

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

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XRD instrument (D8 Advance; Bruker AXS, Karlsruhe/Germany) with Bragg-Brentano geometry. The diffractometer is equipped with a scintillation detector using Cu K α ($\lambda = 1.5406\text{\AA}$) radiation with a scanning range between 5° and 80° 2θ at a scanning speed of $0.5^\circ/\text{step}$ (with $0.008^\circ/\text{step}$). 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 $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ to mimic the ionic content of UHPC pore solution without sulfate. PCE concentration was 0.2 g/L. Charge titration was performed on a Mutek PCD 03 pH titrator (Mutek, 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)

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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 $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ 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 exercising 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

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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 best⁸ 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 $\mu\text{eq/g}$, respectively, refer to Table 5) than PCE 21 (65 $\mu\text{eq/g}$). 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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Table 1—Chemical composition of normal portland cement CEM I 52.5 R used in this study

Component	Content, wt.-%
SiO ₂	21.3
CaO	64.5
Al ₂ O ₃	3.4
Fe ₂ O ₃	5.2
MgO	0.7
SO ₃	2.2
Na ₂ O	0.1
K ₂ O	0.3
Loss of ignition	1.3

Table 2—Phase composition of normal portland cement CEM I 52.5 R used in this study

Phase	C ₃ S monoclinic	C ₂ S monoclinic	C ₃ A	C ₄ AF	CaO free	CaSO ₄ ·0.5H ₂ O	CaSO ₄ ·2H ₂ O
Content, wt.-%	60	21	0.7	14	1.2	0.5	1.8
Methods:	XRD (C ₃ S, C ₂ S, C ₃ A, C ₄ AF); acid titration according to FRANKE (free CaO); DSC/TG (CaSO ₄ ·0.5H ₂ O, CaSO ₄ ·2H ₂ O)						

Table 3—Characteristic properties of cement and silica fume samples

Property	Cement	SF 1	SF 2
Specific surface area, BET [m ² /g]	1.3	16	24
d ₅₀ , μm	6.80	0.24	0.08
SiO ₂ , wt.-%	—	98	97
C, wt.-%	—	0.41	0.47

Table 4—Composition of UHPC mixture reduced to cement, silica fume, and water

Component	Content, kg/m ³
Normal portland cement (CEM I 52.5 R HSR/LA)	832
Silica fume (16 % bwoc)	135
Water	184
w/cement and silica fume	0.19
w/c	0.22
w/silica fume	1.35

Table 5—Properties of methacrylate ester- and allyl ether-based PCEs and of sodium gluconate used in this study

	PCE 11	PCE 21	Na gluconate
Molar mass M_n , g/mol	12,000	8000	218
Monomer ratio a/b/c	12/1/3	1/1	—
Trunk chain length, nm	13	2.3	—
Side chain, n_{EO}	45	34	—
Specific anionic charge density, $\mu\text{eq/g}$	2800	65	5124

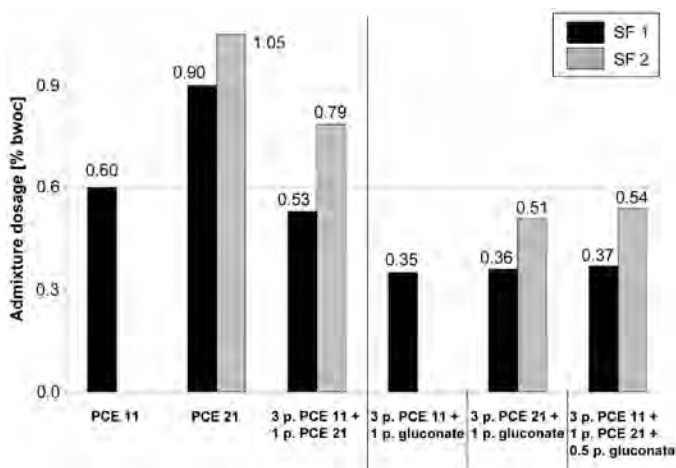


Fig. 1—Admixture dosages required for UHPC paste flow of 26.0 ± 0.5 cm (10.24 ± 0.02 in.); parts (p.) are by weight of solid admixture.

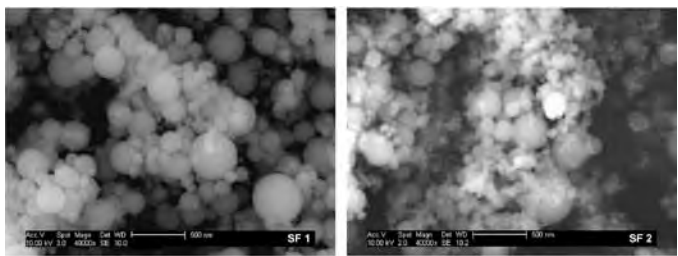


Fig. 2—SEM pictures of silica fume samples SF 1 (left) and SF 2 (right); magnification 40,000x.

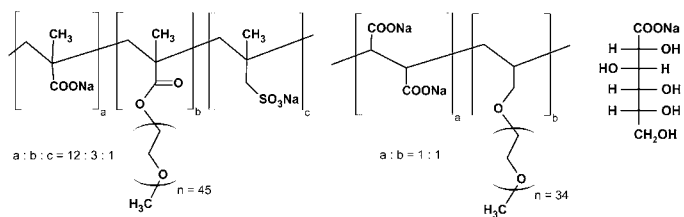


Fig. 3—Chemical composition of methacrylate ester-based PCE 11 (left), allyl ether-based PCE 21 (middle) and of sodium gluconate (right).

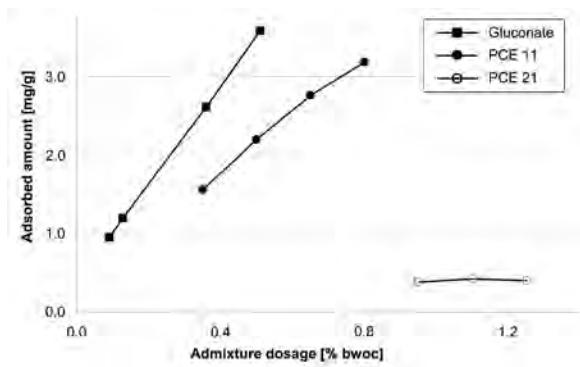


Fig. 4—Adsorbed amounts of sodium gluconate and PCE superplasticizers on cement ($w/c = 0.22$).

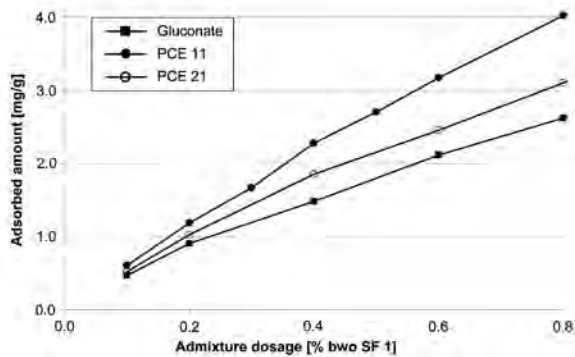


Fig. 5—Adsorbed amounts of sodium gluconate and PCE superplasticizers on silica fume SF 1 (pH 12.2, KOH, $c(\text{Ca}^{2+}) = 11 \text{ g/L}$, w/sf 1.35).

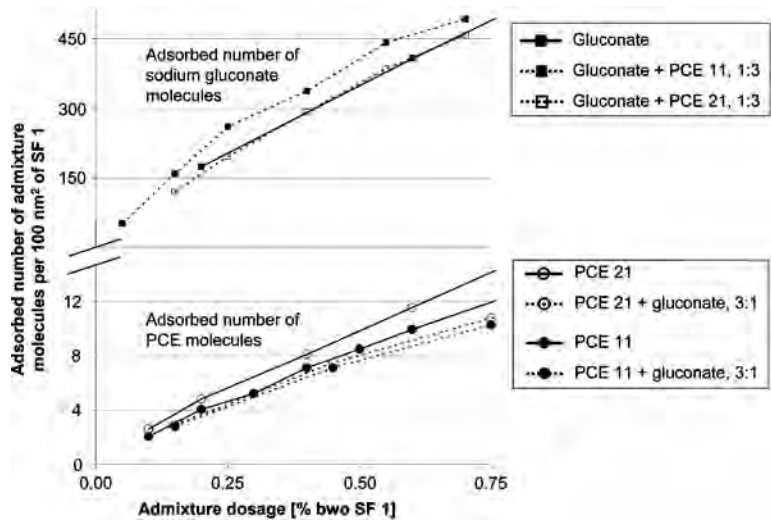


Fig. 6—Adsorbed number of sodium gluconate and PCE molecules per unit area of surface on silica fume SF 1 (pH 12.2, KOH, $c(\text{Ca}^{2+}) = 11 \text{ g/L}$, w/sf 1.35).

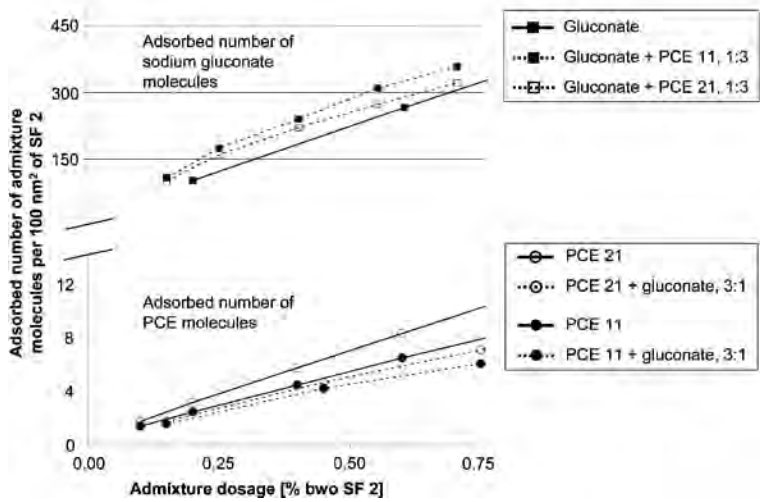


Fig. 7—Adsorbed number of sodium gluconate and PCE molecules per unit area of surface on silica fume SF 2 (pH 12.2, KOH, $c(\text{Ca}^{2+}) = 11 \text{ g/L}$, w/sf 1.35).

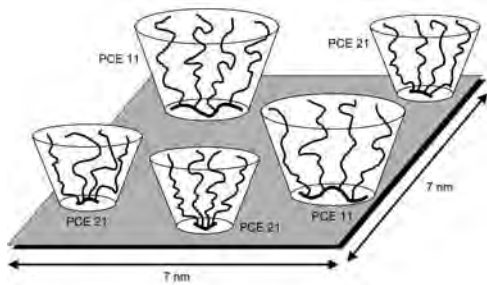


Fig. 8—Schematic representation of the combined adsorption of PCE 11 and PCE 21 on silica fume surface (steric size of PCEs shown to scale).

