspension for separating the lignin-containing fraction. The lignin precipitate was washed with distilled water to pH 5.5 and dried in an oven at 40^{o}C. Anhydrous ethanol was added to the obtained filtrate at the volumetric ratio of ethanol/filtrate close to 4. After addition of anhydrous ethanol, the hemicelluloses-containing fraction precipitated and then was isolated by centrifugation, washed with the ethanol and dried in an oven at 40^{o}C. The content of hemicelluloses- and lignin-containing fractions in the biomass was assessed from the masses of the obtained dried precipitates.

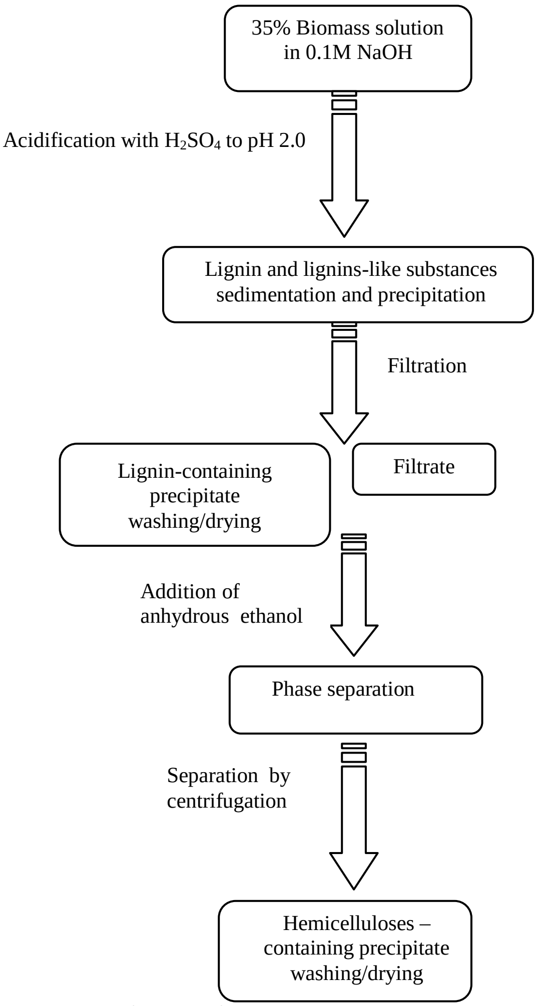

Fig. 5. Scheme of biomass fractionation

The FTIR spectrum of the isolated lignin and the isolated hemicelluloses are given in Fig. 6. In FTIR spectrum of lignin, typical bands can be seen, which are common for hardwood lignins, namely, a band at 1323 cm^{-1} and that at 821 cm^{-1} are assigned to syringyl rings. For FTIR spectrum of the isolated hemicelluloses, typical absorbance bands of glucosidic linkages in the 1200 – 800 cm^{-1} are observed.

The obtained results of the biomass fractionation showed that the content of the lignin and hemicelluloses fractions in the solid biomass corresponded to 13.5% and 75.2%, respectively. At the same time, the low molecular products of the lignocellulosic matrix destruction that were not able to be precipitated by this procedure occupied 11.3% of the solid biomass. The measuring of the content of water-soluble lignin [9] in the filtrate obtained after the Klason lignin extraction corresponded to 5.89%, and the total content of lignin (Klason and water-soluble) in the biomass was 10.9%. As the obtained results have shown, the content of lignin, hemicelluloses and water-soluble degraded wood products in the solid biomass corresponded to the following mass ratio: 1.2/6.7/1.0, respectively.

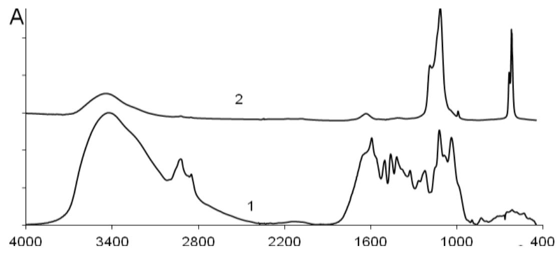

Fig. 6. FTIR spectra of biomass components: lignin (1), hemicelluloses (2).

TABLE 2.

WOOD COMPONENT COMPOSITION OF BIRCH SAWDUST BEFORE AND AFTER THE HYDROLYSIS

Sample	Holo-cellulose, %	Cellulose, %	Hemi-cellulose %	Lignin, %
Untreated	68.5	40.3	28.2	25.2
Treated	70.4	46.8	23.6	25.1

Simultaneously, the changes in the wood composition of birch sawdust due to its hydrolysis were assessed. According to the results listed in Table 2, the main changes in the wood composition caused by the hydrolysis took place for cellulose, i.e., its content increased by 6.5% and hemicelluloses, i.e., their content decreased by 5.6%, while the content of lignin diminished by only 0.1%. It is reasonable to assume that the gain in the cellulose content and the negligible alteration in the lignin content in the pre-treated lignocellulosic matrix were associated with the notable losses of hemicelluloses and water-soluble extractives during the hydrothermal treatment.

The chemical and morphological characteristics of the precipitated birch lignin were studied by Shulga and co-authors [18]. Hemicelluloses in the biomass were identified by a liquid chromatograph. The identifying HPLC analysis (Fig. 7) testified the presence of xylose, mannose, arabinose, rhamnose and glucose monomers in a 1.0% birch hydrolysate

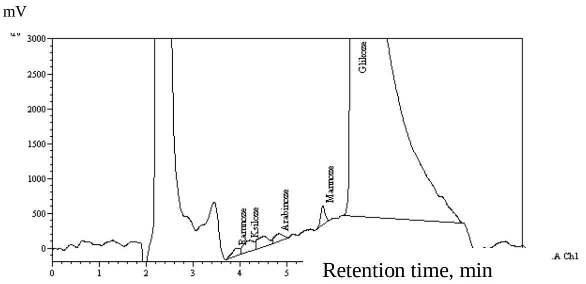

Fig. 7. HLPC chromatogram of a 1% biomass aqueous solution in 0.01M NaOH.

The obtained quantitative data analysis showed that the content of the first four sugars in the obtained hydrolysate was comparatively low and did not exceed 0.1%. This means that the hemicelluloses in the hydrolysate are represented mainly by polysaccharides. At the same time, the glucose content in the hydrolysate was higher and close to 0.4%, which may be associated with the features of the birch lignocellulosic matrix degradation during the hydrolysis.

IV CONCLUSION

For imitating woodworking wastewater, birch sawdust was hydrothermally treated in mild alkaline conditions at 90^{o}C. The yield of the solid biomass did not exceed 7% and contained, mainly, hemicelluloses in the polysaccharide form and lignin. The applied instrumental analysis (FTIR-, UV-, Raman spectroscopy) testify the dominant content of hemicelluloses in the obtained biomass. The study of the biomass with a high performance liquid chromatograph identified, along with xylose, glucose and mannose, also arabinose and rhamnose. The fractionation of the biomass was performed using concentrated sulphuric acid and ethanol. As the obtained results have shown, the content of lignin, hemicelluloses and water-soluble degraded wood products in the solid biomass corresponded to the following mass ratio: 1.2 /6.7/1.0, respectively.

V ACKNOWLEDGMENTS

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Optical Properties of Natural and Synthetic Minerals

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Abstract. **The results of investigation of optical absorption and photoluminescence (PL) of topaz, beryl and yttrium aluminium garnet crystals doped with different concentrations of transition ions exposed to fast neutron irradiation and electron irradiation are presented. We suppose that irradiation leads to the formation of two types of complex centers: "Me^{2+}- F^+ (or F) centre" and complex centers, which consist of a cation vacancy and an impurity (iron, manganese and chromium) ion. Exchange interaction between radiation defects and impurity ions during neutron or electron irradiation gives rise to appearance of additional absorption and luminescence band broadening in investigated crystals.**

Keywords – inorganic compounds, absorption spectra, photoluminescence, neutron irradiation.

I INTRODUCTION

Natural and synthetic minerals such as topaz, beryl and garnet are used not only as gemstone but have a practical application. Topaz crystal is a suitable material for dosimetric applications [1]-[3]. Beryl and garnet crystals doped with transition metal ions find application as laser materials [4], [5]. Most gemstone crystals have an intrinsic color due to the optical absorption and presence of color centers that are produced by impurities like transition metals and elements of Earth-rare, or defects in the crystalline lattice [6]. Defect and disorder creation has been studied in detail, but the renewed interest arises from the use of electron and ion beams for synthesis and modification of materials.

Potential application of this material to a great extent is determined by its optical properties, which in turn are determined not only be structure but also by presence of defects. Therefore it is important to estimate the present material defects and their effect on properties of material.

The paper presents results of the effects of neutron and electron irradiation on optical properties of natural (topaz, beryl) and synthetic (beryl, yttrium aluminum garnet) minerals**.**

II MATERIALS AND METHODS

Oxide materials $Y_3Al_5O_{12}$, natural and synthetic beryl $Be_3Al_2Si_6O_{18}$, topaz $Al_2[SiO_4](F, OH)_2$ have been used for research.

The investigated YAG samples were cut from single crystals grown by the Czochralski technique, crystal had the composition. $Y_3Al_{5-x}Mn_{.x}O_{12}$, where x = 0.012, 0.025, 0,037 and 0.05. Samples of beryl were obtained from variety of sources: natural crystals from Ural Mountains and synthetic grown by flux method in Russia. Natural colourless and blue topaz from Ukraine was investigated. The sample thickness was in the range of 0.1 –2.15 mm.

The neutron irradiation was performed at the Latvian 5 MW water-water research reactor. The fluence of fast neutrons with energy > 0.1 1MeV was in the range $10^{14} – 5{\cdot}10^{18}$ cm^{-2}. A cadmium filter was used for absorption of thermal neutrons. Irradiation by electrons with energy of 3.5 MeV of integral fluence up to 10^{16} cm^{-2} was carried out in accelerator ELU (Salaspils, Latvia). The sample temperature did not exceed 60°C during the electron irradiation and was below 40°C during the neutron irradiation.

The luminescence studies were carried out using two setups for spectral measurements. The first setup was equipped with a SPM-2 monochromator having diffraction grating of 651 lines per mm. The crystals were excited with a high pressure xenon lamp (DKSEL-1000) 1000 W connected to the monochromator SPM-1(Carl Zeiss Iena) with a quartz prism. Signal detection was carried out with a photomultiplier tube (FEU-119) by a synchronic detection method. The second setup was equipped with a deuterium lamp LDD-400 as a source of UV light and a grating monochromator MDR-2 in the excitation channel. In the case of PL measurements the luminescence signal was analyzed by Shamrock monochromator SR-303i-B using a grating with 150 lines/mm and 500 nm blaze and detected with a CCD camera DV420A-BU2 in the accumulation mode. The standard technique to measure absorption spectra has been based on a "Specord M-40" two-beam spectrometer operating in the 200-900 nm regions and "Specord 210" (Analytikjena) double-beam spectrophotometer operating in the spectral region of 190-1100 nm. Optical measurements before and after irradiation were carried out in the temperature range 8-300 K.

III Results and Discussion

A. Topaz crystals

Topaz is an aluminium fluorosilicate with a fairly constant chemical composition $Al_2SiO_4(OH,F)_2$. The only major variation found in different samples is related to the [OH]/[F] concentration ratio. The structure of topaz consists of SiO_4 groups linking octahedral chains of $Al[O_4(F,OH)_2]$ in a zigzag fashion parallel to the crystalline c-axis. Four of six anions surrounding Al^{3+} ion belong to SiO_4 tetrahedron and the remaining two anions are F^- or OH^-group. Topaz crystallizes in the orthorhombic system, space group Pbnm [7], [8] and is normally found as well-developed prismatic crystals with pyramidal terminations

Natural topaz stone has the structure of an aluminum silicate fluoride hydroxide $Al_2[SiO_4](F, OH)_2$, and is usually colorless or has an unattractive color. Figure 1. gives the absorption spectra of topaz single crystals before irradiation (curve 1), after fast neutron irradiation (curve 2) and natural blue topaz from Volodarsk Volynskii, Ukraine (curve 3). Before irradiation some zero-phonon lines were observed in the region of the Cr^{3+} ion electron transition $^4A_{2g} \rightarrow {}^2E_g$ in topaz spectra (Fig. 2). After irradiation in absorption spectra there appears an intense absorption at 230 nm and occur the characteristic maxima at 305, 410, 446, ~590 nm. Two lines around 230 and 305 nm belong to a single defect such as silanone (=Si=O) as it was suggested in [9] basing on similar lines observed in spodumene. Blue color is connected with a broad absorption band in the red part of the spectrum generated by the so-colled R-centers (two F-vacancies with two trapped electrons) [10]. It was previously concluded that the optical absorption band centered at 620 nm is closely correlated with an O^- center interacting with two Al ions of the topaz structure. This O^- center is produced by the irradiation in the hydroxyl sites which substitutes for fluorine in the topaz structure [11], [12]. As suggested Priest V. at al [13] the blue defects in neutron damaged topaz is the doubly occupied dangling silicon bond. We assume that the band ~ 620 nm includes not only the above mentioned bands, but also the bands associated with the presence of impurities of Cr^{3+}, Fe^{2+} and Mn^{2+} ions. The calculations performed in [14] using $AlCrFH_7O_{11}Si$ model molecule with unrestricted CIS method to simulate UV and visible spectra shows that the theoretical spectrum of the model is in a considerably good agreement with experimental one.

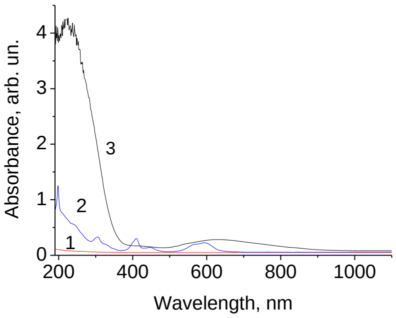

Fig.1. Topaz absorption spectra before (1) and after neutron irradiation (2), (3) natural blue topaz from Volodarsk Volynskii, Ukraine.

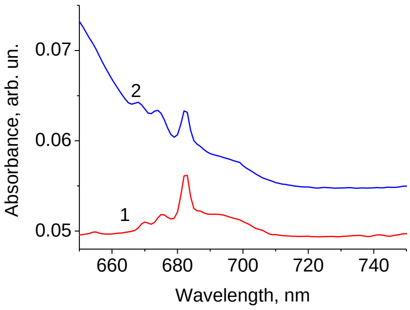

Fig. 2. Topaz absorption spectra before (1) and after neutron irradiation (2)

Photoluminescence spectra in natural colourless topaz excitated at λ_{exc}= 251 nm and λ_{exc}= 447 nm registered at 300 K are shown in Fig. 3. In photoluminescence spectra of topaz crystal exited at 251 nm, it is possible to separate an intensive band 350 nm with shoulder about 364 nm, and less expressed 390 nm, 420 nm and 464 nm bands. Upon excitation 447 nm it is observed two wide bands at maxima at 575 and 800 nm.

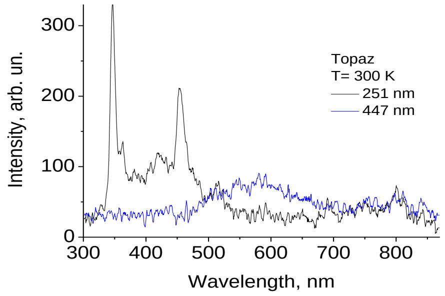

Fig.3. Photoluminescence spectra of topaz crystal at 230 and 447 nm excitation wavelengths.

Luminescence at 390 nm belongs to own $[SiO_4]^{3+}$ hole centers. The emission band with maxima 464 nm is connected with $[AlO_4]^{4-}$ center arising from isomorphic substitution of silicon by aluminum in the silicon-oxygen tetrahedron. Wide luminescence bands at excitation wavelength 447 nm may be connected with presence of Mn^{2+} (~ 600 nm) and Fe^{3+}(~ 800 nm) isomorphically substituting for Si^{4+} in the silicon-oxygen tetrahedron.

B . Beryl crystal

Beryl ($Be_3Al_2Si_6O_{18}$) is a silicate mineral belonging to the cyclosilicate class. It has a honeycomb-like hexagonal structure and belongs to the P6/mcc space group. The axial parameters are c=9.17 ˚A and a=9.21 ˚A [15, 16]. Each ion of Al is surrounded by 6 oxygen atoms located in the vertices of almost regular octahedron. Each octahedral complex AlO_6 is linked to six SiO_4 tetrahedron through common oxygen atoms. The disposition of the octahedral is such that allows the formation of Si_6O_{18} rings. Each beryllium is surrounded by 4 oxygens forming distorted tetrahedron. The Si_6O_{18} rings lay one above the other along the C6 axis forming intercommunicating channels of quite large dimensions. The oxygen that is shared among Si^{4+} ions is an O1 type oxygen and the oxygen that is linked to Al^{3+} and Be^{2+} ions is an O2 type oxygen. Taking into account this configuration, each Si^{4+} ion is surrounded by two O1 oxygens and two O2 oxygens. The diameter of the channels varies from a minimum of 2.8 ˚A in the plane of the Si_6O_{18} ring and a maximum of 5.1 A˚, midway between two neighboring rings. Because of this structure, impurities can be substitutional, interstitial and also located in the channels.

The color of beryl $Be_3Al_2Si_6O_{18}$ is usually determined by its Fe^{2+} and Fe^{3+} content. Fe^{2+} produces pale blue color, Fe^{3+} produces golden-yellow color, and when both Fe^{2+} and $Fe^{3+}$are present, the color is dark blue. Green color in iron-containing beryl usually results from a mixture of blue and yellow components. Green color can also come from Cr^{3+} as it is found in various emeralds. Beryl is naturally transparent, however inclusions and impurities may make it opaque.

Absorption spectra for three beryl crystals are shown in Fig. 4. Beryl, when containing sufficient chromium (about 0.1% or more) is characterized by two broad bands near 430 and 600 nm (Fig. 4, curve 1), as well sharp R-lines (Fig 5.)

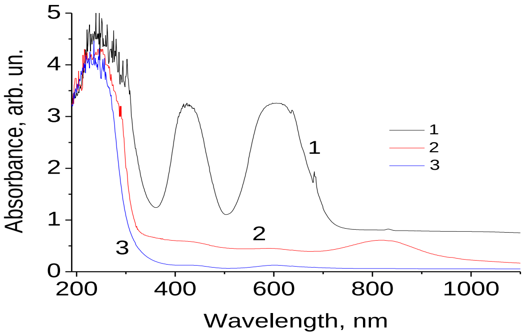

Fig.4. Absorption spectra of beryl crystals: 1. synthetic beryl containing Cr 0.1% chromium impurity, 2. natural beryl from Ural, 3. synthetic flux beryl.

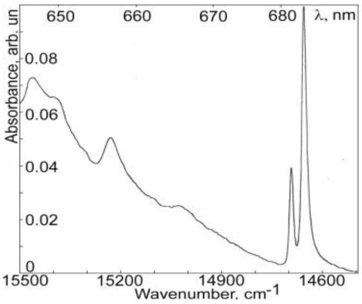

Fig. 5. Absorption spectra of beryl containing 0.1 %Cr:

The observed absorption bands associated with electronic transitions of chromium ion: 630 nm transition $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ and 431 nm transition $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ [17]. The wide absorption band with peak in the near-infrared range at 813 nm is observed in natural beryl spectra. The band is generally ascribed to internal electron transition of $^5T_2$ (^5D) → ^5E (^5D) of $Fe_{VI}^{\ 2+}$ ions localized in octahedral aluminum sites of beryl [18, 19]. Absorption spectra of beryl containing chromium before and after neutron irradiation are given in Fig.6.

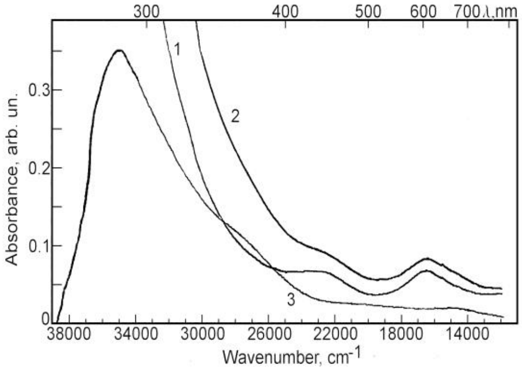

Fig. 6. Absorption spectra of beryl:Cr: 1. before irradiation, 2. after fast neutron irradiation $\Phi=10^{16}cm^{-2}$, 3.additional absorption spectrum.

Fast neutron irradiation produces additional bands with maxima: 286, 370, 500 and 667 nm. Most probably these bands are due to anion intrinsic defects (the F^+, F, F_2, $F_2^{\ +}$ and $F_2^{\ +}$ centers) similar to observed in Al_2O_3 [20], [21]. Natural pale blue beryl crystals contain iron ions and small amount of chromium ions. Prior to irradiation there were not observed absorption bands associated with electronic transitions $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ (630 nm) and $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ (431 nm) of chromium ions. Absorption spectra contain only band 813 nm associated with Fe^{2+} ions. After the impact of fast neutron fluence of 10^{13}-$10^{17}cm^{-2}$ the intensity of 813 nm band reduced and the absorption edge shifted due to appearance of an intense absorption band in the UV region. Besides, after irradiation there appears the additional band with maximum 690 nm (Fig. 7). The crystal color is changed from pale blue to light green.

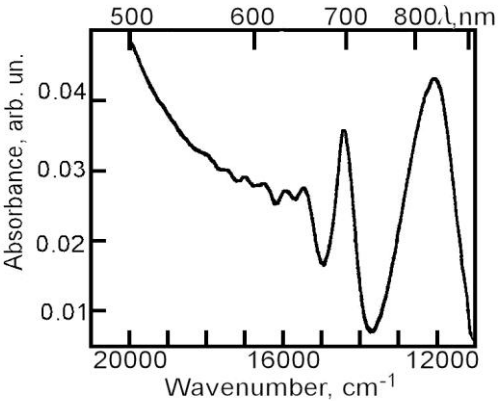

Fig.7. Absorption spectra of natural pale blue beryl after fast neutron irradiation $\Phi = 10^{16} cm^{-2}$.

Dependence of intensity of 813 nm (1) and 694 nm (2) absorption bands on fast neutron fluence in pale blue beryl is shown in Figure 8.

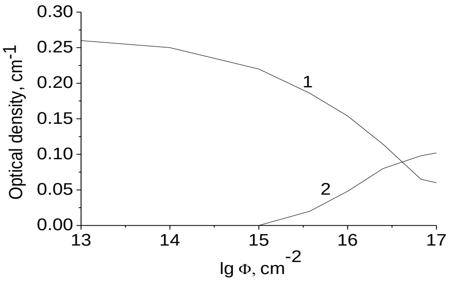

Fig. 8. Pale blue beryl absorption band 813 nm (1) and 694 nm (2) intensities as functions of fast neutron fluence.

As previously reported [22]-[24] irradiation produces radicals NO_3^0 and CO_3^-, which are called Maxixe and Maxixe-type color centers and which seem to be related to blue colors in beryl. We suppose that the band with maxima 690 nm belongs to complex center which consists from Cr^{3+} ions and radiation defects (F or F^+- center). Concentration of F and F^+ centers are increasing with neutron fluence increasing. The number of perturbed chromium sites also increased and the band became more intense. The containing chromium impurity ions may be the chromium ions in the lower valence, such as bivalent Cr^{2+} impurity ions. The Cr^{2+} impurity ions are oxidized into Cr^{3+}. A Cr^{3+} impurity ion has the same valence as the substituted Al^{3+} ion. Possible processes for chromium valence change are:

1. $Cr^{2+} \rightarrow Cr^{3+} + e^+$; 2. $Cr^{2+} + V \rightarrow Cr^{3+} + X_s^-$

(X_s^- -the constituent anions or radical in normal lattice of beryl crystal [25]). Therefore, the newly produced Cr^{3+} impurity ions prefer to lie in the octahedral sites in order to maintain the local charge neutrality of the crystal.

The photoluminescence spectra of flux beryl at λ_{ex}= 271 nm and different temperature are given in Fig. 9. Wide band at 740 nm observed at T= 300 K is connected with Fe^{2+} ions. Narrow lines in region from 680 to720 nm at T= 8 K belong to single Cr^{3+} (R-lines) and Cr^{3+}- pairs (N- lines). The photoluminescence band at 525 nm intensity increases with temperature decrease.

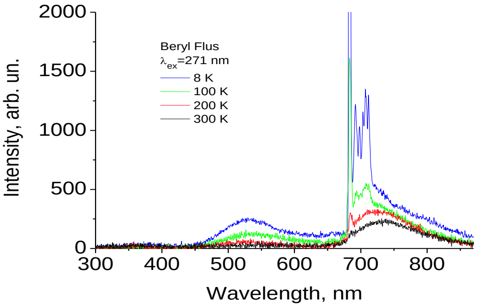

Fig. 9. Photoluminescence spectra of beryl crystal at different temperature, excitation wavelengths 271 nm.

