Recent Developments of Special Self-Compacting Concretes

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

Synopsis:

During the last decades new cementitious materials were available. These represent a technical revolution with respect to the traditional concretes. The most important innovative "High Tech" materials are Self-Compacting Concretes (SCCs).

In the present paper the compositions, the performances and some practical applications of high-performance SCCs are shown. In particular, some performance improvements carried out in our laboratories are shown for these specific uses:

a) SCC for a Building Engineering application (S. Peter Apostle Church in Pescara, Italy) with white concrete characterized by a marble-like skin;
b) SCC in the form of high-strength concrete with compressive strength over 90 MPa devoted to a work in the field of Civil Engineering (World Trade Center in San Marino);
c) SCC in the form of mass concrete structure with a reduced risk of cracking induced by thermal difference between the nucleus and the skin of the elements;
d) SCC in the form of lightweight precast concrete with a density of 1750 kg/m³, 28-day compressive strength of 35 MPa, and 28-day flexural strength of 5 MPa;
e) SCC in the form of a shrinkage-compensating concrete for reinforced concrete walls 8 m high and 55 m long.

Keywords: expansive agent; high performance concrete; lightweight concrete; mass concrete; self-compacting concrete; shrinkage reducing admixture; silica fume; superplasticizer; viscosity modifying agent
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INTRODUCTION

With respect to the traditional concretes, the new cementitious materials, thanks to the availability of new raw materials, allow the concretes to reach much higher performances in terms of execution on job sites, useful service life, and mechanical strength. These new raw materials include:

- New synthetic polymers (poly-acrylates) which, in comparison with naphthalene- or melamine-sulphonated polymers, are able to reduce even more effectively the amount of mixing water and the water-cement ratio with all the consequent benefits [1,2].
- Viscosity Modifying Agents (VMA) to produce thixotropic mixes and then to obtain cohesive fresh concretes even when they are very fluid [3].
- Mineral additions characterized by amorphous silica such as silica fume (waste from silicium-iron alloys) in the form of very fine particles (size of some µm/m) or UFACS (Ultra-Fine Amorphous Colloidal Silica) synthetically produced in the form of very small particles with size of some nm [4].
- Shrinkage Reducing Admixture to improve the dimensional stability of concrete structures with geometric characteristics, in terms of size and form, which may have cracks related to drying shrinkage.
EXPERIMENTALS AND DISCUSSION OF RESULTS

The term Self-Compacting Concrete (SCC) refers to a special type of concrete mixture, characterized by high resistance to segregation, that can be cast without compaction or vibration. With the advent of superplasticizers, flowing concretes with slump levels up to 250 mm were manufactured with no or negligible bleeding, provided that an adequate cement factor was used, that is at least 350 kg/m³ [2]. The most important basic principle for flowing and unsegregable concretes including SCCs is the use of the 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 cement heat of hydration. Some other mineral additions, alternative to fly ash, have been considered for the five works presented in this paper: they are silica fume, ground limestone, and an expansive agent.

In this paper five specific concretes are shown all belonging to the SCC type: for an architectural concrete of the church of S. Peter Apostle in Pescara, Italy; for a HSC of the World Trade Center of San Marino; for a mass concrete placed in a slab foundation near Venice, Italy; for precast lightweight concrete structures, in Milan, Italy; and for shrinkage-compensating concrete devoted to a Museum Center in Rome, Italy.

Pure portland cement (CEM I according to European Norm EN 197/1) was used only for the HSC, whereas blended cements were used in all the other works.

For the mix-design of the three concretes, laboratory and field tests have been carried out. In the following sections the results for each of the five concretes are shown and discussed.

Architectural SCC: The properties required by the structural engineers of the S. Peter Apostle church erected on the sea beach of Pescara (Italy), may be summarized by the following data:

1) high fluidity in terms of slump flow: $\geq 600$ mm after 1 hr at 30°C (ready-mixed concrete placed in summer time);
2) cube compressive characteristic strength: $\geq 35$ MPa;
3) impermeability in terms of water penetration according to the ISO DIS 7031 test: $\leq 20$ mm (this requirement was adopted to guarantee durable concrete exposed to sea water);
4) marble-like effect of the skin of the concrete placed in the absence of vibration due to the very congested reinforcement.
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In order to reach all these requirements, the composition adopted for the concrete mixture was that shown in Table 1.

The performances really obtained are shown in Table 2 and they are all capable of meeting the above first three performances required by the structural designers.

As far as the marble-like effect of the skin is concerned – which was very important for the work from an architectural point of view – it was visually assessed by comparison of two white concretes, both placed without any vibration: the former at a superfluid consistency S5 (slump = 225 mm), and the later in form of SCC. Figure 1 shows, for instance, the marble-like effect of the skin obtained only in the case of the SCC. Then, thanks to the special rheological properties of the SCC in the fresh state, even the fourth requirement needed by the architect was met. Figure 2 shows the splendid appearance of SCC at a white wall of the church placed without vibration.

High-Strength SCC: For the World Trade Center in San Marino (designed by Norman Foster and Partners, London, U.K.), a special concrete was required with the typical properties of SCC as shown in the previous section and, additionally, with a high compressive strength. These are the requirements needed for the work [5]:

1) high fluidity in terms of slump flow: $\geq 600$ mm after 1 hr;
2) cube compressive strength $\geq 40$ MPa at 1 day and $\geq 80$ MPa at 28 days;
3) dynamic elastic modulus: $\geq 40$ GPa;
4) drying shrinkage: $\leq 500$ $\mu$m/m at two months;
5) uniformity in terms of specific mass, elastic modulus, and compressive strength measured on cored specimens through field tests.

Table 3 shows both the adopted composition and the performances of the concrete. These agree with the first four requirements.

One cylinder specimen was cored from the un-vibrated concrete placement 1500 mm thick, and then the following measurements were carried out: density (D) and dynamic elastic modulus ($E_d$) shown in Fig. 3, and compressive strength shown in Fig. 4.

The data obtained on different parts of the cored material indicated that the results obtained for the concrete of the structure are reproducible and agree very well with those obtained for the specimens cast in laboratory. Then, even the fifth requirement (about uniformity) is met.

SCC for mass concrete structures: In order to manufacture such a special SCC (slump flow of 700-800 mm) near Venice [4, 5] the following ingredients were used: blast-furnace slag cement (CEM III/A 32.5 R with portland cement content of only 40%), fly ash, ultra-fine amorphous colloidal
silica (UFACS) to reduce segregation and bleeding, and polyacrilic superplasticizer with retarding effect in order to reduce the early hydration rate (Table 4). The thermal difference between the nucleus (in a quasi-adiabatic condition) and the skin (considered to be in perfect thermal equilibrium with the environment) was lower than 20°C (recommended value to avoid craking risk) as shown in Fig. 5. The properties of these special SCC’s in the fresh state are shown in Table 5.

Figure 6 shows the strength development: the compressive strength was 40 MPa at 28 days with some post-hardening up to 50 MPa at 60 days. Drying shrinkage at RH of 55% was lower than 300 μm/m at 60 days (Fig. 7).

Moreover, laboratory test on SCC’s specimens, exposed to chloride aqueous solution (Fig. 8), carbon dioxide (Fig. 9), and water under pressure (5 atm) indicated that this concrete is durable and watertight (water penetration less than 10 mm) although the portland cement content was as low as 120 kg/m³ (Table 4).

**SCC for precast lightweight structures:** Self-compacting lightweight concrete was used in the form of precast insulating panels (Fig. 10). The main problem was to avoid segregation of expanded clay (Fig. 11): to do this, a relatively high content of the viscosity modifying agent was used as shown in Table 6 which gives a summary of the performance of this special SCC in terms of slump flow, strength, elastic modulus, drying shrinkage at R.H. of 50%, creep, and durability in terms of CO₂ and Cl⁻ penetration.

**Shrinkage-compensating SCC:** For the very prestigious Museum of Modern Arts, in Rome, designed by Zaha Hokhid Architects, London, U.K., a very special shrinkage-compensating SCC was studied in order to avoid the risk of cracks in some special walls (8 m high and 55 m long) without constructions joints. A CaO-based expansive agent in combination with a shrinkage reducing admixture (SRA) was used.

The composition of this special SCC and that of the corresponding SCC mixture without an expansive agent and SRA are shown in Table 7. Figure 12 shows the strength development of the two SCC, with and without an expansive agent and SRA.

Figure 13 shows the length change of the reinforced specimens (manufactured with mix A or B of Table 7) cured by a protective plastic film up to 16 hours and then exposed to unsaturated air (R.H. = 60%) at 20°C.

Due to the presence of SRA [6], the early curing of the reinforced specimens manufactured with the shrinkage-compensating SCC was not carried out under water as required by ACI Committee 233, but only with a plastic film to simulate the protection of the concrete surface from drying by the formwork. Even under this un-favorable but realistic conditions of curing, the expansion at 16 hours was relatively high (520 μm/m) and still good at 2
months (280 μm/m) with R.H. of 60%. In the “ordinary” SCC (mix B), without expansive agent and SRA, the shrinkage at 2 months was about 400 μm/m. Due to this special behavior, the first results obtained by field tests on concrete structures are very encouraging for the crack-free ability of this SCC.

CONCLUSIONS

The results obtained in the present paper show the extra-ordinary properties which can be obtained by using the innovative concretes recently developed in the field of SCC.

SCC appears to be very successful because it is easy to place in a safe way independent of the quality and reliability of the workmanship available today on the jobsites.

The architectural SCC presented in this paper is a very special concrete even for the excellent surface (white and with marble-like aspect) required for architectural reasons.

The high-strength SCC studied in this paper can be considered as market niche in the field of Civil Engineering.

The combined use of CEM III/A 32.5R (300 kg/m³), AP-based superplasticizer (0.8-1.5%), fly ash (130-150 kg/m³), ultra-fine amorphous colloidal silica (1-2%), and aggregate with a maximum size of 20 mm allow the manufacture of self-compacting concretes characterized by low heat development which are particularly suitable for mass concrete structures.

Lightweight SCC can be produced without any segregation of the expanded clay aggregates provided that an adequate dosage of the viscosity modifying agent is used.

Finally, a shrinkage-compensating SCC can be also manufactured with a CaO-based expansive agent and a shrinkage reducing agent as additional ingredients in addition to those usually adopted for SCC (superplasticizer, filler and VMA).

REFERENCES


Table 1 – Composition of Architectural SCC

<table>
<thead>
<tr>
<th>INGREDIENT</th>
<th>kg/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>WHITE Cement CEM/II B-L 32.5R*</td>
<td>400</td>
</tr>
<tr>
<td>COARSE CRUSHED MARBLE (2-16 mm)</td>
<td>875</td>
</tr>
<tr>
<td>FINE CRUSHED MARBLE (0-4 mm)</td>
<td>440</td>
</tr>
<tr>
<td>VERY FINE CRUSHED MARBLE (0-2 mm)</td>
<td>430</td>
</tr>
<tr>
<td>GROUND LIMESTONE</td>
<td>100</td>
</tr>
<tr>
<td>WATER</td>
<td>180</td>
</tr>
<tr>
<td>ACRYLIC SUPERPLASTICIZER</td>
<td>9.6</td>
</tr>
<tr>
<td>VISCOSITY MODIFYING AGENT</td>
<td>0.12</td>
</tr>
<tr>
<td>WATER-CEMENT RATIO</td>
<td>0.45</td>
</tr>
</tbody>
</table>

* portland cement = 70%

Table 2 – Performances of Architectural SCC

<table>
<thead>
<tr>
<th>Specific Mass (fresh mix) (kg/m³)</th>
<th>2417</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concrete Aspect</td>
<td>Cohesive</td>
</tr>
<tr>
<td>Slump Flow (mm) at 30°C after:</td>
<td>0 min. 700</td>
</tr>
<tr>
<td></td>
<td>30 min. 680</td>
</tr>
<tr>
<td></td>
<td>60 min. 650</td>
</tr>
<tr>
<td>Compressive Strength (MPa) at 20°C as a function of time (days)</td>
<td>1 17.2</td>
</tr>
<tr>
<td></td>
<td>7 35.3</td>
</tr>
<tr>
<td></td>
<td>14 39.4</td>
</tr>
<tr>
<td></td>
<td>28 43.0</td>
</tr>
<tr>
<td>Water penetration (ISO-DIS 7031)</td>
<td>6 mm</td>
</tr>
</tbody>
</table>

Table 3 – Composition and properties of High-Strength SCC

| Portland Cement (CEM I 42.5 R) | 465 kg/m³ |
| SILICA FUME                     | 65 kg/m³  |
| WATER                           | 175 kg/m³ |
| GRAVEL (15-22 mm)               | 195 kg/m³ |
| GRAVEL (6-15 mm)                | 720 kg/m³ |
| SAND (0-6 mm)                   | 710 kg/m³ |
| ACRYLIC SUPERPLASTICIZER        | 4.6 kg/m³ |
| water/(cement+silica fume)      | 0.33     |
| Slump flow at 5 and 60 min. (mm) AT 20°C | 730-600 |
| Compressive Strength (MPa) at:  | 1 day 50 |
|                                  | 28 days 95 |
| Drying shrinkage at 60 days (µm/m) | 380     |
| Dynamic elastic modulus (GPa) at 28 days | 45     |
**Table 4** – Composition of SCC mixtures for mass concrete structures.

