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**SIXTH CANMET/ACI
SIXIÈME CANMET/ACI**

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**SUPERPLASTICIZERS
AND OTHER
CHEMICAL ADMIXTURES
IN
CONCRETE**

**LES SUPERPLASTIFIANTS
ET AUTRES
ADJUVANTS CHIMIQUES
DANS
LE BÉTON**

EDITOR • V. M. MALHOTRA • RÉDACTEUR

Sixth CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete

Editor

V. M. Malhotra



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PREFACE

In May 1978, the Canada Centre for Mineral and Energy Technology (CANMET), in association with the American Concrete Institute (ACI) sponsored a 3-day conference in Ottawa, Ontario, Canada, on the use of superplasticizers in concrete. Selected papers from the symposium were published as ACI special publication SP-62.

In 1981, CANMET, again in association with the American Concrete Institute, sponsored a second 3-day international conference in Ottawa on the use of superplasticizers in concrete. The proceedings of the conference were published as ACI special publication SP-68.

The purpose of the third international conference in 1989 was to review the progress made since the meetings in 1978 and 1981, and to bring together representatives of the chemical admixtures, cement, and concrete industries to exchange information and to delineate new areas of needed research. The scope of this conference was expanded to include chemical admixtures other than superplasticizers. The proceedings of this conference were published as ACI special publication SP-119.

In October 1994, CANMET, in association with the American Concrete Institute and several other organizations, sponsored the fourth conference on the subject in Montreal, Canada. The objective of this conference was to bring attention to the new developments in chemical admixtures since the last conference in 1989. The proceedings of this conference were published as ACI special publication SP-148.

In October 1997, the Committee for the Organization of CANMET/ACI International Conferences (ACI Council), in association with the American Concrete Institute and several cement and concrete organizations in Italy, sponsored the fifth conference in Rome, Italy. This conference was aimed at transferring technology in the fast moving field of chemical admixtures. The proceedings of the conference were published as ACI special publication SP-173.

In October 2000, the Committee for the Organization of CANMET/ACI International Conferences (ACI Council), in association with several organizations in Canada and France, sponsored the sixth conference in Nice, France. A total of more than 50 papers from more than 20 countries were received and reviewed by the ACI review panel, and 37 were accepted for publication in the proceedings of the conference. The proceedings were published as ACI special publication SP-195. The co-operation of the authors in accepting the reviewers' suggestions is greatly appreciated.

During the conference a special dinner was held to recognize Prof. Carmel Jolicoeur, Université de Sherbrooke, Sherbrooke, Canada, for his outstanding and sustained contributions in the area of superplasticizers.

Thanks are extended to the members of the review panel for their contributions towards the publication of this volume. The help and assistance of A. Bilodeau, Chairperson of the Slide Review Panel is gratefully acknowledged. Thanks are also extended to Harry S. Wilson, Maria Venturino, and Gordon D. Brearley for their help in the processing of the manuscripts, both for the ACI proceedings and the supplementary volume. Acknowledgment is also made to Rebecca Hartford of ACI and her editorial and production staff, for their help in getting the proceedings ready on time.

V. M. Malhotra, P.Eng.

Editor

Chairman, Sixth CANMET/ACI International Conference
on Superplasticizers and Other Chemical Admixtures in Concrete

October 2000

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Trends in Concrete Chemical Admixtures for the 21st Century

by N. Spiratos and C. Jolicoeur

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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Nelu Spiratos president and CEO of Handy Chemicals Ltd., Candiac, Qué., Canada. He spearheaded the development of superplasticizers at Handy, and vigorously promoted the use of these admixtures in Canada and abroad, namely through sustained and supportive participation to international scientific events in concrete technologies. He was honored by the Canadian Board of Trade in 1996 for his leadership in innovative technologies and received a Honorary Doctorate of Engineering from the Université de Sherbrooke in 1997.

Carmel Jolicoeur is Professor in the Department of Chemistry of the Université de Sherbrooke since 1971; he also heads the Department since 1996. He specializes in solution and colloid chemistry, with applications in materials, particularly cementitious materials and chemical admixtures for the latter. He has co-authored numerous papers in the area of concrete admixture chemistry, mode of action and application. He was recently recognized by ACI-CANMET for his contributions to the Chemistry of Superplasticizers

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).

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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 CO₂, 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).

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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 AAR-preventing 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 shrinkage-compensating 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

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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 oil-burning 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 water-reducers (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

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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 physico-chemical 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., from 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 entrainment;
- 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

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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 and bleeding. Currently, the inherent surfactancy of 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 water-reducing 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 be 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

Superplasticizers and Other Chemical Admixtures in Concrete 11

the course of cement hydration reactions and the nature of the hydration products. For example, superplasticizer molecules can interfere with the nucleation and growth of the hydration products, thus retarding the formation of connective gel between the hydrating particles; this will help maintain fluidity (slump) for longer periods. Also, depending on their chemical composition, superplasticizers molecules may become embedded, or intercalated, in the hydration products, leading to new organo-mineral hydrates (19). In the case of these "chemical" mechanisms, the relationship between the molecular properties of the superplasticizers and the effects observed are only partially understood.

DESIGNING FOR "IDEAL" OR "OPTIMAL" SUPERPLASTICIZERS?

Although there are still considerable detail eluding a quantitative interpretation of all mechanistic aspects, the current level of knowledge on the mode of action of superplasticizers is already sufficient to guide the design of the "ideal" product,..... as long as one specifies beforehand in what respect the product should be ideal! As is readily apparent from the information summarized above, there is no unique ideal product; hence future development in superplasticizers, or in the use of these products, will likely evolve as an overall optimization process, and may involve several families of products.

The design of new superplasticizers must, of course, aim towards maximum water reduction performance, with minimum detrimental effects vis-à-vis other properties. However, it should also take into account various other criteria which, in the end, may supersede performance criteria. Such criteria include:

- availability to all potential users
- ease of production and supply
- suitability for a broad variety of concrete types
- ease of dosage and application
- compatibility with other commonly used admixtures
- adequate knowledge of potential problems resulting from improper applications (e.g., excessive dosage)
- predictability of behavior under unavoidable variations in the experimental parameters (dosage, temperature, mixing shear, etc, a criterion sometimes referred to as "robustness")
- environmental impact of all components (including by-products) and processes
- cost for the particular application.

There is no absolute scale to evaluate the impact of each of the above criterion on future developments in superplasticizers. In the authors opinion,

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however, a cursory evaluation of the different groups of products, using the above combination of criteria, can reliably indicate the direction of the trends

With respect to availability, in the raw chemicals used for superplasticizer synthesis, naphthalene and sulfuric acid rank as most widely available in quantity and in location. Also, the synthesis of naphthalene sulfonate and condensation into polynaphthalene sulfonates are well-established technologies which are no longer proprietary, and thus can be implemented worldwide.

In relation to suitability for a broad variety of applications (e.g., types of cement and cement blends, types of concreting technologies), as well as for compatibility with other chemical admixtures (e.g., air-entraining admixtures, set modifiers, anti-segregation admixtures), the sulfonate-based superplasticizers, PNS and PMS, share the benefit of long-term successful application under a wide variety of conditions (20).

With respect to ease of use and tolerance vis-à-vis improper uses, particularly overdosage, PNS and PMS also exhibit a more predictable behavior than some of the poly-acrylate products recently introduced, as briefly outlined above.

