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# Competitive adsorption between superplasticizer and retarder molecules on mineral binder surface

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## Abstract

In a self-levelling mortar based on the ternary binder system ordinary Portland cement (OPC), calcium aluminate cement (CAC) and anhydrite, a polycarboxylate-based superplasticizer (PC) showed no plasticizing effect in combination with citrate retarder while good flowability was observed with tartrate. The mechanism behind the incompatibility between PC and citrate was investigated by means of adsorption and zeta potential measurements. Also, anionic charge densities of the admixtures were compared. Adsorption measurements revealed that, in presence of citrate, PC adsorption drops dramatically to less than 10% of dosage added, implying a complete loss of fluidity in the paste. In presence of tartrate, however, PC adsorption remains high enough to still provide good flowability. In contrast, adsorption of casein biopolymer is not much affected by addition and type of retarder. Thus it provides high fluidity with both retarders. Comparison of specific anionic charge density of $Ca^{2+}$ retarder complexes and PC reveals a direct correlation between their adsorption behaviour and anionic charge density. Admixtures with higher anionic charge density show higher affinity to the binder surface and thus adsorb preferredly. When several admixtures are present, molecules with lower anionic charge density will adsorb only if, after adsorption of the admixture with higher anionic charge, a cationic surface charge and enough adsorption area still exists. The incompatibility problem between PC and citrate in the self-levelling mortar formulation was solved by increasing the anionic charge density of the PC molecule. Similar to casein, adsorption of this modified PC is not much influenced by retarder molecules.

*Keywords:* Admixture; Superplasticizer; Mortar; Retardation; Adsorption

## 1. Introduction

The use of several admixtures in a building material formulation can cause undesired interactions. In the worst cases, a complete loss of performance is observed [1]. From jobsites, many examples for incompatibilities have been reported [2]. For most of them, the reason remains unknown. One well studied example is the effect of sulphate ions on the adsorption of certain polycarboxylates (PC) [3]. According to this study, higher charged inorganic anions such as sulphate, but also carbonate or phosphate, can hinder the adsorption of a polycarboxylate with low anionic charge density in the main chain. The result is a strong reduction of the achievable flowability.

Self-levelling underlayments (SLUs) are commonly applied on floor screeds in order to level uneven, rough surfaces [4,5]. The mortar levels itself under the influence of gravity and produces a plain and smooth surface. Typically, the binder system for such mortar is OPC (e.g. CEM I 42.5 R). If fast setting and high early strength development are required, a rapid hardening mortar containing OPC, CAC and anhydrite is used [6]. The complete formulation of such a dry mortar is shown in Table 1. Rapid set and hardening of this ternary binder is caused by massive ettringite formation. The mixing water is bound chemically in the ettringite crystals, resulting in much faster drying. Ettringite also provides excellent shrinkage compensation.

In cementitious SLUs, incompatibility between polycarboxylate-based superplasticizers and trisodium citrate retarder is a well known phenomena. Measurement of mortar spread over time according to DIN EN 12706 revealed that a typical PC functions

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Table 1
Complete formulation of a rapid set self-levelling mortar

| Component | Function | wt.% |
|---|---|---|
| Ordinary Portland cement (CEM I 42.5 R) | Binder | 18.5 |
| Calcium aluminate cement (approx. 40% $Al_2O_3$) | Binder | 11.5 |
| $CaSO_4$ (synthetic anhydrite) | Binder | 6.5 |
| Quartz sand (0.1 to 0.315 mm) | Aggregate | 41 |
| $CaCO_3$ filler (10 to 20 μm) | Filler | 19.4 |
| Casein or polycarboxylate ether | Superplasticizer | 0.4 |
| Vinylacetate–ethylene copolymer | Redispersible powder | 2 |
| KNa $C_4H_4O_6{\cdot}4H_2O$ or $Na_3C_6H_5O_7{\cdot}2H_2O$ | Hydration retarder | 0.4 |
| $Li_2CO_3$ (particle size <40 μm) | Accelerator | 0.1 |
| Cellulose ether | Water retention agent | 0.05 |
| Polyglycol | Defoamer | 0.15 |
| Water (for 100 wt.% dry mortar) | | 20 |

only in combination with tartrate (Fig. 1). This behaviour is typical for commercially available PCs. When citrate is present, this PC does not achieve flowability. In comparison, casein performs well with both citrate and tartrate retarder.