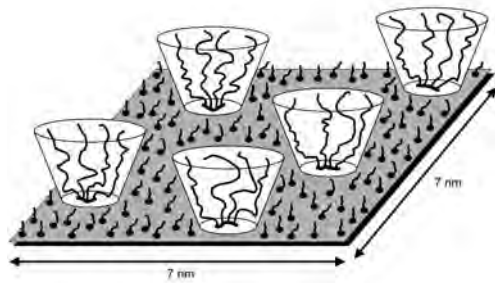


Fig. 9—Schematic representation of combined adsorption of PCE 21 and sodium gluconate on silica fume surface (steric sizes of admixture molecules shown to scale).

Performance of Superplasticizers in Blended Cement Systems

by I. Papayianni and F. Karkantelidou

Synopsis: The combination of different type of blending materials with portland cement such as natural pozzolans, fly ashes, and slags provides high flexibility in designing concrete mixtures with several technical advantages and low cost. However, their addition influences the properties of fresh concrete and causes problems of compatibility in blended cement systems containing superplasticizers that are usually used either for reduction of water demand or for increase of workability.

In this study, two of the widely used type of superplasticizers, one based on sulphonated naphthalene formaldehyde condensate (SNF) and another based on polycarboxylate polymers (PC), were tested with ten blended cement mixtures containing 20, 30, 50, or 80% portland cement replacement with one or more of the above-mentioned supplementary cementitious materials.

The action of superplasticizer on cement pastes was monitored by making zeta potential, pH, and temperature measurements as well as by using DTA-TG method for determining the hydration and hardening process. Porosity and strength development were also measured at different ages. The aim of the research work was to find which type of superplasticizer was more suitable for each type of binder system.

The highest reduction of water demand was achieved with polycarboxylate polymer superplasticizer. Results show that compared to the plain portland cement system, the decrease of water/binder ratio with superplasticizer addition was lower in blended cements.

Keywords: blended cement systems; fly ash; polycarboxylate; porosity; slag; strength; sulfonated naphthalene formaldehyde; superplasticizers; water/cementitious material ratio.

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INTRODUCTION

The use of blended cements in concrete mixtures either by using a blended portland cement or by adding suitable materials directly at the concrete mixer seems to be the answer to the challenge to the concrete industry of 21st century for sustainable development. This concept has been well documented by research work and applications during the last century.¹⁻³ It was also practiced in ancient building technology, as masons in old times used to combine local materials for the construction of long lasting structures.⁴

Between the two methods of using cementitious materials, fly ashes, slags, and natural pozzolans; the first one is more convenient and produces concrete of uniform quality, the second method is more flexible, but requires adequate quality control system. The microstructure and properties of cementitious materials and their hydration products in a blended cement system containing portland cement clinker should be thoroughly investigated to achieve optimum performance. The mineralogical composition of anhydrous phases, fineness, and surface morphology characteristics of particles influence the hydration products and properties of blended cement systems.⁵

In the case of blended cement systems, containing high-calcium fly ash and ladle furnace slag, the water demand of the binding system of a given consistency is increased, resulting in lower strength development compared to plain portland cement system. This behavior presented a barrier to potential exploitation of these industrial by-products although their slow rate of hydration produces a stronger interfacial transition zone between the cement paste and aggregate particles in concrete.⁵

Mahlotra's pioneering work on the use of superplasticizers in mixtures of high-volume fly ash cement systems has removed this barrier.¹

According to Collepardi's comprehensive review,⁶ there are two types of superplasticizers and each type has a different mechanism of dispersive action in hydrated cement pastes. In case of sulfonated naphthalene formaldehyde (SNF) condensate, the mechanism involves electrostatic repulsion provided by sulphonic groups. In case of polycarboxylates, steric hindrance of long graft neutral chains is responsible for the dispersion of cement particles. The purpose of this study was to determine which type of superplasticizers are suitable for use with blended cement systems made with standard portland cements and pozzolanic materials available in Greece.

EXPERIMENTAL

Materials

Ten combinations of binders were used to study the effectiveness of superplasticizers. They consisted of portland cement clinker and locally available cementitious materials, one natural pozzolan and two industrial by-products. A blended portland cement containing one of the by-products was also included for testing. Pastes of standard

consistency according to EN 196-3 were prepared both without and with 1%, by mass superplasticizer. Characteristics of Greek cements and cementitious materials are listed in Tables 1 and 2, respectively. The cementitious materials used were added in different percentages by mass, as shown in Table 3.

Compositions with high content of cementitious materials were selected because of good experience with performance of concrete containing high volume of supplementary materials in pavement and road construction.⁷

In this report, only the water reducing capacity of two widely used superplasticizers, one belonging to sulfonated naphthalene formaldehyde (SNF) class and the other to polycarboxylate polymer (PC) class, was tested in the blended cement mixtures shown in Table 3. Other parameters that influence the performance, such as the time of adding them, temperature of the system, and rheological characteristics and dosage of superplasticizers are not considered here.

Both superplasticizers meet the requirements of EN 934-2:2001 and ASTM C-494, and are free of chlorides (Table 4). The first type is generally used for the production of high strength flowable concrete, while the second is recommended for slump retention even in hot climate. Apart from CEM I 42.5 with 95% portland cement clinker, the blended cement type CEM IV 32.5 with 19% calcareous fly ash was also used. The local available fly ash, a high – calcium type, possesses cementitious and pozzolanic properties. The ladle furnace slag from the steel industry is another by-product pozzolanic material. A natural pozzolan of volcanic origin from Island Milos was also used.

Test Methods

Thirty paste mixtures were prepared according to EN 196-3 standard consistency method. The addition of 1% by mass superplasticizer was made through the mixing water. Five minutes after the water mixing, the pH and temperature of the system were measured. The prepared pastes of standard consistency were cast in steel plate molds of 25 x 25 x 300 mm (1 x 1 x 12 in.), size from which specimens of 25 x 25 x 300 mm (1 x 1 x 12 in.) and 25 x 25 x 25 mm (1 x 1 x 12 in.) size were taken for testing flexural and compressive strength, respectively. Open porosity measurements were made following RILEM CPC 11.3 method. All specimens were placed in curing room at relative humidity $99 \pm 1\%$ and temperature $20 \pm 1^\circ\text{C}$ ($68 \pm 2^\circ\text{F}$) up to testing age. Strength and porosity were determined at 1, 3, 7, 28 and 90 days.

Diluted paste mixtures of 0.1 mg/ml concentration both with and without superplasticizers were used for zeta potential measurements. The rate of hydration and hardening of the mixtures with 30% fly ash and 20% natural pozzolan was also monitored by using DTA-TG method for determination of C-S-H phase.

RESULTS AND DISCUSSION

The reduction of the water/binder ratio of the standard consistency cementitious pastes resulted from the addition of the two superplasticizers (SNF and PC) to different mixed type binding systems is indicated in Figures 1 to 10. It seems that when a mass percentage of portland cement clinker was replaced by a pozzolanic material, even in the form of blended type cement, the water demand for standard consistency was increased. By adding 1% by mass superplasticizers this extra demand was significantly

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decreased so that the resulting water/binder ratios were comparable to control paste mixture without superplasticizer. However, as the percentage of cementitious material increased the effectiveness of the superplasticizer also decreased. It is also obvious that the PC based superplasticizer was more effective with all mixed type binding systems tested. The pH measurements showed that as the content of cementitious material was increased, the first 5 minute pH values were slightly reduced. This reduction was more obvious in the case of ladle furnace slag, where the measured pH value was 12.2, while the pH of control cement CEM I 42.5 paste was 13.2. The effectiveness of PC superplasticizer was relatively lower in the CEM I 42.5 + slag systems. This relationship of pH and effectiveness of PC will be investigated further.

The strength development of the paste mixtures in terms of flexural and compressive strength is given in Figures 11-20 and Figures 21 to 30, respectively. The bars in the figures represent the mean values of 2 prisms 25 x 25 x 100 mm (0.98 x 0.98 x 3.9 in.) and four cubes 25 x 25 x 25 mm (0.98 x 0.98 x 0.98 in.). In all mixed type mixtures the strength was much increased with the addition of superplasticizer, especially with PC type. In the case of CEM I 42.5 + 30% or 50% Fly Ash, strength levels comparable to those of plain CEM I 42.5 and CEM IV 32.5 were obtained.

Furthermore, superplasticizers and especially PC type contribute to early strength development. This is in particular obvious in the case of CEM I 42.5 + Fly Ash systems. The three constituent system, CEM I 42.5 + 20% Pozzolan + 30% Fly Ash, developed with PC, a 90 day strength level comparable to that of CEM IV 32.5 at 28 days. Of course, the higher strength development was expected since it was in accordance with the water/binder reduction. In addition, it seems that less water in the system had an impact on modifying the open porosity, as is depicted in Figs. 31 to 40. As it is well known, decrease of porosity with time is very beneficial for durability of the cementitious matrix.⁵ The higher reduction is observed in mixed type binding systems modified with PC.

In an effort to understand the lower effectiveness of superplasticizers in these systems, zeta potential measurements were made (Table 5) and the hydration process was monitored by using DTA-TG method for determining C-S-H phases in pastes of different ages (Figs. 41 and 42). It seems that the zeta potential values for the blended cement systems with the cementitious materials used in this research were much higher than those of portland cement alone. With the addition of SNF and PC the zeta potential values range are normalized being around the measured values for cement mixtures. Regarding Figures 41 and 42, it is obvious that the rate of C-S-H formation is intense, and superplasticizers and in particular the PC type helps in achieving higher rate of C-S-H formation and consequently better strength.

CONCLUSIONS

The effectiveness of sulfonated naphthalene type and polycarboxylate type admixtures on blended portland cement systems containing relatively large quantities of a calcareous fly ash, a ladle furnace slag, a natural pozzolan was lower when compared to plain portland cement paste. However, the strength development of these blended cement systems was greatly increased followed by a respective decrease in porosity. A higher water reduction in blended cement was achieved with a polycarboxylate type admixture as compared to a sulfonated naphthalene type admixture. In the case of CEM I 42.5 + Fly

Ash systems the water/binder reduction is 20, 17, and 0% for 30, 50, and 80% by mass fly ash content. In CEM I 42.5 + Slag systems, the water/binder reduction ranges from 70 to 15% for 30, 50, and 80% slag content.