<table>
<thead>
<tr>
<th>Mix</th>
<th>Slag Cement* (kg/m³)</th>
<th>Fly Ash (kg/m³)</th>
<th>Sand (kg/m³)</th>
<th>Gravel (kg/m³)</th>
<th>Water (kg/m³)</th>
<th>Acrylic superplasticizer (% by powder)**</th>
<th>UFACS (by % powder)**</th>
</tr>
</thead>
<tbody>
<tr>
<td>FA/0</td>
<td>307</td>
<td>128</td>
<td>965</td>
<td>824</td>
<td>178</td>
<td>0.96</td>
<td>0</td>
</tr>
<tr>
<td>FA/1</td>
<td>300</td>
<td>125</td>
<td>944</td>
<td>806</td>
<td>174</td>
<td>1.14</td>
<td>1</td>
</tr>
<tr>
<td>FA/2</td>
<td>304</td>
<td>127</td>
<td>964</td>
<td>822</td>
<td>176</td>
<td>1.31</td>
<td>2</td>
</tr>
</tbody>
</table>

* Portland cement = 120 kg/m³
** Powder = slag cement + fly ash

**Table 5** Properties of SCC’s for mass concrete structures

<table>
<thead>
<tr>
<th>Mix</th>
<th>UFACS (%)</th>
<th>SLUMP FLOW</th>
<th>Bleeding capacity (% by vol. of concrete)</th>
<th>Aspect**</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>After mixing</td>
<td>After 30 min</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>mm</td>
<td>sec*</td>
<td>mm</td>
</tr>
<tr>
<td>FA/0</td>
<td>0</td>
<td>790</td>
<td>30</td>
<td>750</td>
</tr>
<tr>
<td>FA/1</td>
<td>1</td>
<td>790</td>
<td>29</td>
<td>660</td>
</tr>
<tr>
<td>FA/2</td>
<td>2</td>
<td>800</td>
<td>30</td>
<td>740</td>
</tr>
</tbody>
</table>

* Time needed to research the final slump flow
** Fair = cohesive, good = very cohesive

**Table 6** – Composition and performance of a lightweight SCC with a density of 1750 kg/m³ and a slump flow of 650 mm, and without segregation at all (B in Fig. 12)

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>CEM II/A-L 42.5R*</th>
<th>Fly Ash</th>
<th>Sand (0-4 mm)</th>
<th>Expanded Clay (0-15 mm)</th>
<th>Water</th>
<th>Acrylic Superplasticizer</th>
<th>VMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>400</td>
<td>100</td>
<td>480</td>
<td>570</td>
<td>192</td>
<td>6</td>
<td>0.25</td>
</tr>
</tbody>
</table>

**Mechanical performances at 28 day**
- \( \sigma_c = 35 \text{ MPa} \)
- \( f_r = 5 \text{ MPa} \)
- \( E = 19000 \text{ MPa} \)
- Drying shrinkage at 90 days (R.H. 50%): 675 \( \mu \text{m/m} \)
- Creep at 90 days (with a load of 12 MPa at 28 days): 1000 \( \mu \text{m/m} \)
- CO₂ penetration (30% by vol. of the air) at 90 days: 5.5 mm
- Cl⁻ (3.5% NaCl aqueous solution) penetration at 90 days: 8 mm

* Portland cement = 85%
Table 7 – Composition of shrinkage-compensating SCC (A) and “ordinary” SCC (B)

<table>
<thead>
<tr>
<th>Mix</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement CEM II A/L 42.5R (kg/m$^3$)*</td>
<td>350</td>
<td>347</td>
</tr>
<tr>
<td>Limestone filler (&lt; 100 μm) (kg/m$^3$)</td>
<td>150</td>
<td>183</td>
</tr>
<tr>
<td>Gravel 4-16 mm (kg/m$^3$)</td>
<td>877</td>
<td>871</td>
</tr>
<tr>
<td>Sand 04-10 mm (kg/m$^3$)</td>
<td>908</td>
<td>903</td>
</tr>
<tr>
<td>Water (kg/m$^3$)</td>
<td>167</td>
<td>166</td>
</tr>
<tr>
<td>Acriilic Superplasticizer (kg/m$^3$)</td>
<td>6.3</td>
<td>6.3</td>
</tr>
<tr>
<td>Expansive Agent (kg/m$^3$)</td>
<td>35</td>
<td>-</td>
</tr>
<tr>
<td>SRA (kg/m$^3$)</td>
<td>4</td>
<td>-</td>
</tr>
</tbody>
</table>

* portland cement = 85%

Figure 1 – Skin effect marble-like of SCC with respect to a traditional concrete S5 at a superfluid consistency (slump = 225 mm), both placed without compaction.
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Figure 2 – View of a white wall of the S. Peter Apostle Church in Pescara (Italy).

D = 2383 kg/m$^3$
$E_d = 43619$ MPa

D = 2382 kg/m$^3$
$E_d = 43755$ MPa

D = 2385 kg/m$^3$
$E_d = 44570$ MPa

D = 2381 kg/m$^3$
$E_d = 43887$ MPa

Figure 3 – Density (D) and dynamic elastic modulus ($E_d$) measured on cored concrete of high-strength SCC.
Figure 4 – Cylinder compressive strength measured ($f_{21}$) at 21 days from cored concrete 1 m long (on the right) of high-strength SCC.

Figure 5 – Temperature increase in the nucleus of SCC with FA/2 (Table 4) in a quasi-adiabatic condition [5].
Figure 6 – Cube compressive strength ($R_c$) as a function of time of SCC with fly ash and UFACS (Table 4).

Figure 7 – Drying shrinkage of concrete mixture as a function of time for the SCCs with fly ash and UFACS (Table 4).
Figure 8 – Penetration of CO₂ as a function of time (√t) in SCCs with fly ash and UFACS (Table 4).

Figure 9 – Penetration of Cl⁻ ions as a function of time (√t) in SCCs with fly ash and UFACS (Table 4).
Figure 10 – Precast lightweight concrete: casting of SCC (A); Screeding without vibration (B); demolding of the hardened lightweight panel (C).
Figure 11 – Flowing concrete with segregation of the lightweight coarse aggregate on the top (A) in comparison with the corresponding lightweight SCC without segregation.

Figure 12 – Strength development of shrinkage-compensating self-compacting concrete (Sh-Co SCC) and “ordinary” self-compacting concrete (SCC).
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Figure 13 – Length change of shrinkage-compensating (Sh-Co) SCC and ordinary SCC (mix A and B, respectively in Table 7) after an early curing (16 hr) by protection of a plastic film.
Influence of Internal Friction and Cohesion on the Variations of Formwork Pressure of Self-Consolidating Concrete

by J. Assaad and K. H. Khayat

Synopsis:

A comprehensive research program was undertaken to determine the influence of coarse aggregate concentration, binder type and content, and the use of set-modifying admixtures on lateral pressure exerted by self-consolidating concrete (SCC). Experimental columns measuring 200 mm in diameter and either 2100 or 2800 mm in height were used to determine the distribution of lateral pressure during the plastic stage of cement hydration. The effect of thixotropy of the concrete on pressure variations was investigated.

Test results show that lateral pressure exerted by SCC is significantly affected by the development of shear strength properties of the plastic concrete, namely internal friction and cohesion. Mixtures incorporating greater coarse aggregate volumes and/or lower binder contents were found to exhibit higher degree of internal friction. This can reduce the mobility of the concrete and result in lower initial pressure. However, given that internal friction is an inherent property of the material which remains constant with time, the rate of drop in pressure was shown to depend mainly on the increase in cohesion. Therefore, mixtures containing higher binder contents and/or a set-accelerating admixture can exhibit sharper rate of pressure drop with time.

Concrete with higher degree of thixotropy was found to develop lower initial lateral pressure and higher rate of pressure drop with time. This is attributed to the stiffening effect which enables the material to re-gain its shear strength when left at rest without any shearing action.

Keywords: aggregate; binder; cohesion; formwork lateral pressure; internal friction; self-consolidating concrete; set-modifying admixture; thixotropy
INTRODUCTION

Self-consolidating concrete (SCC) is a new class of high-performance concrete that flows readily under its own weight and achieves good consolidation without any mechanical vibration. Given its high consistency, formwork systems prepared to receive SCC are often designed prudently by considering that the concrete exerts full hydrostatic pressure until the setting. This increases the construction costs and reduces the allowable rate of rise of the concrete in the formwork.

Numerous laboratory and field tests were carried out to evaluate formwork pressure of concrete with normal consistency. For example, Rodin (1) reported that formwork pressure depends mainly on the rate of casting, method of consolidation (hand consolidation or mechanical vibration), concrete temperature, setting time, mixture proportioning, consistency, as well as size and shape of the formwork. When external vibrators are used, the author concluded that the formwork should be designed for full hydrostatic pressure of a fluid having the same unit weight as the concrete. For design purposes, ACI Committee 347 proposed that lateral pressure should be hydrostatic from the upper free surface down to some limiting value beyond which it remains constant until the bottom of the formwork (2).

To evaluate the effect of cement content, Roby (3) investigated a series of rich, normal, and lean concrete mixtures made with different cement:sand:coarse aggregate ratios of 1:1.25:2.25, 1:2:3.5, and 1:2.5:5, respectively. An ordinary portland cement was used and the slump values of the mixtures varied between 50 and 150 mm. The author reported that the cement content has a significant effect on lateral pressure. The rich mixtures developed 40% greater pressure than the normal mixtures, which in their turn, developed 15% greater pressure than the lean ones. This was indirectly related to the lower volume of coarse aggregate in the lean mixtures (3). A greater volume of aggregate particles can lead to higher degree of internal friction which reduces the mobility of the concrete, and thereby the transformation of vertical load in lateral pressure.

Limited information exists regarding the effect of portland cement replacement by supplementary cementitious materials (SCM) on the
development of lateral pressure. Gardner (4) investigated the influence of cement replacement by fly ash for mixtures with slump values ranging between 65 and 115 mm. The fly ash replacement varied between 0 and 50%. Concrete mixtures containing fly ash were found to develop higher lateral pressure than similar concrete prepared with only Type 10 cement. According to Gardner (4), the incorporation of fly ash increases the mobility of fresh concrete and reduces the rate of strength gain, thus resulting in higher lateral pressure.

Ore and Straughan (5) reported that cement hydration tends to limit the formwork pressure after the initial vibration used for concrete placement, but does not prevent an increase in pressure due to revibration after an elapsed time from casting. The effect of incorporating a set-retarding agent on cement hydration was found to have limited influence on initial formwork pressure.

Limited information exists on the factors affecting the initial maximum formwork pressure of SCC and its rate of drop with time. More recently, the CEBTP (6) carried out a large-scale field experiment on diaphragm wall elements measuring 12 m in height to determine the lateral pressure developed by SCC. The mixture was made with a water-to-cementitious materials ratio (W/CM) of 0.46 and a slump flow of 700 mm. The results showed that the pressure envelope is not linear. At the base of the formwork, the deviation from the hydrostatic distribution was found to be 30% and 35% in the case of SCC pumped from the bottom of the formwork and that cast using a bucket from the top, respectively.

This paper presents an overview on the effect of coarse aggregate volume, binder type and content, and the use of set-modifying admixtures on both initial pressure and rate of pressure drop developed by SCC with 650 ± 15 mm slump flow consistencies. The influence of thixotropy on pressure development is also investigated.

