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New Generation Chemical Admixtures in Concrete Construction

It is interesting to observe that the reinforced concrete construction that made its debut as far back as in 1880 is still evolving. The boundary of imagination in concrete technology is still advancing. All this is not so much due to developments in cement as much due to the advances in chemical admixtures.

Admixtures of various classes provide a means to control and improve the quality of concrete, permit concreting to continue under adverse climate conditions and facilitate design and construction techniques not readily practicable with concrete not containing such materials. The topical high performance concrete (HPC) often contains a mixture of admixtures that has enabled the development of specific applications such as placement in areas of limited access or ensuring proper consolidation coupled with labour savings.

Superplasticisers, so widely known to-day in the field of concrete construction, can be used for three different purposes or a combination of these :

I.   To obtain concretes with very high flowability – slumps in excess of 180 mm – with no alteration in w/c ratio to enhance placing characteristics;

II. To make concrete with low w/c ratio to attain high early and ultimate strengths and improved durability;

III. To reduce both water and cement, at a given workability and strength, in order to reduce creep, drying shrinkage, and thermal strains caused by heat of hydration in mass concrete.

All these objectives have become achievable due to the rapidly increasing diversity in superplasticisers. For nearly half a century, the superplasticizer group comprised mostly two types of polymers, derived from sulphonated naphthalene and sulphonated melamine. In the past decade, however, the introduction of acrylic-type polymers has considerably broadened the group, which now includes dozens of different carboxylated polymers. These are often referred to as "polycarboxy superplasticisers".

The carboxylic group (COOH) being a weaker acid than the sulphonic group (SO_3H), polycarboxylates are ionized or charged only in alkaline environments, whereas polysulphonates are highly ionized even in moderately acidic solutions. Moreover, polycarboxylates are more effective complexants for di- and tri-valent metal ions than sulphonated polymers, a feature which can also contribute to their functional properties. It is also interesting to learn that the inclusion of various side chains or functional groups into acrylate derived polymers leads to a still broader group of products having mixed functionality.

Looking at the immensely expanding potential of functionality of superplasticizers, we thought of devoting this issue of the newsletter to the chemical admixtures, offering you extracts of a few interesting publications.

Apart from polycarboxy superplasticizers we bring to you in this issue some flavours of two other admixtures viz., Viscosity Modifying Admixtures (VMA) and Shrinkage Reducing Admixtures (SRA), which have emerged as very significant modifiers of fresh concrete properties.

In the design of highly flowable and self-compacting concrete mixtures, the use of VMAs has become very essential in order to keep the mixes cohesive. The use of a combination of admixtures in flowing concrete makes compatibility of admixtures a key requirement. Many of the viscosity inducing admixtures compete with the superplasticisers for absorption sites on the cement particles and render the first and second generation superplasticizers less effective. These effects should be considered in the selection of a VMA.

Drying shrinkage is another unavoidable property of concrete that often results in cracks. Most chemical admixtures have little effect on shrinkage but the use of accelerators may often increase the drying shrinkage of concrete. In order to tackle this issue, Shrinkage Reducing Admixtures (SRA) were developed and introduced in the 1980s. Propylene glycol and polyoxyalkylene alkyl ether have been used as shrinkage reducers without any adverse effects on slump and air loss. They are generally known to be compatible with other admixtures. Because of its increasing significance in modern concreting, we decided to draw your attention to this special chemical admixture as well.

These are obviously not all but they are important. We hope you will find the coverage on some modern classes of chemical admixtures interesting and useful.

We look forward to your feedback.

The New Variety of Polycarboxylate Dispersants

Polycarboxylate admixtures (PCs) were introduced in Japan in the early 1980s.Since then they have come a long way through their molecular design in polymer technology for tailor made market oriented applications for different conditions and then engineered molecules to achieve that result.

ASTM covers the use of chemical admixtures for the production of flowing concrete in ASTM C 1017. In this standard, the focus is on treating a concrete mixture with a chemical admixture for the express purpose of producing high-slump concrete while not reducing any of the mix water. In most cases admixtures classified as C 494 Type F or G also would be used in the manner prescribed by ASTM C 1017. These high-range water-reducing admixtures do more than simply reduce water; they disperse cement particles. This dispersive action then allows one to either reduce water, to generate higher slump, or both. Therefore, more flexibility and value is available than the name implies.

Polycarboxylate dispersants

Significant advances in dispersant chemistry have been made in the last decade. This includes the introduction and use of polycarboxylate dispersants across all segments of the concrete industry. Prior to that, most dispersant chemistries had limitations with respect to making modifications to the molecule. However, the introduction of polycarboxylate dispersants has paved the way for developing molecules that will influence performance in specific and tailored ways. This is a tremendous technological advancement for the concrete industry as this enables the use of molecules developed for the sole purpose of dispersing Portland cement, whereas previous dispersants were mainly byproducts of other industries.

Dealing with molecules designed for concrete applications has real advantages for concrete producers. Considering the architecture of a polycarboxlyate molecule allows one to better understand why there is so much promise and flexibility in their application to the concrete industry. First, polycarboxylates are classified as being comb polymers (Figure 1).The name itself implies much about the structure of these molecules in that they are characterized as consisting of a backbone having pendant side chains, much like the teeth of a comb. For these molecules to be effective as dispersants, they must be attracted to the surface of a cement particle. The backbone of the polycarboxylate molecules typically serves two functions: as the location of binding sites (to the surface of the cement particle) and to provide anchoring sites for the side chains of the molecule. The pendant side chains serve as a steric, or physical, impediment to reagglomeration of the dispersed cement grains.
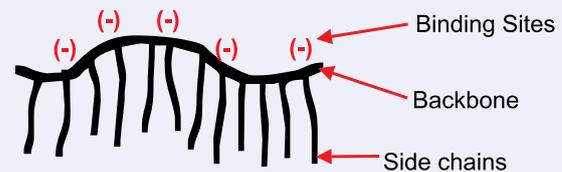

Figure 1 : Comb like molecular structure of PC

Due to the nature of the processes used to manufacture early synthetic dispersants, a chemist's ability to manipulate their structure was limited. Typically, the structures obtained were complex and the processes were relatively difficult to control from a molecular design point of view.

However, the nature of the chemistry that leads to polycarboxylates is rich with possibilities. It allows a chemist to design a dispersant that is an excellent water reducer versus a dispersant that may maintain high levels of workability over longer periods of time. However, the powerfully flexible chemistry behind polycarboxylates is helpful only if one truly understands the nuances of the other materials in the concrete mixture. Ultimately, differences seen in concrete behavior often can be traced back to mineralogical differences in the cements and aggregates. This opens up the door for chemists to optimize a dispersant's performance based on the predominant mineralogies found in a given material. The design of these next generation dispersants may be based on careful and intelligent manipulation of any of the design parameters for polycarboxylates, or through customized formulations, or both. One thing is for certain—game changing performance is often the result. The various properties of PCs which play an important role in concrete are discussed below.

