Use of a Supplemental Agent to Improve Flowability of Ultra-High-Performance Concrete

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Synopsis: Ultra-high-performance concrete (UHPC) possesses a very low water-cement ratio (< 0.25). Additionally, a large amount of fines, such as silica fume, are used to achieve optimum packing density. Because of its specific surface chemistry and higher surface area, silica fume is more difficult to disperse than cement. Previously, it was found that methacrylic acid-MPEG methacrylate ester type PCEs disperse cement effectively whereas allylether-maleic anhydride-based PCEs work better with silica fume. Apparently, PCEs with different molecular architectures are required to achieve optimum coverage of the different surfaces of cement and silica fume. Thus, a blend of methacrylate- and allylether-based PCEs used at approx. 0.5% by weight of cement is more effective than when they are utilized individually.

To further enhance the performance of the formulation, sodium gluconate was introduced as a "supplemental" agent. The combination of PCE with gluconate allowed a reduction of approximately 50% in the dosage of PCE. The final blend contained 0.28% of allylether-based PCE and 0.10% of gluconate by weight of cement.

A mechanistic study established that sodium gluconate adsorbs very strong on cement and to a less extent also on silica fume, whereas the allylether PCE almost exclusively adsorbs on the silica surface. Thus, the surface of cement is covered by gluconate molecules whereas the silica surface shows concomitant adsorption of both PCE and sodium gluconate molecules. The small gluconate molecules fill the space between the huge PCE molecules on the silica fume surface.

Keywords: adsorption; dispersion; polycarboxylate; silica fume; sodium gluconate; ultra-high-performance concrete.

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INTRODUCTION AND BACKGROUND

Ultra-high performance concrete (UHPC) is designed for compressive strengths of more than 150 MPa (25,400 psi). To achieve this, a ratio of water to cementitious materials powders below 0.25 is necessary. Additionally, the packing density of the binder matrix has to be optimized.[1] Intergranular voids between the cement and aggregate particles are filled by finer particles. Silica fume possessing a particle size of about one-tenth of that of cement is commonly used as a fine material, typical additions to UHPC range between 10 and 25% by weight of cement (bwoc). In addition to the filler function, silica fume acts as a pozzolanic compound to strengthen the binder matrix. Silica reacts with Portlandite released by the cement and further C-S-H phases will grow. However, workability of such no-slump concrete mixtures is very poor. Thus, high-performance superplasticizers are needed to obtain good flowability and workability or even self-compacting properties. Concrete mixtures containing significant amount of silica fume have been reported to be difficult to disperse.[2] Recently, several rheological studies on concretes containing silica fume have been published.[3,4] These studies provide an insight into the flowability aspect of this concrete, but do not illuminate the mode of interaction between the superplasticizer and the surfaces of cement and silica fume.

Comb shaped superplasticizers based on polycarboxylate chemistry have been used successfully to disperse UHPC.[1] Their working mechanism is based on a steric effect which prevents particle agglomeration.[5-7] Polycondensate-based superplasticizers such as BNS were found to be much less effective in UHPC. Their working mechanism of electrostatic repulsion between particles is not sufficient to disperse the fines in UHPC.

In a previous investigation on the specific interactions between cement, silica fume, and PCE superplasticizers, we found that our synthesized methacrylate ester-based PCEs primarily disperse cement whereas allylether-based PCEs are highly effective dispersants for silica fume, but less for cement.[8] Thus, in a mineral system with heterogenic surface characteristics, surface-selective superplasticizers are required for optimum dispersion. To achieve maximum interaction with each surface, the specific stereochemistry of the superplasticizer needs to be tailored to this surface. The specific stereochemistry of allylether-maleic anhydride copolymers seems to favor stronger interaction with a silica fume surface than with cement hydrates. In contrast, methacrylate-type PCEs perform better with cement. A potential explanation for these differences in behavior is the difference in calcium chelating capability (calcium binding capacity) by these two polymers. Recently, it was shown that, because of their vicinal dicarboxylate groups, allylether-based PCEs possess a much higher calcium chelating capability than methacrylates.[9] Adsorption of PCE molecules on a mineral surface generally involves the coordination of calcium atoms and/or ions located on the surface. Location of these calcium atoms/ions on the surface and their coordination spheres will differ on the cement hydrates and silica fume. Therefore, it is to be expected that structurally different PCE molecules will in turn perform differently with components developing different surface chemistry.