With regard to environmental impact, superplasticizers imbedded in a hardened cement matrix cannot represent a significant environmental risk, particularly so since the polymers themselves are usually selected on the basis of minimal toxicity for obvious reasons. It is interesting to note, on the other hand, that the PNS superplasticizers are prepared using, for the most part, chemicals extracted from secondary industrial products: naphthalene separated from coking or petroleum distillation residues, and sulfuric acid obtained from flue gas combustion or from processing of sulfide minerals. Hence, for a large part, PNS products consume industrial by-products, rather than value added chemicals. This is very much in line with the raw materials conservation, and minimum environmental impact trends currently promoted in the development of blended cements.

Considering the combined requirements and criteria outlined above, it seems safe to predict that future developments in superplasticizer applications will favor sulfonate-based superplasticizers, albeit not necessarily in their present form. Relative to some new synthetic polymers developed recently, PNS and PMS exhibit shortcomings noted earlier, namely in slump retention and in their dosage-response curve. To enable their use in applications with more demanding specifications, it seems probable that their "optimization" will be pursued via the co-polymerization approach mentioned earlier; in the latter, only a minor part of the PNS or PMS is substituted with other compatible chemicals.



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ANTICIPATING GENERAL TRENDS FOR OTHER ADMIXTURES

Referring to the above discussion on the trends in superplasticizer development, it seems reasonable to expect that the development of all concrete chemical admixtures will be driven by similar forces, and submitted to the same constraints. Beyond the specific performance criterion of each admixture, the criteria used to evaluate the relative merits of new admixtures should be the same as those outlined above for superplasticizers.

When considering concrete admixtures as a whole, additional trends can be seen to emerge:

- Chemical admixtures are increasingly used in a large variety of applications, involving vastly different technologies (e.g., from in-plant to on-site production; from “normal” strength concrete to 1 000 MPa reactive powder concrete; from dry cast to flowing concrete, etc). The development of optimal admixtures to meet the specific needs of each technology is likely to emphasize the development of “specialty” or “niche” type admixtures.
- In contrast, the global need for construction technology will favor chemical admixtures that can support the broadest possible range of applications.

Considering further that,

- there now exists many families of admixtures to achieve different functions,
- that each family of admixtures usually represents a variety of chemical compounds, and
- that, most often, several chemical admixtures are used simultaneously in a given mix,

it is quite clear that development of new chemical admixtures must be pursued in an integrated approach, i.e., developments to fulfill a particular requirement should not be achieved at the expense of other functional properties.

The chemical complexity deriving from simultaneous use of different admixtures strongly underlines the need for adequate chemical knowledge on these systems and proper technical information for the end user. It further seems desirable, and probable, that adequate codes of practice and corresponding regulatory measures be introduced to provide an adequate framework for optimum design of cementitious materials.

CONCLUDING REMARKS

As noted in the introductory section, chemical admixtures, which were first introduced into concrete as beneficial supplements, are rapidly becoming essential components of virtually all quality concrete materials. It thus seems

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realistic to expect that the global use of concrete admixtures will continue to expand, driven both by technical factors and socio-economic pressures.

The technical factors include:

- new knowledge on the chemistry of cementitious systems and on the mode of action of the admixtures in these systems,
- performance specifications,
- “field” requirements for reliable, low labor, cost-effective technologies.

The socio-economic factors will typically promote:

- broad geographic accessibility,
- affordability in the prevailing economic context,
- concrete performance and durability optimization using locally available materials,
- minimum negative environmental impact and maximum environmental benefits, i.e., through the use of supplementary cementitious materials, reduced diffuse carbon dioxide emission.

Given this overall context, the development of chemical admixtures, as well as the applications of these admixtures, will most certainly be pursued in an incremental optimization mode.

As is usually the case, new basic knowledge on the chemistry of concrete admixtures will evolve from systematic studies on reference systems (cementitious materials and others) and “ideally designed” chemical products. Such studies will generate information, which will support both, the development of new “ideal” admixtures and the optimization of admixtures to accommodate all relevant field requirements.

On the other hand, given the nature of the construction industry (including cement, concrete and admixtures), the implementation of technological advances resulting from admixture developments, will likely proceed through a continuous optimization mode. Also, in view of the increasing number of different technological segments in the construction industry, the evolution will likely emphasize the development of specific “niche”-type admixtures.

Finally, in view of the broad variety and increasing number of chemical admixtures currently available, or in development stages, there will be a growing need to provide the industry with appropriate codes of practice and regulations to guide the introduction of new products and/or applications. Since cementitious systems continue to react (mature) over long periods of time, and considering the variety of chemicals to which concrete elements may be exposed to, improper combinations of admixtures carry the potential to affect the long-term properties of concrete materials in less than desirable ways.

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Effect of Superplasticizer Type on Performance of High-Volume Fly Ash Concrete

by A. Borsoi, S. Collepardi, L. Coppola, R. Troli, and M. Collepardi

Synopsis: Superplasticized high-volume fly ash concretes with 50% of portland cement replacement were made by incorporating two different chemical admixtures based on sulfonated naphthalene (*SN*) or acrylic polymer (*AP*).

Portland cement with a Blaine fineness of about 400 or 500 m²/Kg was replaced by 50% of ground or un-ground fly ash. The content of the cementitious material (portland cement + fly ash) was about 470 kg/m³. The concretes with *SN* were manufactured with a slump in the range of 190-200 mm, whereas the slump of the concretes with *AP* was in the range of 220-230 mm. Due to the different effect of the superplasticizers, the water-cementitious material ratio (*w/cm*) was 0.32 or 0.29 for the *SN* or *AP* admixture, respectively, although the dosage was slightly lower for the latter.

Cube specimens, 150x150 mm in size, were cured at 5°C or 20°C and compressive strength was measured at 1 to 90 days. Due to the lower *w/cm*, the strength of the concretes with the acrylic polymer was significantly higher with respect to those with *SN*.

The better performance of the *AP* superplasticizer, in terms of compressive strength, was obtained at early and later ages independently of the curing temperature (5 and 20°C), and the fineness of the portland cement and fly ash.

Due to the lower *w/cm* of concrete with the *AP* admixture with respect to those with the *SN* superplasticizer, the durability of high-volume fly ash concrete can be improved in terms of lower penetration rate of CO₂ or chloride ions.

Keywords: durability; fly ash; superplasticizer

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INTRODUCTION

Initial studies works on high volume fly ash (*HVFA*) concrete characterized by high portland cement replacement (50-65% by mass), low water-cementitious material ratio (w/cm), and use of naphthalene-based superplasticizer were carried out by Malhotra and coworkers (1-4).

The main purpose of this research was to study the influence of the superplasticizer type, in terms of differences in chemical composition, on the performance of *HVFA* concrete. Superplasticizers based on sulfonated naphthalene (*SN*) or acrylic polymer (*AP*) were studied.

Another purpose of this research was to study the influence of the specific surface area of the blended cements on the performance of *HVFA* concrete.

MATERIALS

Cementitious materials: The chemical analysis of the two ingredients (portland cement and fly ash) used to manufacture blended cements are shown in Table 1.

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Portland cement was available at the Blaine fineness of 395 and 504 m²/Kg. Each portland cement was blended with fly ash which was available at three different Blaine fineness levels: 351 m²/kg (unground fly ash), 395 and 482 m²/kg (both ground). Four blended cements (*A, B, C*, and *D*) were manufactured (Table 2), all with 50% by mass of portland cement replaced by fly ash, and characterized by different Blaine fineness (from 368 m/Kg for cement *A* to 487 m²/Kg for cement *D*). Other properties of these cements, such as setting time, compressive strength, and classification according to the European Standards have been published elsewhere (5).

