SP 195-1

Trends in Concrete Chemical Admixtures for the 21st Century

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Synopsis: Chemical admixtures play a central role in modern concrete materials and technologies. In conjunction with mineral additives such as silica fume, chemical admixtures have enabled major improvements in many of the properties of concrete, particularly, compressive strength and durability. Chemical admixtures have also assisted in developing new concrete technologies, for example, concrete pumping and self-leveling, underwater concreting and shotcreting. Chemical admixtures have further promoted the use of secondary industrial materials (blast furnace slag and fly ash) in cementitious systems, contributing to resource conservation and environmental sustainability. In the continuing quest for more cost-efficient and environmentally acceptable materials and technologies, it may thus be expected that chemical admixtures will continue to play an important role in future generations of concrete.

Probing into the future, how will concrete chemical admixtures evolve in the coming decades? What trends can be anticipated in future developments and use of these admixtures? What will be the driving influences for these developments?

This paper addresses some of the issues that are considered relevant driving forces to promote changes in the use of currently available chemical admixtures, or in the development of new admixtures. The trends already apparent in cementitious materials and concrete applications provide a reasonable basis for proposing probable trends in the evolution of concrete admixtures into the 21st Century.

Keywords: admixture (water-reducing); admixtures; concrete

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INTRODUCTION

Modern concrete materials and applications have come to rely strongly on chemical additives both, to enhance the properties of the fresh or final materials, and to broaden the scope of concrete technologies and applications. Currently, quality concrete, and more so high-performance concrete (HPC), contain several chemical admixtures selected from the following partial list, and added individually or as pre-formulated combinations (in addition to clinker grinding aids frequently used in the cement production process):

- set modifier: retarder or accelerator
- water reducer
- superplasticizer (high-range water-reducing admixture)
- air entraining agent
- corrosion inhibitor
- alkali-aggregate reaction control
- shrinkage-reducing, or shrinkage-compensating admixture
- anti-bleeding, -segregation or -washout admixture
- anti-freeze additive
- defoamer

As amply demonstrated elsewhere (1-5), each of these types of admixtures has shown specific benefits. Used in appropriate combinations, they have enabled, first, to meet with increasingly stringent demands on concrete strength and durability, and second, to promote greater use of secondary industrial products as supplementary materials. However, recognizing the inherent composition variability of cementitious binders, and the fact that each family of chemical admixtures comprises a variety of different chemical compounds, the

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combined use of several types of chemical admixtures greatly increases the chemical complexity of the cementitious system. This has several immediately obvious consequences:

- the design and preparation of concrete mixes must increasingly rely on adequate chemical information on the system;
- the probability of occurrence of chemical "incompatibility" situations will be greatly increased.

In such a context, what trends can be anticipated in future requirements and in applications of concrete chemical admixtures? What will be the driving force underlying these trends?

Any attempt to predict the evolution of concrete admixtures must, of course, consider the current trends in all key aspects of modern concrete technologies. Given the scale, importance and impact of concrete construction technologies, "holistic" approaches (6) must be adopted which aim the simultaneous optimization of:

- material properties
- short- and long-term economic viability
- raw materials conservation
- energy consumption
- environmental impact of all components of the cementitious system and of the concrete.

Many of these considerations derive, of course, from a global consensus to pursue sustainable development of all technologies, as demonstrated, for example, through the recent Kyoto Protocol on carbon dioxide emissions into the atmosphere.

TRENDS IN CEMENTITIOUS SYSTEMS

In approximately the first two-thirds of the present century, considerable efforts were devoted to the chemical optimization of portland cement (7,8). Through extensive studies on the hydration behavior of portland cement and its silicate (C_2S , C_3S) and aluminate (C_3A , C_4AF) phases, and from detailed investigations on the role of sulfate in the hydration process, as well as on the importance of the form under which sulfate is introduced, portland cement has evolved into a highly specified reactive mineral system. To achieve proper control of the early hydration phenomena, convenient lag phase and setting periods, adequate rate of early strength development and optimum long term consolidation behavior, the components of portland cement required extensive "fine tuning", in accordance with selected key applications (cement types).

In following developments however, various types of mineral additives were progressively introduced to supplement the reactive mineral phases in portland cement (9). Such supplementary materials, typically, silica fume, blast furnace slag and fly ash, are included in the cementitious system, both to improve its mechanical and durability properties of the concrete, and to take advantage of secondary industrial products that are widely available in large quantities. Hence, in addition to drawing benefits from these secondary industrial products, the use of supplementary materials reduces the consumption of portland cement, with concomitant benefits in raw materials conservation, energy consumption and release of CO_2 , i.e., from the production of cement clinker.