C. *Yttrium aluminum garnet*

The cubic cell of garnet compound $A_3B'_2B''_3O_{12}$ contains eight formula units, where A, B', B" are metal ions occupying sites of different symmetry [26]. The crystal structure of $Y_3Al_5O_{12}$ (YAG) has a bcc structure (space group Ia3d or O^{10}_h) with 160 atoms in the cubic (primitive) cell. Y ions (A atoms) occupy 24 (c) sites and each of them is dodecahedrally coordinated to eight oxygen ions. Oxygen atoms occupy 96 (h) sites whose exact location depends on three structural parameters - x, y, and z and are different for different garnet oxides. There are two different sites for Al: Al_{oct} (B' atoms) occupy 16 (a) sites with octahedral point symmetry (C_{3i}); and Al_{tet} (B") atoms occupy 24 (d) sites with tetrahedral point symmetry (S_4). The garnet structure may be considered as interconnected octahedrons, tetrahedrons, and dodecahedrons with shared oxygen atoms at the corners [26]. Each oxygen ion is a member of two dodecahedrons, one octahedron, and one tetrahedron. Y^{3+} and Al^{3+} in YAG can be replaced by many kinds of other cations with different valence and size within a suitable range.

The optical absorption spectra of four garnet single crystals measured at room temperature before irradiation are similar. Figure 10. gives the absorption spectra of yttrium aluminum garnet single crystals (curve 1) before irradiation, after fast neutron irradiation (curve 2) and after electron irradiation (curve 3). Before irradiation there are observed bands at 370, 500 and 830 nm. After neutron irradiation additional bands with maxima 549.5, 595.2 and 714.3 nm appear in absorption spectra of YAG containing manganese impurities. The 370 and 500 nm bands intensity increases but the 830 nm band intensity decreases after fast neutron irradiation. A weak band 370 nm corresponds to F-type centers [27].

Broad orange luminescence band in the range 580-620 nm appears at room temperature (Fig. 11, curve 1). Luminescence spectrum of $Y_3Al_{5-x}Mn_xO_{12}$ single crystal measured at liquid nitrogen temperature contains the following main features: a sharp line at

587 nm and a series of weaker lines on the long wavelength side of the sharp lines (curve 2, Fig.11).

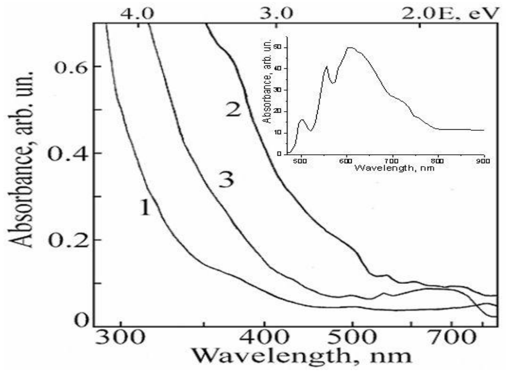

Fig. 10. . Absorption spectra of $Y_3Al_{5x}Mn_xO_{12}$: 1. before irradiation, 2. after neutron irradiation $\Phi = 10^{16}cm^{-2}$, 3.after electron irradiation $\Phi = 10^{16}cm^{-2}$. In the inset: additional absorption spectrum of neutron irradiated $Y_3Al_{4.963}Mn_{0.037}O_{12}$ crystal.

After irradiation with fast neutrons at fluence $6{\bullet}10^{18}cm^{-2}$ the photoluminescence spectrum at liquid nitrogen temperature consists of a broad structureless band with a maximum at 607 nm (Fig. 11, inset). A little sharp line is seen also as a shoulder of the main band. Neutron irradiation causes production of anion and cation vacancies in the crystal. F-centre absorption band at 370 nm arises. After PL and optical measurement thermal annealing of the $Y_3Al_{4.988}Mn_{0.012}O_{12}$ and $Y_3Al_{4.975}Mn_{0.025}O_{12}$ crystals has been carried out. The crystals were heated in air at 473 K during 2 hours. The PL spectra measured after annealing at liquid nitrogen temperature are similar to the PL spectra before irradiation.

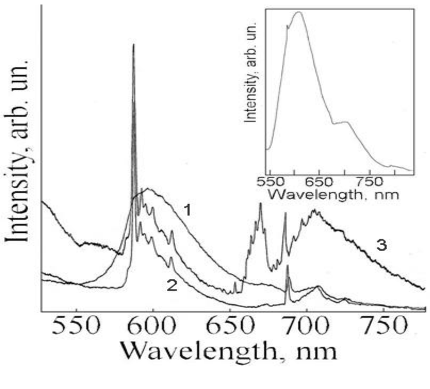

Fig. 11. Photoluminescence spectra of Y3Al5-xMnxO12 at λex=470 nm: 1. at room temperature, 2. at 80 K, and 3. after electron irradiation. The inset shows photoluminescence spectrum of a neutron- irradiated crystal.

It is suggested, that the reversibility of broadening of luminescence lines of Mn2+ ions is the evidence of the structure ordering reconstruction after annealing. The relatively low annealing temperature shows, that the structure changes after neutron irradiation concern only cation sublattice. Photoluminescence spectra of Y3Al4.988Mn0.012O12 carried out at liquid nitrogen temperature after electron irradiation have discovered a series of relatively narrow lines in 645-680 nm spectral regions. Mn2+ ions have a 3d5 electron configuration. All electron transitions for this configuration are forbidden by the selection rules of spin and parity. The restrictions caused by the selection rule are removed owing to the exchange interaction. The emission with maxima around 590 nm is attributed to the 4T1g→ 6A1g transition of Mn2+ ions in octahedral sites. Luminescence spectrum of Mn4+ (3d3), which is isoelectronic to Cr3+ consists of the sharp R lines peaked around 645-675 nm, which are caused mainly by the 2Eg → 4A2g transitions and partly by the 4T2g→ 4A2g transitions. These bands are observed after electron irradiation of Y3Al5-xMnxO12 together with the Mn2+ ion luminescence in octahedral sites. In contrast to paper [5] the green luminescence was not observed in our single crystals. The broad band emission of Cr3+ with a maximum at 695 nm is ascribed to the 4T2g→ 4A2g transition, the sharp and narrow bands at 685 nm are due to 2Eg → 4A2g. The diffused band centered at 675 nm (anti-Stokes vibronic sidebands) and two sharp diffused bands at 710 and 725 nm corresponding to the vibronic sidebands are observed in all investigated YAG crystals before and after irradiation (Fig.10). Hodges et al. [28] pointed out that Mn2+ in yttrium aluminum garnet can enter into any of three kinds of sites which are located in the center of dodecahedron, octahedron and tetrahedron, respectively [29, 30]. The presence of a nearby F or F+ center can modify the neighborhood the Mn2+ impurity site to produce an effective increase in the crystal field. In addition to the shift in energy, the perturbation induced by the F or F+ center can increase the oscillator strength by introducing odd components to the crystal field, or by exchange coupling between the F or F+ center and the Mn2+ impurity. The enhancement of the oscillator strength by the exchange interaction has been previously observed between F centers and transition metal impurity ions in MgF2, MgAl2O4 and MgO [31, 32]. As the concentration of F and F+ centers increased, the number of perturbed manganese sites also increased, so that the excitation peaks became more intense as a function of neutron dose. It is possible to assume that the band broadening is connected with a complex center "Mn2+-F+ (or F centre)". A part of holes generated after irradiation are trapped by Mn2+, which then produces Mn3+ and Mn4+ ions.

IV CONCLUSIONS

The absorption and luminescence spectra behaviour of natural (topaz, beryl) and synthetic (beryl, yttrium aluminum garnet) minerals containing transition metal ions exposed to a fluence of fast neutrons up to $10^{18}cm^{-2}$ (E>0.1 MeV) and electron are investigated.

We assume that the band ~ 620 nm in topaz crystals is associated with the presence of impurities of Cr^{3+}, Fe^{2+} and Mn^{2+} ions. Band with maxima 690 nm in beryl crystal belongs to complex center which consists from Cr^{3+} ions and radiation defects (F or F^{+}- center). Band broadening in aluminium yttrium garnet is connected with a complex center "$Mn^{2+-}F^{+}$ (or F centre)". Electron irradiation produced broad band with a complex structure related to Mn^{4+} ions. Exchange interaction between radiation defect and impurity ions during neutron irradiation and electron irradiation leads to appearance of additional absorption and luminescence bands and bands broadening in investigated crystals.

V ACKNOWLEDGMENTS

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Reduction of Oil Shale Losses

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Abstract. **Oil shale utilisation losses reach 70% in some cases. These are closely related to legislation, backfilling and waste rock usage. Much smaller sections include production of oil, electricity and chemicals in which most of the research and development is performed today. Current urgent topics for investigating, testing and developing of oil shale mining related questions are backfilling, mechanical extracting of shale, fine separation, selective separation and optimised drilling and blasting. Reducing oil shale losses will be more actual in the future, because the depth of mining increases and the taxes for resource and pollutants are increasing as well.**

Keywords **– oil shale, losses, mining, extraction.**

I INTRODUCTION

Oil shale utilisation losses reach 70% in some cases. These are closely related to legislation, backfilling and waste rock usage [9]. Much smaller sections include production of oil, electricity and chemicals in which most of the research and development is performed today. Current urgent topics for investigating, testing and developing of oil shale mining related questions are backfilling, mechanical extracting of shale, fine separation, selective separation and optimised drilling and blasting [43].

Mining related waste is mainly solid waste from separation and processing, operating solid waste from overburden removal and drifting, liquid waste from dewatering, processing and washing processes [13]. Mining losses include tonnage, mining waste water, mining influenced water, surface water, soil water, groundwater and mining water, mining influenced land and ground layers [17]. Origin of mining waste is separation waste form Heavy Media Separation (HMS), processing waste, crushing and screening waste [15].

The main usage of solid mining waste is filling material, construction material and cementing material [44][45]. Liquid waste can be used as heat carrier or as source for kinetic energy of water or for industrial usage. Waste as used land is used mainly as space for depositing, construction and recreation [27][28]. The principal direction of developing mining technology is filling the mined area. This provides control over majority of environmental effects [16]. Filling the workings decreases the loss of resources and land subsidence, and at the same time provides usage for stockpiling. Filling the spoils of surface mine decreases dewatering; harmless waste can be used for filling surface mines and in this manner offer new building land [48]. The methods are: mapping the modelling criteria, indicators and processes of the mined areas; experimenting the possibilities of application, compatibility and results of mining software; applying laboratory experiments and fieldwork in modelling; creating models for blanket deposits; applying seismological methods for developing theory for collapse risk [10]. The key question of current study is related to resource wastage, if it is possible to decrease resource wastage or has it reached its limits.

II Methods

Series of analytical and testing methods have been applied in current study **Error! Reference source not found.**.

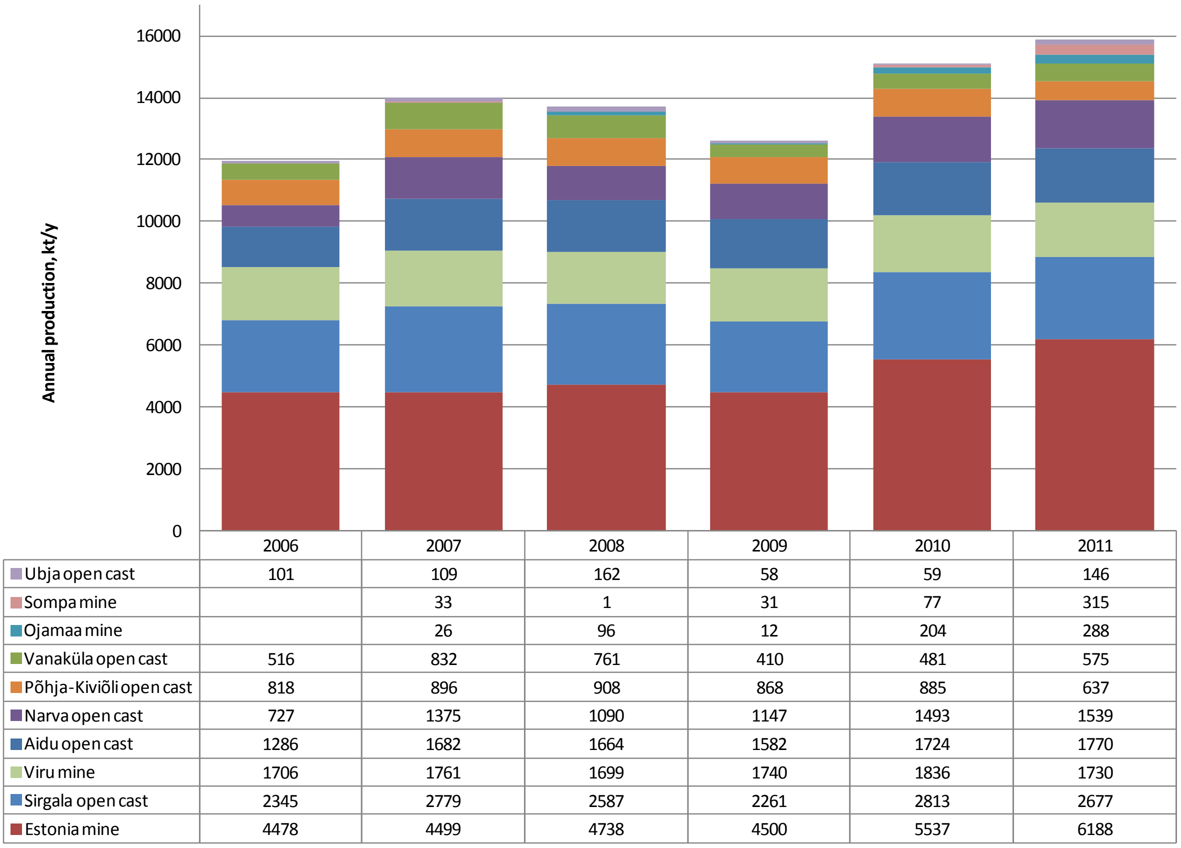
Beginning from resource analyses and followed by tests of extracting processes have been performed [20][31]: selective oil shale seam blasting, longwall mining, high selective surface mining, selective extraction by mechanical shovel, bulldozer ripper and hydraulic excavator ripping in several oil shale mining fields [18]. Separating tests included fine separation, dry separation and jigging.

Resource analyses and availability of resources are crucial part of the study influencing the base of the industry [22].

Although based on quality parameters oil shale resource could be evaluated as economically mineable resource [21], some resource is lost by geological dislocations and nature protection zones [14]. According to the Estonian Nature Protection Law it is prohibited to mine oil shale on nature protection zones. It is not specified how deep in the ground the law applies [23]. For example south-western part resources of Estonia oil shale mine may be estimated as not mineable resources because of Selisoo mire above the mine.

There is not enough adequate information about oil shale processing or extracting losses available. Official data from mining companies are kept in secret and will not be public. Only overall losses and changes of the mineral reserves of the deposits can be seen in official balance of mineral recourses in the Environmental Register. The authorized processors of the Environmental Register are the Ministry of the Environment and Estonian Land Board. This part of the register consists of mineral reserves of the deposit, mined amounts of the mineral reserves and changes of the mineral reserves of the deposits [26].

Overall losses are higher in underground mines because of roof supporting pillars and it grows with depth increase [29][30]. Deepest oil shale mine Estonia has up to 30% overall losses (Fig. 6, Fig. 7, Fig. 8). At the same time largest losses are in the largest mine. In the future this trend continues [11][12]. Mining depth and amount of losses is related to the stability of the overburden rocks [5][6][7]. Losses and stability are influencing each other if backfilling is not used [19]. At the same time monitoring systems have developed rapidly [24][25].



	2006	2007	2008	2009	2010	2011
■ Ubja open cast	101	109	162	58	59	146
■ Sompa mine		33	1	31	77	315
■ Ojamaa mine		26	96	12	204	288
■ Vanaküla open cast	516	832	761	410	481	575
■ Põhja-Kiviõli open cast	818	896	908	868	885	637
■ Narva open cast	727	1375	1090	1147	1493	1539
■ Aidu open cast	1286	1682	1664	1582	1724	1770
■ Viru mine	1706	1761	1699	1740	1836	1730
■ Sirgala open cast	2345	2779	2587	2261	2813	2677
■ Estonia mine	4478	4499	4738	4500	5537	6188

Fig. 6 Annual oil shale production in Estonia, thousand tonnes per year

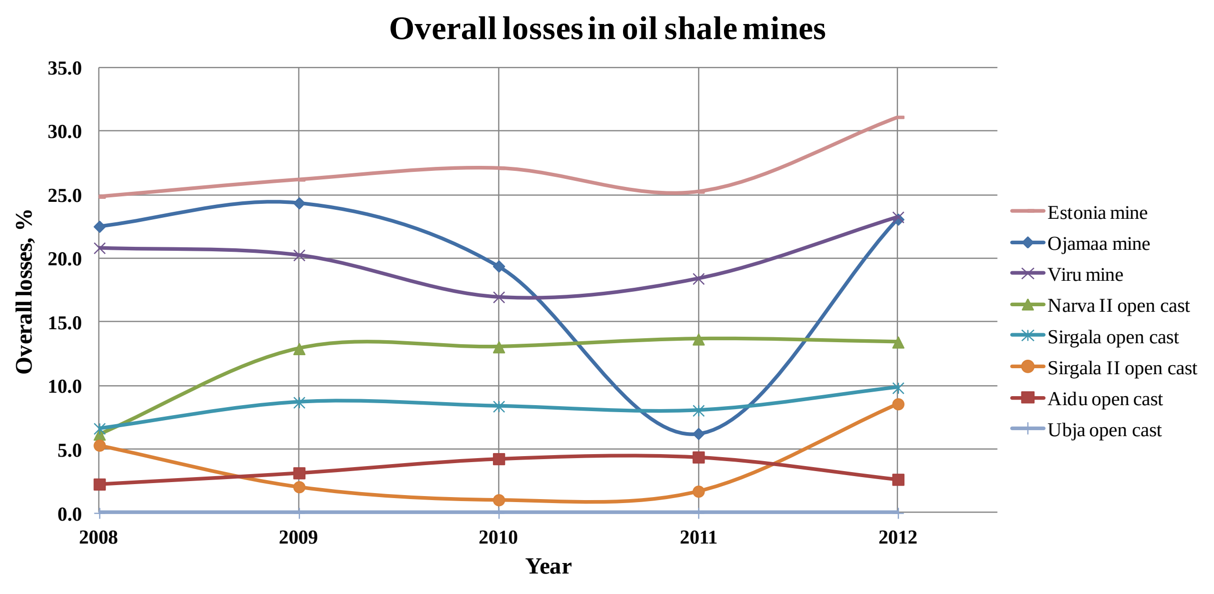


Fig. 7 Overall losses in oil shale mines during last five years [Environmental Register]

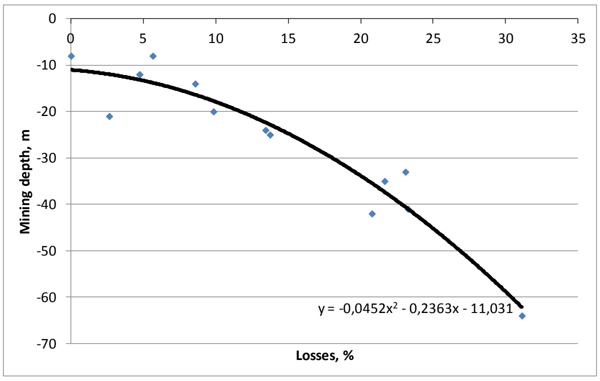


Fig. 8 Amount of losses depending on mining depth

A. *Processes*

The main processes affecting resource usage are resource management, extracting, crushing, separating and processing.

B. *Extracting*

Several extraction technologies have been used for mining oil shale during last 96 years [42]. In first years high selective hand mining was used due to absence of machines. The main problem related to losses and dilution was the rock that contained both oil shale and limestone what could not be separated by hand [3].

Later, when drilling and blasting was applied, only sorting or selective blasting influenced losses and dilution. Both full seam and selective seam blasting was used. In case of underground mining full seam and partial seam blasting was used. In years 1970 to 2000 partial seam longwall mining was used [32][33][34][35].

Due to weak limestone layers on top of underground room and pillar mining sections in Estonia mine, dilution is high and not only full seam, but in some cases 1.3 times higher seam is extracted [35].

Also surface miners have been used for selective mining of the oil shale [46][47]. For analysing possibilities of selective mining, range of tests and theoretical studies have been carried out during last decades [2]. Tests of high selective mining have been carried out in Estonia in limestone, dolostone and oil shale mining areas [42]. As well selective extraction has been performed by mechanical shovel, bulldozer ripper and hydraulic excavator ripping in several oil shale mining fields [38][39].

Several separation technologies have been used for processing the run of mine [40][41]. Due to the complex chain of mining processes optimisation is performed in some cases for finding optimal solution between losses, dilution, yield and other factors [4]. At the same time extraction technology has not been well analysed [36][37].

Surface miners productivity result show great variation in different oil shale layers and in other minerals layers. Surface miner Vermeer T1255 studies in 2012 show that surface miner productivity in F3 layer is 736 t/h and in C/D interlayer 591 t/h. The cutting speed in F3 layer is 0,12 m/s and in C/D interlayer 0,05 m/s.

Surface miner Wirtgen 2500SM studies in 2009 show that surface miner productivity in limestone interlayer H/J layer is 594 t/h and cutting speed is 0,06 m/s. Initial studies show that 80% of material pass through 25mm mesh and 30% through 3mm mesh (Fig. 9). Larger pieces are required for vertical oil generators. Solid heat carrier could use such material more easily.

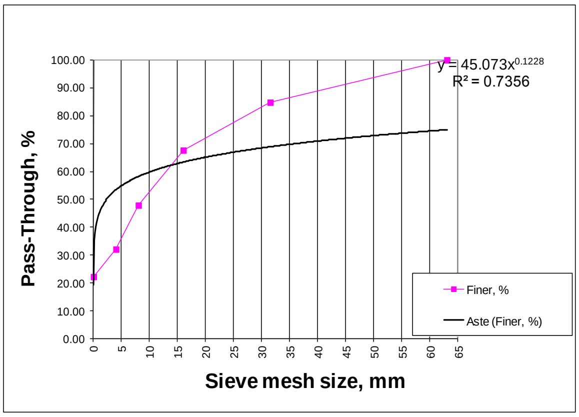


Fig. 9 Mechanical sieving analyses

C. *Crushing*

Initial tests with bucket crushers have been performed, showing promising dry separation results.

D. *Separating*

Fine separation machine, with the aim to separate fines from the separation pulp before it goes to sedimentation pond (Fig. 10).

Fig. 10 Fine separation cyclones

The fine separation machine is a hydro cyclone, what could process 50 m^3 in hour. The testing was done in two ways, first was with coagulant and the second one without it. Coagulant is additive what combines fine particles together and it should increase the amount of material. Fine particles were divided into the size 0-8 mm and 0-5 mm.

Fine particles with size 0-8 mm productivity were 162 kg/h and 0-5 mm 29 kg/h. Hydro cyclone productivity was 191 kg/h. Also was tested separated fine particles moisture, calorific value, ash value and were done mechanical sieving (Fig. 9). Initial tests showed that it is not possible to concentrate higher calorific value with coagulant.

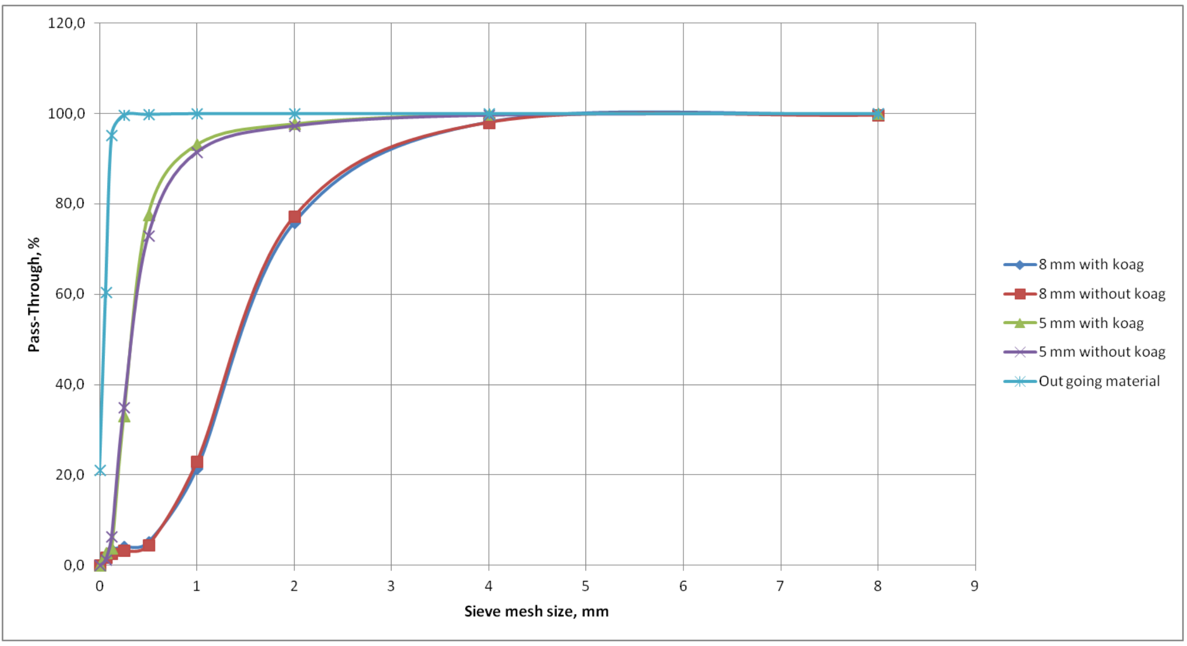


Fig. 11 Mechanical sieving results

III CONCLUSION

Reducing oil shale losses will be more actual in the future, because the depth of mining increases and the taxes for resource and pollutants are increasing as well. In several cases selectivity is the key solution for extraction, separation or processing. Fine separations has not shown good results for oil shale, but limestone fine separation, granulating or jigging should still be analysed with more options. In addition dry separation with sizers, drum crushers and roll-crusher sieves should be considered.