Aggregates: Natural sand (fineness modulus of 3.09) and two coarse aggregates were used. For all concrete mixtures a combined aggregate was used with 25% of sand, 40% of 4-16 mm gravel and 35% of 10-25 mm gravel.

Superplasticizers: Two commercially available superplasticizers, both from Mapei (Milan, Italy), were used. One admixture was a 40% aqueous solution of sulfonated naphthalene-based polymer (*SN*). The other superplasticizer was a 30% aqueous solution of acrylic polymer (*AP*). Additional data on the chemical structure and performance of these two superplasticizers can be found in reference (6).

Concrete mixtures: Table 3 shows the composition of the eight *HVFA* mixtures, all manufactured with about 470 Kg/m³ of cementitious material which corresponds to a portland cement content of about 235 Kg/m³. In four mixtures (No. 1-4) the superplasticizer *SN* was used, whereas the other four concretes (No. 5-8) were treated with the superplasticizer *AP*.

TEST METHODS

After measuring specific gravity and slump, fresh concrete was compacted and cured at 5°C or 20°C. The following properties were then determined on cube specimens 150x150 in size

- compressive strength up to 90 days after curing at 5°C or 20°C;
- depth of carbonation measured by phenolphthalein test (RILEM CPC-18) of concrete specimens exposed to air at room temperature after demolding at 1 day;
- chloride diffusion at 20°C through the AgNO₃ and fluorescein test (7) of concrete specimens exposed to a 10% NaCl aqueous solution after a wet curing of 1 week, and an air curing at room temperature of 3 weeks.

RESULTS

Workability: Concrete mixture (Table 3) with the *AP*-based admixture ($w/cm=0.29$) performed better, with respect to those with the *SN*-based superplasticizer ($w/cm=0.32$) in terms of:

- higher slump level (220-230 mm vs. 190-200 mm);
- lower slump loss

These data confirm the superior performance of the *AP*-based superplasticizer (6,8) with *HVFA* concretes independent of the fineness of the cementitious materials. In particular, more flowable mixtures were obtained, with lower w/cm , not only at the end of the mixing time (Table 3) but even, and more importantly, at a given time, up to 60 min, after mixing (Fig. 1).

In addition, the data shown in Table 3 indicate that when the fineness of both portland cement and fly ash is increased up to about 500 m²/Kg (cement *D*) a higher amount of superplasticizer (about 20% more) is needed for the *HVFA* concrete to attain the same slump level, at a given w/cm , with respect to the corresponding concretes with blended cements *A*, *B*, and *C* at lower fineness (368-415 m²/Kg).

Compressive Strength: Figures 2,3,4 and 5 show the compressive strength development at 5°C and 20°C up to 90 days for concrete mixtures with cement *A*, *B*, *C* and *D* respectively. In each Figure strength values of *HVFA* concretes with the same cement and different superplasticizer type (*SN* vs. *AP*) are shown.

Independently of the cement type and curing temperature, the compressive strength of *HVFA* concretes with the *AP*-based superplasticizer is significantly higher than that of the corresponding *HVFA* mixtures with the *SN*-based superplasticizer. This behavior is related to the more effective action of the *AP*-based superplasticizer in further reducing the w/cm by 10% less when compared to the *SN*-based admixture. On the other hand, the early retarding action of the *AP* admixture on the portland cement hydration — which is responsible for negligible slump loss of the fresh *HVFA* concrete within 60 min (Fig. 1) — does not interfere with the early strength development. Therefore, with the *AP*-based superplasticizer, *HVFA* concretes with 1-day strength of more than 30 MPa and 90-day strength of more than 80 MPa are manufactured by using only 235 Kg/m³ of portland cement.

The best combination of cement, fly ash and superplasticizer seems to be:

- fine portland cement (Blaine fineness: 504 m²/Kg)
- unground fly ash (Blaine fineness: 351 m²/Kg)
- *AP*-based superplasticizer (1% by mass of cementitious material).

This combination corresponds to the mixture No. 7 with cement *C* and 1% of *AP*-based superplasticizer (Table 3). This concrete performs very well in terms

of low slump loss (Fig. 1) and high compressive strength (Fig. 4). The compressive strength of the concrete No. 8 with cement *D* (Fig. 5) is a little higher than that of the concrete No. 7 with cement *C* (Fig. 4) due to the higher fineness of the ground fly ash (Blaine: 482 vs. 351 m²/Kg). However, just because of this increase in fineness, the amount of the *AP*-based superplasticizer must be increased by 20% to keep the same workability level and *w/cm* (Table 3)

Carbonation: Due to the relatively small amount of portland cement in *HVFA* concrete and the pozzolanic reaction of fly ash, the amount of Ca(OH)₂ in *HVFA* concrete is expected to be negligible compared to that in control concrete without fly ash. Therefore, there would be a potential risk of quicker carbonation in *HVFA* concrete due to the lower amount of Ca(OH)₂ that should be neutralized by the CO₂ ingress from the environment. However, the results shown in Fig. 6 indicate that the CO₂ penetration in *HVFA* concrete is so slow (Fig. 6) that after one year the carbonation depth is about 1 mm when the *SN*-based admixture is used, and only 0.2 mm with the *AP*-based superplasticizer. These results confirm that carbonation would not pose any problem for corrosion of the metallic reinforcements, due to the very low permeability of *HVFA* to the CO₂ penetration (1). The CO₂ penetration is so slow that is difficult to detect any difference related to the fineness of portland cement.

Chloride penetration: Figure 7 shows the chloride penetration depth with time for *HVFA* concretes. The penetration depth is lower in *HVFA* concretes with *AP*-based superplasticizer due to the lower *w/cm* when compared to those with *SN*-based superplasticizer.

The penetration depth is in general so low that any difference related to the fineness of portland cement and fly ash cannot be detected.

CONCLUSIONS

In *HVFA* concrete the *AP*-based superplasticizer performs significantly better than the *SN*-based admixture, in terms of higher slump level, lower slump loss and lower *w/cm*.

Consequently, *HVFA* concretes with higher compressive strength and better durability behavior (in terms of lower CO₂ and chloride penetration) can be manufactured with *AP*-based superplasticizer rather than with the *SN*-based admixture.

The retarding action of the *AP* admixture on the early portland cement hydration is beneficial for the low slump-loss of the fresh *HVFA* concrete, and it does not cause any retardation in the early strength development of the hardened concrete even at low temperatures.

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Table 1 - Chemical composition of portland cement and fly ash used to produce blended cements.

Oxyde (%)	Portland cement	Fly Ash
SiO ₂	21.25	59.94
Al ₂ O ₃	4.33	22.87
Fe ₂ O ₃	1.85	4.67
TiO ₂	0.13	0.94
CaO	64.30	3.08
MgO	1.81	1.55
So ₃	3.70	0.35
K ₂ O	0.71	2.19
Na ₂ O	0.17	0.62
LOI	1.50	3.34

Table 2 - Composition and Blaine fineness of blended cements and individual ingredients.