Superplasticizer addition to blended cement systems modified the microstructure of hardened cement pastes. Lower porosity pastes resulted even at the first day after hydration. The reduction of porosity and increase of strength was higher with the polycarboxylate admixture. The high-strength paste of CEM I 42.5 + 30% Fly Ash showed 113 MPa (16,390 psi) at 90 days. The CEM I 42.5 + 50% Fly ash system developed strength of the same order as that of the blended type cement, CEM IV 32.5. For the CEM I 42.5 + 80% Fly Ash, the dosage of superplasticizer was obviously inadequate. Similar results were reported during investigations for the construction of Platanovrvyski RCC dam with 82% high-calcium fly ash and 18% CEM I 42.5 cement.⁷

In the case of CEM I 42.5 + Ladle Furnace Slag the water/binder reduction ranged from 2 to 12% of the control mix. Again, the polycarboxylate admixture was more effective than the sulfonated naphthalene admixture decreasing the porosity and improving the strength development. However, it seems that the cement-slag blended system did not perform as well as the cement-fly ash system.

The superplasticizer addition in the system CEM I 42.5 + 20% Pozzolan, resulted in reduction of the water/ binder ratio from 11 to 17% when compared to the control cement. The polycarboxylate admixture produced lower porosity and higher strength, which was comparable to that of blended cement (CEM IV 32.5) paste of the same age.

The three component cementitious systems, CEM I 42.5 + 20% Pozzolan + 30% Fly Ash, developed a paste strength level of 50 MPa (7250 psi) at 90 days with polycarboxylate type admixture. The water/binder reduction in the system was comparatively lower.

Generally speaking, it is obvious that superplasticizing admixtures especially the polycarboxylate type have made it possible to replace large amounts of portland cement with by-product cementitious materials while reducing the cost and enhancing the durability of concrete.

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Table 1—Characteristics of Greek cement types CEM I 42.5 N and CEM IV 32.5 W

Characteristics	Portland clinker CEM I 42.5	Blended CEM IV 32.5
Chemical composition (% by mass)		
Na ₂ O	0.57	2.10
K ₂ O	1.08	1.90
CaO	66.84	59.19
MgO	3.91	3.30
Fe ₂ O ₃	8.11	1.01
Al ₂ O ₃	2.40	6.54
SiO ₂	19.55	21.64
Loss of ignition	1.91	4.32
Insoluble residue	0.8	—
Fineness, retained on 45 µm sieve	1.5	6.0
Apparent specific density	3.141	2.780

Table 2—Characteristics of cementitious materials used in binding systems

Characteristics	Calcareous fly ash	Ground ladle furnace slag	Pozzolan from Milos
Chemical composition (% by mass)			
Na ₂ O	0.38	0.46	2.67
K ₂ O	0.80	0.31	3.42
CaO	41.70	55.96	17.91
MgO	7.30	6.82	7.96
Fe ₂ O ₃	5.26	1.60	0.92
Al ₂ O ₃	6.69	1.28	8.81
SiO ₂	29.42	17.99	50.43
SO ₃	3.85	—	—
Loss of ignition	8.46	15.58	7.89
Insoluble residue	9.93	3.93	5.74
Fineness, retained on 45 µm sieve	38%	28%	6%
Pozzolanicity index EN 450-1 with cement, 28 days	85%	81%	—
Pozzolanicity index ASTM C593 with lime, 28 days	4.64 MPa	1.56 MPa	4.5 MPa
Apparent specific density	2.556	2.555	2.170

Table 3—Composition of pastes at blended cement systems

Composition	Portland cement clinker	Blended cement	Calcareous fly ash	Ground ladle furnace steel slag	Natural pozzolan from Milos	Standard consistency EN 196-3 Vicat plug penetration, mm	Temperature of paste mixture after 5 min., °C	pH of paste mixture after 5 min.
CEM I 42.5	+	-	-	-	-	5	30.9	13.20
CEM I 42.5+SNF 1%	+	-	-	-	-	7	28.7	13.19
CEM I 42.5+PC 1%	+	-	-	-	-	5	28.2	13.18
CEM IV 32.5	-	+	-	-	-	7	24.5	13.12
CEM IV 32.5+SNF 1%	-	+	-	-	-	6	23.9	13.09
CEM IV 32.5+PC 1%	-	+	-	-	-	5	23.4	12.96
CEM I 42.5+30%Fly Ash	+	-	+	-	-	7	27.9	13.20
CEM I 42.5+30%Fly Ash +SNF 1%	+	-	+	-	-	7	27.0	13.15
CEM I 42.5+30%Fly Ash+PC 1%	+	-	+	-	-	5	26.3	13.10
CEM I 42.5+50%Fly Ash	+	-	+	-	-	7	25.3	13.02
CEM I 42.5+50%Fly Ash+SNF 1%	+	-	+	-	-	5	24.8	13.00
CEM I 42.5+50%Fly Ash+PC 1%	+	-	+	-	-	5	24.7	12.84
CEM I 42.5+80%Fly Ash	+	-	+	-	-	5	33.4	12.23
CEM I 42.5+80%Fly Ash+SNF 1%	+	-	+	-	-	5	29.9	12.21

Table 3—Composition of pastes at blended cement systems (con't)

Composition	Portland cement clinker	Blended cement	Calcareous fly ash	Ground ladle furnace steel slag	Natural pozzolan from Milos	Standard consistency EN 196-3 Vicat plug penetration, mm	Temperature of paste mixture after 5 min., °C	pH of paste mixture after 5 min.
CEM I 42.5+30%Ladle Furnace Slag	+	-	-	+	-	5	31.4	12.68
CEM I 42.5+30%Ladle Furnace Slag+SNF 1%	+	-	-	+	-	5	29.5	12.46
CEM I 42.5+30%Ladle Furnace Slag+PC 1%	+	-	-	+	-	5	30.1	12.65
CEM I 42.5+50%Ladle Furnace Slag	+	-	-	+	-	5	27.7	12.42
CEM I 42.5+50%Ladle Furnace Slag+SNF 1%	+	-	-	+	-	5	27.0	12.39
CEM I 42.5+50%Ladle Furnace Slag+PC 1%	+	-	-	+	-	5	25.8	12.45
CEM I 42.5+80%Ladle Furnace Slag	+	-	-	+	-	5	26.1	12.13
CEM I 42.5+80%Ladle Furnace Slag+SNF 1%	+	-	-	+	-	6	25.7	12.38
CEM I 42.5+80%Ladle Furnace Slag+PC 1%	+	-	-	+	-	5	25.6	12.20
CEM I 42.5+20% Pozzolan	+	-	-	-	+	7	-	-
CEM I 42.5+20% Pozzolan +SNF 1%	+	-	-	-	+	5	-	-

Table 3—Composition of pastes at blended cement systems (con't)

Composition	Portland cement clinker	Blended cement	Calcareous fly ash	Ground ladle furnace steel slag	Natural pozzolan from Milos	Standard consistency EN 196-3 Vicat plug penetration, mm	Temperature of paste mixture after 5 min., °C	pH of paste mixture after 5 min.
CEM I 42.5+20% Pozzolan +PC 1%	+	-	-	-	+	5.5	-	-
CEM I 42.5+20% Pozzolan +30%Fly Ash	+	-	+	-	+	6	-	-
CEM I 42.5+20% Pozzolan +30%Fly Ash+SNF 1%	+	-	+	-	+	7	-	-
CEM I 42.5+20% Pozzolan +30%Fly Ash+PC 1%	+	-	+	-	+	6	-	-
CEM I 42.5+80%Fly Ash+PC 1%	+	-	+	-	-	5	30.6	12.31

Table 4—Superplasticizers' technical data

Superplasticizer	Appearance	Specific gravity at 20 °C (g/mL)	pH value at 20 °C	Chloride content, %
SNF	Brown liquid	1.185 – 1.205	8.5 – 9.8	≤ 0.01
PC	Brown liquid	1.080 – 1.150	~ 6.6	≤ 0.01

Table 5—Zeta potential of blended cement systems

Binding systems	Z—potential value without superplasticizer, mV	Z—potential value with 1% SNF, mV	Z—potential value with 1% PC, mV
CEM I 42.5	0.157	−19.16	−4.85
CEM IV 32.5	−0.187	−27.45	−10.45
CEM I 42.5+30% Fly Ash	5.60	−19.17	−2.25
CEM I 42.5+50% Fly Ash	8.91	−16.49	−3.97
CEM I 42.5+80% Fly Ash	11.49	−18.35	−4.50
CEM I 42.5+30% Ladle Furnace Slag	8.11	−19.50	−1.81
CEM I 42.5+50% Ladle Furnace Slag	9.98	−16.75	−1.29
CEM I 42.5+80% Ladle Furnace Slag	14.26	−16.43	−0.82

Figs. 1 to 10—The water/binder ratio of standard consistency pastes of different binding systems and reduction resulted from superplasticizer addition.

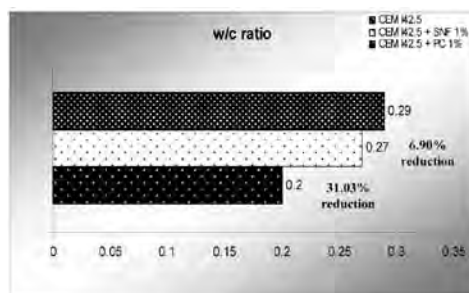


Fig. 1—System: CEM I 42.5 N.

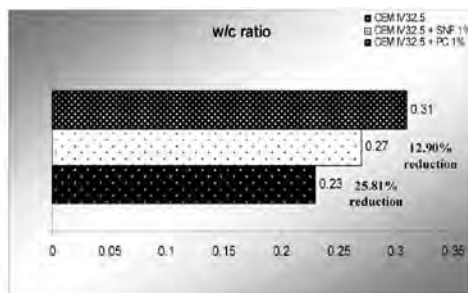


Fig. 2—System: CEM IV 32.5 W.

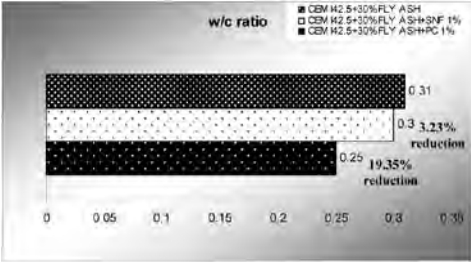


Fig. 3—System: CEM I 42.5+30% Fly Ash.