IV ACKNOWLEDGMENTS

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Functionalized Bark for Recycled Polypropylene-Based Composites

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***Abstract*. A new method for the modification of the bark surface using N,N-diethyl-2,3-epoxypropylamine (DEEPA) was developed. As a result, the part of the bark phenolic hydroxyl groups were replaced with amine groups. The conditions of the modification were found, and the modified products were analysed. The different amount of the introduced amino groups in hardwood and softwood bark was gained by the various contents of lignin in the wood species. The recycled propylene-based composites filled with the modified bark were characterised by higher mechanical parameters in comparison with the composites filled with unmodified bark. The differences in the mechanical properties of the polymer composites filled with softwood - pine (Pinus sylvestris) bark and hardwood - grey alder (Alnus incana) bark has been established.**

***Keywords* – composite, epoxyamination, modified bark, secondary polypropylene.**

I INTRODUCTION

Nowadays one of the parameters of social welfare is the produced amount of waste. Due to developing economical situation in the world within the last decades also production of municipal and hazardous waste has increased rapidly. Waste management depends on the legislation and waste management infrastructure in each country. In any case there are always problems with waste deposition and directly with leachate.

Logging and mechanical processing of wood are well developed in Latvia. The annual output of these industries is about 6.8 million solid m^3 of different types of lignocellulosic by-products, including bark. Wood bark normally constitutes a considerable volume of a log – from 10% to 20%, depending on the wood species and log diameter [1]. This lignocellulosic by-product is commonly burned up or stored, not finding much more rational utilisation.

Polyolefins such as polyethylene and polypropylene are the main constituents of polymeric municipal solid wastes. A perspective practice for recovering these polymers may be their processing together with the use of lignocelluloses as reinforcement agents [2], [3]. At the same time, the wood fillers in polymer composites have several disadvantages, the main of which being their low compatibility with the synthetic polymeric matrix.

One of the possible modification ways of a bark as a filler for the composite materials is the replacement of phenolic hydroxyl groups of lignin in the lignocellulosic structure of the bark with amine groups. It is known that lignin nitrogen-containing derivatives are obtained by a variety of methods [4] – [6]. In our previous work, carried out at the Latvian State Institute of Wood Chemistry, various lignins have been aminated with N,N-diethyl-2,3-epoxypropylamine (DEEPA) [7]. The content of nitrogen in the obtained amino derivatives is 1.7–3.8%. A good correlation is observed between the nitrogen content in aminolignin and the content of phenolic groups in the initial lignin.

The aim of the present study was to apply the developed method of lignin modification with DEEPA for the modification of bark, taking into account the presence of lignin, and to study mechanical properties of the obtained polymer composites filled with the modified bark.

II MATERIALS AND METHODS

Raw material

The initial pine (Pinus sylvestris) and grey alder (Alnus incana) bark (Table 1) were used as a filler for the wood-polymer composites. At first, they were milled, using “Retsch SM-100” cutting mills, for obtaining the filler particles with a size < 500 mk, and then modified. The thermoplastic polymer matrix used was a powder recycled polypropylene (PP). The content of the wood filer in the wood-polymer composites does not exceed 50 mass %.

TABLE 1.
CHEMICAL COMPOSITION OF INITIAL BARK [8]

Bark species	Cellulose (%)	Klason lignin (%)	Extractives soluble		Ash (%)
			In water (%)	In organic solvent (%)	
Pine	18.1	51.2	4.4	7.9	2.4
Grey alder	20.7	36.5	5.6	15.1	4.6

Chemical modification

The amination reagent was synthesised from diethylamine and epichlorohydrin according to the two-stage advanced method by Zakis [9]. At the first stage, 2 ml of water was added to diethylamine (71 ml, 0.69 M) and epichlorohydrin (54 ml, 0.70 M) to initiate the reaction. The mixture was stirred for 5–6 h at a temperature of 28–30°C (cooling in water bath) to form diethylamino-oxy-propoxy-chloride. At the second stage, sodium hydroxide (32.5 g, 0.82 M) and water (53 ml) were added for dissolving the residue to form DEEPA.

Testing of composites

The samples were prepared by the extrusion method on an extruder “RHEOCORD 90” (HAKKE, Germany) at the temperature 170–180°C as well as by moulding under a pressure in a casting machine at a temperature of 180°C. The mechanical tests were carried out in a universal machine “Instron” (USA). The surface structure of the obtained composites was examined on a scanning electron microscope Tesla (Czech Republic).

III RESULTS AND DISCUSSION

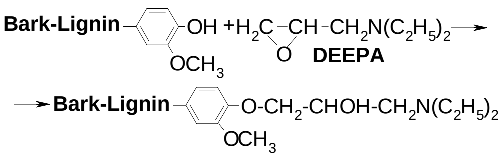
Bark modification

For many modes of the chemical modification of lignin, hydroxyl groups play the leading role [10], [11]. The heating of bark with DEEPA aqueous solution results in the formation of bark amino derivatives containing 2-hydroxy-3-diethyl-amine-propoxy groups.

Optimum amination conditions were achieved at a modulus of 1:15 (bark : water solution), a reagent mass ratio of 1:1.5 (bark : DEEPA), a reaction time of 1h, and a temperature of 98±2°C, with stirring.

The highest yield and N-content of amino derivatives were, when the active component DEEPA was separated from the whole synthesis mixture.

The interaction between lignin and the modifier may be represented according to the mechanism shown in scheme:



Our study has revealed that, on the average, up to 3% of nitrogen may be introduced in the bark (Table 2). It is supposed that the different amount of the introduced amino groups in hardwood and softwood is gained by the various contents of lignin in pine bark and grey alder bark (Table 1). With increasing the lignin content, the amount of the introduced amino groups grows.

TABLE 2.

NITROGEN CONTENT IN BARK DEPENDING ON MODIFICATION CONDITIONS

Bark species	With all synthesis mixture		Active component DEEPA	
	Yield of N-polymer (%)	N-content in N-polymer (%)	Yield of N-polymer (%)	N-content in N-polymer (%)
Pine	76	3.04	135	3.84
Grey alder	57	1.37	92	2.61

Bark-polymer composites

The analysis of the physico-mechanical properties of the obtained polymer composites indicates that the composites filled with the amino-containing pine and grey alder bark, on the whole, are characterized by better physico-mechanical properties in comparison with those of the composites containing the unmodified bark (see Fig. 1–4). This demonstrates an increase in the tensile strength and the rupture deformation by 31–50% and 14–52%, respectively, in comparison with those of the composite containing unmodified bark. At the same time, the values of modulus of elasticity and tangential modulus increase by 7–11% and 9–24%, respectively. The elevated values of the composite deformation may testify the additional plasticizing effect of the modified bark due to the presence amino groups.

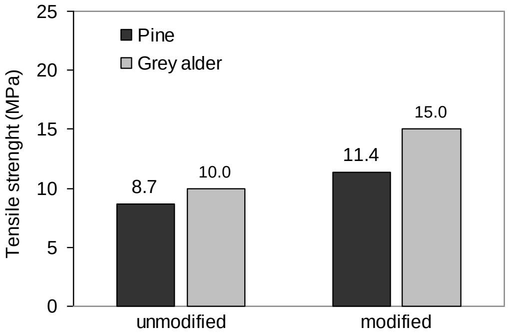


Fig. 1. Tensile strength of polymer composites filled with intial wood bark and modified ones

Fig. 2. Rupture deformation of polymer composites filled with initial wood bark and modified ones

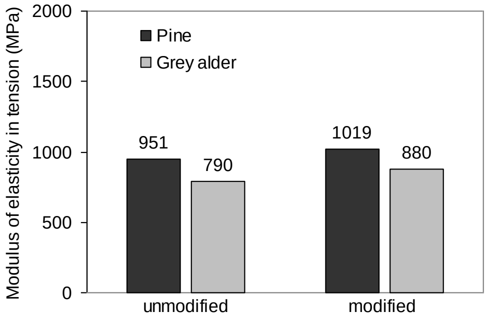


Fig. 3. Modulus of elasticity of polymer composites filled with initial and modified wood bark

Fig. 4. Tangential modulus of polymer composites filled with intial wood bark and modified ones

The results show that the composite materials filled with modified grey alder bark are characterised by higher physico-mechanical properties than those filled with modified pine bark (see Fig. 1, Fig. 2 and Fig. 4). It is supposed that the worsening of mechanical properties for the softwood filler may be governed by the enhanced content of resins in pine wood, which can negatively influence the compatibility of the polymer matrix with the filler. The morphology of the polypropylene composite filled with the aminated pine bark was examined by SEM. The microphotography given in Fig. 5 demonstrates a good homogenity of the obtained composite structure.

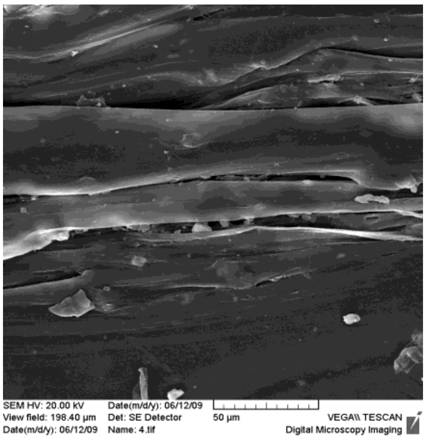


Fig. 5. Structural consolidation of filler particles in the composite, containing pine bark modified with DEEPA (50% recycled polyprolylene/50% modified pine bark)

The conducted moisture sorption study at a relative humidity of 98.9% during 90 days showed that a moisture sorption of 4.0–5.0% was characteristic for the composites filled with the modified bark both hardwood and softwood. The free hydroxyl groups presented in the modified bark were responsible for the absorption of water that decreased the mechanical properties of the obtained polymer composites. Our future investigation will be directed to the improvement of hardwood and softwood bark modification with the aim of obtaining the propylene-based composites with a lower moisture sorption.

IV CONCLUSION

A new method for the modification of the bark surface using DEEPA was developed. The optimal conditions of the bark modification were found, and the modified lignocellulosic products were obtained and analysed. The content of nitrogen in the modified bark was 1.7–3.8%. It is established that the application of the modified bark increases up to 50% of the tensile strength of the polymer composites in comparison with those containing unmodified bark as a filler. At the same time, the modified bark of hardwood effects more favourable on the composite mechanical properties than the modified softwood bark. The morphological study of the polypropylene composite filled with the aminated pine bark testifies a good homogenity of the obtained composite's structure.

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Environmental Resource - Economized Processes of Recycling Mineral Raw Materials of Complex Composition

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***Abstract*. The results of the studies on the justification of technological processes providing recycling of the warehoused ferruginous quartzites of complex composition and waste non-ferrous metals allowing to receive additional commodity products are given. The example of amphibole and biotite varieties of ferruginous quartzites of CMA and tailings of copper-zinc sulphide Ural ores determines the reasons of ineffective use of traditional technology solutions for recycling. The reasons of environmental hazards concerning varieties of technogenic mineral substances to the environment are identified. The presence in ferruginous quartzites complex composition of various silicates, carbonates and iron sulphides change their technological properties. So to get the iron concentrate from them suggests a new combination of technological operations performed in specially selected operating conditions. The specifics of the presence of mineral components in solid mineral wastes of nonferrous metal ores indicates the possibility of obtaining additional marketable products. With the use of laboratory multiscale modelling and physical methods of analysis regularities of variation of fractionation, separation and mineral concentration operations efficiency by varying its composition and the various influencing factors are identified. To improve the efficiency of the individual technological operations it is recommended to use different techniques, using physical and physico-chemical effects on the polymineral systems. The flow diagrams for the considered varieties of technogenic processing of mineral substances, allowing them to obtain standard quality products (metal-containing concentrates), and the results of their testing are submitted. The suggested technological solutions can reduce the amount of environmentally hazardous mineral substance, hosted in technogenic formations.**

***Keywords* – resource conservation, ferruginous quartzites, non-metal ores, mineral resources, technogenic formations**

I INTRODUCTION

Intensive development of mineral deposits is often accompanied by deterioration of the geological conditions of their mining, leads to an increase in the amount of recoverable from the subsoil complex composition mineral raw. Because of the significant difference of technological properties from conditional varieties of minerals, its processing in the production capacity of existing enterprises is not carried out [1].

Thus, on the average, only 10 - 20% of the recovered from the depths of the mineral matter (the rock) is used to obtain the final commercial product. The rest of it, although it contains useful components placed in man-made formations (tailings, sludge warehouses, etc.) that adds up to Russia about 2.5 billion tons per year. This situation has a negative impact on the economic performance of enterprises.

Accumulated in the central regions of Russia manmade mineral waste of mining and mineral processing occupied the total area of about 0.7 million hectares, situated mainly in industrialized regions with high density of population.

Disintegrated state of located on the surface man-made mineral substance provides free access to a natural fluids (liquids and gases) causes an intensive flow of hypergenic processes (oxidation, hydration, interaction of the components), and the presence of heavy metals and toxic elements in solid-phase contributes to migration of hazardous components including the hydrosphere and, as a consequence, the deterioration of the environmental situation in the mining regions [2].

Along with this, the mineral substance of technogenic formations contains useful components, shortage of which have various industries, so it can be considered as an additional resource base.

II MATERIALS AND METHODS

Radical solution to the resource and environmental problems associated with the formation and storage of unused types of mineral matter of natural and anthropogenic origin, is to reduce its volume, through their recycling using specially developed technology.

Ferruginous quartzite of complex composition of Lebedinsky ore deposit and tailings of copper-zinc sulphide Ural ores (for example, waste ore at JSC "Svyatogor") is the subject of the research.

The study of the composition, structure and structural condition features of mineral matter of ferruginous quartzite of complex composition and tailings of copper-zinc sulphide Ural ores was carried out with the use of complex methodological approach that uses multiple physical and physico-chemical analysis of mineral matter which data cannot only confirm, but also complement each other.

The purpose of the study is to develop technological methods of processing of man-made mineral matter which gained a conditioning commercial products that improve the environmental situation in the regions

Ferruginous quartzite *of* complex composition

Studies have shown that ferruginous quartzites of complex composition of Lebedinsky deposit are typical very finely disseminated ores and significant differences in material composition, variety of textural and structural features of non-uniform impregnation of metallic and non-metallic minerals with similar physical and chemical properties/

By ferruginous quartzite complex of composition are kummangtonit-magnetite and biotite-magnetite ferruginous quartzite species; the features of their structure can be judged on the basis of the data presented in Table 1.

TABLE 1

THE DIFFERENCES OF THE MINERAL COMPOSITION OF THE MINERAL PROCESSING SAMPLES OF FERRUGINOUS QUARTZITE OF LEBEDINSKY DEPOSIT

Minerals	Magnetite quartzites	Cummingtonite-magnetite quartzites	Biotite-magnetite quartzites
Quartz	29,5 - 34,5	32,2 - 37	12,5 - 17,5
Magnetite	34 - 39	26,6 - 31,5	30 - 35
Hematite	1,73 - 2,0	0,15 – 0,2	-
All carbonates	2,6 - 3,5	8,1 - 13	2,5 - 5,0
All amphiboles	13,5 - 17,0	18,5 - 22,5	30 - 35
Aegirine	0,5 – 2	-	-
Biotite + green mica	2,5 - 4,5	7,6 - 11,5	9 - 13,5
Pyrite + pyrrhotite	0,23 - 0,25	0,43 - 0,52	5 - 7

The information about presented in this table group of minerals - amphibole includes varieties:

1) monoclinic amphiboles: cummingtonite, actinolite, tremolite, grunerite;

2) alkaline amphiboles: riebeckite, glaucophane;

3) rhombic amphiboles: anthophyllite.

On the strength of the weakest intergranular contacts is iron-mica-magnetite quartzite, followed by alkali-magnetite quartzite, cummingtonite-magnetite quartzite and biotite-magnetite quartzite.

Sulphides in the ferruginous quartzites of complex composition are mainly pyrite. Dimensions of pyrite formations vary between 0.005 to 3-5 mm. Forms of emphasis of pyrite are very diverse: from the rounded, equant, euhedral grains with well-educated faces (it is usually the smaller individuals from 0.005 to 0.1 mm) to the needle, elongated curved, corrosive, skeletal, as well as patterns of substitution after magnetite , siderite silicates

It was found that ferruginous quartzite of complex composition of Lebedinsky deposits are rich in amphibole (35%), mica (14%), sulphides (up to 7%).

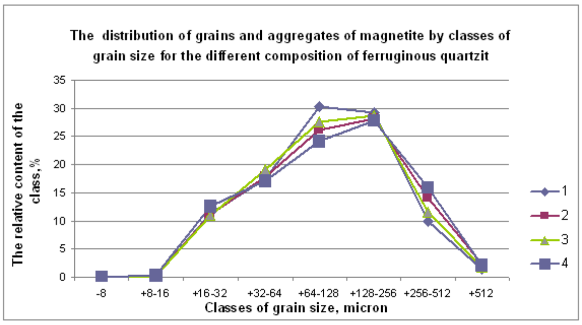

Fig. 1 The distribution of grains and aggregates of magnetite by class size for the ferruginous quartzite of different composition (1 - magnetite, 2 - magnetite with cummingtonite, 3 - magnetite with alkaline amphibole, 4 - cummingtonite-magnetite)

The study of grain size distribution of useful component in different ferruginous quartzite species showed a significant difference in the magnetite grain size in quartzites of complex composition. This is confirmed by the data presented in Figure 1.

The difference in the magnetite grain size in quartzites of complex composition results in significant changes of their physical and technical properties, and results in inefficiency in the traditional technological schemes of processing [3].

Analysis of the data showed that it is advisable to extract useful components using fractional magnetic separation followed by of coarse- and fine-grained enrichment by the individual schemes.

Further experimental study of the effectiveness of individual recycling processes and the choice of optimal conditions and modes was performed using multiscale modeling methods of disintegration processes, fractionation and concentration of mineral matter.

Tailings of non-ferrous metals

The studies of the composition and structure of mineral matter tailings of nonferrous metals in the man-made formation "Svyatogor" showed that there are useful components in their composition. The result of the composition of a representative sample of the mineral matter is presented in Table 2.

The study of representative samples made by using X-ray diffractometry showed that they contained: chalcopyrite (1.67%), sphalerite (1.2%), pyrite (57.6%), quartz (25.8%), feldspar (8%) and mica (6%).

It was found that chalcopyrite in classes minus 2.0 plus 0.63 mm is full of incorrect inclusions in pyrite or occupying his veins in intergranular space. In the class minus 0.63 plus 0.40 mm appear loose grains of chalcopyrite, which quantity is in the range of minus 0.074 plus 0.043 mm increased to 70%, and in the class minus 0.043 mm increased to 80%.

Сфалерит в классах +0,40 мм встречается только в сростках с пиритом и с

The sphalerite in classes +0.40 mm is found only in intergrowths with pyrite and non-metallic inclusions in the rare forms or small abnormal secretions in the intergranular space of pyrite. In the class minus 0.40 plus 0.315 mm appear free sphalerite grains (14%), the number of which is gradually increased, reaching 87% (class minus 0.074 plus 0.043 mm) and 91% (class minus 0.043 mm).

TABLE 2

TABLE OF CONTENTS OF EXTRACTED ELEMENTS IN THE NON-FERROUS METAL ORE WASTES STOCKPILED IN THE TECHNOGENIC FORMATION

Grain size classes, mm	Output, %	Content, %		
		copper	zinc	sulfur
+2,8	0,07	0,52	1,38	27,79
-2,8+2,0	0,53	0,79	2,61	32,40
-2,0+1,4	0,61	0,81	0,31	28,29
-1,4+0,63	4,83	0,66	0,54	22,09
-0,63+0,40	6,91	0,61	1,29	22,36
-0,40+0,315	6,46	0,55	0,93	20,74
-0,315+0,2	16,90	0,62	0,65	23,44
-0,2+0,125	23,73	0,49	0,55	28,70
-0,125+0,09	0,89	0,54	0,76	36,05
-0,09+0,074	14,24	0,52	0,68	32,66
-0,074+0,043	13,84	0,49	0,68	33,14
-0,043	7,99	0,60	0.78	40,32
Total	100,00	0,55	0,72	8,18

Grain size classes, mm	Output, %	Distribution, %		
		copper	zinc	sulfur
+2,8	0,07	0,06	0,13	0,06
-2,8+2,0	0,53	0,76	1,93	0,52
-2,0+1,4	0,61	0,90	0,26	0,59
-1,4+0,63	4,83	5,78	3,64	3,68
-0,63+0,40	6,91	7,65	12,43	5,33
-0,40+0,315	6,46	6,45	8,37	4,62
-0,315+0,2	16,90	19,02	15,35	13,70
-0,2+0,125	23,73	21,11	18,31	23,54
-0,125+0,09	0,89	3,81	4,12	4,84
-0,09+0,074	14,24	13,44	13,49	16,07
-0,074+0,043	13,84	12,31	13,29	5,86
-0,043	7,99	8,71	8,69	11,12
Total	100,00	100,00	100,00	100,00

The pyrite during grinding released from intergrowths significantly faster: if in a class minus 2.0 plus 1.4 mm it is found only 8% free grains of it, then in the class minus 0.074 mm plus 0.043 - 97%, and in the class minus 0.043 mm pyrite almost disclosed. It often grows together with chalcopyrite (2-11%), rarely sphalerite (1-6%) and non-metallic (3-8%).

These results indicate that the waste of non-ferrous metal ores keeping for a long time in man-made tailings are rather difficult target of enrichment, as valuable minerals in them closely grow together with pyrite. Thus sphalerite released from pyrite intergrowths much better than chalcopyrite (respectively 91% and 80% in the class minus 0.043 mm). To extract chalcopyrite and sphalerite very fine grinding of the sample is necessary, which leads to overgrinding of pyrite and formation of sludge, complicating the selective separation of minerals [4].

The difference of the structure and composition of the mineral substances extracted from man-made formation and incoming to the enrichment is illustrated by the graphs shown in Figures 2 and 3.

It was found that when the grinding time is 20 min the content of the class minus 0.074 mm from the waste ore is a 35% increase than in the ore crushed material.

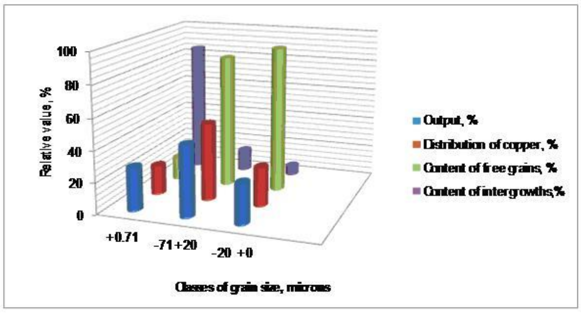

Fig. 2. The characteristics of different grain size classes of disintegrated ore coming onto the enrichment

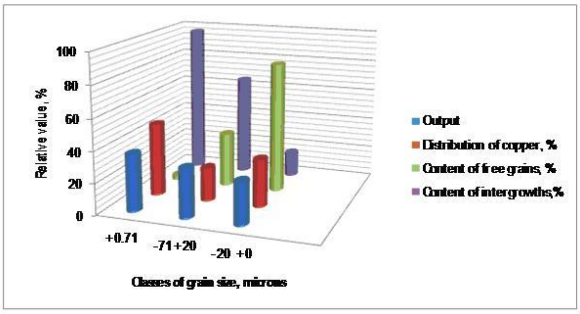

Fig. 3. Characteristics of the different grain size classes of mineral matter in nonferrous metals technogenic tailings

In Figures 2 and 3 it the results of particle size, mineralogical and chemical analysis of disintegrated mass and waste of ore Volkovsky deposits on JSC "Svyatogor" are shown.

These results revealed a significant difference in the distribution of the useful components in mineral matter. Studies have shown that most of the copper minerals in the raw material (55%) (Figure 2) is in a class of -71+20 microns, with 86% in the form of free grains, in class +71 micron copper minerals are represented by intergrowth (85%) in the class -20 microns dominate free grains (95%). In the tailings (Figure 3) the character of the distribution of copper minerals is different: most of the copper accounts for class +71 microns (47.26%), and in the class -71 + 20 micron there is a minimum distribution of copper - 21.8%.

Comparing the data presented in Figures 2 and 3, it can be noted that the major losses occur in aggregates of copper minerals in a class of 71 microns, and to a large extent on the availability of grain in classes -71+20 and -20+0 microns.

The study found that non-ferrous minerals of stale tailings represent the transformed mineral association with specific surface and technological properties different from the ore mineral associations.

The investigations have shown that the processing characteristics of stale ore wastes and disintegrating ores vary due to the changes in the surface properties of their constituent minerals. Experiments have shown that the changes in the technological properties of mineral matter are associated with the manifestation of the following factors:

- an increase in technogenic material of fine fractions;
- the presence of oxidized forms of copper minerals, which are suppliers of copper cations in the liquid phase;
- oxidation of the surface of the non-ferrous metal sulphides;
- preservation of pyrite flotation activity.

Further experimental studies of disintegration processes, fractionation and separation of mineral matter of ferruginous quartzite of complex composition and waste of non-ferrous metal ores made using multiscale modelling allowed us to establish patterns of changing the efficiency of these processes, depending on the conditions and characteristics of their implementation.

On the basis of the pilot study the selection of the optimal parameters of the individual processes to ensure efficiency of mineral substances processing is carried out.