The aim of this study was to investigate the mechanisms behind the incompatibility between the PC and citrate, and to find ways for preventing such undesired interactions in admixture formulations.

## 2. SLU formulation

### 2.1. Materials and methods

In this study, the use of a complete SLU mortar formulation would have impeded most analytical results. For example, adsorption measurement of PC via the TOC method is impossible in the presence of several other organic admixtures. Because of this, a simplified, more basic system containing only the admixtures under study (superplasticizer and retarder) and without sand and mineral filler as shown in Table 2 was chosen for all further investigations. At a water/binder ratio of 0.5, it produced a flowability of 15 cm on the Hägermann table [7].

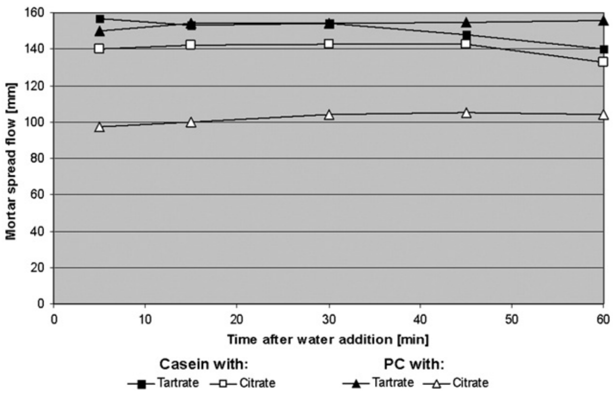

Fig. 1. Flowability versus time for self-levelling mortar containing different combinations of superplasticizers and retarders (dosage of all admixtures: 0.4% by weight of binder).

Table 2
Basic SLU formulation used in the study

| Component | Function | wt.% |
|---|---|---|
| Ordinary Portland cement (CEM I 42.5 R) | Binder | 48.1 |
| Calcium aluminate cement (approx. 40% $Al_2O_3$) | Binder | 32.1 |
| $CaSO_4$ (synthetic anhydrite) | Binder | 18.7 |
| Casein or polycarboxylate ether | Superplasticizer | 0.4 |
| $KNaC_4H_4O_6{\cdot}4H_2O$ bzw. $Na_3C_6H_5O_7{\cdot}2H_2O$ | Hydratation retarder | 0.4 |
| $Li_2CO_3$ (particle size <40 μm) | CAC accelerator | 0.27 |
| water (for 100 wt.% dry mortar) | | 50 |

### 2.2. Superplasticizers and retarders

Two polycarboxylates and the biopolymer casein were used as superplasticizers. The chemical structure of the polycarboxylates is shown in Fig. 2. The first polycarboxylate (PC 1) possesses a molecular mass ($M_w$) of 73,000 Da and a polydispersity index of 2.1 (GPC analysis). Furthermore, a similarly structured, modified polycarboxylate (PC 2) having a higher amount of acrylic acid in the backbone was used. As a reference, commercial casein obtained by acid precipitation from bovine milk was used. Casein is a heterogeneous, partly glycosilated phosphoprotein consisting of a mixture of approx. 49% $\alpha_{S1}$-casein, 37% β- and 14% κ-casein [8,9]. In aqueous solution, casein forms micelles with average diameters between 90 and 140 nm. This micelle consists of sub micelles with average diameters of 20 nm. Each sub-micelle contains 20–25 casein molecules [10]. The intermicellar space between the sub micelles is filled with calcium phosphate clusters of the formula $Ca_9(PO_4)_6$. The surface of the casein micelle has a layer enriched with κ-casein whereas the core of the micelle predominantly consists of α- and β-caseins. Several models of the casein micelle exist. A schematic representation of the most widely accepted model from WALSTRA is shown in Fig. 3 [11]. At high alkaline pH in cement pore solution, casein micelles disintegrate into sub micelles and the casein proteins [12]. Furthermore, depolymerisation of the proteins and even decomposition of the amino acid building blocks may occur, leading to the release of ammonia [13].

Very recently, preparative separation of casein into its α-, β- and κ-protein fractions revealed that pure α-casein provides the main dispersing-effect whereas β- and κ-caseins are little effective [14].