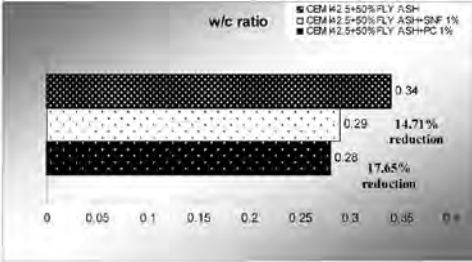


Fig. 4—System: CEM I 42.5+50% Fly Ash.

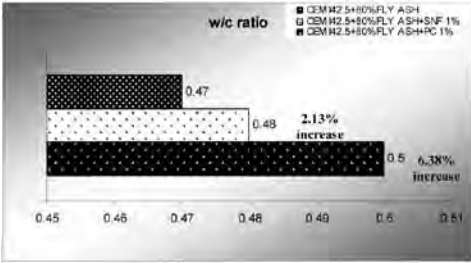


Fig. 5—System: CEM I 42.5+80% Fly Ash.

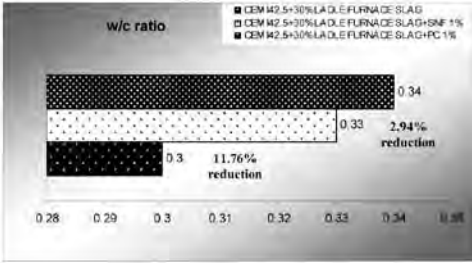


Fig. 6—System: CEM I 42.5+30% Ladle Furnace Slag.

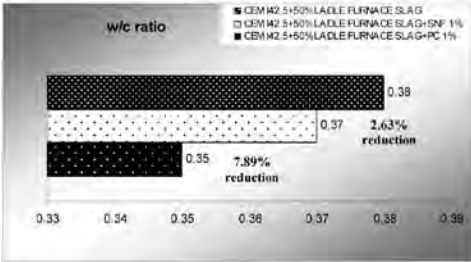


Fig. 7—System: CEM I 42.5+50% Ladle Furnace Slag.

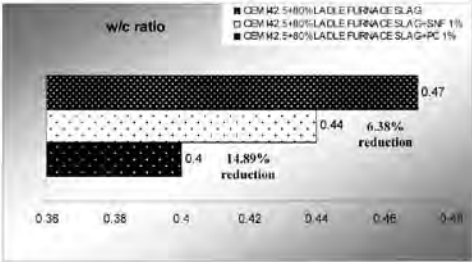


Fig. 8—System: CEM I 42.5+80% Ladle Furnace Slag.

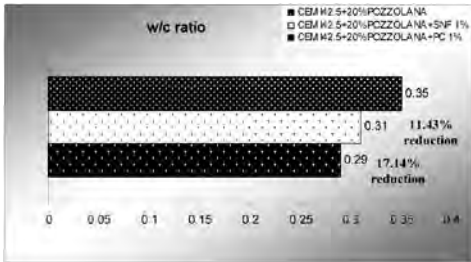


Fig. 9—System: CEM I 42.5+20% Pozzolan.

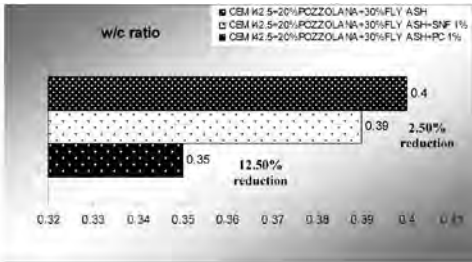


Fig. 10—System: CEM I 42.5+20% Pozzolan+30% Fly Ash

Figs. 11 to 20—Flexural strength development of standard consistency pastes of different binding systems.

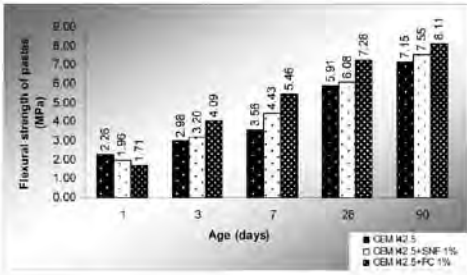


Fig. 11—Binding system: CEM I 42.5 N.

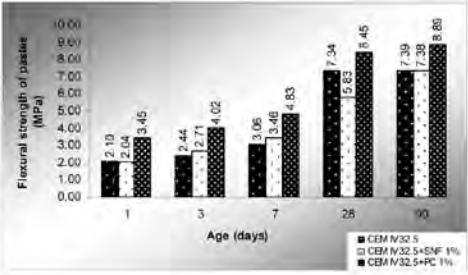


Fig. 12—Binding system: CEM IV 32.5 W.

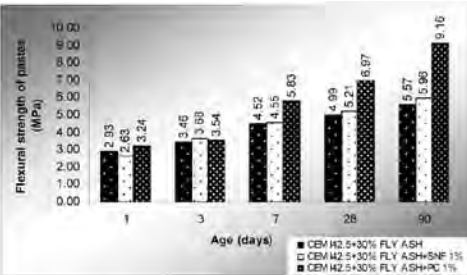


Fig. 13—Binding system: CEM I 42.5+30% Fly Ash.

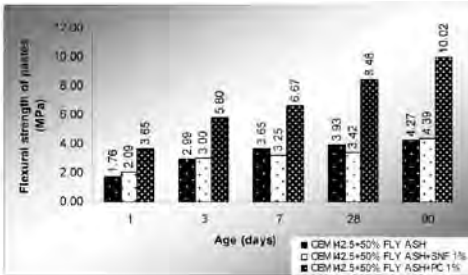


Fig. 14—Binding system: CEM I 42.5+50% Fly Ash.

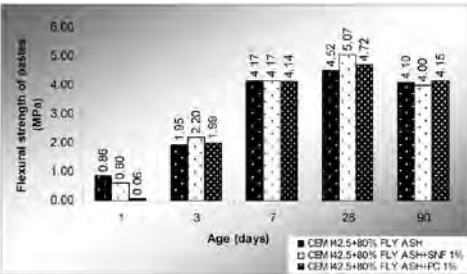


Fig. 15—Binding system: CEM I 42.5+80% Fly Ash.

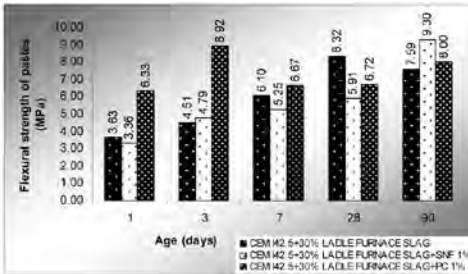


Fig. 16—Binding system: CEM I 42.5+30% Ladle Furnace Slag.

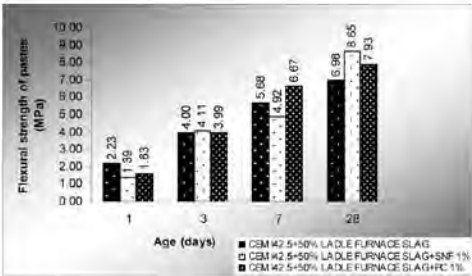


Fig. 17—Binding system: CEM I 42.5+50% Ladle Furnace Slag.

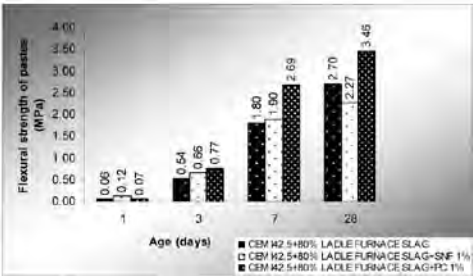


Fig. 18—Binding system: CEM I 42.5+80% Ladle Furnace Slag.

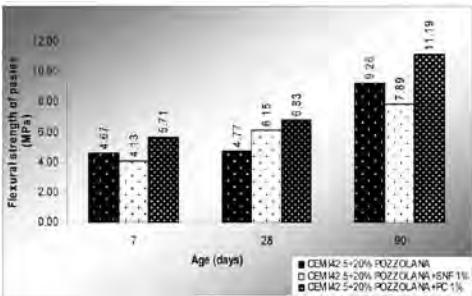


Fig. 19—Binding system: CEM I 42.5+20% Pozzolan.

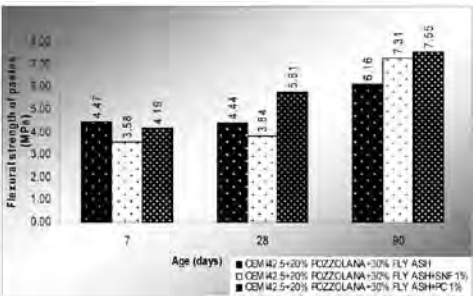


Fig. 20—Binding system: CEM I 42.5+20% Pozzolan+30% Fly Ash

Figs. 21 to 30—Compressive strength development of standard consistency pastes of different binding systems.

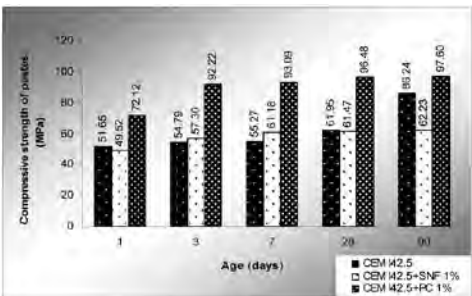


Fig. 21—Binding system: CEM I 42.5 N.

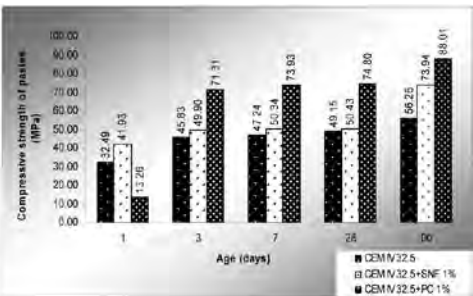


Fig. 22—Binding system: CEM IV 32.5.

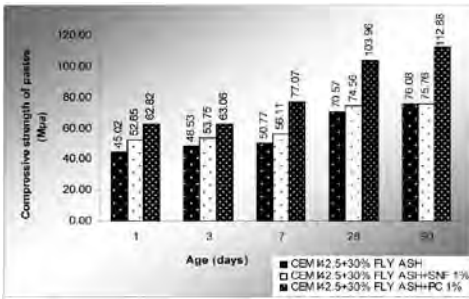


Fig. 23—Binding system: CEM I 42.5+30% Fly Ash.

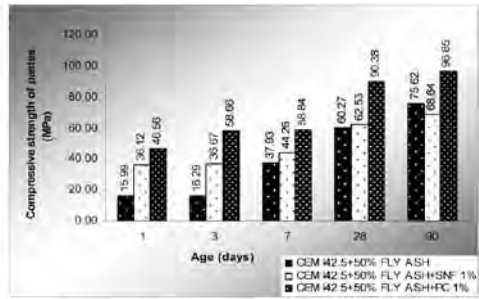


Fig. 24—Binding system: CEM I 42.5+50% Fly Ash.

