

Self-Compacting Concrete: What Is New?

by M. Collepardi

Synopsis:

The paper summarizes the results on flowing and cohesive superplasticized mixtures studied and placed in the 1970's and 1980's with properties very close to those of Self-Compacting Concretes (SCCs) presently considered to be the most advanced cementitious material.

Case histories (from Hong Kong, New York, and Trieste, Italy) concerning placing of superplasticized self-levelling concrete without any vibration at all, published in the 1980's, are re-examined to compare them with the present SCCs.

In particular, the paper deals with the ingredients of these mixtures (superplasticizer, cement, fly ash, ground limestone, silica fume, etc.) by examining their specific role in determining the main properties of these concretes, such as fluidity, on the one hand, and resistance to segregation, on the other. Some interesting new materials, such as ground fly ash or powder from recycled aggregates, appear to be very promising for manufacturing SCC in agreement with the requirements needed for sustainable progress.

Keywords: bleeding; fly ash; ground fly ash; recycled aggregate; self-compacting concrete; silica fume; superplasticizer

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INTRODUCTION

The term *Self-Compacting Concrete (SCC)* refers to a “new” special type of concrete mixture, characterized by high resistance to segregation, that can be cast without compaction or vibration. According to the opinion of the author of the present paper such a concrete – or a sort of its very close precursor – was studied and used in practice 20-25 years ago in many countries.

Data available in the international literature indicate that self-levelling and cohesive concretes were firstly studied in 1975-1976 [1, 2]. At that time the maximum slump level admitted by ACI was 175 mm [3]. Moreover, case histories concerning placing of self-levelling concretes **without any vibration at all** were published in the 1980's [4-8].

The present paper summarizes the main progressive advances in concrete technology from the middle of 1970's, after the advent of superplasticizers, until the end of 1990's when the term *SCC* was coined. During this period of time, other concrete ingredients, beside superplasticizers, were found to play an important role in determining or improving the rheological properties needed for *SCCs*. In the following sections of the present paper these ingredients will be examined along with their effect on the properties of these concretes.

THE ROLE OF SUPERPLASTICIZERS AND POWDER MATERIALS

Figure 1 shows the bleeding capacity as a function of the slump level for three different concretes with a cement factor of 300-350-400 kg/m³ in the absence of superplasticizer [2]. The slump was increased by increased the amount of mixing water. When the slump is over 175 mm the bleeding increases too much and this was the reason why ACI in 1973 did not recommend slump higher than 175 mm [3].

With the advent of superplasticizers, flowing concretes with slump level up to 250 mm were manufactured with no or negligible bleeding (Fig. 2), provided that an adequate cement factor was used [2]. In the middle of 1970's, it was suggested [1, 2] to define “*rheoplastic*” as a concrete which,

besides being very flowable, is also very cohesive and therefore has a low tendency to segregation and bleeding.

The most important basic principle for flowing and cohesive concretes including SCCs is the use of superplasticizer combined with a relatively high content of powder materials in terms of portland cement, mineral additions, ground filler and/or very fine sand. A partial replacement of portland cement by fly ash was soon realized to be the best compromise in terms of rheological properties, resistance to segregation, strength level, and crack-freedom, particularly in mass concrete structures exposed to restrained thermal stresses produced by the heat of hydration of the cement [6-7].

Table 1 shows the composition of two typical concrete mixtures which were used to place self-compacting and cohesive concretes at the end of 1970's and at the beginning of 1980's. Special attention was used in selecting coarse aggregate with maximum size smaller than 20 mm (preferably smaller than 15 mm), in order to enhance the mobility of all the concrete ingredients without any significant segregation effect.

Mixture A in Table 1 corresponds to the composition adopted for 40,000 m³ of concrete placed under water (Fig. 3 and 4) by using the Tremie method for the construction of a dry dock at the end of 1970 [4, 5]. Mixture B with fly ash (Table 1) corresponds to the composition typically adopted for massive structures, such as reinforced concrete foundations for skyscrapers [6,7] or very high chimneys at the end of 1970 (Fig. 5 and 6).

The following two statements quoted from reference [8] indicate that the precursor of the SSC at the beginning of 1980 was already available not only for laboratory studies but even for practical and important applications. The first statement refers to a work described in references [4,5]: *"The placement of the foundation slab for the construction of the dry dock, where 40,000 m³ of rheoplastic concrete were poured under water, exploited the self-levelling underwater placement without vibration, on one side, and the great cohesion of the mix to minimize the washing away by sea water, on the other"*.

The second statement refers to a mass concrete for foundation slabs: *"For the contractor the rapid placement of concrete allows economies to be realized during the execution of the work. Obviously the saving due to the employment of less manpower and less time of execution, must be higher than the cost of the addition of superplasticizer. This usually occurs in most reinforced concrete works and is more and more advantageous the more intricate the reinforcement and the more complicate the shape of the structure are"*.

There is an other interesting statement of the engineers involved in the placement of concrete (190 m³/hr with maximum of 350 m³/hr) for the Hong Kong slab foundation in 1983-84 [7]: *"It was decided to use poker vibrators initially, to ensure the concrete was adequately compacted under and round the bottom mat of reinforcement. At the end it was considered unnecessary to continue vibrating the concrete, as the superplasticizer produced a 'flowing concrete' which was self-compacting. The self-compacting property of the concrete was shown by the apparently large volume of water displaced during*

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the pour which finally had to be pumped away to allow surface finishing-off to proceed”.

The above sentences seem to be quoted from a present paper on SCC rather than on its precursor of least 20 years before.

Table 2 shows some interesting results on the degree of compaction, in terms of density, and compressive strength of the concrete used for a 4.7 m thick slab in the Tin Hau Station of the Mass Transit Railway Island Line of Hong Kong [7]. There is no difference in the density of the specimens and that of the cores taken from 0.5 m, 1 m and 3 m below the surface of the reinforced slab foundation **placed without any vibration at all**. Moreover, the range as percentage of the average strength is a little higher for the laboratory specimens at 28 days (7.1%) than for cores taken at 96 days from the slab foundation (6.2%). This indicates that, even in the absence of vibration, the concrete of the structure was as reliable as that of the laboratory specimens.

THE ROLE OF SILICA FUME

Silica fume or *microsilica* (very fine amorphous silica particles $< 1 \mu\text{m}$) was studied as concrete mineral admixture in the early 1950's at the Norwegian Institute of Technology [9]. However, only in the mid 1970's, after the advent of superplasticizers, silica fume both in practice and in laboratory started in several Scandinavian countries: Norway, Sweden, Denmark and Iceland. After then, research work and practical use of silica fume in concrete started in many countries outside Europe.

Silica fume and superplasticizer are complementary materials to manufacture self-levelling concretes with great cohesion of the fresh mix. Due to this special behavior, silica fume in the presence of superplasticizer can compensate the absence of fine materials, such as fly ash or ground limestone in relatively lean cement mixtures (about 300 kg/m^3).

THE ROLE OF VISCOSITY MODIFYING ADMIXTURES

The use of *Viscosity Modifying Admixtures (VMA)* is definitely the most innovative material for the present self-compacting concretes with respect to those manufactured in the 1970's and 1980's [10]. These admixtures (0.1-0.2% by mass of cementitious materials) allow the manufacture of self-compacting concrete with a reduced volume of fine materials.

There are two basic types of *VMA*:

- Traditional pumping aids, admixtures used to improve the cohesiveness of lean concrete mixtures to be pumped, and chemically based on modified cellulose or hydrolized starches.

- Poliethielen-glycol and biopolymers [11] which appear to be the most effective *VMAs* for self-compacting concretes.

Figure 7 shows the molecular structure of the biopolymer *welan gum*. Due to its molecular composition (Fig. 7), hydrogen-bonds are present between two glucosidic rings belonging to polymer chains. This produces a significant different increase in the viscosity of the aqueous phase. Moreover, since these polymers can be adsorbed to the surface of cement particles, they produce a long-range bridging effect throughout the cement paste involving the aqueous phase and many cement grains. This can explain the strong increase in the yield stress of the cement paste and the subsequent cohesiveness of the concrete mixture at rest or under a moderate shear stress. However, when a shear stress much higher than the yield stress is applied, the hydrogen bonds between the different polymer chains are broken and the biopolymers align in the direction of the movement of the cement mixture without any adverse effect on the fluidity of the concrete mixture.

OTHER RECENT ADVANCES FOR SCC

Due to the progress in the last 30 years, concrete can be considered to be one of the most innovative building materials. Even for the *SCC* technology there are promising advances related to new available ingredients. Two of these are discussed below.

Acrylic Polymers

During the last three decades the main ingredients in the superplasticizers were synthetic water-soluble polymers, such as sulfonated melamine formaldehyde (*SMF*) condensate, sulfonated naphthalene formaldehyde (*SNF*) condensate, and modified sugar-free lignosulfonate (*MLS*). Advances in superplasticizers, containing alternative water soluble synthetic products, were proposed in the last decade [12] to reduce the slump-loss drawback which can partly or completely cancel the initial technical advantage associated with the use of superplasticizers (low *w/c* ratio or high slump level). More recently, these new superplasticizers - all based on the family of acrylic polymers (*AP*) - have been deeply investigated, and numerous papers on these admixtures were presented at the Fifth CANMET-ACI International Conference on "Superplasticizers and Other Chemical Admixtures", in Rome (Italy), 1997 [13].

Ultra Fine Amorphous Colloidal Silica (UFACS)

Ultra fine amorphous colloidal silica (*nanosilica*) is based on silica particles of 5-50 nm [14] and they are much smaller than those of silica fume (*microsilica*) which contains particles as "big" as 0.1-1 μm . Precipitated silica

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(another type of amorphous silica) also contains particles with the same size of colloidal silica, the main difference being that the former tends to aggragate (Fig. 8).

UFACS is available in the form of an opalescent liquid solution (10-50% of solid content). At a dosage of 3-5%, it is able to reduce bleeding and increase the resistance to segregation. Due to the very high specific surface area (80-1000 m²/g) and the spherical shape of the colloidal silica particles (Fig. 9), *UFACS* enhances the stability of *SCC*, particularly when the filler content is low [15]. Moreover *UFACS* increases the tolerance levels in *SCC* arising from errors in water additions made under mixing.

Ground Fly Ash

Ground fly ash (*GFA*) was studied [15] by Collepardi et al for manufacturing *SCC* with improved properties in terms of lower bleeding capacity and higher compressive strength with respect to corresponding concretes where fly ash (*FA*) or ground limestone (*GL*) was used as cementitious fillers.

Table 3 shows the composition of three mixtures with *GL*, *FA* or *GFA*, all with a reduced cement content (310 kg/m³) of slag cement (*CEM III A* according to the European Norm EN 197/1) in order to produce special *SCC* mixtures for massive concrete structures without any risk of cracks induced by thermal stresses. Table 4 indicates that, at equal slump flow properties, in the presence of *GFA* the bleeding capacity is lower than that with *GL* or *FA*. On the other hand, due to its higher reactivity *GFA* increases the compressive strength of *SCC* with respect to that of the corresponding mixtures containing *FA* or *GL* (Fig. 11).

Fine powder from recycled aggregates

Corinaldesi et al. [16] have found that the use of fine powder from recycled aggregates produced by grinding demolished concrete performs very well as fine filler for the manufacture of *SCC*. The behavior of this powder in reducing segregation and increasing compressive strength is much better than fly ash and very close to that of silica fume. These results appear to be very encouraging and promising for the production of *SCC* in agreement with the requirements needed for a sustainable progress.

