LIMESTONE – AN INERT MODEL SYSTEM OF CEMENT?
KAĻĶAKMENS – SAISTVIELU INERTO SISTĒMU MODELIS?

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Abstract. *The adsorption of small organic anions like those of benzoate, tartrate, citrate and glutamate on Portland composite cements CEM II and CEM III can be influenced by the present limestone (industrial* $CaCO_3$*). Therefore, the replacement of ordinary Portland cement CEM I is not a trivial matter, although using these materials reduces the cement production and hence the* CO_2 *emission providing the solution of an up-to-date environmental problem. A systematic study is shown here by zeta potential determination on the* $CaCO_3$ *suspension containing the organic anions. The effect of increasing pH was further considered and correlated to the adsorption on* $CaCO_3$ *surface. The study gives an insight on the compatibility between cement and organic additives in presence of limestone that has very similar surface properties to cement.*

Keywords: *adsorption, carboxylic acids, zeta potential.*

Introduction

The arising request for modern building materials that show better workability and durability can only be fulfilled by the application of different construction-chemical admixtures. Although some very good recipes have been developed e.g. for dry mix mortars, problems of compatibility between cement and organic admixtures have arisen. Substitution of CEM I by CEM II and CEM III cements, which clearly possess different chemical-mineralogical compositions, results in changes in the reaction behavior. A common admixture in that field resembles limestone (industrial $CaCO_3$). Its interaction with organic matter was ignored and its inertness was taken for granted. Therefore, a systematic study seemed necessary. For this purpose, the interaction of some organic molecules with different functionalities on a model system like $CaCO_3$ was studied. The results should give some fundamental understanding in how far the cement industry can reduce the production of cement clinker by replacing it with limestone as admixture and consequently the CO_2-emission will be reduced, which is of high environmental interest.

In aqueous suspension, calcitic limestone develops a positive zeta potential. Its surface properties are very similar to the properties of cement hydrate phases such as ettringite or calcium aluminium monosulfate. Numerous works have been published on adsorption of small organic anions such as salicylate and succinic, phthalic and maleic acid on $CaCO_3$ [1, 2,]. Surface complexation occurs between the carboxylate groups of these molecules and hydrated calcium atoms located on the $CaCO_3$ surface which is exposed to the liquid phase [3]. Structural parameters influencing the interaction of numerous low molecular weight organic acids with goethite surface has been studied extensively by surface complexation modeling [4].By comparing the adsorption behavior of phthalate, salicylate and p-hydroxybenzoic acid on an α- Fe_2O_3 surface, Gu *et al.* [5] have found that a second –COOH group in ortho position of a molecule greatly increases the adsorbed amount in comparison to the same compound with an –OH or –COOH group in *para* position. Similarly, Das *et al.* [6] have shown that on α-alumina, phthalate adsorbs higher than benzoate because of the two adjacent –COOH groups in phthalate. For small organic anions on a given positive surfaces, the adsorbed amount and ratio between adsorbed and dissolved anion (adsorption equilibrium) generally depends on the functionality of the adsorbate molecule. Benzoate, tartrate and citrate were used because of their carboxylate functionality and their widespread use to retard cement hydration in concrete and dry-mix mortars containing limestone powder. Glutamate was studied because of its additional N-functionality which might lead to a different adsorption behavior. For this purpose, adsorption isotherms, as well as zeta potentials of $CaCO_3$ suspensions containing these anions were determined at pH = 9 (native pH of the $CaCO_3$ slurry) and pH = 12.5, respectively.

Materials and methods

The experiments were performed with aqueous suspensions of $CaCO_3$ (SCHAEFER Precal 18, Schaefer Kalk GmbH & Co KG, Diez, Germany). Its medium particle size D_{50} was 12.58 µm and the specific surface area was 0.283 m^2 /g (BET method) and 0.345 m^2/g (BLAINE method), respectively. The density was found to be 0.2688 g /m^3. Sodium benzoate, di-sodium tartrate dihydrate, tri-sodium citrate dihydrate and sodium L-glutamate monohydrate (all from Merck) were used without further purification.