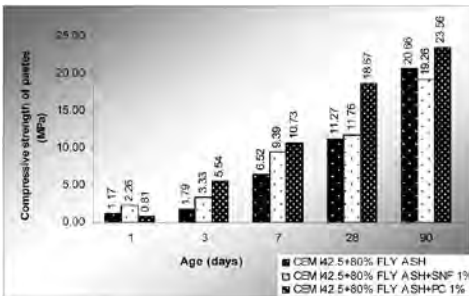


Fig. 25—Binding system: CEM I 42.5+80% Fly Ash.

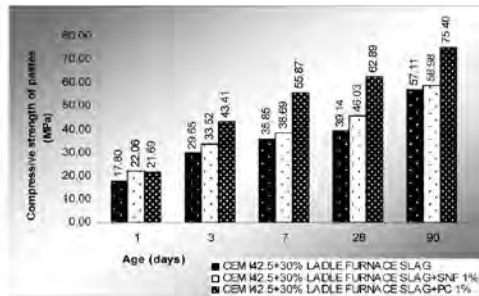


Fig. 26—Binding system: CEM I 42.5+30% Ladle Furnace Slag.

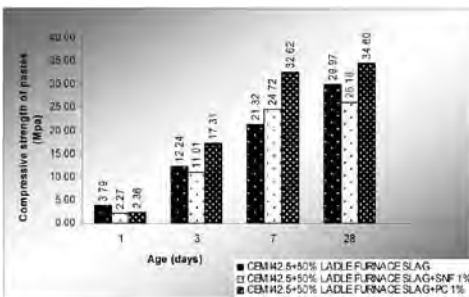


Fig. 27—Binding system: CEM I 42.5+50% Ladle Furnace Slag.

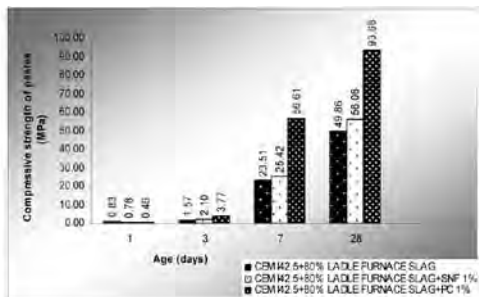


Fig. 28—Binding system: CEM I 42.5+80% Ladle Furnace Slag.

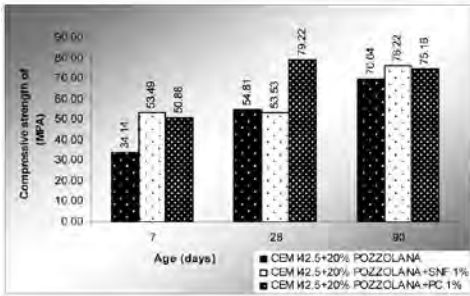


Fig. 29—Binding system: CEM I 42.5+20% Pozzolan.

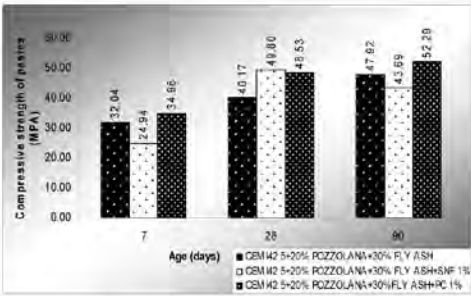


Fig. 30—Binding system: CEM I 42.5+20% Pozzolan+30% Fly Ash.

Figs. 31 to 40—Evolution of open porosity with time in blended cement systems without and with superplasticizers.

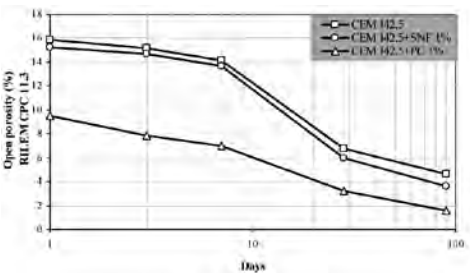


Fig. 31—Binding system: CEM I 42.5 N.

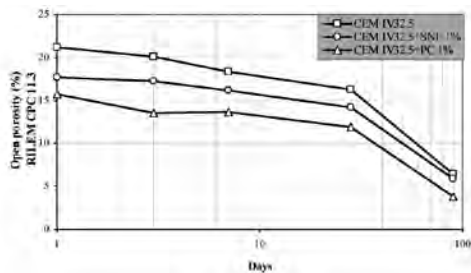


Fig. 32—Binding system: CEM IV 32.5 W.

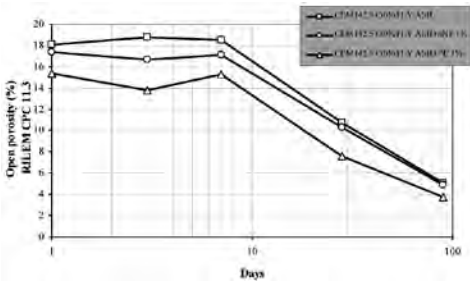


Fig. 33—Binding system: CEM I 42.5+30% Fly Ash.

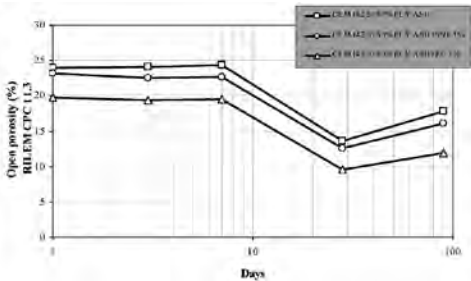


Fig. 34—Binding system: CEM I 42.5+50% Fly Ash.

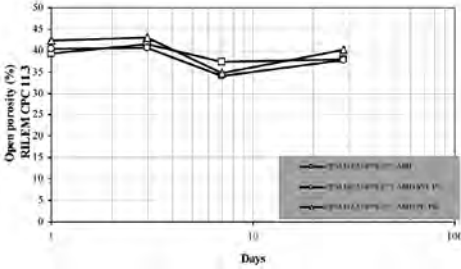


Fig. 35—Binding system: CEM I 42.5+80% Fly Ash.

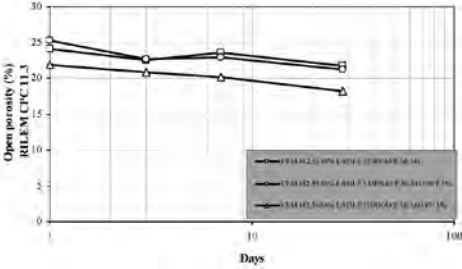


Fig. 36—Binding system: CEM I 42.5+30% Ladle Furnace Slag.

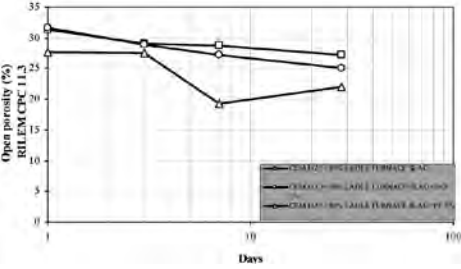


Fig. 37—Binding system: CEM I 42.5+50% Ladle Furnace Slag.

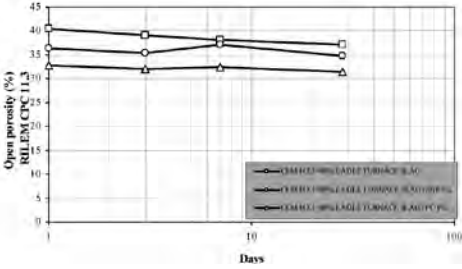


Fig. 38—Binding system: CEM I 42.5+80% Ladle Furnace Slag.

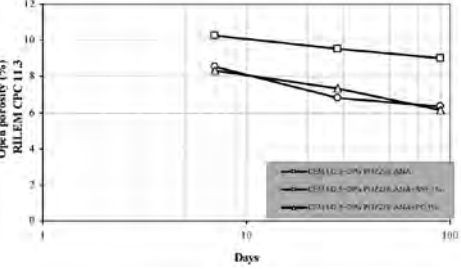


Fig. 39—Binding system: CEM I 42.5+20% Pozzolan.

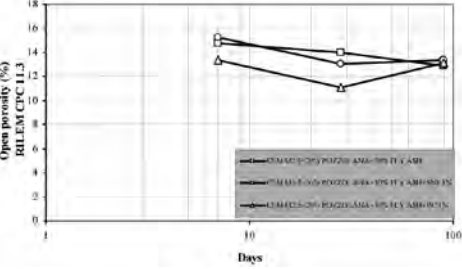


Fig. 40—Binding system: CEM I 42.5+20% Pozzolan+30% Fly Ash.

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Figs. 41 to 42—Rate of C-S-H phase development in pastes of different binding systems with and without superplasticizers.

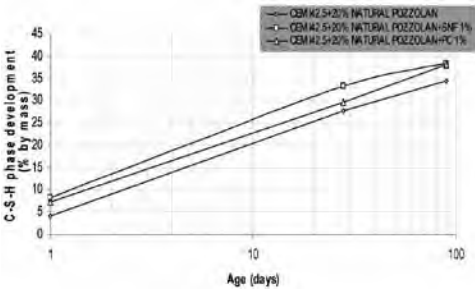


Fig. 41—Binding system: CEM I 42.5+20% Pozzolan.

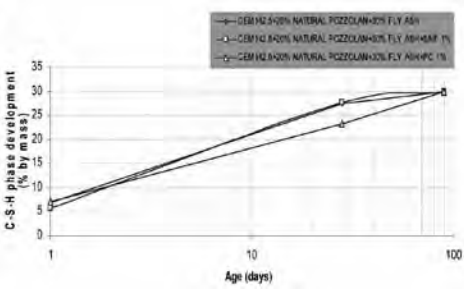


Fig. 42—Binding system: CEM I 42.5+20% Pozzolan+30% Fly Ash

Multifunctional Chemical Admixture to Reduce Quality Control Requirements of Self-Consolidated Concrete

by A.A. Jeknavorian, E. Koehler, A. Abelleira, D. Geary,
and R. Cook

Synopsis: Self-consolidated concrete (SCC) is increasingly being used for both precast and ready mixed concrete applications. For ready mixed concrete, slump flow retention becomes a concern when the concrete is transported for long distance, and when delays in placing the concrete occur due to unexpected traffic problems or incomplete jobsite preparations. In this study, the performance of a special multifunctional superplasticizer is discussed that can enable SCC mixtures to have slump flow retention up to two hours without any significant extended setting properties and delay in strength gain. Furthermore, during the period of extended slump-flow, the SCC demonstrates rheological properties adequate to ensure segregation resistance once the concrete has been placed, as well as good moisture tolerance. This capability provided by the special superplasticizer formulation is expected to significantly reduce quality control operations and facilitate the successful production and placement of self-consolidating ready mixed concrete by imparting an appropriate amount of thixotropy to the SCC mixture without compromising suitable flow properties.