Rheology

PCs is an anionic surfactant, when adsorbed on cement particles becomes negatively charged causing a repulsive effect with each other, consequently its fluidity increases; in addition, the side chains preserve water molecules in contact via hydrogen bonding creating osmotic pressure which increases the movement of these cement particles. PCs improve the fluidity of cement pastes by the dispersion of cement particles. The adsorption of PCs superplasticizer molecules on the cement particles hinders their flocculation as a result of the electrostatic repulsion forces and/or through steric hindrance. Consequently, the particles are homogenously distributed in the aqueous solution, minimizing the amount of water needed for then to be dispersed, which leads to the higher fluidity and workability of cement pastes.

Initial setting time

Figure 2 shows the effect of PCs on initial setting time of cement pastes. PCs forms a complex with Ca^{2+} ions liberated on the surface of C-S-H gel or Ca $(OH)_2$ crystals; the interweaved net structure consists of ion bonded large molecular system bridged by means of Ca $(OH)_2$. In the presence of PCs, it appears that only a few number of Ca^{2+} ions go into the solution and do not becomes supersaturated with respect to Ca $(OH)_2$, i.e. PCs inhibits the growth of hydrates, leading to retard of the setting. Initial setting time of OPC paste extended as the dosage of PCs increases. Adding silica fume with the paste setting time increases upto 40% as PCs content increases up to 0.75%. Also setting times decrease by 5% at higher dosages of PCs.
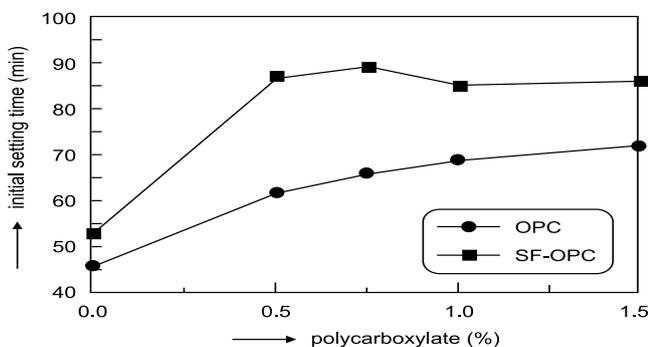
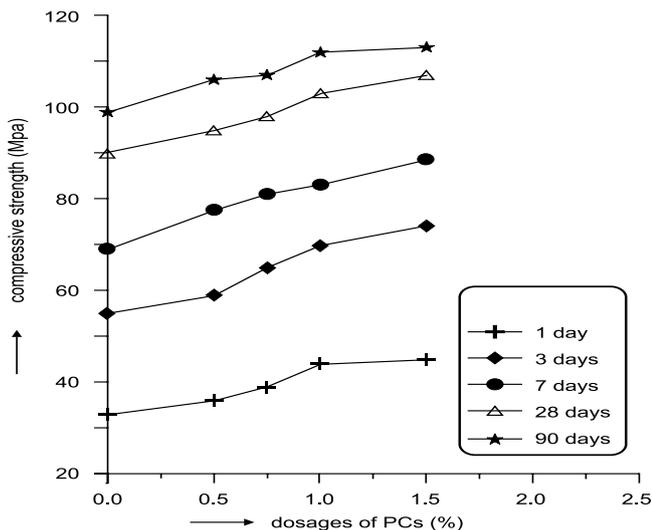Figure 2 : Effect of PC on initial setting time

Figure 3 : Compressive Strength of OPC cement paste

Porosity and Compressive strength

The increase of the dosages of PCs causes reduction of total porosity. As the porosity decreases, the compressive strength increases and electrical conductivity decreases. The compressive strength of all cement pastes increases with curing time. As the dosages of PCs increases upto a maximum of 1.5%, the compressive strength of all samples increases but an over dosages beyond 1.5% causes a reduction of strength (figure 3). This is mainly due to decrease of the total porosity that affects positively the compressive strength of the cement pastes.

Effect on self-compactability

The effect of PC-based SPs on self-compactability of concrete mixtures depends on dosages of PC and water/powder (W/P) ratios. A dosage of 0.8% to 1.5% along with a mix proportion is sufficient to pass the flow tests by U-flow, slum-flow and funnel tests. The various formulaes available can be used to establish a rational method for adjusting the water-powder ratio and superplasticizer dosages to achieve appropriate deformability and viscosity which are known as the index for the dispersing effect by superplasticizer.

The requirements for super plasticizer in self-compacting concrete are given below

- High dispersing effect of low water/powder (cement) ratio : less than approx. 100% by volume
- Maintenance of the dispersing effect for at least two hours after the mixing
- Less sensitivity to temperature changes

There have been many examples of the development of new type of superplasticizer for self-compacting concrete. Characterization of the dispersing effect of superplasticizer independent of the effect of water flow is indispensable for self-compacting concrete.

Figure: 4 Use of PCs in self-compacting concrete in Delhi Metro

The next generation

The latest generation of polycarboxylate admixtures is based on this cutting-edge molecular design and synthesis. One can now take into consideration a significant number

of factors and create a dispersant molecule that is custom designed for that scenario. As has been previously mentioned, the concept of these polycarboxylate dispersants being labeled simply as "water reducers" is somewhat outdated. Polycarboxylates do reduce water; however, additional performance characteristics that benefit the concrete construction process also are possible via molecular design. These additional benefits include previously unreachable levels of slump retention, which can result in significant material and production efficiencies for the concrete producer and the contractor. Figure 5 shows the slump retention comparison between three polycarboxylates tailor made for specific applications.
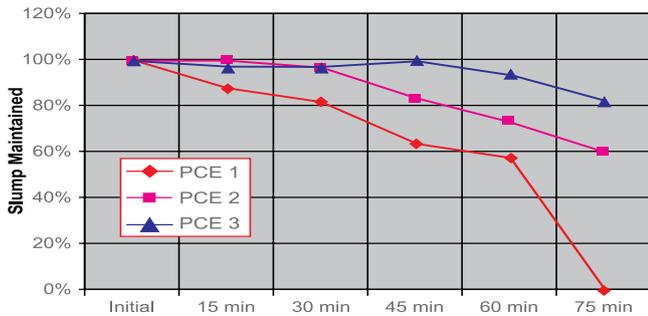

Figure 5 : Slump retention comparisons of three different types of PCs

Impressive levels of high early compressive strength also can be achieved, which will impact production efficiencies for contractors, as well as precast concrete producers. Some of these new molecules provide combinations of the previously mentioned characteristics resulting in never before seen concrete performance. For example, a molecule has been developed that will provide slump retention for 45 to 60 minutes while still providing high early strength. Historically, some level of retardation was required to provide slump retention to high early strength concrete mixtures, however, too much retardation would negatively impact the early compressive strength. Because of this need to balance retardation and strength gain, a compromise twas required that would not allow one to capture the full benefits of both slump retention and early compressive strength.