CONCLUSIONS

Self-Compacting Concrete is considered to be the most promising building material for the expected revolutionary changes on the job site as well as on the desk of designers and civil engineers. However, the basic principles of this

material are substantially based on those of flowing, cohesive, and superplasticized concretes developed in the mid of 1970's.

The necessary ingredients for manufacturing SCC are superplasticizers and powder materials (including cement, fly ash, ground fillers or other mineral additions even in the form of fine recycled aggregate) at an adequate content ($> 400 \text{ kg/m}^3$ of cement and filler), with some limits in the maximum size of the coarse aggregate ($< 25 \text{ mm}$).

Supplementary materials, particularly for lean SCC mixes (about 300 kg/m^3), are silica fume and/or viscosity modifying admixtures.

The most important progress achievable in the future for this technology depends on the availability and use of some new ingredients such as:

- More effective superplasticizers (those based on acrylic polymers) with respect to the traditional ones (naphthalene or melamine based) in terms of lower slump loss.
- Viscosity modifying admixtures (based on organic polymers) and ultra fine amorphous colloidal silica, both focused to reduce bleeding and to increase the resistance to segregation particularly in SCC with low content of fillers and/or cement.

Modified mineral additions such as ground fly ash and/or crush recycled aggregate.

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Table 1 – Typical Self-compacting concretes in 1970's and 1980's

Ingredient/Property	Mix A*	Mix B**
Ordinary Portland cement	400 kg/m ³	300 kg/m ³
Fly ash	-	90 kg/m ³
Very fine sand (0.075 – 0.60 mm)	180 kg/m ³	-
Sand (0-5 mm)	990 kg/m ³	670 kg/m ³
Gravel (5-15 mm)	630 kg/m ³	305 kg/m ³
Gravel (10-20 mm)	-	710 kg/m ³
Water	190 kg/m ³	187 kg/m ³
Superplasticizer	7 kg/m ³	4 kg/m ³
Water/cement	0.47	0.62
Water/binder (c+f.a.)	0.47	0.48
Slump	260 mm	220 mm

* Typical self-levelling and very cohesive concrete placed under water [4.5].

** Typical self-levelling concrete for mass concrete foundations [7].

Table 2 – Density and strength of laboratory specimens and cores taken 0.5-1.3 m below the surface of the 4.7 m thick slab foundation placed without any vibration at all [7].

SPECIMENS			CORES		
Density (kg/m ³)	Cube (150 mm) Strength (MPa)		Below the concrete surface (m)	Density (kg/m ³)	Equivalent* Cube Strength (Mpa) at 96 days
	7 days	28 days			
2320	24.5	43.0	0.5	2310	57.5
2320	25.0	43.5	1.0	2320	57.5
2310	24.0	40.0	3.0	2320	54.0
		Average = 42.2			Average = 56.3

*Equivalent cube strength = Cylinder strength/0.80

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Table 3 –Composition of SCC at w/c of 0.58 [15].

Mix	Cement * (kg/m ³)	Mineral addition:		Sand (kg/m ²)	Gravel (kg/m ²)	Water (kg/m ³)	AP (%)***
		amount (kg/m ³)	s.s.a.** (m ² /kg)				
GL	306	157	310	964	824	178	0.70
FA	307	128	350	965	824	178	0.96
GFA	312	130	2100	981	838	181	1.12

* Slag cement CEM III A 32.5 R according to EN 197/1 with 60% of GGBS

** s.s.a.: specific surface area

*** By cement and mineral addition

Table 4 –Properties of SCC mixtures in the fresh state [15].

Mix	Specific gravity (kg/m ³)	SLUMP FOW				Bleeding capacity (% by vol. of concrete)	Aspect (Visual Rating)
		After mixing		After 30 min.			
		mm	sec*	mm	sec*		
GL	2429	790	20	720	25	0.12	Slight segregation
FA	2402	790	30	750	35	0.11	Slight segregation
GFA	2442	790	20	700	25	0.06	Cohesive

*time needed to reach the final slump flow

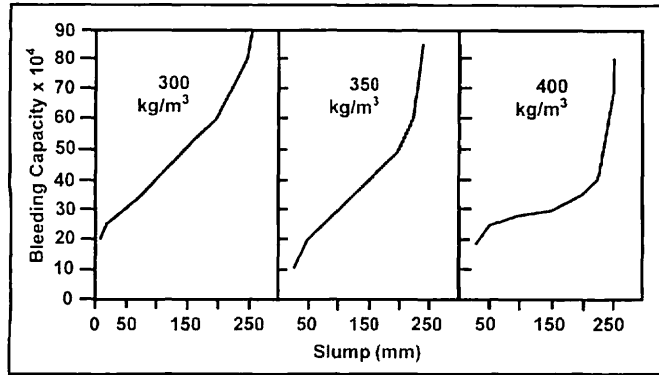


Fig. 1 – Bleeding capacity as a function of slump for concretes not containing additives [2].

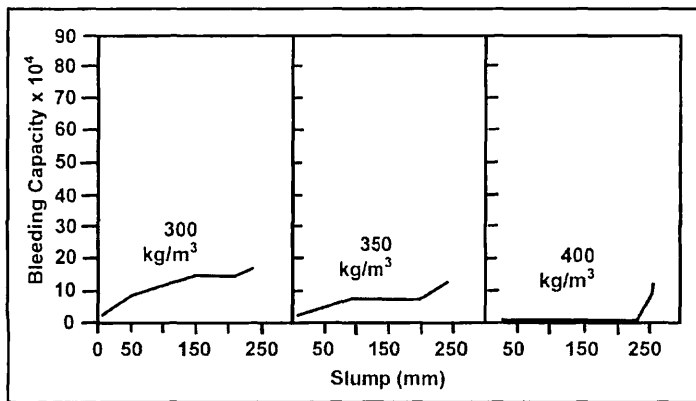


Fig. 2 – Bleeding capacity as a function of slump for concretes containing superplasticizer [2].

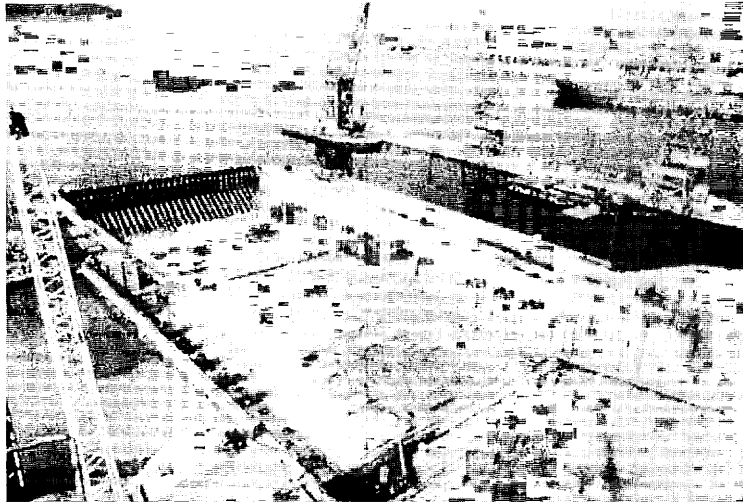


Fig. 3 – Aerial view of the dry dock after removing sea water [4].

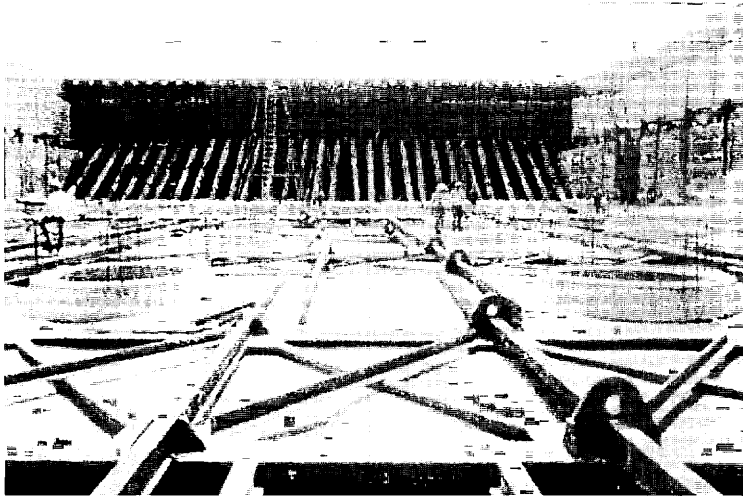


Fig. 4 - View of the reinforced slab foundation placed under water without vibration [4].

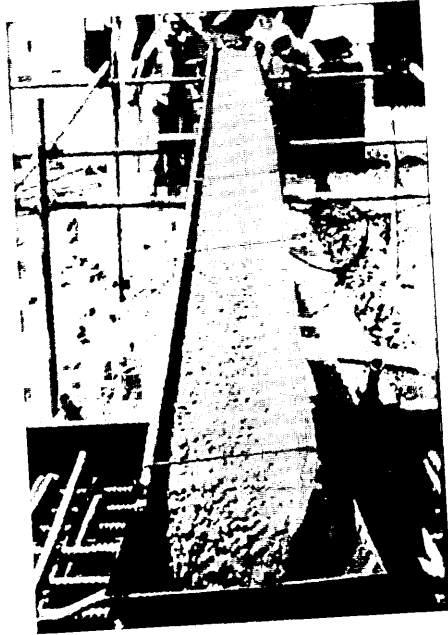


Fig. 5 - Self-compacting concrete placed by chute [8].

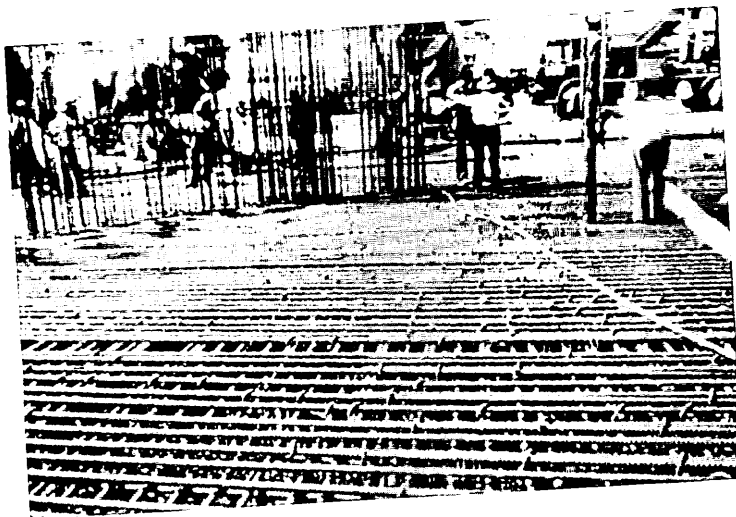


Fig. 6 - Congestion of reinforcement of a slab foundation where concrete (in the background) is placed without vibration [8].