**EXPERIMENTAL PROGRAM**

**Concrete Proportions**

The effect of coarse aggregate concentration on lateral pressure variations was investigated by evaluating various SCC mixtures with different sand-to-total aggregate ratios (R), by volume (7). A commercially available ternary cement containing 6% silica fume and 22% Class F fly ash replacements was used at a fixed dosage of 450 kg/m³. The W/CM was held constant at 0.40, and the maximum aggregate size was set at 10 mm. Some typical mixtures are presented in Table 1.

A Type 10 Canadian cement along with three blended cements were used to determine the effect of binder type on pressure development (8). The blended cements included a binary cement with 8% silica fume replacement, a ternary
cement such as the one specified earlier, and finally a quaternary cement with 6% silica fume, 26% Class F fly ash, and 18% blast furnace slag replacements, by mass of total binder. Further, a Type 30 Canadian cement was employed. The binder content ranged between 400 and 550 kg/m³ (Table 1). The W/CM and R values remained constant at 0.40 and 0.46, respectively, throughout this study (8).

A non-chloride-based set-accelerating admixture and a lignosulfonate-based set-retarding admixture were used to determine the effect of set-modifying admixture on pressure variations (9). These mixtures were prepared with 450 kg/m³ of ternary or binary cement. The W/CM was set at 0.42, and the R values varied from 0.44 to 0.50 (Table 1).

All of the investigated mixtures had initial slump flow consistencies of 650 ± 15 mm, concrete temperatures of 20 ± 2 °C, initial air contents of 6 ± 2%, and unit concrete weights of 2200 ± 200 kg/m³.

**Instrumented Formworks for Measuring Lateral Pressure**

Instrumented PVC columns measuring 200 mm in diameter and either 2100 or 2800 mm in height were used to determine lateral pressure distributions. The tubes had a smooth inner face to minimize any friction. The lateral pressure was determined using five pressure sensors of 100 kPa capacity mounted at 50, 250, 450, 850, and 1550 mm from the bottom. The face of each sensor was set flush with the inside of the formwork. The sensors were properly calibrated using a free head of water prior to use.

**Testing Program**

The L-box flow characteristics and surface settlement of SCC mixtures were evaluated. The L-box test is an L-shaped apparatus with a gate separating the vertical and horizontal compartments (10). The vertical part of the box is filled with concrete and left at rest for one minute before opening the gate separating the two compartments. The ratio of the height of concrete remaining in the leading edge \(h_2\) to that remaining in the vertical section \(h_1\) was determined. In general, values greater than 0.80 were obtained, indicating good self-levelling characteristics.

The surface settlement was assessed by casting concrete in a PVC column measuring 200 mm in diameter and 800 mm in height (11). The settlement was monitored using a linear dial gauge fixed on top of a thin plate positioned and anchored at the concrete surface. Values lower than 0.5% were obtained, indicating that the mixtures are stable with minimum degree of bleeding or segregation.

The protocols adopted for evaluating the thixotropy of SCC are presented elsewhere (12). Four structural breakdown curves determined at rotational
speeds of 0.3, 0.5, 0.7, or 0.9 rps were determined for each mixture. Immediately after the vane drive mechanism is started, readings of the torque were noted as a function of time without any delay. The first reading is considered as the initial maximum torque value, and the mean of the five smallest measurements over the 25 sec duration at each rotational speed is taken as the equilibrium torque value. The time required to perform each of the structural breakdown tests at a given rotational speed was 7.5 min (in some cases 12.5 min), of which 5 min (or 10 min) when the concrete was at rest in the rheometer bowl and 2.5 min required for the testing and rehomogizing the concrete before subsequent measurements. In total, 30 min (or 60 min) were necessary to determine the four structural breakdown curves during the first time interval ($T_1$). In order to determine the variations of thixotropy with time and its influence on changes in lateral pressure, two additional series of measurements, referred to as $T_2$ and $T_3$, were performed at time intervals of 60-90 (or 60-120) and 120-150 (or 120-180) min, respectively.

The general procedure of filling the experimental columns consisted of discharging continuously the SCC at a rate of rise of 10 ml/hr without any vibration. Given that the PVC column had to be emptied prior to stiffening, the monitoring of lateral pressure distributions was stopped once the concrete had an approximate slump of 125 mm.

TEST RESULTS AND DISCUSSION

Variations in Lateral Pressure with Respect to Height and Elapsed Time

A typical example showing the drop in lateral pressure with time after placement is given in Fig. 1 for a mixture made with $550$ kg/m$^3$ of ternary cement and $0.40$ W/CM. The loss in slump flow consistency with time is also indicated. Right after casting, the lateral pressure exerted by the SCC corresponded to 94% of hydrostatic pressure. Three hours latter, the pressure envelope decreased to approximately 52% of the hydrostatic.

Effect of Shear Strength Properties on Lateral Pressure Development

The lateral pressure exerted by plastic concrete is highly affected by the development of shear strength properties which include (i) the frictional resistance and interlocking among solid particles and (ii) the bond among the particles due to cement hydration (13). The former component of shear strength is termed internal friction and requires strain to be mobilized, while the latter component is referred to as cohesion. Cohesion results from cement hydration, and therefore depends on the elapsed time after the initial contact of water with cement (13). The influence of each component is further discussed below.

Effect of Internal Friction--An example showing the variations of the ratio of maximum pressure measured using the 2800-mm high experimental column to
the hydrostatic pressure \((P_{\text{maximum}}/P_{\text{hydrostatic}})\) is plotted in Fig. 2 for mixtures made with various R values. The slump consistency measured at the end of lateral pressure monitoring is noted. Mixtures prepared with low concentrations of coarse aggregate (higher R values) are shown to develop higher initial relative pressure and lower rate of pressure drop with time. For example, the reduction in the R value from 1.0 to 0.50 and 0.30 resulted in lower initial relative pressures corresponding to 99%, 92%, and 77%, respectively. Given that the SCC mixtures are prepared with the same binder content of 450 kg/m\(^3\) and W/CM of 0.40, such variations can predominantly be attributed to the various degrees of internal friction resulting from coarse aggregate (7). After placement, aggregate particles surrounded by the cement-mortar matrix tend to consolidate and settle down, hence achieving greater granular packing. When the mixture has relatively high R value corresponding to low aggregate concentration, aggregate particles can have greater freedom to translate and rotate within the matrix. In consequence, given that fresh concrete behaves in a dilatant fashion and expands when subjected to a given vertical load (14), it can be expected that the reduced degree of internal friction resulting from lower coarse aggregate concentration can increase the mobility of the fresh concrete. This can therefore increase the expanding response and result in higher lateral pressure.

Increased degree of internal friction within the freshly cast concrete can be achieved by the incorporation of higher volume of coarse aggregate as well as by substituting the Type 10 cement by SCM. The effect of binder type on the variations of \(P_{\text{maximum}}/P_{\text{hydrostatic}}\) values for mixtures made with 450 kg/m\(^3\) of binder is illustrated in Fig. 3. It is important to note that the coarse aggregate concentration was held constant at 0.46 throughout this study (8). The SCC made with only Type 10 cement developed the highest initial pressure of 98% of the hydrostatic value and the lowest rate of pressure drop with time. Mixtures made with quaternary, binary, or ternary cement yielded respectively lower initial pressures. The substitution of part of the Type 10 portland cement by an equal mass of silica fume, fly ash, or granulated blast furnace slag results in an increase in the solid volume of the powder materials. It is to be noted that the specific gravities of the Type 10 cement, silica fume, fly ash, and blast furnace slag are 3.14, 2.22, 2.53, and 2.88, respectively. Their surface areas are 325, 20250 (B.E.T.), 410, and 445 m\(^2\)/kg, respectively. This can increase the degree of flocculation and inter-particle links leading to higher level of particle interlock (8). In consequence, the use of blended cements can increase the degree of internal friction within the cement paste, thus resulting in lower development in lateral pressure.

Even though the replacement of portland cement by SCM can reduce the initial lateral pressure and increase the rate of pressure drop, such beneficial effect can decrease beyond certain limits of Type 10 cement replacements. This is the case of the mixture proportioned with 50% SCM compared to SCC made with binary or ternary cement containing 8% and 28% SCM, respectively. Higher contents of SCM was shown to increase the demand of high-range water-
reducing admixture (HRWRA), thus resulting in relatively lower loss in consistency with time (8). As can be seen in Fig. 3, after approximately 250 min from casting, slump values of 150 and 140 mm were measured for mixtures made with binary and ternary cement, respectively. This increased to 240 mm for the SCC prepared with quaternary cement. The material can then behave like a fluid for a longer period of time and result in higher lateral pressures.

The SCC prepared with Type 30 cement exhibited the lowest initial relative pressure of 78% and the highest rate of pressure drop (Fig. 3). This can be due to the increased surface area of the Type 30 cement (600 m²/kg) that increases significantly the degree of flocculation and number of inter-particle links (8). The high surface area, as well as the chemical composition of the cement, can lead to faster rate of hydration which increases the loss in slump flow and thereby the rate of pressure drop following casting.

Effect of Cohesion—The \( \frac{P_{\text{maximum}}}{P_{\text{hydrostatic}}} \) values determined on the 2800-mm high column are plotted in Fig. 4 for four SCCs made with various contents of ternary cement. The R value and W/CM were set at 0.46 and 0.40, respectively. Mixtures prepared with higher binder contents developed greater initial pressure. This can be related to the relatively lower coarse aggregate volume that can reduce the degree of internal friction, thus increasing the mobility of the concrete and yielding greater initial pressure (7). However, unlike the effect of binder content on the initial pressure, the rate of pressure drop is enhanced with the increase in binder content. Alexandridis and Gardner (13) reported that internal friction is an inherent property of fresh concrete that remains constant with time and temperature changes. For longer elapsed periods after casting, it is the increase in cohesion that enables the plastic concrete to develop higher shear strength through the formation of a gel structure capable of carrying an increasing fraction of the vertical load (13). In consequence, mixtures made with higher binder contents can result in increased development of cohesion, thus leading to higher drop in lateral pressure. It is important to note that the HRWRA dosage can also indirectly affect the rate of reduction of lateral pressure. Mixtures prepared with lower binder contents necessitated higher HRWRA dosage that can enhance fluidity retention. This can therefore enable the material to behave like a fluid for longer elapsed times, thus reducing the rate of pressure drop.

The effect of using set-modifying admixture on variations in \( \frac{P_{\text{maximum}}}{P_{\text{hydrostatic}}} \) values for SCC mixtures made with 450 kg/m³ of ternary cement, 0.42 W/CM, and R of 0.50 is plotted in Fig. 5. The rate of pressure drop is shown to be significantly increased by the incorporation of a set-accelerating admixture (9). As already mentioned, the increase in cohesion as a result of cement hydration allows the plastic concrete to develop higher shear strength at longer elapsed periods after casting. Knowing that the rate of hydration can be controlled by incorporating a set-modifying agent, the use of such admixtures can have direct influence on cohesion and thereafter on the drop in lateral pressure with time.
Relationship Between Thixotropy and Lateral Pressure

The relationship between the values of the breakdown area evaluated during the first time interval \(T_1\) of rheological measurements and the corresponding residual pressure, \(P(\text{maximum})/P(\text{hydrostatic})\), determined right after filling the formwork is illustrated in Fig. 6. This figure also illustrates the relationship between the values of the breakdown area evaluated during the \(T_2\) and \(T_3\) time intervals and the \(P(\text{maximum})/P(\text{hydrostatic})\) calculated at 100 and 200 min after casting, respectively. For the three correlations, the \(P(\text{maximum})/P(\text{hydrostatic})\) ratio decreases for mixtures exhibiting a higher degree of thixotropy. Such decrease becomes more accentuated with time as indicated by the sharper slope obtained at 100 and 200 min after casting.

As already mentioned, lateral pressure exerted by fresh concrete depends largely on shear strength development. On the other hand, it is well established that thixotropy is a reversible phenomenon that takes place as soon as the material is left standing at rest (12). The onset of the structural build-up phase causes the structure to flocculate and increase its cohesiveness. For mixtures having greater degree of thixotropy, the increased kinetics of the build-up phase can cause a faster increase in the shear strength properties, thus precluding the development of higher lateral pressure.

CONCLUSIONS

Based on the above results, the following conclusions can be drawn:

1. Depending on the type of structure and major requirements of the field, one could recommend lower initial pressure or higher rate of pressure drop with time. The former could be of special interest to reduce the design loads, whereas the later could be important for scheduling issues of concrete placement.

2. The initial lateral pressure developed by SCC is significantly affected by the degree of internal friction. Mixtures prepared with greater coarse aggregate volumes and/or lower binder contents can exhibit higher internal friction and lower initial pressure. For a given content of coarse aggregate, the use of blended cement can also increase the degree of internal friction compared to mixtures made with Type 10 cement without any SCM.