Blended Cement		Portland Cement		Fly Ash		
Type	Fineness*: m ² /Kg	Fineness*: 395 m ² /Kg	Fineness*: 504 m ² /Kg	Un-ground. Fineness*: 351 m ² /Kg	Ground. Fineness*: 395 m ² /Kg	Ground. Fineness*: 482 m ² /Kg
A	368	50%	—	50%	—	—
B	388	50%	—	—	50%	—
C	415	—	50%	50%	—	—
D	487	—	50%	—	—	50%

*Blaine fineness was determined on individual ingredients (Portland cement and fly ash) and blended cement

Table 3 - Composition of concrete mixtures.

Mix No.	Blended Cement		Gravel (10-25 mm)	Gravel (10-25 mm)	Sand (0-4 mm)	Water	Superplasticizer	w/cm	Slump (mm)
	Type	Kg/m ³	Kg/m ³	Kg/m ³	Kg/m ³	Kg/m ³	Type %cem.*		
1	A	463	453	729	641	148	NS-1.00	0.32	200
2	B	465	455	732	643	145	NS-1.05	0.32	190
3	C	463	453	729	641	148	NS-1.05	0.32	190
4	D	465	455	732	643	145	NS-1.25	0.32	190
5	A	464	455	731	642	133	AP-0.90	0.29	230
6	B	470	460	740	650	134	AP-1.00	0.29	230
7	C	464	455	731	642	133	AP-1.00	0.29	220
8	D	473	463	745	655	135	AP-1.20	0.29	230

* by mass of blended cement

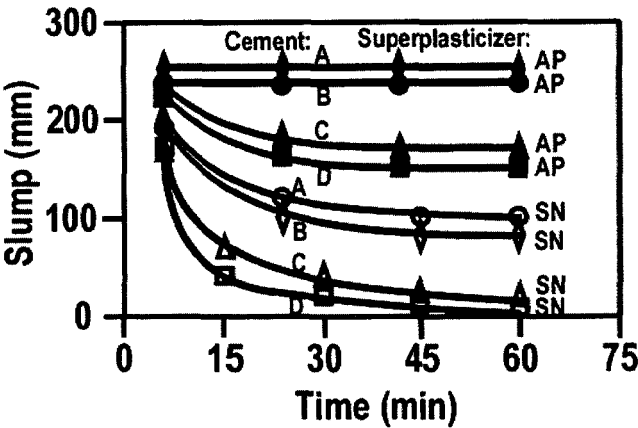


Fig. 1 - Slump-loss of concrete mixture with AP or SN superplasticizer (cements A, B, C and D in Table 2).

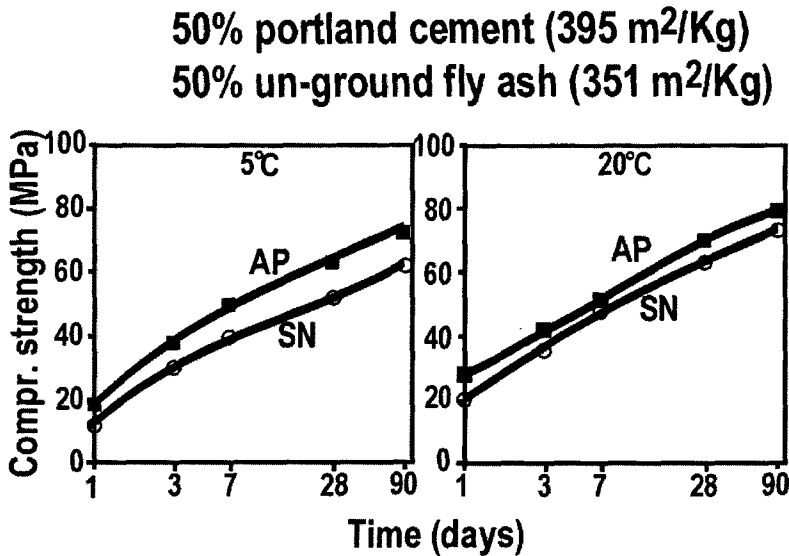


Fig. 2 - Influence of temperature and superplasticizer type on compressive strength versus time (cement A).

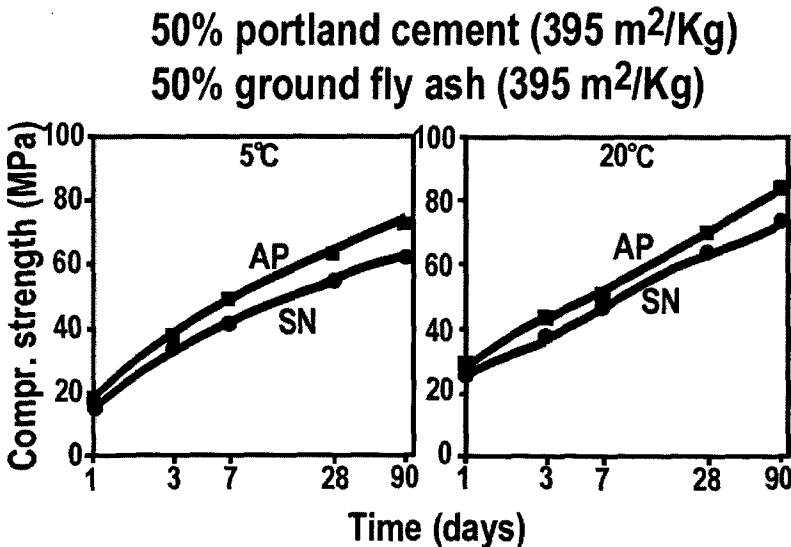


Fig. 3 - Influence of temperature and superplasticizer type on compressive strength versus time (cement B).

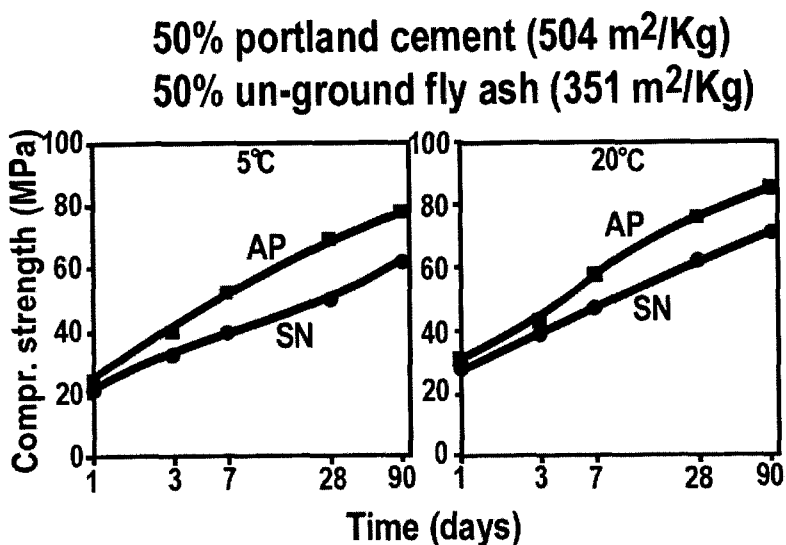


Fig. 4 - Influence of temperature and superplasticizer type on compressive strength versus time (cement C).