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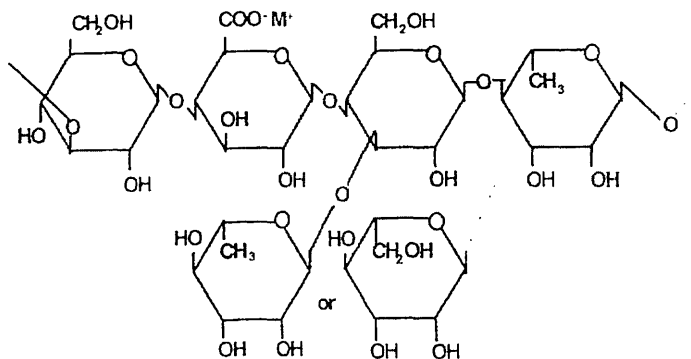


Fig. 7 - Molecular structure of the welan gum biopolymer

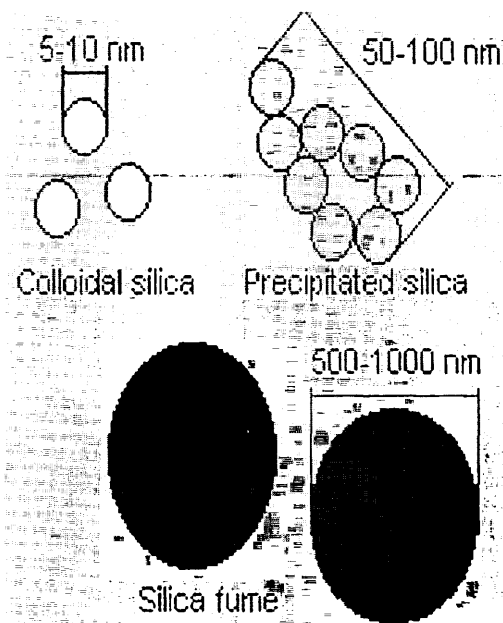


Fig. 8 – Colloidal silica vs. precipitated and silica fume [9].

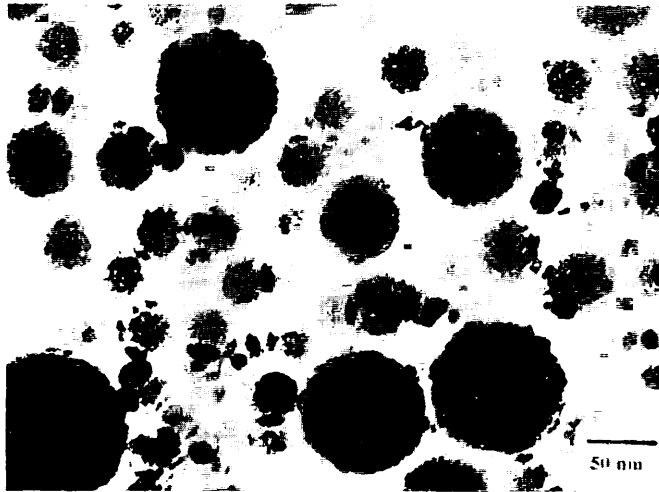


Fig. 9 - Ultra fine amorphous colloidal silica particles under transmission electron microscope [13].

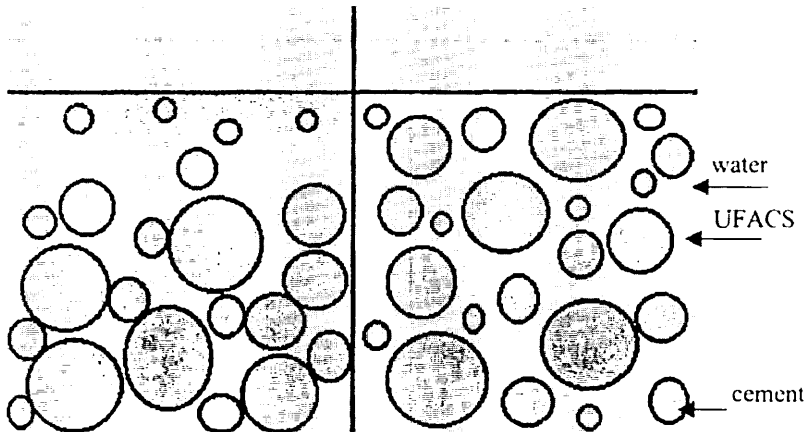


Fig. 10 – UFACS improves safety and tolerance towards errors in the addition of mixing water [15].

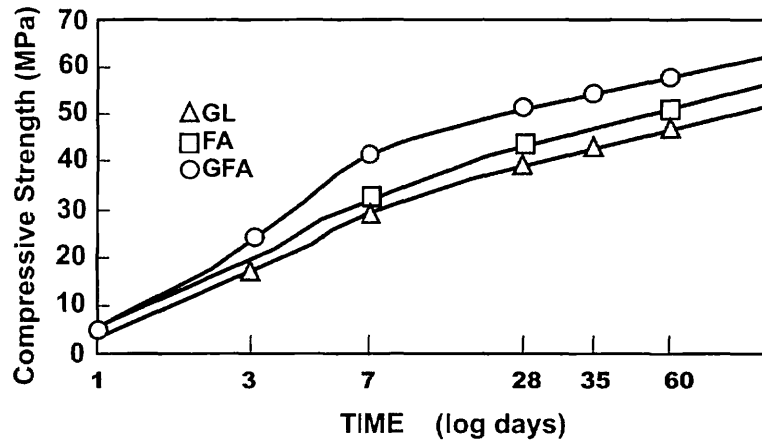


Fig. 11 – Cube-compressive strength as a function of time of SCC with ground fly ash (GFA), fly ash (FA) and ground limestone (GL).

Durability of Concrete Made with Different Chemical Admixtures Under Marine Splash Environment

by T. U. Mohammed, H. Hamada, and T. Yamaji

Synopsis:

A detailed investigation on the concrete specimens made with different chemical admixtures was carried out after 10 years of exposure in the marine splash environment. Chemical admixtures include air-entraining admixture (vinsol), water-reducing admixture (lingsulfonate group), various high-range water-reducing and air-entraining admixtures (naphthalene, melamine, polycarboxyl and amino-sulfonate group), and drying shrinkage reducing admixture (glycol ether plus amino alcohol derivatives). The specimens were tested for carbonation depths, chloride ingress, oxygen permeability, electrochemical and physical evaluations of corrosion of steel bars in concrete, porosity and mineralogy of the mortar portion, and SEM (Scanning Electron Microscopy) investigation of steel-concrete interface.

Naphthalene group of high-range water-reducing and air-entraining chemical admixture shows relatively better performance with respect to the strength development and chloride ion ingress in concrete. The use of shrinkage reducing admixture shows no harmful effect after 10 years of exposure. The specially adopted method of casting concrete used in this study causes a formation of good steel-concrete interface that prevents the initiation of corrosion even for water soluble chloride concentration around 1.5% of cement mass.

Keywords: chemical admixture; chloride; concrete; corrosion; durability; marine environment; steel bars; steel-concrete interface

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INTRODUCTION

Water-reducing chemical admixtures are used to produce concrete of higher strength, obtain a specified strength at lower W/C, or increase the slump of a given mixture without an increase in water content. Numerous studies on the properties of fresh concrete (or at the early age of exposure) mixed with different chemical admixtures were carried out. Also several international conferences had been held focusing on the chemical admixtures in the last couple of decades. However, detailed studies on the long-term performance of concrete mixed with different chemical admixtures are very scarce (1). Therefore, studies on the long-term performance of chemical admixtures will be very useful for the sustainable development of concrete technology. With this background, a detailed study on the concrete specimens exposed to the marine splash environment was carried out. In addition to the water reducing admixtures, shrinkage reducing admixture was also investigated. Other factors, such as slag with different fineness, W/C, and slag contents were also included. Moreover another series of the specimens was also exposed in the marine tidal environment. The results of this series were reported separately (2, 3).

RESEARCH SIGNIFICANCE

Different types of high-range water-reducing and air-entraining chemical admixtures were developed in the last few decades. Most studies on these admixtures have been carried out to judge the properties of fresh concrete, or the properties of concrete at the early age. Studies on the long-term performance of concrete made with different water-reducing admixtures are very scarce. Therefore, this long-term study of different chemical admixtures will be very useful to the concrete professionals.

SCOPE

Reinforced cylindrical specimens (100 mm diameter and 200 mm height) of sixteen different cases were investigated. The variables include air entraining (vinsol) chemical admixture, water reducing (lignosulfonate type) chemical admixture, high-range water-reducing and air-entraining (naphthalene, melamine, polycarboxyl, and amino-sulfonate types) chemical admixture, drying shrinkage reducing chemical admixture (glycol ether plus amino alcohol derivatives), slag fineness (4000 and 8000 cm^2/g), slag content (40%, 55%, 70%), and W/C (0.4, 0.47, and 0.5). The specimens were exposed in an artificial marine splash zone for 10 years utilizing seawater directly from the sea. In each case, three specimens were investigated. The specimens were tested for carbonation depths, chloride ingress in concrete, and chemical and physical evaluations of corrosion of steel bars in concrete, and others. Unfortunately there were no plain concrete specimens exposed to the splash zone for the evaluation of compressive strength. The compressive strength of another series exposed to the tidal exposure was reported here. For further deterioration of the specimens after 10 years exposure, some specimens were exposed in an artificial accelerated chamber for 22 cycles. Each cycle consists of seven days, three days spraying of seawater at temperature 60°C and four days drying at atmospheric temperature. Some specimens are still retained at the exposure sites for investigation at the age of 15 and 20 years of exposure.

MATERIALS

Blended cements by replacing a portion of the cement with slag were used. Two kinds of slag were used with Blaine fineness of about 8000 cm^2/g (Slag 1) and 4000 cm^2/g (Slag 2). In the case of shrinkage reducing admixture, normal portland cement was used with and without blending. The physical properties and chemical analysis of the cement and slags are listed in Table 1. River sand and crushed granite coarse aggregates were used. The specific gravity, water absorption, and fineness modulus of sand (< 5 mm) are 2.63, 1.63 and 2.73, respectively. The values for coarse aggregates (<25 mm) are 2.64, 0.6 and 6.64, respectively. Chemical admixtures used in this study include air-entraining (AEA) based on vinsol, water-reducing (WRA) based on lignosulfonate group, high-range water-reducing and air-entraining (HRWRAEA) based on naphthalene, melamine, polycarboxyl and amino-sulfonate chemical admixtures, and shrinkage reducing chemical admixture. Combination of glycol ether and amino-alcohol derivatives was used as shrinkage reducing admixture. The chloride, total alkali content, and specific gravity of the chemical admixtures are listed in Table 2. Japanese Industrial Standard steel bars (JIS SR 24) were used. The mill-scale over the steel bar was removed by chemical method before embedding into concrete. The chemical compositions of the steel bars are listed in Table 3.

MIXTURE PROPORTIONS

Mixture proportions of concrete are summarized in Table 4. Sixteen cases were investigated. The variables include type of chemical admixtures (Case 3, 11~13, Case 1~6), fineness of the slag (Case 1~6), replacement amount of cement (Case 3, 7 and 8), water-cement ratio (Case 3, 9 and 10), and shrinkage reducing admixture (Case 14 ~ 16). More detail of the variables is explained earlier. The slump of the fresh concrete was 120 ± 10 mm for all cases. Air content was set at 4 ± 1 % for Case 1~13 and 1 ± 0.5 % for Case 14~16.

SPECIMENS

Cylindrical specimens of diameter 100 mm and height 200 mm were investigated as shown in Fig. 1. Round steel bars of diameter 9 mm and length 140 mm were embedded at cover depths of 20 and 45.5 mm. The method of casting concrete specimens with steel bars is shown in Fig. 2. First a wooden frame was inserted at the location of the steel bars after pouring concrete in the mould. Then it was removed about an hour and the steel bars were inserted manually through the hole left in concrete. Concrete surrounding the steel bar was compacted with repeated wooden hammer blows on the mould. This special casting technique was adopted to neglect the influence of spacers provided at the bottom of the mould. Generally, it was found that chloride easily penetrates through the weak interface surrounding the spacers and causes unexpected corrosion of steel bars in concrete. After 28 days of standard curing, three plain concrete specimens were tested for compressive strength of concrete. The reinforced specimens were exposed in an artificially created marine splash environment beside the sea at latitude of about 35° N and longitude of about 138° E. Natural seawater was automatically sprayed onto the specimens with a cycle of 4 hours wetting and 8 hours air drying. The average monthly temperature at the exposure site varies from $5 \sim 26^\circ\text{C}$ in a year. The average annual rainfall at the exposure site is about 1650 mm/year. The specimens were free from freezing and thawing effect. The physical properties and chemical composition of seawater are listed in Table 5.