However, because of the inherent composition variability of the supplementary cementitious materials, the chemical complexity of the reactive system is increased and the chemical optimization developed initially in the normal portland cement system is lost. In principle, this situation could be addressed through at least two routes:

- an *ad hoc* reformulation of the portland cement: alternative combinations of silicates and aluminates could possibly be better suited (overall) than normal portland cement for systems containing high volumes of supplementary materials, such as high volume fly ash (HVFA) concrete;
- addition of appropriate chemical admixtures: the latter can be introduced in the dry cementitious system, or in the fresh concrete, to compensate for changes in the chemical composition of the supplementary cementitious materials.

In the foreseeable future, it may be expected that the second approach will be emphasized since optimization using chemical admixtures is considerably more versatile than reformulating cement compositions, particularly to correct local situations on a case-by-case basis. The addition of chemical admixtures directly into the dry cementitious system is thus likely to gain increasing acceptance.

On the other hand, as chemical knowledge and practical experience accumulate on the design and application of mixed cementitious systems, the first approach (alternatives to normal portland cement), may also prove rewarding.

TRENDS IN CONCRETE TECHNOLOGIES

In the final third of the present century, the development of concrete technologies has been mostly driven by the need to increase the performance of concrete materials and the necessity to optimize concrete production, handling, placing and curing operations in order to accelerate construction rates (10-12).

Concrete Material Performance

With respect to improvements in concrete properties, considerable progress has been achieved in several areas through a combination of experimental approaches. Some of the most significant challenges which were successfully met include:

- increase of compressive strength and reduction of concrete permeability through reduction of pore volume which was made possible by water reducers and superplasticizers, and the addition of ultra-fine supplementary or pozzolanic materials;
- improvement in the freezing and thawing resistance of concrete through the controlled introduction of a air void network using air entraining admixtures;
- minimization of deleterious alkali-aggregate reactions (AAR) through AARpreventing admixture allowing the use of marginal aggregate.
- reduction in the corrosion of concrete steel reinforcement through addition of corrosion inhibitors, and the use of sealers or water-proofing membranes;
- minimization of microcracking due to drying shrinkage through shrinkagecompensating or shrinkage-reducing admixtures, curing compounds and more appropriate curing methods;
- minimization of early thermal micro-cracking in large concrete elements, by improved control of reaction rate and heat generation, using both supplementary cementitious materials and chemical admixtures.
- increase in concrete service life resulting from enhanced durability, corrosion resistance, freezing and thawing resistance, etc.

Concrete Fabrication, Handling and Placing Technologies

In line with the "just-in-time" approach adopted in many other industries, the production of concrete has been increasingly carried out using high-speed, high-shear batching systems, with addition of chemical admixtures in the batching process. Ideally, the fresh concrete properties (slump, homogeneity, air entrained, air void system) should remain constant for sufficient time to eliminate all "on-site" adjustments. This aspect will remain a major challenge for chemical admixtures in years to come.

A possible extension of concrete fabrication technologies may be in "continuous flow mixes", allowing constant on-line monitoring and adjustments

of the mix composition and properties. Such approaches would likely generate additional requirements in the performance of chemical admixtures.

Developments in other aspects of the production and handling of concrete are also largely driven by turnover rates and minimum labor requirements. In the future, these considerations will continue to favor such concrete technologies as: flowable, or pumpable concrete; self-compacting concrete; "dry", zero-slump concrete (e.g. roller compacted concretes, dry cast); anti-washout concrete for under-water concreting; shotcrete. In all of these applications, stringent requirements are imposed on the properties of the fresh concrete (rheology, segregation), and these can only be controlled through appropriate combinations of chemical admixtures.

OTHER INFLUENTIAL TRENDS

Several other observable trends are likely to influence the development course of concrete chemical admixtures and their applications; these trends may either be driven directly by requirements from the "field", or indirectly, by various external factors. Some of these are identified below.

Developing countries will continue to require huge quantities of "normal strength-good quality" concrete (e.g., 30-40 MPa) for housing and industrial infrastructure. Because of economic pressures, the production of such concrete will aim to minimize cement contents, using all supplementary cementitious materials locally available (natural pozzolans, fly ash, calcined clay, etc.); the admixtures required in conjunction with the supplementary materials will be selected for optimal cost/performance ratio, for these specific concrete materials and applications.