Figures 6 and 7 compare a first generation high early strength polycarboxylate molecule coupled with a retarder (for slump retention) versus a next generation polycarboxylate designed specifically for slump retention and high early strength without a retarder. The figures show slump retention, rate of hardening, and 14-hour compressive strength respectively.
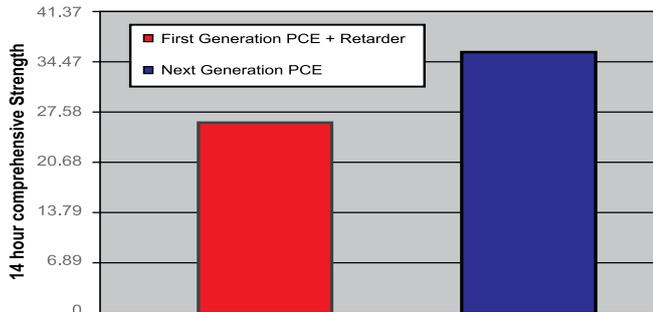

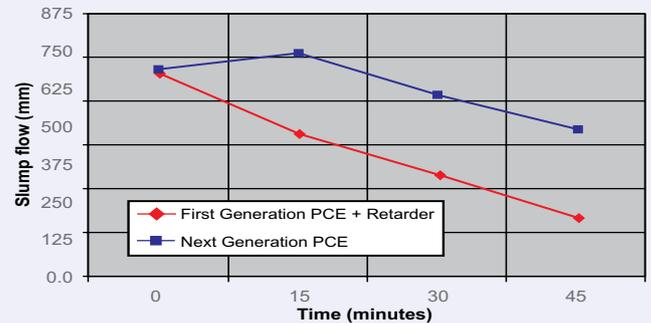Figure 6 : Compressive Strength (MPa) of two different types of PCs after 14 hour.

Figure 7 : Slump Flow vs. Time of two different types of PC

These new performance combinations provide significantly greater value to the concrete producer and contractor than previous dispersants. In considering the concrete performance, one must take the next step and relate that to actual value for the industry. Performance characteristics, such as slump retention, can provide the following benefits:

- Eliminate or reduce retempering at the jobsite allowing for more consistent and efficient concrete placement
- Improved surface aesthetics due to consistent workability resulting in a reduction in surface patching
- Overall more consistent and higher quality concrete

The sensible lower cement contents and a consequent reduction in the risk of thermal cracking and higher concrete consistency as standard at lower cost are other benefits to the end-user. PCs are compatible with air entrainment in concrete, and have no adverse impact on freezing and thawing durability and also compatible with other mineral admixtures such as GGBS and Silica Fume.

These well engineered mixtures are being used in a variety of concrete applications and the new polycarboxylates have become an important component in these mixtures. Additionally, several large precast concrete producers have begun using the high early strength/slump retaining polycarboxylates to facilitate the placement of high-performing SCC mixtures. This results in more consistent concrete production as well as further improvements to the surface finish of the elements cast with concrete.

This next generation of polycarboxylate superplasticizers is being recognized as more than just a high-range water-reducing admixture. They are being recognized as "performance admixtures." The incredible feat of this technology is to allow concrete producers to find new ways of producing concrete as well as creating concrete mixtures with new levels of performance. This is perfect timing for an industry moving towards performance-based concrete. One thing is for sure—this is just the beginning.

Comparing the properties of superplasticizers in terms of dosage and effectiveness, -OH terminated poly (ethylene glycol) methacrylate macro monomers offer an attractive alternative to -OMe terminated methacrylates. However, by using appropriate polymerization technique, superplasticizers of high quality can be synthesized.

New Developments in Shrinkage Reducing Admixtures

(Partly extracted from "Influence of Shrinkage-Reducing Admixtures on Early-Age Properties of Cement Pastes" by Dale P. Bentz, Journal of Advanced Concrete Technology Vol.4,No.3,423-429,October 2006 and "Admixtures:The niche generation" by Don Talend ,A Publication # J960742 of The Aberdeen Group, Boston, MA 02210)

In recent years, shrinkage-reducing admixtures (SRAs) have moved successfully from the research laboratory to being commercially viable admixtures that are often employed in field concrete to reduce drying shrinkage. While the specific chemical compositions of the SRAs vary amongst manufacturers, they generally reduce the surface tension of the pore solution (or of distilled water) by as much as 50% or more, at typical recommended addition rates. It is worth noting that while SRAs will influence the surface tension and viscosity of the pore solution; these materials are usually dosed according to the mass of cement in the concrete mixture. The SRAs is based on polyoxyalkylene alkyl ether or aliphatic propylene glycol ethers.

Shrinkage-reducing admixtures (SRAs) provide a method to reduce the associated strains caused by drying and the resulting stresses. Differences in autogenous deformation (Jensen and Hansen 1996) for cement mortars (w/cm=0.35) with and without SRA, cured under sealed conditions at 30ºC are shown in Figure 1.
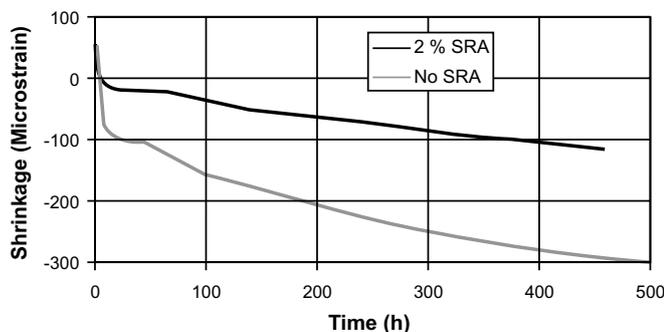

Figure 1: Autogenous deformation for cement mortars with and without SRA

Advantages to this method are that with the exception of the added SRA, concrete mixture proportions and mixing requirements remain relatively unchanged. Thus, the drying shrinkage can be reduced for essentially any currently used concrete. Also increase moist curing reduces long-term drying shrinkage, concrete with SRA exhibits reduced drying shrinkage even if the moist curing is shortened. Random cracking caused by drying shrinkage is always undesirable, but it's particularly objectionable in bridge decks and parking garage slabs, where the cracks make rebar corrosion more likely. Cracking must also be controlled in secondary containment structures and vaults for hazardous material storage. Particularly, a polypropylene

glycol based Shrinkage-reducing admixture (SRA) helps in arresting such types of cracks.

Drying shrinkage is a complicated process, but in simple terms, the cement paste binder shrinks as larger pores within the paste lose moisture. As drying occurs, a meniscus forms at the air-water interface, and surface tension in this meniscus pulls the pore walls inward, causing the concrete to shrink. The test for shrinkage can be made as per ASTM C157 (Standard Test Method for Length Change of Hardened Hydraulic-Cement Mortar and Concrete). Figure 2 shows length change (%) versus time with SRA and without SRA.

