*Environment. Technology. Resources, Rezekne, Latvia*
*Proceedings of the 10th International Scientific and Practical Conference. Volume I, 200-204*

# Alkali Activated Binders Based on Metakaolin

**Laura Sele, Diana Bajare, Girts Bumanis, Laura Dembovska**
*Department of Building Materials and Products, Institute of Materials and Structures,*
*Riga Technical University*

***Abstract.*** **According to research conducted in last 25 years, alkali activated binders have been considered as one of the most progressive alternative binders, which can effectively replace Portland cement. Production of alkali activated binders differs from the Portland cement production and is associated with lower $CO_2$ emissions. The use of recycled industrial by-products and wastes is also possible, what corresponds to the future guidelines and principles of sustainable binder production in the world.**

**The aim of this study was to create innovative alkali activated binders by using secondary raw materials, which will be different from the ones described in the scientific literature – alkali activated binders with porous structure. Raw materials used for the binders were metakaolin containing waste, waste from aluminium scrap recycling factory and recycled lead-silicate glass; solid contents were activated with modified sodium silicate solution with an addition of sodium hydroxide.**

**The physical properties of alkali activated binders, such as density, water absorption, open and total porosity, were determined and flexural and compressive strength of hardened alkali-activated binders were tested at the age of 28 days. Durability was examined by sulphate resistance test, which was performed according to SIA 262/1, appendix D: applicability and relevance for use in practice. 40x40x160 mm prismatic specimens were used for expansion measurement and determination of compressive strength.**

**The open porosity of obtained materials was up to 45%, density from 380 to 1720 kg/m$^3$, compressive strength up to 29,8 MPa, water absorption 6 – 114 wt.%. After analysing the results from the sulphate test it was concluded that glass additive reduced the alkali activated binder resistance to sulphate attack.**

***Keywords:*** **Alkali Activated Binder, Aluminium Recycling Waste, Waste Metakaolin.**

## I INTRODUCTION

The production of different types of alkali activated binders results in a near zero-carbon dioxide emission, which is significantly less compared to the production of ordinary Portland cements (OPC) or lime binders [1]. For example, in case study of geopolymer concrete mixes based on typical Australian feed stocks, the results indicated a potential for a 44-64% reduction in greenhouse gas emissions while the financial costs varied from 7% lower to 39% higher compared with OPC [2]. It is clear that alkali activated binders can exhibit performance properties such as high compressive strength [3]; high level of resistance to a range of different acids and salt solutions [4]; high resistance to freeze–thaw [4]; not being subject to deleterious alkali–aggregate reactions [4]; low shrinkage [5]; effective solution for the stabilization of industrial by-products and the immobilization of heavy metals [6] as well as other important technologic and functional properties which depend from the chemical composition of raw materials used and the composition of mixes. Therefore alkali-activated binders (AAB) are receiving increased attention as an alternative to OPC and lime because of their high functionality and low environmental impact.

Alkali activated binders traditionally are made by mixing powdered alumosilicates based raw materials such as fly ash, metakaolin, slag or other materials rich with amorphous $SiO_2$ and $Al_2O_3$ with an alkali activation solution [7] [8].

A key attribute of alkali activation technology is the robustness and versatility of their process of production; it enables products to be tailor-made from a range of alumosilicate raw materials so that they have specific properties for a given application at a competitive cost [9]. Although several researchers demonstrated an excellent durability of alkali activated materials in their experiments, the major unsolved problem in the development and application of alkali activation technology is still related to the durability, because it seems to depend strongly on the application of adequate curing regimes and composition of mixes. Also carbonation can be quite problematic in these systems, as there is no reservoir of available calcium to provide a pH buffer; therefore durability performance is critically dependent on the development of a compact and refined pore structure