Commercial sodium/potassium (2R,3R)-tartrate (seignette salt, made from naturally occurring L-tartaric acid, Merck) and trisodium citrate dihydrate (Sigma-Aldrich) were used to retard binder hydration and to allow sufficient workability time. Their chemical structures are shown in Fig. 4. Generally, the effect of retarders is based on the formation of very stable calcium complexes and their adsorption on binder and hydrate surfaces. In some cases, the calcium retarder complexes can also precipitate on the surface because of low solubility [15].

### 2.3. Preparation of SLU paste

In order to produce filtrate for the adsorption tests, 222 g of dry SLU formulation as shown in Table 2 was poured into 111 g deionised water within 1 min and allowed to soak for another

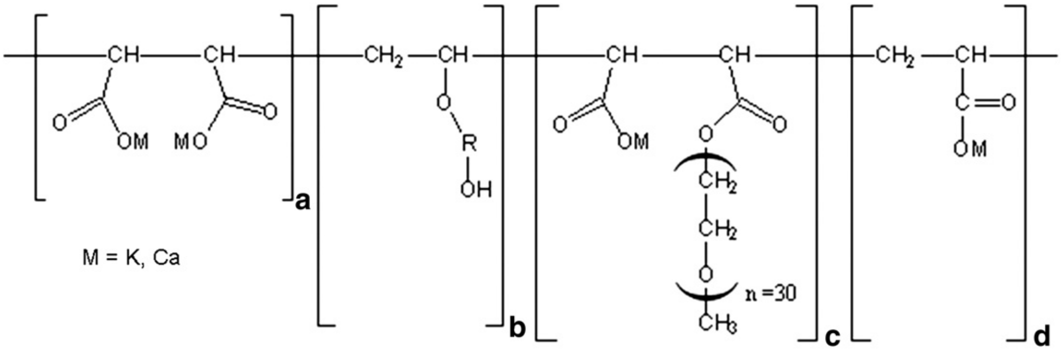

Fig. 2. Chemical composition of the polycarboxylate superplasticizer.

minute. Then the binder paste was stirred manually in a porcelain casserole for another 2 min. The binder slurry was filtered off in a chromium steel filter press as shown in Fig. 5 using glass fibre filters and a compression force of 250 kN.

For further analysis, the filtrate was treated as follows: for TOC measurement, the filtrate was diluted 1:50 with ultra pure water. For ion chromatography (IC), the filtrate was acidified with conc. HCl in case of citrate and with nitric acid in case of tartrate (dosage of acids: 20 µl/ml filtrate). The samples were diluted 1:10 (citrate), 1:50 (tartrate) and filtered with a 0.2 µm filter (Pall Life Sciences Acrodisc).

### 2.4. Quantitative analysis of citrate and tartrate

Quantitative analysis of unadsorbed citrate and tartrate occurring in the SLU paste filtrate was performed by ion chromatography (IC). A DIONEX ICS 2000 reagent free ion chromatograph with auto sampler AS 40 was used. A combination of MetPac CC-1 (for polymeric impurities) and IonPac NG1 (to remove heavy metal cations) from Dionex were used as protective pre-columns. The analytic column was AS 11 HC with 2 mm diameter (Dionex). Different KOH gradients necessary for the separation of tartrate and citrate were programmed by use of the eluent generator. Figs. 6 and 7 show example chromatograms, demonstrating the method to quantitatively determine citrate and tartrate concentrations in the SLU paste filtrates. The quantitative determination of the analyte ions was done by comparison of relative peak areas (µS·min) obtained from aqueous solutions with known concentrations of citrate and tartrate, resp., and the filtrate samples.

### 2.5. Adsorption measurement

For quantification of organic carbon in filtrate samples, a High TOC apparatus from Elementar was used. Filtrates were acidified with 0.1 n HCl to remove inorganic carbon (carbonates) from the sample. Then, sample is oxidized in a glass pipe at 1000 °C on a platin catalyst using synthetic air. The exhaust gas is dried with phosphorous pentoxide and the carbon dioxide is determined in a NDIR-Cell. The amount of organic carbon being present in the sample is calculated based on calibration standards.

### 2.6. Zeta potential

Zeta potential measurements were made with a DT 1200 electro-acoustic spectrometer from Dispersion Technology. This instrument allows to measure samples with very high volume fraction such as SLU paste without dilution [16–18].

