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Conference Report

RILEM International Symposium on the Role of Admixtures in High Performance Concrete; Monterrey, Mexico, 21–26th March 1999

The RILEM International Symposium on the Role of Admixtures in High Performance Concrete took place in Monterrey, Mexico, from 21–26th March 1999. It was organized by the RILEM Technical Committee TC-158 AHC (Admixtures for High Performance Concrete), The Civil Engineering Concrete department at the University Autonoma de Nuevo Leon (UANL) in Mexico and the Civil Engineering Materials Unit (CEMU) at the University of Leeds, UK. Forty papers from fourteen countries are included in the proceedings, published by the RILEM Publications s.a.r.l., France; 30 papers were presented at the conference out of which 6 were key note papers. The conference was divided into seven sections. The themes covered were; Cement–Concrete–Chemical Admixtures Interaction, New Molecular Structure of Chemical Admixture, Corrosion Protection, Frost Resistance, Abrasion Resistance, Rheological Effects and Engineering properties.

Cement–concrete–chemical admixture interaction: High performance concretes (HPC) generally have high cementitious materials. It causes difficulties in obtaining good workability and in its homogeneous dispersion. This problem is solved by using water reducing admixtures. Concrete made with high cementitious material and low water to binder ratio may show early age cracking. It occurs due to the loss of workability and the very quick drying at the open surface caused by the dual effects of lack of bleeding, and the lack of bleed water to move up to the surface. High heat of hydration is another major factor causing thermal cracking with high cement concrete. It is reported that slag reduces the temperature rise during hydration, and can be designed to give early high strength to the concrete. However, a combination of high range water reducer and fine grounded slag significantly improves durability properties and strength development.

Influence of cement type on superplasticizing admixture: It is now recognized that superplasticizers (SP) behave differently with the same cement and different cements behave differently with the same superplasticizer. These are also known as high range water reducers, fluidifiers, plasticizers etc. The various superplasticizers available are neither equivalent in their chemical characteristics nor in their functional properties. Even if the superplasticizer meets standard specification, it does not mean that they are the same. The standard specification only defines minimum or maximum values of certain parameters so that a particular SP may meet the minimum standard, while the other may exceed this minimum specification by a large margin.

The behaviour of superplasticizers with different cements mainly depends upon the sulfate minerals in the cement and cement clinker. The type of sulfate in the cement has a major effect on viscosity and yield. It is reported that the anhydrite gives substantially greater yield values than gypsum. The type of SP has influence on the workability of cement paste. For example, SNF makes the paste more workable than SMF followed by LS. Influence of variation in the composition of clinker mineral and SP is elaborated by the following example:

Cements which varied in the clinker composition, C_3S, C_2S, C_3A, C_4AF and in fineness were tested with the superplasticizers synthesized in the laboratory (methacrylic water soluble polymers, MSPs). Their molecular weight varied between 37 000 and 43 200. Comparison was done with β-naphthalene-based polymer. Cements used were, Low heat Portland cement L1, belite rich Portland cement L2, Normal Portland cement N, and early High strength Portland cement H. Their specific surface area was 3350, 4080, 3250 and 4340, respectively).

It is reported that the apparent saturated adsorption of MSPs was significantly lower than that of NSF, and MSPs with longer polyethylene graft chains led to the lower adsorption. This may be because MSPs with graft chains form a bulky, stereostructural layer when adsorbed by cement particles. This is in contrast with the NSF, a copolymer in the shape of stiff chains, forming a flatter layer on cement particles. In other words, MSPs are considered to produce strong steric repulsion (entropy effect), rather than electrostatic repulsion, by being adsorbed by cement particles and forming a barrier, which provides an excellent cement-dispersing capability. It is also shown from the exothermic rate curves of cement pastes made with Portland cement and a constant dosage of MSPs that the longer the POE chain, the weaker is the set retarding effect on hydration.