*ISSN 1691-5402*

*DOI: http://dx.doi.org/10.17770/etr2015vol1.204*

[10]. The sulphate attack is a topical issue similarity as it is in systems made of OPC because of chemical reaction in wet media between sulphate ions and aluminate component of hardened cement paste [11]. A mineral formation increases internal stresses due to expansion of tricalciumaluminates (C3A) up to 227% from its initial volume [12]. This leads to irregular micro-crack pattern and degrades material durability. Similarities can be found with high calcium amount contained alkali activated systems, where sulphate salts can react with free lime and form ettringite and/or gypsum. Bakharev has reported that magnesium sulphate, compared to sodium sulphate, has more deleterious effect on sulphate resistance of concrete made of OPC or alkali activated slag. No visual signs of degradation were detected for alkali activated slag concrete while OPC specimens expanded significantly after long-term immersion in sodium sulphate solution [13]. El-Sayed has reported that compressive strength decreased up to 52% of alkali activated slag concrete when samples were exposed to magnesium sulphate attack for 6 months [14]. Also diffusion of alkali ions from structure of alkali activated materials to solution can cause stresses; deep vertical stresses can be observed [15]. However, using slag cements could lead to failure of material structure due to weakening and disintegration of structure before expansion could be observed [16].

Incorporation of pozzolans like fly ash, rice husk ash in OPC reduces the total calcium amount in cement system; therefore material, which is more durable to the sulphate attack, could be obtained [17]. The increased resistance to the sulphate attack of low–calcium alkali activated material could be sulphate caused by low calcium content available for reactions. AAB based on fly ash could reach superior sulphate resistance compared with OPC materials or high calcium amount contained AAB systems [18]. Bakharev has reported that specimens made of low-calcium AAB have increased durability to sulphate attack but it depends on type of activator used and cation type in sulphate media. At the end it was concluded that activator containing NaOH can lead to improved resistance of AAB to sulphate attack [15].

Resistance to the sulphate attack of alkali activated materials depends from polymerization degree of the material structure; highly cross-linked aluminosilicate polymer structure will be more stable even in comparison with OPC system [19]. Intensity of polymerization reaction and development of specimens' strength are affected by chemical composition of the system, ratio of solid raw material and activator, concentration of activator as well as curing conditions [14] [20] [21] [22]. There are many variables that could affect sulphate resistance of AAB but information on tried and tested solutions for the best performance is not available in literature.

The presented research focuses on a low-calcium alkali activated binders with high porosity and their resistance to the sulphate attack. Porous binders were obtained from metakaolin containing waste (WMK) by incorporation of industrial wastes from aluminium scrap recycling (ASRW) as foam forming agent.

## II MATERIALS AND METHODS

### *Materials*

Low-calcium alkali activated binder (AAB) was obtained from industrial by-products and alkali activation solution. Waste metakaolin (WMK) was obtained from the expanded glass granule production plant "Stikloporas" UAB (Lithuania), where kaolinite clay is used as a substance for anti-agglutination in the final stage of expanded glass granule production and the obtained metakaolin containing material is defined as by-product. During processing WMK was calcined at 850 °C for about 40-50 minutes and fraction <0.25 mm was used as base material for alkali activation. Glass waste (GW) received from the glass recycling factory "Lampu Demerkurizacijas Centrs" Ltd. (Latvia) was used to modify the composition of AAB. Aluminium scrap recycling waste (ASRW) received from aluminium scrap recycling industry facility "Dilers" Ltd. (Latvia) was used as a foaming agent for creating of porous AAB structure [23]. The amount of ASRW in the mixture composition of AAB can define the final physical and mechanical properties of the obtained material. Chemical composition of the raw materials is given in Table 1. In order to increase homogeneity and fineness of ASRW and WG, both raw materials were ground in planetary ball mill Retsch PM 400 with speed 300 rpm for 30 minutes.

TABLE 1

CHEMICAL COMPOSITION OF RAW MATERIALS, $W_T$ %

| CHEMICAL COMPONENT | ASRW | WMK | WG |
|---|---|---|---|
| $Al_2O_3$ | 63.2 | 51.7 | 1.0 |
| $SiO_2$ | 7.9 | 34.4 | 68.1 |
| CaO | 2.6 | 0.1 | 1.4 |
| $SO_3$ | 0.4 | - | - |
| $TiO_2$ | 0.5 | 0.6 | - |
| MgO | 4.4 | 0.1 | - |
| $Fe_2O_3$ | 4.5 | 0.5 | 0.2 |
| PbO | - |  | 20.0 |
| $Na_2O$ | 3.8 | 0.6 | 8.0 |
| $K_2O$ | 3.8 | - | 1.2 |
| Other | 2.6 | - | 0.1 |
| LOI, 1000°C | 6.2 | 12.1 | - |