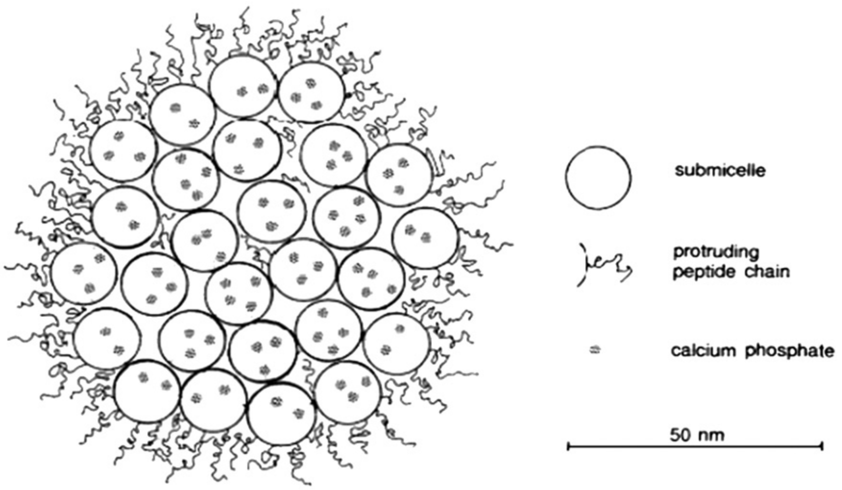

Fig. 3. Schematic representation of a casein micelle [11].

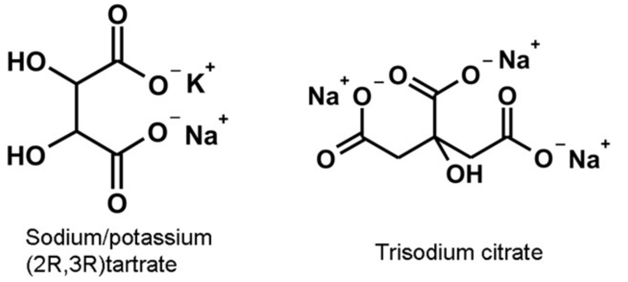

Fig. 4. Chemical structures of the α-hydroxycarboxylic acid based retarders used in this study.

### 2.7. Quantitative analysis of admixture combinations

When only SP was present, its concentration was measured by total organic carbon (TOC) method. Pastes containing only retarder in the filtrate were analysed by IC. When both admixtures, superplasticizer and retarder, were present in the filtrate, at first the retarder concentration was measured by IC and subtracted from the TOC concentration, allowing to calculate SP concentration remaining in the filtrate. The amount of admixture adsorbed on the mineral surface was assumed to be the difference between the admixture dosage added to the SLU formulation and the concentration detected in the filtrate.

### 2.8. Anionic charge density of polyelectrolytes

For determination of the anionic charge density of the polymers, a particle charge detector PCD03 PH (BTG Muetek GmbH) was used. The charge detector consists of a PTFE cylinder with an oscillating PTFE piston in the centre. The polyanionic polymer adsorbs onto the Teflon surface, while the counter ions are being separated from the polymer when the piston is moving. This creates a streaming current, measured by two Pt electrodes inside the Teflon cylinder. For the polymer titration, a cationic polyelectrolyte (0.001 N poly(dimethyl diallyl ammonium chloride)) was added dropwise to the solution until zero point of charge was reached.

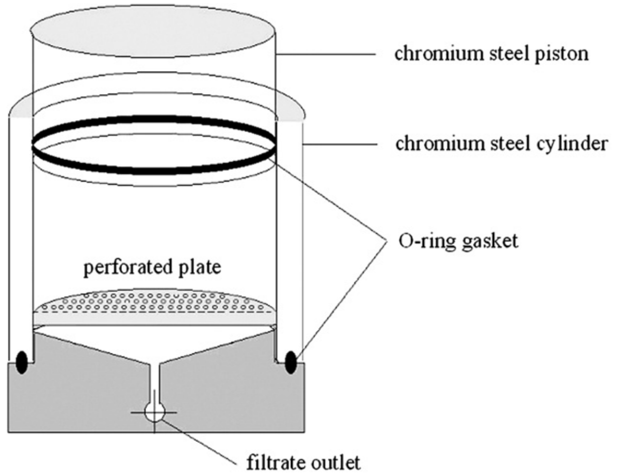

Fig. 5. Schematic drawing of the filter cell used to produce filtrate from SLU paste.