Secondly, it was found that in the UHPC formulation used, good dispersion of silica fume instead of cement is the key to achieve a highly workable UHPC. The reason for this is the larger surface area of silica fume in comparison to that of cement. Note that in cement pore solution, silica fume possesses a positive surface charge, similar to cement hydrates.[8] Thus, silica fume competes with cement for adsorption of superplasticizers. A 3:1 blend (wt./wt.) of a methacrylate- and an allylether-based PCE was found to provide an optimized superplasticizer formulation for this paste of cement and silica fume. It is significantly more effective as compared to the usage of the individual PCEs only (Fig. 1). The PCE blend allowed a decrease in PCE addition from dosage levels of approx. 1.5% bwoc when only one PCE was used to about 0.5% bwoc. This way, a more economical formulation with improved early strength was obtained.[8]

In a separate study concerning admixture incompatibility in oil well cements, it was found that a small, short-chain dispersant (acetone-formaldehyde-sulfite polycondensate) possessing a molecular weight M_n of only 11,000 g/mol can adsorb simultaneously with a high molecular weight water retention agent (CaAMPS®-*co*-NNDMA, M_n 1.2 mio. g/mol).[10] Apparently, the small molecules of the dispersant adsorb side by side, for example, in the interstitial space between the large molecules of adsorbed CaAMPS®-*co*-NNDMA. Here, concomitant adsorption of two admixtures differing in chemical composition and steric size resulted in a highly effective admixture combination.

The aim of this study was to apply the concept of combining a small and a large molecule admixture to the problem of UHPC dispersion in order to further optimize the admixture formulation. As large molecules, a methacrylate-type and an allylether-type PCE were used. As small molecule, sodium gluconate was employed. The goal was to study the dispersing effectiveness of such a PCE/small molecule combination and to develop a mechanistic understanding for their interactions.

MATERIALS AND METHODS

Materials

Cement—A high sulfate resistant, low alkali normal portland cement CEM I 52.5 R was used. Its chemical and phase composition is presented in Tables 1 and 2, respectively. Oxide content in the cement was identified by X-ray fluorescence (Röntgenspektrometer SRS 303; Siemens, Karlsruhe/Germany). Phase composition was determined using an

XRD instrument (D8 Advance; Bruker AXS, Karlsruhe/Germany) with Bragg-Brentano geometry. The diffractometer is equipped with a scintillation detector using Cu Kα (λ = 1.5406Å) radiation with a scanning range between 5° and 80° 2θ at a scanning speed of 0.5 s/step (with 0.008°/step). Physical properties of the cement sample are given in Table 3. The specific surface area was measured by nitrogen adsorption (BET method; Porotec, Hofheim im Taunus/Germany) whereas the particle size (d_{50} values) was determined using the laser granulometer CILAS 1064 (Quantachrome, Odelzhausen, Germany).

Silica fume—Two samples of silica fumes (denoted as SF 1 and SF 2) were employed. Their physical and chemical properties are given in Table 3. SEM pictures of SF 1 and 2 are displayed in Figure 2. The silica fume particles show a spherical shape. SF 2 clearly reveals finer particles than SF 1. Particle size distribution (d_{50} values, refer to Table 3) was measured by acoustic attenuation spectroscopy in a DT-1200 acoustic and electroacoustic spectrometer from Dispersion Technology (Bedford Hills, NY/USA).

Ultra-high performance concrete mixture—Instead of a complete UHPC mixture which typically contains normal portland cement, silica fume, quartz flour, crushed basalt, superplasticizer, and water,[11] a simplified mixture containing only cement, silica fume, water and admixture was used (Table 4). This reduced formulation was chosen due to its ease of preparation. Moreover, as cement and silica fume possess much larger surface areas than any other component in UHPC, they are most critical for the study of the effectiveness and interactions of the admixtures in the UHPC blend.