Adsorption measurements on $CaCO_3$ were carried out at 20°C by determining the unadsorbed organic carbon content in the centrifugate via High TOC II analyser (Elementar). 0.1 - 5% bwo$CaCO_3$ of the organic salts were added to the aqueous $CaCO_3$ suspension (water/$CaCO_3$ ratio = 0.413) and mixed thoroughly with the help of a test tube shaker (VWR International) for 1 min. The suspension was then centrifuged for 20 min at 8500 rpm. Adsorption measurements performed over 4 h confirmed that the state of equilibrium was fully attained after 2 min.

Zeta potential of aqueous $CaCO_3$ suspensions containing different concentrations of the anions were measured at different pH using Model DT-1200 Electro-acoustic Spectrometer (Dispersion Technology, Inc.). The following mixing procedure was used to prepare the $CaCO_3$ suspensions: 400 g of $CaCO_3$ were added to 165.2 g water within 1 min. This slurry was let sit for one more minute. Afterwards, the mixture was vigorously stirred for 2 min in a casserole with a spoon. Filtration gave the mother liquor for the measurement of the ionic background of the $CaCO_3$ suspension that was subtracted from the zeta potential values of the $CaCO_3$ slurries containing the organic anions.

Results and Discussion

Adsorption

The adsorbed amounts of benzoate, tartrate, citrate and glutamate on $CaCO_3$ surface determined at dosages of 0.1- 5.0 % bwo$CaCO_3$ and at pH = 9 are shown in **Figure 1**. As can be seen, the adsorbed molar amount of all organic anions increases with dosage. Benzoate shows the highest adsorbed molar amount and citrate the lowest. Because citrate possesses three carboxylic groups, it achieves compensation of the surface charge at lower dosages than anions with only two or one carboxylic function. No saturation points of adsorption were obtained at the dosages tested here. Zeta potential measurements described later showed that saturation points were achieved at dosages between 10-20 mMol anion/ m^2 $CaCO_3$ surface. The adsorbed molar amounts of tartrate and glutamate are nearly the same.

For Ca-citrate, the ratio between adsorbed and the total amount added has been reported to range from 19-52%, depending on dosage [7]. This is in good accord with our findings for Trisodium citrate showing that about 20% of citrate is adsorbed. Adsorption of disodium tartrate onto $CaCO_3$ was found to correspond to a Type II isotherm [8]. In the vast majority of cases, physical adsorption gives rise to a Type II isotherm. In this case, only the forces between the adsorbent and the adsorbate molecules (vertical interactions) are considered, whereas the forces between neighboring adsorbate molecules on the surface (horizontal interactions) are neglected. Considering the nature of such intermolecular forces, adsorbate-adsorbate interactions must be taken into account when a layer is approaching the saturation point of adsorbed anion and the distance of adsorbed molecules becomes small in relation to their size [8].

Effect of pH on adsorption behavior

To investigate the effect of pH on the adsorbed amount of anion, the pH of the $CaCO_3$ suspension was adjusted to 12.5 with NaOH. The dosage of the anions added varied from 0.1 to 5% bwo$CaCO_3$. The results are displayed in **Figure 1**. Surprisingly, adsorption of the organic anions depends very little on the pH. An increase in pH to 12.5 causes only a slight increase in the amount of adsorbed benzoate, tartrate, citrate and glutamate, due to further deprotonation of the hydroxyl groups. Interestingly, no saturation point for adsorbed amount is observed even at concentrations as high as 5 % bwo$CaCO_3$.