The shrinkage-reducing admixture is unique because it works on water molecules, not the concrete structure. By reducing surface tension in the pore water, it reduces shrinkage forces on the pore structure when moisture leaves the concrete during drying. The percentage of shrinkage reduction for low and high dosage SRA for different days are given in Table 1.
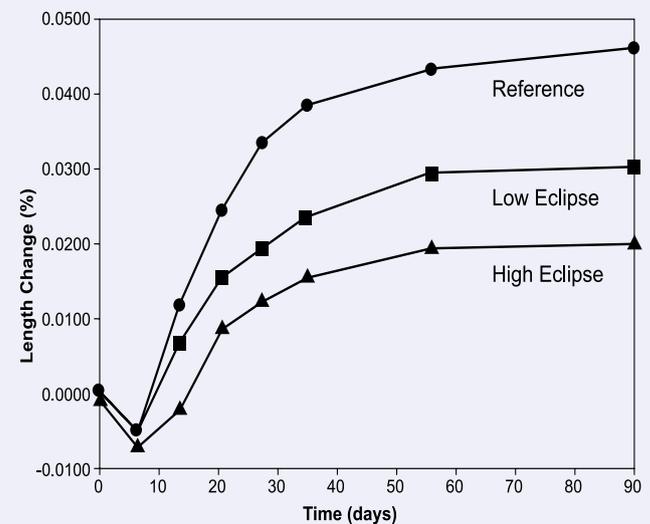

Figure 2 : Length Change (%) versus Time (Eclipse is SRA of Grace Construction Products, USA)

SRA Concrete versus Reference Concrete Shrinkage Performance

(expressed as % Shrinkage Reduction of Reference)

Table 1

	28 Days	90 Days	365 Days
Low dosage SRA	41	34	36
High dosage SRA	62	55	56

Effect of SRA on Compressive Strength:

There is an undesirable side effect as 2% SRA in the mix can reduce compressive strength by as much as 15% at 28 days. To offset this effect, it is recommended to add

enough superplasticizer to reduce mixing water by 7% to 10% while keeping cement content constant.

But studies by 'Brookes and Jiang' shows a reduction of 28% in 28-days compressive strength with an SRA of 1.5% by mass of cement addition with w/c=0.42 and cured at 100% RH against controlled specimens prepared without the SRA.

Also studies by 'Folliard and Berke' shows a reduction of 6% to 8% in 28-days compressive strength with a SRA of 1.5% addition, cured at 20°C and 100% RH for concretes with and without silica fume and w/s ratio of 0.35.

However studies by 'Benz,Geiker and Hansen shows that a reduction of 15% and an increase of 14% in 7-days & 28-days compressive strength, with and without SRA respectively, with a w/s ratio of 0.35 containing 8% silica fume and 2% SRA, cured at 30°C and 100% RH. The higher 28-days compressive strength may be due to addition of silica fume along with controlled curing with higher internal RH during which silica fume reacts pozzolanically with the calcium hydroxide formed from the cement hydration, leading to higher degrees of reaction and higher strengths. But it seems that SRA does not contribute significantly in 28-days compressive strength.

Interaction between SRA and Cement Paste's Solution:

• The mixture of SRA and pore fluid forms an oil water-surfactant emulsion which may or may not be stable depending on the concentration of SRA. At some intermediate concentrations (7.5% to 15 % for the synthetic pore solution),the emulsion becomes unstable and separates into two distinct phases; an SRA-dilute phase which contains approximately 7.5% SRA and a SRA-rich phase which contains the excess SRA (i.e., in excess of 7.5%).Below 7.5% and above 15% the emulsion is stable, clear and macroscopically homogeneous.

• SRA reduces the surface tension of pore fluid when added up to a threshold concentration (e.g., 7.5% for the synthetic pore solution).Beyond this critical threshold, further addition of SRA results in accumulation of surfactant molecules within the bulk solution rather than the solution-air interface. As such ,beyond the critical threshold, further reduction in pore fluid's surface tension becomes marginal.

• The addition of SRA reduces the polarity of mixing water. This results in lowering the affinity of alkalis (e.g, K_2SO_4) to dissolve and ionize in the mixing water. Consequently, the resulting pore fluid contains a smaller concentration of alkali ions compared to the pore fluid of a plain cement paste. The reduced alkalinity of the pore fluid has a direct impact on the rate of cement hydration and can contribute to retardation in hydration and strength development of concrete containing SRA.

• A delayed addition of SRA (e.g, addition of SRA to concrete at job site instead of addition during the initial mixing at concrete plant) can be beneficial in alleviating the hydration retardation. The absence of SRA in the original mixing water promotes the dissolution of alkalis. As a result, a higher alkali concentration may be achieved when SRA is added after the initial mixing.

• SRA concentration in the pore fluid increases as hydration progresses. This stems from the fact that water is consumed in the hydration process while SRA is not taken up by the hydration products (at least not at the same rate as water).As such, the concentration of SRA increases in the remained pore fluid. A similar phenomenon can occur when concrete is exposed to drying as water is removed by evaporation while SRA remains in the pore fluid.Figure.3 shows degree of hydration as a function of curing time for a w/c=0.35 ordinary Portland cement paste with various SRA additions by mass of cement, cured under saturated conditions at 20°C.
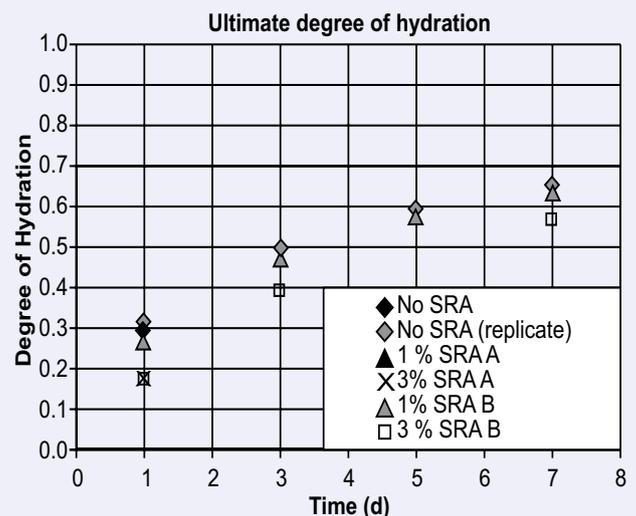

Figure 3 : Degree of hydration versus time

• Although the SRA accelerates the drying of bulk solutions, in cement paste with a w/c ratio=0.35, it actually reduces the measured drying rate.

• A change in the drying profile from uniform drying to a sharp drying front for W/C = 0.35 cement pastes exposed to drying conditions occurs.