After 10 years of exposure, it was found that the steel bars were not corroded at all even for a high level of chloride content at the steel bars. Therefore, some specimens (Case 3, 11~13) were exposed for further deterioration in an accelerated chamber for 22 cycles of wetting and drying. One cycle consists of seven days: three days of spraying with seawater at temperature 60°C and four days of drying at atmospheric temperature.

ITEMS OF INVESTIGATION

At the age of 28-days, plain concrete specimens were tested for compressive strength as per JIS A1108. After 10-year of continuous exposure, the reinforced specimens were transferred from the exposure site to the laboratory, then cleaned and tested for the following properties:

Carbonation depth of the specimens was evaluated after spraying a 1% phenolphthalein solution on freshly broken or cut surfaces. To measure chloride ion concentration, a 50 mm disc was cut from the mid-height of the plain concrete specimens. It was cut again to take samples at the depths of 0-5, 5-15, 15-25, 25-40 and 40-50 mm. The samples were powdered and both water and acid soluble chloride concentrations were measured as per JCI SC4.

The polarization resistance of the steel bars and concrete resistance were measured by the AC impedance method. For this, the low frequency was set at 10 mHz and high frequency at 20 Hz. The measurements were carried out keeping the specimens submerged in natural seawater. A stainless steel counter electrode was placed surrounding the specimens. Ag/AgCl half-cell was placed beside the specimen in the seawater. Utilizing polarization resistance data, micro-cell current density of the steel bars was evaluated from the Stern-Geary equation given below (4):

$$I_{mic} = \frac{B}{R_p} \times 10^6 \quad (1)$$

$$B = \frac{\beta_a \beta_c}{2.3(\beta_a + \beta_c)} \quad (2)$$

Where, I_{mic} is the micro-cell current density in $\mu A / cm^2$, the value of the B depends on the slopes of the anodic (β_a) and cathodic (β_c) polarization curves. Assuming, β_a and β_c as 120 mV/decade, the value of B can be estimated at 0.026 V (4). R_p is the polarization resistance in $\Omega.cm^2$.

Anodic polarization curves of the steel bars were also measured. For this, the natural potential of the steel bars shifted to 1 V gradually at the scanning speed of 1 mV/sec and the corresponding anodic current was measured. The specimens were submerged in seawater during the measurement. A stainless steel counter electrode was placed surrounding the specimens in seawater and a half-cell (Ag/AgCl) was placed beside the specimens.

The oxygen permeability was calculated from the following equation (5):

$$\frac{dQ}{dt} = - \frac{I_{lim}}{nF} \quad (3)$$

Where, $\frac{dQ}{dt}$ is the oxygen permeability in concrete in mole/cm².sec (on steel surface), I_{lim} is the limiting cathodic current density in A/cm², F is the

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Faraday's constant (96500 coulombs/mole) and n is 4. The potential was shifted by -850 mV from its natural potential and the limiting current density was measured. During this measurement, the specimens were submerged in seawater. A stainless steel counter electrode and a reference half-cell (Ag/AgCl) were placed beside the specimen.

All specimens were split opened along the steel bars to check the condition of the steel bars and surrounding concrete visually. The corroded areas over the steel bars were traced on a transparent sheet, if any. Then the area was measured by a digital planimeter. The concrete surface surrounding the steel bars was also checked visually after removing the steel bars to identify the presence of visible voids surrounding the bar.

EXPERIMENTAL RESULTS AND DISCUSSION

Compressive Strength

Compressive strengths of concrete at 28-day and after 10-year of exposure in the tidal environment are shown in Fig. 3. There were no specimens in the splash zone exposure. Therefore, these data are noted from another series of specimens exposed to the tidal zone. More results of this series can be obtained in References 2 and 3. Compressive strength of concrete is increased in most of the cases. The increment is more in the case of coarse slag cement (Case 4~6). It is expected due to the slower hydration reaction of coarse slag. The more the slag content the more is the strength development from the 28-day strength (Case 3, 7 and 8). However, 55% replacement shows the maximum compressive strength (Case 3). At the early age (28 days), the strength development for the naphthalene group of chemical admixture was the highest (Case 3). This tendency is also the same after 10 years of exposure. However, after 10 years of exposure, polycarboxyl group (Case 11) shows a 20% reduction in strength from 28-day's strength. In the case of shrinkage-reducing admixture, the increment of compressive strength is observed irrespective of the cement types, such as normal portland cement and blended cements (Blaine fineness of slag 4,000 and 8,000 cm^2/g).

Carbonation Depth and Chloride Ion Profile

The carbonation depth of the specimens was negligible for all cases investigated here. Water and acid soluble chloride concentrations at the average sampling depths of 2.5, 10, 20, 32.5 and 45.5 mm from the surface of the specimens are shown in Fig. 4 for the Case 1~3 and 11~13. The use of water-reducing admixture (WRA or HRWRAEA) reduces chloride ingress in concrete (Case 1~3). Comparing the different type of HRWRAEA, such as naphthalene (Case 3), polycarboxyl (Case 11), melamine (Case 12), and

amino-sulfonate (Case 13) type of chemical admixture, it is found that chloride penetration at the deeper region is relatively lower for naphthalene group (Case 3). Contrary, relatively a higher chloride concentration is observed at the deeper region for polycarboxyl group. The difference was clearer in the tidal environment explained in References 2 and 3.

The water and acid soluble chloride profiles for the specimens, which were exposed in an artificial chamber for further deterioration are shown in Fig. 5. Same as before, it is found that relatively a higher chloride concentration is observed at the deeper region of the specimens in the case of polycarboxyl group (Case 11), and a lower chloride concentration at the deeper region for naphthalene group (Case 3).

To verify the reasons for having more chloride ingress in the case of polycarboxyl type of chemical admixtures, the chemical composition of the chemical admixtures were reviewed. In the case of melamine, naphthalene and amino-sulfonate group of chemical admixture negatively charged short side sulfonate chains exist with the main polymer chain (6). However, in the case of polycarboxyl group long neutral graft chains exist in addition to the negatively charged short side carboxyl chains. Therefore, the dispersion mechanism for polycarboxyl group is the combination of ionic repulsion and steric hindrance. For other cases, it is only ionic repulsion. It is expected that an ordered or interconnected pore structures is created for polycarboxyl group of chemical admixture that results in more chloride penetration and also more oxygen permeability explained later. The interconnectivity of the pore system is much more important rather than the total pore space for chloride ingress as well as oxygen permeability. The presence of carboxyl side chain may also have some influence. The exact reason cannot be concluded from the scope of this investigation. Further detail investigation is recommended.

Micro-cell Corrosion

The micro-cell current density of the steel bars embedded at different cover depths are shown in Fig. 6. A current density of less than $0.1 \mu\text{A}/\text{cm}^2$ is generally defined as negligible or the current density at passive condition (7). The current density is less than $0.3 \mu\text{A}/\text{cm}^2$ in most of the cases. In some cases, it is even less than $0.1 \mu\text{A}/\text{cm}^2$. After splitting open the specimens also no corrosion over the steel bars was found. These data are explained later. With increasing the slag content, the current density seems to reduce (Case 3, 7, 8). Higher W/C also shows relatively more current density (Case 3, 9 and 10). A tendency of having less current density is observed for the case made with naphthalene group (Case 3, 11–13). However, rigid conclusions cannot be made due to a very low level of current density.

The low level of current density as well as no corrosion over the steel bars indicates that the steel bars are in passive condition after 10 years of

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exposure in the marine splash environment. The water soluble chloride threshold level is defined at 0.4 % of cement mass (8). If it exceeds 2% of cement mass, an active corrosion is expected. The chloride level exceeds the threshold level at 20 mm cover depth for all cases. In some cases, it is even more than four times of the chloride threshold value (Fig. 4). It indicates that the steel-concrete interface is improved significantly due to the special method of casting as explained in Fig. 2, which delays the onset of corrosion. Related SEM micrographs are explained later.

The micro-cell current density of the specimens exposed to an accelerated chamber after 10 years exposure in the splash zone is shown in Fig. 7. A very high level of current density is observed for the specimen made with polycarboxyl type of chemical admixture, especially at cover depth of 20 mm.

Anodic Polarization Curve

To check the passivity of the steel bars embedded in concrete, the anodic polarization curves were measured for all of the sixteen cases investigated here after 10 years of exposure. It was found that the anodic polarization curves are very close to the potential axis irrespective of the cases investigated. For comparison, the current densities at 0.25 V and 0.65 V are summarized in Table 6. Same as before, rigid conclusions cannot be made based on the anodic polarization curves due to the very low level of current density.

Utilizing the anodic polarization current densities at 0.25 and 0.65 V, the condition of the passivity of the steel bars was evaluated based on Reference 9 from scale 0 (complete loss of passivity) to 5 (excellent passivity). The evaluated passivity grades of the steel bars embedded at 20 and 45.5 mm of cover depths are listed in Table 6. In most of the cases, the passivity grade is four, which is a very high level of passivity. In some cases, the passivity grade is five, which is an excellent grade of passivity. Lower level of micro-cell current density is also observed for this reason as explained in "Micro-cell Corrosion" subsection (Fig. 6).

The anodic polarization curves of the steel bars (cover depth = 20 mm) in concrete for the specimens exposed for further deterioration in an accelerated chamber are shown in Fig. 8. It is found that the anodic polarization curve for polycarboxyl group (Case 11) is far from the potential axis compared to the others. The passivity grades are evaluated as 1 for Case 11, 4 for Case 13, and 3 for Case 3 and 12.

Oxygen Permeability

The oxygen permeability through cover concrete was only measured for the specimens exposed to an accelerated chamber for further deterioration. Also, the oxygen permeability was measured utilizing the steel bars located at

45.5 mm cover depth only. The steel bars located at 20 mm of cover depth were used for the measurement of anodic polarization curve. The oxygen permeability data per unit area of the steel bars located at the 45.5 mm cover depth are shown in Fig. 9. Higher oxygen permeability through the concrete specimens made with polycarboxyl group (Case 11) is observed.

Porosity and XRD Results

The pore size distributions of the mortar samples at depth 15-25 mm are shown in Fig. 10 for Case 3 and 11. For the naphthalene group (Case 3) the pore volume is relatively higher compared to the polycarboxyl group. More fine pores in polycarboxyl group of chemical admixture are mainly observed at around average pore diameter of 1 μm . The possible reason is explained below.

The results of the XRD analysis are listed in Table 7. The Friedel's salt and ettringite peaks were not so prominent for Case 3 compared to Case 11. The reduction of the pore volume for Case 11 is expected due to the more Friedel's salt and ettringite formation. No $\text{Ca}(\text{OH})_2$ peaks were observed for Case 11. It is also expected that in case of polycarboxyl group of admixture, the pore channels may interconnect with fine pores with less voids in their paths. It causes more chloride ingress and more oxygen permeability even though the pore space is relatively lower for the case of polycarboxyl group.