Polycarboxylates—Two superplasticizers of different chemistry were used. PCE 11 is a methacrylate-type, PCE 21 is an allylether-type polycarboxylate.

- ***Preparation***—PCE 11 was synthesized by aqueous radical copolymerization from the three comonomers methacrylic acid, ω-methoxypolyethyleneglycol-methacrylate (MPEG-methacrylate, n_{EO} = 45), and methallyl sulfonic acid. The graft density of side chains along the backbone was determined by the molar feed ratio of methacrylic acid to MPEG-methacrylate to methallyl sulfonic acid which was 12:3:1. Details of its synthesis are described in Reference 12. Molecular characteristics are presented in Table 5 and the molecular structure is shown in Figure 3. PCE 11 is a low viscous, brownish liquid possessing a polymer content of 18 wt.-%.

  PCE 21 is an α-allyl-ω-methoxypolyethyleneglycol-maleic anhydride copolymer. It was synthesized via aqueous radical copolymerisation of maleic anhydride with the allylether macromonomer at a molar ratio of 1:1. Details of the synthesis process have been described in Reference 13. The characteristic properties of PCE 21 are shown in Table 5 and its molecular structure is illustrated in Figure 3. The copolymer possesses a strictly alternating monomer sequence (ABAB) as the allylether macromonomer does not homopolymerize. PCE 21 is a yellow, low viscous fluid with 38 wt.-% polymer concentration.
- ***GPC characterization***—Polymer characterization was performed by aqueous size exclusion chromatography (SEC) using a 2695 SEC separation module (Waters, Eschborn/Germany), equipped with a 2414 RI detector (Waters, Eschborn/Germany) and a Dawn EOS 3 angle light scattering detector (Wyatt Technologies, Clinton, IA/USA). Ultrahydrogel columns 500, 250, and 120 (Waters, Eschborn/

Germany) with an operating range (PEO) of M_w = 100 to 1,000,000 g/mol were used. Eluent was 0.1 mol/L $NaNO_3$ solution with pH 12 adjusted by NaOH.

- ***Anionic charge densities***—The anionic charge density of the PCEs was determined in NaOH (pH 12.8) containing 0.5 g/L Ca^{2+}. The Ca^{2+} was added in the form of $CaCl_2 \cdot 6H_2O$ to mimic the ionic content of UHPC pore solution without sulfate. PCE concentration was 0.2 g/L. Charge titration was performed on a Mütek PCD 03 pH titrator (Mütek, Herrsching/Germany) using Poly-DADMAC standard solution (0.001 mol/L) as cationic counter polymer. Details of the experimental procedure have presented in Reference 9. From the consumption of cationic polyelectrolyte required to neutralize the anionic charge of the polymer, the anionic charge density of the PCEs was calculated.

Sodium gluconate—Reagent grade sodium gluconate was applied. Its chemical structure is illustrated in Figure 3.

The anionic charge density of sodium gluconate was calculated from its molecular weight as the method of polyelectrolyte titration is not applicable to small molecules such as gluconate.

Procedures

Preparation of cement-silica fume paste—Cement and silica fume were preblended in dry form while the admixture was dissolved in the mixing water (weight proportions for components, refer to Table 4). Pastes were mixed in a commercial, blade-type high shear blender (WARING blender 7011S, Waring Laboratory, Torrington, CT/USA). This blender was chosen because its shear force best simulates the high friction forces occurring when UHPC is prepared in a high speed mixer.[14] Within 30 seconds, the dry blend was poured into the water containing the dissolved admixture while the mixer was stirring at 18,000 rpm. After this, mixing was continued for 30 seconds at 22,000 rpm. Pastes prepared by this method were used for mini-slump tests and adsorption measurements.