Flow values of cement paste made with normal Portland cement and MSPs at *W/C* ratio 0.30 were

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similar. But when the *W/C* decreased to 0.25 and 0.20, the differences between the cement dispersing capabilities of MSPs became significant. Polyoxyethylene with the longest chain showed the highest dispersing capability. Further it is reported that it needs lower dosage of MSPs compared to NSF for good cement dispersion. With the use of MSP1 and MSP3, the fluidity of cement L1 was the highest followed by N and H. It was observed that at $W/C = 0.50$, the fluidity retaining capability of polymers with shorter graft chains is higher than that of the polymers with longer chains. However, the differences are narrowed in the range of low *W/C* ratio. MSPs impart the highest fluidity to low heat cement followed by normal cement and high-early strength cement. In the low *W/C* range, low heat cement requires lower dose of MSP than normal cement. This curbs the adiabatic temperature rise of concrete without retardation in setting. It is concluded that MSP3 and low heat cement used in combination make possible the production of high performance concrete having high fluidity, low heat of hydration, and high strength. Further it is reported that the incompatibilities of cement/superplasticizers can be overcome by the use of high molecular weight SP for normal alkali cement. For low alkali cements the use of a SP having a high residual sulfate content improves the rheology with time and decreases the SP dosage.

The time at which the SPs are added also plays an important role. It is reported that the differences of flow of cement paste with NS and AS between simultaneous addition and later addition were larger than those with PC and LC. Particularly, the flow of cement paste with NS added by later addition was larger than that added by simultaneous addition. For coarsely ground cements having a low C_3A content, a small amount of a viscosity enhancing agent such as Welan gum is recommended to prevent bleeding and segregation in high slump concretes. In such cases higher dosage of SP can be used to have better rheological properties.

Fluidity and temperature: The fluidity and the setting time are influenced by the ambient temperature. It is reported that an increase in the ambient temperature leads to an increase in the fluidity of cement paste over the range 5–45°C. However the saturation dosage of the SP is not affected by the change in the temperature. This confirms that the adsorption of SP molecules on the cement particles depends on the surface area and once this surface area has been covered, any further increase in the dosage does not lead to an improvement of the fluidity. Further it is reported that the copolymer of oxyethelene–oxypropelene is more effective than the SNF, since the former acts principally by generating a repulsive force between the cement particles through steric hindrance as a consequence of the adsorption of the large molecules that prevent the proximity between the cement particles, while the latter acts due to the electrostatic repulsion due to the electrical charge of the adsorption layer.

The water demand of cement at normal paste consistency increases with temperature and decreases with the incorporation of SP. This decrease occurs until a certain dosage beyond which the water demand is practically constant. It is the same for all temperatures. SP leads to the retardation of the setting process which increases significantly with the increase in SP dosage up to the saturation point.

The slump of concrete is also very much influenced by the ambient temperature. It is reported that the slump loss of mixes prepared at 30°C/40% RH was faster than those prepared at 20°C/65% RH. The setting time was also influenced by increase in the temperature. However the presence of SP resulted in extended setting time, compared to the reference mixes. Bleeding has been reported less in dryer exposure conditions than at 20°C/65% RH. Concrete containing SP gained more compressive strength than the reference mixes. Mixes containing SP had lower capillarity and lower total water adsorption than the control mixes. This difference was more pronounced at higher temperature.

Mechanism of interaction of SP with cement: Commercially known superplasticizers are; sulfonated naphthalene formaldehyde condensates, sulfonated melamine formaldehyde condensate, and alkali salts of lignosulfonates. New SPs based on polycarboxylic acid, and aminosulphonic acid which are developed were discussed in detail.

Polycarboxylic acid based admixtures (*PC*): There are two types of PC; (i) Those containing mainly copolymers of unsaturated chain hydrocarbon olefins with carboxylates including maleic acid (CHOOC–HC–CH–COOH): admixtures composed of copolymer of olefin with maleic acid, however have limited water reducing ability. Therefore it is not widely used at present but the admixtures composed of acrylic acid with acrylic ester occupy the position of the popular high range water reducer, (ii) This includes a copolymer of an acrylic acid ($CH_2{=}CHCOOH$) with acrylic acid ester with many ester bonds (–C–O–C–) in the side chain forming so called graft polymer. This structure increases the steric repulsive force and contributes to the dispersion of solid particles. Recently a new type of admixture composed of water soluble methacrylic polyethylene graft polymers containing both carboxyl groups and sulfone groups is developed. However the slump loss using this admixture is extremely small though the range of dosage without separation of material is narrow.

Amino sulfonic acid based admixtures (*AS*): AS is a three dimensional polycondensation product of an aromatic aminosulphonic acid with trimethyl phenol.