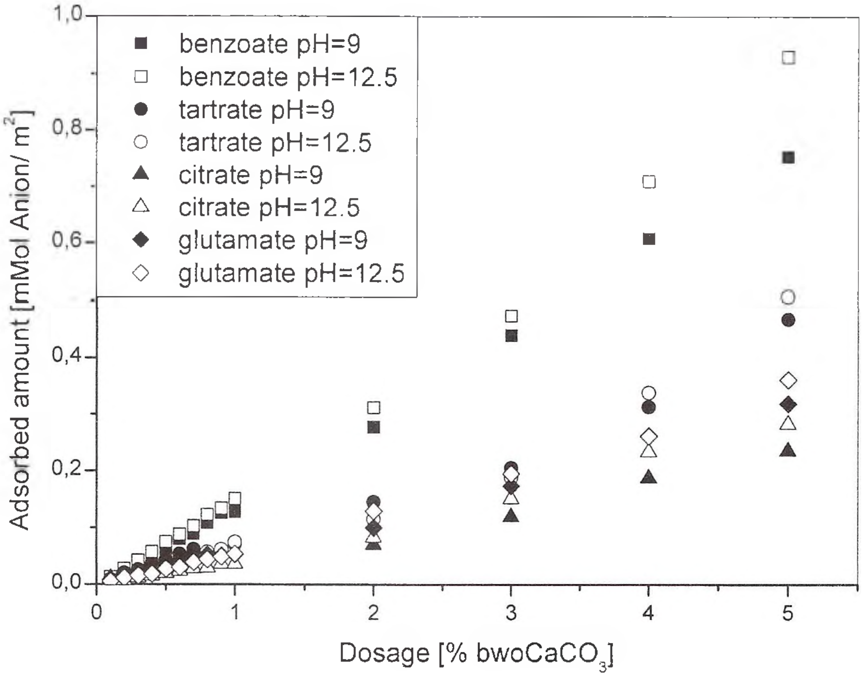

Fig. 1. **Comparison of dosage dependent adsorbed molar amounts of benzoate, tartrate, citrate and glutamate on $CaCO_3$ surface at pH = 9 and 12.5, respectively**

Zeta potential measurements

Zeta potential measurements were performed to determine the surface charge of the calcium carbonate particles in presence of varying dosages of the anions. Generally, charge, spatial arrangement and conformation play an important role in the adsorption behavior of the anions. Solvent, temperature and ionic strength can influence adsorbent structure and properties. This is reflected by the zeta potential of the particle. Calcium carbonate particles suspended in water containing an organic salt form a STERN layer of adsorbed ions while hydrated ions remain in solution. Further organic molecules may be adsorbed on the STERN layer. In consequence, a diffuse electric double layer (EDL) surrounds the particle. The concentration of ions oppositely charged to the STERN layer decreases exponentially with increasing distance from the $CaCO_3$ particle. In the vast majority of previous zeta potential measurements, highly diluted suspensions with water/$CaCO_3$ =1 to 1000 were used. In many practical applications such as dry-mix mortars, however, highly concentrated $CaCO_3$ suspensions with water/$CaCO_3$ <1 are commonly used. Therefore, a $CaCO_3$ suspension with water/$CaCO_3$ = 0.413 was studied by using the electroacoustic method which allows to obtain results that correspond to practical conditions in building materials.

First, the zeta potential of the $CaCO_3$ suspension was measured at pH = 9 to pH = 12.5 by adding dilute sodium hydroxide solution. As seen in **Figure 2**, the zeta-potential at pH = 9 is +40 mV. The surface potential decreases to negative values as the pH of the suspension increases. This effect is caused by the adsorption of hydroxide ions on the initially positive surface. At pH = 12.5, the surface charge of $CaCO_3$ is -15 mV.