3. The rate of drop in lateral pressure following casting is mainly dependent on the development of cohesion with time. Mixtures containing higher binder contents or a set-accelerating admixture can exhibit greater degree of cohesion, hence sharper rate of pressure drop.

4. The formwork pressure of SCC mixtures can be directly related to the magnitude of thixotropy. The greater the degree of thixotropy, the lower the
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initial lateral pressure can be and the faster is the rate of pressure drop with time.

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High Vertical Form Faces before Setting of Cement”; (in French), Doctoral
Table 1 – Typical SCC mixtures used in this study

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<thead>
<tr>
<th>Effect of coarse aggregate concentration (7)</th>
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<tr>
<td>Ternary cement = 450 kg/m³ and water = 180 kg/m³ (W/CM = 0.40)</td>
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<td>Coarse aggregate = 970 kg/m³ and sand = 640 kg/m³ (R = 0.40)</td>
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<tr>
<td>Ternary cement = 450 kg/m³ and water = 180 kg/m³ (W/CM = 0.40)</td>
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<tr>
<td>Coarse aggregate = 810 kg/m³ and sand = 810 kg/m³ (R = 0.50)</td>
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<tr>
<th>Effect of binder type and content (8)</th>
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<tr>
<td>Binary cement = 450 kg/m³ and water = 180 kg/m³ (W/CM = 0.40)</td>
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<tr>
<td>Coarse aggregate = 890 kg/m³ and sand = 760 kg/m³ (R = 0.46)</td>
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<tr>
<td>Ternary cement = 400 kg/m³ and water = 160 kg/m³ (W/CM = 0.40)</td>
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<tr>
<td>Coarse aggregate = 940 kg/m³ and sand = 800 kg/m³ (R = 0.46)</td>
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<tr>
<td>Ternary cement = 550 kg/m³ and water = 220 kg/m³ (W/CM = 0.40)</td>
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<tr>
<td>Coarse aggregate = 780 kg/m³ and sand = 660 kg/m³ (R = 0.46)</td>
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<th>Effect of set-modifying admixture (9)</th>
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<tr>
<td>Ternary cement = 450 kg/m³ and water = 189 kg/m³ (W/CM = 0.42)</td>
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<tr>
<td>Coarse aggregate = 890 kg/m³ and sand = 710 kg/m³ (R = 0.44)</td>
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<td>Set-retarder = 75 mL/100 kg of CM</td>
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<td>Ternary cement = 450 kg/m³ and water = 189 kg/m³ (W/CM = 0.42)</td>
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<tr>
<td>Coarse aggregate = 890 kg/m³ and sand = 710 kg/m³ (R = 0.44)</td>
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<td>Set-accelerator = 1000 mL/100 kg of CM</td>
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Fig. 1 – Typical example on lateral pressure developed on formwork (8)

Fig. 2 – Effect of coarse aggregate concentration on lateral pressure variations (7)
Mixtures made with 450 kg/m$^3$ of binder, W/CM of 0.40, and R of 0.46

Type 10 cement
Slump = 160 mm

Quaternary cement
Slump = 240 mm

Binary cement
Slump = 150 mm

Ternary cement
Slump = 140 mm

Type 30 cement
Slump = 105 mm

Fig. 3 – Effect of binder type on lateral pressure variations (8)

Mixtures made with various contents of ternary cement, W/CM of 0.40, and R of 0.46

SCC with 400 kg/m$^3$
Slump = 210 mm

SCC with 450 kg/m$^3$
Slump = 140 mm

SCC with 500 kg/m$^3$
Slump = 120 mm

SCC with 550 kg/m$^3$
Slump = 100 mm

Fig. 4 – Effect of binder content on lateral pressure variations (8)
Fig. 5 – Effect of set-modifying admixture on lateral pressure variations (9)

Fig. 6 – Relationship between thixotropy and lateral pressure
Self-Consolidating Concrete at Padgett-Thomas Barracks—The Citadel

by G. Amekuedi, R. Morrow, M. Nigels, and B. Guedel

Synopsis:

The Citadel in Charleston, South Carolina is steeped in tradition down to the buildings at the campus. Currently under construction is a replacement for the Padgett-Thomas Barracks, which was demolished in 2001. The new structure will be identical to the original barracks. It will showcase a classic fortress design that requires intricate forming and careful planning in the proportioning and placement of the concrete mixtures, in order to minimize/eliminate cost over-runs that have been experienced in previous construction projects at the campus.

Through a cooperative effort involving all parties in the construction of the new barracks, self-consolidating concrete (SCC) is now being used in lieu of the originally specified regular slump concrete. The use of SCC in the construction of the narrow 150mm (6 in.) thick walls have significantly increased placement/construction efficiency. It has also resulted in a greatly enhanced surface finish and sharper edges.

This paper chronicles the project from the pre-construction meetings and trial placements to the placement efficiencies that have been realized due to the use of SCC. About 7646 cubic meters (10,000 cubic yards) of SCC are going to be used for this project, which is scheduled for completion in 2004. Data on the properties of the SCC mixture from the field and companion laboratory studies are presented and discussed.

Keywords: compressive strength; flexural strength; self-consolidating concrete; shrinkage
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Mack Nigels is currently a structural engineer with Davis & Floyd overseeing the Padgett-Thomas Barracks Replacement at the Citadel in Charleston, South Carolina. He has experience in all aspects of this, one of the largest self-consolidating concrete projects in the region. He has 35 years of experience in the pre-stressed concrete industry and 9 years as a structural engineer. A 1955 graduate of the Citadel with a bachelor of science in civil engineering, he is a licensed professional engineer in the state of South Carolina.

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Richard Morrow is the manager of North and South Carolina for Master Builders. A former President of the ACI-Virginia Chapter he has been involved in concrete technology for 19 years and specialized in concrete mixture design, admixtures, anti-washout concrete, and troubleshooting. He has experience with large-scale projects including sunken tube tunnels, shipbuilding facilities, and bridges containing silica fume. He graduated from Christopher Newport University, Newport News, Virginia, and is an NRMCA certified concrete technologist.

INTRODUCTION

Established in 1822. The Citadel – The Military College of South Carolina. is an academy rich in history and tradition. Located on .712 km² (176 acres) on the banks of the Ashley River in Charleston, South Carolina. the picturesque campus has 24 major buildings, where students pursue studies in 19 different degree programs. Originally an all-male institution, women were admitted in 1996. The Citadel has long been respected as a premier educational institution and is consistently ranked among the best colleges in the region.
At The Citadel, "students" are called "cadets" and the word "barracks" is used in place of "dormitories". Four barracks house roughly 1900 cadets who attend the college. Constructed in 1922, the Padgett-Thomas Barracks was the oldest building and the largest student housing facility on campus. For eighty years, it served as perhaps the best-known symbol of the military college and a model for all other barracks on the campus. An imposing, brilliant white unreinforced masonry structure complete with turrets and a large clock tower overlooking the parade ground to the east, the center of the Padgett-Thomas Barracks was designed as a quadrangle onto which each room opened, and spiral stairways graced each of the four corners.

By 2000, the venerable structure -- with its narrow dorm rooms with high ceilings and hardwood floors -- was declared a safety hazard with collapsed ceilings, fallen concrete, backed-up sewer lines, and structural instability. In the early part of 2000, The Citadel made the decision to demolish and replace the Padgett-Thomas Barracks.

DESIGN

The Structure

Architect Davis & Floyd, Inc. of Charleston, SC, began work on the design of the new Padgett-Thomas Barracks in 2000. The goal - design a new structure, identical in appearance to the landmark building but incorporating modern conveniences and designed to withstand strong hurricanes. In addition, the design had to accommodate the fact that Charleston is on top of an ancient fault line. A devastating 7.3 magnitude earthquake struck the city in 1886 (1) and recent changes to the International Building Codes' seismic requirements meant doing things differently. They delivered a plan for a four-story building that is a work of art and a showcase of excellence. Almost an exact replica of the original, it features a classic fortress design with precast concrete battlements and reconstruction of the magnificent eight-story tower, complete with the original clock, wrought iron gates, and brass seal. The 10,400 m² (112,000 ft²) building was to be constructed entirely of cast-in-place concrete walls and slabs. And not simple walls and slabs -- nearly half of the construction would be 150 mm (6 in.) thick. 3.7 m (12 ft) high walls that required intricate forming to achieve nearly 1000 block-outs for doorways, window casings, archways, and utilities. Because of the new seismic code requirements, the 150 mm (6 in.) thick bearing walls would have two mats of steel reinforcement, leaving no room for pump hoses or vibrators. The cadet room walls would be exposed, only receiving paint for their
finished surface, requiring better than normal surface finish with these difficult constraints.

**Concrete Mixture**

The specifications called for 27.6 MPa (4000 psi), air-entrained concrete with a maximum water-cement ratio (w/c) of 0.40 and a maximum slump of 100 mm (4 in.). With the addition of a high-range water reducer (HRWR), the maximum slump was extended to 180 mm (7 in.). The maximum size coarse aggregate allowed was 25 mm (1 in.) and fly ash was initially not permitted.

Locally available aggregates are conducive to proportioning concrete mixtures with good characteristics with respect to gradation, cleanliness, and water demand. A crushed granite meeting the ASTM C 33 requirements of a #67 material (Table 1) and natural sand having a fineness modulus of 2.57 (Table 1) were initially chosen. The cement to be used was an ASTM C 150 Type I/II portland cement.

It was known that a large portion of the project would be constructed in the typically very hot summer Charleston, S.C. is renowned for. Therefore, limits were placed on initial concrete temperature with a minimum of 10 °C (50 °F) and a maximum of 32 °C (90 °F). In addition, a time limit of 1½ hours from batch until unloading was specified. The size of the walls required slow placement and careful consideration of these necessary precautions.

**PRE-CONSTRUCTION PLANNING**

The success of concrete placement on a project is often determined by the timeliness and thoroughness of good pre-construction meetings. In the case of the Padgett-Thomas Barracks, it was crucial. The construction team consisting of the owner's representative, the design engineer, the concrete supplier, the admixture supplier, and facilitated by a forward-thinking contractor's superintendent, was assembled in the Spring of 2002. It was noted that previous attempts to place the designed concrete in 150 mm (6-in.) thick walls with two layers of steel reinforcing mats had proved problematic. The inability to insert internal vibrators had left severe honeycombing and poor surface finish. The amount of rubbing required to achieve a smooth enough texture to accept a heavy paint had been devastating. Rubbing costs alone had approached $32/m² ($3/ft²).

During the pre-construction meeting, the concept of higher slumps utilizing HRWR admixtures was introduced and this led to the introduction of self-
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consolidating concrete (SCC). Data were provided showing SCC's engineering properties as comparable to or better than the properties of conventional concrete.(2) The team agreed that something out of the ordinary would be required to place the walls as designed in a cost effective manner. It was agreed to begin wall construction using a polycarboxylate HRWR at 180 mm (7-in.) slumps to ease placement. At the same time, the ready mix supplier would begin trials with SCC.

SELF-CONSOLIDATING CONCRETE TRIALS

Implementing SCC into this project took on the following seven-step process:

1. Consider Hardened Property Requirements
2. Evaluate Element Characteristics
3. Evaluate Raw Materials
4. Establish Fresh Performance Targets
5. Proportion Mixtures
6. Run Trial Batches
7. Production/Field Trials

Hardened Properties

The hardened properties had been established by the specification – 27.6 MPa (4000 psi), air-entrained concrete at 28 days with a w/c of 0.40 for corrosion protection of the reinforcement from the chloride-laden air. The structural element characteristics were the impetus for the SCC mixtures - narrow walls with tight reinforcement and the need to strip the walls in reasonable time with minimal surface defects.

Raw Materials

Evaluation of raw materials focused on aggregate selection and the amount of cementitious material that would be required to keep the mixture stable. In order to proportion SCC mixtures, it is important to utilize fine and coarse aggregates in such a way as to minimize the potential for segregation. This implies developing a blend of aggregates that best fits together, eliminating the amount of gaps in the gradations and thus the potential for settlement in high-flow mixtures. Practicality dictates the use of readily available aggregates but
evaluation of other options that would not normally be considered may be required. In the case of the Citadel, the concrete producer had available the #67 coarse stone previously submitted and a #789 stone that could fill some gaps (Table 1). The proportions of these aggregates and the fine aggregate, natural ASTM C 33 concrete sand, were plotted against a best-fit curve for both total % passing (Fig. 1) and total % retained (Fig. 2). This best-fit curve was also utilized to arrive at a sand-to-aggregate ratio (s/a) that would minimize the chance for segregation. This curve was developed from the modification of similar equations in an attempt to take into consideration the high fluidity of these mixtures. Early guidelines for SCC often stressed an elevated s/a as high as 0.50. Due to the concerns about durability and increased shrinkage, this ratio had been optimized to keep it as close as possible to that normally associated with normal slump concrete and thus resulted in an s/a value of 0.46.