Physical Evaluation of Corrosion

The reinforced specimens were spilt opened after electrochemical investigations. No significant corrosion was observed over the steel bars after 10 years of exposure even though there was countable numbers of visible voids over the steel bars as shown in Fig. 11. The size of the voids varies from several hundreds micrometer to the order of millimeter. Over the steel bars, deposit of hydration products adhered at the locations having visible voids at the steel-concrete interface. SEM results of the porous matrix and steel-concrete interface are explained later.

The corroded areas of the specimens exposed to an accelerated chamber for further deterioration are shown in Fig. 12. More corroded area was observed for the case with polycarboxyl group (Case 11).

SEM Micrographs of the Porous Matirx and the Steel-Concrete Interface

Typical SEM micrographs of the fractured porous concrete (15~25 mm) of Case 3 and 11 are shown in Fig. 13. In Case 11, more deposit of calcium aluminate hydrate with chloride is observed at the void region. The point analysis also showed the presence of chloride peak in addition to the calcium and aluminium peaks indicating the possible formation of Friedel's salt. The result supports the data of more chloride ingress in Case 11. Typical SEM

micrographs related to the steel-concrete interface (20 mm concrete cover) are shown in Fig. 14. A compact steel-concrete interface is visualized. The diameter of the micro-voids is less than $5\text{ }\mu\text{m}$ over the steel surface. Ettringite is randomly distributed at the interface (close-up view). Also, calcium aluminate hydrates crystals are observed. Same as before, the point analysis showed the presence of chloride peak in addition to the calcium and aluminium peaks indicating the possibility of the Friedel's salt formation. The fractured steel-concrete interface (concrete cover = 20 mm) is shown in Fig. 15. A dense steel-concrete interface is observed with the average thickness less than $10\text{ }\mu\text{m}$. In another investigation with the series of specimens exposed to the tidal environment, it was confirmed that calcium silicate hydrates adhered on the steel bars associated with the voids at the steel-concrete interface (3). In this study, the adhered deposit on the steel bars at the void region was not analyzed.

Generally, at the interface a porous region in the order of $40\sim 50\text{ }\mu\text{m}$ is often found due to the particle packing surrounding the steel bars or wall effect. The compact steel-concrete interface is formed due to the special method of casting concrete as explained in Fig. 2. It is expected due to the less influence of bleeding effect as well as the compaction of the interface due to the sliding of the steel bars through concrete. As a results chloride threshold value improves significantly. The results strongly support that the improvement of steel-concrete interface is essential to make sustainable concrete structures in the marine environment.

CONCLUSIONS

Based on the results of this experimental investigation under marine splash environment, the following conclusions are drawn:

- (1) Naphthalene group of high-range water-reducing and air-entraining chemical admixture shows relatively better performance against chloride ingress and strength development. Relatively a poorer performance is observed for polycarboxyl group of chemical admixture.
- (2) No significant harmful effect is found for other chemical admixtures including shrinkage reducing chemical admixtures investigated in this study.
- (3) The special method of casting concrete used in this study causes the formation of a good steel-concrete interface that prevents the initiation of corrosion even for chloride concentration much more than the so-called chloride threshold limit.
- (4) The improvement of steel-concrete interface is essential to make sustainable concrete structures in the marine environment.

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Table 1 Physical and Chemical Compositions of Cement and Slags

	NPC	Slag 1	Slag 2
Specific Gravity	3.16	2.90	2.90
Blaine Fineness, cm ² /g	3190	7900	4080
Ignition Loss, %	0.7	-	-
SiO ₂ , %	21.3	32.7	33.2
Al ₂ O ₃ , %	5.3	13.8	14.1
CaO, %	64.4	42.4	42.3
MgO, %	2.2	5.9	5.9
SO ₃ , %	1.9	2.0	2.0
Na ₂ O, %	0.28	-	-
K ₂ O, %	0.6	-	-
Fe ₂ O ₃ , %	2.6	0.2	0.2

- Indicate not measured items

Table 2 Chloride and Alkali Contents, and Specific Gravity of Chemical Admixtures

Chemical Admixtures	Chloride and Alkali Content (%)		Sp. Gr.
	Chloride	Total Alkali	
Vinsol	-	-	-
Lignosulfonate	0.03%	0.7%	1.06
Naphthalene	0.01%	0.2%	1.14
Polycarboxyl	0.00%	0.1%	1.04
Melamine	0.01%	5.1%	1.23
Amino Sulfonate	0.01%	3.5%	1.13
Shrinkage Reducing Adm.	-	-	0.99

- Not available

Table 3 Chemical Compositions of Steel Bar

C (%)	Si (%)	Mn (%)	P (%)	S (%)
0.1	0.21	0.66	0.02	0.02

Table 4 Mixture Proportions of Concrete

Case	Cement Type	Slag Content (%)		Slump mm	Air %	Types of Chemical Admixture	W/C	s/a %	C kg/m ³	W kg/m ³	S kg/m ³	G kg/m ³	WRA or HRWRAEA	AEA % of C
		8000 cm ² /g	4000 cm ² /g											
1	Slag 1	55	-	120 ± 10	4 ± 1	Vinsol	0.56	44.8	330	183	786	972	-	0.06
2						LS Group	0.53	44.8		174	797	985	250mL/100kg C	0.006
3						N Group	0.47	45.3		155	828	1001	1.5% of C	0.006
4	Slag 2	-	55	120 ± 10	4 ± 1	Vinsol	0.53	45.6	330	174	810	972	-	0.04
5						LS Group	0.50	45.5		165	821	985	250mL/100kg C	0.003
6						N Group	0.47	45.5		155	831	1001	1.5% of C	0.005
7	Slag 1	40		120 ± 10	4 ± 1	N Group	47.0	45.5	330	155	834	1001	1.5% of C	0.005
8		70				N Group	0.47	45.4			828	1001	1.5% of C	0.0095
9	Slag 1	55	-	120 ± 10	4 ± 1	N Group	0.40	44.0	388	155	784	1001	1.5% of C	0.008
10						N Group	0.50	46.0	310		849	1001	1.5% of C	0.006
11	Slag 1	55	-	120 ± 10	4 ± 1	PC Group	0.47	45.5	330	155	831	1001	1.1% of C	0.006
12						M Group							1.3% of C	0.015
13						AS Group							1.5% of C	0.003
14	NPC	-	-	120 ± 10	1 ± 0.5	GED plus AAD + AS Group	0.525	49.0	330	170	923	964	1.5% of C + 10 kg/m ³	-
15	Slag 1	55	-	120 ± 10	1 ± 0.5	GED plus AAD + AS Group	0.52	48.6	330	170	907	964	1.5% of C + 10 kg/m ³	-
16	Slag 2	-	55	120 ± 10	1 ± 0.5	GED plus AAD + AS Group	0.52	48.6	330	170	907	964	1.5% of C + 10 kg/m ³	-

W-water, C-Cement, S-Sand, G-Gravel, s/a - Sand-Aggregate Ratio, AEA – Air-Entraining Admixture, WRA-Water-Reducing Admixture, HRWRAEA- High-Range Water-Reducing and Air-Entraining Admixture, LS – Lignosulfonate, N – Naphthalene, PC-Polycarboxyl, M-Melamine, AS-Amino-sulphonate, GED – Glycol Ether Derivative, AAD – Amino-alcohol derivative.

Table 5 Physical Properties and Chemical Composition of Seawater

Specific Gravity	pH	Na ppm	K ppm	Ca ppm	Mg ppm	Cl ppm	SO ₄ ppm	CO ₃ ppm
1.022	7.77	9290	346	356	1167	17087	2378	110

Table 6 Anodic Current Densities at 0.25 and 0.65 V

Specimen	Anodic Current Density ($\mu\text{A}/\text{cm}^2$)				Passivity Grade	
	20 mm Cover		45.5 mm Cover		20 mm Cover	45.5 mm Cover
	0.25 V	0.65 V	0.25 V	0.65 V		
1	3.26	5.57	0.27	1.36	3	4
2	1.09	2.18	0.14	1.09	3	4
3	0.14	0.82	0.27	1.63	5	4
4	0.27	1.09	0.27	1.36	4	4
5	0.27	1.09	0.27	1.09	4	4
6	0.27	1.09	0.27	1.09	4	4
7	1.63	3.26	0.27	1.36	3	4
8	0.27	0.54	0.25	0.54	5	5
9	0.82	1.63	0.27	1.63	4	4
10	0.27	1.09	0.82	1.63	4	4
11	0.54	2.72	0.27	1.09	4	4
12	0.27	1.09	0.27	0.82	4	5
13	0.27	0.95	0.27	0.95	5	5
14	0.54	1.09	0.27	0.82	4	5
15	0.27	1.09	0.27	1.09	4	4
16	0.27	0.82	0.27	0.82	5	5

Table 7 Summary of the XRD Data (15 ~ 25 mm from the surface)

Mineralogy	Case 3	Case 11
Ca(OH) ₂ (Calcium Hydroxide)	△	-
3CaO.Al ₂ O ₃ .3CaSO ₄ .32H ₂ O (Ettringite)	△	O
3CaO.Al ₂ O ₃ .CaCl ₂ .11H ₂ O (Friedel's Salt)	△	O
CaCO ₃ (Calcite)	O	O

“O” means clearly observed, and “△” means observed but not so clear,
“-” means not observed.

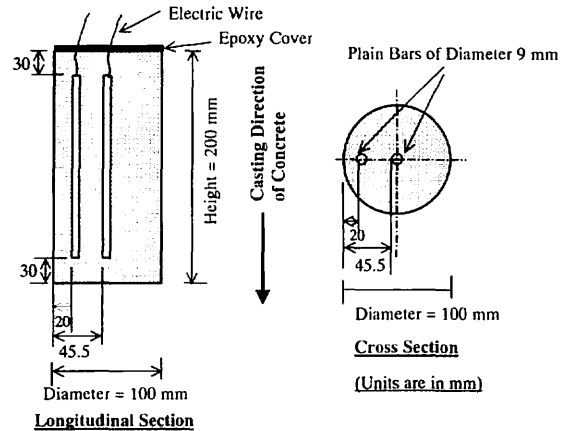


Fig. 1. Layout of the Specimens

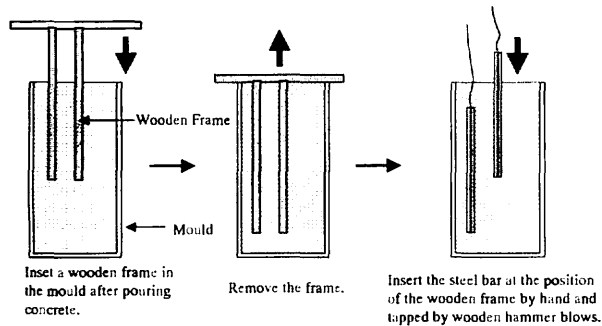


Fig. 2. Casting Method of the Specimens

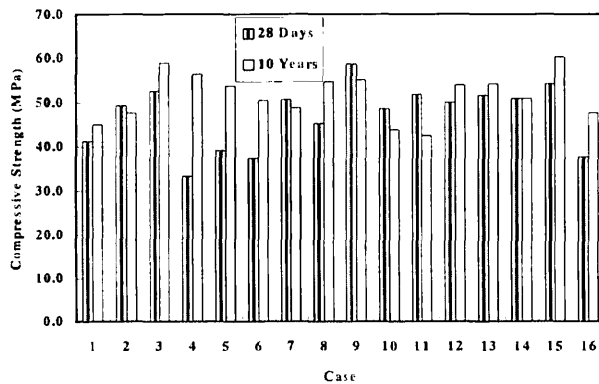


Fig. 3. Compressive Strength of Concrete (Tidal Exposure)