The mechanism of interaction of superplasticizers with cement is a complex process. However adsorption of SP on the solid particles is thought to be mainly responsible for dispersion of cement. These form an adsorption layer on the solid surface. The adsorption in the water medium depends upon the kind of solid particles including cement compounds, blending components, cement hydrates and the type and molecular weight of the polymer.

The motive force for the adsorption of the admixture to the surface of the cement particle includes van der Waals force, the electrostatic forces by the ion exchange, formation of ion pair and polarization of -electron, the hydrogen bonds of atoms in the admixture with the atoms on the surface of cement particles, formation of complexes with Ca-atoms on the surface of cement particles and the hydrophobic bonds with cement particles by the affinity of the hydrophobic group in the admixture. It has been reported that the mechanism of the adsorption of the admixture by the cement hydrates in addition includes the substitution of the OH groups in the cement hydrates for sulfonic acid and carboxylic groups in the molecule of the admixture, and the entering of the admixture between the layers of the hydrates with laminated structure.

Adsorbed amounts of admixture to cement compounds, blending components and cement hydrates: The adsorption is different on different clinker minerals. It is more on C_3A, C_4AF and CaO compared to those on C_3S, C_2S etc. This subsequently depends upon the type of cement and the type of SP used. It is generally in the following order: NS = AS > PC > LS.

Since calcium sulfates and alkali sulfates contained in cement are rapidly dissolved in the liquid phase in the form of SO_4^{2-}, the ion adsorption of an admixture containing a sulfonic acid group to the interstitial material is decreased and the calcium concentration increases. The dispersion of the solid particles depends upon the interactive force between cement particles coexisting with organic admixture which depends upon the distance between them, and is related to the interactive energy.

Influence of the type of admixture on the morphology of hydrates: Besides influencing the dispersion process of the solid particles, SP also influences the hydration process. It is reported that at 0.27 *W/C* the Ettringite (Aft) crystals are of the same dimension as in the case without SP. After 2 h the crystal size became a little larger but have the same morphology. At the age of three days the type III C–S–H crystals produced at the surface of unhydrated cement particles are about 0.2–0.3 mm while the large crystals of $Ca(OH)_2$ are not seen. On the other hand, the equidimensional irregular Aft crystals of the size as large as 0.2–0.3 mm are observed in the case of NS after 5 min. After 2 h the structure of the hydrates is similar to the one produced after 5 min. After three days the surface of the unhydrated cement particles is covered with type III C–S–H crystals; their agglomerates and large crystals of CH are not seen. With the increase in the water to cement ratio, the crystals of hydration products including Aft, C–S–H and CH are enlarged, and the surface of unhydrated cement particles becomes almost covered with type I C–S–H crystals. The crystallinity is improved.

Mechanism of change in performance of fresh concrete by cements: The rapid decrease of fluidity and increase of slump loss with time often observed in the fresh concrete using admixture are not clearly understood. It is reported that the depositing time and amounts of ettringite (Aft) and monosulfate (Afm) in the early stages of hydration of cement and the thickness and density of the adsorption layer of admixture on the surface of the cement particles and cement hydrates are responsible for change in the performance of concrete in the early stage. Aft gives stronger influence on stiffening than Afm because of its morphology and produced amounts in the early stage of hydration.

Production of Aft is more accelerated by calcium sulfates than alkali sulfates. Na_2SO_4 gives higher acceleration effect than K_2SO_4 although the morphology of Aft varies according to the kind of admixture used and water to cement ratio. The small crystals produced during the hydration with the use of SP increase the specific surface area of hydrated cement.

SO_4 concentration in mixing water of fresh concrete in the initial stage is higher when the cement contains great amounts of hemihydrate, particularly β-form and alkali sulfates. In the case, SO_4 is preferentially adsorbed and combined with the interstitial material of cement forming Aft and reducing the adsorption of the admixture. As a result, repulsion by the adsorption of admixture to the cement particles and cement hydrates is reduced and large amount of Aft is produced, causing rapid decrease of fluidity and the increase of the slump loss with time.

In the PC, COOH is located on the outer side of the polymer and thus have good possibility to come into contact with the cement particles and cement hydrates. On the contrary, in general cases the calcium sulfates and alkali sulfate coexist; the COOH group is embedded in the inner side of polymer because alkali sulfate decrease the polymer rotation radius, that is the spread of the polymer. Therefore the opportunity for the COOH group to make contact with the cement particles and cement hydrates is decreased. Consequently, the adsorbed amount and thickness of the adsorption layer of polymer is remarkably reduced and the steric hindrance of the adsorbed admixture is weakend. This brings depression of cement particles and cement hydrates. This decreases the fluidity.