- ***Mini-slump test***—Dispersing effectiveness of the admixtures was tested in a mini-slump test using a VICAT cone [height 40 mm (1.57 in.), top diameter 70 mm (2.76 in.), bottom diameter 80 mm (3.15 in.)]. The paste was filled into the cone placed on a glass plate. Lifting the cone allowed the paste to spread. Dispersing effectiveness of the admixture was derived from the dosage of superplasticizer which is necessary to obtain a paste flow of 26.0 ± 0.5 cm (10.24 ± 0.02 in.).
- ***Adsorption measurements***—PCE adsorption was determined by the depletion method. The pore solution containing the non-adsorbed portion of the admixtures was obtained from the cement paste by filtration, following a procedure specified by the American Petroleum Institute.[15] After pouring the UHPC paste into the filter cell of a 500 mL HTHP filter press (high temperature – high pressure filter press, part. no. 171-00; OFI Testing Equipment, Houston, TX/USA), a differential pressure of 70 bar (1000 psi, N_2) was applied to the top of the cell. Filtration proceeded through a 3.5 $in.^2$ mesh metal sieve and filter paper placed at the bottom of the cell. The filtrate produced by the differential pressure was collected for 15 minutes. Afterwards, it was filtered through a 0.2 µm syringe filter (Pall, Newquay/UK) and diluted with deionized water. The total organic carbon (TOC)

content of the solution was determined by combustion at 890°C (1634°F) in a HIGH TOC II (Elementar, Hanau/Germany). The adsorbed amount of PCE was calculated from the difference between the TOC content of mixing water and the TOC content of filtrate.

Admixture depletion resulting from precipitation was excluded by a solubility test of the admixtures in UHPC pore solution. For this purpose, 1.3 g of dry admixture (prepared by freeze-drying from PCE solution) were dissolved in 10 mL UHPC pore solution, producing a 13 wt.-% admixture solution. This concentration corresponds to a PCE dosage of 2.8% bwoc. After one day of rest, no precipitate was observed. This observation confirms that adsorption is the sole reason for admixture depletion.

Silica fume paste—As mixing water, a synthetic pore solution made of 9.72 g $Ca(NO_3)_2 \cdot 4H_2O$ in 148.5 mL of a 0.56 wt.-% KOH (pH 12.2) was employed. This was used to mimic Ca^{2+} and K^+ contents and pH value of the UHPC pore solution. Use of this saline solution is important to obtain results on the interaction between admixtures and silica fume which represent application conditions.[8] For preparation of the silica fume paste, admixtures (PCE, gluconate) were dissolved in the mixing water. In tests with PCE and gluconate, both types of admixtures were dissolved and preblended in water. Thus, simultaneous contact of PCE and gluconate with the silica fume surface was ensured. Next, dry silica fume [110 g, water-to-silica fume ratio (*w/sf*) 1.35, refer to Table 4] was poured into the mixing water within 1 minute. Then, the slurry rested for 1 minute. Afterwards, it was mixed by hand with a spoon for 3 minutes.

- ***Mini-slump test***—The same method as described above for cement-silica fume pastes was used.
- ***Adsorption measurements***—After the mini-slump test, the paste was collected and centrifuged (8,500 rpm for 10 minutes). The supernatant was separated by a 0.2 μm syringe. Samples containing only PCE or only gluconate, respectively, were characterized by TOC analysis as described above.

  Samples containing both gluconate and PCE were characterized as follows: Gluconate contents in the mixing water and the filtrate were determined by ion chromatography (ICS 2000, Dionex, Idstein/Germany). Subtraction of the gluconate content present in the centrifugate from that contained in the mixing water gives the amount of adsorbed gluconate. Furthermore, the TOC value for the total amount of non-adsorbed admixtures present in the filtrate was determined by TOC method. From this total TOC content, the TOC value stemming from non-adsorbed gluconate was subtracted. The amount of non-adsorbed gluconate was determined by IC and converted into the corresponding TOC value. The difference produces the TOC value of non-adsorbed PCE, from which the adsorbed amount of PCE was calculated.