The activation of solid raw materials was done with modified sodium silicate solution. Commercially available sodium silicate solution from "Vincents Polyline" Ltd. (Latvia) characterized by the silica modulus Ms 3.22 was modified with sodium hydroxide flakes from "Tianye Chemicals" (China) with 99% purity and alkali activation solution with silica modulus Ms 1.67 was obtained

*Methods*

Physical properties of AAB, such as density, water absorption, open and total porosity, were determined in accordance with EN 1097-6 and EN 1097-7. Flexural and compressive strength of hardened alkali-activated mortar bars were tested according to LVS EN 1015-11 at the age of 28 days. Sulphate resistance test was performed according to SIA 262/1, appendix D: applicability and relevance for use in practice. 40x40x160 mm prismatic specimens aged 28 days were used for expansion measurement and determination of compressive strength.

*Sample preparation*

The compositions of solid raw materials are given in Table 2. Two series of AAB were prepared: samples without WG in mixture composition (mixture composition with index G0) and samples with WG in mixture composition (with index G1, respectively). The incorporation of WG in the mixture composition of AAB increases the $SiO_2$ content; therefore the obtained AAB can possess different properties. The ASRW in both series were added from 0 to 1.0 mass ratio calculated from the amount of WMK resulting in materials with different porosity.

All dry components were weighted and mixed together to obtain homogenous powder, and alkali activation solution (AAS) was added to the mixture with a constant AAS/solid content ratio of 0.75. After mixing, the pastes were immediately poured into prismatic moulds measuring 4×4×16 cm. Moulds were covered to limit expansion of pastes and then placed in heating chamber at 80 °C for 24 h for the final setting in order to obtain porous AAB.

TABLE 2

MIXTURE COMPOSITION OF AAB

| MIXTURE COMPOSITION | COMPOUND MASS RATIO | | | |
|---|---|---|---|---|
| | ASRW | WMK | WG | AAS/SOLID RATIO |
| 0G1 | 0 | 1 | 1 | 0.75 |
| 0.1G1 | 0.1 | 1 | 1 | |
| 0.5G1 | 0.5 | 1 | 1 | |
| 1.0G1 | 1.0 | 1 | 1 | |
| 0G0 | 0 | 1 | 0 | |
| 0.1G0 | 0.1 | 1 | 0 | |
| 0.5G0 | 0.5 | 1 | 0 | |
| 1.0G0 | 1.0 | 1 | 0 | |

## III RESULTS AND DISCUSSIONS

### *Physical properties of AAB*

Due to the chemical reactions between ASRW and high alkalinity of the activation solution, gas evaporation was observed and porous structure of AAB was obtained (Fig.1). Highly porous AAB was obtained with the addition of ASRW even with 0.1 mass ratio to WMK in mixture composition. The pore volume, pore structure and density depend from the amount of ASRW and WG used in the AAB composition. The physical properties of AAB are given in the Table 3.

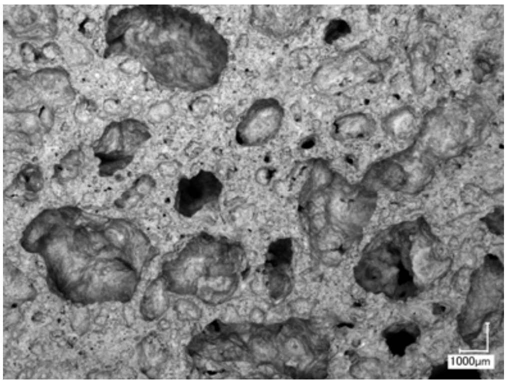

Fig. 1. Porous structure of AAB with ASRW (weight part 0.5) and without WG additives.

Samples without ASRW in the mixture composition provide the highest density and the density greatly depends from WG (1400 kg/m$^3$ for 0.0G0 and 1720 kg/m$^3$ for 1.0G1). Glass additive in mixture composition provides glassy and compact structure of AAB while structure of AAB without WG is more porous thus influencing porosity of the material (Table 3). All samples with glass additive in the mixture composition have higher density in comparison with samples without glass. Most likely glass additive dissolves in the alkali media and fills microporous of the material structure. This phenomenon also explains the difference of water absorption among samples with and without glass additive. Thus samples with glass in the composition have significantly lower water absorption compared with the rest. Water absorption for samples with glass in the mixture composition was from 6 to 93% while for the samples without glass additive in mixture composition – from 26 to 112%. Water absorption increases with the increase of open porosity of the samples which was determined by the amount of ASRW in the mixture composition. Porous AAB are characterized with high open porosity and it can be up to 44% (1.0G0). Glass additive in the mixture composition reduced open porosity which could be explained by the glassy structure of AAB.