The influence of molecular weight of Polynaphthalene sulfate (PNS) SP on the rheological behavior of cement pastes depends on alkali content in cement. It is reported that molecular weight PNS is more effective in fluidizing pastes made with high alkali cements than low molecular weights PNS. However PNS molecular weight has little effect in fluidizing pastes made with low alkali cement. The adsorption is much more with low alkali cements than with high alkali cements. In high alkali cement, the addition of PNS SP initially retards cement hydration in the first few hours then accelerates it. The differences in the molecular weight of PNS SP do not appear to significantly affect cement hydration in high alkali cement. In low alkali cement, the induction period is increased by the addition of low molecular weight PNS, but not by the addition of relatively high molecular weight PNS.

Corrosion Inhibitors: Corrosion inhibitors discussed were: calcium nitrates (CN) and calcium nitrites (CNi), lithium and a penetrating inhibitor. CN and CNi are to be mixed with the concrete whereas the penetrating inhibitor (a modified amino alcohol) and lithium nitrate are to be applied on the surface after the concrete is ready. It means that even if the concrete is old and have shown reinforcement corrosion, this can be applied upon the surface to protect the concrete from further damage. It is reported that the use of CNi is harmless and improves the resistance against corrosion. In the case of good quality concrete. It seems to be effective even in the region of cracks with a crack width of 0.3 mm. It is further reported that the CNi decreased the slump and setting time of the fresh concrete and increases the compressive strength.

The concrete surface applied with amino alcohol inhibitor decreased the corrosion rate of corroding bars. It is reported that the time to achieve a significant reduction in corrosion current increased with increasing depth of cover of concrete and quality of concrete. The presence of admixed CNi produced delay between the application of amino alcohol inhibitor and the point at which the corrosion rate first decreased. The effect was biggest at high quality concrete. However the time from the surface application to the corrosion current reaching 0.1 mA/m^2 was independent of the presence of the calcium nitrite.

In another paper it is reported that CN can work as a multifunctional admixture for high performance concrete. It has been demonstrated that it posses the properties which enable its use as: (i) a set accelerator, (ii) a long term compressive strength enhancer, and an anodic corrosion inhibitor for the reinforcing steel in concrete. In addition to this CN can be used as a major component in anti-freeze admixture for concrete. Use of some other inhibitors like DCI-S giving resistance to the reinforcement corrosion have also been reported.

It is further reported that besides improving the resistance to the reinforcement corrosion, impregnation with $LiNO_2$ of the concrete significantly improves resistance to the alkali silica reaction.

Freeze–thaw resistance: Mechanism of freeze–thaw resistance of concrete was discussed and some theories have been put forward. It was emphasized that besides the bubble spacing factor of 0.2 mm, there are some other factors also to be considered such as the thermal behavior and compatibility of aggregates, rate of cooling etc. Besides the material properties and the pore size distribution, the mechanical properties of the concrete are also important. These depend very much upon the curing conditions and the type of cement used to make the concrete. It is reported that the concrete to be tested for freezing should have a strength of 28 MPa

The chemical admixture like air entraining agents, superplasticizer and corrosion inhibitors often are not compatible and hinder each other influence. This hinderance is more pronounced with the use of supplementary cementing materials like silica fume, fly ash and blast furnace slag. It is reported that the NSF based HRWRA has a tendency to decrease the air content in concrete. None of these specialty admixtures cause a synergistic effect with low dosage of AEA. At an intermediate dosage of AEA, in the absence of HRWRA, some of these admixtures tend to entrain more air while others detrain air. Very similar results are obtained when the combination of specialty admixtures were used.

It was emphasized that the dosage of AEA needs to be increased by 150–300% to obtain 4–6% air entrainment in the presence of HRWRA. Phase mineralogy of cement appears to have no distinctive effect on air entrainment, and the above conclusions are valid even for the cement containing high C_3A, high alkali cements and plain cement concrete without fly ash. Microstructure studies did not show any distortion in the shape of air voids, but the size varied from one concrete mixture to the other, with the air voids tending to grow coarser in some mixtures. Concentration of air voids at the paste-aggregate interphase can occur in some concrete with high air content.