Keywords: dynamic and static yield stress; moisture tolerance; rheology; self-consolidating concrete (SCC); slump flow; superplasticizers; thixotropy; viscosity; workability box.

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INTRODUCTION

Self-consolidating concrete (SCC) must exhibit proper slump flow and other rheological parameters at the time of placement.^{1,2} While different types of high-range water reducers (HRWRs) have been used to produce various SCC mixtures, polycarboxylate (PC)-based HRWRs have become the most common form of superplasticizer technology versus those based on either naphthalene and melamine sulfonates because of a number reported benefits such as reduced water demand and reduced surface settlement upon placement (static stability),³ extended workability retention,⁴ and increased thixotropy of the in-place concrete.⁵ These attributes, along with imparting a desired cohesiveness to SCC mixtures, is made possible because the polymeric structure of polycarboxylate-based superplasticizers can be configured for a wide range of concrete applications, including SCC mixtures.⁶ Figure 1 provides one form of the general PC chemical structure, which features a “comb” polymer architecture wherein the comb backbone adsorbs onto cement surfaces, and the comb teeth extend into the pore water producing a steric repulsive force between agglomerated hydrating cement particles. Teeth length (Z), teeth density [$Y/(X+Y)$], and backbone length (X+Y) are three of the many parameters that can influence performance. Figure 2 provides data showing the impact of PC structure on the rheology of SCC. The superplasticizer PC B was designed to impart increased viscosity to the SCC mixture, which can contribute to greater stability.⁷ Relative to PC A, superplasticizer PC B is designed with relatively longer teeth, a higher teeth density and a longer backbone length. With these differences in comb polymer structure, for any slump flow (or admixture dose), the mixtures made with PC B will generally have a higher viscosity. Moreover, at a given slump flow, polycarboxylates can impart different rheological properties over time, such as workability retention and thixotropy based on polymer architecture.⁸ This, in turn, can have significant consequences on placeability, pumpability, segregation resistance, formwork pressure, and robustness or the ability of the mixture to withstand certain variations in raw material characteristics and/or process conditions, which can lead to significant dynamic and static segregation of the SCC mixture. Therefore, in order to consistently produce and place stable SCC mixtures with adequate flow properties, there is a critical need to understand how superplasticizers can impact concrete rheology over time.

In this study, two test protocols are introduced designed to compare the suitability of

several PC-based superplasticizers, especially a multi-purpose PC formulation, PC078, for use with SCC mixtures. One protocol involves assessing PC performance using the so-called “workability box” concept, which defines the ranges in yield stress (slump-flow) and viscosity (T_{50} or V-funnel) within which an SCC mixture must be maintained to assure proper fluidity and stability. In a second protocol, key rheological properties of an SCC mixture, dosed with PC078 along with another PC-based superplasticizer, were measured using a portable rheometer. Changes in slump flow, v-funnel flow time, yield stress, plastic viscosity, and thixotropy over time were compared.

TEST PROGRAM

Superplasticizer PC 068 is based on a range of polycarboxylate-type polymers optimized to provide multifunctional performance for both highly flowing and self-consolidating cementitious mixtures. Key performance properties include workability retention in excess of two hours without extended set times, capability to impart rheology control including dynamic and static yield stress, viscosity, and thixotropy, and the ability to provide resistance to segregation that could result from moisture variations. To evaluate the robustness of the multi-purpose superplasticizer, PC078, an SCC mixture having mixture proportions corresponding to marginal stability, was treated with successive increments of water to simulate the variations in water content that could occur during daily ready-mix production (Table 1). The mixing process was adopted from the protocol described in the ASTM C494 standard for chemical admixtures. After each increment of water was added to the SCC mixture, slump-flow, T_{50} , and visual stability index (VSI) were measured according to procedures cited in ASTM C 1611-05, and static segregation by the method reported in ASTM C 1610-06a. Using this protocol, a workability box was created by plotting slump-flow versus T_{50} measurements and noting areas on the plot where the VSI was greater than 1, indicating the possible instability of the SCC mixture.

A second set of SCC mixtures was fabricated to investigate the rheological performance of the multifunctional PC 068 admixture versus two other PC formulations, PC 059 and PC 915. All the PC-based admixtures were added with the mixture water at a dosage of 0.17% admixture actives by weight of cement. These admixtures are also based on polycarboxylate technology, but incorporate a different polymer structure. PC 915 was also co-admixed with a set retarding admixture to help promote extended slump life. To evaluate sensitivity to uncompensated changes in aggregate moisture content, a water amount equal to 2% of the sand mass were added to the mixture with no other changes to the mixture proportions including the HRWR dosage. Slump flow, T_{50} , VSI, and segregation were measured in 30 minute increments over a 2 hour period. The V-funnel test was performed as described in EFNARC Report on SCC, May 2005. Rheology was measured with a portable vane-type rheometer. The rheometer protocol consisted of placing concrete in the rheometer, pausing for 3 minutes, and performing a stress growth test followed by a flow curve test. The stress growth test was used to calculate static yield stress by rotating the vane at a speed of 0.05 rps and measuring the maximum torque achieved. The flow curve test was performed by increasing the speed from 0.05 to 0.50 rps in 7 increments, holding the speed constant at 0.50 rps for 20 seconds, and decreasing the speed from 0.50 to 0.05 rps in 7 increments.

Dynamic yield stress and plastic viscosity were calculated from the downward portion of the flow curve, and thixotropy was calculated as the area between the upward and downward portions of the flow curve. The proportions for the second set of mixtures are reported in Table 2. The composition of the cement for both series of SCC mixtures is shown in Table 3.

For both test protocols, the admixtures were added with the concrete batch water.

TEST RESULTS

For the first set of mixtures dosed with PC 068 and designed to evaluate the robustness SCC mixtures through the workability box concept, the VSI was plotted versus static segregation to understand if the far less labor intensive VSI observation could be used as an approximate indicator of in-place stability. The correlation in Figure 3 indicates that with the selected materials and mix design, the VSI appears to be a somewhat effective predictor of segregation resistance, contrary to the understanding that the two measurements correspond to different rheological properties: (a) VSI is influenced by dynamic yield stress, while (b) column segregation is a function of static yield stress. When excess water is added to the SCC mixture reported in Table 1, the effects on slump-flow and T_{50} , shown in Figures 4 and 5 indicate a water tolerance of approximately 20 liters/m³ before significant change in VSI occurs. The slump-flow, T_{50} , and VSI results are combined in Figure 6 to establish a workability box, which begins to set the ranges in rheological parameters (yield stress as represented by the slump-flow, and viscosity estimated by T_{50}) within which stable SCC mixtures can be produced.

For the second set of concrete mixtures reported in Table 2, the three admixtures, PC 068, PC 059, and PC 915, were all capable of providing over 2 hours of slump-flow retention (Figure 7), which was also consistent with the trends in dynamic yield stress as a function of time (Figure 8). In the case of PC superplasticizers 059 and 915, the additional use of a retarding admixture was required. However, significant differences in the static yield stress (Figure 9) and thixotropy (Figure 10) as a function of time were evident between PC 068 versus PCs 059 and 915, which can be associated with the unique polymer architecture of PC 068. The consequences of the differences in static yield stress and thixotropy can be seen from the static segregation results (Figure 11), whereby the smallest values for percent segregation and change in segregation due to uncompensated variations in moisture content were evident with PC 068. Moreover, the unique capabilities of PC 068 become quite apparent by combining the results from Figures 10, 11, and 13, where the SCC mixture admixed with PC 068 exhibits the most significant increase in thixotropy as a function time, relatively low viscosity, and the least changes in column segregation and viscosity when the sand moisture is increased versus superplasticizer PC 059.

The T_{50} and V-funnel results were found to correlate well with plastic viscosity (Figures 12 and 13), which in turn corresponded with the thixotropy of the SCC mixtures (Figure 14). Furthermore, the intentional variations in sand moisture were most evident in plastic viscosity, T_{50} , and V-funnel times (Figures 15 and 16), which indicates that the T_{50} and V-funnel tests would seem to be quite effective in identifying unexpected batch-to-batch moisture variations.

CONCLUSIONS

The inherently low yield stress and viscosity of SCC mixtures, along with its more complicated mix design, place an enhanced critical importance on the role of robustness for successful production/use of SCC. Establishing a “Workability Box” and understanding the sensitivity of mix proportions, especially water tolerance, is a key approach to improving the robustness of SCC mixtures. Critical test parameters for defining the limits of the workability box are yield stress and viscosity. Careful selection of the appropriate chemical admixtures and test protocol is required for robust production of SCC mixtures. PC o68 clearly demonstrates preferred performance in terms of the critical requirement for good moisture control. The higher values for static yield stress and thixotropy, inherent with PCo68, is expected to allow SCC mixtures with this HRWR to have a larger “workability” box, or range of allowable yield stress and viscosity, with which stable SCC mixtures can be produced and placed.

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Table 1—Mixture proportions to evaluate moisture tolerance of SCC mixture

	Batch wt., kg/m ³
Cement	418
Sand	855
Stone 1, 16 mm	270
Stone 2, 10 mm	625
Water	181
W/C	0.43
PC o68	0.22% s/s*

Notes: Moisture tolerance was evaluated by incremental addition of 10, 20, 25, 30, and 40 l/m³.
Admixture dosage is expressed as % admixture solids by weight of cement.

Table 2—SCC mixture proportions for evaluating rheological performance of PC o68, PC o59, and PC 915

	Batch wt., kg/m ³
Cement	418
Sand	855
Stone 1, 16 mm	255
Stone 2, 10 mm	590
Water	209
W/C	0.50
PC o68	0.22% s/s

Note: Rheological properties were measured before and after adding an increment of water equivalent to 2% of mass of sand.