III RESULTS AND DISCUSSION

Recycling of ferruginous quartzite of complex composition

The research of process of complex composition ferruginous quartzite recycling was carried out with specifics of existing manufacturing base for processing of their conditioned varieties.

The analysis of data on the distribution of magnetite in the products of disintegration has shown that for a quality magnetite concentrate of ferruginous quartzite of complex composition it is advisable to use a scheme realizing the fractional magnetic separation with split-flow disintegrated masses by size. In this case the disintegration of multimineral aggregates should be carried out in three stages (see Figure 4).

The experiments showed that the disintegration of the ferruginous quartzite with the use of autogenous grinding mills the performance of the operation depends on the mass fraction of grinding media and of milled classes in nutrition, as well as the water consumption. It was found that the maximum performance is achieved when the ratio between the grinding and milling classes is 2.3 - 2.6.

It was found that as the number of stages of wet magnetic separation increases the metal extraction into concentrate, and the number recleanings for ores of complex composition, should be: three - "basic" and two - "roughing" [5].

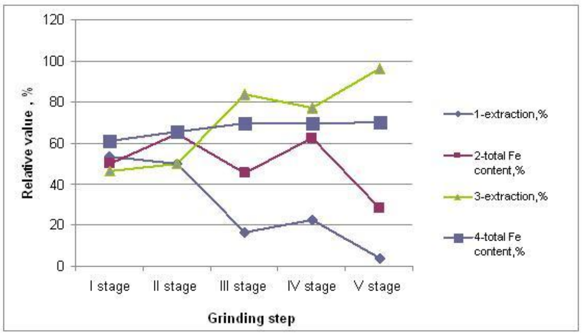

Fig. 4. The influence of the grinding step to retrieve the value (in%) and the concentration of Fe total. (in%) in the products of disintegration of the ferruginous quartzite of complex composition with grain size + 0.045 mm (lines 1, 2) and - 0,045 mm (lines 3, 4)

Experiments have shown that the use of the processing of ferruginous quartzite thin fractionation of complex composition that uses high-frequency vibration exposure, reduces the amount of material to be sent to the secondary disintegration, and ensures growth of mass fraction of iron in the concentrate, as well as smaller overgrinding of iron minerals than using hydrocyclones. The study of the influence of various schemes disintegration of the ferruginous quartzite of complex structure on the efficiency of the process, different by ratio of the number of primary and secondary crushing mills, showed that the obtained magnetite concentrates are similar in mass fraction of iron (65,98-66,22%), however, waste of concentrating cycles for different disintegration schemes differ significantly. Their output ranged from 10.02 to 11.04% when the mass concentration of total iron content varies from 8.99 (Figure 3-2) to 11.45% (1:1) and magnetic iron content varies from 0.77 to 1.65% respectively.

Conducted research of polymineral masses fractionation process showed that the increase of solid mass fraction in griddle nutrition from 30% to 40% reduces the effectiveness of sifting for 8%, the increase up to 50% - for 10%, and increase the frequency of griddle vibration from 42 to 50 Hz reduces the efficiency of sifting by 4% when the mass concentration of solid in griddle nutrition is 30%; when the mass concentration of solid in grate nutrition is 40% the effect of vibration frequency on the effectiveness of sifting is insignificant.

Recommended scheme of treatment of complex composition ferruginous quartzite stipulates ragging in boulder crusher KKD 1500/180. Crushed to a particle size 0-350 mm product is transported by conveyors into the enrichment house, where conveyor system distributed it over bins.

At the processing plant crushing and enrichment of ferrous quartzites is carried out on the scheme of three-way grinding with five stages of magnetic separation (ratio of volume of mills in stages is 3:2).

Experiments have shown that the scheme 3:2 is a basic scheme that will ensure the raw magnetite concentrate of ferrous quartzites complex composition, providing the production of concentrate with Fe content 66,6-68,7%.

Crushed ore is fed to the horizontal conveyor, where reloaded onto conveyors filing the ore to the primary mills.

The first stage of grinding is carried out in three wet grinding mills operating in a closed cycle with spiral classifiers. The first stage provides grinding to a particle size of 65-75% of the class - 0,071 mm. The drain of spiral classifier enters the first stage separation. Each block of separators contains a sequentially installed three drums, i.e. separation is carried out in three stages. Tails of the first stage of magnetic separation are sent to the tail tray. The first stage middlings of magnetic separation enters the dibhole from which is fed to the classification at the griddle of fine screening. Oversize material of fine screening comes to the secondary grinding. Discharge of the mill supplied to the second stage of wet magnetic separation. Wastes of the second stage of wet magnetic separation are sent to the tail tray, and middlings return to thin fractionation.

Undersize material of fine screening fed to an additional classification in hydrocyclones. Hydrocyclone separation occurs on a class -0.071 mm. Discharge of the hydrocyclones, containing 85% of the class -0.045 mm, fed to the third stage of wet magnetic separation in two steps. Tails of the third stage of magnetic separation are sent to the tail tray. Magnetic product after the third stage of magnetic separation is the final product, corresponding to the requirements for ordinary magnetite concentrate.

A high-quality magnetite concentrate is carried out on an additional scheme in which produced magnetite concentrate fed into the radial thickening, where they compacts up to the solid mass fraction of 60%. Underflow solids are pumped to the average in the stirrer.

After compaction and stirring ordinary average magnetite concentrate fed to the grinding to a particle size minus 0.045 mm of 98%. Discharge of the mill is supplied to the first stage of wet magnetic separation. The obtained concentrate is fed to the classification at the thin fractionation griddles, and tails are sent to the tail tray. Oversize material of fine fractionation returned to the mill, and the underflow material is fed to the slime removal, which discharge with solid mass fraction of 0.12% goes to the recycling of water and sand is applied fed to the second stage of magnetic separation. The obtained product - high quality magnetite concentrate with Fe content of 70.0% is the final product.

Conducted research trials showed the promising use for the operation of magneto-gravitational condensation of the concentrator (MGS-0,5). It was found that the mass fraction of solids in the initial nutrition of magneto-gravity concentrator does not affect mass fraction of SiO_2 in the concentrate, and the mass fraction of solid in concentrate affects slightly.

It was found that the mass concentration of Fe_{total} 68.56% in the nutrition while using magnetic-gravity concentration the concentrate with Fe_{total} 69.69% and SiO2 3,36% is obtained. The experiments also showed that the reduced magnetic field strength of MG-concentrator allows to produce concentrate with a smaller mass fraction of SiO_2.

Recycling of non-ferrous metals enrichment

Implementation of a complex research processes of non-ferrous metal ores waste processing, in which the flotation separation techniques of polimineral systems used, allowed to choose an optimal combination and modes of specific operations execution.

Investigations have shown that pyrite, which is the main ore-forming mineral of pyrite deposits (up to 90% of the sulfide) has a significant effect on the oxidation of sulphides of nonferrous metals and on precious metal mineral associations. Processes of oxidation of sulphides are intensified by mikro galvanic couple (nonferrous metal sulphides with pyrite, which play the cathode role).

It is stablished that in the processing of the mineral matter it is expedient to use the combined technological schemes and additional fractionation with a conclusion in the final products of fractions that have similar technological properties. This allows to recycle them using individual technologies, which improves the technological parameters and the complexity of the use of raw materials [6]. Occurring in the technogenic formation hypergenic processes cause a high acidity which was produced at the contact of heterogeneous system with water.

The study of the effect of old tailings grinding time on the pH shows that with increasing the duration of grinding and thus reducing the size of the solid phase, the acidity of the environment is stabilized (Figure 5).

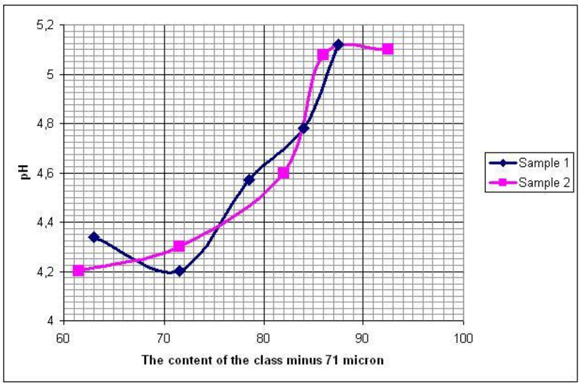

Fig. 5.Change in pH with a decrease in size of the solid phase during the grinding process to investigated old tailings tests

The study of the kinetics of the oxidation rate of ore minerals change during grinding in the liquid phase of different compositions allowed to select rational methods of purposeful changing their ability to flotation recovery.

Figure 6 shows the dependence of the oxidation rate of unit mineral surface by oxygen during grinding in a saturated solution of lime to time. The curves of sulfide oxidation rate of unit mineral surface by oxygen unit surface show that the highest rate of sulphides oxidation in the prescribed range observed in the first minutes of grinding, and then with increasing grinding time is tapering off.

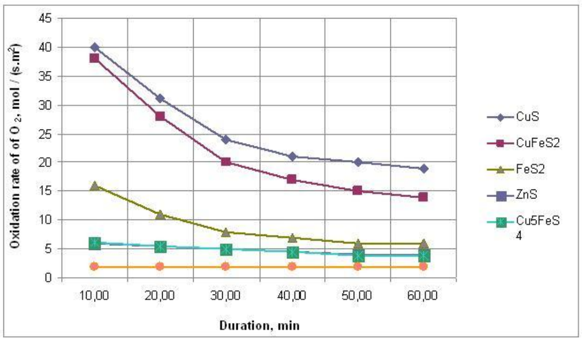

Fig. 6. rate of absorption of oxygen by a unit surface sulphides during grinding in a saturated solution of lime in time

Decrease with time of the rate of oxidation per unit area of sulphide minerals in the grinding process is mainly due to the fact that the oxidation of sulfides in highly alkaline medium occurs with the consumption of alkali, and with a decrease of alkalinity the rate of oxidation of sulfide minerals decreases. Other, less significant cause of it, and the fact that oxidation of the oxygen concentration in the solution is reduced as long as the rate of dissolution of oxygen in the slurry reaches the speed of oxidation.

The experiments showed that the highest rate of oxidation chalcopyrite has, leading to significant changes in surface properties, complicating its flotation recovery. When the natural duration of redox processes in the tailings, along with the activation of the surface of sphalerite by copper cations, sphalerite oxidation occurs with the formation of oxidized forms of zinc minerals - smithsonite, zincite and calamine, which are practically not extracted with flotation methods of enrichment. Pyrite, which in redox processes acts as the cathode, the most remains flotation activity.

It was found that fine regrinding of large fraction of old waste of ores for subsequent gravitational and flotation extraction of useful components is a necessary operation, allowing for the inter-cycle operation of gravity or flotation of copper extraction.

Investigations have shown that the use of aeration in the collective and selective flotation, can improve performance of the process. Moreover, the best results are obtained with continuous aeration during 5-10 minutes. At the same time the extraction of copper in obtained after gravity separation concentrate increased by 20%, in the collective copper concentrate by 20-25%, zinc more than 2 times, greatly improving the quality of concentrates, and the extraction of zinc in rough zinc concentrate at any lime consumption by 10 20% higher than without aeration when mixed with reagents.

It was also found that with increasing temperature up to 60 °C, the efficiency of the separation process in the zinc flotation of pyrite and sphalerite with different duration of mixing zinc recovery increased average by 10%, followed by a further increase in temperature decreases. Extraction of iron in the rough zinc concentrate with increasing temperature up to 95 °C decreases by 2 times. The optimum temperature is in the range 40-65 °C, and the duration of the mixing has a significant effect of up to 20 °C. Oxidation-thermal effect on the sulfide polymineral mixture increases the difference in the oxidation of sulphide minerals surface and the various changes in their flotation properties. As reagents accelerating the oxidation of sulfides by heating, used lime, calcium hypochlorite, hydrogen peroxide.

Investigations have shown that the technology of recycling of non-ferrous metal ores should include operations - disintegration; washing; classification; desliming on class minus 0.010 mm; gravitational extraction of useful components, regrinding of sand fraction; selective flotation to produce copper and pyrite products, copper zinc middlings and tailings; selective flotation of copper-zinc product.

IV CONCLUSION

The executed researches have shown that the processing of mineral substances of complex composition ferruginous quartzites and previously stockpiled wastes of non-ferrous metals produces quality conditioned metal concentrates. The use of specially selected for each object of the study complexes of technological operations carried out in specific conditions and modes, provides reception the concentrate of complex composition ferruginous quartzites with Fe content of at least 68, and 5% from the previously stockpiled tailings base metal ores concentrates with no less 16% of copper and at least 48% of zinc. Use of the proposed technology solutions will reduce the amount of that will be hosted on the surface of environmentally hazardous mineral matter, and is able to improve the environmental situation in the regions.

V ACKNOWLEDGMENTS

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Vertical Flue Gas Heat Absorption System with Option for Fuel Drying

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***Abstract*. The publication will describe research that produced vertical inglenook type innovative vertical flue gas heat absorption system with option for fuel drying. Innovative arrangement of smoke ducts will be developed for the flue gas heat absorption inglenook. The inglenook will be heating up in the bottom therefore the lower level of premises will be heated more efficiently and provide higher degree of comfort. Considering fire safety regulations above the inglenook 4 arches will be built for storing and drying firewood before burning.**

***Keywords*: firewood drying, oven-couch, energy efficiency, microclimate of buildings.**

I INTRODUCTION

Usually there are two types of heating. The first is operating by small capacity during heating time without heat accumulator. The second is operating with considerably higher capacity, heating up heat accumulator and stops. Accumulated heat energy heats up interior of the building. Implementation of the first system is usually cheaper than the second. But exploitation costs of the second system are more profitable. Preparation of firewood bricks in right size is very important. For the first kind of heating rough size logs are recommended, because they must burn long time and give heat. Unfortunately also heat losses via flue gases are high. For the second kind of heating thin size logs are recommended, because they must burn fast and heat up accumulator. In short burning time with high temperature and capacity it is possible to produce more heat and decrease heat losses by flue gas. Considerable improvement of working conditions of heating system is possible by additional drying and pre-heating of firewood. That is easy to set on fire, is burning by high temperature, increases capacity of boiler for 10…15%. Regulations of fire safety must be kept carefully and solution has to be found to suitable use of heat energy of the boiler surface, which usually produces losses [1].

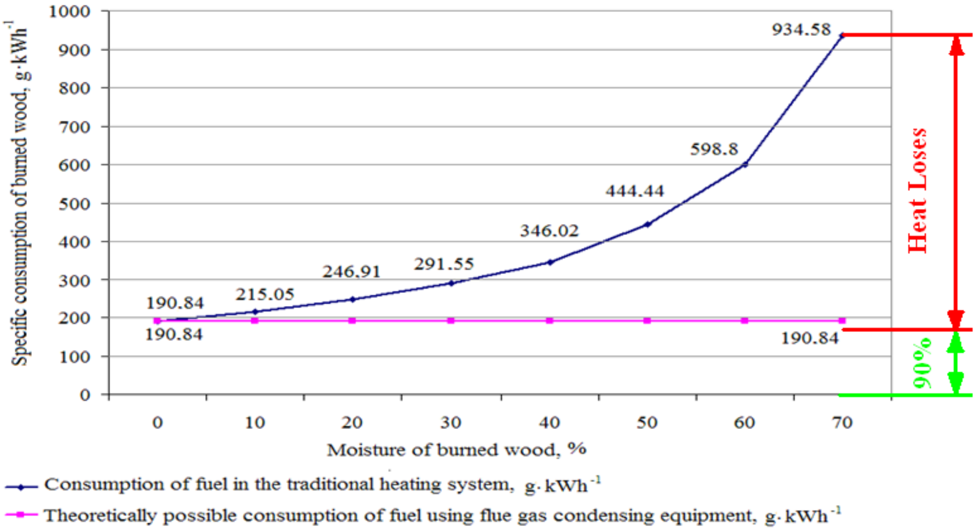

Fig.1.Dependence of the heat energy losses from the wood fuel moisture [1, 2]

When dry fuel is burnt in the heating equipment, efficiency factor of which is indicated in the technical passport for example as 90%, the heat losses arising from the discharge of flue gas into atmosphere are amounting to 10%. If this is moist fuel, thermal energy from the combustion process is used for its drying, and the latent thermal energy of the generated steam together with flue gas is discharged into atmosphere. In order the heating equipment to ensure a constant amount of the obtained thermal energy, the blue curve represents increase in consumption of fuel depending on the amount of moisture in the fuel (Fig 1). This demonstrates that in order the heating equipment without condensation of flue gas and the steam latent heat recovery system to function with the specified efficiency factor and the fuel to be used economically, prior to combustion it should be sufficiently dried. The solution proposed in the publication relatively makes it possible to perform without using additional thermal energy, since in order to ensure for an individual optimum microclimate of the room to be heated, unnecessary evaporization of water during the winter can be avoided to maintain moisture appropriate for comfort in the atmosphere of the room to be heated.

II MATERIALS AND METHODS

The firewood will be dried for about a month (each arch to be used for a week) thus reducing moisture content by 25-35% in the firewood which previously has been stored under a shelter outdoors till 5–10% of moisture. This will significantly ease firing, improve quality and intensity of a burning process, shorten duration of the burning, will reduce firewood consumption and emissions of the flue gases, their temperature and amount of hazardous particles in them. It also will reduce possibility of condensate build up on the surfaces of the ducts and chimney, increase the coefficient of performance of the heating system etc. Humidity produced during drying process will be used to humidify air in the heated premises when due to freezing temperatures humidity in the fresh air introduced from outdoors is reduced and dropped below optimum of 45–55%. The collected data will be processed using Excel software and the results of the scientific research will be shown in graphs.

Description of the construction of experimental object: the experimental object is located within the building to be heated in such manner as the oven-couch to function also as a partition wall between two rooms to be heated and both sides of the oven-couch to heat it. Monolithic concrete foundations were constructed. On these an oven-couch has been built from side-facing 400 clay furnace bricks, on which four arched shelves for additional drying of fuel have been built from 100 bricks. A mantel façade from 250 bricks has been built close by in compliance with fire-prevention regulations. As a binding agent for oven-couch were used 400kg, for shelves 80kg, but for mantel façade 200kg of sand-cement-lime mixture PM Super. A steel fire furnace connected with oven-couch and the existing brick chimney was inserted in the mantel façade. Oven-couch is horizontally divided in two parts (see Fig. 2).

Working of the experimental object: open valves (2) and (3). Place the fuel into fire furnace (1) and set fire. Flue gases are mainly flowing through valve (2) to chimney (4) and warming it up for 5-10min. When the fuel has well caught fire and draught has become sufficiently strong, the valve (2) is closed. From fire furnace the hottest flue gases are flowing through flue gas shafts (5) of the lower part forward to the oven-couch end and more warming up its lower part. The more intensive infra-red radiation radiated from the oven-couch warms up the lower part of the room to be heated. It provides for a more even heat distribution and a more comfortable conditions in the room to be heated. At the oven-couch end flue gases are considerably cooled down and flow into flue gas shafts (6) of the upper part and dissipate a part of the remaining heat. When the fuel has fully burnt down, the valve (3) is closed and the oven-couch continuously releases the accumulated heat in the room. This solution fully complies with the fire safety requirements in order to firewood could be placed above the oven-couch on drying shelves(7) for additional drying before combustion. Shelves are divided into four parts. Fuel of each part is intended to be combusted approximately within one week and at once to be filled up again. In this way the fuel is intended to be subject to additional drying approximately for one month before incineration. Since upper portion of the oven-couch is considerably cooler than the lower one, drying of the fuel is predominantly ensured by the warm air accumulated in the upper part of the room and ventilated by its free flow. Moisture contained in the fuel is considerable reduced during the additional drying process. Such decision allows to use an existing chimney built from bricks, since notwithstanding high efficiency factor of the heating system due to which flue gas is cooled down to a comparatively low temperature, actually no condensate is developing and no stainless steel casing has to be inserted in the brick chimney, or no other heat-insulated steel chimney has to be built. From the fuel the dried out moisture contributes to more optimal microclimates of the rooms to be heated during the heating season, when the fresh outdoor air is cold and excessively dry.

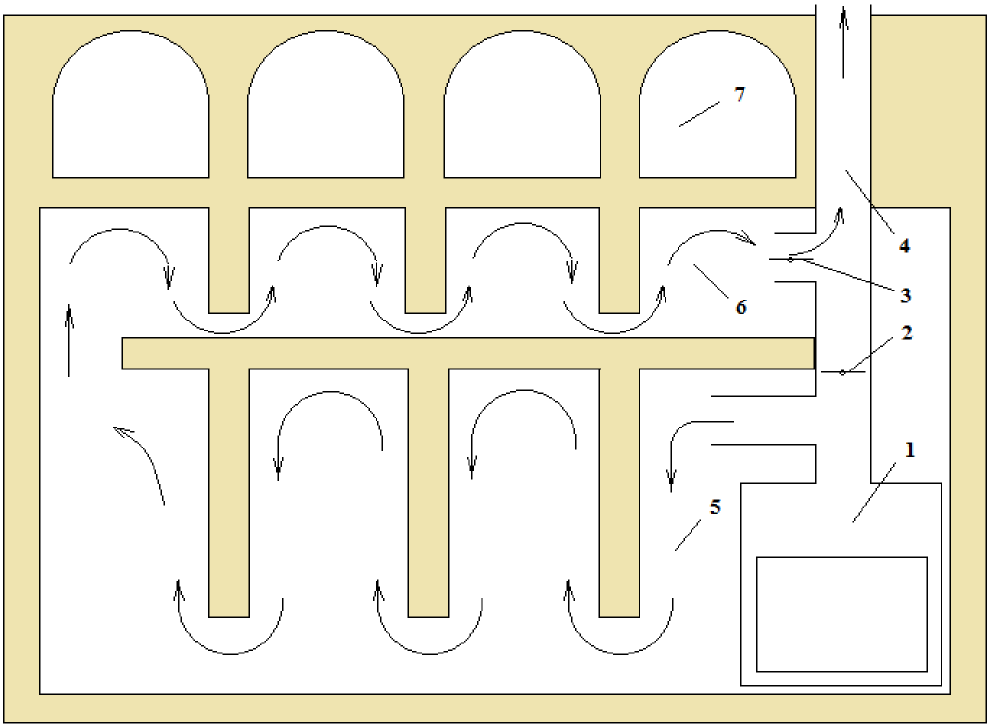

Fig. 2. The vertical flue gas heat absorption structure with the fuel additional drying option

1- furnace; 2- flue gas flow regulating valve to chimney or oven-couch; 3- oven-couch seal; 4- chimney, 5- forward shaft of the hottest oven-couch flue gas; 6- backward shaft of the coolest oven-couch flue gas; 7- additional drying shelves for fuel

Description of the experiment. In order to bring conditions as close as possible to the real situation, experiments were performed during the winter heating season each day from 1 February to 20 February 2013.

Each time 7kg of different wood species with moisture 10% were inserted into the furnace. By means of an electronic multimeter the outdoor air temperature (average -5ºC), the room air temperature, air temperature at inlet to the furnace, on flue gas pipe surface from the furnace and in flue pipe from the oven-couch to the chimney was detected. Experimental measurements were read off at intervals of 30 minutes, heating duration of 2 hours, duration of indication readings as 3 hours. Upon summary of data obtained in 20 repeated experimental measurements, average temperatures were calculated (see tab. 1), but for the resulting curves see Figures 3 and 4.

TABLE 1.

EXPERIMENTAL STUDIES OF THE OPERATION OF VERTICAL FLUE GAS HEAT ABSORPTION STRUCTURE

Experiment duration, min.	Average temperature, °C					
	Indoor air	Air inflow to furnace	Discharge of fuel gas from furnace	Discharge of fuel gas from oven-couch	Oven-couch lower part	Oven-couch upper part
0	18	18	18	18	18	18
30	22	19	215	25	28	23
60	24	20	230	28	32	25
90	28	22	185	30	40	27
120	28	22	125	29	40	27
150	27	-	-	-	38	28
180	27	-	-	-	37	28

Description of data obtained in experimental studies of the operation of vertical flue gas heat absorption structure.

The data obtained resulting from experimental studies were entered into the Excel program by creating a Table 1, from which Figures 3 and 4 were obtained. Processing of the data obtained resulting from experiment was carried out using the Excel program. Distribution in energy is demonstrated by Fig. 4, representing the areas taken by the flue gas temperatures from the furnace and from the oven-couch.