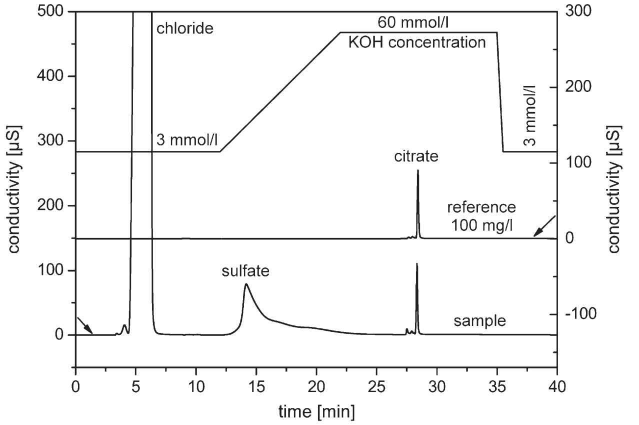

Fig. 6. Ion chromatograms of SLU paste filtrate sample containing citrate (left scale) and reference sample containing 100 mg/l citrate (right scale).

## 3. Results and discussion

### 3.1. Anionic charge density of admixtures

To explain the different behaviour of SPs in combination with retarder, the specific anionic charge densities of PC and casein were measured in the filtrate of the basic SLU formulation (Table 2). The results are shown in Table 3. Casein shows almost twofold higher anionic charge density than the PC molecule. This indicates that casein may adsorb in higher amount than PC as will be shown later. Unfortunately, the method of polyelectrolyte titration does not allow measuring the anionic charge of small molecules such as citrate or tartrate. Their charge density can be calculated, however. In aqueous solutions containing $Ca^{2+}$ ions, both citrate and tartrate form soluble calcium complexes. Their stoichiometric composition depends on the pH value and the $Ca^{2+}$ concentration. In cement pore solution, a strongly alkaline pH exists. According to literature, both retarders form highly negatively charged dimeric

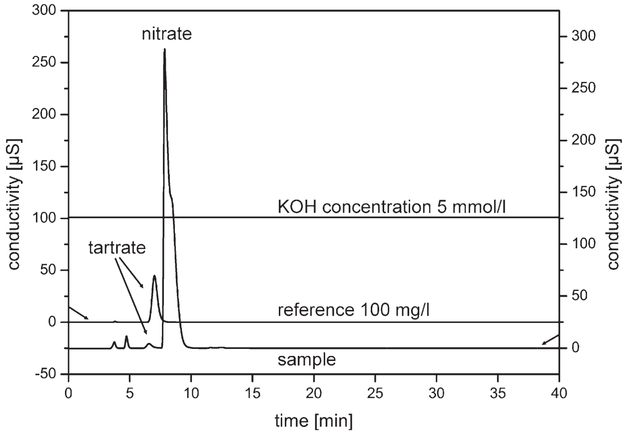

Fig. 7. Ion chromatograms of SLU paste filtrate sample containing tartrate (right scale) and reference sample containing 100 mg/l tartrate (left scale).

Table 3
Anionic charge densities of superplasticizers used in the study and $Ca^{2+}$ retarder complexes existing in the binder pore solution

| Admixture | Specific anionic charge density [C/g] |
|---|---|
| PC | 99[a] |
| Modified PC | 158[a] |
| Casein | 180[a] |
| $[Ca(Tartrate)_2]^{2-}$ | 574[b] |
| $[Ca(Citrate)_2]^{4-}$ | 923[b] |

[a] Experimentally determined in the pore solution of the basic SLU formulation.

[b] Calculated from the composition and charge of the Ca complex.

complexes under these conditions. Citrate exists as $[Ca(citrate)_2]^{4-}$ complex [19] (Fig. 8) and tartrate as $[Ca(tartrate)_2]^{2-}$ complex [20] in strong alkaline solution. From their molar masses and charge, the anionic charge density of these anions was calculated.