TABLE 3

PHYSICAL PROPERTIES OF AAB

| MIXT. DESIGN | DENSITY KG/M$^3$ | WATER ABSORPTION % | OPEN POROSITY, % | TOTAL POROSITY, % |
|---|---|---|---|---|
| 0.0G1 | 1720 | 6±0.4 | 10±0.6 | 20±0.5 |
| 0.1G1 | 770 | 17±0.7 | 12±0.4 | 64±0.3 |
| 0.5G1 | 490 | 78±0.9 | 36±0.8 | 78±0.2 |
| 1.0G1 | 390 | 93±2.0 | 37±0.3 | 83±0.4 |
| 0.0G0 | 1400 | 26±0.3 | 30±0.8 | 31±0.7 |
| 0.1G0 | 520 | 68±2.1 | 32±0.7 | 74±0.3 |
| 0.5G0 | 430 | 86±1.3 | 35±0.7 | 80±0.3 |
| 1.0G0 | 380 | 112±3.8 | 44±0.9 | 83±0.5 |

ASRW mass content increase in the mixture composition leads to significant decrease of density for all samples. Even 0.1 weight part of ASRW in the composition decreased density up to 60% (from 1720 to 770 kg/m$^3$ for samples with glass additive and from 1400 to 520 kg/m$^3$ without glass). By increasing the amount of ASRW in the composition to 1.0 weight part from the amount of WMK, the changes in sample density are less critical and it decreased to 390-390 kg/m$^3$. By increasing amount of ASRW in the composition, influence of glass additive on the physical properties of obtained samples decreased but density of samples decreased below density of water.

Obtained samples with ASRW over 0.5 weigh part in mixture composition have total porosity around 80% and it is explained by the specific pore structure where more than 50% of pores are closed. This phenomenon ensures floating of samples in the water for unlimited time. Comparing porosity of denser samples without ASRW and samples with minimal amount of ASRW (0.1 with parts) in the composition, total porosity increased more than 2.5 times.

It can be concluded that WG and ASRW additives have great influence on the physical properties of samples made by alkali activation technology.

### *Mechanical properties of AAB*

Compressive strength of hardened samples was in range from 0.5 MPa to 29.8 MPa and it strongly depends from composition (Table 4). Comparing series with and without WG in mixture composition, AAB samples with glass additive were with higher compressive strength compared (0.5 to 30 MPa) to AAB samples without WG (from 0.5 to 8 MPa).

By increasing the amount of ASRW in the mixture composition, compressive strength decreased to 0.5 MPa for both series of samples (Table 4). By incorporating ASRW even to 0.1 weight part to WMK, the compressive strength reduction was significant which can be explained by the increase of porosity for obtained material.

TABLE 4

MECHANICAL PROPERTIES OF AAB

| MIXT. DESIGN | FLEXURAL STRENGTH, MPA | COMPRESSIVE STRENGTH, MPA | REDUCTION OF COMPRESSIVE STRENGTH AFTER SULPHATE ATTACK, % |
|---|---|---|---|
| 0.0G1 | 2.1 | 30.1 | 72 |
| 0.1G1 | 0.9 | 3.2 | 25 |
| 0.5G1 | 0.7 | 1.2 | 20 |
| 1.0G1 | 0.4 | 0.5 | 5 |
| 0.0G0 | 1.3 | 8.0 | 15 |
| 0.1G0 | 0.6 | 1.1 | 4 |
| 0.5G0 | 0.5 | 0.8 | 3 |
| 1.0G0 | 0.4 | 0.5 | 2 |

The flexural strength results were similar to the compressive strength and it strongly depends on WG content and ASRW ratio in the mixture composition. As it is shown in Table 4, the flexural strength of samples with WG additive was from 0.4 to 2.1 MPa but without WG additive – 0.3 to 1.5 MPa. Porous structure obviously affects flexural strength and the results of flexural strength test show that samples without ASRW provide 3 times higher flexural strength.