- A decrease in the internal Relative Humidity (RH) reduction in low w/c ratio cement pastes and mortars cured under sealed conditions takes place. Fig. 4 shows differences in internal RH (Jensen and Hansen 1995) for ultrafine cement pastes (w/c=0.3) with and without SRA, cured under sealed conditions at 25°C.
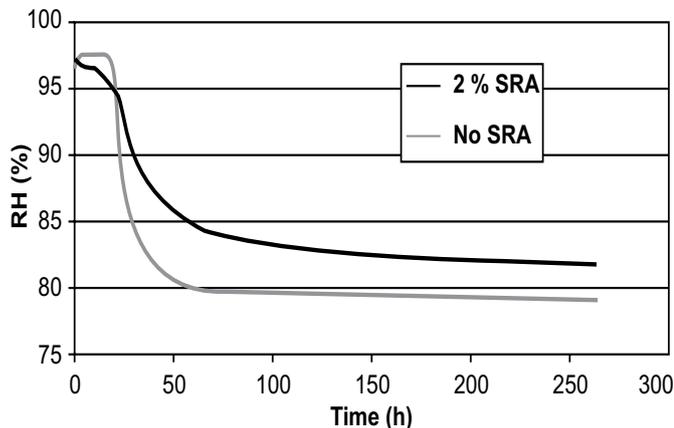

Figure 4 : RH versus time

- Also, a significant decrease in autogenous shrinkage in low w/c ratio mortars cured under sealed conditions occurs.

The above facts suggest that SRA is helpful for the mitigation of early-age cracking in low w/c ratio concretes and possibly for the design of improved curing systems and methodologies.

Figure 5 : Application of SRA Concrete in basement Parking

In addition to their well known influence on drying shrinkage, SRAs also affect drying profiles and drying rates of fresh cement-based materials, internal RH and autogenous deformation at early ages, freezing point depressions within the porous networks, and the viscosity of the pore solution (and potentially diffusion). SRAs may be used beneficially to reduce evaporative water loss from fresh concrete, to reduce autogenous shrinkage, and thus to reduce early-age cracking whether due to plastic shrinkage or autogenous deformation. The significantly greater quantity of freezable water (at around -15°C) in specimens prepared with a SRA will require that appropriate attention be paid to the placement and curing of SRA-containing concretes in cold climate conditions. Finally, in addition to reducing the surface tension of the pore solution, the addition of a SRA should also significantly increase the pore solution viscosity, which could potentially have beneficial implications for reducing the diffusion coefficients of deleterious ions (chloride, sulfate, etc.) in cement-based materials.

The various application areas of SRAs are indoor slab - on - grade concrete construction, bridge decks, parking garages, marine structures and containment structures. It can also be used to extend joint spacing and help reduce cracking in high value flooring.

Reference:

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2. Jensen, O.M., and Hansen, P.F. (1995a). "Autogenous Relative Humidity in Silica Fume Modified Cement Paste," Advances in Cement Research, 7 (25) 33-3 8.

3. J.J. Brooks, X. Jiang, The influence of chemical admixtures on re-strained drying shrinkage of concrete, in: V.M. Malhotra (Ed.), Super-plasticizers and Other Chemical Admixtures in Concrete, Am. Concr. Inst., SP 173 (1997) 249-265.

4. K.J. Folliard, N.S. Berke, Properties of high-performance concrete containing shrinkage-reducing admixtures, Cem. Concr. Res. 27 (9) (1997) 1357-1364.

5. Eclipse: Shrinkage Reducing Admixture, Technical Bulletin TB-1000, Grace Construction Products, USA

Performance of new viscosity modifying admixtures in enhancing the rheological properties of cement paste

Viscosity modifying admixtures (VMAs) are water-soluble polymers that increase the viscosity of mixing water and enhance the ability of cement paste to retain its constituents in suspension. The use of VMA along with adequate concentration of high-range water reducer (HRWR) can ensure high deformability and adequate workability leading to better resistance to segregation of such a concrete. Commonly used VMA in cement-based materials include polysaccharides of microbial or starch sources, cellulose derivatives and acrylic-based polymers.

Mixture containing VMA exhibits shear-thinning behavior whereby apparent viscosity decreases with the increase in shear rate. Such mixture (paste, mortar or concrete) is typically thixotropic where the viscosity buildup is accelerated due to the association and entanglement of polymer chains of the VMA at a low shear rate that can further inhibit flow and increase viscosity.

The investigation by authors was carried out to evaluate the performance of four different types of new VMAs whose properties are given in the Table: 1 based on various tests of rheological properties, fluidity, segregation and washout resistance of the cement pastes. A series of tests using viscometer to obtain rheological data such as yield stress and apparent and plastic viscosity along with minislump and washout tests were carried out to determine the robust mixture proportions for the cement pastes incorporating various dosages of superplasticizer (SP) and VMA. Rheological properties and consistency of cement paste play an important role in controlling the rheology and consistency of concrete.

Table 1 : Chemical and physical properties of VMA

VMAs					
	A	B	C	D	COM
Total solid(%)	80.7	80.2-81.4	80.4-81.6	82.1	42.5
pH	4.9	4.9	4.8	4.8	7.0
Specific Gravity	1.42	1.42	1.42	1.42	1.21
Viscosity (cP) 26^0C	81,000	81,000	54,000	25,000	-
Viscosity (cP) 60^0c	2500	2500	1600	1000	-

Four novel polysaccharide-based VMAs in liquid form classified as A–D and a known commercial VMA widely used in Canada and designated in this paper as "COM" were also used to perform a comparative study. The chemical composition of COM is a proprietary secret and it is composed of a combination of SP and VMA. The percentages of VMA and SP were calculated based on total solid content. New VMAs are soluble in water and dispersed homogeneously to create robust mixtures.

Fluidity tests:

The minislump tests on paste were designed to study the performance of novel form of VMAs. This test could also be used for studying the cement/SP compatibility. The proportions for the cement paste mixes identified as Series 1–4 are summarized in Table 2. The variable parameters in the mixes were VMA and SP contents. Investigations on pastes with COM suggested that the addition of SP was necessary to generate slump flows comparable with those of new VMAs. Even then, higher dosages of COM were necessary in the pastes to generate slump flows comparable with those of new VMAs.

Table 2 : Mix design of paste for minislump tests

VMAs			
	A, B, C or D	COM	Control
W/c	0.45	0.45	0.45
VMA (%C)	0.25	0.25	0
	0.50	0.37	
	0.75	0.62	
SP(%)	0.25	0.25, 0.75	0.25, 0.75
Number of mixes	12	6	2

Washout tests:

The mix proportions of the cement pastes used to investigate washout mass loss are presented in Table 3. These pastes were used to determine the effect of VMA–SP combination on washout mass loss.

Table 3 : Mix design of pastes for washout and rheological tests

	Washout Tests		Rheological Tests
	VMA Type A-D, COM	Control	VMA Type A-D, Com
W/C	0.45	0.45	0.45
VMA (%C)	0.025	0	0.025
	0.050		0.075
	0.075		
SP (%)	0.25, 0.5, 0.75	0.25, 0.5, 0.75	0.25
Number of mixes	45	3	10

Tests on rheological properties of cement pastes:

The purpose of using VMA in cement-based pastes is to improve the stability (bleeding) and rheological properties (viscosity, cohesion and internal friction or bond) to enhance the penetrability and flow characteristics. Ten paste mixes shown in Table 3 were used. The mixing sequence was similar to that used in minislump test. The rheological measurements of paste were conducted by using a commercially available digital Brookfield viscometer (Model RVDV-II) equipped with disc spindles at normal room temperature of about 22–25^{0}C.