As can be seen from Table 3, both retarder complexes possess significantly higher anionic charge densities than the SPs. Consequently, in a situation where SP and retarder molecules are present at the same time, the retarder shows higher electrostatic attraction by the surface and will adsorb in a higher amount. SP molecules will adsorb only if their anionic charge density is more similar to the charge of the retarder complex. From Table 3 it is obvious that the anionic character of PC is not pronounced enough to compete with retarders whereas casein is more anionic. Thus, a PC molecule possessing higher anionic charge density should also adsorb in higher amount in the presence of retarder. It can be expected to provide high dispersing effect also when citrate is present.

### 3.2. Zeta potential measurements

Adsorption of PC and casein on binder surface was confirmed by zeta potential measurements using OPC-slurry (w/c = 0.5) (Fig. 9). Casein increases the negative surface charge of binder particles to more negative values when dosage is increased.

This confirms that adsorption of the biopolymer is taking place. The increase in negative surface charge with higher dosage indicates that the casein molecule possesses a significant charge density. In contrast, addition of PC results in a less negative zeta potential approaching the isoelectric point. This behaviour is due to the steric effect of adsorbed PC side chains and has been described before [21,22]. It hints that the side chain length of this PC is longer than 20 ethylene oxide units. Addition of citrate or tartrate retarder to the cement slurry also results in a more negative zeta potential. This confirms that the anionic $Ca^{2+}$ retarder complexes adsorb onto the cement surface. Apparently, the citrate complex is more negatively charged than the tartrate complex. It implies a higher negative charge on the binder particles (Fig. 10). This result is in line with the calculated anionic charges of the two complexes (Table 3).

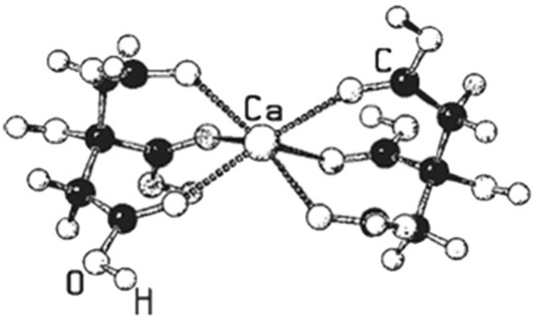

Fig. 8. Chemical structure of the $[Ca(citrate)_2]^{2+}$complex [19].

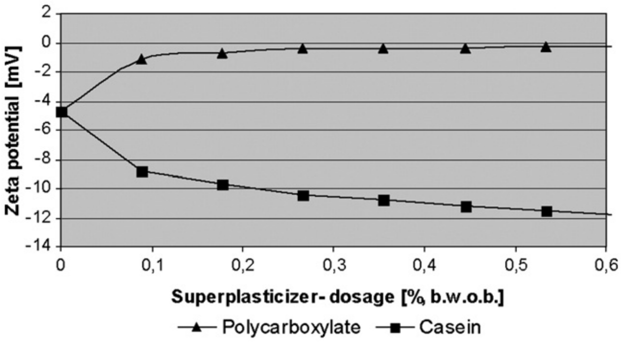

Fig. 9. Zeta potential of OPC slurry upon addition of polycarboxylate and casein.

### 3.3. Adsorption of SPs and retarders

To investigate potential interactions between the additives, adsorption of the superplasticizers and retarders present as single admixture and in combination with each other was measured using the basic SLU formulation shown in Table 2. Dosage for each admixture was 0.4% by weight of dry SLU formulation, when only one admixture was present. The adsorptions were as follows: polycarboxylate 67% of dosage added, casein 80%, tartrate 87% and citrate 55%, resp. Thus, when present only by themselves, relatively high adsorption is observed for all admixtures. When combinations of one SP and one retarder are used, however, major changes with respect to SP adsorption occur: The addition of retarder has dramatic effects on PC adsorption (Fig. 11). Tartrate reduces PC adsorption from 67% to 20% and citrate even causes adsorption to 7% only. This means that, in presence of citrate, hardly any PC is adsorbed. This explains why PC cannot produce any dispersing effect. Obviously, citrate prevents adsorption of the

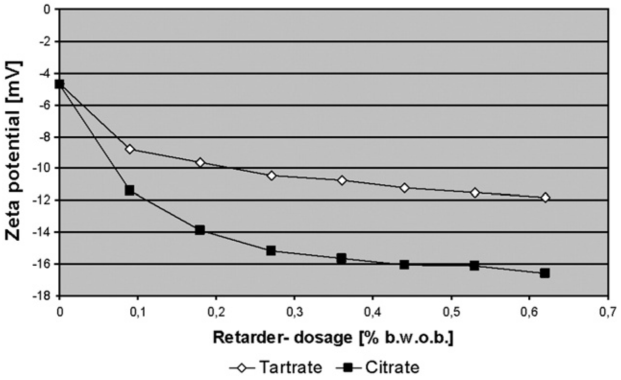

Fig. 10. Zeta potential of OPC slurry upon addition of citrate and tartrate.