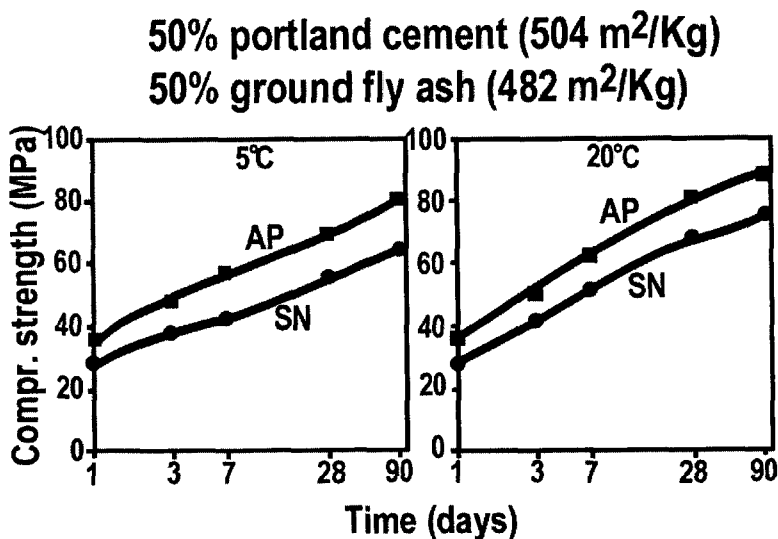


Fig. 5 - Influence of temperature and superplasticizer type on compressive strength versus time (cement D).

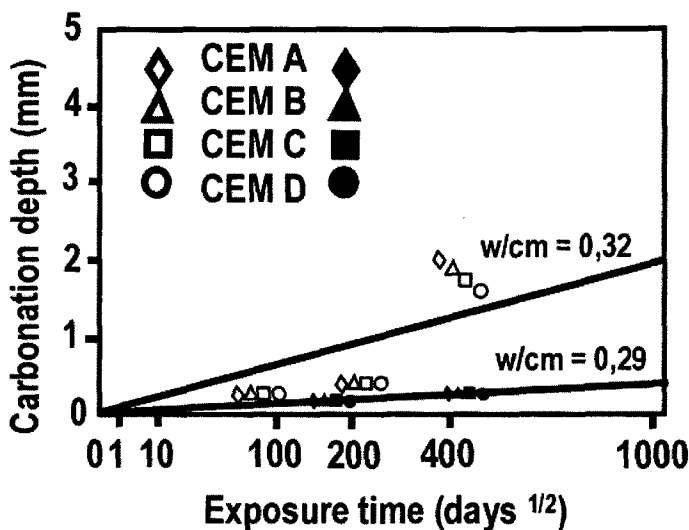


Fig. 6 - Carbonation of HVFA concretes as a function of cement fineness (Table 2) and superplasticizer type (SN or AP).

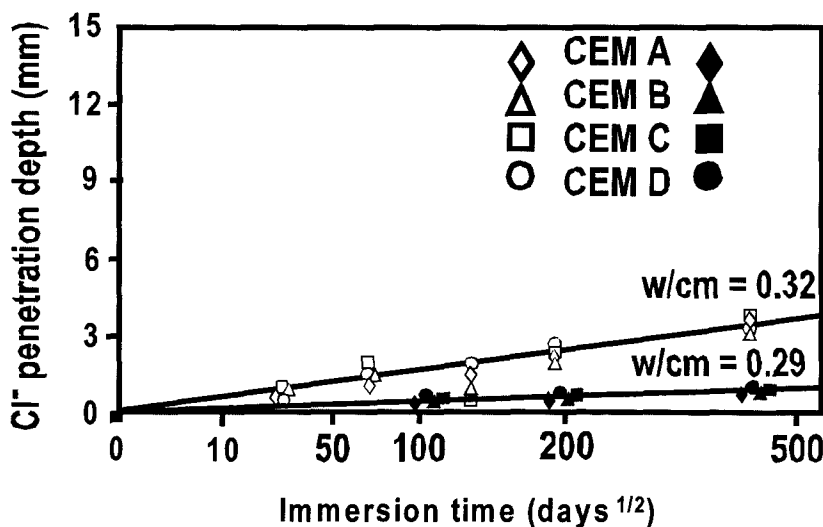


Fig. 7 - Chloride penetration in HVFA concretes as a function of cement fineness (Table 2) and superplasticizer type (SN or AP).

Electrosteric Repulsion Induced By Superplasticizers between Cement Particles —An Overlooked Mechanism?

by R. J. Flatt, Y. F. Houst, P. Bowen, and H. Hofmann

Synopsis: Dispersion mechanisms of superplasticizers have received much attention over the past years. Recent developments have brought very efficient superplasticizers where the dominant stabilizing mechanism is thought to be via steric repulsion. These new superplasticizers contain an adsorbing backbone onto which non adsorbing side chains are grafted with the objective of getting them to stretch out into the solution from the cement particle surface and induce the steric repulsion upon approach of other particles. Another feature of these polymers is that they induce only very small zeta potentials. Calculations of interaction energies indicate that these polymers act predominantly through steric repulsion. However, the same calculations could lead to the conclusion that all polymers can only act through steric repulsion. The calculation of the steric and electrostatic contributions are greatly dependent on the polymer adsorption conformation and the distribution of charge at the particle surface associated with these adsorbed polyelectrolytes. Many of the assumptions made in calculating interparticle forces are not necessarily good approximations for polyelectrolytes. This paper discusses the limits of the approximations currently used in such calculations and presents a more accurate model for the calculation of these forces. The main result, applicable for a wide range of superplasticizers, is that both electrostatic and steric repulsions should be taken into account, provided the electrostatic charge can be assumed to lie at the outer-bound of the adsorbed layer of superplasticizers. Such information is of primary importance for understanding and solving cement and superplasticizer incompatibilities, as well as for developing novel products.

Keywords: dispersion mechanisms; electrostatic repulsion; steric repulsion; superplasticizers

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INTRODUCTION

Understanding mechanisms by which superplasticizers improve the workability of concrete is a topic, which has received much attention over the recent years. In part, this has been stimulated by the so-called cement-superplasticizer incompatibilities [1,2]. Another important aspect is the development of new superplasticizers. The most significant achievement in this field has been the introduction of polymers onto which side chains have been grafted. This is believed to lead to a surface configuration, often referred to as comb-type adsorption, in which a backbone is in contact with the surface, while side chains extend into solution [3-5].

All ionic polymers can be expected to induce both electrostatic repulsion and steric hindrance in proportions depending on the ionic strength of the solution, on the molecular structure and molar mass of the polymers. The magnitude of these forces in cementitious systems has been both calculated [3] and determined experimentally by surface force measurements [4-5]. Experimental results indicate that comb-type copolymers disperse cement agglomerates by steric hindrance. This contrasts with superplasticizers of an earlier generation such as sulfonated formaldehyde condensate (SNFC), lignosulfonates or salts of polycarboxylic acids (PCA) where electrostatic repulsion was assumed to be dominant. In fact, certain calculations suggest that dispersion by these polymers could be largely linked to steric repulsion [6], which would lead to a serious reevaluation of a widely spread idea that such superplasticizers act mainly by electrostatic repulsion.

In this paper, the approximations assumed in the majority of the interparticle force calculations published so far in the cement literature are reviewed. Its intention is to refocus attention on a certain number of critical issues, which if overlooked could lead to either misinterpretation of cement and superplasticizer incompatibilities or to poorly oriented development of new superplasticizers.