Because of the slump flows that would be required to successfully place SCC in The Citadel walls, it was determined that a minimum of 445 kg/m$^3$ (750 lb/yd$^3$) of cementitious material should be employed to ensure there would be enough fines to avoid segregation. For economic reasons and to aid in lowering the heat of hydration, class F fly ash was utilized at 26% of the total cementitious material. Permission was obtained from the structural engineer for this deviation from the specifications and the concrete producer supplied past compressive strength performance data with similar mixtures for review.

In order to achieve the fluidity required, a new generation polycarboxylate HRWR was utilized in conjunction with an ASTM C 494 Type A water reducer. To provide stability at high slump flows, and to maintain the required properties in the hardened state, a viscosity-modifying admixture (VMA) was utilized.

**Fresh Performance Targets**

Because of the high fluidity of SCC, additional measurements must be considered to measure properties with respect to fluidity and stability. The slump flow test measures fluidity. It is used in conjunction with the T$_{50}$ test, which measures how much time is required for a mixture to achieve a slump flow of 50 cm (20 in.). T$_{50}$ is a simple measurement of viscosity. The U-box measures the ability of a mixture to flow from a 680 mm (26.8 in.) column through reinforcement and into an identical column. The reinforcement varies depending on the type of structure in which the mixture will be placed and is categorized by rank. A rising height of 300 mm (12 in.) is considered passing. The Visual Stability Index (VSI) for the categorization of mixtures with respect to stability was applied on all slump flow tests (3).

Using a chart (Fig. 3), developed by Constantiner and Daczko (4), that evaluates flow properties with respect to element characteristics, a slump flow of at least
660 mm (26 in.) was required to handle the form intricacy, finish importance, form length/depth, and wall thickness. The same matrix also suggested a U-box rank of 1, meaning a high level of passability. The mixtures performing best had T50 times less than 2 seconds. This meant that the viscosity was low enough to transport the mixture well and not trap air at the finished surface, but high enough to minimize segregation and help with aggregate transport around the steel reinforcement.

**Trial Mixtures**

The ready mix supplier and admixture representatives, Daczko et al., began work using the parameters developed by the specifications and above criteria. Trials were conducted with small batches produced in a modern central-mixed concrete plant instead of a trial mixer. Initially, only the #67 coarse aggregate was utilized as it was thought the gradation was adequate. A small 1.5 m³ (2 yd³) slab was placed at the plant. Slump flow attained 510 mm (20 in.), and T50 time was 2.5 s. The VSI was observed to be 2.5, indicating minor aggregate piling in the center of the spread patty. Additional full loads of 6 to 7.6 m³ (8 to 10 yd³) were evaluated in highway barrier forms with increased slump flows. This also allowed for a placement similar to the walls on the project that required transport through a narrow section without segregation and a good surface finish upon stripping. As slump flows were increased to 660 mm (26 in.), it became apparent that the #67 coarse aggregate alone was inadequate—resulting in segregation and poor surface finish with some voids. A #789 stone was added at 35% of the total coarse aggregate amount, a value obtained from the blending program mentioned previously. Also, a VMA was added to aid with stability at the higher slump flows. Additional trials were completed using the barriers and all criteria improved to acceptable levels. The engineering team from the project was invited to observe the mixture being placed at the plant and agreed to allow a test placement on the project.

**Field Trials**

A critical step, the field trial at the project, was conducted on the first stage of an elevator pit wall. Conditions were quite similar to the walls to be placed using SCC and accessibility was such that all could easily observe the placement both during the pour and after stripping. Although slump flow was below the desired 660 mm (26 in.), the placement was a success and the surface finish was greatly improved over normal slump, vibrated concrete. Next, an actual wall was placed. Again, conservative slump flows of 510 to 560 mm (20 to 22 in.) were used. The concrete was placed by boom pump and because of the steel
reinforcement spacing; the flexible hose end could not be inserted into the form. Concrete was allowed to fall 3.7 m (12 ft), and although segregation was not observed, aggregate trapped between the steel and the form and was able to build up such that after stripping, there were "rock pockets" in several small areas. The remainder of the non-vibrated concrete surface finish was excellent.

A meeting among all parties to review the field trial accomplished several enhancements that greatly contributed to the project's success. In order to allow insertion of the pump hose, the horizontal extra piece of steel from an incomplete portion of the mat was removed at the end of one of the walls. This allowed the pump to be inserted to the bottom of the wall like a tremmie during placement, allowing the SCC to flow to the other end, turn and go until a bulkhead. This eliminated the "rock pockets". In addition, results from U-Box testing confirmed the need for highly fluid 610 to 710 mm (24 to 28 in.) slump flow SCC.

**PRODUCTION**

After modifications were made, the SCC mixture performed well. All parties were so pleased that attention focused on improving the process - not only taking advantage of time and energy savings, but looking for newfound advantages that had not been expected.

**Contractor**

The contractor began to realize advantages with SCC immediately. Placement times required to place 15 to 23 m$^3$ (20-30 yd$^3$) had been reduced from 2 hours to 1 hour. Crew size was reduced from six men to two men on the wall. No vibration was used; however, a vibrator was kept ready in case of delays or unforeseen problems. Perhaps the greatest advantage was afforded by the extremely smooth finish and clean sharp edges (Figs. 3 and 4) made possible by a mix that was truly self-consolidating. Rubbing costs were reduced by a factor of ten. Because of the relatively high cementitious factor, stripping strengths as well as 28-day strengths were well within the requirements and in most cases greatly exceeded specification (Table 2). Form building required special attention to prevent leakage and blowouts. Steel forms were used and had no problem accommodating the pressure head. At one point, unavoidable leakage into a utility space formed by the intersection of two walls created a need to reduce slump flow. The mix was adjusted to produce a 560 mm (22 in.) slump flow, which solved the problem. U-Box testing confirmed the mixture did not impede the flow required to fill the walls uniformly and without vibration. After the first level of walls this leakage was not a problem and the mix was adjusted
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back to a 660-mm (26-in.) slump flow. Pour sizes were increased to as large as 54 m$^3$ (70 yd$^3$) as the time required for placement was reduced.

**Ready-Mixed Concrete Producer**

The concrete producer undoubtedly spent more time and effort developing and insureing quality with the SCC mixture. Attention to aggregate moisture condition becomes critical in producing SCC mixes. Aggregate storage silos and moisture probes in the weigh hoppers that were interfaced with the batch computer aided in this process. Typically, the concrete was batched with all ingredients except approximately 10% of the HRWR. Slump flows of 510 to 610 mm (20 to 24 in.) were produced to allow for larger load size 6 m$^3$ (8 yd$^3$) without spillage in transit. At the project site, slump flow and T$_{50}$ times were tested on each truckload and adjusted by quality control personnel to the final desired level – ideally 630 to 710 mm (25 to 28 in.). The U-box was also used on the first few placements to ensure the mix would pass through the reinforcement as designed. Shortened pour times provided greater truck mixer delivery efficiency and less concern about time limit constraints and temperature rise.

**Results**

As of this writing, over 3440 of approximately 3670 m$^3$ (4500 of 4800 yd$^3$) have been placed in walls using SCC. None of the SCC concrete was vibrated. The surface finish, formed edge sharpness, and general appearance of the concrete is reported by all parties to be excellent. Statistical analysis of the compressive strength performance shows the average 28-day strength to be 38.1 MPa (5530 psi) with a standard deviation of 4.65 MPa (674 psi) for 110 tests. These results as reported by the contractor, concrete producer and laboratory, are superior to projects utilizing normal slump 27.6 MPa (4000 psi) concrete. The project is nearing completion ahead of schedule.

**LABORATORY ANALYSIS**

Because of the great success realized with the SCC mixture on this project, the concrete producer and admixture supplier agreed to perform more in-depth analysis of the properties of the mixture in the admixture supplier’s headquarters laboratory. The goal of the project was to record more comprehensive data in both the fresh and hardened states and to identify the properties that made this
mixture perform so well. Development of data to facilitate the use of the product on future projects was also considered.

**Procedures**

All mixture constituents were transported from the concrete supplier's inventories to the laboratory in sealed steel drums. 0.057 cubic meter (two cubic foot) batches of the mixture utilized at The Citadel were prepared and plastic properties tests performed included slump flow, T50 time, U-Box rising height, bleed %, column segregation, and initial and final set. Yield stress and viscosity measurements were recorded by an IBB rheometer. Results are summarized in Table 2.

The hardened tests included compressive and flexural strength at 1, 7, and 28 days, and rapid-chloride permeability at 28 days. An additional laboratory mixture was prepared to measure shrinkage at 4, 7, 14, and 28 days after 7 days moist curing (Table 2).

The original mixture was also modified in the laboratory to observe changes with respect to water-cementitious materials ratio (w/cm) and HRWR dosage.

**CONCLUSIONS**

It is likely that self-consolidating concrete technology will be adopted for use in concrete structures similar to the Padgett-Thomas barracks as well as many other applications. Based on the success observed on this project, the advantages to be gained by contractors will undoubtedly be utilized in the competitive bid process – thus driving the technology and the impetus to improve it forward.

This example upholds the process of defining and communicating the challenges facing a concrete project before construction begins. It also provides a successful model for the presentation of new technology and the importance of data collection to further that technology. The procedure used to arrive at SCC mixture proportions that are appropriate for the project was successful.

The data presented from the analysis of the Citadel SCC mixture is unique in that laboratory data have been developed on a mixture that is known to be successful on a current project. The new test procedures developed to evaluate SCC mixtures were helpful in the comparison of different mixtures and seem to provide some interesting correlation between slump flow, w/cm and viscosity. Strength analysis seems to indicate that the use of similar SCC mixtures may as a
by-product, enhance the compressive strengths over a normally designed mixture and therefore limit potential delays for investigations of low strengths. These mixtures may accelerate the construction process without additional cost.

It is hoped that the construction industry will see the value of SCC based on the types of benefits presented here. If the value chain can be sustained from the concrete producer through to the owner, this technology will produce higher quality concrete structures and hopefully allow the industry to invest in the continuous improvement of this most versatile material.

REFERENCES


Table 1. Aggregate Gradations

<table>
<thead>
<tr>
<th>Sieve Size</th>
<th>Fine Aggregate</th>
<th>#67 Stone</th>
<th>#789 Stone</th>
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<tr>
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<td>% Passing</td>
<td>% Passing</td>
<td>% Passing</td>
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<td>100</td>
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<td>3/4 in.</td>
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Table 2. Plastic Properties of Field and Laboratory Mixtures

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<th>Field Trial #1 (100% #67)</th>
<th>Citadel Final Mix #1 (Field)</th>
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<th>Citadel Final Mix #2 (Lab) w/ Shrinkage</th>
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<td>Sand to coarse</td>
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<td>W/C</td>
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<td>HRWR fl oz/100 lbs.</td>
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<td>VMA * fl oz/100 lbs.</td>
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<td>Air Content, %</td>
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<td>4.0</td>
<td>4.7</td>
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<tr>
<td>Slump Flow, mm</td>
<td>508 (20 in)</td>
<td>685 (27 in)</td>
<td>635 (25 in)</td>
<td>629 (24.7)</td>
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<td>Visual Stability Index</td>
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<td>Slump Flow T_{90}, seconds</td>
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<td>1.59</td>
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<td>U-Box rising height,</td>
<td>330 (13 in)</td>
<td>360 (14.2)</td>
<td>370 (14.6)</td>
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<td>Bleed %</td>
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<td>Column Segregation, %</td>
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Table 3. Hardened Properties of Field and Laboratory Mixtures

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<td>8.7 (1260)</td>
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<td>7-Day</td>
<td>30.7 (4450)</td>
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<td>29.6 (4290)</td>
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<td>44.7 (6480)</td>
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<td>2.0 (285)</td>
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<td>7-Day</td>
<td>4.3 (625)</td>
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<td>28-Day</td>
<td>5.2 (750)</td>
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<td>28-Day RCP (coulombs)</td>
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<td>4-Days</td>
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<td>-0.012</td>
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<td>28-Days</td>
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<td>-0.043</td>
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Fig. 1 Aggregate Blending Curve - Percent Passing

Fig. 2 Aggregate Blending Curve – Percent Retained
**Fig. 3. Structural Element Characteristics Evaluation for SCC Target Properties**

*The white boxes represent generally acceptable performance ranges that can be used to establish the initial performance targets.