The mechanical properties of AAB are strongly affected by physical properties of AAB. The mechanical properties of samples were defined with the amount of ASRW used in composition but influence of glass additive is essential in cases, when ASRW is not used or the amount of ASRW is low. The difference between series of samples with ASRW mass ratio to WMK from 0.5 to 1.0 was less significant and more comparable.

### *Sulphate test*

Resistance to sulphate attack was tested for 28 days old samples (6 samples from each composition). Change of compressive strength after sulphate test is given in Table 4. The sulphate attack deteriorates the structure of AAB and the decrease of compressive strength was detected. Reduction of compressive strength was significant for AAB samples with WG in the mixture composition – compressive strength reduced even up to 72% (0.0G1) and the structure integrity of AAM was damaged. The strength loss of AAB made without WG and ASRW (0.0G0) was 15%.

Although ASRW provides porous structure and decreases compressive strength of AAB, the ASRW has significant effect on AAB resistance to sulphate attack. For sample series with WG in mixture composition the increase of ASRW reduced the compressive strength loss down to5 % (1.0G1) while for samples with 0.1 and 0.5 mass ratio of ASRW to WMK was 25 and 20% respectively. Samples without WG in mixture composition provided low strength loss after sulphate test even with low ASRW content in mixture composition (4% for 0.1G0); therefore ASRW not only increases porosity and reduces initial compressive strength but also increases the AAB resistance to sulphate attack.

## IV CONCLUSIONS

Alkali activated binders (AAB) were obtained by using industrial by-products such as aluminium scrap recycling waste (ASRW), lead-silicate glass waste (WG) from recycling of florescent lamps and waste metakaolin (WMK) after using as a substance for anti-agglutination in the final stage of expanded glass granule production as a secondary raw material.

The obtained material was characterized by density from 380 to 1720 kg/m$^3$. The density can be controlled by ASRW mass ratio and WG additive. Because of wide range of density, all physical and mechanical properties were varied depending on the mixture composition. Compressive strength up to 30.1 MPa and flexural strength up to 2.1 MPa can be achieved by selecting appropriate mixture composition.

Results of sulphate test evidently shows the effect ASRW and WG have on resistance to sulphate attack. Samples with higher proportion of ASRW have lower compressive strength changes. Samples with proportion of ASRW from 0.1 to 1.0 show 2-4% reduction of compressive strength after sulphate attack, while samples with the same proportion of ASRW and WG additives have 5-25% reduction.

In further research it would be essential to improve mixture composition for samples with high $SiO_2$ and low ASRW content to ensure high mechanical properties of AAB (compressive strength 30 MPa) after sulphate attack. It would also be necessary to test such durability properties as freeze-thaw resistance.

## V ACKNOWLEDGEMENT

The research work was carried out in the frame of the Latvian Council of Science Project: "Development of sustainable effective lightweight construction materials based on industrial waste and local resources" (No. Z12.0412).

## VI REFERENCES

[1] G. Habert, J. B. D'Espinose De Lacaillerie and N. Roussel, "An environmental evaluation of geopolymer based concrete production: Reviewing current research trends," J. Clean. Prod., vol. 19, no. 11, pp. 1229–1238, 2011.

[2] B. C. McLellan, R. P. Williams, J. Lay, A. Van Riessen and G. D. Corder, "Costs and carbon emissions for geopolymer pastes in comparison to ordinary portland cement," J. Clean. Prod., vol. 19, no. 9–10, pp. 1080–1090, 2011.

[3] W. K. W. Lee and J. S. J. van Deventer, "The effect of ionic contaminants on the early-age properties of alkali-activated fly ash-based cements," Cem. Concr. Res., vol. 32, no. 4, pp. 577–584, Apr. 2002.

[4] F. Pacheco-Torgal, Z. Abdollahnejad, a. F. Camões, M. Jamshidi and Y. Ding, "Durability of alkali-activated binders: A clear advantage over Portland cement or an unproven issue?," Constr. Build. Mater., vol. 30, pp. 400–405, May 2012.

[5] A. Elimbi, H. K. Tchakoute and D. Njopwouo, "Effects of calcination temperature of kaolinite clays on the properties of geopolymer cements," Constr. Build. Mater., vol. 25, no. 6, pp. 2805–2812, Jun. 2011.