THEORETICAL CONSIDERATIONS

Agglomeration

It is widely accepted that superplasticizers modify the rheology of concrete by modifying the forces between cement particles [3-6]. Their magnitude depend on the material dielectric properties, particle-size distribution, geometry, and on the charge and concentration of the electrolytes present. The van der Waals forces, which have an electromagnetic origin [7, chapter 5], come predominantly from the interaction between instantaneous dipoles. At larger separations ($> 5\text{-}10\text{nm}$), the instantaneous dipole in particle 1 may no longer be correlated with that induced in the second particle, thus reducing the interaction. This effect is known as retardation. The intervening electrolyte can also reduce the attractive force by interaction with the fluctuating electromagnetic field. This effect is known as screening. The dispersion forces can be simply described by equation 1:

$$F_{disp} = -A H_{(a,h)} \quad (1)$$

Where A is the Hamaker constant and H a geometric function (a is particle radius and h the distance between particle surfaces). The retardation and screening effects can be taken into account by calculating a screened and retarded Hamaker constant [7]. The objective is to reduce the magnitude of the attractive forces between particles sufficiently for them to be broken easily. Superplasticizers therefore allow a decrease of the effective size of the agglomerates. This in turn decreases the effective volume of solids in suspension, thereby increasing fluidity.

The attractive forces leading to agglomeration are mostly the van der Waals forces. Other attractive forces can arise between particles having different surface potentials [7, chapter 4]. In addition, situations can be encountered in which divalent cations such as calcium lead to attraction for a given separation range [8]. These are situations, which deserve further study but are beyond the scope of this paper and have been discussed elsewhere [9].

Dispersion

To prevent this agglomeration, the main modes by which superplasticizers might be acting is either by inducing an important electrostatic potential by adsorption onto the cement particles, or by preventing the close contact of the particles (steric repulsion).

For colloids (1-1000 nm), agglomerates can be separated by the thermal energy of the surrounding media. It is therefore common to discuss the stability of suspensions in terms of interparticle potentials. For suspensions, such as cement which only have a primary minimum one considers that agglomerates may be dispersed by Brownian motion if the attractive potential is less than a certain

multiple of the thermal energy. In other words, Brownian motion can produce the energy necessary to move particles away from the thermodynamically stable state, which is agglomeration.

Thermal energy is independent of particle size, so small particles are moved efficiently. On the other hand, attractive forces (or potentials) increase with particle size, making the dispersion of large particles difficult. For particles larger than $1\mu\text{m}$ applied shear forces, which increase with the square of particle size, are needed to break-up cement agglomerates. It therefore seems more relevant to discuss dispersion of cement particles in terms of the relative magnitude of balances between the maximum interparticle forces and forces arising from applied shear fields rather than attractive potential wells with respect to Brownian energy [9, chapter 10]. This is the reason for which this paper focuses on interparticle forces, rather than interparticle potentials as has been widely done so far [3-6].

Links to rheology

In order to correlate such calculations to the rheology of cement suspensions, it is necessary to take into account the particle size distribution of the cements considered. This approach, along with a detailed development of interparticle forces allowed Flatt [9] to reach a semi-quantitative relationship between calculated and experimentally determined yield stresses of cement suspensions.

It therefore appears that a good treatment should allow the determination a priori of the performance, which can be expected from different polymers. However, this is strongly linked to the accuracy of the interparticle force calculations.

Electrostatic repulsion

Flatt [9] has shown that it is possible to describe the aqueous phase of cement suspensions, which contains many different electrolytes by an equivalent binary electrolyte. He was then able to assess the validity of the extended three parameter Debye-Hückel approximation (valid up to 1 mol/l for instance for a monovalent electrolyte) for the electrostatic repulsion between spheres. Its range of validity falls within the ionic strength of current cement suspensions [9, chapter 3]. An identical and constant potential upon approach of the particles was also assumed. His calculations used thermodynamics of non-ideal solutions to take into account the ion pair associations taking place in the aqueous phase of cement suspensions. This repulsive force can be written as:

$$F_{ES} \equiv -2\pi\epsilon\epsilon_0\bar{a}\psi^2 \frac{\kappa e^{-\kappa\bar{a}}}{(1 + e^{-\kappa\bar{a}})} \quad (2)$$

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Where:

ϵ is the relative dielectric constant of the water

ϵ_0 is the permittivity of vacuum

$\bar{a} = \frac{2a_k a_l}{a_k + a_l}$ is the harmonic average radius of particles of radius a_k and a_l

ψ is the electrostatic potential

κ^{-1} is the Debye length

h is the separation distance between particles

With the Debye length given by:

$$\kappa^{-1} = \sqrt{\frac{\epsilon \epsilon_0 k_B T}{2e^2 z_+^2 n_+^b}} \quad (3)$$

Where:

k_B is the Boltzmann constant

T is the absolute temperature

e is the charge of an electron

z is the valence of the symmetric electrolyte

n^b is bulk density of the electrolyte

One of the problems for calculating this electrostatic force, is the evaluation of the surface potential ψ . This is the potential at the outer bound of the Stern layer, which is the layer in which ions are linked to the surface and not greatly influenced by Brownian motion. Often, the experimentally determined zeta potential is used, which is the potential at a shear plane. This plane is situated somewhat farther from the surface than the Stern plane. So, it leads to an under-evaluation of the electrostatic force. In many situations however, this approximation might be valid.

In our case, the charge is induced by adsorption of ionic polymers. Zeta potential measurements are based on relative motion between particles and the surrounding fluid. This motion can compress somewhat the layer of adsorbed polymers, thus modifying the distance at which the potential might be measured. Polymer layers can be compressed up to a certain limit beyond which, in the scaling theory of steric interactions [12], the steric force goes to infinity.

Flatt [9] discusses the case of a polycarboxylate polysulfonate polymer (PCA-1) for which the adsorption onto MgO, a good model powder for cement [10], is $753 \mu\text{g m}^{-2}$. Assuming the density of this layer to be $1400 \mu\text{g mm}^{-3}$ (the density of the pure polymer), and that 75% of the mass can be attributed to the polymer, then we have $1050 \mu\text{g mm}^{-3}$. This leads to the conclusion that the

totally compressed thickness would be about 0.7 nm, giving a minimum separation of 1.4 nm.

This is of the order of the Debye length of the cement suspension with a water cement ratio of 0.35, measured by Yang et al [11]. So, if the potential plane were placed at the surface of the particle, the force would already have dropped by about 90% of its value [9]. Placing the plane of origin of the electrostatic force at the surface of the particle instead of the surface of the compressed layer would therefore lead erroneously to completely neglecting any electrostatic effects. We emphasize that in reality the plane is probably even further away from the surface, and that electrostatic interactions will contribute to repulsion as soon as adsorbed layers begin to overlap.

In fact, de Gennes [12] states that the hydrodynamic layer thickness scales in the same way as the adsorbed layer thickness. He mentions that this is confirmed by experimental data, though in some cases the hydrodynamic layer might be even larger. For this reason we will consider that during zeta potential measurements, hydrodynamic forces are not sufficient to significantly compress the adsorbed layer. Therefore we place the plane of origin of electrostatic forces at the surface of the adsorbed layer.

So, we can reformulate the electrostatic force, integrating the adsorbed layer thickness L :

$$F_{ES} = -2\pi\epsilon\epsilon_0\bar{a}\psi^2 \frac{\kappa e^{-\kappa(h-2L)}}{(1 + e^{-\kappa(h-2L)})} \quad (4)$$

As the layer gets compressed we will adjust the value of L , thus maintaining the electrostatic force constant during compression. In fact, we will show that compression is negligible in the determination of the maximum attractive force. This approximation therefore does not have major consequences for our calculations.