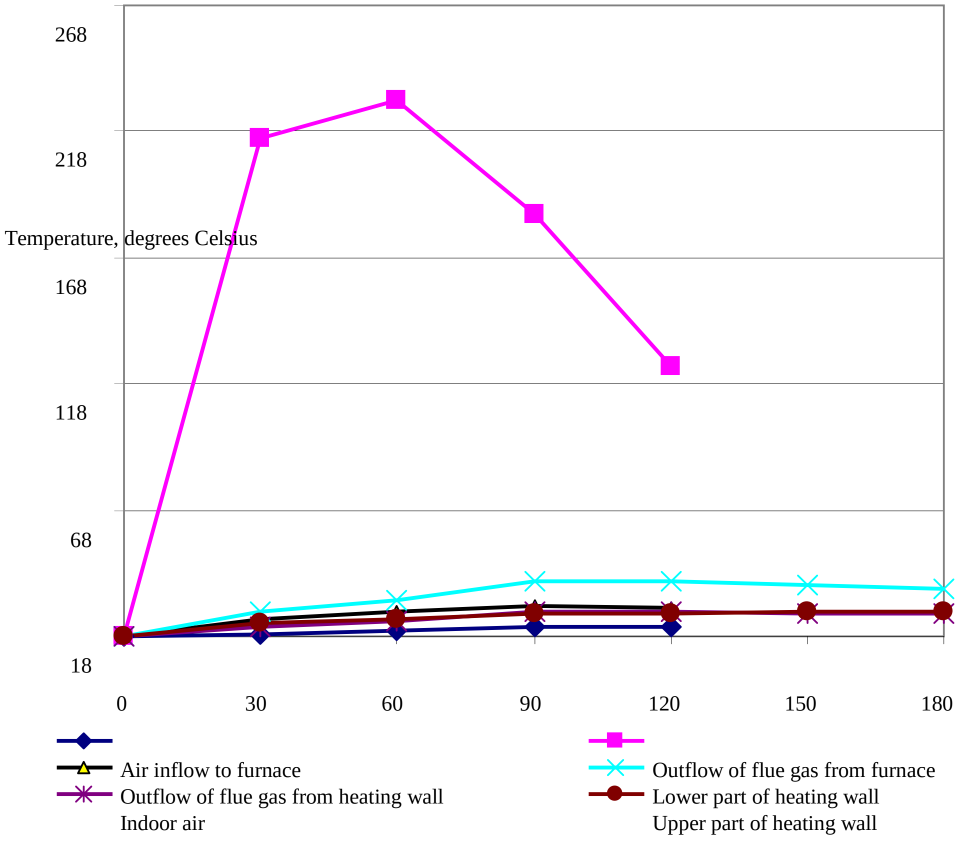

Fig.3. Average temperature of the operation of vertical flue gas heat absorption structure

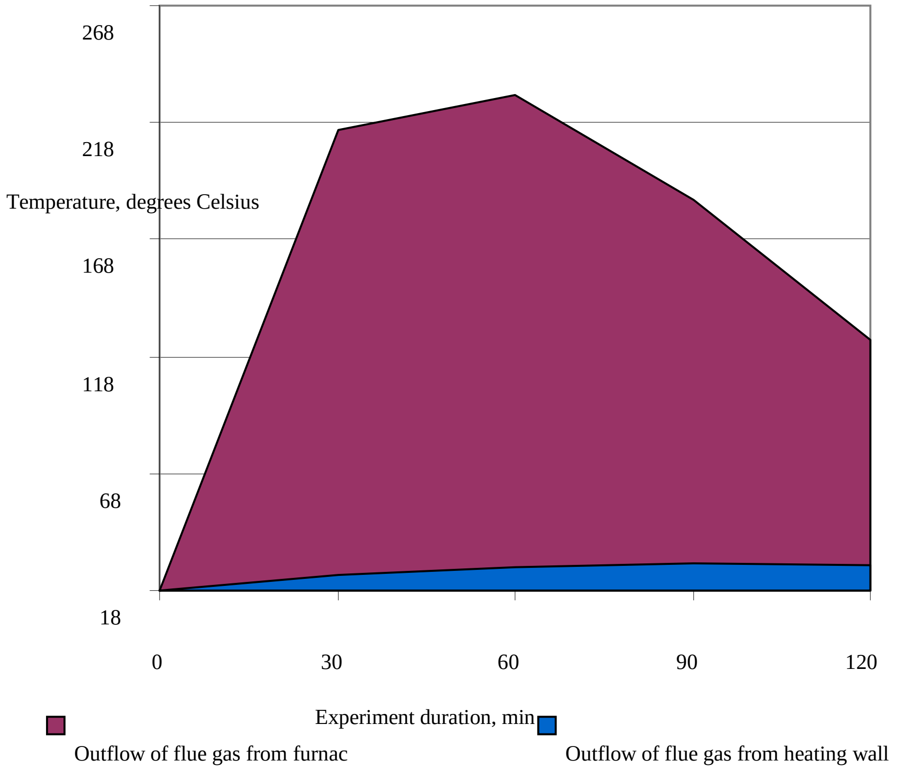

Fig. 4. The heat quantity recovered from flue gas as a result of the use of vertical flue gas heat absorption structure

The claret field, filled by flow of the flue gas from the furnace to the oven-couch, pro rata indicates how much heat is removed from the flue gas and accumulated in building structures of the oven-couch. The blue field, filled by flow of the flue gas from the oven-couch to the chimney, pro rata indicates how much flue gas heat is discharged into atmosphere.

After comparison of sizes of the blue field and the claret field, a rough estimate can be made, how much amount of heat is taken and accumulated by the oven-couch. This improves efficiency of the heating system and increases overall efficiency factor exceeding nominal efficiency factor of the heat generator.

Calculation of efficiency for use of the flue gas heat in the oven-couch

In combustion of mixed wood with moisture content of 10%, the maximum quantity of heat, which can be obtained from one kg of wood amounts to Q_A = 18864 kJ*kg^{-1} (4,65 kWh*kg^{-1}) heat, taking into account gross calorific value or Q_Z = 16740 kJ*kg^{-1}(5,24 kWh*kg^{-1}) by consideration of net calorific value [3, 4].

Having regard of the composition of such wood it is possible to determine the composition and the amount of flue gas.

Estimated wood composition by mass percentage [5] (by consideration of moisture content W=10%) is as follows: A=1.3%, C=43.9%, H=5.5%, O=39.3%.

In theory, the air required for burning per 1 kg of wood subject to combustion:

$$V^0 = 0{,}0889 * C + 0{,}266H - 0{,}033 * O = 4{,}07\ m^3 * kg^{-1}$$

Composition of flue gas generated through combustion of 1 kg wood at the excess air factor α=1.3, shall be composed of:

- the amount of carbon dioxide:

$$V_{CO_2} = 0{,}0187 * C = 0{,}83\ m^3 * kg^{-1}$$

- theoretical amount of nitrogen:

$$V_{N_2}^0 = 0{,}79 * V^0 = 3{,}21\ m^3 * kg^{-1};$$

- the water vapour amount:

$$V_{H_2O} = 0{,}111 * H + 0{,}0124 * W + 0{,}0161 * \alpha * V^0 = 0{,}82\ m^3 * kg^{-1}.$$

Total amount of flue gas from M=7 kg wood:

$$V_d = M * \left(V_{CO_2} + V_{N_2}^0 + V_{H_2O} + (\alpha - 1) * V^0\right) = 42.5 m^3.$$

According to experimentally obtained data found in Table 1, the average flue gas temperature at outflow from the furnace reaches t_{mk}= 154.6 ^{0}C, at outflow from the oven-couch reaches t_{ms} = 26 ^{0}C.

Flue gas heat, when leaving the furnace consists of heat $H_{d154}{}^0$ contained in the combustion reaction products and heat content of the air getting into flue gas H_{g154}:

$$H_{d154}^0 = \left(c'_{CO_2} * V_{CO_2} + c'_{N_2} * V_{N_2}^0 + c'_{H_2O} * V_{H_2O}\right) * t_{mk} = 1056{,}1\ kJ * m^{-3},$$

where: c’$_{CO2}$, c’$_{N2}$, c’$_{H20}$ – according to CO_2, N_2 and water vapour calorific capacity at a given temperature t_{mk}, kJ*m^{-3}*^{0}C^{-1}.

$$H_{g154} = c'_g * V^0 * t_{mk} = 832{,}4\ kJ * m^{-3},$$

where: c’$_g$– air calorific capacity at a given temperature t_{mk}, kJ*m^{-3}*^{0}C^{-1}.

Heat quantity Q_{dk} contained in the flue gas outflow from the furnace with average temperature of 154.6 ^{0}C, through combustion of 7kg wood, shall be:

$$Q_{dk} = V_d * \left(H_{d154}^0 + (\alpha - 1) * H_{g154}\right) = 55497\ kJ$$

Flue gas heat, at outflow from the oven-couch, consists of heat $H_{d26}{}^0$ contained in the combustion reaction products and heat content of the air getting into flue gas H_{g26}:

$$H_{d26}^0 = \left(c'_{CO_2} * V_{CO_2} + c'_{N_2} * V_{N_2}^0 + c'_{H_2O} * V_{H_2O}\right) * t_{ms} = 174{,}7\ kJ * m^{-3}$$

$$H_{g26} = c'_g * V^0 * t_{ms} = 139{,}8\ kJ * m^{-3}.$$

Heat quantity Q_{dm} contained in the flue gas outflow from the oven-couch at combustion of 7kg wood, shall be:

$$Q_{dm} = V_d * \left(H_{d26}^0 + (\alpha - 1) * H_{g26}\right) = 9207{,}2\ kJ$$

Thus, the amount of heat that has been recovered from the flue gas in the oven-couch can be calculated as:

$$Q_m = Q_{dk} - Q_{dm} = 46289{,}8\ kJ.$$

Portion of the amount of heat, which is recovered from flue gas through the built oven-couch, by applying to total heat to be obtained in the combustion process, shall be as follows:

- applying to the gross calorific value:

$$Q_{ia} = {Q_m}/{M * Q_A} * 100\% = {46289,8}/{7 * 18864} * 100\% = 35\,\%$$

- applying to the net calorific value:

$$Q_{ia} = {Q_m}/{M * Q_Z} * 100\% = {46289,8}/{7 * 16740} * 100\% = 39,5\,\%$$

Portion of the heat recovered from total heat possessed by flue gas at the furnace outlet shall be:

$$Q_{at} = {Q_m}/{Q_{dk}} * 100\% = {46289,8}/{55497} * 100\% = 83,4\,\%$$

Definitely, if more heat is removed in the boiler, then the temperature of flue gas at the furnace outlet will also be reduced, efficiency factor of the boiler itself will increase and the impact of oven-couch in improving of the efficiency will be reduced. Flue gas temperature over 100^0C at the boiler outlet permanently leads to inadequate thermal loss. For steel boiler the flue gas temperature along the surfaces may not be reduced below 60 ^{0}C, to avoid formation of condensate, which contributes to corrosion. This means that for the boiler these temperatures are the extreme minimum limit. By reducing the flue gas temperature close to the ambient temperature (such as in the experimental object at intensive combustion the outlet temperature from the oven-couch does not exceed 30^0C) a substantial amount of heat is recovered. This process may be executed by building additional structures with the surfaces made from materials to which the condensate is not dangerous.

III CONCLUSIONS

1. The built experimental oven-couch significantly increases the heat using efficiency, by recovering the flue gas- contained heat at furnace outlet of the flue gas heat generator. The amount of heat dissipated by flue gas at given circumstances for the existing structure constitutes 35% of the maximum available heat with consideration of the fuel gross calorific value, or 39.5% with consideration of the net calorific value.
2. Experiments demonstrate that a very high proportion of thermal loss is the loss with fuel gas, which temperature is above the ambient temperature. Cooling down the fuel gas to the temperature close to the ambient temperature can significantly improve overall efficiency of the heating system.
3. Construction of additional structures for recovery of the flue gas heat, allows to maintain a sufficiently high temperature in the boiler to prevent development of corrosion-inducing condensate and to stimulate the burning intensity and completeness of combustion.
4. When making analysis of the experimental data obtained in the built heat recovery system, it is estimated that through such a system it is possible to recover at the furnace outlet approximately 83% from the heat contained in the flue gas, using the given conditions. This proportion is affected by the flue gas composition, the flow conditions and the initial temperatures.

IV ACKNOWLEDGMENTS

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Microorganisms Producing Biosurfactant Selection and Characterization of New Discovered Bioemulsifier that will be Used to Create Ecological Heating Production Technology

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***Abstract*. The chemical synthesis of surface active compounds is economically inefficient. It requires much energy expense, raw materials and harmful reagents. Biological biosynthesis of surface active substances happens in milder conditions without the use of dangerous chemical reagents. The main goal of this work was to select a microorganism strain capable of producing a bioemulsifier with an ability to create a stable water / fuel-oil emulsion that could be used to design a new ecological heating technology. To this end, 3 microorganism strains displaying a high emulsification activity were used. The new discovered surface active substance (SAS) was investigated with different methods (hydrocarbon overlay agar method, emulsification activity determination, microscopic observation). The production of bioemulsifier (BE) was studied by using soluble and insoluble carbon sources. It was found that *Arthrobacter sp.* Pr82 is the best bioemulsifier producer. Oleic acid was ascertained as the best carbon source for the production of discovered BE.**

***Keywords* – bioemulsifier, microorganism selection, water-oil emulsion, carbon sources**

I INTRODUCTION

The decreasing prospects of oil resources and continuous emissions from gas due to fossil fuel consumption have raised keen attention as urgent problems around the world. As one of the different solutions to these problems, emulsion fuel technology has received close attention, because it may provide better combustion efficiency and would contribute to a reduction in emissions, such as NO_x or particulate matter (PM). There are also great expectations that it would lead to a reduction in fossil fuel consumption and carbon dioxide emissions on a global level and eventually provide a final solution to environmental problems, such as effluent gas.

Emulsion fuels refer to the emulsified mixture of petroleum-based fossil fuels, including gasoline, light oil, heavy oil, kerosene and waste oil, and water. In emulsion fuels, a mechanism which improves the combustion efficiency of the emulsified fossil fuel by virtue of the emulsified water is assumed to work.

Unfortunately, water-oil emulsions are not stable enough and are usually created before use, as they cannot be transported or stored for long periods of time. In order to stabilize them, surfactants with emulsifying qualities, i.e., emulsifier, need to be used. Synthetic emulsifiers are expensive and their synthesis requires not a small amount of energy expense and pure reagents. These chemically synthesized surfactants are mainly petroleum based and are usually non-biodegradable thus remain toxic to the environment they find themselves [1]. The use of synthetic emulsifiers for fuel emulsions increases its price twice; additionally there might be environmentally undesirable elements within the composition of the synthetic emulsifier [2].

As an alternative, bioemulsifiers – surface active substances, gained through biological methods and produced by bacteria and yeast strains *Arthrobacter, Bacillus, Pseudomonas, Acinetobacter, Rhodococcus* , *Sphingomonas, Thiobacilus thiooxidans, Serratia marcescens, Agrobacterium, P.fluorescens, Debaryomyces polmorphus, P.aeruginosa, Clavibacter, C.tropicalis, Yarrowia, Candida, Torulopis, Pseudozyma, Saccaromyces* [3-9], can be used. Bioemulsifiers are categorized mainly by their chemical composition and microbial origin. BSAS secreted by different microorganisms are composed of lipids, phospholipids, polysaccharides, proteins and other biological macromolecules; they contain various functional groups including carboxyl, amino and phosphate groups [10-14].

Biological surface active substances commonly have the advantages of biodegradability, low toxicity, selectivity, and biocompatibility over chemically synthesized surfactants, as well as being effective at the extreme ranges of pH, temperature, and salinity [15]. Bioemulsifiers easily degrade and do not pollute environment [16]. Biosurfactants can be produced from very cheap raw materials which are available in large quantities.

By comparing the properties of the acquired bioemulsifier with those of the synthetic emulsifier used in fuel emulsions, it is possible to choose the most suitable BE secreted by microorganisms. By optimizing the growth conditions, the maximal yield of bioemulsifier can be gained.

The aim of this study is to assess bacterial strain able to produce bioemulsifier which could stabilize water/fuel-oil emulsion, and to select carbon source in order to get the highest emulsification activity.

II MATERIALS AND METHODS

Microorganisms

Arthrobacter sp. N3, *Arthrobacter sp.* Pr82 and *Azotobacter vinelandii* 21 bacteria strains producing surface active substances obtained from the culture collection of JSC "Biocentras" were used for investigation. The selected bacterial isolates were preserved and kept under refrigerated conditions (-70 °C).

Chemicals

All chemicals used for media preparation were obtained from the following companies: Oxoid (Basingstoke, United Kingdom), Sigma – Aldrich Chemie (Sternheim, Germany), Fluka (Sternheim, Germany), Merck (Darmstadt, Germany), Roth (Karlsruhe, Germany), Eurochemikals (Bratislava, Slovakia), Penta (Prague, Czech Republic), (***Lach-Ner***, Czech Republic*)*. Fuel-oil and crude oil were obtained from oil refinery Public Company ORLEN Lietuva (Lithuania).

Inoculum preparation

Nutrient broth (Oxoid, United Kingdom) was used for preparation of the inoculum. 0.1 ml of bacterial strain suspension from the stock culture was inoculated into 50 ml nutrient broth in Erlenmeyer flask. The inoculated 250 ml flasks were incubated at 30 ºC in rotary shaker (Innova 43, New Brunswick Scientific Co. Inc, USA) for 5 h at 200 rpm. Inoculum was used at the 5 % (v/v) level in the all experiments with submerged cultures.

Culture media and cultivation conditions

For bioemulsifier selection, bacterial strains were cultivated in a mineral medium with the following composition (g/l): NH_4NO_3 – 2.5, $Na_2HPO_4 \times 2H_2O$ – 1, $MgSO_4 \times 7H_2O$ –0.5, $Fe(SO_4)_2 \times 5H_2O$ – 0.01, $CO(NO_3)_2 \times 6H_2O$ – 0.005, $CaCl_2 \times 2H_2O$ – 0.001, KH_2PO_4 –0.0005, $MnSO_4 \times 2H_2O$ – 0.0001, $(NH_4)_6Mo_7O_{24} \times 4H_2O$ – 0.0001, yeast extract – 0.1. The carbon source was octadecane 1 % (w/v) and the final pH of medium was 7.2 ± 0.2. LB medium consisted of peptone – 10, yeast extract – 5 and NaCl – 10 g/l. The carbon source was octadecane 1 % (w/v) and the final pH of medium was 7.2 ± 0.2. Cultivations were performed in 250 ml Erlenmeyer flasks containing 40 ml of medium at 30 °C in the rotary shaker at 200 rpm for 48 h.

The influence of carbon source on the emulsification activity was investigated in the same mineral and LB media. The carbon sources used were oleic acid (1 % w/v), dodecane (1 % w/v), olive and sunflower oil (1% w/v) (local commercial production), glucose (10 g/l), starch (10 g/l), sodium acetate (10 g/l), and glycerol (1% w/v). Cultivations were performed in 250 ml Erlenmeyer flasks containing 40 ml of medium at 30 °C in the rotary shaker at 200 rpm for 24 h.

Hydrocarbon overlay agar (HOA) method

Hydrocarbon overlay agar method was performed with slight modifications [17]. Nutrient agar (Oxoid, UK) plates were coated with 40 μL of crude oil. Pure bacterial isolates were streaked on to the coated plates and incubated for 48 hours at 30 °C. A streak surrounded by emulsified halos indicates biosurfactant producers.

Emulsification measurement

Emulsifier activity was measured by calculating EI according to the slightly modified method of Cooper and Goldenberg (1987) [18]. 6 ml of kerosene were added to 4 ml of 25 % suspension of culture liquid in 0.1 M Na_2CO_3, and homogenized with T18 Ultra-Turrax homogenizer. The mixture was allowed to stand in room temperature for 24 hours prior to measurement. Emulsification index (EI) was calculated by measuring the height of the emulsion layer (a), dividing it by the total height (b) and multiplying by 100 ($EI = a/b \times 100$).

Preparation and microscopy of the water/ fuel-oil emulsion

Water (30 %)/fuel-oil emulsion (20 g) has been created using homogenizer (T18 Ultra-Turrax, Ika-Werke GmbH & Co. KG, Germany). Emulsion agitation was performed at 60 ºC, introducing small amounts of bioemulsifier and water into fuel-oil (fuel-oil + BE + water). A sample smear was taken with a piece of wire, jabbing it to the bottom after 5 days incubation at 60 ºC. The stuck-on emulsion was carried over to the microscope slide and covered with a cover slip. Observation and taking of photos were carried out under the magnification of x1000.

III RESULTS AND DISCUSSION

Bioemulsifier selection

Bioemulsifiers are a very convenient alternative to chemical surfactants due to displaying little to no toxicity, high temperature stability and activity at extreme ranges of salinity and pH. In addition, they can be modified by genetically engineering the microorganism producing it, employing biological and biochemical techniques [19, 20].

In this study, the best bioemulsifier was chosen from among the three species of bacteria: *Arthrobacter sp.* N3, Pr82 and *Azotobacter vinelandii 21.* The selection was performed using hydrocarbon overlay agar (HOA) method and analyzing emulsion activity.

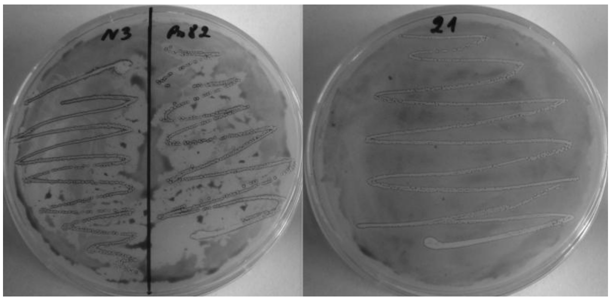

Fig. 7. Biosurfactant production by bacterial strains

During the assessment of bacteria strains using HAO method, pure bacterial culture was streaked onto the Petri dishes covered with crude oil and they were incubated for two days at a temperature of 30 °C. As shown in Fig. 1, *Arthrobacter sp.* N3 and Pr82 streaks were surrounded by emulsified halos, however *Azotobacter vinelandii* 21 didn‘t show any activity after two days of incubation. This method is only qualitative and colonies surrounded by emulsified halos are the direct indication of SAS producers, however it is unreliable to detect potential BS/BE producer using a single method.

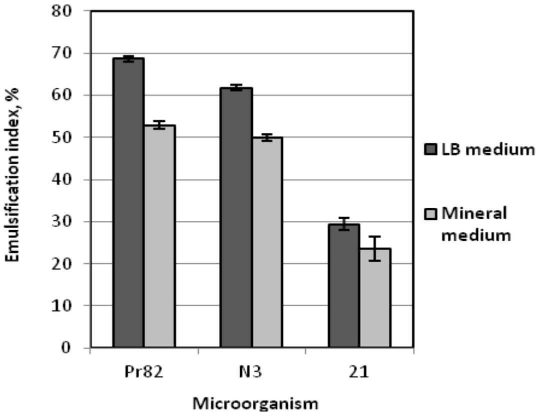

Fig. 8. Emulsification activity, using octadecane as a substrate

The bioemulsifier production may also be detected using emulsification measurement; this method was applied for the selection of bacterial strains. The results of the selection are presented in Fig. 2. The greatest emulsification activity was shown by *Arthrobacter sp.* Pr82 bacterial strain; in LB medium EI was 68.6 and in mineral medium - 52.9 %. *Arthrobacter sp. N3* bacterial strain also displayed big activity – EI was 61.8 % in LB medium and 50.0 % in mineral medium. The emulsification index of *Azotobacter vinelandii* 21 was lower than 30 % in LB and mineral media. Seeking to verify the stability of emulsion, the samples were kept in the temperature of 40°C for 5 days. After 5 days emulsion layer was measured and EI calculated. The most noticeable drop of EI has been noticed with *Arthrobacter sp. N3* (30 %) and *Azotobacter vinelandii* 21 (32 %). Emulsion containing *Arthrobacter sp. Pr82* remained the most stable, with the drop of only 11 %.

In order to research an influence the *Arthrobacter sp.* Pr82 BE has on water / fuel-oil emulsion stability, the emulsion agitation and microscopic observation was performed.

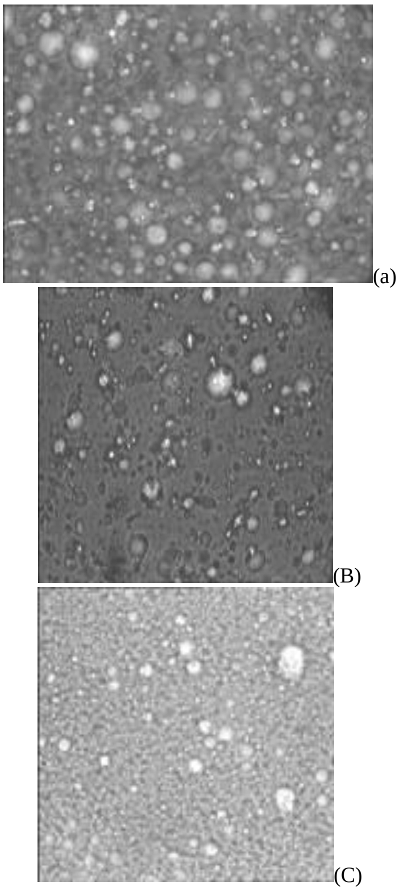

Fig. 9. ×1000 magnification of water in fuel-oil emulsion

The results are shown in Fig. 3. (A – emulsion with BE from *Arthrobacter sp.* Pr82; B – emulsion with BE from *Arthrobacter sp.* N3 and C – emulsion with BE from *Azotobacter vinelandii* 21). The greatest emulsification illustration obtained with *Arthrobacter sp.* Pr82, second – with N3 and with *Azotobacter vinelandii* 21 visible only noises. All above discussed assays have confirmed that the greatest BE producer is *Arthrobacter sp.* Pr82 bacterial strain.

Influence of carbon source

A number of attempts have been made to increase bioemulsifier production by manipulating medium composition. The choice of a suitable carbon sources has a huge influence on the production of surface active substances; however its importance is organism dependent. Microorganisms can grow on various substrates, but they do not necessarily produce BSAS. The carbon source may come from raw materials, hydrocarbons, carbohydrates, lipids or from their combinations [20, 21, 22]. BS/BE are gained by growing microorganisms with olive oil, glucose, starch, n-hexadecane, mannitol, sodium acetate, maltose, peptone, hexadecane [23, 24].