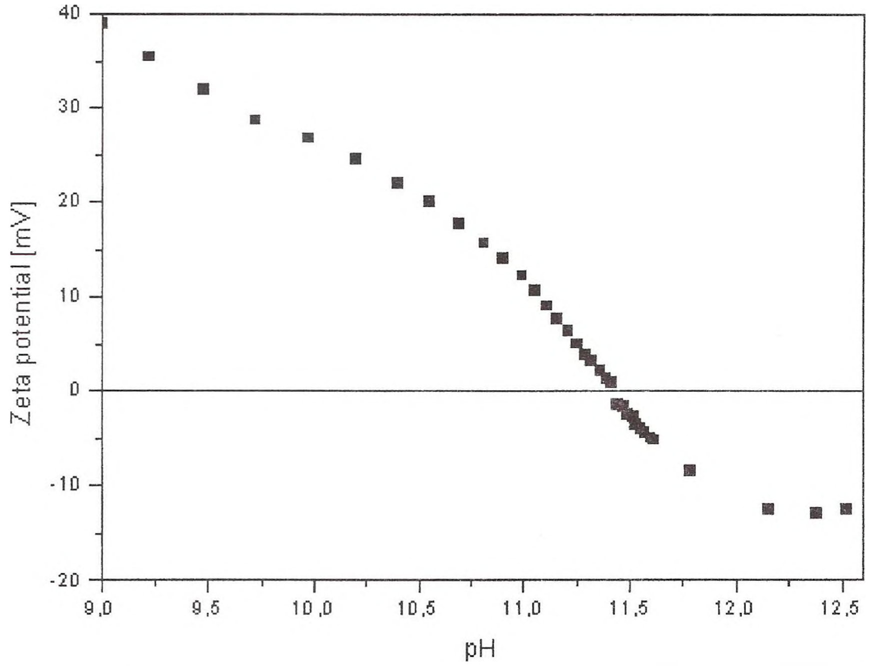

Fig. 2. **Zeta potential of the $CaCO_3$ suspension at pH = 9 to 12.5**

Secondly, the $CaCO_3$ suspension with pH = 9 was treated with 0.1 - 5% bwo$CaCO_3$ of benzoate, tartrate, citrate and glutamate. Untreated $CaCO_3$ shows a zeta potential of +40 mV. Addition of increasing amounts of organic anions results in a decrease of the zeta potential as shown in **Figure 3**.

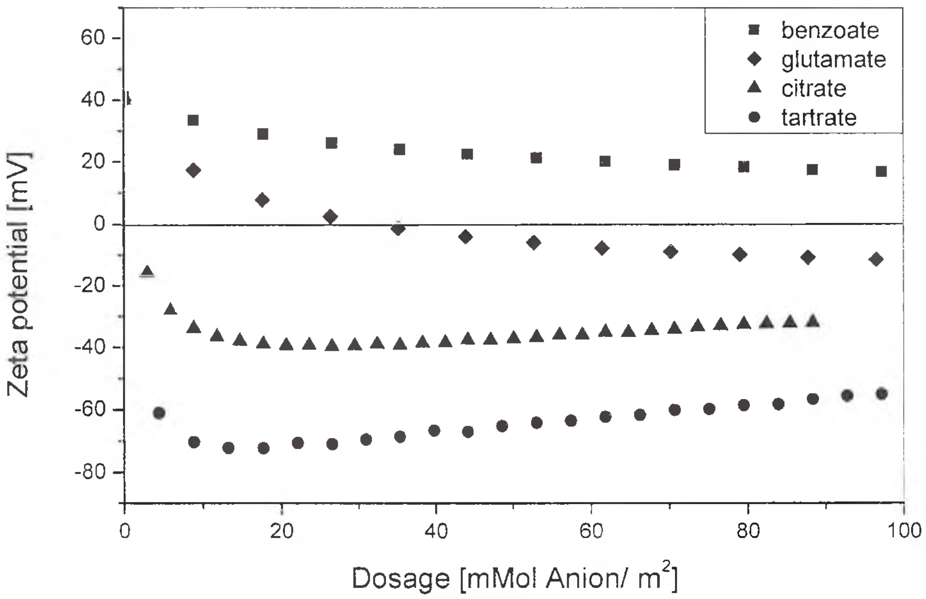

Fig. 3. **Zeta potential of aqueous $CaCO_3$ suspensions at pH = 9, treated with 0-100 mMol anion/ m^2 of benzoate, tartrate, citrate and glutamate**

The decrease is most strong for tartrate and less strong for citrate and glutamate. Benzoate shows the least change in zeta potential with dosage. For example, addition of 20 mMol/m^2 of benzoate decreases the zeta potential only to approximate +20 mV whereas the same amount of tartrate produces a zeta potential of about –70 mV.