Test results and discussion

Fluidity of pastes:

Fig. 2 compares the influence of different types of VMA by showing typical variation of minislump diameter with time for pastes. The fluidity of new VMA pastes is much better than the control mix without VMA and commercial VMA COM. The minislump value (Fig. 2) in VMA pastes ranges between 127 and 132 mm at 0 min compared with 116 mm in control paste (0% VMA). To achieve similar fluidity at a particular dosage of SP (0.25% in Fig. 2), the paste needed much higher commercial VMA COM (about 0.37% compared with only 0.05% of new VMAs in Fig. 2). A number of trial paste mixes using different dosages of COM were tested to verify this conclusion. The minislump value also decreases with the increase of time. The minislump value decreases from a range of 127–132 mm to a range of 93–98 mm in new VMA pastes, from 130 to 82 mm in COM paste and from 118 to 65 mm in control paste (Fig. 2) within 2 h. This clearly indicates a better fluidity retaining capacity for pastes with the combinations of new VMA–SP than the COM-VMA and the control. The requirement of lower dosages to achieve satisfactory fluidity and better fluidity retaining capacity with time can be very useful in developing a satisfactory and cost-effective SCC with new VMAs. Fig. 3 shows the influence of dosages of Type a VMA and time on the fluidity of the paste. The slump value increases with the increase of dosages of VMA in the mixes. Similar phenomena were also observed in pastes with other new VMAs. All VMAs (with Type A marginally better) prove to be quite effective in all the paste mixes and shows better results compared with commercial VMA COM.
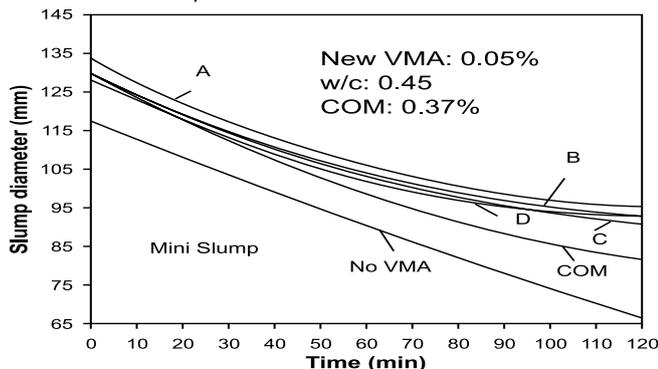

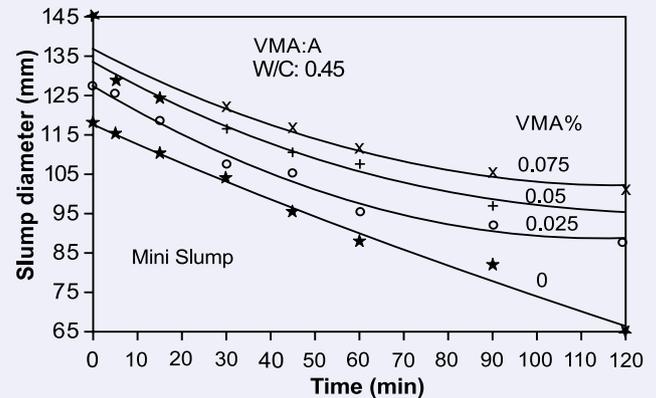Figure 2 : Effect of type of VMA on the slump of paste (SP=0.25%)

Figure 3 : Effect of VMA content on the slump diameter of paste (SP=0.25%)

Washout resistance of pastes

Typical washout resistances of paste with VMAs A and B and COM are compared with those of control paste without VMA in Fig. 4. For similar dosages of VMA and SP, washout resistances of new VMAs A and B are found to be better than the commercial COM and control pastes. Washout mass losses were higher in COM pastes (ranges between 12.6% and 14.9%) compared with VMA Types A (ranges between 6.7% and 12.4%) and B (ranges between 7.5% and 13%) pastes. The washout resistance of the control paste was similar to that of COM pastes. Improvement in washout resistance was not observed in pastes with COM compared with control pastes for the SP–VMA combinations of dosages used in this study. VMA Types A and B pastes are found to have similar washout resistances. Similar behavior was also observed in pastes with VMAs C and D. These results are similar to those obtained by Khayat and Yahia in their investigation on the combination of Welan gum–HRWR. Washout resistance improves with increasing concentration of VMA coupled with a greater content of SP to maintain the desired fluidity. Therefore, by adjusting the combination of VMA–SP, a washout-resistant paste with adequate fluidity can be obtained. The increase in the dosage of SP in paste disperses the cement grains and increases the amount of free water in the system. The higher SP dosage may be the cause for no improvement in washout resistance of pastes with COM compared with control paste. As COM is a combination of SP and VMA, the actual SP content in the COM paste is higher than the pastes with new VMA. This leads to the higher washout mass loss in pastes with COM (Fig. 3). The combined addition of SP and VMA can improve both fluidity and washout resistance. The improvement in washout resistance is due to the enhancement in the degree of water retention by the VMA, whereby some of the free water made by the addition of SP can be physically adsorbed by hydrogen bonding onto polymer molecules of the VMA. Furthermore, some of the VMA polymer becomes adsorbed onto cement grains along with the imbibed water, resulting in further retention of suspended cement particles. The use of VMA increases the viscosity of the paste, which reduces the rate of sedimentation of cement grains, thus resulting in highly stable paste even at elevated fluidity levels.
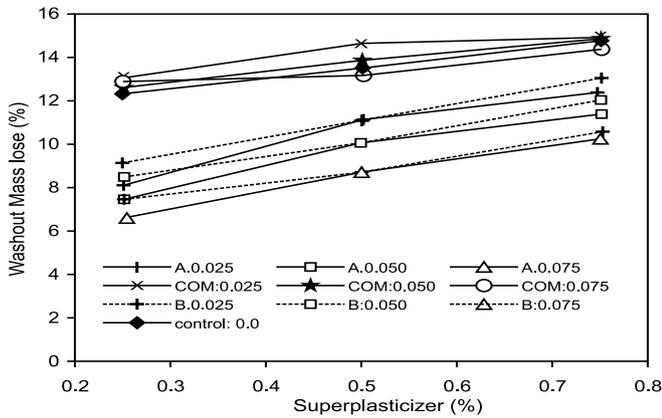
Figure 4 : Washout mass loss of paste