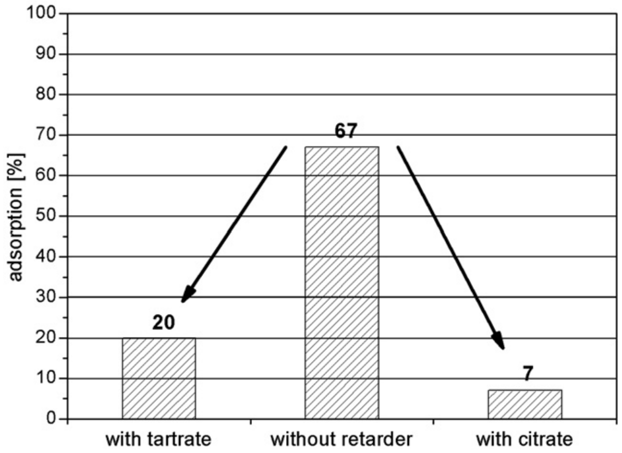

Fig. 11. Adsorption of PC in basic SLU formulation without retarder and in presence of tartrate and citrate.

PC. Tartrate has a less strong effect. It still allows enough PC to adsorb and to achieve fluidity of the SLU paste. The behaviour of casein is different in comparison to PC (Fig. 12). Addition of citrate retarder causes casein adsorption to drop only slightly from 80% to 50% of initial casein dosage. Tartrate does not even impact casein adsorption at all. Hence it is demonstrated that casein adsorption is quite stable in presence of α-hydroxy carboxylic acid-based retarders. Therefore, no decrease in fluidity of the SLU paste is observed.

The results demonstrate that the presence of retarders can greatly influence SP adsorption. Additional measurements showed that retarder adsorption is the same in absence or presence of SPs (PC or casein). Thus, SPs have no influence on retarder adsorption. This result hints that retarder molecules have a much stronger affinity towards the binder surface.

## 3.4. Optimization of PC molecule

To verify this concept, the PC 1 molecule which was tested before was modified by slightly increasing the amount of acrylic acid in the polymer composition (see Fig. 2). This simple modification produced a new PC (PC 2) with higher anionic charge density of 158 C/g (Table 3). As expected, adsorption of the modified PC is generally higher than for unmodified PC (82% vs. 67%). Most important, adsorption remains high in the presence of retarders (Fig. 13). This clearly confirms that, when several admixtures are present in the same formulation, an important contribution for allowing simultaneous adsorption and effectiveness of all admixtures is their anionic character which needs to be somewhat comparable. Unsurprisingly, flowability tests conducted with the modified PC proved that this PC works well also in presence of citrate (Fig. 14). Thus, the incompatibility problem between these two admixtures was solved.

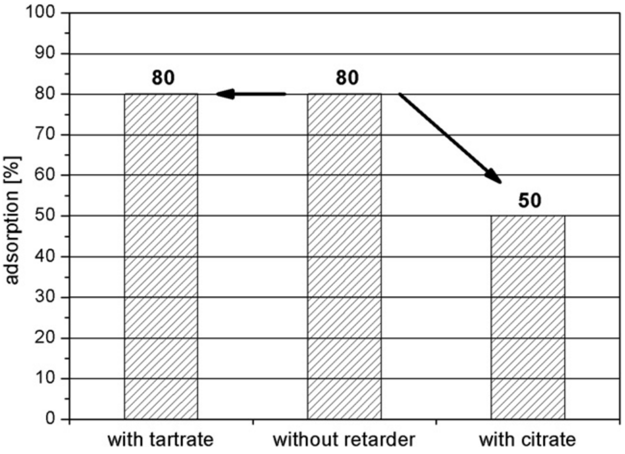

Fig. 12. Adsorption of casein in basic SLU formulation without retarder and in presence of tartrate and citrate.