At pH = 12.5 (**Figure 4**), the zeta potential of the initial $CaCO_3$ suspension without further additives is -15 mV. In the case of benzoate, the zeta potential value decreases towards the isoelectric point with increasing dosage of the anion. Glutamate shows almost no effect of dosage on the zeta potential whereas citrate as well as tartrate initially causes a sharp decline to highly negative zeta potential values. This effect can be explained by desorption of initially adsorbed hydroxyl anions from the $CaCO_3$ surface. Both citrate and tartrate can load more negative charge per unit area onto the $CaCO_3$ surface than OH^- anions. At higher concentrations, the zeta potentials of citrate and tartrate treated $CaCO_3$ suspensions become slightly less negative.

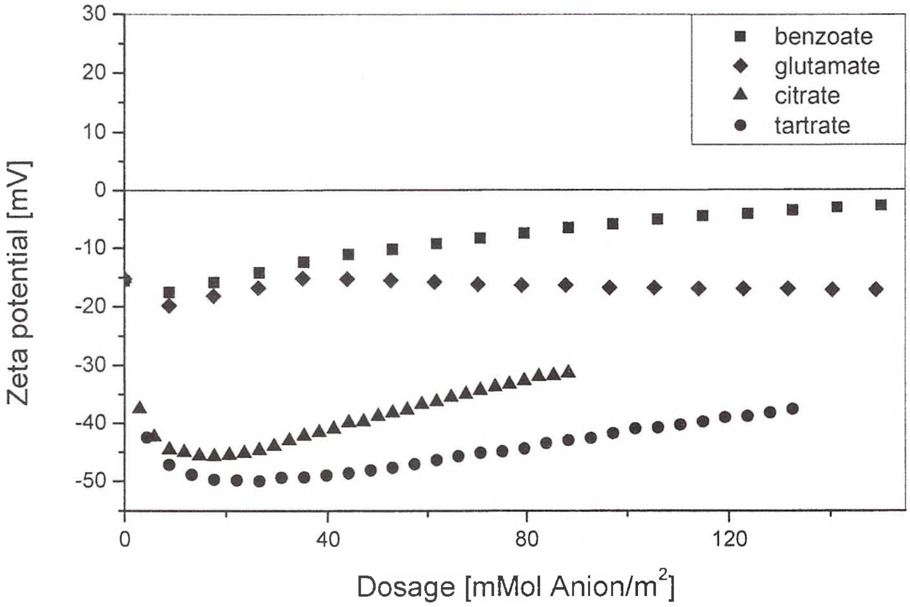

Fig. 4. **Zeta potential of aqueous $CaCO_3$ suspensions, treated with 0-140 mMol/m^2 of benzoate, tartrate, citrate and glutamate at pH = 12.5**

Conclusion

The adsorption behavior of salts of carboxylic acids is greatly influenced by the number of carboxylate functions in the molecule. High numbers of carboxylate groups require a less molar amount of the organic anion to achieve charge compensation on the $CaCO_3$ surface. This is also shown in zeta potential measurements. The pH has practically a very slight effect on the adsorption behavior of the anions studied here because their deprotonated salts were used. With respect to construction applications, the results confirm that limestone powder which is now being used as a supplemental constituent in Portland composite cements (e.g. CEM II / A-LL) has the potential to adsorb significant quantities of anionic admixtures such as polycarboxylate superplasticizer or sodium gluconate retarder.

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