Steric force

The steric force begins as soon as the adsorbed layers begin to overlap. It increases strongly and reaches infinity as the maximum compression is reached. The functionality of this increase is highly dependent on the adsorption mode (conformation) of the polymer. Pedersen and Bergström [13], under their experimental conditions, reached the conclusion that polyacrylic acid (PAA) adsorbed in a mushroom like conformation. Though their surface has a significant negative charge, which increases the layer thickness, we consider there are enough similarities with our suspensions to also assume a mushroom conformation. For such adsorption modes, the scaling theory developed by de Gennes is increasingly used to calculate the steric force. We have for the steric force:

$$F_{ste} = \bar{a} \frac{6\pi k_B T}{s^2} \left[\left(\frac{2L}{h} \right)^{\frac{5}{3}} - 1 \right] \quad (5)$$

Where s is the distance between the centers of gravity of two neighbouring mushrooms. This is twice the radius obtained from adsorption data, assuming a compact layer of spheres, disks or mushrooms. L is the maximum length extending into the solvent.

Dispersion force

Flatt [9, chapter 3], showed that for the size range of interest to cement suspensions, the dispersion force could be written as:

$$F_{Disp} = -\frac{A_{(h)}}{6} \left(\frac{-\bar{a}}{2h^2} + \frac{-1}{2\bar{a}} + \frac{1}{h} \right) \quad (6)$$

For small separations, this simplifies to:

$$F_{Disp} \cong A_{(h)} \frac{\bar{a}}{12h^2} \quad (7)$$

Because the aqueous phase of cement suspensions is a concentrated electrolyte, the static term in the dispersion interaction potential is screened. Retardation, which describes the decrease of the Hamaker constant $A_{(h)}$ with increasing separation is taken into account.

Because proper Hamaker constants of cement components are not yet available at the time of writing this section, the Hamaker constant for magnesium oxide has been used. Indeed the only estimation of a Hamaker constant for a cement phase was presented by Sakai and Daimon [3], who only gave a value of a non-retarded, non-screened Hamaker constant for C_3S of 4.55×10^{-20} J/mol using old dielectric data for water [14]. If the same dielectric data of water as Sakai and Daimon [3] is used, MgO gives a non-retarded and non-screened Hamaker constant of 4.2×10^{-20} J/mol. Since both values are close, MgO seems to be a reasonable model for calculating the retarded and screened dispersion forces (for details see [9]) using more recent evaluation of the dielectric data for water [14].

Total interaction

The total interaction force can be obtained by taking the sum of (4), (5) and (7). Since all these equations depend linearly on $\bar{a}$, it is possible to introduce an interparticle force parameter $G_{(h)}$ given by:

$$G_{(a_1, a_2, h)} \cong F_{Disp} + F_{ES} + F_{Ster} \quad (8)$$

In Fig. 1, this interparticle force parameter is plotted as a function of separation distance, for two adsorbed layer thicknesses of 1 nm (a) and 3 nm (b). In both

cases electrostatic potentials of 0, 10, and 15 mV are considered, placed at 1 and 3 nm from particle surface. In Fig 1c, interparticle forces are plotted for three values of the adsorbed layer thickness, assuming that the surface potential is 15 mV. Positive values indicate attraction and negative values repulsion (recall that the force is the derivative of a potential with respect to separation). These figures show clearly that compression of the adsorbed layer is not significant at the point where the maximum attractive force is reached. Indeed, in absence of electrostatic repulsion this maximum is reached for separations of about twice the maximum length of the layer extending from the surface into the solvent. When electrostatic effects come into play, the point of maximum repulsion is beyond this distance. Note that this does not mean that the particles will not come into sufficient contact to lead to layer compression. It means that the maximum force, which we are concerned with for yield stress calculations, i.e. the amount of shear force needed to separate particles, is barely affected by the capacity of the layer to be compressed.

The differences between the maximum attractive force at 0 mV for the 1 nm and 3 nm layers is an order of magnitude. To quantify these effects an accurate assessment of effective thickness of the adsorbed layer is of key importance. So, we can say that there is an important steric effect. This effect can be significantly complemented by electrostatic repulsion, provided it is reasonable to place the potential (as a measured zeta potential) at the outer bound of the adsorbed layer. When the potential is placed at the surface of the particle for 1 nm layer, a maximum normalized attractive force of 395 pN/ μ m is calculated instead of the low value of 60 pN/ μ m when placed at the exterior of this 1 nm layer, for a surface potential of 10 mV. If this potential is 15 mV, the maximum normalized attractive force goes down to 40 pN/ μ m.

Maximum interparticle force

The maximum interparticle force was determined numerically for a series of polymer layers and potentials. Results using MgO spectral information for the calculation of a retarded screened Hamaker interaction are given both in Fig. 2 and 3. They show the dominant effect of the adsorbed layer thickness. It also indicates, that for thin layers, the electrostatic contribution must not be overlooked, provided the plane of origin may be placed at the outer-bound of the adsorbed layer. This will be applicable for non-conducting particles such as those formed in cement suspensions.

Fig. 2 illustrates the effects of both electrostatic potential ψ and adsorbed layer thickness L . However, it is not convenient for identifying the precise value of G for specific combinations of ψ and L . For this we also plot a projection of this graph in Fig. 3. Here we see that with an adsorbed layer thickness of 1.5 nm the maximum attractive force decreases from more than 60 pN/ μ m to less than 40 pN/ μ m, if the surface charge is increased from 0 to 10 mV. Typical polymers of the comb type induce a potential of around -10 mV and would thus decrease the

force needed to separate particles by over 30 %. This illustrates that, although the dominant mechanism for stabilization is steric without which a strong attractive force is always predicted, small increases in surface charge can play a significant role. These results of electrostatic repulsion are still using a single plane of homogeneous charge distribution which is unlikely to be the case with adsorbed polyelectrolytes. Further work on the actual conformation and layer/charge inhomogeneities needs to be carried out to further confirm the above predictions.

CONCLUSIONS

Many of the parameters needed to make theoretical calculations of interparticle forces are difficult to determine for real complex systems, such as adsorbed polymer thickness and surface charge distribution. In this paper, the main assumptions have been looked at rigorously and the dominant effect of most superplasticizers is probably linked to the thickness of their adsorbed layer, even if this layer is quite thin (1-3 nm).

Electrostatic contributions can be significant if the plane of charge used to calculate the repulsive forces is placed at the outer-bound of the adsorbed layer of superplasticizers and not at the particle surface. What is the most adequate choice remains an unsettled question.

Interparticle force calculations were made with the rigorous treatment for electrolytes expected in cement suspensions in addition to using screened and retarded Hamaker constant with more recent data for dielectric properties of water.

If the electrostatic plane is placed at the particle surface, attractive interparticle forces can be overestimated by at least 30%. The conformation of adsorbed superplasticizers onto cement particle surfaces is to a certain degree uncertain and further work on this aspect will help clarify to what degree the plane of electrostatic charge is best approximated and will further elucidate the role of superplasticizers in cement suspensions.

Solving such questions is of primary importance in the development of new superplasticizers and in problem tracking of cement and superplasticizer incompatibilities.