Abrasion resistance: Abrasion can be defined as the separation of particles when an object slides or moves over the surface of another creating friction. It depends on the speed of movement and the weight of the object moving. It is reported that in the case of fluid concrete, addition of densifying agent (DA) eliminates the formation of hydroxide dust over the surface. Superplasticizer addition produces a concrete with higher abrasion resistance compared to the reference. Further, it is reported that in fluid concrete when DA was used at $W/C = 0.50$ the abrasion resistance noted was the same as for the concrete made with a $W/C = 0.35$. Furthermore a concrete with SP and DA cured for three days had the same abrasion resistance as the concrete made without admixtures after 28 days. Fluid concrete fabricated with SP has shown similar abrasion resistance to that of the same concrete without admixture with the advantage that the concrete can be made with less amount of cement and increase the workability. With the use of carboxylic ether superplasticizers concrete of very high strength and very high abrasion resistance can be produced.

Efflorescence: Some times concretes made with the addition of sulfonated naphthalene or melamine condensate superplasticizers show white or yellow spot. It is known as efflorescence and is thought that it appears from the use of superplasticizers. It creates some uneasiness among the producers of superplasticizers. The efflorescence is caused by the formation of calcium salts, sodium sulfate (thenardite) and potassium sulfate Aphthitalite (Glaserite). Calcium efflorescence appears when the cement used is rich in alite C_3S and concrete is fluid. With the evaporation of water, the wide spread lime base efflorescence appears on the surface and may cause problems. In the case when the alkali content is high and the NaOH/KOH ratio is high, thenardite efflorescence can appear. Thenardite crystals expand by absorbing water and may cause peeling off. The efflorescence observed with the use of superplasticizers is different than appearing due to the crystallization of calcium and sodium salts. Crystals formed on the surface are localized and spotty. It is reported that these crystals do not reduce the compressive strength of the concrete and can be washed away. Nevertheless addition of 1% cumene sulfonate to melamine sulfonate reduces the formation of Glasserite. Reducing of bleeding by the addition of mineral additives is another alternative to reduce efflorescence. The efflorescence caused by the superplasticizers even though is not deleterious, it is advisable to avoid the use of high alkali cement.

Functionality of SP: Functionality of concrete can be enhanced by retarding the setting time of fresh concrete and to retain the slump for a long time. It will enable long transportation of fresh concrete without change in their properties. It is reported that by the use of gluconate SPB (polycarboxylate type) as a superplasticizer, slump can be maintained for 3–4 days. These do not adversely effect the compressive strength of concrete and the final setting time. It is further reported that compared with the four superplasticizers based upon aminosulfonate type (SPA) naphthalene sulphonate (SPC) type and melamine sulfonate type (SPD), the percentage of SPB remaining in the liquid phase is highest followed by order SPA, SPD and SPC. This agrees with the order of high slump retention of mortar. Higher the percentage of superplasticizer in the liquid phase higher will be the slump retaining power for long time.

Engineering properties: Superplasticizers or high range water reducing admixtures have led to the development of very low water to cement ratio; high strength, high performance concrete both for new construction and for repair; rehabilitation of deteriorated infrastructure. Innovative concretes have been developed of superplasticized high performance concretes containing high volume fly and slag, ultra high strength concrete incorporating silica fume, fiber reinforced concrete, heavy weight and lightweight concretes, rice husk ash and meta kaolin concretes, low heat, high performance concrete and reactive powder mortars. Besides new construction, it is reported that the use of superplasticized silica fume concrete performs better as a repair material as it provides higher strength and lower shrinkage.

Mixing technique: Mixing technique also plays an important role on the properties of concrete made with SP. The concretes with superplasticizers and PFA and micro silica made with two stage mixing technique is reported to have better strength and durability properties. It is attributed to the decrease in transition zone, the weakest point between the aggregates and the cement paste. It is further reported that the settlement of the coarse aggregates becomes negligible. Besides the non-segregating characteristics noted, SEC concretes have high workability than conventionally made concrete with the same overall water/cement ratio. Microstructure analyses have shown smaller pore size distribution of the paste at 28 days in addition to the continuous and dense structure. Calcium silicate hydrates are enriched with small homogeneous calcium hydroxide crystals well attached to the glassy side.

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