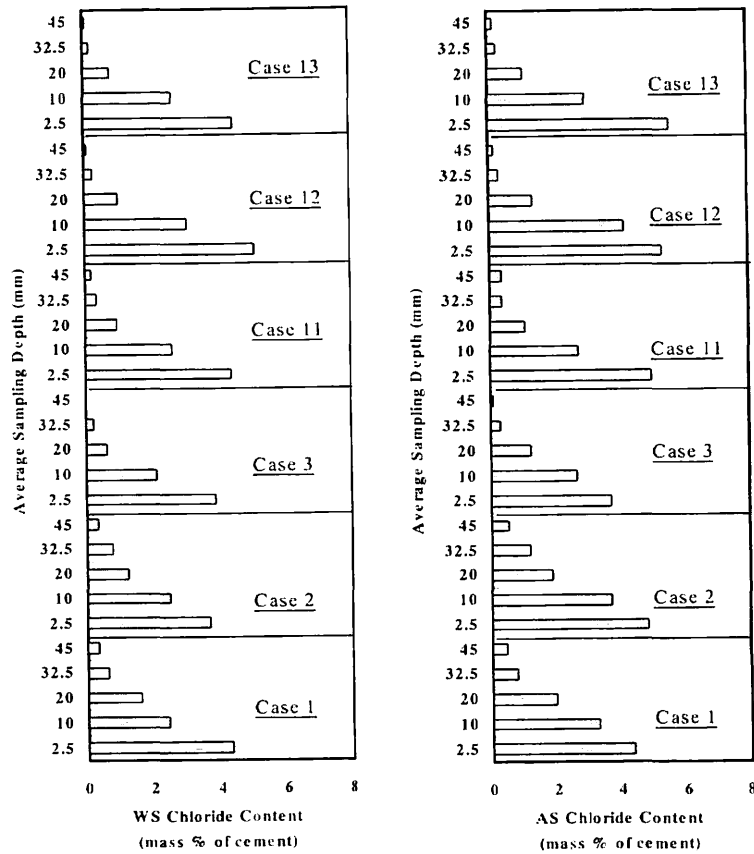


Fig. 4. Water Soluble (WS) and Acid Soluble (AS) Chloride Contents at Different Depths (Splash Zone Exposure)

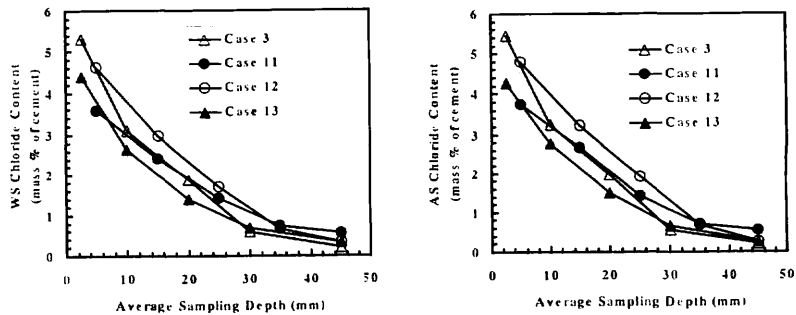


Fig. 5. Water and Acid Soluble Chloride Contents (Splash Zone Plus Accelerated Exposure)

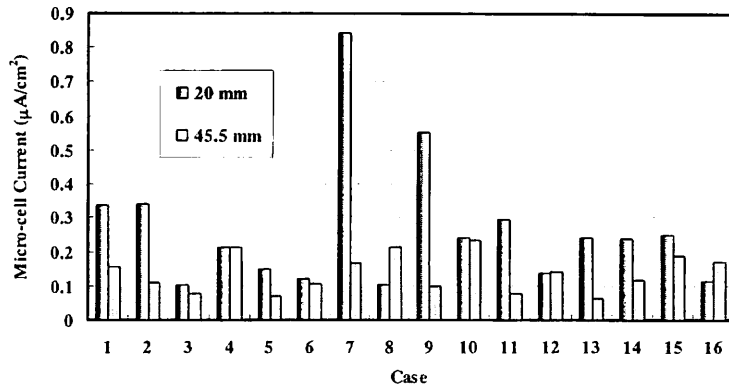


Fig. 6. Micro-Cell Corrosion Current Density (Splash Zone Exposure)

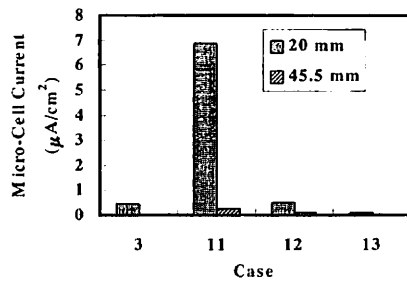


Fig. 7. Micro-Cell Corrosion Current Density (Splash Zone Plus Accelerated Exposure)

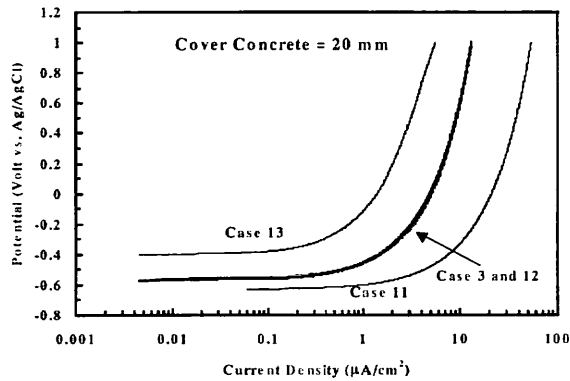


Fig. 8. Anodic Polarization Curves (Splash Zone Plus Accelerated Exposure)

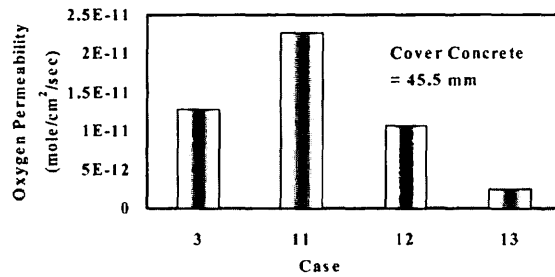


Fig. 9. Oxygen Permeability in Concrete (Splash Zone Plus Accelerated Exposure)

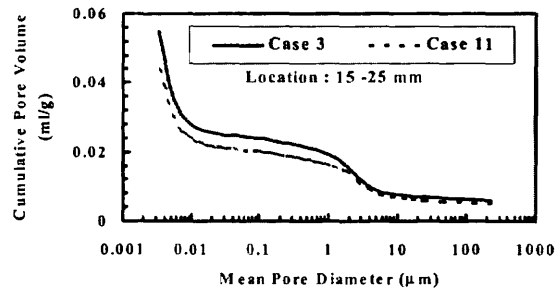


Fig. 10. Cumulative Pore Volume Versus Pore Size (Splash Zone Exposure)

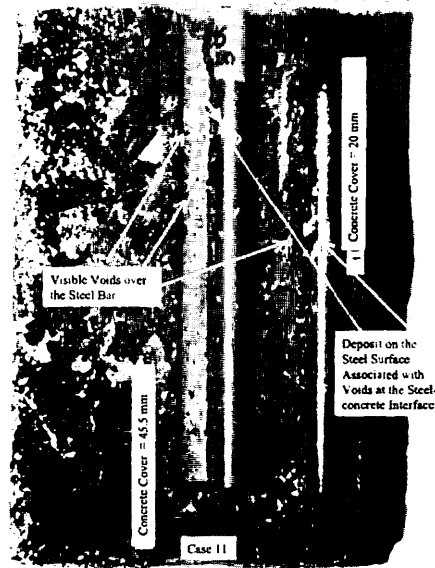


Fig. 11. Steel Bar Surrounding Concrete (Splash Zone Exposure)

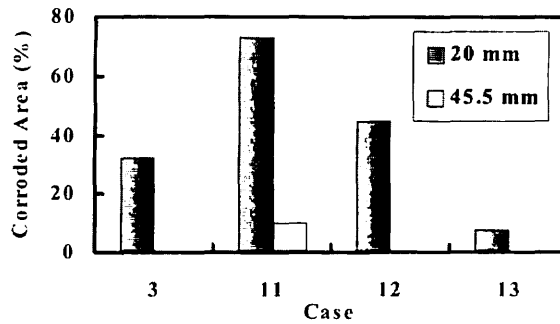
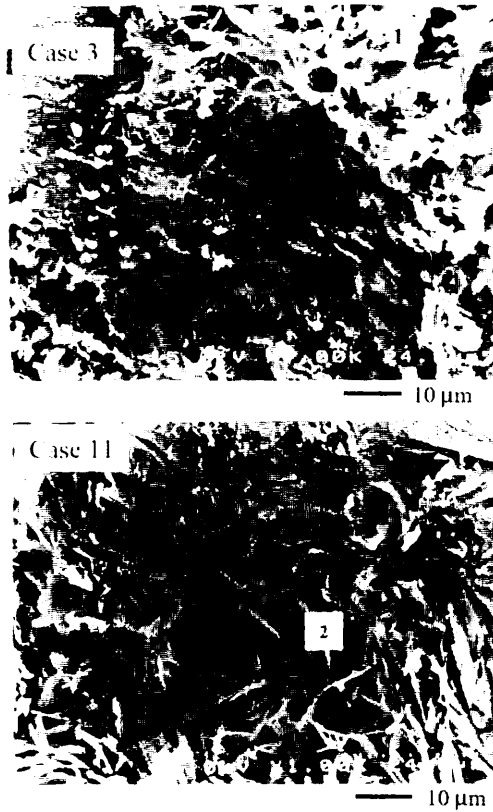


Fig. 12. Corroded Area (Splash Zone Plus Accelerated Exposure)



1 -C-S-H, 2 - Calcium Alluminate Hydrate

Fig. 13. SEM Micrographs of Porous Matrix (Splash Zone Exposure)

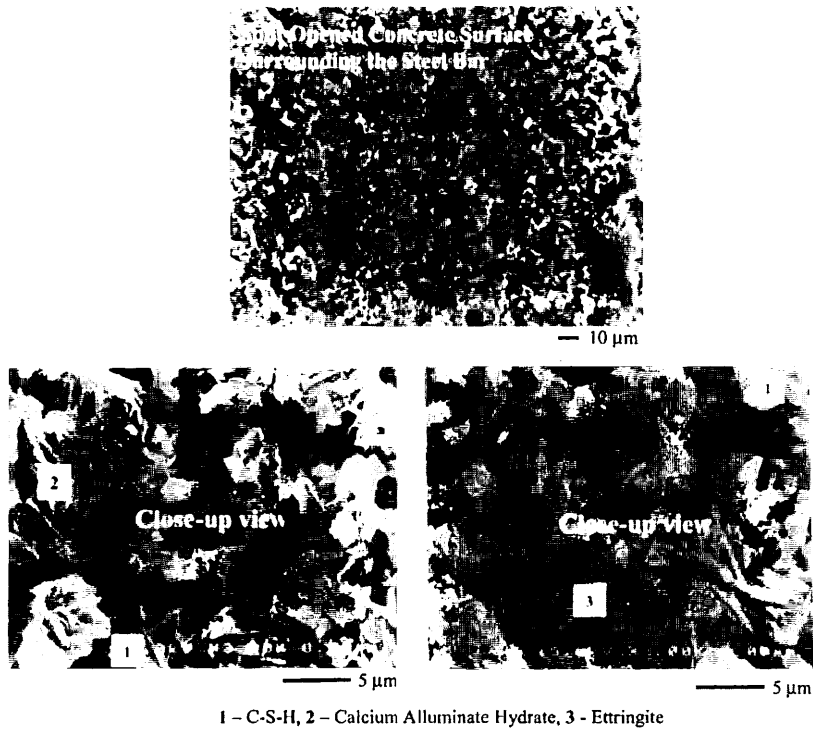


Fig. 14. SEM Micrographs of Concrete Surface Surrounding the Steel Bar (Case 3, Splash Zone Exposure)