  For the silica fume pastes, adsorption was confirmed to be the sole reason for admixture depletion by a solubility test of the admixtures in the synthetic pore solution. After one day of storage, no precipitate was observed.

RESULTS AND DISCUSSION

To achieve optimum dispersion of cement-silica fume paste, the surfaces of both cement and silica fume need to be covered with a layer of adsorbed superplasticizer molecules which provide maximum electrostatic repulsion and steric hindrance. The primary working mechanism of PCE superplasticizers is based on steric hindrance between particles.[5-7] The presence of a highly anionic, small molecule admixture possessing no side chains and therefore exercizing only an electrostatic, but no steric effect, may be advantageous. It can load more anionic charge per surface area unit onto the mineral surface than a PCE. This way, it may enhance dispersion by adding more electrostatic repulsion between particles. Based upon this concept, the supporting effect of sodium gluconate was investigated. It was hoped that this small molecule may act as a supplemental admixture for PCE.

Commonly, gluconate is added to cementitious materials as a retarder. Commercial admixture blends contain a blend of several chemical substances which are supposed to develop individual effects (PCEs to plasticize, gluconate to retard). These components are supposed to perform independent effects. However, so-called incompatibilities can occur when one component interferes with another and the intended effects are inhibited. From a mechanistic point of view, not only negative interferences can occur, but positive (synergistic) effects are possible as well.

In our work, the retarding effect of gluconate was investigated as well (results not shown). Isothermal calorimetry of hydrating cement-silica fume pastes revealed that retardation times of the optimized PCE/gluconate blends as shown below are in a similar range of the individual PCEs when they are applied without gluconate. Additionally, early compressive strength development of UHPC cylinders containing the optimized amount of PCE/gluconate blend is similar to pure PCE. Thus, due to the very low dosages of PCE and gluconate in the optimized blends, retardation is not extended by the addition of gluconate to the PCE.

1) PCE blends with sodium gluconate

First, sodium gluconate alone was tested in the cement-silica fume mixture at concentrations of 0 to 2% bwoc. It showed no liquefying effect at all. This result is no surprise because the primary function of gluconate is known to be retardation, and not dispersion.

Next, the effectiveness of adding sodium gluconate to PCE 11, PCE 21 and to the 3:1 blend (wt./wt.) of PCE 11 and PCE 21 was investigated. The results are presented in Figure 1. There, admixture dosages required to achieve a paste flow of 26.0±0.5 cm (10.24±0.02 in.) are shown.

With PCE 11 and in presence of silica fume SF 1, gluconate addition caused a substantial reduction in total admixture dosage from 0.60% (for PCE 11 only) to 0.35% bwoc. Here, the beneficial effect of the small molecule already becomes apparent. Still, this blend failed to disperse the paste containing silica fume SF 2 which possesses a higher specific surface area than SF 1, rendering it more difficult to disperse. Because in previous work PCE 11 was found to interact mainly with cement,[8] it can be concluded that sodium gluconate does not interact sufficiently with silica fume SF 2 to achieve dispersion of this UHPC blend.

A striking effect, however, was observed when allylether-based PCE 21 was combined with sodium gluconate (refer to Figure 1). There, the paste containing silica fume SF 2 also was dispersed very effectively. Total admixture dosage was reduced from 0.90% (for PCE 21 only) to 0.36% bwoc (for 3:1 wt./wt. PCE 21/gluconate blend) when SF 1 was present, and from 1.05% (for PCE 21 only) to 0.51% bwoc (for the blend) when SF 2 was present. Obviously, combination of the allylether-type PCE 21 with sodium gluconate produces a highly effective and economical admixture formulation.

Finally, addition of sodium gluconate to the 3:1 blend (wt./wt.) of PCE 11 and 21 which had been found in our previous study to perform best[8] was studied. Various formulations of PCE 11, PCE 21, and gluconate, their weight portions ranging between 3:1:0.5 and 3:1:3, were prepared and tested, but none of them exceeded the performance of the PCE 21/gluconate combination described in the previous experiment. At best, comparable performance to PCE 21/gluconate was achieved with 3 parts PCE 11, 1 part PCE 21 and 0.5 parts (wt./wt.) gluconate. This blend, however, is less attractive than that of PCE 21/gluconate because it contains more of the expensive PCE polymer.