[6] L. Zheng, C. Wang, W. Wang, Y. Shi and X. Gao, "Immobilization of MSWI fly ash through geopolymerization: effects of water-wash.," Waste Manag., vol. 31, no. 2, pp. 311–7, Feb. 2011.

[7] M. C. G. Juenger, F. Winnefeld, J. L. Provis and J. H. Ideker, "Advances in alternative cementitious binders," Cem. Concr. Res., vol. 41, no. 12, pp. 1232–1243, Dec. 2011.

[8] D. Bajare, G. Bumanis and A. Korjakins, "New Porous Material Made from Industrial and Municipal Waste for Building Application," Mater. Sci., vol. 20, no. 3, pp. 3–8, 2014.

[9] P. Duxson, J. L. Provis, G. C. Lukey and J. S. J. van Deventer, "The role of inorganic polymer technology in the development of 'green concrete,'" Cem. Concr. Res., vol. 37, no. 12, pp. 1590–1597, Dec. 2007.

[10] R. R. Lloyd, J. L. Provis and J. S. J. van Deventer, "Pore solution composition and alkali diffusion in inorganic polymer cement," Cem. Concr. Res., vol. 40, no. 9, pp. 1386–1392, Sep. 2010.

[11] H. F. W. Taylor and R. S. Gollop, Some chemical and microstructural aspects of concrete durability. London: E & FN Spon, pp. 177–184,1997.

[12] S. E. Wallah and B. V. Rangan, "Research Report GC2," Australia, 2006.

[13] T. Bakharev, J. G. Sanjayan and Y.-B. Cheng, "Sulfate attack on alkali-activated slag concrete," Cem. Concr. Res., vol. 32, no. 2, pp. 211–216, Feb. 2002.

[14] H. El-Sayed and E. Abo, "Resistance of Alkali Activated Water-Cooled Slag Geopolymer to Sulphate Attack," Ceram., pp. 153–160, 2011.

[15] T. Bakharev, "Durability of geopolymer materials in sodium and magnesium sulfate solutions," Cem. Concr. Res., vol. 35, no. 6, pp. 1233–1246, Jun. 2005.

[16] O. S. B. Al-Amoudi, S. N. Abduljauwad and M. Maslehuddin, "Magnesium-Sodium Sulfate Attack in Plain and Blended Cements," J. Mater. Civ. Eng., vol. 6, no. 2, pp. 201–222, May 1994.

[17] P. Chindaprasirt, P. Kanchanda, A. Sathonsaowaphak and H. T. Cao, "Sulfate resistance of blended cements containing fly ash and rice husk ash," Constr. Build. Mater., vol. 21, pp. 1356–1361, 2007.

[18] S. E. Wallah, D. Hardjito, D. M. J. Sumajouw and B. V. Rangan, "Sulfate and acid resistance of fly ash-based geopolymer concrete," in Proceedings Australian structural engineering conference, 2005.

[19] V. Sata, A. Sathonsaowaphak and P. Chindaprasirt, "Resistance of lignite bottom ash geopolymer mortar to sulfate and sulfuric acid attack," Cem. Concr. Compos., vol. 34, no. 5, pp. 700–708, May 2012.

[20] D. L. Y. Kong and J. G. Sanjayan, "Damage behavior of geopolymer composites exposed to elevated temperatures," Cem. Concr. Compos., vol. 30, no. 10, pp. 986–991, Nov. 2008.

[21] G. Bumanis, D. Bajare and J. Locs, "The Effect of Activator on the Properties of Low-Calcium Alkali-Activated Mortars," Key Eng. Mater., vol. 604, pp. 169–172, Mar. 2014.

[22] G. Bumanis, D. Bajare and A. Korjakins, "Influence of the carbonate-free clay calcination temperature and curing conditions on the properties of alkali-activated mortar," The International Scientific Conference „Innovative Materials, Structures and Technologies". pp. 24–28, 2014.

[23] D. Bajare, A. Korjakins, J. Kazjonovs and I. Rozenstrauha, "Pore structure of lightweight clay aggregate incorporate with non-metallic products coming from aluminium scrap recycling industry," J. Eur. Ceram. Soc., vol. 32, no. 1, pp. 141–148, Jan. 2012.