The environmental regulations on emissions from coal-, or crude oilburning plants are likely to become increasingly severe, for example with regard to NO_X emissions. The changes in the operational conditions of the plants to meet such regulations can markedly influence the physical and chemical properties of the combustion ashes (fly ash). In some cases, this results in fly ash with high levels of carbon; the latter can interact with chemical admixtures (for example, air-entraining admixtures), interfering with their action. Chemical admixtures must be able to accommodate, or even compensate for, changes in the properties of the supplementary materials.

The ongoing globalization of markets for raw materials enhances the worldwide trading of clinker and supplementary cementitious materials. Hence, cement producers can grind/mix materials from various sources, a practice which may tend to introduce greater variability in the properties of the resulting blends. Quite probably, chemical admixtures, added in the dry mix or in the concrete

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batching process, will be increasingly called upon to alleviate any shortcomings of the blended cements.

Recent climatic perturbations have shown unprecedented variations in temperature which may cause concern for appropriate protection of exposed concrete; this should also lead to increasing use of chemical admixtures, for example, air entraining agents to increase the freezing and thawing resistance of concrete.

Finally, the behavior of concrete exposed to intense heating, such as may occur in fires, has recently attracted considerable interest, particularly with high performance concretes(13); the extremely low porosity of these materials results in fewer mechanisms to relieve localized expansive thermal stresses, and the escape of gaseous products formed within the mass. These situations may require development of new types of admixtures, or innovative combinations of admixtures and concrete technologies.

TRENDS IN CHEMICAL ADMIXTURES

From the foregoing considerations, it is quite apparent that the future of concrete chemical admixtures will be subjected to many influences from within the construction industry, as well as from external sources, that may not be easily predictable; some of these influences will, moreover, be in direct opposition. However, the direction of future trends in the development of chemical admixtures may become evident through the following simple question: Which of the various types of admixtures listed in the introductory section are absolutely essential for the production of high quality concrete? i.e., by opposition to those which are highly beneficial, convenient and cost-effective, but not strictly essential.

For example, set modifiers, curing compounds, or corrosion inhibitors are extremely valuable admixtures; however, what they achieve could, at least in part, be obtained by changing other components, or parameters, of the system (e.g., adjusting the mixing temperature to control the setting time; modifying the curing conditions to minimize shrinkage cracking; and using galvanized steel or stainless steel to avoid corrosion).

In this perspective, there appears to be relatively few chemical admixtures that are truly indispensable for making HPC (high performance referring here to strength and durability); three such admixtures would be: high-range waterreducers (superplasticizers), air entraining admixtures and colloidal admixtures. Superplasticizers are unavoidable in any HPC formulation, particularly those containing significant quantities of silica fume or fly ash, as both frequently increase the water demand. Air entraining agents are also generally required in

making concrete with adequate resistance to freeze-thaw cycling. Colloidal admixtures designed may also be considered essential to prevent segregation in fresh self-compacting concrete. Each of these "essential" admixtures will evolve further according to a combination of need and opportunity; in attempt to understand this evolution process, the particular case of concrete superplasticizers is elaborated below.

TRENDS IN SUPERPLASTICIZER DEVELOPMENT

Historical Notes

The evolution of water-reducing admixtures followed a relatively simple pattern, basically responding to the need for greater and greater reduction of concrete porosity in order to enhance both, the strength of the material, and its durability. As noted earlier, the introduction of supplementary materials, also to enhance concrete properties, often imposes further need to minimize the water demand of concrete mixtures.

The chemical admixtures designated as "water reducers" could include a broad variety of organic chemicals which can interfere with the various physicochemical processes occurring in fresh concrete (see below). However, the actual number of chemicals used, to date, as water reducers on a large scale are rather few.

Lignosulfonates

As is well known, the first chemical admixture to find extensive and sustained use as a water reducer was lignosulfonate. This derivative of lignin, obtained as a by-product of Kraft wood pulping, provides moderate water reduction, which has proven satisfactory for many earlier concrete applications. As the requirements for water reduction were increased, i.e., form 8-10%, the lignosulfonates began to evidence inherent shortcomings, namely:

- at the dosages necessary to achieve workability in low W/C mixtures, lignosulfonates induce considerable set retardation;
- because of their surfactancy, lignosulfonates often lead to high levels of undesirable air entrainement;
- due to the intrinsic variability of these by-products, i.e., from different types of wood, processing technologies and post fermentation processes to reduce sugar levels, the performance and detrimental effects of lignosulfonates are sometimes difficult to predict.