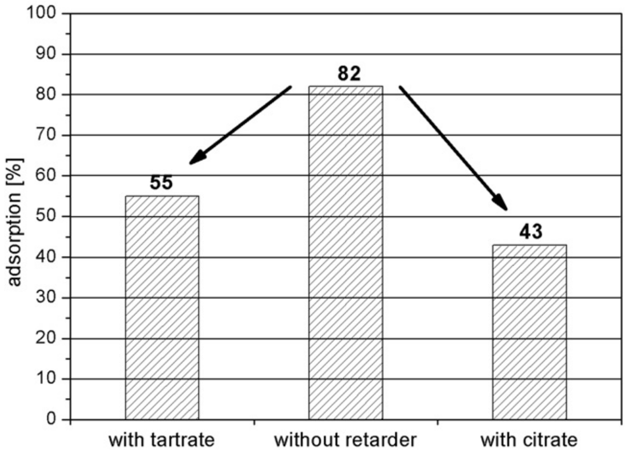

Fig. 13. Adsorption of modified PC in basic SLU formulation without retarder and in presence of tartrate and citrate.

## 3.5. Competitive adsorption

In complex admixture systems, the processes on the mineral binder surface can be explained with a competition of the anionic additives for the positively charged surface area: Adsorption of molecules with higher anionic charge density is preferred. If several additives are present, then the adsorbed amounts correspond to the order of their relative anionic charge. The anionic charge density can be measured experimentally by charge titration. It should be noted that besides charge density, also stereochemical factors, intermolecular forces and entropic effects, e.g. from adsorbed water molecules being desorbed

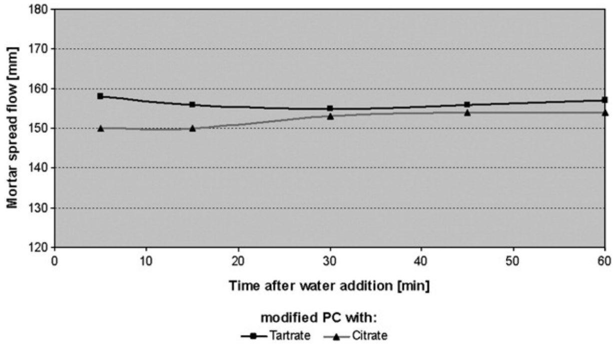

Fig. 14. Flowability versus time for self-levelling mortar containing the modified PC and retarders (dosage of all admixtures: 0.4% b.w.o.b.).

from the binder surface, may contribute to the free energy change, thus determining the adsorbed amount. For example, with respect to their order of adsorption, PC molecules can be compared only if their general composition (main monomers) is similar. Likewise, when comparing PCs with different side chain lengths, the charge per mole of polymer should be comparable.

On general terms, adsorption means desorption (replacement) of water molecules or anions attached to the binder surface by anionic admixture molecules. The free energy change (ΔG) for this process is described by Eq. (1).

$$\Delta G = \Delta H - T \cdot \Delta S. \quad (1)$$

While the electrostatic interaction between the admixture and the binder surface is expressed by the adsorption enthalpy ($\Delta H$), the desorption of water/anions and the adsorption of the admixture results in an entropy change ($\Delta S$). Thus, higher adsorption of an admixture molecule can be achieved not only by higher anionic charge, but also by less entropic loss upon its adsorption due to relatively compact or rigid molecule conformation in the water phase.

## 4. Conclusions

The order of admixture adsorption on a binder surface follows specific rules. From our study, the following conclusions can be made:

(1) Admixtures with high anionic charge density strongly adsorb onto the binder surface.
(2) When several additives are present, molecules with the higher anionic charge density adsorb in the highest amount. Additives with low anionic charge density adsorb only if the first admixture does not achieve surface charge compensation and if some surface area is still available for adsorption. However, this statement only holds completely if the additive molecules possess similar chemical structures.
(3) Additives with high anionic charge density can dramatically reduce or even completely prevent adsorption of additives with low anionic charge density.
(4) The anionic charge density of polymeric admixtures can be derived from charge titration measurement.

The rules described above allow assessment of admixture behaviour in combinations. The predictions are more accurate if the chemical structures of the admixtures are comparable.

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