Rheological properties of pastes

The variation of apparent viscosities with shear rate for pastes with 0.025% and 0.075% of various VMAs at 15 and 30 min is shown in Fig. 5 and Fig. 6. Apparent viscosity decreases with the increase of shear rate. The apparent viscosities of pastes with Types A and B VMA are found to be higher than those of the other VMAs including commercial COM. The apparent viscosity is also increased with the increase of the dosages of VMA from 0.025% to 0.075% as can be seen from the typical graphs shown in Fig. 7 and Fig. 8 for Types A and B VMA. For any given concentration of SP (0.25% in the current study), the increase in VMA content should increase the viscosity at both high and low shear rates, and this was observed in the study (Fig. 7 and Fig. 8).
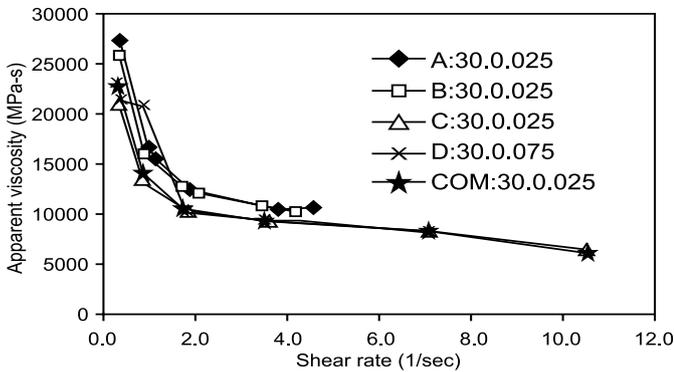

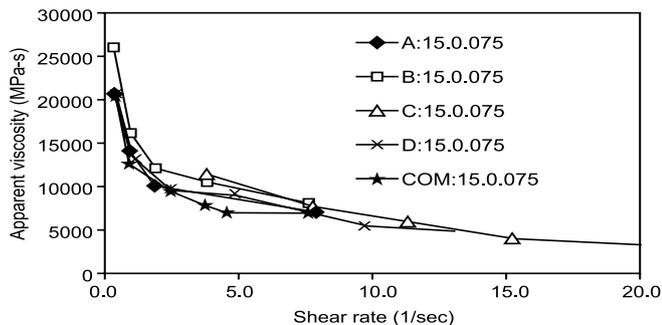Figure 5 : Variation of apparent viscosity with types of VMA 1

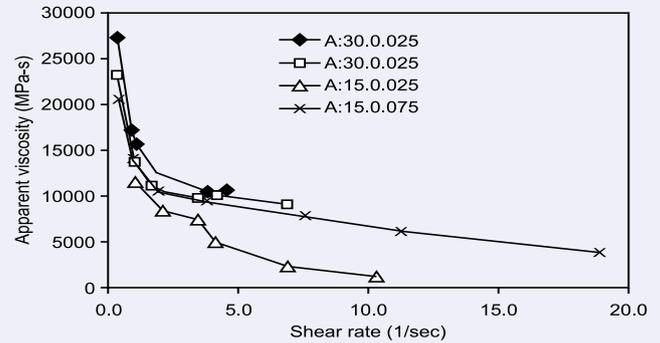Figure 6 : Variation of apparent viscosity with types of VMA

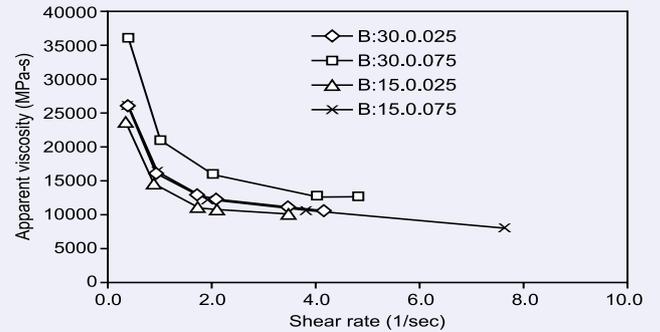Fig. 7 : Variation of apparent viscosity with time and dosages of VMA

Fig. 8 : Variation of apparent viscosity with time and dosages of VMA

The apparent viscosity of paste with 0.025% of Type A VMA is increased from 1500 MPa s at 10 s^{-1} to 11,500 MPa s at 1.5 s^{-1} compared with 7000 MPa s at 10 s^{-1} and 20,500 MPa s at 1.5 s^{-1} in paste with 0.075% Type A VMA (Fig. 7). Similar behavior is also observed in pastes with Type B VMA (Fig. 8).

This can be attributed to the fact that the degree of water retention and the free water needed to lubricate the paste increases with the dosage of VMA that acts on the aqueous phase. The addition of VMA also increases the degree of pseudo plasticity or shear thinning of cement paste regardless of the concentration of SP. Pastes with VMA exhibit high apparent viscosities at low shear rates and significantly lower viscosities at greater shear rates. For the same dosage of SP, the use of VMA results in a greater apparent viscosity at low shear rate than at high shear rate (Fig. 5, Fig. 6, Fig. 7 and Fig. 8).

The increased pseudo plastic response in the presence of VMA is believed to be because the polymer chains of the VMA entangle or associate, resulting in an increase in apparent viscosity, especially at low shear rate. With the increase in shear rate, the entangled chains dislodge and align in the direction of flow, thus decreasing the resistance of the grout to undergo deformation. The apparent viscosity is then decreased with an obvious improvement in flowability at high shear rate regimes.

The effect of the increase in the concentration of VMA on viscosity depends on the shear rate. For a given concentration of SP, the increase in the dosage of VMA is more effective in increasing viscosity at low shear rate than that at high shear rate (Fig. 5 and Fig. 6).

Fig. 9 compares the yield stress of pastes with different dosages and types of VMA. The yield stress is decreased with the increase of dosages of VMA from 0.025% to 0.075%. The yield stress, viscosity and apparent viscosity values are affected by the combination of dosages of VMA and SP. It is then important to find out the combinations of dosages of VMA and SP to secure a stable paste with required fluidity and rheological properties. This can be achieved by testing trial mixes with various combinations of dosages of SP and VMA as illustrated in this study.
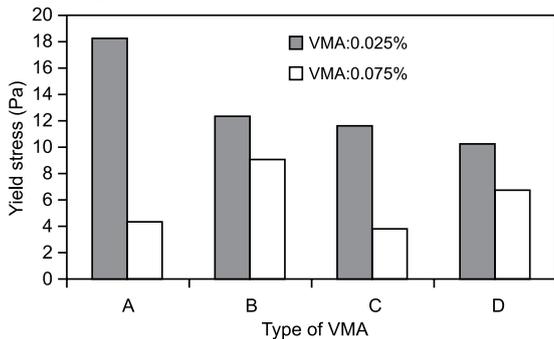

Figure 9 : Variation of yield stress with VMA concentration

Fig. 10 shows a typical variation of viscosity of paste with time (elapsed between mixing and testing) for various types of VMA. Viscosity is found to increase with the increase of elapsed time. This can be attributed to the hydration of cement with time that made the paste stiffer as time progresses. This also indicates somehow that the new VMAs are not inhibitors for the cement hydration.
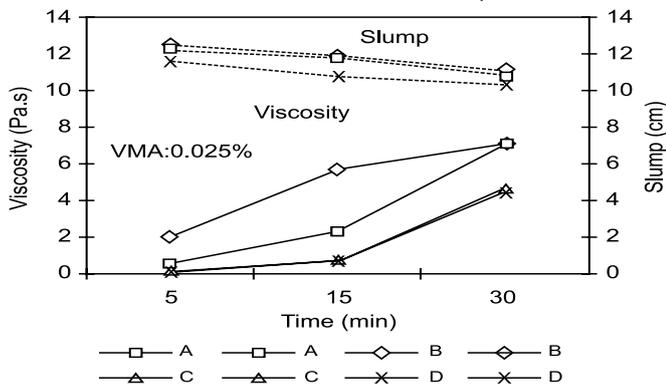

Figure 10 : Viscosity and slump as a function of time and types and dosages of VMA.