Table 3—Chemical composition of portland cement, % by mass

Compound	#078 Cement
SiO ₂	20.84
Al ₂ O ₃	4.45
Fe ₂ O ₃	3.08
CaO	62.88
MgO	3.46
SO ₃	2.91
Alkali as Na ₂ O	0.58
LOI	1.54
C ₃ S	53
C ₂ S	20
C ₃ A	7
C ₄ AF	9
C ₃ A/SO ₃	2.4
Fineness blaine cm ² /g	3940
% Retained 45 μm sieve	5.33%

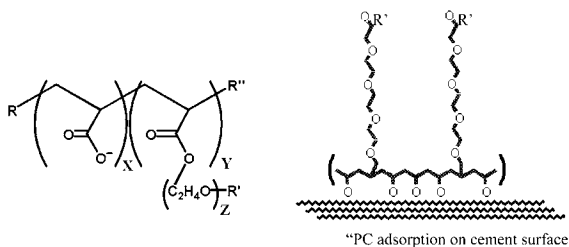


Fig. 1—Key structural attributes of polycarboxylate-based superplasticizers, where X, Y, and Z can be optimized for SCC mixtures.

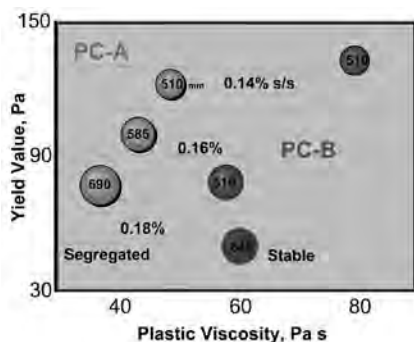


Fig. 2—Impact of PC structure on rheology of SCC. Mixture proportions are identical (445 kg/m³ cement, $w/c = 0.39$) except for the type of comb polymer (superplasticizer PCE A vs. PCE B). Admixture dosage expressed as % admixture actives by mass cement.⁶

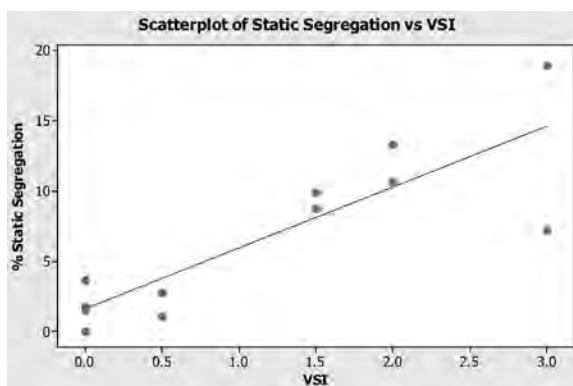


Fig. 3—Correlation of VSI with percentage static segregation.

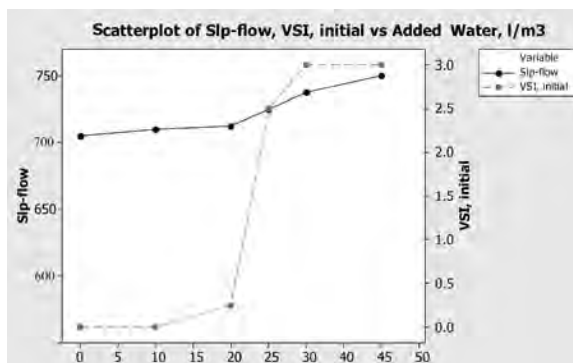


Fig. 4—Slump-flow and VSI as a function to water addition.

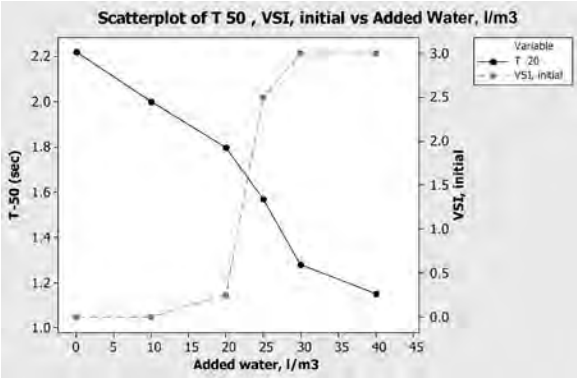


Fig. 4—Slump-flow and VSI as a function to water addition.

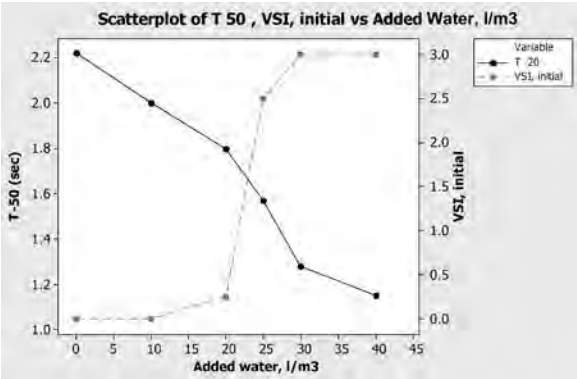


Fig. 5—T50 and VSI as a function to water addition.

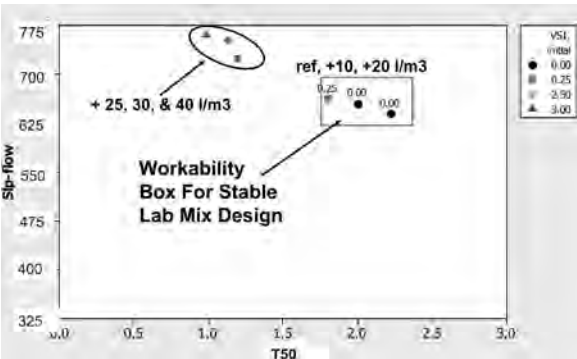


Fig. 6—Workability box for moisture tolerance.

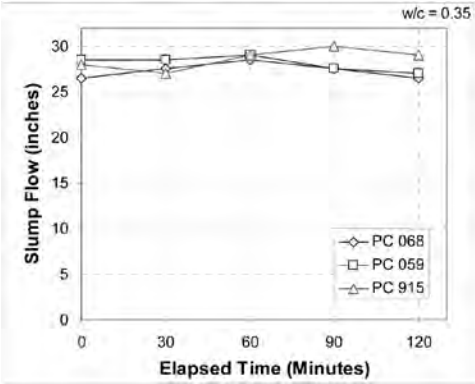


Fig. 7—Slump-flow as a function of elapsed time.

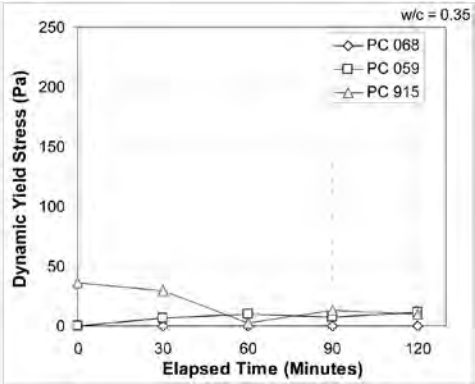


Fig. 8—Dynamic yield stress as a function of elapsed time.

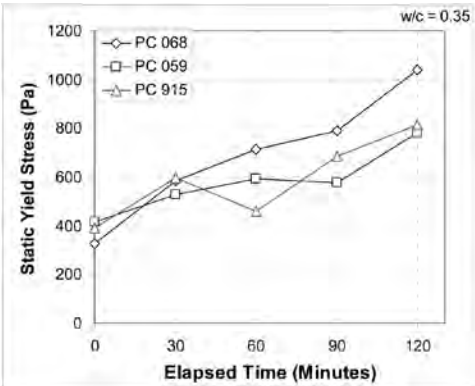


Fig. 9—Static yield stress as a function of elapsed time.

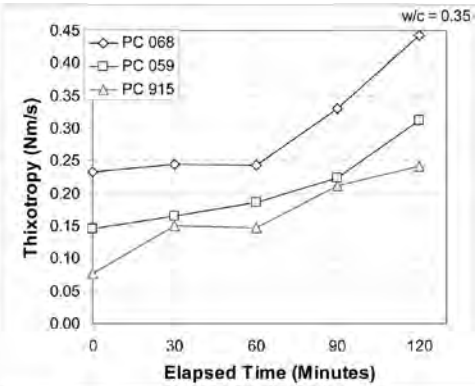


Fig. 10—Thixotropy as a function of elapsed time.

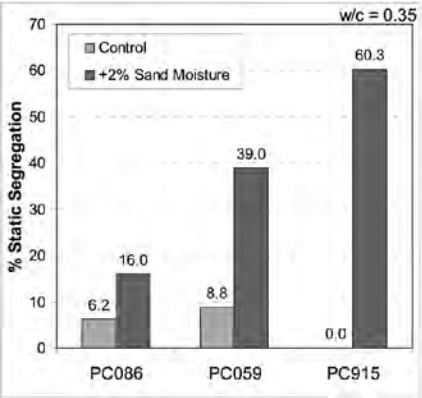


Fig. 11—Column segregation as a function of change in sand moisture content.

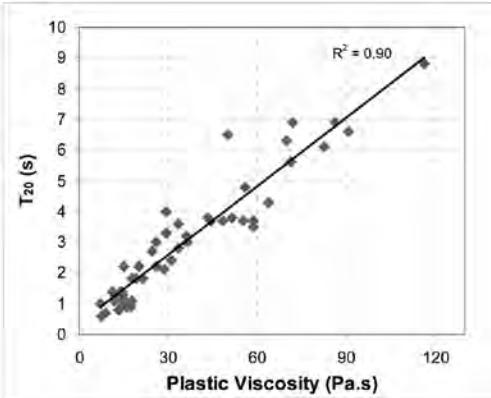


Fig. 12— T_{20} as a function of plastic viscosity.

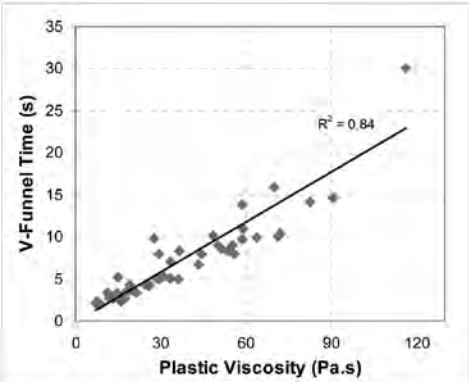


Fig.13—V-Funnel time as a function of plastic viscosity.

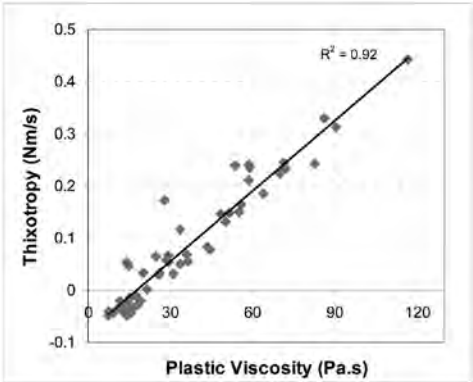


Fig. 14—Thixotropy as a function of plastic viscosity.