** Rank 1 – most dense reinforcement, rank 2 – medium density, rank 3 – no reinforcement in U-box.
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Fig. 4 Form Finish and Sharp Edges on Archway

Fig. 5 Comparison of SCC and Conventional Concrete Finishes
Fig. 6 View from Quadrangle of Turret, Wall Intricacy, and Form Finish
Static Stability of Self-Consolidating Concrete

by J. A. Daczko

Synopsis:

Self-Consolidating Concrete (SCC) is recognized by those in the industry as a mixture that can flow into place and completely fill formwork with little or no vibration. This concept immediately brings to mind an image of a highly fluid concrete mixture that flows like water. It is the level of fluidity that provides the self-consolidation and ease of placement characteristics that both precast concrete producers and concrete contractors are anticipating when they use SCC. The characteristic of fresh concrete stability, however, is also important although it may sometimes be overlooked. Stability is critical both during the placement operations (dynamic stability) as well as once placement is complete (static stability). Because the stability of the SCC mixture has significant impact on the final hardened properties of the concrete, it should be considered during the mixture development and quality control process. This paper outlines some of the variables that influence SCC static stability and provides insight on how to control them.

Keywords: aggregates; bleeding; gradations; self-consolidating concrete; slump flow; stability; test methods
Joseph A. Daczko is manager of the Concrete Technology group for Master Builders Research and Development Department. He has 12 years experience in the development and application of concrete construction materials. He is Chairman of ACI Committee 237 Self-Consolidating Concrete and is a member of the ASTM committee currently developing standards for self-consolidating concrete.

INTRODUCTION

Self-Consolidating Concrete (SCC) is being used in daily production in many precast facilities across North America. The basic characteristics of acceptable SCC are high fluidity and adequate stability. The proportioning variables influencing fluidity, such as water content and high-range water reducer (HRWR) dosage are well known. However, the proportioning variables that influence SCC mixture stability have not been thoroughly discussed. There are two facets of stability, dynamic and static, that are important to SCC. Dynamic stability is the stability of the mixture during transport and placement and static stability is the resistance of the mixtures to segregation once all placement activities have ceased. This paper illustrates some of the main mixture and proportioning variables that can influence the static stability of SCC.

Static stability is an important characteristic and has been shown to influence the hardened properties of SCC (1,2). Significant effort has been put into developing methods to quantify this characteristic (3,4,5). Of the techniques developed, a column segregation test has been used in various forms by several researchers (3,5,6). This technique is based on measuring coarse aggregate segregation in a small column. This type of test, in combination with the standard ASTM C 232 bleed test can provide a good indication of the static stability performance of a concrete mixture (7). These two tests, in addition to the slump flow test, were used to characterize SCC stability performance in this study.

TEST METHODS

The column segregation test method selected for this study was performed by placing a sample of freshly-mixed concrete into a cylindrical mold measuring 200-mm in diameter and 650-mm in height (Fig.1)(5). The concrete is placed in one lift and allowed to self-consolidated without mechanical agitation or rodding. The mold is separated into four sections (200-mm dia x 165-mm
height) representing different levels of the column. After 15 minutes of sitting, the unhardened concrete from the top and bottom section is removed and wet-washed through a 4.75-mm sieve leaving the coarse aggregate retained on the sieve. The mass of the coarse aggregate from the top and the bottom sections of the column is determined. The column segregation factor is calculated as follows.

\[
\left( \frac{MCA, \text{Bottom} - MCA, \text{Top}}{(MCA, \text{Bottom} + MCA, \text{Top}) \times 0.5} \right) \times 100 = \text{Column Segregation Factor}
\]

where MCA = Mass of Coarse Aggregate

The larger the column segregation factor, the greater the aggregate settlement. As noted earlier, the other test methods used for this evaluation were the standard ASTM C 232 Bleed test and the slump flow test. During the slump flow test, the Visual Stability Index Rating (VSI) is noted as a visual indication of stability. The VSI rating criteria can be found in Table 1.

**EXPERIMENTAL STUDIES**

Four specific variables were investigated for their influence on static stability: fluidity level (as measured by slump flow), aggregate (both fine and coarse) grading and content, cement content and water content. A single polycarboxylate-based HRWR was used throughout the testing and no Viscosity-Modifying Admixtures (VMA) were used. All mixing was performed in a standard laboratory, revolving drum mixer.

**Experiment 1**

The influence of fluidity level on static stability was investigated using two non-air-entrained mixtures. Each mixture used a crushed ASTM #57 limestone coarse aggregate at a constant amount of 975 kg/m³, a set water content of 180 kg/m³ and either 430 or 490 kg/m³ of an ASTM Type I cement. Each mixture was evaluated at four levels of slump flow: 500-550-mm, 575-625-mm, 650-700-mm, 725-775-mm. The different levels of slump flow were achieved by varying the amount of a polycarboxylate-based HRWR. At each level of slump flow, the column segregation and bleed tests were performed. Separate concrete batches were evaluated for each of the slump flow levels.
Results of Experiment 1—As can be seen in Figs. 2 and 3, as slump flow increases, both the column segregation factor and the bleed of the mixtures increase. It is also noted that the two mixture proportions behave differently, indicating that the relationship between slump flow and stability will be dependent upon the individual mixture proportions and raw materials used.

Experiment 2

In this experiment, non-air entrained mixtures were proportioned using three coarse aggregates and two fine aggregates of different origin and gradations. The fineness modulus, specific gravity and gradation information on these aggregates are presented in Table 2. Of the three coarse aggregates used, two were considered ASTM #57 gradation and one was a #8. Twenty-four mixtures were evaluated using an ASTM Type I cement at either 430 or 490 kg/m$^3$, two sand-to-total aggregate ratios (s/a) of 0.46 and 0.55 and a water content of 180 kg/m$^3$. Based on the results from Experiment 1 that indicated a high aggregate settlement at slump flows of 650-mm and higher, all mixtures in this evaluation were evaluated at a 675-700-mm slump flow. The column segregation, VSI and bleed tests were performed.

Results of Experiment 2—The results from experiment 2 are shown in Figs 4 to 6 and Table 3. No significant trend between the variables tested and the column segregation test data could be found in this data set. Only 2 of the 24 mixtures tested had column segregation factors lower than 10%, the remainder ranged from 13-35%. A trend between the column segregation and the bleed test results was not observed. Fig. 4 shows the results of the two tests plotted one versus the other with the two sands distinguished by different symbols. This figure also demonstrates that bleed and coarse aggregate segregation are two different and independent phenomena. Fig. 4 also demonstrates that the type of fine aggregate used has a significant impact on the bleed characteristics of a mixture but not necessarily on the coarse aggregate segregation potential.

Further analysis of the bleed data shows that in conjunction with the sand, the cement content has a significant impact on the bleed of SCC. Fig. 5 shows a plot of the sum of the cement weight and the weight of material passing the 600-μm sieve from the fine aggregate. In essence the relationship between fine material in the mixture and bleed can be established. It was assumed that the water content of the mixture would impact this relationship. However, for the water content tested, the amount of bleed water increased rapidly as the finer material in the mixture fell below 800 kg. This relationship was not significantly influenced by the coarse aggregate.

A comparison of the VSI values with the column segregation and the bleed results was performed and no unique correlation between VSI and column
segregation was determined. However, a relationship between VSI and bleed was seen. Fig. 6 shows VSI as a function of bleed. This figure shows that to have a low VSI (below 2) the bleed of the concrete should be below 6%. However, upon reviewing the data as presented in Table 3, these mixtures may have a column segregation factor greater than 20%. For the mixtures evaluated, when the VSI increases and is greater than 2, all of them had either a bleed percentage greater than 17% or a column segregation value greater than 20%. This indicates that the VSI can be useful in identifying mixtures with poor performance, and therefore useful as a quality control tool.

**Experiment 3**

The final experiment evaluated the influence of water content, cement content, and coarse aggregate gradation and amount on stability. Fig. 7 shows the gradations of the two #57 coarse aggregates. This figure shows that aggregate #57C has a more continuous grading than #57D. Sixteen total mixtures were evaluated, eight for each coarse aggregate. The other variables examined were cement contents of 415 and 475 kg/m³, water contents of 163 and 178 kg/m³ and s/a values of 0.40 and 0.48. All mixtures were run to a slump flow of 625-675-mm using a polycarboxylate HRWR and were non-air-entrained.

**Results of Experiment 3**—For all of the mixtures evaluated, the content of fine material passing the 600-μm sieve was greater than 800 kg/m³ and all of the bleed results were under 2.5%. The most significant variable influencing aggregate segregation was the water content of the mixtures. Fig. 8 shows this influence. As water content increases, segregation also increases presumably due to the general decrease in the paste viscosity, which allows for a more free movement of the aggregate particles. At the low water content, 75% of the results are below 10% segregation, while at the higher water content 75% are above 10% segregation. This figure also demonstrates the interaction between coarse aggregate grading and water content. The more continuous grading (#57C) has a consistently lower segregation than #57D.

**CONCLUSIONS**

Based on the data presented the following conclusions can be made;
1. The fluidity level influences the stability of SCC mixtures. All other things being equal, as the fluidity level increases both the aggregate settlement and bleed will also increase. The relationship between fluidity and stability is unique and will be dependent upon the individual mixture proportions.
(such as water content) as well as the characteristics of the raw materials used.

2. At a given fluidity level, the amount of water has a significant impact on the degree of aggregate settlement in a SCC mixture: Higher water increases aggregate settlement.

3. The content of fine material in the mixture is a significant variable that controls bleed. Both the cement content and the amount of material in the sand that passes the 600-µm sieve should be used to determine this relationship.

4. The VSI rating is a good indicator of concrete bleed, with a rating greater than 2 being caused by either excessive bleed or aggregate settlement. This method is appropriate only for quality control testing.

5. The coarse aggregate grading, sand to aggregate ratio and cement factor influence coarse aggregate settlement, but to a lesser degree than water content.

REFERENCES


7. 2002 Annual Book of ASTM, Standards Volume 4.02

Table 1. Visual Stability Index (VSI)

<table>
<thead>
<tr>
<th>VSI Value</th>
<th>Criteria</th>
</tr>
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<tbody>
<tr>
<td>0 = Highly Stable</td>
<td>No evidence of segregation in slump flow spread</td>
</tr>
<tr>
<td>1 = Stable</td>
<td>No mortar halo or aggregate pile in the slump flow spread</td>
</tr>
<tr>
<td>2 = Unstable</td>
<td>A slight mortar halo (&lt;10-mm) and/or an aggregate pile in the slump flow spread</td>
</tr>
<tr>
<td>3 = Highly Unstable</td>
<td>Clearly segregating by evidence of a large mortar halo (&gt;10-mm) and/or a large aggregate pile in the center of the concrete spread</td>
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Table 2. Aggregate gradations for experiment 2 (percent passing)

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<tr>
<th>Sieve Size</th>
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<th>#57B Coarse Aggregate</th>
<th>#8 Coarse Aggregate</th>
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Table 3. Comparison of VSI to bleed and column segregation values

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Fig. 1. Column segregation Test

Fig. 2. Segregation as a function of slump flow level
Fig. 3. Bleed as a function of slump flow level

Fig. 4. Bleed versus aggregate segregation
Fig. 5. Bleed as a function of the amount of fines in an SCC mixture

Fig. 6. Bleed versus VSI
Fig. 7. Coarse aggregate gradations for Experiment 3

Fig. 8. Segregation as a function of water content and coarse aggregate grading
Delayed Ettringite Formation: Suggestion of a Global Mechanism in Order to Link Previous Hypotheses

by X. Brunetaud, L. Divet, and D. Damidot

Synopsis:

Ettringite observed in macroscopic paste cracks during DEF is often held responsible for concrete deterioration. However, some authors have raised the hypothesis of an homogeneous paste expansion resulting from ettringite crystallisation in the C-S-H porosity, which does not attribute any mechanical effects to the subsequent formation of ettringite crystals in the voids. Thus the role of ettringite is still controversial.