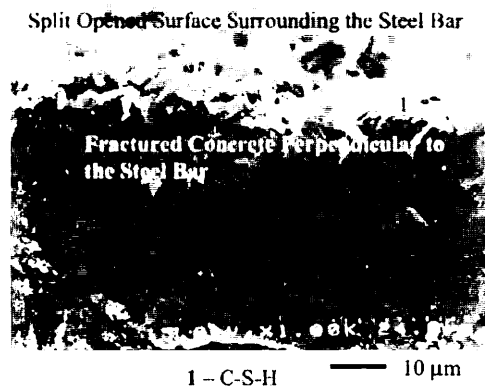


Fig. 15. SEM Micrograph of Steel-Concrete Interface (Case 3, Splash Zone Exposure)

Improving Concrete Performance with Shrinkage-Reducing Admixtures

by N. S. Berke, L. Li, M. C. Hicks, and J. Bae

Synopsis:

Concrete is one of the most durable construction materials. However, cracking adversely affects its durability, appearance, and functionality. A major cause of the cracking is related to shrinkage-induced strains creating stresses when concrete is restrained. Shrinkage reducing admixtures (SRA's) have been used for several years to reduce drying and autogenous shrinkage. However, their uses in temperate environments were limited due to difficulties in producing good quality air void systems needed for freezing and thawing resistance. In this paper we show that good air void systems and freezing and thawing performance are obtainable with a new formulation of a glycol ether SRA. This formulation is very compatible with polycarboxylate type superplasticizers and calcium nitrite corrosion inhibitor. Furthermore, it is demonstrated that in addition to improving shrinkage and cracking performance, permeability and corrosion performance are improved.

Keywords: admixtures; air entrainment; chloride; corrosion; corrosion inhibitors; diffusion; durability; freezing and thawing; reinforced concrete; shrinkage; shrinkage reducing admixture; superplasticizers

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INTRODUCTION

Shrinkage Reducing Admixtures (SRA's) provide a method to reduce the strains caused by drying shrinkage and subsequently drying shrinkage stresses. Advantages to this method are that with the exception of the added SRA, concrete mixture proportions and mixing remain relatively unchanged. Also, since no expansion is induced as with shrinkage compensating cements or admixtures, no change in restraint is necessary in the engineering design. Thus, the drying shrinkage can be reduced for essentially any currently used concrete.

Shrinkage reducing admixtures have been discussed in the literature for several years. Various authors (1-11) have shown the reduction of free shrinkage can translate to a reduced frequency of restrained drying shrinkage cracks, and extended time to cracking. In addition, there is evidence that autogenous shrinkage is reduced (10). The mechanism by which the reduction

in shrinkage occurs is thought to be from the reduction of the surface tension of the pore water solution (11). However, the reduction in surface tension can have an effect on the formation of a satisfactory air void system, which is needed for good performance in freezing and thawing environments (12,13,14).

In this paper it will be shown that recent developments can result in an air void system meeting the recommendations in ACI 201.2R and ACI 211.1, and that concretes produced perform well in ASTM C666 Standard Test Method for Resistance of Concrete to Rapid Freezing and Thawing, Method A. Other advantages shown by additional research are that the SRA reduces permeability and long-term corrosion performance is improved.

EXPERIMENTAL

Concrete aggregates used in the production of concrete in this work met the requirements of ASTM C 33 Standard Specification for Concrete Aggregates. Cements met the requirements of ASTM C 150 Standard Specification for Portland cement, and unless otherwise stated were Type I. Admixtures, where applicable, met the requirements of one or more of the types in ASTM C 494 Standard Specification for Chemical Admixtures for Concrete. There are no ASTM specifications at this time for SRA's. Two commercial SRA's based upon glycol ether chemistry were used. The first is a commercial product (Eclipse® Shrinkage Reducing Admixture) designated, as SRA 1 and the other is a newly introduced product (Eclipse® Plus Shrinkage Reducing Admixture) formulated to produce a better air void system, designated as SRA 2.

Laboratory specimens were made according to ASTM C 192 Standard Practice for Making and Curing Concrete Test Specimens in the Laboratory. Plastic properties of the concretes were determined by ASTM C 138 Standard Test Method for Unit Weight, Yield, and Air Content (Gravimetric) of Concrete, ASTM C 143 Standard Test Method for Slump of Hydraulic Cement Concrete, and ASTM C 231 Standard Test Method for Air Content of Freshly Mixed Concrete by the Pressure Method.

Compressive strengths were determined at the times noted according to ASTM C 33 Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens. Shrinkage beams were tested according to ASTM C 157 Standard Test Method for Length Change of Hardened Hydraulic-Cement Mortar and Concrete with curing times as indicated in this paper. Freezing and thawing tests were conducted in accordance with ASTM C 666 Standard Test Method for Resistance of Concrete to Rapid Freezing and Thawing, Method A, freezing and thawing in water, was used. Finally, air void analyses were conducted in accordance with ASTM C 457 Standard Test Method for

Microscopical Determination of Parameters of the Air-Void System in Hardened Concrete.

Corrosion properties were determined on specimens subjected to ponding in 3% NaCl. The specimens were 75 mm diameter x 150 mm tall concrete cylinders with an embedded reinforcing bar, as described in reference 14. Corrosion rates on these specimens were determined by using polarization resistance with IR interruption.

Additionally, chloride profiles were determined for 76 mm diameter cylinders with one exposed face immersed in 15% NaCl at 40°C. Total acid soluble chloride was measured according ASTM C1152. Diffusion coefficients and surface concentrations were calculated using a nonlinear regression analysis to a one-dimensional solution to Fick's second law.

RESULTS AND DISCUSSION**Air Voids and Freezing and Thawing Behavior**

Table 1 shows concrete data for concretes produced with and without SRA-1. The data show that with a polycarboxylate superplasticizer and tall oil based air entrainer; a good air void system can be obtained for concretes with and without SRA-1. In this case there was an improvement in slump and strength with SRA-1, even though this is not always observed.

Air void parameters plus freezing and thawing results for the two concretes in Table 1 are shown in Table 2. Both concretes had spacing factors under 0.20 mm and specific surface areas over 24/mm, indicative of a good air void system according to ACI 201.2R and ACI 211.1. Thus, it is not surprising that both concretes exhibited excellent performance in the ASTM C 666 Method A testing with RDME factors above 99% and mass loss under 0.25%. These results show that concretes with SRA-1 can be freeze-thaw durable when a good air void system and good strength are present.

The good freezing and thawing results are consistent with Schemmel's work (12) in which concrete with SRA-1 using a tall oil based, air entrainer and a higher strength mixture design had good freezing and thawing performance. Schemmel showed poor performance when air entrainment was not achieved, especially at lower compressive strength values. Cope and Ramey (13) showed reduced freezing and thawing performance with SRA-1; however, they did not alter the mixture design or admixtures to achieve higher strength (only the SRA mixture had a 28-day compressive strength under 35 MPa). Also, the air void system was not as good as can be obtained by modifying admixture types and dosage rates. Nevertheless, the results from Schemmel, Cope and Ramey indicate that getting a good air void system with SRA-1 can be difficult. In addition, when SRA-1 was used in conjunction with calcium nitrite, it was very

difficult to entrain air in our laboratory and in the field. This resulted in not recommending the use SRA-1 with calcium nitrite in freezing and thawing applications, thus losing the benefit of potentially less cracking in concretes exposed to chlorides.

SRA-2 has been recently developed to enhance the air entrainment capability of concrete mixes with a SRA. In particular, SRA-2 works well with calcium nitrite corrosion inhibitor and non-chloride set accelerators. Concrete properties for SRA-2 mixtures with and without calcium nitrite are given in Table 3. The mixture with calcium nitrite (DCI® S Corrosion Inhibitor) had an 8% strength increase at 28 days, which is typical for mixtures with calcium nitrite. Air void parameters and freezing and thawing results are in Table 4. Both mixtures had air void systems exceeding the recommendation in ACI 201.2R and ACI 211.1, and results in ASTM C 666 were excellent. The mixture with calcium nitrite corrosion inhibitor had lower mass loss and a higher RDME than SRA-2 and SRA-2 and the control in Table 2. This is most likely due to the higher strength.

Table 5 provides additional data on the properties of several concrete mixtures produced with SRA-2 using either a NFSC or polycarboxylate superplasticizer, with rosin and tall oil type air entrainers. In all cases it was possible to get plastic airs in the 5 to 8% range and compressive strengths exceeded 35 MPa for all of the mixtures.

Fig. 1 provides additional freezing and thawing performance data for several mixtures produced with SRA 2 given in Table 5. Good performance is obtained in all cases, however, the combination of rosin based air entrainer and naphthalene sulfonate based superplasticizer showed a larger drop in RDME values than the other combinations. This drop in performance is related to the significantly lowered hardened air content and subsequently greater spacing factor as seen in Table 6. Thus, the use of NFSC superplasticizer and rosin type AEA might not produce a good air void system, and further work is needed to understand this. Nevertheless, the concrete specimens still passed ASTM C666. The other specimens that performed well had very good air void parameters as seen in Table 6.

Shrinkage data comparing performance of SRA-1 to SRA-2 are given in Fig. 2. Performance is essentially the same for both SRA's and much better than that of the control mixture.

Air void analyses from concrete produced in ready-mix trucks with SRA-2 were discussed recently (11). These results show that a good air void system can be obtained under field conditions using two commercially available polycarboxylate-based superplasticizers. In field conditions, tall oil and rosin type air entrainers gave good results. At 18 and 25 °C spacing factors

were obtained that were below 0.15 mm with both rosin and tall oil based air entrainers. In addition, spacing factors with calcium nitrite at 18 and 32 °C were also under 0.15 mm, and produced better air void parameters than the mixtures without calcium nitrite.

Corrosion and Permeability

Fig. 3 shows long-term corrosion performance data for concretes produced with SRA 1 versus a control. The improvement in corrosion performance is most likely due to a reduction in chloride ingress as can be seen from chloride data from beams that were in another test given in Table 6 (1). More work is underway to determine if the reduction in chloride ingress and subsequent improvement in corrosion behavior is typical.

Figure 4 shows good shrinkage performance with calcium nitrite and Fig. 5 shows that corrosion performance with calcium nitrite and SRA-1 (without the air improving additives) is very good. The ability to get good air void systems with the combination of calcium nitrite corrosion inhibitor and SRA 2 makes this a desirable combination for freezing and thawing environments where deicing salts are used, or in marine applications where a reduction in shrinkage is needed.