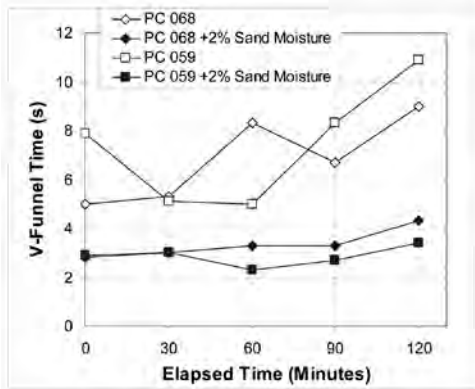


Fig. 15—Effect of change in water content on V-funnel times.

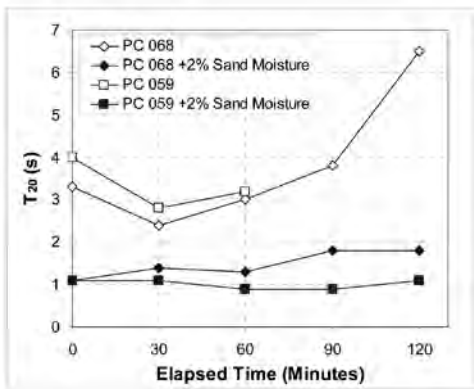


Fig. 16—Effect of change on water content on T_{20} .

Polycarboxylate and Polyether Admixture Compatibility with Different Cement Compositons

by M.M. Alonso, F. Puertas, and M. Palacios

Synopsis: The use of polycarboxylate (PC)- and polyether (PE)-based superplasticizers often generates segregation, inadequate flowability or similar problems due to the incompatibility between the cements and admixtures used. In light of the widely varying composition of these admixtures, not all cement- and superplasticizer-related factors which could affect compatibility have been defined to date. In this study, therefore, rheological trials were conducted with a rotational viscometer and adsorption tests were conducted in a total organic carbon (TOC) analyzer to explore the compatibility between different PC - PE admixtures and cements employed in a variety of compositions and additions.

Three admixtures (PC₁, PC₂, and PC₃) with different carboxylate (CA) and polyether (PE) group contents were used, along with seven standard cements whose chemical and mineralogical compositions and active additions varied.

The structural characteristic of the admixtures affecting compatibility most intensely was found to be the carboxylate (CA) to polyether (PE) group ratio. In cements with no active additions, characteristics such as fineness and the C_3A to calcium sulphate and C_3S to C_3A ratios were also observed to have marked effect on compatibility. On the other hand, in cements with limestone or fly ash additions, no fundamental differences were identified with respect to a standard CEM I 42.5R cement in terms of admixture compatibility.

In calcium aluminate cement (CAC) the fluidizing effect of polycarboxylate superplasticizers led to very significant declines in yield stress.

Keywords: adsorption; compatibility; portland cement; rheology; superplasticizers.

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INTRODUCTION

For some years now, organic admixtures, along with cement, water and aggregate, have become a basic component of concrete. Ninety per cent of all concrete prepared in Europe are estimated to contain some admixture, and 70% of these are plasticizers or superplasticizers. The use of superplasticizers has revolutionized concrete technology in essentially two ways:¹⁻³ enhancing workability and reducing water content by up to 40%, and producing mixtures with improved mechanical properties and better durability.

Up until the late 1990s, the superplasticizers most commonly used were based on melamine or naphthalene derivatives. The development of polycarboxylate (PC)-based superplasticizers has largely eclipsed such conventional admixtures, because of the versatility of the new formulas and the improvements in concrete properties that their use entails.

Polycarboxylate admixtures are characterized by a “comb”-like structure⁴ in which the backbone is a linear chain of carboxylate groups with lateral ether groups. Their adsorption onto cement particles, mediated by their carboxylate groups, induces cement grain dispersion as a result of both the electrostatic and especially the steric repulsion generated by the long ether group chains.⁵⁻⁶ More recently, admixtures with shorter backbones and longer polyether (PE) chains have been synthesized.⁷

Nonetheless, the use of superplasticizers may encounter obstacles associated with variations in flowability, uncontrolled setting, rheological behaviour and so on, which are due in most cases to cement-admixture incompatibility. A number of authors⁸⁻¹² have provided detailed descriptions of the effect that of factors associated with cement and conventional superplasticizers admixtures such as SMF and SNF that could affect cement-admixture interaction. The main cement-related factors of relevance are found to be fineness and composition of the cement. It is important to note that the cement composition covers not only the type and content of aluminates or silicates, but also the amount and type of calcium sulphate and alkaline sulphates present. Moreover, the use of a cement substitution, be it blast furnace slag, fly ash, silica fume, limestone, or other fillers, can modify paste flowability and rheology, because of the

particle size and morphology differences with respect to portland cement. At the same time, reactions taking place parallel to portland cement hydration may alter the $\text{SO}_4^{2-}/\text{C}_3\text{A}$ /superplasticizer equilibrium, and with it, admixture adsorption. The factors that determine admixture behaviour and its fluidizing effect, in turn, are the dosage, the manner and addition time, and chemical and structural composition of the admixture.

The wide variety of designs in PC- and PE-based admixtures, however, has led to lack of complete understanding of factors associated with admixtures and the way they affect both paste microstructure¹³ and cement-admixture compatibility. In particular, little is known about the effect of the relationship between carboxylate (CA) and ether (PE) groups, and the length and density of the ether side chains. Certain authors¹⁴ have reported that the higher the carboxylate group content in the admixture, the greater is the adsorption: therefore, the longer the main chain, the more effective is the adsorption. In addition, the greater the number and the longer the lateral polyether chains, which are responsible for the steric effect, the greater is particle dispersion in the mix.⁴

According to Winnefield et al.,¹⁵ however, in admixtures consisting in short lateral polyether chains, the fluidizing effect induced does not depend on the proportion of these chains. On the contrary, in compounds with medium or long lateral chains, the smaller the number of lateral chains, the greater is the increase in flowability generated by the admixture in cement pastes. Furthermore, not only admixture structure, but molecular weight and distribution of molecular weights have an effect on compatibility issues. Magarotto et al.¹⁶ noted that the higher the molecular weight, the greater was the adsorption and induced flowability, whereas flowability was greater when the molecular weight were not widely distributed.¹⁷

Lastly, at this time accurate scientific knowledge is lacking regarding the mechanism involved in PC and PE admixture action and compatibility, particularly when used with cements with different chemical and mineralogical compositions that contain varying proportions of additions of different nature. The purpose of the present paper is to determine the compatibility between differently structured PC and PE based admixtures and cements having different mineralogical compositions and fineness, via rheological and adsorption studies.

EXPERIMENTAL

Materials

Seven standardized Portland cements were used:¹⁸ (a) CEM I 42.5R with 95-100% of clinker; (b) CEM I 52.5R with 95-100% of clinker, but with higher Blaine fineness than CEM I 42.5R; (c) CEM I 52.5N/SR, sulphate resistant with a C_3A content between 5-8%; (d) BL I 52.5R type I cement, with the additional whiteness characteristic ($L^* \geq 85.0$)¹⁸; (e) limestone-blended cement CEM II/BL 32.5R, with 21-35% limestone; (f) fly ash-blended cement CEM II/AV 42.5R, with 6-20% fly ash; and (g) calcium aluminate cement, CAC 32.5R, whose mineralogical composition differed significantly from the others and whose main mineralogical phase was monocalcium aluminate.

The trials were run on the seven cements, whose chemical composition and specific surface as determined with the Blaine method¹⁸ are given in Table 1. Table 2 shows the mineralogical composition found by Rietveld analysis,¹⁹⁻²⁰ along with the amorphous material content in some of the samples. Table 3, in turn, gives the particle size

distribution of the seven cements used. Lastly, the physical-chemical characteristics of the three polycarboxylate/polyether superplasticizer admixtures, with different carboxylate (CA) and polyether (PE) group contents, are listed in Table 4. The functional group estimates were found using the methodology described in the literature.²¹⁻²²

Physical-chemical and structural characterization revealed that PC1 is a PC admixture with a long carboxylate main chain, small lateral ether group chains and a CA to PE ratio of 0.656. Conversely, PC3 had a short main chain, with very few carboxylates, and long lateral chains for a CA to PE ratio of 0.057. PC2 occupied an intermediate position, with a CA/PE value of 0.240. The structures proposed for these admixtures are given in Figure 1.

Tests conducted

Rheological behavior—Pastes were prepared from the different cements, with the water-cementitious materials ratios given in Table 5 to conduct the rheology tests. Yield stress was evaluated using a Haake Rheowin Pro RV1 rotational viscometer fitted with a grooved cylindrical rotor.

The cement paste was prepared with a sample of 100 g (0.22 lb) of cement and the amount of liquid needed to obtain the liquid/solid ratio specified in Table 5. The paste was stirred for three minutes with a blade stirrer. Admixture dosages were 0.1 and 0.3% by mass of cement, which correspond to 2.32 and 6.97 mg of polymer/g of cement for PC1 and 2.5 and 7.5 mg of polymer/g of cement for PC2 and PC3. Admixtures were introduced at the same time as the mixing water.

The pastes were subjected to a rheological test consisting on pre-stirring at 100 s^{-1} for one minute to ensure full dispersion. The rotor speed was then reduced to 10 s^{-1} and then steadily increased to 100 s^{-1} over 2.5 minutes and finally reduced in the same period of time to 10 s^{-1} .

Admixture adsorption curves in cement paste—Twenty grams (0.044 lb) of cement and 40 g (0.088 lb) of a solution containing polycarboxylate-based admixture were mixed and stirred for 30 minutes at $25\text{ }^{\circ}\text{C}$ ($77\text{ }^{\circ}\text{F}$) to determine the adsorption isotherms for PC1, PC2 and PC3 admixtures. The suspensions were subsequently ultra-centrifuged, and the liquid phase was siphoned off. The total organic carbon content was found with a total organic carbon (TOC) analyzer (SHIMADZU model TOC-VCSH/DSN). The amount of admixture adsorbed by the cements studied was considered to be the difference between the initial amount of admixture and the residual amount present in the liquid phase measured by TOC. At high polymer concentrations, a layer of white admixture was observed on the surface of the cement, due to admixture precipitation. In light of this, successive centrifugation and water rinsing operations were performed to extract this layer of admixture. These dilutions were taken into account in the adsorption calculations.

RESULTS AND DISCUSSION

The results and their interpretation are presented here from the standpoint of the differences inherent in the seven investigated cements (different fineness, C_3A and calcium sulphate content, mineral additions and mineralogical composition, refer to see Tables 1, 2, and 3).