The performance of Types A and B VMA is found to be better than the other VMAs for similar dosages of VMA and SP used in this study.

Figure 10 shows a typical variation of viscosity and slump diameter with time. The viscosity increases and the slump value decreases with time. It can be seen that an increase in the viscosity of the paste reduces the flowability. The increases in Types A and B VMA content from 0.025% to 0.075% can increase the viscosity in wider range than the other VMAs (Fig. 7 and Fig. 8). This justifies the suitability of Types A and B VMA and the need of finding an optimum dosage that can develop adequate viscosity to ensure an optimum flowability.

Conclusions

The performance of four different novel VMA designated as Types A–D compared with a commercial VMA designated as "COM" was investigated. The influence of various dosages and types of VMA in addition to the dosages of SP on fluidity, viscosity, yield stress and washout resistance of cement pastes made with a W/C of 0.45 was studied. Based on the results presented in this paper, the following conclusions can be derived:

1. Minislump value increases with the increase of dosages of VMA from 0.025% to 0.075% for a fixed dosage of SP. Minislump value decreases with the increase of elapsed time between mixing and testing, somehow indicating that the hydration of the cement pastes is not inhibited. Based on investigation, all new VMAs prove to be quite effective (with Type A marginally better) in enhancing the consistency of all the paste mixes, showing better flowability compared with commercial VMA COM.

2. The apparent viscosity of the cement paste is increased with the increase of dosages of VMA from 0.025% to 0.075%. The viscosity of Types A and B VMA is found to be higher than other new VMAs and commercial COM particularly at low shear rate of up to 5 s^{-1}. Viscosity of the pastes also increases with the increase of elapsed time between mixing of paste and testing. Based on viscosity data, Types A and B VMAs are found to be more efficient than other new VMAs and would provide better rheological properties.

3. The washout resistance is enhanced by the increase in VMA dosage and reduction in SP content. However, with a proper use of VMA–SP combination, highly flowable yet washout-resistant mixtures can be secured. Washout resistance of Type A, B, C or D VMA is found to be higher than that of commercial VMA COM for similar dosages of VMA–SP combination.

4. The minislump test results correlate roughly with the yield stress of the cement paste even if there is a scatter of data. General trend shows a decrease in yield stress of the paste with the increase in slump. This suggests that a correlation between rheological properties and consistency of paste can be achieved with sufficient test data.

5. A correlation between viscosity and minislump of paste shows a decrease in minislump with the increase in viscosity of the paste.

6. Based on the current investigation, cement pastes with 0.05% of either Type A or Type B VMA would provide better rheological properties at W/C of 0.45 and SP content of 0.25%.

7. The conclusions reached based on the tests on paste in the selection of type and dosage of new VMA (in this case, VMA Types A or B) could be used in the development of a SCC with satisfactory properties, and research is now focused in that direction. The future research will also validate the prediction of the influence of VMA on SCC rheology based on that on the rheology of cement paste.

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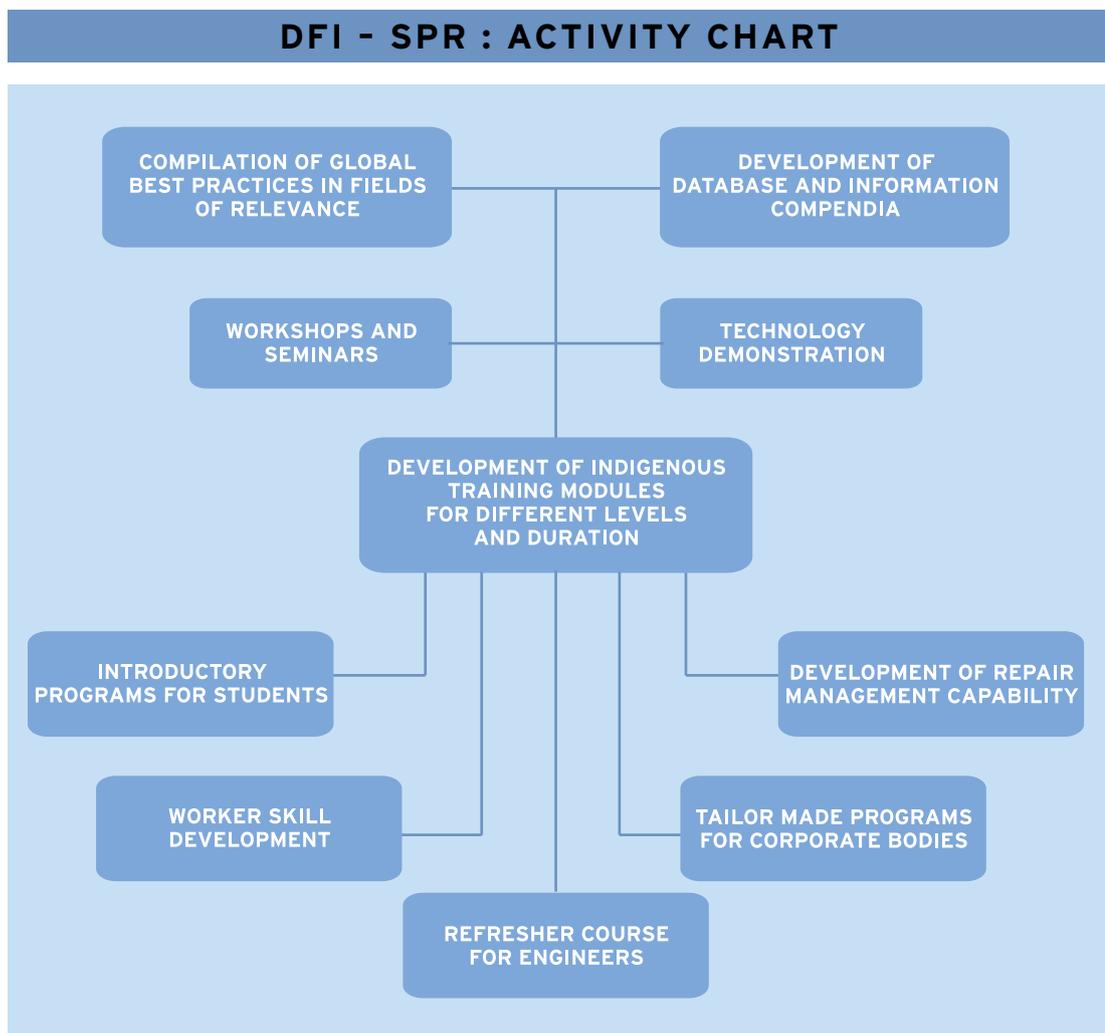### Dr. Fixit Institute of Structural Protection and Rehabilitation

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