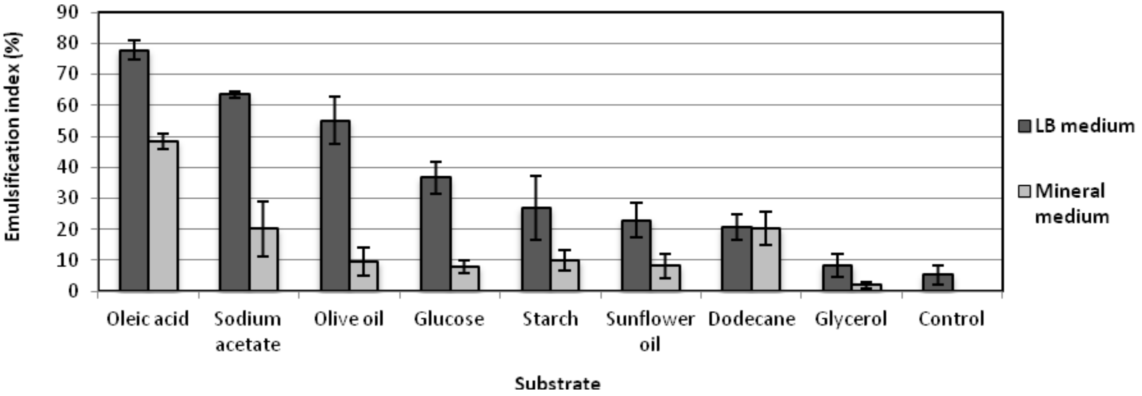

Fig. 10. An influence of carbon source on the emulsification activity

In order to research an influence the carbon source has on *Arthrobacter sp.* Pr82 strain, these carbon sources were picked: oleic acid, sodium acetate, olive oil, glucose, starch, dodecane and glycerol.

The maximum BE production was occurring only with oleic acid with sodium acetate and olive oil (Fig. 4) it showed better than 50 % emulsification index in LB medium. The greatest emulsification activity was achieved by adding oleic acid into LB and mineral medium: EI was 77.8 % and 48.4 % respectively.

IV CONCLUSION

Three bacterial strains with a high surface active substances production capacity were screened out using hydrocarbon overlay agar method, emulsification activity determination and microscopic observation of water/fuel-oil emulsion. *Arthrobacter sp.* Pr82 showed the best results in all cases and it showed that could be used in the further studiesto designing new ecological heating technology.

Oleic acid, sodium acetate, olive oil, glucose, starch, dodecane and glycerol have been employed previously to enhance *Arthrobacter sp.* Pr82 bioemulsifier production. The maximum BE production was occurring with oleic acid and showed 77.8 % EI after 1 day of cultivation.

V ACKNOWLEDGMENTS

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III

ENVIRONMENTAL EDUCATION, ECONOMICS

Integrated Regional Development Concepts: Case of Rezekne City

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***Abstract.* As to impact of European level planning activities and initiatives on planning practice in the Member States of the European Union, an important issue is practical application of theoretical aspects of planning that includes results of discussions on basic conditions for elaboration of a high quality and effective integrated planning documents and concepts in accordance with theoretical conclusions. The significance of cities with regard to regional development is testified by political and strategic documents – the strategy "Europe 2020" (EC, 2010) and others. Attractiveness is now linked to economic growth to provide a broader framework for the analysis of the process during which cities will reach higher standards of their inhabitants' life quality, as well as the most favorable environment for attraction of investments and visitors. Therefore it is important to understand what creates the attractiveness of cities for residents, investors and visitors and the way it could become an element of policy and planning process to contribute to balanced regional development.**

The aim of the research is to explore the importance of elaboration of integrated development concepts to increase the city attractiveness and the way it could become an element of policy and planning process to contribute to balanced regional development. Three tasks have been set within the framework of the research:

- **to investigate the theoretical aspects of planning methodology and city attractiveness;**
- **to identify the most important factors of city attractiveness for Rezekne city;**
- **to set up the integrated regional development concepts' priorities of the Rezekne city to enhance its attractiveness.**

***Keywords*: integrated approach, city attractiveness, planning documents, spatial planning, strategic planning, regional development.**

I INTRODUCTION

The terms "regional development" and "development planning" are closely related with regional development theory, the main task of which is to determine causes and regularities of differences between economic growth and competitiveness of regions. Lately, academic literature has started paying more attention to elaboration of new theories and concepts, the task of which is to solve long – term problems in an innovative way. An impressive number of empirical researches in the fields of spatial planning and city attractiveness in integrated way have been carried out.

In the recent academic and the European Union debates on regional development territorial assets and spatial qualities have increasingly been understood as factors for attracting inhabitants and economic activities and, consequently, as important features for local development planning documents (like development concepts strategies, spatial plans and development programs e.g.). However, the capacity and potential of cities and regions to elaborate a high quality policy and planning documents to attract population, investors and visitors is unexplored [1]. Ezmale S. (2012) concluded that local governments having a higher quality of spatial planning documents have better conditions for territorial development [2].

As to impact of European level planning activities and initiatives on planning practice in the Member States of the European Union, an important issue is practical application of theoretical aspects of planning that includes results of discussions on basic conditions for elaboration of a high quality and effective integrated planning documents and concepts in accordance with theoretical conclusions. Spatial and non-spatial policies, planning documents, particularly those of the EU, may have a significant role in enhancing the attractiveness of cities by changing endogenous factors (determined mostly by geographical, cultural, institutional and historical factors) and producing shifts related to the relative positioning of regions [3].

The significance of cities with regard to regional development is testified by the European Union political and strategic documents – the strategy "Europe 2020", European Union Territorial Agenda 2020, the Leipzig Charter and others. Attractiveness is now linked to economic growth to provide a broader framework for the analysis of the process during which cities will reach higher standards of their inhabitants' life quality, as well as the most favorable environment for attraction of investments and visitors. Therefore it is important to understand what creates the attractiveness of cities for residents, investors and visitors. Also the documents on the regional policy of Latvia determine that for enhancing polycentric development it is especially important to sustain the medium-sized and small cities which, as prescribed by the planning and political documents of the state, are distinguished as the centres of development of national, regional and municipal-scale importance.

The aim of the research is to explore the importance of elaboration of integrated development concepts to increase the city attractiveness and the way it could become an element of policy to contribute to balanced regional development. Three tasks have been set within the framework of the research:

to investigate the theoretical aspects of planning methodology and city attractiveness;

to identify the most important factors of city attractiveness for Rezekne city;

to set up the integrated regional development concepts' priorities of the Rezekne city to enhance its attractiveness.

The object of the research – city attractiveness in the context of regional development planning.

The subject of the research – integrated approach in planning documents of municipalities based on the Rezekne city case.

The novelty of the research – it is the first time in Latvia when a research of integrated development planning is prepared, regarded as a tool for improving cities' attractiveness for residents, business and visitors considering the case of Rezekne city.

The methods of the research – theoretical analysis of scientific literature, comparative analysis, different tools of strategic planning (brainstorm, visioning, situation analysis, public involvement e.g.).

II MATERIALS AND METHODS

Many theoretical researches characterize the "good practice" of spatial planning documents by analysing the key – elements for elaboration of a high – quality, effective and successful planning document (Larsson, 2006; Adams, Harris, 2005; Healey, 2009; Hudalah, 2010; Forinos, 2004; Aldens, 2006; Böhme, 2002; Böhme, Waterhout, 2008; Healey, 2009; Forinos, 2004; Healey, Khakee, Motte , Needham, 1997; Lichfield, 1998, 2001a; Olivera, 2010; Madanipour, 2010; Böhme, 2002; Archibugi, 2008; Aitken, 2010; Adams, Ezmale, Paalzow, 2006; Boelen, 2010; Bäcklund, Mäntysalo, 2010; Hudalah, 2010; Tosics, Szemzo, Illes, Gertheis, 2010; Olivera, Pinho, 2010; Mehmood, 2010 e.g.) [4]. By summarizing conclusions analyzed in theoretical researches, it can be concluded that the key – elements characterizing the compliance of spatial planning documents with the "good practice" of planning are as follows: (1) aims of planning documents, planning horizon and status; (2) vertical and horizontal coordination; (3) integrated approach; (4) participation and awareness of the society; (5) strategic dimension or vision, aims and strategy e.g. [5].

There is a range of elements, observance of which is substantial for elaboration of a high – quality planning document, and these elements are as follows:

- in the document, it is important to analyse institutional, economic, environmental and social context;
- strategy of a planning document must suggest a clear vision, aims and values, as well as a clear strategy for introduction of the latter;
- it is necessary to involve broad target groups during the entire process of document elaboration;
- it is necessary to organize a well – considered and appropriate information and communication strategy aimed at target groups;
- a good planning document must be strategic, short and easy to understand; it should contain a limited number of priorities;
- a good planning document should be integrated, namely, it must be related with other field policy documents, compatible with planning documents of a higher level, as well as according the needs and preferences of different target groups;

it is important to identify a clear introduction mechanism to introduce resources, as well as to establish a simple though effective frameworks for monitoring activities [6].Servillo L., Atkinson R. and Russo A. (2011) outline that the empirical assessment of the attractiveness of cities and regions is addressed in two main ways: through the measurement of the most important aspects of a city's or region's factor endowments and by evaluation of the outcome of these endowments in terms of the actual economic performance [8]. Clark T.N. (2000) describes the need for creating cities more attractive not only for companies, but also for people, since human resources are an important factor for companies. He argues that city attractiveness strategies must be related to policies aimed to enhance the quality of life of inhabitants by improving the local economy [9]. Van den Berg L., Van der Meer J. and Otgaar A. H. J. (2007) emphasize criteria which reflect city attractiveness from the point of view of inhabitants (employment opportunities, a clean and safe environment, high – level education, cultural, health and social care services e.g.), entrepreneurs/ investors (a real estate, tax environment, labour force, the presence of a supplier and customer e.g.) and visitors (accommodation, access to entertainment, restaurants, public transport and other amenities attractive to visitors) [10]. Servillo L., Atkinson R. and Russo A. (2011) noted that attractiveness of places consists of three main aspects: (1) the asset side of the attractiveness of a place and its different characteristics, called "territorial capital"; (2) different potential users for whom attractiveness should be measured; (3) the way such assets are mobilized by governmental and non-governmental organizations and institutional actors [11]. Consequently, increase of attractiveness of territories and places (regions, cities e.g) is an important topic in the regional policies of the Member States of the European Union nowadays. Development planning coordinates the location efficiency of infrastructure and economic activities, as well as it addresses the region – scale issues such as environment, social and economic concerns [12]. The governments at different levels develop and manage space through the development planning documents (development concepts, strategies, spatial plans and development programs e.g.) and their implementation. It makes it necessary at all levels of government to use an integrated approach, in the policy and planning process to promote the growth of territories and places and attract new inhabitants, investments, enterprises and visitors, simultaneously creating attractive places. An integrated approach emphasizes that promoting development requires close coordination of public policies and activities, as well as it is necessary to take into account the needs and preferences of different target groups. Aldens (2006) indicates, however, that the unique possibilities of spatial planning are related with its inter – disciplinary nature binding the social and the economical spheres, as well as the dimensions of culture and environment in the framework of regional development. Studying the most significant factors of city attractiveness indicated by various target groups, local governments can adopt decisions related to a set of the most effective strategies and measures for enhancing the attractiveness of cities. As a result, the integrated approach relies primarily on integrated regional development planning documents [13]. Development planning should be oriented to target groups with regard to the needs and preferences of each group, thus facilitating the attractiveness of the city (see Figure 1).

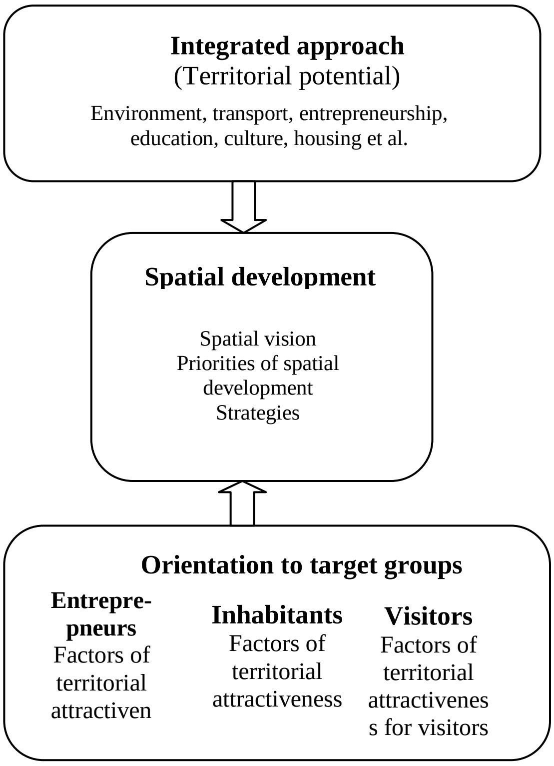

Fig. 1. Spatial strategies for territorial attractiveness

The source: Ezmale S., 2012 [14].

III RESULTS AND DISCUSSION

Pursuant to the results of theoretical, empiric researches and working groups the author has elaborated suggestions for integrated development planning for facilitating the attractiveness of Rezekne city. The results are summarized in the document "Conception of Rezekne City Attractiveness" [„Rēzeknes pievilcības koncepcija"] [15]. Cities compete with each other to attract new companies or fields, inhabitants, tourists and visitors. The author suggests that city development planning should be organized according to the target groups needs and desires, as well as taking into account territorial assets.

Every city has unique combination of attractiveness criteria and factors, and each city in its development may focus to the advantages, unique assets and values/ competencies in relation with other cities. The crucial step in this process is to identify the most important factors of the attractiveness of the city. Within the framework of the RHEI ESF project "Linguo-Cultural and Socio-Economic Aspects of Territorial Identity in the Development of the Region of Latgale" (TILRA Project) during the period 2010 – 2011 inhabitants of Rezekne city (380 respondents) were surveyed to collect information for a qualitative assessment of the cities' attractiveness and to elaborate particular measures for the city development concept and increasing attractiveness in the future. Within the framework of the survey of the Rezekne city's inhabitants their opinion on such aspects of city attractiveness and life quality as the welfare, work and employment perspectives, ecological quality, health, social care, culture, leisure time, education, sports, safety and security, public transportation, the quality and availability of services et al. was asked. In total, 81 question of the survey was answered and information about 252 variables or indications was obtained; however, there was found out the inhabitants' satisfaction with the living conditions in the city and the assessment of their attractiveness. Investigating the Rezekne city inhabitants' opinion of a city's attractiveness factors, the method of correlation and factor analysis was applied for processing the data obtained by the survey. To gather information about the most significant Rezekne's city attractiveness factors, 108 indications characterizing the city attractiveness criteria were analyzed. Applying the method of factor analysis combining the abovementioned indications, three most significant factors which characterize the attractiveness of a city from the inhabitants' viewpoint were outlined: (1) culture, (2) welfare, employment and security, (3) education, sports and leisure activities [16].

Within the framework of the RHEI ESF project "Linguo-Cultural and Socio-Economic Aspects of Territorial Identity in the Development of the Region of Latgale" study , an entrepreneurs' survey was carried out (130 respondents) to find out the point of view of economically active market units in the cities of Latgale region (EAMU) regarding the essential criteria for decision making on setting up business in a particular place, as well as the business environment in the cities of Latgale region. The chosen sampling method – determinate quota sampling. Using the factor analysis method has identified three factors to determine the key factors influencing a decision on setting up business in a particular place in Latgale region:

1. local business environment: good accessibility, favorable local taxes, fees and normative regulations, safe environment for business;
2. quality of life: leisure time activities, availability of housing, safe living environment;
3. technical infrastructure and real estate: competitive real estate prices, appropriate real estate availability, provision and quality of technical infrastructure [17].

The city - visitors look for a temporary accommodation offer (hotels, apartments, camping, family houses, etc.), as well as good accessibility and availability of these facilities. Such factors as cost and accommodation facilities, access to entertainment and restaurants, public transport and other amenities are attractive for visitors. The urban habitats (landscape, tress, rivers) and urban landscape, which has been developed by people (architecture, parks), contribute to attractiveness of Latgale cities [18].

By taking measures for increasing the attractiveness factors in the city planning documents, it would create favourable conditions for attractiveness improvement in the future. Regarding an analysis of the attractiveness criteria, as well as identifying Rezeknes city's most important factors of attractiveness from the point of view of different target groups, the author worked out proposal for the "Conception of Rezekne City Attractiveness" [„Rēzeknes pievilcības koncepcija"] in collaboration with scientists of Rezekne Higher Education Institution and representatives of Rezekne Municipality. Proposals from "Conception of Rezekne City Attractiveness" will be incorporated in the "Rezekne Sustainable Development Strategy" [„Rēzeknes ilgstpējīgas attīstības stratēģija"] developed by Rezekne City Council.

In the studies of Healey (1997) there is analysed the role of the vision and outlined the need to formulate a clear framework for the desired spatial development perspective, as well as a strategic framework for regulatory and investments activities in the future. In the other studies (Adams, etc., 2005, and Myers, 2000) it is proposed to formulate a vision, which reflects the views of all target groups [19]. The author holds an opinion that it is necessary to elaborate the document "Conception of Rezekne City Attractiveness" in respect to different fields regarding to spatial issues and target groups (inhabitants, entrepreneurs/ investors and tourists/ visitors) which would thus ensure an integrated approach. The proposed vision of Rezekne city is: "Rezekne is an internationally recognized, attractive, environmentally and socially friendly, innovative and easy accessible city for citizens, businessmen, tourists and visitors. It is an important economic, cultural, educational and research center of Eastern Latvia with a well-developed international co- operation network. Rezekne is a popular tourism destination, where everyone can find Latgalian culture. The strengths of Rezekne enrooted in its inherited and created values of education, culture, in its Latgalian language and culture, in its industrial traditions, as well as its favorable geographic location between the European Union and global world" [20].

In relation to the development strategies several scientists (Alden, 2005, Albrecht 2004; Healey, 2009; Scheer, 2006, Mintzberg, 1994; Mehmood, 2010) highlight that it is important to: (1) ensure integration between the objectives of the economic, social and environmental sectors with a focus to a small number of priorities; (2) comply with the principles of sustainability; (3) focus on the priorities; (4) provide the link between vision, strategy, objectives and measures, as well as to formulate a logical and clear a implementation mechanism of strategies, which focuses on vision and goals; (5) to ensure the harmonization of interests of different target groups and sectors, (6) to define a clear institutional framework and resources for implementation. There are many approaches to strategic planning but in the Rezekne case the Situation-Target-Proposal (Situation - evaluate the current situation and how it came about is used, Target - define goals and/or objectives, Proposal - map a possible route to the goals/objectives), as well as an appropriate techniques is used.

The proposal for improving of attractiveness of Rezekne city is prepared according to the theoretical and empirical research (see Figure 2). In the document "Conception of Rezekne City Attractiveness" [„Rēzeknes pievilcības koncepcija"] there was brought four strategic priorities linked to strategic aims:

P1. Rezekne – economic development centre of international and national significance.

P2. Rezekne – The Capital City of Latgalian culture, creativity and national identity.

P3. Rezekne – Eastern Latvian Educational, Research and Sport centre.

P4. Rezekne – a people and environment friendly, modern and safe city in the eastern Border area of the EU (See Figure 3).

The manner, in which the vision and its content were formulated, generally influences the favourable development. The vision of Rezekne is complemented by the strategy, which outline 4 strategic aims, 4 priorities and 11 strategic development directions (measures) for achieving the vision (See Figure 2).

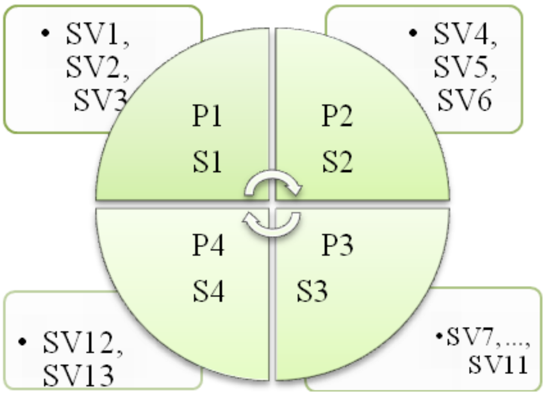

Fig. 2. The schematic illustration of strategy for Rezekne attractiveness.

Essential part of any planning document is implementation of the strategy – is there defined a mechanism for implementation of the strategy according defined aims, objectives and priorities, as well as is there included an action plan that reflects implementation of the strategy [23].

It will be next important step in the process of elaboration the "Rezekne Sustainable Development Strategy" [„Rēzeknes ilgstpējīgas attīstības stratēģija"]. Implementation depends, amongst other things, on a number of key factors: the institutional and legal framework, the available delivery mechanisms and resources. The importance also designing frameworks for monitoring evaluation and review is clear.

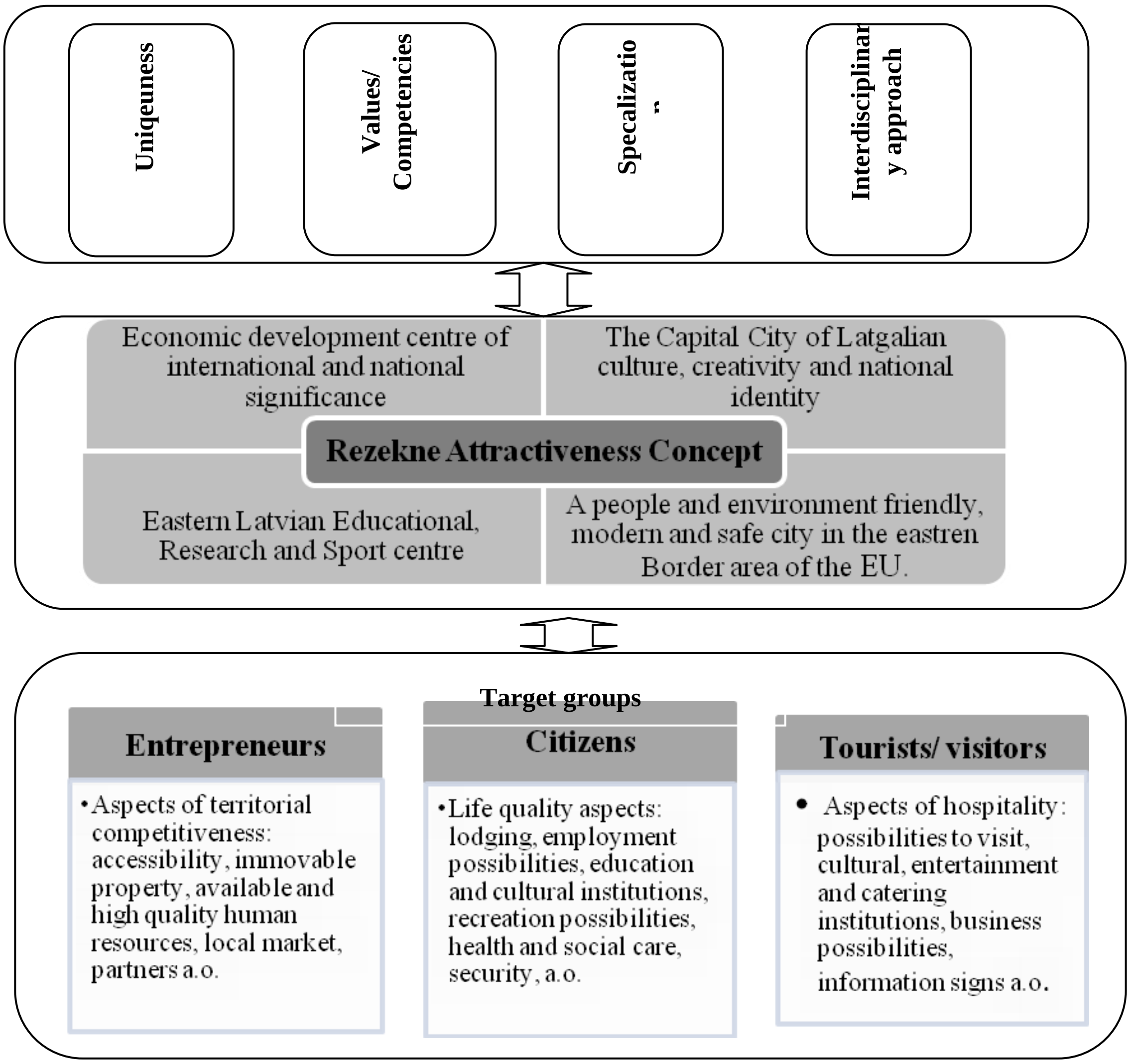

Fig. 2. The pattern of Rezekne Attractiveness Concept

IV CONCLUSIONS

There has been a growing interest and academic literature in recent years in developing new paradigms of regional development to find new ways of tackling longstanding regional problems. An impressive number of empirical researches in the fields of spatial planning and city attractiveness in integrated way have been carried out.

City attractiveness can be defined both as the capacity to attract new residents, visitors, enterprises and investments as well as the ability to retain and develop these mobile communities and assets. Cities compete one with another to attract new inhabitants, visitors, and business or investments that create jobs and thus provide increased material welfare. It makes it necessary at all levels of government to use an integrated approach in the policy and planning process to promote the growth of territories and places and attract new inhabitants, investments, enterprises and visitors, simultaneously creating attractive places. In order to strengthen the role of planning to increase attractiveness in Rezekne city it is necessary to pay more attention:

to such factors as culture, welfare, employment and security, education, sports and leisure activities in order to make the city to be attractive to residents as a target group;

to such factors as competitive local business environment and technical infrastructure and real estate, safe environment for business activities in order to attract new business and investments;

to such factors as a temporary accommodation offer (hotels, apartments, camping, family houses, etc.), a high quality urban landscape, as well as good accessibility and availability of these facilities in order to attract new tourists and visitors. Therefore there was brought four strategic aims and priorities in "Conception of Rezekne City Attractiveness" [„Rēzeknes pievilcības koncepcija"] to improve the attractiveness of Rezekne city: (1) Rezekne – economic development center of international and national significance; (2) Rezekne – The Capital City of Latgalian culture, creativity and national identity; (3) Rezekne – Eastern Latvian Educational, Research and Sport center; (4) Rezekne – a people and environment friendly, modern and safe city in the eastern Border area of the EU. The strategic aims and priorities of Rezekne is complemented by the 11 strategic development directions (measures) for achieving the vision.