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Synthetic Sulfonated Aromatic Polymer

The first group of truly high-range water-reducers admixtures (superplasticizers) broadly used in concrete consisted in synthetic polymers of sulfonated aromatics, condensed with formaldehyde. Two such products were developed and optimized: one uses naphthalene as the aromatic building block, yielding poly-naphthalene sulfonates (PNS); the other uses melamine which leads to poly-melamine sulfonates (PMS). These two types of products can achieve comparable water-reduction when used at their respective optimal dosage, although they exhibit minor differences in some practical aspects of their application. The main limitation currently reported for these products is, in some cases, their inability to retain the initial slump of the fresh concrete for an extend period, ideally for two hours.

Other Synthetic Polymers and Copolymers

To further improve the water reduction and overall performances of superplasticizers, several approaches may be followed:

- first, a complementary admixture (co-admixture) may be added into the superplasticizer to alleviate its shortcomings;
- second, the optimization of the widely available PNS and PMS products through changes in molecular parameters (molecular weight and distribution, degree of sulfonation), or replacement of part of the naphthalene or melamine monomers by other compatible monomers to form co-polymers;
- third, the search for completely different, "ideal" polymers having molecular features designed from available knowledge on the mode of action of these admixtures.

In recent years, all of these approaches have been pursued to varying extents.

The co-admixture approach has been, and still is, widely practiced to provide optimal formulations for local materials and applications, from the superplasticizers and other chemicals available. Typically, mild set-retarding admixtures may be incorporated into the superplasticizers to reduce the rate of cement hydration, thus improving slump retention.

The co-polymerization approach for modification of PNS and PMS products has also been pursued, at least at the R&D level, indicating promising results(14,15).

In the search for new "ideally designed" products, various polymers derived from acrylic, or substituted acrylic monomers, have recently occupied an important part of the chemical and technical literature on superplasticizers (see publications cited in ref. 16, 17)). Many of these new compounds exhibit higher

water reduction ability, compared to earlier PNS and PMS products; in some cases, they offer the additional advantages of a more linear dosage-response curve and a better slump retention. In some cases, these qualities are, however, associated with a few drawbacks: surfactancy (air entrainment), set retardation the inherent surfactancy of and bleeding. Currently, poly-acrylate superplasticizers (generally bearing long poly-ethoxylated side chains) requires the addition of defoamers to minimize their air-entraining propensity (with potential interference with air-entraining admixtures). Perhaps also because of their intrinsic surfactancy (and possibly due to their weaker adsorption on cement particles (see below)), poly-acrylate superplasticizers tend to induce bleeding more readily than conventional PNS and PMS products in high slump concrete.

Interestingly, the concrete industry now has a wide variety of waterreducing admixtures available to select from, a situation resulting directly from recent advances in understanding how superplasticizers work. Today, many of the complex phenomena which occur during cement hydration in the presence of water-reducing and other admixtures are reasonably well understood at the molecular, colloidal and microstructural levels (18).

HOW SUPERPLASTICIZERS WORK

Superplasticizers are water soluble, electrically charged organic polymers having molecular weights in the range 1 000 – 100 000 Daltons. The action exerted by these molecules in an aqueous slurry (paste) of cement particles may viewed as resulting from a superimposition of "physical" and "chemical" effects.

The "physical" effects are those which would be observed in any dense slurry of "inert" mineral particles (e.g., limestone, titanium dioxide); in such slurries, superplasticizer molecules can exert a strong fluidizing effect at constant water content, or a major water reduction at constant fluidity. The mode of action of superplasticizer molecules in these systems (and, generally, in any slurry of mineral particles), first relies on the adsorption of part of the molecules onto the surface of the particles. The superplasticizer molecules convey an electrical charge to the particle surface, and this favors a better dispersion (de-flocculation) of the particles via electrostatic repulsive forces. The adsorbed superplasticizer polymers also act as a physical barrier to keep particles apart (i.e. steric repulsion), further assisting the dispersion of the particles and fluidification of the slurry. The molecular properties of the superplasticizer which optimize the "physical" contribution to the mode of action superplasticizers have now been largely elucidated (18).

The "chemical" role of superplasticizers in cement pastes may be qualitatively pictured as the way in which these polymer molecules can influence