It can be concluded that relatively minor additions of sodium gluconate to PCEs allow a substantial reduction of the admixture dosage required to disperse the UHPC mixture. The effect is particularly strong when PCE 21 is present in the formulation. Combination of PCE 21 with sodium gluconate works better than the blend with methacrylate-based PCE 11.

2) Mechanistic study

To investigate the working mechanism of the synergistic blends between the PCEs and sodium gluconate, interactions between these admixtures, cement and silica fume were studied.

First, adsorption of the individual admixtures on cement and the silica fume samples SF 1 and SF 2, resp., was determined. The results are shown in Figures 4 and 5.

On cement only, sodium gluconate adsorbs in very high amounts. PCE 11 shows lower adsorbed amounts whereas PCE 21, even at very high dosages, hardly adsorbs at all (Fig. 4). This explains previous results indicating that with cement, PCE 11 works better than PCE 21.[8] At comparable dosages, the adsorbed amounts of PCE 11 are 30-50% less than that of gluconate. Thus, sodium gluconate has an even stronger affinity to the surface of cement than PCE 11 whereas PCE 21 does not much interact with it.

On silica fume SF 1, both PCEs and sodium gluconate show significant adsorption (Fig. 5). Different from cement, PCE 21 now adsorbs in higher amounts, indicating its higher affinity to the silica fume surface than to cement. Interestingly, sodium gluconate also adsorbs on silica fume, but at lower amounts than any of the PCEs. Similar trends relative to the adsorbed amounts were found for all admixtures when silica fume SF 2 was used instead of SF 1 (results not shown here).

The experiments allow the following conclusions:

- Sodium gluconate adsorbs very strong on both cement and silica fume surfaces, but the adsorbed amount on cement is higher than that on silica fume. Thus, in a cement/silica fume blend, it is expected to interact preferably with cement and less with silica fume.
- The allylether-type PCE 21 predominantly adsorbs on the silica fume surface, and little on cement. Therefore, it is more suitable to disperse silica fumes, and less cement.

- The methacrylate-type PCE 11 adsorbs in significant amounts both on cement and silica fume. Compared to sodium gluconate, it appears to have a slightly higher preference for silica fume than for cement.

An explanation for the adsorption behavior of the admixtures relative to cement is given by the anionic charge densities of the admixtures. Apparently, there the adsorbed amounts of the admixtures are much determined by their anionic charge densities. Sodium gluconate and PCE 11 possess much higher charge densities (5,124 and 2,800 μeq/g, respectively, refer to Table 5) than PCE 21 (65 μeq/g). Therefore, PCE 21 cannot adsorb in significant amount on cement and at these low *w*/*c* ratios, is a poor cement dispersant. Consequently, when applying a PCE 21/sodium gluconate blend to the UHPC mixture, sodium gluconate is expected to predominantly adsorb onto cement whereas PCE 21 covers the silica fume surface and achieves its dispersion.

While the behavior of the admixtures relative to cement is quite explainable, the situation on silica fume seems to be more complicated. For example, there is a disconnect between the high adsorbed amount of PCE 11 and its poor dispersing performance with silica, compared to PCE 21. To investigate, not only the adsorbed amounts, but also the number of molecules adsorbed per unit area of surface were looked at. Calculation of molecular dimensions of the PCEs and their demand for adsorption space on the silica fume surface was done following the method described earlier by OHTA.[16]. Figures 6 and 7 show the results for the two PCEs and sodium gluconate, adsorbed onto the surfaces of the silica fume samples SF 1 and SF 2, respectively.