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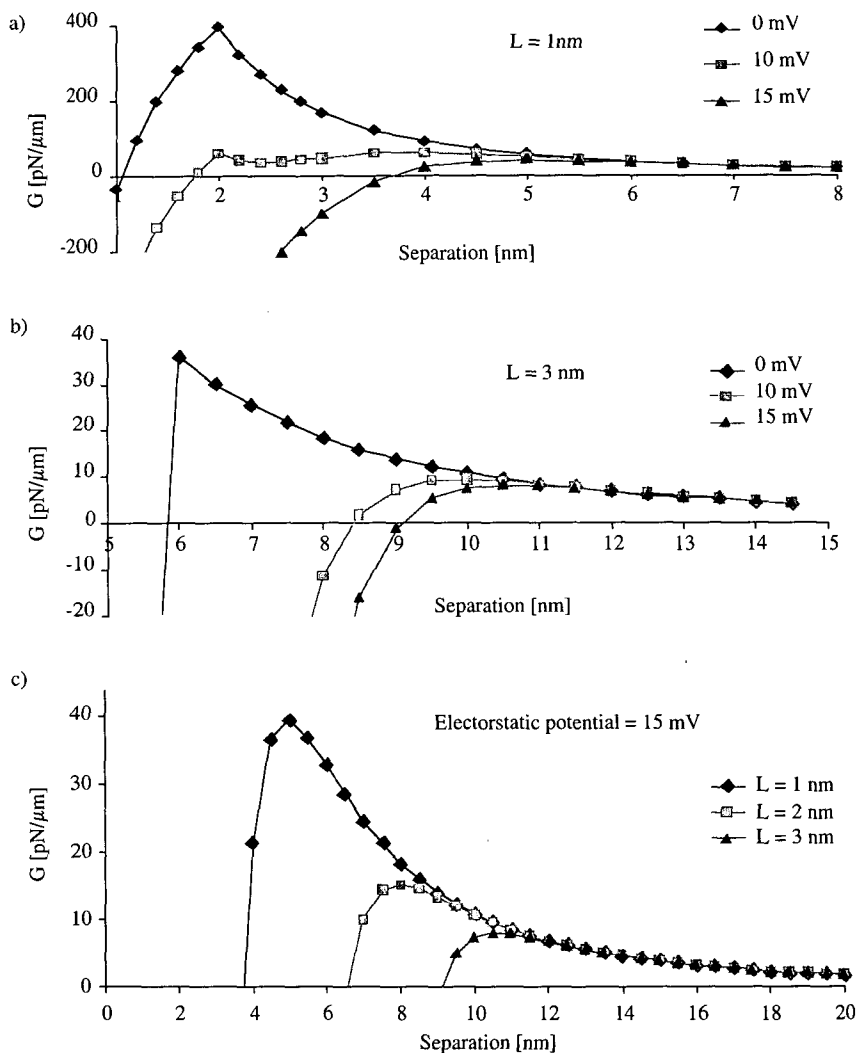


Fig. 1. Normalized interparticle force as a function of separation. Positive values indicate attraction and negative values repulsion. Computed for MgO particles, in the equivalent symmetric electrolyte representation of a cement suspension.

- (a) Adsorbed layer 1 nm, surface potential: 0, 10, 15 mV
- (b) Adsorbed layer: 3 nm, surface potential: 0, 10, 15 mV
- (c) Surface potential: 15 mV, adsorbed layer: 1, 2, 3 nm.

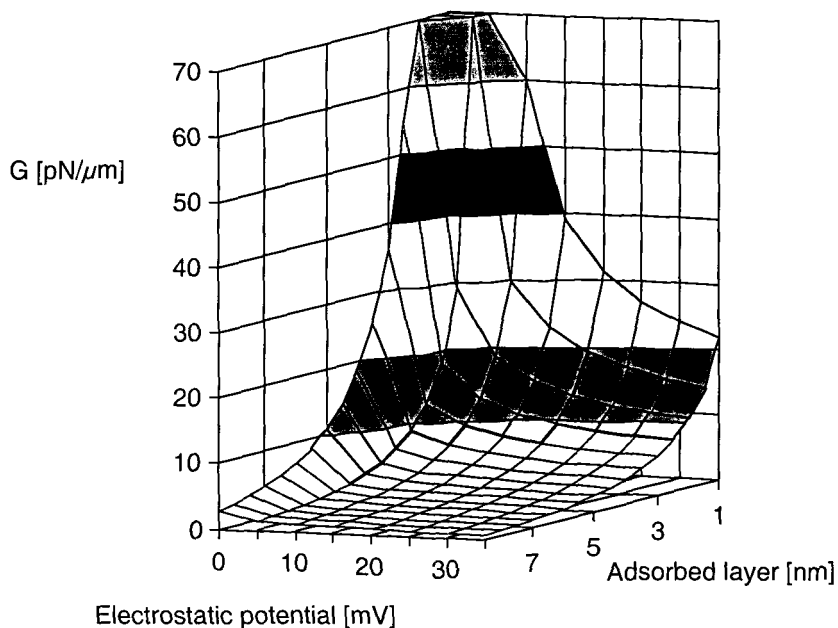


Fig. 2. Normalized maximum attractive force G , determined using the equivalent symmetric electrolyte representation for a cement suspension and using optical data of MgO particles. All adsorbed layers are considered to have a minimum compressed thickness of 0.7 nm .

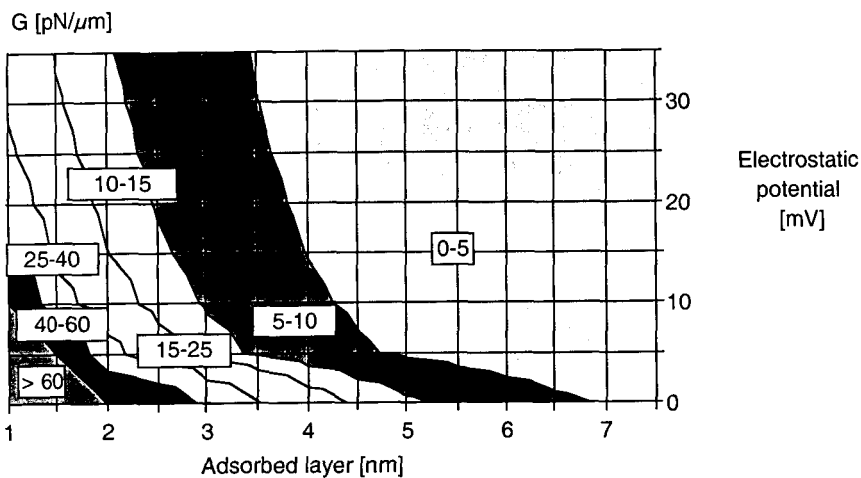


Fig. 3. Normalized maximum attractive force between two MgO particles. All adsorbed layers are considered to have a minimum compressed thickness of 0.7 nm.

Valorization of Modified Starch in Mortars

by J. L. Wolf and J. Péra

Synopsis: This research was aimed at the use of agroresources as admixtures for mortar and concrete. Thirteen modified starches from potato, wheat, corn and waxy corn were investigated. They were compared to methylhydroxyethylcellulose (MHEC) and Welan gum for the following properties: thickening effect, water retention, setting time and 28-day compressive strength.

The study was carried out on standard mortars and the starch dosage was either 0.75 % or 0.25 % of the total dry matter (sand + cement). The results obtained show that the recommended dosage is 0.25 %, which is still economic compared to MHEC and Welan gum. The best performances were obtained with waxy corn starches and, to a less extent, with potato starches. The latter performed well except for water retention.

Keywords: bleeding; compressive strength; flow; mortar; setting time; starch; thickening effect