FURTHER DISCUSSION

The data show that good air void systems are obtainable with glycol ether based SRA's. However, as others have shown, this is not always the case (12-13), especially when changes in the admixtures and mixture proportions were not made to improve the quality of the air void system and increase strength. The ability to obtain a good air void system is significantly improved when the SRA's are used with a polycarboxylate superplasticizer and tall oil based air entrainer. A new SRA-2 extends use to rosin type air entrainers as well as the use of calcium nitrite and non-chloride based accelerators. This is significant as in many applications, such as a bridge or parking deck, low shrinkage and improved corrosion resistance to deicing salts are desired. In these applications, the w/cm is usually at 0.40 or lower, and 28-day strengths exceed 35 MPa. Furthermore, the SRA's in this study were shown to improve corrosion performance and reduce chloride ingress.

CONCLUSIONS

Good freezing and thawing resistance can be obtained with glycol ether based SRA's. The ability to produce the air void system needed to achieve good freeze-thaw resistance is related to the proper choice of compatible admixtures, and it is recommended that a polycarboxylate based superplasticizer be used if a superplasticizer is utilized.

Newly developed SRA-2 works well with both tall oil and rosin based air entrainers, as well as with calcium nitrite. This now opens up the use of a combination system with calcium nitrite corrosion inhibitor and SRA-2 in applications where chloride induced corrosion is a concern, and cracking needs to be minimized.

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TABLES

Table 1: Concrete data for SRA-1 vs. control.

Mixture	Super-plasticizer* (ml/100 kg)	Air Entrainer** (ml/100 kg)	Slump (mm)	Plastic Air (%)	28-day Compressive Strength (MPa)
Control	228	19.6	127	6.3	39
5 l/m ³ SRA-1	228	6.5	172	7.5	42

Cement Factor: 390 kg/m³

w/c = 0.4

*Adva® Flow Superplasticizer

**Darex® II AEA

Table 2: Freeze-thaw data and air void analyses of concretes in Table 1.

Mixture	% Mass Loss	RDME (%)	Hardened Air (%)	Specific Surface (mm ⁻¹)	Spacing Factor (mm)
Control	0.13	99.1	5.8	34.6	0.13
5l/m ³ SRA-1	0.24	99.6	6.3	28.1	0.15

Table 3: Concrete data for SRA-2 with and without calcium nitrite corrosion inhibitor.

Mixture	Super-plasticizer* (ml/100 kg)	Air Entrainment** (ml/100 kg)	Slump (mm)	Plastic Air (%)	28-day Compressive Strength (MPa)
5 l/m ³ SRA-2	209	98	114	5.6	43
5 l/m ³ SRA-2 + 15 l/m ³ CN***	160	179	102	6.4	46

Cement Factor: 390 kg/m³

w/c = 0.4

*Adva® Flow Superplasticizer

**Darex® II AEA

***DCI® S Corrosion Inhibitor (30% calcium nitrite)

Table 4: Freeze-thaw data and air void analyses of concretes in Table 3.

Mixture	% Mass Loss	RDME (%)	Hardened Air (%)	Specific Surface (mm ⁻¹)	Spacing Factor (mm)
5l/m ³ SRA-2	0.38	98.2	5.8	35.1	0.13
5l/m ³ SRA-2 + 15 l/m ³ CN	0.07	100.9	4.9	34.1	0.14

Table 5. Properties of concretes with 5-l/m³ of SRA-2 using different superplasticizers and air entrainers.

Mix #	AEA	Superplasticizer	Slump (mm)	Air (%)	28day (MPa)	f _c
1*	Tall Oil	Polycarboxylate	152	6.3	46.6	
2	Tall Oil	Polycarboxylate	152	7.7	35.4	
3	Rosin	Polycarboxylate	133	6.3	41.8	
4	Tall Oil	Polycarboxylate	121	5.6	40.0	
5	Rosin	Polycarboxylate	133	7.4	37.3	
6	Tall Oil	NFSC	159	7.5	39.0	
7	Rosin	NFSC	159	5.6	45.6	

*Control mixture without SRA-2

Table 6. Air Void Analysis for Concretes shown in Figure 1 and Table 7

Mix #	Hardened Concrete Air (%)	Average Chord Length (mm)	Spacing Factor (mm)	Specific Surface (1/mm)	Voids/cm
1	NA	NA	NA	NA	NA
2	7.84	0.102	0.089	39.7	7.8
3	6.21	0.127	0.140	31.7	4.9
4	5.42	0.109	0.130	36.6	5.0
5	8.08	0.117	0.102	33.9	6.9
6	6.68	0.117	0.124	33.9	5.7
7	3.22	0.178	0.264	22.6	1.8

Table 7 Chloride data after 3 months at 40 °C for concretes at 0.5 w/c from (1).

Depth (mm)	Reference	2.5% s/s SRA
0-13	10.1	7.6
13-25	5.2	3.1
25-38	2.1	1.0
38-51	0.7	0.4
D_e (m ² /s)	3.2×10^{-12}	2.2×10^{-12}
D_e (m ² /s) (at 22 °C)	1.0×10^{-12}	0.8×10^{-12}

Figures

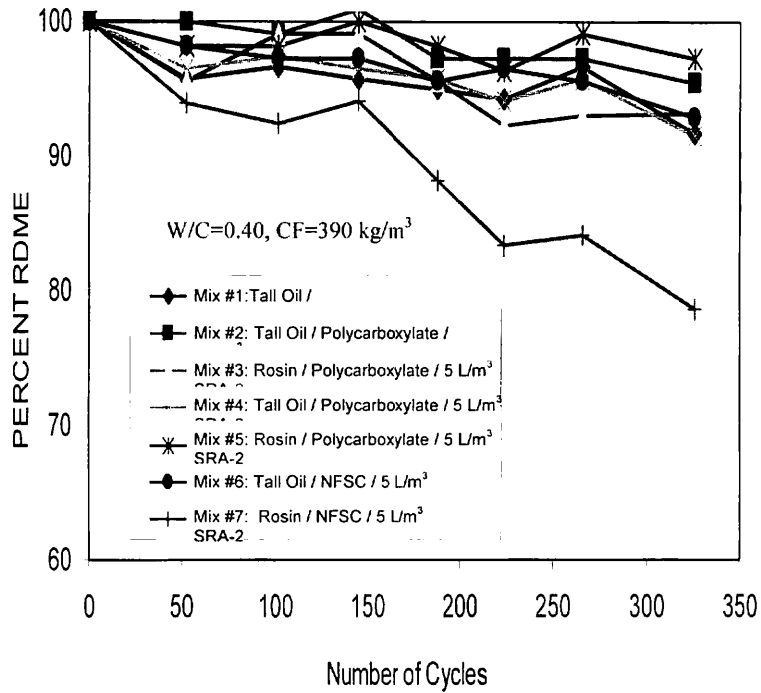


Fig. 1 Freezing and thawing data in ASTM C 666 Method A for various combinations of superplasticizers and air entrainers with SRA 2.

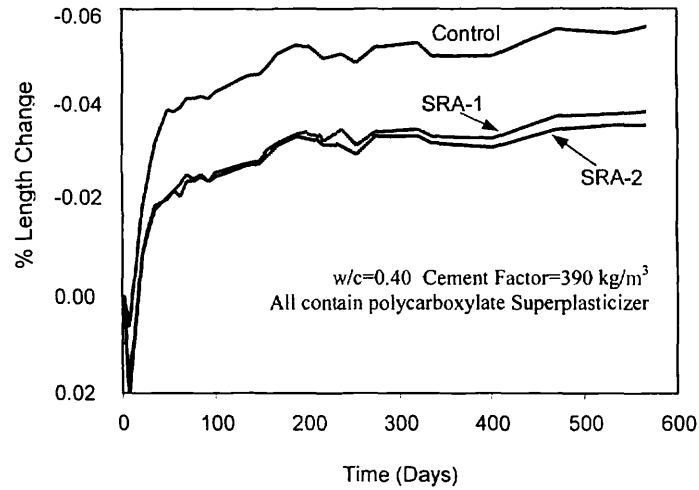


Fig. 2. Comparison of SRA-1 and SRA-2 in Shrinkage

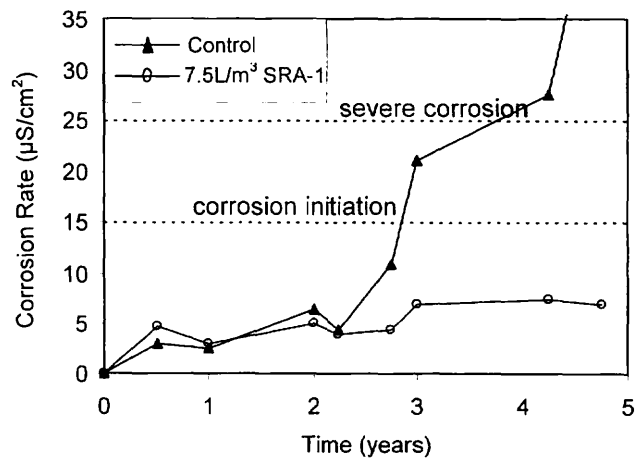


Fig. 3 Corrosion performance of SRA versus Control

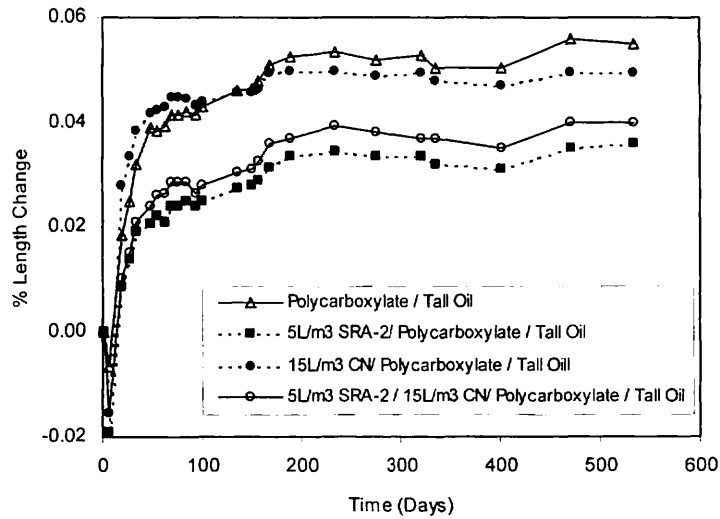


Fig. 4 Shrinkage performance of SRA with and without calcium nitrite at $w/c=0.41$.

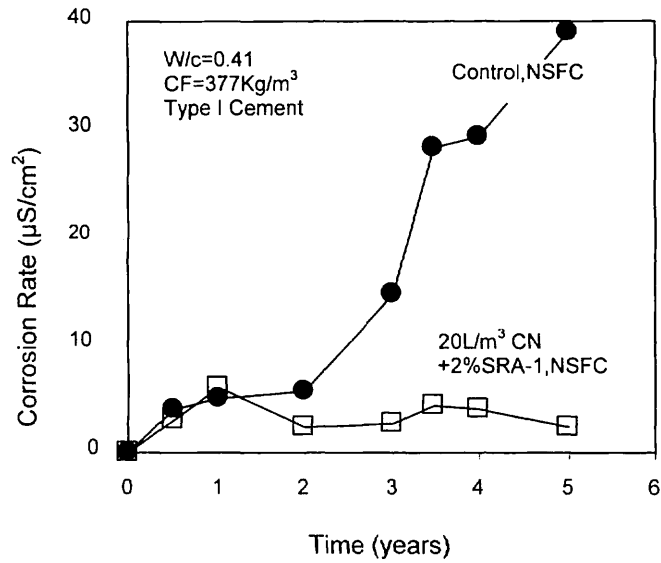


Fig. 5 Corrosion performance of concretes with SRA and Calcium Nitrite