As expected, the number of adsorbed gluconate molecules per unit area is about 30-50 times higher than that of any of the PCEs. The small size of sodium gluconate allows the packing a large number of these molecules onto the surface, resulting in a considerable anionic charge load (Fig. 6). In presence of the PCEs, the number of adsorbed gluconate molecules remains unchanged (PCE 21) or even increases slightly (PCE 11; refer to the top of Fig. 6). At the same time, the presence of sodium gluconate slightly decreases the number of adsorbed PCE molecules (refer to the bottom of Fig. 6). Very similar results were obtained for silica fume SF 2, the only difference being that there, at comparable dosage levels for the admixtures, less gluconate and PCE molecules adsorb per unit surface area than on SF 1 (Fig. 7).

From these experiments, we now can develop a better understanding of the multiple interactions occurring between the admixtures, cement and silica fume.

In the 3:1 (wt./wt.) blend of PCE 11 and PCE 21, the first admixture predominantly adsorbs on and disperses cement. From the remaining non-adsorbed amount of PCE 11, some will also adsorb on silica fume, resulting in a side by side adsorption with PCE 21 which almost exclusively adsorbs on silica fume. The side by side adsorption of the two different PCE molecules on silica fume is illustrated in Figure 8. Thus, from Figures 6 and 7, it is apparent that the number of adsorbed PCE 21 molecules is slightly higher than that of PCE 11 (the ratio is approx. 3:2). On silica fume, the allylether-based PCE 21 generally produces a thicker and more densely packed layer of adsorbed polymer than the methacrylate-based PCE 11. This explains the better performance of PCE 21 with the silica fumes and UHPC mixtures.

When PCE 21 is combined with sodium gluconate, this small molecule will first adsorb in high amount on cement. Second, from the remaining non-adsorbed gluconate, a considerable amount adsorbs onto the silica fume surface, supplementing the effect of PCE 21 which also occupies this surface. This way, a hybrid admixture layer is formed on the silica surface. Considering the steric dimensions of both admixture molecules, it seems to be likely that the small gluconate molecules occupy the interstitial space between the large PCE molecules. A schematic representation of this mixed adsorbed organic layer is shown in Figure 9. Therefore, it becomes obvious that sodium gluconate can provide additional negative charge to the surface of silica fume, and thus enhances the dispersion mechanism of PCE 21.

CONCLUSIONS

When cementitious materials in UHPC hydrate, different surfaces with different chemistry resulting from cement and silica fume are developed. They demand superplasticizers with specific chemical structures to cover these surfaces best. In cement, mainly ettringite surfaces are available for superplasticizer adsorption, whereas silica fume has silanolate groups covered by a layer of adsorbed Ca^{2+} ions. In the progress of hydration, early C-S-H phases develop and offer further adsorption sites for Ca^{2+}, superplasticizer and gluconate. Obviously, the chemistry of these surfaces is quite different. Superplasticizers based on methacrylate polycarboxylates primarily adsorb onto and disperse cement, whereas those based on allylethers interact more with silica fume. Thus, a blend of methacrylate-based and allylether-based PCEs is most effective in cement-silica fume pastes.

Due to steric reasons caused by the size of the side chains of adsorbed PCE, the number of PCE molecules which can adsorb is limited. Thus, when using PCE only, a limited coverage of grain surface area is accomplished. The voids in between the truncated cones occupied by the adsorbed polymer molecules remain uncovered. They can be covered effectively, however, by addition of a small organic admixture. This way, such admixture increases the anionic charge loaded onto the surface and supports the effectiveness of the adsorbed PCE. Inexpensive small anions like gluconate are applicable for this purpose. By addition of gluconate, PCE dosages in cement-silica fume mixtures were reduced to as little as 0.28% bwoc. The selective adsorption of the gluconate on cement and the simultaneous adsorption of both PCE and sodium gluconate on silica fume shows a highly positive ("synergistic") effect with respect to the flow properties of cement-silica fume paste. Thus, gluconate is an admixture which can well supplement the effect of polycarboxylate superplasticizers.

The concept of using a small organic, non-polymeric admixture as a supplement to a large, polymeric admixture to build up more densely packed organic layers on mineral surfaces seems to provide a viable method to enhance the performance of admixture systems.

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