In this paper, we are tempting to link the two previous hypotheses in a more global mechanism:

During heat treatment, thermal decomposition of ettringite can occur, whereas higher amount of sulphate and aluminate are trapped into C-S-H porosity. Then, at ambient temperature, ettringite forms in the porosity corresponding to the network of C-S-H layers. If the volume of ettringite reaches the limit of C-S-H porosity, the following ettringite crystallisation induces an homogeneous expansion of the paste. This expansion can generate peripheral cracks around aggregates. Then, the local shrinkage around voids resulting from the dissolution of the small ettringite crystals incorporated in C-S-H layers and the following precipitation of ettringite massive crystals in the cracks due to Ostwald ripenning, outbreaks radial cracks. When the material is weaken by a multidirectional crack network, the pressure exerted by massive ettringite crystallisation can propagate existing cracks by strain localisation at the crack’s tip, even if the crystallisation pressure is small in these conditions.

Keywords: concrete; cracking; crystallization pressure; delayed ettringite formation; internal sulfate attack; mechanism of expansion
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Dr Loïc Divet is civil engineer, head of concrete pathology, protection and expert evaluation service at the Laboratoire Central des Ponts et Chaussées, Paris, France. He’s main fields of interest include physico-chemistry of concrete and expert evaluation of structure’s deterioration.

Pr Denis Damidot is head of the civil engineering department at Ecole des Mines de Douai, France. He’s main fields of interest are the physico-chemistry and the numerical simulation of the hydration of hydraulic binders and their durability.

**INTRODUCTION**

Delayed Ettringite Formation (DEF) can be defined as the formation of ettringite in a material that contains Portland cement, generally concrete, after setting and without an external sulphate supply but with a water supply. It may result in expansion of the order of one percent leading to severe damage. The first identified cases of delayed ettringite formation by internal sulphate attack [1] involved steam cured precast concrete. However, massive concrete members that have undergone no heat treatment may also suffer from the pathology [2]. In this latter case, the heat generated by hydration of the cement can lead to the development of temperatures close to those applied during steam curing, but here the high temperatures are maintained for much longer.

In relation with its role of monitoring the durability of engineering structures, the Laboratoire Central des Ponts et Chaussées has taken on the task of modelling the consequences of endogenous diseases such as the Alkali-Silica Reaction (ASR) and DEF. This modelling work has already reached a fairly advanced stage in the case of ASR [3], but will only be able to start for DEF when the damage mechanisms involved are understood. Although a considerable amount of research has investigated these mechanisms no consensus has yet been reached [4,5,6]. Our first task will therefore consist of an attempt to identify the sequence of events that leads to damage of the cementitious microstructure as a result of DEF before going on to consider damage at the structural level.

Observations using a Scanning Electron Microscope (SEM) have revealed that concrete affected by the pathology invariably contains massive ettringite crystals which are preferentially located at the paste-aggregate interface and the cracks in the cement paste. Ettringite crystals, in needle form, are usually present in healthy concrete. What characterizes this form of sulphate attack is that ettringite crystals are agglomerated together to form wide bands in cracks [5,6,7].
THE DAMAGE MECHANISMS PROPOSED IN THE LITERATURE

Considered from a theoretical standpoint, the formation of ettringite crystals in a hardened material could lead to expansion as a result of a number of causes: the pressure of crystallization due to the growth of crystals, osmotic pressure due to the growth of colloidal ettringite or, alternatively, the existence of a double electric layer between the surface of the crystals and the pore surfaces.

If we consider the pressure of crystallization hypothesis, which is the most prevalent, there are two main theories about how damage is caused in the material:

- **Hypothesis 1:** The measured macroscopic swelling is due to homogeneous expansion of the paste. During heat treatment, the ettringite becomes extremely soluble and large quantities of sulphates and aluminates are adsorbed on the C-S-H. With the return to ambient temperature the sulphates are progressively released by the C-S-H, leading to the formation of ettringite nanocrystals. The nanocrystals grow within the porosity of the C-S-H in the cement paste generating high pressures of crystallization which push back the nanopore surfaces. This results in homogeneous isotropic expansion of the paste [4,8,9,10]. According to this mechanism the subsequent formation of ettringite bands at the paste-aggregate interfaces and in the cracks has no main effect on the macroscopic expansion [4].

- **Hypothesis 2:** The measured macroscopic swelling is due to the localized crystallization of ettringite in the form of wide bands in the cracks and at the paste-aggregate interfaces. In this case the ettringite precipitates preferentially in the zones with the highest porosity such as the paste-aggregate interfaces, as observed by SEM [5,7]. Growth of these crystals could fill this porosity and then generate sufficiently high pressures of crystallization to fracture the paste and open cracks.

A MORE GLOBAL MECHANISM

As suggested by Diamond [5], these apparently conflicting theories may in fact complement one another. Scherer [11] has shown that homogeneous expansion of the paste can lead to the development of cracks around aggregate particles [12], opening the way for the possible subsequent precipitation of ettringite in the generated voids once these have been filled with water. It is thus probable, initially, that the presence of ettringite at the paste-aggregate interfaces is a consequence of the homogeneous expansion of the paste and not the cause of the measured macroscopic expansion. However, the pressures required to propagate existing cracks are much lower than those required to cause cracking in the matrix. As it is assumed that the microcrystals are able to generate pressures of crystallization in the small pores, the large ettringite bands which totally fill a crack (massive crystals [6]) can also, with much lower pressures, generate stresses at the crack sides in order to propagate them.

The mechanism proposed in this paper consists of 4 stages: the initial period, the latency period, the phase of accelerated deterioration, and the
**final phase.** This sequence of phases is the consequence of various principles such as the origin of homogeneous expansion [4,10] and the mechanical consequences of this expansion and Oswald ripening [11,12].

**Initial period**

The ettringite formed during the first hours of hydration (initial hydration ettringite [6]) dissolves. This breakdown is principally determined by the temperature of the material which is one of the main parameters that causes a modification of thermodynamic equilibrium [13]. A temperature rise increases the solubility of the ettringite, that is to say that the concentrations of sulphate and aluminate ions in solution needs to be much higher in order for ettringite formation to continue. A direct consequence of this change is therefore an increase in the concentrations of sulphate and aluminate ions during heat treatment. Above 70°C, there is almost no ettringite observed at the end of heat treatment [4]. An increase of alkali [6], measured by the pH as calcium concentration is very low, also increases the solubility of ettringite. Thus, the combination of temperature and alkali content influences the concentration of the different ions in solution during the heat treatment and the quantity of the different phases that contain aluminates and sulfates which precipitate (ettringite and AFm phase essentially consisting of hydrated calcium monosulphoaluminate).

The C-S-H, which is the principal hydrated phase, has a high specific surface: approximately 200 m²/g [14]. These hydrates can therefore trap ions such as sulphates and aluminates by adsorption on their layers and release them later when the concentrations in solution are lower [9,15,16]. The aluminates can even enter within the silicate chains at the place of silica bridging tetraedra. For a given C/S ratio in the C-S-H, the quantity of ions adsorbed onto the layers will principally depend on the concentrations (and therefore indirectly the temperature and the alkali content) and the duration of period in question. The initial period stops at the end of the heat treatment, when the decrease of temperature leads to a situation of thermodynamic disequilibrium. The main cause is the reduction in temperature and possible leaching of alkalis. The ettringite, and other phases, are therefore in a supersaturated state with respect to the aqueous phase composition.

**Latency period**

By definition, this phase corresponds to a period of apparent inactivity with regard to the degradation at the macroscopic level. This phase begins when the material returns to ambient temperature. Expansion measurements reveal no unusual swelling. During this phase, it is assumed that the ettringite precipitates in accordance with the hypothesis set out below, which results in a homogeneous expansion of the paste. However, the presence of "inert" inclusions which attach themselves to the swelling paste impedes this expansion. We know from the results of Pavoine [6] that the final expansion during this
phase would not exceed 0.3%, which is not a critical value for a pathology of concrete.

The origin of the homogeneous expansion--The thermodynamic disequilibrium caused by the temperature drop provokes the precipitation of ettringite. The rate of ettringite crystallization will depend on the supply of water and the supersaturation degree of ettringite, which depends on the concentrations in the aqueous phase and the temperature. The local concentrations depend on the rate of desorption of sulphate and aluminate ions from the C-S-H, which itself depends on the adsorption temperature [15,16], on the local transport conditions within the material and on the distances between the sites of nucleation and the sources of ions. The available space should allow the crystal to grow unhindered, otherwise the required concentration for precipitation will be higher and the restricted growth of the crystals will generate a pressure of crystallization. This pressure is given by Riecke’s principle:

\[ P=\ln(S)RT/V_M \]

where \( S \) is the supersaturation index (the ratio between the product of effective concentrations and the concentrations at equilibrium without pressure), \( R \) is the perfect gas constant, \( T \) is the temperature and \( V_M \) is the molar volume of the formed solid.

If the nucleation sites are sufficiently close to the ion sources, local zones of supersaturation can occur, due to the lower diffusion speed of certain ions. When the quantity of water present is small, this local supersaturation is encouraged because transport is limited. Thus, while ettringite is more stable in the large pores where its crystals can grow without generating pressure, local supersaturation permits crystallization within a finer porosity. According to the theory put forward by Taylor, Famy and Scrivener [4], ettringite precipitates rapidly in a very fine porosity [16]. When unconstrained, crystal growth is determined by the minimization of surface energy, which gives the ettringite crystal its characteristic thin needle shape. If the pore imposes its curvature on the crystal, pressure will be exerted at the crystal-pore interface, on condition that the level of supersaturation is sufficient [11]. Thus, the growth of crystals in a very fine porosity will generate pressures of crystallization which depend on the level of supersaturation [8]. Likewise, the morphology of these crystals which are formed “under pressure” will be imposed by that of the pores, and this will differ from their usual needle like morphology. The fact that these crystals are very small and of a none specific shape explains why they may be difficult to detect under scanning electron microscopy, even by MET.

Large crystallization pressures are produced only in nanopores but the resulting pressures are too localized to make the flaws that determine the material’s strength growth [11]. However, if we assume that this process is sufficiently homogeneous, these pressures will lead to homogeneous and, in principle, isotropic expansion of the cement paste [4].
The mechanical consequences of homogeneous expansion of the paste--

As can be seen in Fig. 1, homogeneous expansion of the paste leads to the appearance of voids around those inclusions which do not swell, for example aggregate particles. This change can be considered to be homothetic with the ratio $1+\Delta l/l_0$ in the case of the paste and consists of a simple translation in the case of inclusions. In the case of a spherical aggregate particle with no bonding to the matrix, the space generated will be proportional to the expansion and the particle's diameter [12]:

$$e = r\Delta l/l_0$$

According to Garboczi [12], the case of a non-spherical aggregate particle is not fundamentally different from that of a perfectly spherical inclusion, and we can therefore use this simplified representation to evaluate the mechanical consequences of the homogeneous expansion of the cement paste. An important consequence of this is that irrespective of its morphology, the space generated around an aggregate particle will be proportional to its size.

If there is a total absence of bonding between the aggregate particle and the paste, movements are free and no stress will be generated at the interface. Fortunately bonding, which depends on the mineralogical nature of the aggregate and its surface state, occurs at the interface. Bonding at the paste-aggregate interface limits separation of the paste and the aggregate and produces radial tensile stresses, which are at their maximum at the interface [12]. In the same manner that the space generated without bonding is proportional to the expansion and the size of the aggregate, so are the stresses that are generated when bonding exists [12]. Once the stresses exceed the ultimate tensile strength of the interface, the interface breaks, the sides of the created crack move apart and the stresses are dissipated; case 1 in Fig. 2.

When an interface is partially cracked (real case), the stresses will concentrate at the crack lips in order to equalize the forces around the aggregate particle. The ultimate strength will be reached more rapidly in these areas. The result is propagation of the crack until the stresses reach equilibrium below the ultimate tensile strength. This is a gradual process which does not necessarily lead to total debonding of the interface, and it is shown by case 3 in Fig. 2.

This debonding of the interface occurs even when expansion is very small. On the basis of the equations put forward by Garboczi [12], a longitudinal expansion of $10^{-4}$ (0.01%) can produce cracking at the interfaces. However, this value is not considered to be characteristic of deteriorated concrete.