Essential part of any planning document is implementation of the strategy – is there defined a mechanism for implementation of the strategy according defined aims, objectives and priorities, as well as is there included an action plan that reflects implementation of the strategy. Therefore the next important step is to elaborate implementation mechanisms for the strategy, as well as to develop the framework for monitoring and review system.

The planning documents of local governments that take into account the investigation results of attractiveness of each territory or place may facilitate development of a many spatial assets and attractiveness factors that play a substantial role in development of particular territory or place.

V ACKNOWLEDGMENTS

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The Research on Environment Protection Knowledge and Competencies in Non-Formal Education

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Abstract**. In Lithuania, as well as all over the world in developed countries, the society is starting to become a new kind of the information society. Under modern conditions it is increased the role of educated personality, personality capable of not only absorb the previously accumulated knowledge, but also to summarize, analyze, develop new and innovative ideas, information technologies, services and products. Implementing the EU common agricultural and rural development policy and adapting it to the local conditions, special attention must be paid to the qualitative aspects of human capital and education. Environment protection problems are deeply rooted in. The extensive agricultural policy of EU is in active formation process as a serious counterweight and feasible alternative to intensive, almost industrial farming [1]. According to this policy, farmers are supported for reducing negative impact on the environment and fostering an attractive landscape; therefore it is important to develop professional qualification. It is possible to distinguish three forms of education in formation of farmers' human resources: formal, non-formal and informal learning [2]. Formal education takes place in accordance with the statutory procedure, approved and registered training programs witch lead to the acquisition of a primary, secondary, or higher non-university education and qualifications. Non-formal education is learning through a range of educational needs, training, and acquisition of additional skills. It typically involves workshops, community or interest based courses, conference style seminars. Informal education is continuous self-learning, based on the person gaining knowledge from various sources and practical experience. Non-formal and informal education is relevant to farmers who already have some formal education and seek to continually enhance and update their knowledge. Professional development is important to the farmer during all the farming period. The paper deals with environment protection competencies and qualification development gained during non-formal education course of farming basics. The study found out environment protection motivation and tendencies of knowledge use in practical activities.**

Keywords**: environment protection, non-formal education, competence, fundamentals of farming.**

I INTRODUCTION

The rapid society changes, economic reform, scientific and technical progress requires regeneration of environmental system in Lithuanian. Researches on environment protection are one of instrumentalities which have impact on changes of the urban environment and in general agriculture. Studies and collective action based on research results promote social changes. Ecology issues must be solved at national and cross levels. One of the most important tasks is to consistently educate ecological consciousness of adults. This must be visible for everyone and this approach should be developed from early years. Theoretical knowledge should be applied in order to protect natural resources. Finding acceptable organic forms of education in adult education, combining environmental cognition methods and techniques helps them reinforce the idea that people are not just consumers of nature, but each of us is responsible for the development and conservation of the environment. A number of scientists and educators worked in eco-education areas. J. M. Hines, I. Gabiavo prepared methodological materials and accumulated knowledge about environmental awareness. R. Repin, V. Lukankina, E.Sapokiene, A.Sidelkovskis, R.Makartsakaite, O. Motiejunaite investigated the effectiveness of various supplementary environmental education forms like clubs, radio shows, etc. Residential environment on ecological education studied V. Latiuskinas and I. Coriander. L. Keirans, P. Baltrunas, E. Sapokiene and others considered issues of ecological education researching students [8].

The aim of work is to assess the ecological importance of education, the need for developing environmental skills for adults.

The objectives of work:

1. To summarize development of organic farming in Lithuania and farm certification results.
2. To analyze training grounds and environmental motivation of the non-formal education courses listeners.
3. To evaluate environmental skills of non-formal education course listeners and to provide means of improving.

II MATERIALS AND METHODS

1. Theoretical: a systematic and comparative analysis of scientific literature, statistical comparative analysis.
2. Empirical: a survey (questionnaire).

III RESULTS AND DISCUSSION

Theoretical grounding of environmental skills' formation need.

Nowadays, environment protection is widely recognized as a priority area. Ecologists, educators and andragogues have an important mission in environmental education. These are people who purposefully prepare young people to live with the changing labor market conditions. Environmental protection competencies of teachers and andragogues have influence on how young people will be able to create and work with new environment-friendly technologies.

Environment protection is taught as a separate subject or is integrated into various professions subjects. Environment protection is an important subject for any professional training [8].

Agricultural activities are considered multifunction, because here are the main functions of food, fiber, feed, energy, raw materials, and manufacturing, supplying private trade goods, carried out many other additional features. This is the vitality of rural areas, natural resources, biodiversity, cultural heritage, cultural landscape maintenance, food safety and quality assurance [4]. Goods (products or services) created by these functions are considered public and are generally non-marketable. People created public goods are produced as a product of human activity (cultural heritage, traditions and technological devices). Proportions of public values vary in different areas, they depend on nature and human interaction degree.

Residents of rural areas at the same time face several interrelated tasks:

- To produce agricultural products;
- To maintain adequate natural resources (soil, water, air) quality;
- To ensure food safety and quality;
- To preserve and maintain biodiversity, cultural (also natural) landscape;
- To preserve and maintain for new purposes rural material and spiritual heritage;
- To establish and properly operate rural infrastructure for public use. [1].

These tasks meet challenges as continuously ongoing migration of the population (Table 1). During the migration of the population in rural areas, changes in living conditions, the needs and provisions. These changes have the impact on the old and young rural habitants, both men and women.

TABLE 1

INTERNAL MIGRATION FLOWS (%) IN 2009-2011 [5]

Year Migration	2009	2010	2011	Increase / decrease in 2011 compared to 2009
Total urban arrivals	30,1	30,3	31,8	+ 5,64
urban-to-urban	13,6	13,7	14,3	+5,14
rural-to-urban	16,5	16,6	17,5	+6,06
Total rural arrivals	19,4	19,5	20,3	+4,64
urban-to-rural	15,8	16,3	17,0	+7,59
rural-to-rural	3,6	3,2	3,3	-8,33

Based on data from first table, the number of internal migrants is increasing, as well as rural population mobility.

Environmental researches are one of the steps to change the situation of the urban environment and agriculture. Rural habitants comply best with the requirements of environment protection in organic farming, because the production line is closely related with their own viewpoint and way of life. The analysis of scientific literature and public institution "Ekoagros" data showed that organic farming in Lithuania in 2003-2007 increased rapidly gaining popularity and has stabilized lately. Despite this fact the certified organic area is growing. 158,060 hectares certified in 2011 [7]. Quantities and assortment of certified organic products was increasing. New processing plants was established, therefore number of organic raw materials and finished products exported to other EU countries.

The total area under organic farming increased, but the number of organic producers decreased in 2009-2011 (Fig. 1).

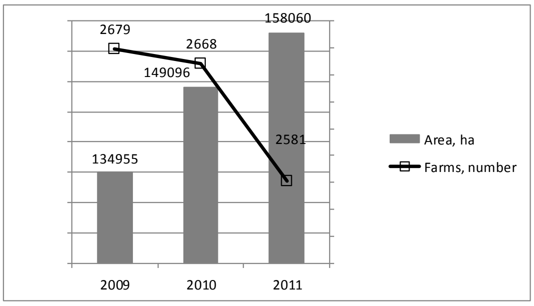

Fig. 1. Total organic area and farms (including fish farms), 2009-2011 [7]

The average organic farm size is increasing every year. There are currently 61.2 ha organic farms, which are larger five times than the Lithuanian average. The number of certified farms owned by woman is increasing slowly (Fig. 2).

Fig. 2. The change in organic farms' number owned by women in 2009-2011 [7]

There are a lot of researches on organic production dealing with economic performance changes, the transition from conventional to organic production problems.

V.Grakauskas, Z.Gineitiene, J. Zvinklys, A. Poviliunas, E. V. Vabalas analysed organic farming as a business, A. Astromskienė, J. Ramanauskienė, R. Rukuižienė [3] analyzed rural entrepreneurship, its determinants and measures. Organic farming factors, their modeling studied V. Skulskis, V. Vitunskienė [6].

Environmental education is necessary condition for the implementation of sustainable development, replacing the consumerist approach to human resource and its values, unfortunately researches on farmers environmental approach is not much.

A research on environmental knowledge and competencies gained during non-formal education course of farming basics.

In 2010-2012, the research on environmental knowledge and competencies gained during non-formal education course of farming basics was carried out at Landscaping faculty of Kauno kolegija/University of Applied Sciences. The research involved 148 women and 256 men (Fig. 3).

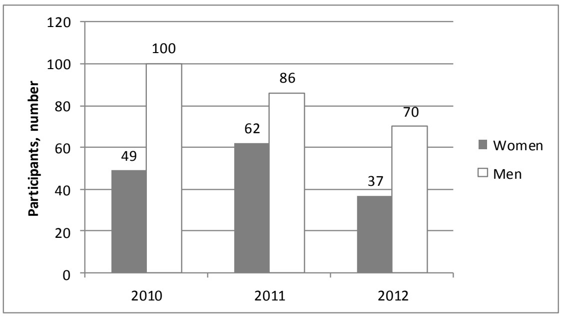

Fig. 3. Distribution of respondents by gender, 2010-2012

The survey results suggest that during analyzed period, percent of women in groups of listeners changed from 49 percent in 2010 to 72 percent in 2011.

A survey collected data about respondents' reasons for choosing non formal education (Fig. 4).

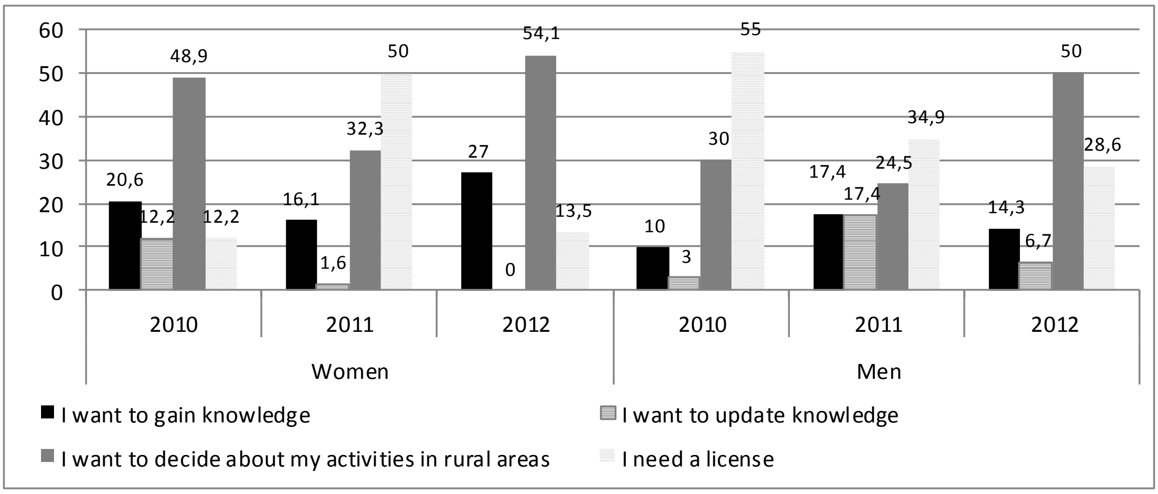

Fig. 4. Motives for the choice of non-formal education study

Analysis of the results suggests that the majority of respondents, both women and men, have chosen farming basics course because they need license or want to decide about their activities in rural areas.

The answers of respondents are not encouraging, because many of the respondents need a certificate only to build a country house, but the number of women who want to gain knowledge is increasing by about 10 percent every year.

Skilled and educated people from various regions were chosen as respondents, so it was important to determine motivation of the course choice.

During the analysis some environmental aspects were discussed. Respondents had to describe a number of environmental terms. Table 2 shows respondents' awareness of environmental concepts.

TABLE 2

AWARENESS OF ENVIRONMENTAL CONCEPTS, %

Concepts	2010		2011		2012	
	men	women	men	women	men	women
Sustainable development	20	48,9	34,88	32,25	28,57	27,02
Ecosystem	50	24,5	34,88	50,0	57,14	54,05
Biodiversity	30	48,9	50,0	58,06	50,0	59,45
“Agenda 21”	5	12,2	11,62	16,12	14,28	18,90
Movement "Let's do it"	90	100	100	100	100	100

It can be seen from Table 2 that number of respondents is increasing every year (especially women), who are known to the terms listed. It should be noted that the best known concept is movement "Let's do it" (100 percent of women and 96.66 percent of men in 2009-2011). Women were aware of concept “Biodiversity” 12 percent more than men and concept “Agenda 21” more than 6 percent. Movement "Let's do it” is well known, but it turns a relatively small number of respondents (Table 3).

TABLE 3

RESPONDENTS' ATTITUDE TO THE MOVEMENT "LET'S DO IT", %

Concepts	2010		2011		2012	
	men	women	men	women	men	women
Yes, I participate every year	0	24,5	5,81	32,25	28,57	27,02
I took part once	20	36,7	34,88	32,25	28,57	40,52
I would like, but I do not have time	60	26,6	53,5	35,5	28,58	26,96
I'm not interested	20	12,2	5,81	0	14,287	5,50

It can be seen from Table 2, that 28 percent woman and only 11.46 percent men each year participate in the movement "Let's do it". On average, 29.68 percent women and 47.36 percent men would like to participate but do not have time, only 4 percent female and 13.36 percent men were not interested in this movement.

An attitude to the environment begins with our individuality, the environment in which we live. Therefore, it was important to find out respondents' practical experience in an environmental field. Responses received showed that even 69 percent women and 58 percent men believe that their way of life has a positive impact on the nature, the environment and society, but 20 percent women and 22.5 percent men do not realize about it (Table 4).

TABLE 4

PRACTICAL APPLICATIONS OF ENVIRONMENTAL KNOWLEDGE, %

Statements	2010		2011		2012	
	men	women	men	women	men	women
I save water	45	55	55,81	66,12	64,28	67,48
I save electricity	65	60	73,25	58,06	78,57	67,48
I sort waste	5	45	11,62	32,25	14,28	40,52
I eat more fruits and vegetables	5	75	11,62	90,31	28,57	81,07
I use eco-friendly laundry detergents	0	30	5,81	32,25	7,14	40,52
No longer needed clothing, shoes, toys, home appliances I give to charities	3	30	5,81	58,06	14,28	27,02
I use reusable shopping bags	50	30	5,81	32,25	7,14	13,53
I do not use disposable hygiene products	10	30	5,81	32,25	14,28	13,53
I use public transport, bicycle	10	30	11,62	17,76	14,28	26,96
I teach children to love nature	75	100	84,88	100	92,85	100
I handle environment where I live	100	100	100	100	100	100

The results suggest that the majority of respondents save water, electricity, maintenance of nature as well as teaching their children of environmental skills. Women in the practical environmental activities are much more active than men. However, it is appropriate to promote a wider integrated theoretical and practical knowledge of environmental education, as there are little of the respondents, who sort wastes, are using eco washing, and cleaning, re-usable shopping bags. Completion of non-formal education courses creates preconditions for the respondents to live or work in rural areas.

When a follow-up question was asked about what kind of farming system respondent plan to choose, the results showed an increase in popularity of organic farming among women and intensive agriculture popularity among men (Table 5).

TABLE 5

RESPONDENTS PERSPECTIVES ON CROPPING SYSTEMS, %

Cropping systems	2010		2011		2012	
	men	women	men	women	men	women
Intensive farming system	25,0	24,5	23,2	16,1	28,6	5,9
Organic farming system	5,0	48,9	30,2	24,2	7,1	54,1
Subsistence farm	10,0	20,5	11,6	30,2	14,3	13,5
Other	60,0	6,1	34,8	29,4	50,0	27,0

Focus on subsistence agriculture is associated with the respondents (about 30 percent responses) need to build a farm in the rural area and provide a healthy meal for family.

IV CONCLUSIONS

1. The analysis of scientific information and public enterprise “Ekoagros” data indicates that the certified organic area remained constant in 2011 and was 158,060 hectares in Lithuania. An average organic farm in the area is currently 61.2 hectares. There were growth of certified organic products not only in quantity but also the assortment, new refineries, a number of organic raw materials and finished products exported to other EU countries in 2009-2011. Also increased number of organic farms runs by women.

2. In 2010-2012, non-formal education course of farming basics was carried out at Landscaping faculty of Kauno kolegija/University of Applied Sciences. The research involved 148 women and 256 men. Analysis of the results suggests that the majority of respondents have chosen farming basics course because they needed license. Course participants believe that their way of life has a positive impact on the environment, the environment and society.

3. The survey of their knowledge and skills in the field of environment presented that most of the respondents know the basic environmental provisions, but in practice for a variety of reasons do not implement. Women show initiative and are much more active in practical environmental performance. There is also increasing both: organic farming and women in the number of farms and popularity of non-formal education in organic farming courses in the audience of women. The environmental education aims are to provide the knowledge, abilities and skills, to develop interest in a particular activity. Therefore subject programs of farming basics course must be supplemented with environmental material, also basics of organic and exceptional quality production.

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Production and Foreign Trade of Mineral Products in Latvia and Belarus

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Abstract. **Latvia and Belarus are small countries with limited scope of natural resources. However, the available mineral resources play important role in production of mineral products for domestic and foreign consumption. Main goal of the paper is to characterize the role of extraction industry in national economy and mineral products trade in two neighboring countries – Latvia and Belarus. To achieve the goal, the role of mining and quarrying industry in Latvia and Belarus was identified; trade of mineral resources in Latvia was analyzed. The main trends in the development of its own mineral resources of the Republic of Belarus were identified, the role of mineral resources in the commodity structure of foreign trade of the Republic of Belarus was shown, ways to increase the level of security of the country's own organic and mineral resources were determined, including the improvement of the legal framework. The research was performed in 2012; the following methods were used in the paper: comparative analysis and synthesis, statistical analysis and monographic methods.**

Keywords **– mineral resources, subsoil use, mineral products, economic development, foreign trade.**

I INTRODUCTION

The global economy of mineral resources and mineral commodities is being characterized by the presence of such processes as the emergence and development of the market of mineral bases and intensification of the processes of globalization of markets of mineral mineral products.

The development of national economies and the world economy as a whole depends on how fully meet their needs in mineral commodities.

II THE PLACE OF MINING INDUSTRY IN NATIONAL ECONOMY AND MINERAL'S FOREIGN TRADE IN LATVIA 2005-2011

An insight into the mining industry's role in the economy can be obtained by analysis of value added, as well as foreign trade data, which describes dynamics of foreign and domestic consumption of mineral products.

The value added of mining and quarrying in Latvia is almost 10% of the EU-27 average, there are about 200 companies operating in the industry. Compared with its Baltic neighbours, the value added in mining industry in Latvia is lower: value added in Estonia in 2010 was 140 million EUR, in Lithuania 71 million EUR, but in Latvia only 59 million EUR. The share of value added, created in mining and quarrying industry in Latvia in 2011 was 0.5% of GDP [1]. In comparison, in Republic of Belarus the share was higher: 1.1% of GDP [11].

The mineral resource range of Latvia basically meets the needs of the construction sector as well as the foreign demand for non-metallic mineral products.

During the period from 2005 to 2011, the import of goods and services in Latvia exceeded the export value.

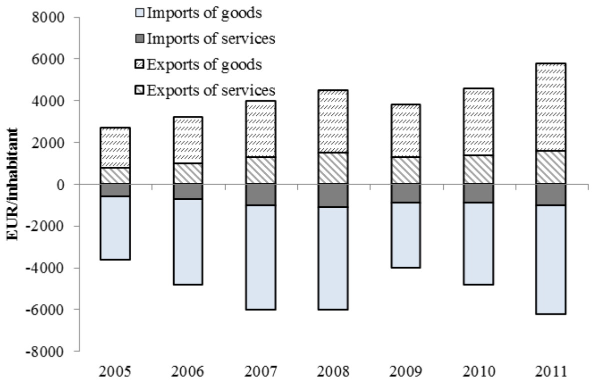

Fig.1. Foreign trade of goods and services in Latvia, 2005-2011

The foreign trade of mineral products has increased following the transition to the market economy (Table I).

TABLE I
SHARE OF MINERAL PRODUCT EXPORTS AND IMPORTS IN LATVIA, % OF TOTAL TRADE VALUE [1]

Indicator / year	**2005**	**2009**	**2010**	**2011**
Total import value	**100.0%**	**100.0%**	**100.0%**	**100.0%**
Mineral products import value % of total, of which	15.5%	17.2%	15.4%	17.3%
-diesel oil	34.2%	27.6%	31.8%	32.8%
-motor spirit (excl. aviation spirit)	16.8%	13.8%	10.8%	9.7%
-coal; briquettes and similar solid fuel	0.6%	0.6%	0.9%	0.9%
Total export value	100.0%	100.0%	100.0%	100.0%
Mineral products export value % of total, of which	9.2%	5.5%	6.0%	9.1%
-cement	0.3%	2.7%	7.6%	6.2%
-peat	11%	27%	23%	13%

As shown in Table I, mineral product import in Latvia in year 2011 accounted for 17.3% (1 903 mln.EUR) from the value of all imported commodities. Machinery and mechanical appliances; electrical equipment accounted for a similar proportion (17.3%) of total goods imports. The third largest group of imported goods is food and agricultural products (15.1% of total imports). These three commodity groups account for 50% of the total value of imported goods in 2011. Thus, compared with 2005, the proportion of mineral products in the total value of imported goods has increased by nearly two percentage points.

When assessing the value dynamics of imported mineral products during the period from 2005 to 2011, it can be concluded that the most rapid increase in import is attributable to solid fuel (coal, briquettes and similar solid fuel).

The export of cement and peat accounts for 20% of exported mineral product revenues, the income from cement exports is rising since 2005. In 2005 the exported cement value was 1022 thsd.EUR and in year 2011 - 48054 thsd.EUR.

According to the foreign trade data, the trade (both export and import value) with Belarus is growing over time. However, the Latvian foreign trade balance with Belarus since 2005 has worsened. In 2005, the difference between the export income from marketed products in Belarus and import expenditure was -94 million EUR, but in 2011 it was -305 million EUR. This can be explained by the fact that the value of imported goods from Belarus has historically been higher than the export earnings of the trade. The value of foreign trade in non-metallic mineral manufactures has increased significantly over the time: according to statistical data, the export income rose 8 times since year 2000, but import value - doubled in 2011/2000. Table II demonstrates Latvian foreign trade value of non-metallic mineral manufactures by region in year 2011.

TABLE II

MINERAL PRODUCT EXPORTS AND IMPORTS BY PARTNER IN LATVIA (2011), MLN.EUR [3]

Product/partner	**Belarus**	**EU27-extra (incl.Belarus)**	**EU27-intra**
Total imports	**483.5**	**2620.5**	**9082.0**
Non-metallic mineral manufactures (SITC 66)	3.9	24.3	138.8
Lime, cement, construction materials (SITC 661)	0.4	7.4	14.1
Clay construction materials, refractory construction materials (SITC 662)	0.3	1.7	25.3
Mineral manufactures, n.e.s. (SITC 663)	1.7	4.5	39.5
Glass (SITC 664)	0.5	5.9	23.2
Total exports	179.4	3208.2	6224.5
Non-metallic mineral manufactures (SITC 66)	6.0	59.2	92.0
Lime, cement, construction materials (SITC 661)	4.6	22.1	29.1
Clay construction materials, refractory construction materials (SITC 662)	0.2	15.1	6.8
Mineral manufactures, n.e.s. (SITC 663)	1.0	7.6	35.2
Glass (SITC 664)	0.1	10.3	15.7

When assessing the foreign trade value dynamics of mineral products between Latvia and Belarus, the following trends can be identified.

In the 3rd SITC group of mineral fuels, lubricants and related materials, Belarus is an important petroleum, petroleum product and related material import market. In 2000, the EU share was 27% of the import value of petroleum, Belarus 27% and other countries - 46%. In year 2011 the role of the third countries in petroleum imports decreased, while the share of the EU increased. Thus, 69% of the petroleum import value is attributable to the EU-27, 24% to Belarus and 7% to other countries.

In the 66th SITC group of non-metallic mineral manufactures since 2005 the foreign trade balance has improved. In 2005 the value of non-metallic mineral manufactures, imported from Belarus was 4 million EUR; the export income was 0.5 million EUR. In 2011 the value of imported non-metallic mineral manufactures was 4 million EUR, but export income rose to 6 million EUR.

Mineral manufactures not specified (group 663) accounted for 44% of mineral product import from Belarus. Glassware (SITC 665) was next most significant import product from Belarus in 2011, following by glass (SITC 664) with share of 24% and 12% accordingly.

In non-metallic mineral manufactures trade, 77% Latvian income was guaranteed by the export of the sub-group 661 (lime, cement, and fabricated construction materials, except glass and clay materials). Trade in these construction materials provided a positive balance of foreign trade with Belarus in both the 2010 and 2011. In comparison, in year 2005 the import value of construction materials from Belarus was 1.5 mln.EUR, and export income 0.3 mln.EUR.

Summarizing, it can be concluded, that trade in mineral products between Latvia and Belarus is increasing in observed time period 2005-2011.

III MINERAL PRODUCT INDUSTRY AND TRADE CHARACTERISTICS IN BELARUS 2005-2011

The Republic of Belarus refers to a group of small countries that do not have sufficient own mineral resources, therefore forced to import them, so far as based on mineral commodities to end use or for produce a finished product the following industries have been functioning: fuel industry, chemical and petrochemical industry, electricity, ferrous metallurgy, building materials industry (Table III).

TABLE III

DYNAMICS OF PRODUCTION OF MAJOR PRODUCTS IN THE REPUBLIC OF BELARUS IN 2005-2011 YEARS BASED ON MINERAL COMMODITIES

Product type	**Unit**	**2005**	**2006**	**2007**	**2008**	**2009**	**2010**	**2011**
Fuel industry								
Oil (including gas condensate)	thous. tonnes	1785	1780	1760	1740	1720	1700	1681
Natural gas	mln m^3.	228	219	201	203	205	213	222
Peat fuel (of conventional moisture content)	thous. tonnes	2307	2125	2502	2361	2216	2352	2823
Chemical and petrochemical industry								
Total mineral fertilizers, of which:	thous. tonnes	5669	5469	5880	5870	3390	6176	6288
nitrogenous	-“-	684	711	751	728	728	761	798
potassium	-“-	4844	4605	4972	4976	2485	5223	5306
phosphate	-“-	141	153	157	175	177	192	185
Fodder yeast (based substrates oil fractions)	-“-	24,3	31,8	32,9	32,5	33,6	20,3	7,6
Production of major products of refining industry								
Primary crude oil processing	thous. tonnes	19802	21253	21349	21304	21634	16455	20474
Petrol	-“-	3763	3931	3702	3709	3671	3477	3693
of which motor petrol	-“-	3330	3498	3181	3330	3372	3158	3135
Diesel fuel	-“-	6426	6616	6679	661	6588	5331	6709
Fuel oil (gross output)	-“-	6313	6329	6195	5913	6202	4421	5589
Production of thermal and electrical energy								
Electrical energy	billion kWh	30,961	31,811	31,829	35,054	30,405	34,890	32,192
The thermal energy	mln Gcal	73,496	74,383	69,733	67,454	67,769	72,475	68,960
Building materials industry								
Cement	thous. tonnes	3131	3495	3821	4219	4350	4531	4604
Wall materials, all of them:	mln standard bricks	2960,4	3640,6	4193,9	4389,2	3729,3	4087,3	4249,0
building bricks	-“-	838,1	934,9	1084,4	1102,8	960,4	1002,3	955,9
wall blocks of cellular concrete	-“-	1964,3	2477,6	2829,8	2982,0	2456,2	2772,4	2971,5
Lime	thous. tonnes	785	853	925	900	788	804	793
Limestone and dolomite flour	mln tonnes	2,506	2,273	2,092	1,874	1,940	1,929	1,684
Non-metallic building materials – total of which:	thous. m^3	23154	27029	29819	34315	36567	41621	43785
rubble stone	-“-	36,1	130,1	66,9	49,3	69,3	107,9	104,1
crushed stone	-“-	8553	9493	10100	10753	11338	12089	13152
mortar sand	-“-	8934	10343	11137	11256	12720	15835	16677
gravel	-“-	649	781	1069	1448	1410	1369	1673
Glass - (all totally for SUP. Elektroarmaturnogo glass), including by type:	thous. m^2	23746	23249	21268	21357	20880	21364	25354
building glass	-“-	1461	1322	1370	1130	1419	1711	1948
polished glass	-“-	20349	20151	18022	18428	17551	17275	20606
glass (stalinite)	-“-	93	130	153	138	101	121	160
patterned glass	-“-	475	397	420	558	380	546	692
glass reinforced	-“-	966	833	951	791	1138	1384	1720
Glass elektroarmaturnoe	thous.unit	402	416	352	312	291	327	228
Ferrous metallurgy								
Cast iron	thous. tonnes	270	301	346	366	276	303	359

Steel	-“-	2076	2297	2387	2660	2449	2672	2779
Finished rolled products	-“-	1839	2047	2192	2470	2298	2458	2454
Steel pipes	-“-	108	134	148	146	107,4	183,7	218
Metal cord	-“-	78,5	86,4	87,2	96,5	68,5	92,9	94,1

In the depths of Belarus found over 10 thousand deposits of various mineral resources, the most important of which are fields of energy resources (oil, associated gas, peat, lignite and oil shale), potash and rock salt, variety of minerals used in the production of building materials (building and facing stone, raw materials for the production of cement, lime, sand and glass construction, sand and gravel material, clay ceramic, refractory and lightweight aggregates, and other), fresh and mineral underground waters. In addition, deposits of iron ore, gypsum, rare metals, phosphorus, alumina-soda raw materials and industrial brines were identified. While Belarus buys oil, gas, raw materials for steel production, facing stone, glass sand, bentonite and kaolin clay, plaster and building materials based on gypsum, apatite, phosphorus.

The Republic of Belarus is now being developed oil fields, peat, potash and rock salt, dolomite, fresh and mineral underground waters on the basis of which work successfully industry.

At the present stage of development and the future site of the mineral resources base of Belarus is sufficient to provide of mineral commodities only industry of building materials (except for the production of glass), chemical and petrochemical industries in the production of potash and nitrogen fertilizers and fuel industries of the country.

Almost all industries have a high degree of dependence on imported mineral commodities and mineral resource production, which adversely affects the competitiveness of commercial products, the formation of the balance of foreign trade of the Republic of Belarus and the state of the economy as a whole.

Mineral resources play a dominant role in the commodity structure of foreign trade of the Republic of Belarus: in 2010 year, their share of total exports amounted to 28.2% and 35.4% of total imports. In 2011 year - 36.0% of total exports and 41.7% of total imports (Fig. 1, 2).

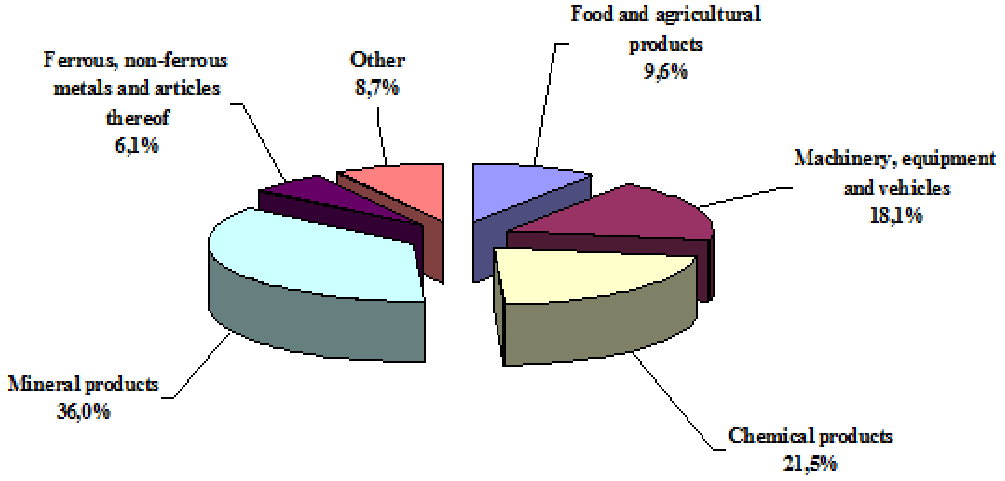

Fig. 1. – Commodity structure of exports in Belarus, 2011

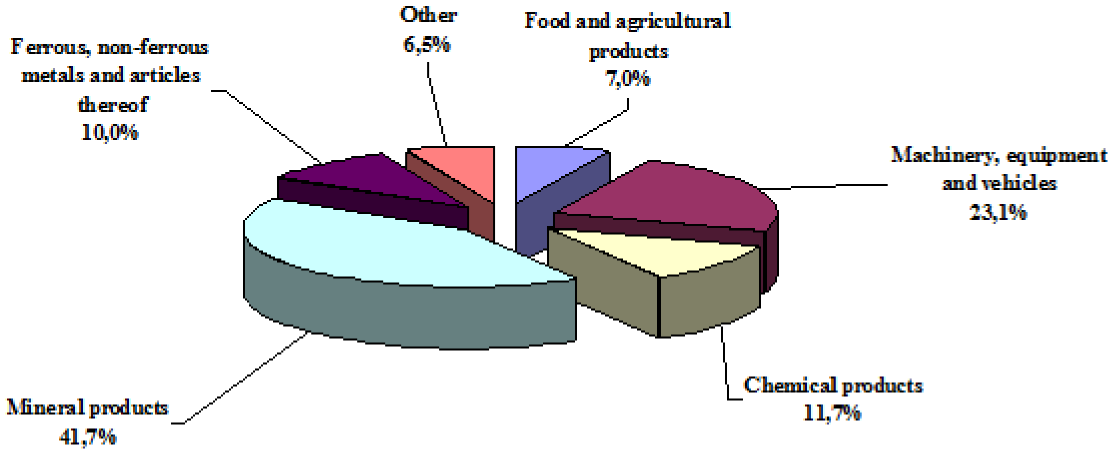

Fig. 2. – Commodity structure of imports in Belarus, 2011.

The main consumers of exports from Belarus mineral commodities are Russia, Ukraine, Moldova, Lithuania, Latvia, Poland [4, p. 25].

Given that the mineral resources is the basis of national security and sustainable development, to regulate its formation should be special state programs.

Belarus has adopted and implemented legal normative acts, which are a part of the national legislation, aimed at integrated use of mineral resources, including fuel and energy resources, improving performance for the involvement in the development of mineral deposits:

State exploration program for the development of mineral resources of Belarus for 2006-2010 and for the period up to 2020, approved by Edict of the President of the Republic of Belarus from 28 March 2006 № 184 [5],

Subsoil Code of the Republic of Belarus (14 July 2008),

The development strategy of the energy potential of the Republic of Belarus, approved by the Regulation of the Council of Ministers of the Republic of Belarus from 9 August 2010 № 1180 [6],

The program of development of mineral deposits and the development of mineral resources of the Republic of Belarus for 2011-2015 and for the period up to 2020, approved by the Regulation of the Council of Ministers of the Republic of Belarus from 4 April 2011 № 431 [7],

Water Code of the Republic of Belarus (15 July 1998),

National program of local and renewable energy sources for the period 2011-2015, approved by the Regulation of the Council of Ministers of the Republic of Belarus from 10 May 2011 № 586, etc.

Regulation similar public relations for the use of mineral resources, including fuel and energy resources, is carried out in the Russian Federation and other countries - members of the Commonwealth of Independent States [8, p. 131], and in the Commonwealth of Independent States. In particular, the basis of international legal cooperation among states in the use of mineral resources are:

Mining Charter of countries - members of the Commonwealth of Independent States from 27 March 1997,

Pact on cooperation in the field of exploration, development and use of mineral resources from 27 March 1997,

Pact on the basic principles of cooperation in the field of rational use and protection of transboundary waters from 11 September 1998,

Pact on cross-border cooperation in the field of exploration, development and protection of the subsoil from 31 May 2001,

Pact on cooperation of countries - members of the Commonwealth of Independent States in the field of energy efficiency and energy savings from 7 October 2002, and Memorandum of Cooperation between the Government of the Republic of Belarus and the Government of Latvia in the energy sector from 18 February 2009 [9].

Of particular interest to Belarus is expanding economic ties with the Baltic states - Lithuania, Latvia and Estonia. This is due to many factors, among which is the geographical proximity, and the overall economic past [10, p. 341].

Improving the legal security subsoil and the introduction of economic incentives of geological study of the subsoil and reproduction of mineral resources and the rational use of mineral resources will increase the investment attractiveness of the subsoil, to remove administrative barriers in regulating geological study of the subsoil and reproduction of mineral raw materials.

IV CONCLUSIONS

The share of value added, created in mining and quarrying industry in Latvia in 2011 was 0.5% of GDP.

Belarus is an important petroleum, petroleum product and related material import market for Latvia. 69% of the petroleum import value is attributable to the EU-27, 24% to Belarus and 7% to other countries outside the European Union.

In 2010 and 2011 trade in construction materials (lime, cement, and fabricated construction materials) turned to a positive balance of Latvian foreign trade with Belarus.

Mineral resources play a dominant role in the commodity structure of foreign trade of the Republic of Belarus: in 2011 year, their share of total exports amounted to 36% and 41.7% of total imports.

The strategic goal for Belarus is to increase the security of the country's own organic and mineral resources, a rational use and minimizing the negative impact of extraction on the environment, reducing the dependence on imports, as well as improving the quality of use of surface and ground water.

To achieve this goal in Belarus it is necessary:

-to improve the economic mechanism of production and use of mineral resources for complex processing environment;

-develop a comprehensive state program for the development of mineral resources of the country in which the strategy of exploration industry should be closely linked with the economical use of natural resources and increasing need in their separate ways;

-oriented economy to rational use of mineral resources;

-ensure the expansion of exploration on promising areas, the search for new deposits, as well as the use of related types of minerals, certain types of waste and recycled materials;

-support material and technical base of exploration industry at an optimal level;

-improve the regulatory framework in the sphere of subsoil use in order to ensure the best possible country own minerals.

V ACKNOWLEDGMENTS

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Trends in Education for Sustainable Development in Some Former Soviet Countries (Use of ESD Potential for Provincial and Regional Studies)

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Abstract. **The major part of the decade for education on sustainable development declared by United Nation in 2005 is over and it is the time to review the outcomes of the efforts of national and international educational and research communities. These results differ greatly. One of the ways to grasp the picture is to look at the map of regional centres of expertise on education for sustainable development organized under the aegis of United Nations University and with its help. The biggest states formed on the ruins of the collapsed Soviet Empire are the most backward ones in this respect. For instance on the huge territory of Russia there are only two such centres, in Samara and Nizhny Novgorod. There are certain political, geographical, economic, social and even linguistic factors deterring the implementation of sustainable development methodology in national education systems. Nevertheless it can be fruitfully used on a regional level. This was proved at a number of international research conferences on provincial life and environment held at Samara State University of Architecture and Civil Engineering. A great potential of this philosophy for regional studies even in such restrictive conditions was revealed.**

Keywords **– sustainable development, CIS countries, regional studies, provincial identity.**

Most of the former Soviet Union Republics (with the exception of Baltic countries and Georgia) still share many common features inherited from the collapsed empire. For example, the organizational structure of the higher education systems of such countries as the Russian Federation, Ukraine or Kyrgyzstan are similar to a great extent. Nevertheless nowadays all of them are undergoing substantial changes caused by the rapid introduction of the Bologna principles for HE coming from the West. That is why there are still two parallel ways of acquiring HE in these countries: a traditional one-level educational system leading to a specialist diploma (5-7 years depending on the chosen specialty) and an European «newcomer», a two-level training system with bachelors and masters degrees, following the European model. The Bologna process was supported by official documents. Russia joined it officially in 2003 at the Berlin Meeting of European Ministers of Education [1]. In 2005 the Bologna Declaration was signed by the Minister of Education of Ukraine[2]. Kyrgyzstan is going to join it and is already adopting this system as well [3]. At the moment there is an overall transition to this new system which is ousting the former one, but there are also attempts to adjust specialist diplomas as an alternative to master degrees in post-bachelor education. Postgraduate education still includes the two academic degrees inherited from the Soviet system, the Candidate of Science and Doctor of Science, which are not easily comparable with European doctoral degrees.

The most common university model in all the three countries is still a state centered institution operating on prescriptions of state regulative bodies.

There are two general types of such institutions of higher education: state (public) and private. In all these countries the number of state universities prevails over the number of private universities: in Russia the number of state universities is 653 out of the total number of 1115 (59%), in Ukraine this proportion is 316 to 451 (70%) and in Kyrgyzstan the percentage is even higher, it is 72% (36 out of 50). If we compare the numbers of university students with the whole population we shall see that there are relatively more students in Ukraine (5,7%), than in Russia (4,9%) and Kyrgyzstan (4,3%) though in absolute figures Russia is taking the lead due to its immense size. But in the public spending on education the Kyrgyz Republic is ahead with circa 18.7% of the total national budget while in Russia it is 16.7%, and in Ukraine it is only 12.6% of the budget.

The key institutions responsible for HE policies are corresponding national Ministries of Education and Science and their subordinate or authorized agencies. They set federal or national state educational standards which rather precisely define obligatory requirements for the structure and content of higher professional education. The standards allow some freedom of choice only in some minor or elective courses. ESD is not included in the content of the standards, because the notion of Sustainable Development is relatively new for the general public in these countries. Only recently it has started to be used in official speeches and documents and mainly only for "decorative" purposes: e.g. new educational standards are said to be developed for the sake of sustainable development. (cf: Federal State Educational Standard – Strategic Resource of Multinational Society Sustainable Development) [4]. In the same way the term SD was used in an article by Russian PM V. Putin in "Komsomolskaya Pravda" on 12/02/2012. This notion is neither included in the content of the federal or national state educational standards nor it is expressed in the national educational programs or state education development projects, except for those involving EU institutions.

The idea of SD was first mentioned in Russia at the legislative level in 1994 by Presidential Decree №236 "On the Russian Federation National Strategy of Environmental Policy and Providing Sustainable Development" of 04.02.1994 [5]. A similar situation could be observed in Ukraine, where the issue of SD was first raised in the framework of the "Conception of Settlements Development", adopted by the Verkhovna Rada of Ukraine on the 24th of December 1999. In both countries it has not made any immediate impact on HE and generally speaking no real measures necessary for implementing principles of SD have followed. In the Kyrgyz Republic the issues of education for sustainable development were first considered in "Conception for Transfer of Kyrgyz Republic to Sustainable Development until 2010", which was adopted in 2002 and all initiatives in the sphere of SD since than have been supported by the Government and Ministry of Education. The reason for such a difference between national approaches to SD implementation may be the relative compactness of Kyrgyzstan in comparison with the Russian Federation and Ukraine combined with the fact that SD ideas were introduced later when they were more clearly defined and made more applicable for implementation in HE. The first definition of SD borrowed by all these countries from the West was rather general - SD was defined in 1987 by the World Commission on Environment and Development as a development that satisfies the needs of the present time, but doesn't endanger the ability of future generations to satisfy their needs. Only later was it further elaborated, specified and clarified.

There are still some differences in the national attitudes to this term. For example, in Russia the idea of SD is still perceived with a kind of skepticism. The main reason for this is a disbelief in the possibility of its implementation under the conditions of present day Russia; it is often regarded as utopian and excessively ambitious. The other reason is that the Russian translation of this term is not accurate and is understood by Russian speakers primarily as "stable" development without considering the multifaceted complexity of this notion. There is also a political reason: many influential politicians say it should be not applicable in Russia or other non-western civilizations because of its Western origin. We can add to that the widespread fear that the concept of sustainability could have a negative impact on industrial development and the limitations of the latter would lead to undesirable consequences.

In Ukraine there are no explicit anti-western arguments, but the other reasons are mainly the same. There is less anti-Westernism in Kyrgyzstan as well. This country focuses more strongly on cooperation with Europe.

In all the given countries the notion of SD was historically closely related with that of ecological protection. Even now these issues and terms are often interchanged and SD is limited to environment protection in the minds and practices of the general public. At the same time there is one thing common for all the countries - concerns for all the aspects inherent for SD, namely social, health, educational, ecological, economic and other priorities, regularly formulated in spite of various conceptual and ideological differences. These challenges nowadays are faced separately, each within its own domain or sphere. Unfortunately there is no awareness that the idea of SD could provide a unified remedy for the successful joint and balanced treatment of those challenges. To be efficient SD needs to be mainstreamed, in education it could find its expression in transdisciplinarity.

Regrettably in Russia and Ukraine there is no national strategy for introducing SD into HE, developed and approved at the legislative level. Since its coming in the 90-s to Russia these ideas have been closely associated mainly with the sphere of ecology, starting with Presidential Decree № 236 of 4.02.1994 and then followed in other official documents such as the National Action Plan of the Environment and Natural Resources Ministry of the Russian Federation "On Environmental Education in Educational Institutions of the Russian Federation" (1994); Presidential Decree № 440 of 1.04.1996 "On Concept of Russian Federation's Transition to Sustainable Development"; and the "Concept of Secondary Ecological Education"[6].

None of these documents pay attention to HESD, neither do they consider other, non-environmental aspects of sustainable development. Maybe that is why a comprehensive strategy of ESD has not been developed up to the present in spite of the fact that it was many times declared. Even the mass media are still not greatly involved in the process of promoting ESD.

At the moment some awareness and activities related to HESD can be seen at regional and local levels. Several specialized institutions have been created (i.e. the Institute for Globalization and SD at the International Independent Ecological University in Moscow), a number of UNESCO Chairs related to SD have been organized at some Russian Universities, ESD ideas are being developed rather sporadically at HEIs such as Moscow State University, the Russian State Humanitarian University, the Mordovian State

Pedagogical Institute and many others. Under the aegis of the UN University two Regional Centers of Expertise on Education for Sustainable Development were created in Russia, at Samara State University of Architecture and Civil Engineering (2007), and at Nizhny Novgorod State University of Architecture and Civil Engineering (2009). Another RCE on ESD was organized in Kyrgyzstan.

In Ukraine as well as in Russia there is no real national policy strategy. SD is not on the list of national priorities. It is also mentioned in some national documents, but the main initiatives are coming from NGOs. We can mention here the Regional Social Ecological Organization "Center of Sustainable Development "Roza Vetrov", the World Social-Ecological Union, the World Data Centre on Geoinformatics and Sustainable Development (WDC-Ukraine), and the Municipal Governance and Sustainable Development Programme. Special courses on SD have been organized in some universities, such as Kievo-Moghilyanskaya Academy, Kiev National University, Odessa Ecological University, and the Management Education University. In these universities special chairs were set up and new educational programs were developed.

More positive tendencies can be noticed in the Kyrgyz Republic. The Government here is constantly expanding the range of issues related to SD. Certain significant commitments were made as a result of different international projects. They are oriented to the integration of SD topics into study programs, such as "Biological and Landscape Diversity", "Citizenship, Democracy and/or Management", "HIV/AIDS, Drug Abuse", "Healthy Life Style", "Cultural Diversity" and "Climate Change". A cross-curricular approach in the sphere of ESD is under active development at the moment in Kyrgyzstan. A broad awareness campaign on ESD issues for schools and institutions of higher education of Kyrgyzstan is underway. Many teachers of higher educational institutions in recent years have been trained in the frameworks of various international projects.

In comparison with the situation in Russia and Ukraine the ESD issues in Kyrgyzstan are reflected in some national strategic documents, such as the State Doctrine of Education of the Kyrgyz Republic (adopted in August 2002 by order of the President of the Kyrgyz Republic), the Concept of Education Development of the Kyrgyz Republic up to 2010 (adopted in 2002), the Concept of Continuous Environmental Education in Kyrgyzstan, adopted by decision of the Ministry of Education and Science Board of the KR on September 17th, 2003.

In relation to the issues of environmental education, it is important to notice that they are partially reflected in the following national political documents, such as the President Education Program "Human Resources of the XXI century" (by Order of the President of the KR on September 11th, 1995, # OP-218), laws "On Environmental Protection" and "On Environmental Expertise" (1999), Conception for Transfer of Kyrgyz Republic to Sustainable Development until 2010 (August 2nd, 2002) and the KR Law "On Education" of April 30th, 2003, # 92.

In Kyrgyzstan state and non-state organizations were created for the implementation of Sustainable Development principles. Such state organizations as the State Agency of Environment and Forestry, the State Environmental Fund and the Forestry Development and Coordination Council of Education for Sustainable Development could be mentioned. Non-State Organizations include the Ecological Movement "BIOM", RCE Kyrgyzstan, EHD Aleine" and the non-state public organization "Institute of Equal Rights and Opportunities". Kyrgyz National University, Kyrgyz State University and Kyrgyz Russian Slavonic University also support and develop the ideas of SD.

Thus, Kyrgyzstan can be regarded as the leader among the above-mentioned countries in promoting HESD. Due to its small territory it's easier to integrate the ideas of SD in all spheres of society. Besides, all reforms in the educational sphere are willingly supported by the Government.

Coming back to the issue of using ESD for regional and provincial studies we can refer to the experience of RCE Samara, where a number of international conferences on the topic were held recently.

I CONCLUSIONS

Summing up we should underline that there still exist certain challenges in implementing / disseminating sustainability in higher education:

1. There are no political/state/legal documents which explicitly promote SD in Education. Sustainable Development as a specialized course started to appear in curricula mostly in ecological specialities only a couple of years ago and it is still at the developmental stage.
2. Universities are very strictly controlled by the Ministry of Education: universities should plan the curricula according to the instructions of the Ministry of Education but not to the current challenges in the ecological, economical, and social spheres. Poor financing of research in SD at HEIs limits the progress of its implementation.
3. Low awareness about the idea of SD among the majority of professionals. Mostly only ecologists and sometimes economists are involved.
4. There are relatively few examples of successful practice in these countries to be used as case studies for students. Many SD initiatives have been recently cancelled because of political and financial pressure as well as because of corruption.
5. Implementing / disseminating of sustainability is done mostly via NGOs. It is necessary to develop interactions between NGOs and high school institutions. Unfortunately such cooperation is not very common currently. Especially after the notorious law was adopted in Russia.

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