Ostwald ripening and its mechanical consequences--The homogeneous expansion is able to generate voids around inclusions which do not swell. As already explained, this expansion could be caused by precipitation of ettringite nanocrystals within a very fine porosity, the growth of these crystals generating a pressure of crystallization. However, to generate such pressures, the aqueous phase must be supersaturated with respect to ettringite. In free space, the concentrations required for ettringite crystals to precipitate would be much less than in stressed conditions. Thus, the small crystals are in thermodynamic
disequilibrium with respect to crystals which can grow unhindered. Furthermore, the largest crystals are more stable as they minimize surface energy in comparison with smaller crystals. It is possible to define a dissolution potential that corresponds to the concentration which is required locally for ettringite to be stable. This dissolution potential is therefore higher in the zones where the ettringite is nanocrystalline and assumed to be compressed than in the free spaces that are filled with water. The ettringite requires a higher concentration of ions when its crystals are compressed than when they can grow unhindered.

Figure 3(a) provides a representation of variations in the dissolution potential, in the case where homogeneous expansion has just opened a crack at an interface. In the case of homogeneous expansion, in the final state (when the nanocrystals are no longer growing), the potential tends to achieve an equilibrium as a result of the diffusion of ions from the zones containing the confined nanocrystals into the free zone. Supersaturation in the zone where swelling is taking place diminishes, leading to the gradual dissolution of the microcrystals, while the ettringite crystals which are free to grow precipitate in the empty zone. This migration is represented in Fig. 3 (b).

The equilibrium state is shown in Fig. 3(c) and corresponds to the equalization of potential throughout the material. As long as sufficient ions are available in C-S-H, undissolved nanocrystals will remain in the paste, still under pressure although it will be lower. This has two main consequences: the ettringite which takes up the previously free space will tend to become compressed, in order to conserve the equilibrium of dissolution potential with other crystals that are compressed in the paste; expansion of the paste will be reduced as the partial dissolution of the microcrystals responsible for expansion takes place, the paste-aggregate interface will therefore retreat towards the paste (expansion still occurs, but, compared to the situation of swelling, relative shrinkage occurs).
Application of Ostwald ripening to inclusions--The ettringite dissolution/precipitation process which is due to Ostwald ripening causes the paste-aggregate interface to retreat towards the paste. In addition, if the quantity of ettringite is sufficient, crystal formation completely fills the porosity, and the packed crystals take on a massive appearance. Dissolution/precipitation due to Ostwald ripening is localized around a zone where empty space is available. In the case of inclusions, distant expansion is unaffected and the near zone continues to retreat towards the paste. Figure 4(a) shows the effect of the interface retreat in the case where the matrix does not provide any mechanical resistance. The result in this case is an increase in the external diameter of the void. Here the space between the paste and the aggregate is given by the equation $e' = r*\Delta l/l_0 + \Delta z$ where $\Delta z$ corresponds to the retreat of the paste due to Ostwald ripening. The effect of homogeneous expansion is therefore accentuated.

The mechanism is slightly different when the paste is coherent and has limited mechanical strength, that is to say in the case of a cementitious matrix. Figure 4(b) shows what happens when the interface retreats. The initial perimeter of the interface (on this diagram, the inner green circle) must increase in size to become the final perimeter (on this diagram, the outer green circle). However, as the paste has retreated in this area, it will be more difficult to extend this perimeter. The relative retreat due to Ostwald ripening is localized around the inclusion, the paste which has not undergone this retreat prevents the contracted zone from closing around the inclusion. As it is kinematically impossible to push back the interface the paste will be subjected to all the radial tensile stresses. If these stresses exceed the tensile elastic limit of the concrete, they will tend to relax generating radial cracks as shown in Fig. 4(b).

It is interesting to note that because of the fragile behaviour of concrete under tension, this cracking can occur in a highly local manner, even if, overall, the process is gradual. Thus, SEM observations of cracks that traverse the paste or paste-aggregate interfaces which are not filled with ettringite do not mean that this process is not taking place. The cracks in question may have opened recently and not yet be in equilibrium with the rest of the material.

Phase of accelerated deterioration

This phase follows the latent phase. Expansion measurements taken during it reveal swelling whose rate depends on the nature of the concrete, its heat treatment and its storage. It is during this phase that macroscopic expansion measurements provide grounds for suspecting that an endogenous reaction such as DEF is occurring.

It is important to note that in many cases the reaction goes no further than the latent phase. Just because ettringite crystals can be observed in cracks under scanning electron microscopy does not mean that the reaction will lead to large-scale expansion that will damage the material. However, at a more advanced stage, the crack network in the matrix and the amount and appearance
of the ettringite in the cracks can allow us to estimate the level of damage to the material [17].

One possible reason for the reaction not continuing past the latent stage is a lack of water. Without water, the nanocrystalline ettringite which requires high levels of supersaturation to grow would not be able to dissolve and diffuse within the material. Ion concentrations will therefore remain locally high, which will prevent the C-S-H from continuing to release other ions which were previously adsorbed on the C-S-H layers. The system will therefore remain set in a situation where highly localized pressures of crystallization generate swelling which is too small to affect the mechanical characteristics of the material.

The phase of accelerating deterioration may be explained by a combination of these two processes:

- First, homogeneous expansion leads to cracking of the material which, once the percolation threshold has been exceeded, will considerably increase the supply of water and induce equalization of the potential by ionic diffusion and thus the appearance of Ostwald ripening effects.
- Subsequently, when a sufficient quantity of ettringite is available, the system will tend towards the state shown in Fig. 3(c), i.e. an equilibrium between the confined microcrystals and the massive crystals in the cracks. From this point, if the C-S-H continues to release ions, the entire aqueous phase will be supersaturated with respect to ettringite. The pressure of crystallization exerted by the massive crystals will be applied directly to the entire surface which is in contact with the crack sides, which will permit rapid crack propagation even with low pressures of crystallization.

It is also necessary to consider the fact that as the material weakens, the matrix resists less and less to the various pressures of crystallization. Thus, smaller levels of supersaturation will be sufficient to damage the material. This will allow the C-S-H to continue to gradually release adsorbed ions, because the concentration required for supersaturation will fall.

Two main parameters are therefore involved in determining whether a transition takes place from the latent phase to the accelerated damage phase, namely the microstructure of the cementitious matrix and the quantity of ions adsorbed on the C-S-H. The microstructure determines the distribution and the size of the pores, which must offer sites which are sufficiently small for ettringite nanocrystals to generate high pressures of crystallization. It also determines the stiffness of the matrix, that is to say its ability to resist expansion and thus avoid reaching the water percolation threshold due to critical cracking.

The microstructure of concrete is the result of the hydration of cement. The cement itself, the cement-water ratio, additives such as filler and silica fume and the heat treatment temperature [18] will modify the quantity, nature and texture of the hydrates which are formed. All the above parameters therefore affect the strength of the matrix, the nature of the phases that are available for reactions and the adsorption capacity of the C-S-H.
The quantity of adsorbed ions will influence the maximum expansion. It is also important to note that if the ions are adsorbed at high temperature, the rate of release will be lower than if the same quantity of ions had been adsorbed at a lower temperature, however the quantity of adsorbed ions will be greater [9,16]. The duration of adsorption also affects the quantity of ions that are trapped, which makes it difficult to evaluate in advance the impact of the adsorption temperature on the desorption phase.

**Final phase**

This is the phase when no further change in the macroscopic measurement of expansion occurs. With regard to the mechanism, it is possible that the desorption of ions from the C-S-H reaches an equilibrium state with the levels of supersaturation required for further weakening of the material. The system remains in the same state due to the lack of additional available ions.

**COMPARISON WITH THE DAMAGE MECHANISM FOR EXTERNAL SULPHATE ATTACK**

Santhanam, Cohen and Olek [19,20] have proposed a several stage mechanism to explain damage due to external sulphate attack. This mechanism also involves an initial latency period which leads to cracking of the material because of differential expansion in the attacked zone and the healthy zone. The cracks then become the preferential sites for the formation of more massive crystals. It is at this stage that damage accelerates.

The main differences with respect to DEF lie in the source of the sulphates and the progression of the deterioration. In the case of external sulphate attack, the sulphates are provided by an external solution and the disorder progresses via a number of damage fronts towards the core of the material. In the case of damage due to DEF, the mechanism proposes that the sulphates originate principally from the C-S-H and the damage progresses at a more local level from the C-S-H towards the inclusions or the macroporosity.

Both mechanisms are based on the same process: the first cracks are generated by differential expansion in an attacked zone (the cement paste or the surface that is in contact with the sulphate solution) and the healthy zones (inclusions or as yet unattacked zones). In both cases, the presence of these cracks accelerates the damage process, which otherwise would seem to remain latent. These similarities would tend to show that internal and external sulphate attacks are sensitive to the same parameters, the principal differences arising from the scale of the processes involved and the location of the initial damage.

**CONCLUSION**

Two major schools of thought with regard to explaining the role of ettringite in expansion during DEF are currently proposed. One view is that the homogeneous expansion is due to ettringite nanocrystallization in a very fine porosity of the C-S-H and the other view is that expansion is caused by pressures of crystallization which act on the whole surface of contact between
the massive ettringite crystals and the sides of the cracks or voids. Both of these hypothesis are based on the principle of pressures of crystallization and they both have weaknesses in relation to numerous observations [5]. However, it would seem that these theories may complement each other to produce a more global mechanism which would be better able to answer some questions which have been ignored until now.

This suggestion of a global mechanism, which has many features in common with a recently proposed mechanism for explaining the damage due to external sulphate attack [19,20], appears to present a theoretical advance in a direction already anticipated by certain researchers [5,11]. It would therefore be interesting to examine it in the light of a larger number of observations conducted on concrete with DEF damage with a view to validation.

This mechanism is based solely on the principle of the forces generated by crystallization pressures. Osmotic pressures and the double electric layer have not been considered. It would certainly be beneficial to investigate the contribution of these to the mechanism, in particular with a view to analyzing the role of water in DEF damage.

REFERENCES


Fig. 1: effect of homogeneous expansion of the cement paste

1st case: completely debonded interface. 2nd case: perfect bonding

No bonding therefore no stresses.

If there is bonding, stresses develop at the paste-aggregate interface.

3rd case: real case, partial debonding at interface.

Appearance of localized stresses at crack tips

Crack propagation

Fig. 2: Expansion generates or propagates interfacial cracks
Fig. 3: Retreat of the paste-aggregate interface as a result of Ostwald ripening
3 (a): initial state, 3 (b): intermediate state, 3 (c) equilibrium state

Fig. 4: Application of Ostwald ripening to inclusions
4 (a): case of a paste without stiffness, 4 (b), case of a coherent paste
DEF-Related Expansion of Concrete as a Function of Sulfate Content in the Clinker Phase or Cement and Curing Temperature

by M. Collepardi, J. J. Ogoumah Olagot, D. Salvioni, and D. Sorrentino

Synopsis:
Delayed ettringite formation (DEF) occurs at late ages and the related heterogeneous expansion in a hardened concrete can produce cracking and spalling. There are two different types of DEF depending on the sulphate source: DEF caused by external sulphate attack (ESA) or internal sulphate attack (ISA). In the present paper only ISA-related DEF is studied with reference to the following three parameters: a) the sulfate content in the clinker phase of the cement; b) the curing temperature; c) the presence of preliminary cracks in concrete specimens.

Concretes manufactured at room temperature (20°C) do not show any form of DEF-related expansion independently of the SO₃ content of the clinker (1–2%) or the portland cement (2–4%). On the other hand, concretes steam-cured at 90°C and then kept under water show significant expansion related to DEF provided that the SO₃ content of the portland cement is relatively high (> 4%). The higher SO₃ content in the clinker phases (> 2%) or the presence of preexisting cracks accelerates the DEF-related expansion. Deposition of ettringite fiber crystals occurs in the preexisting cracks or within the new microcracks. Curing at temperatures lower than 80°C, preferably lower than 70°C, is strongly recommended to avoid DEF-related risk. Blended cements with a lower SO₃ content should be used in case this limit in curing temperature cannot be safely ensured.

Keywords: delayed ettringite formation; expansion; external sulfate attack; internal sulfate attack; sulfate attack
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INTRODUCTION

Ettringite formation is associated with expansion and many hypotheses of ettringite related expansion have been advanced [1-4]. However, not necessarily any ettringite-related expansion produces damaging disruption of concrete structures.

Early Ettringite Formation: When ettringite (C₃A · 3C₅S · H₃₂) occurs homogeneously and immediately (within hours), it does not cause any significant localized disruptive action (early ettringite formation, EEF). This type of harmless ettringite formation happens, for instance, when gypsum (CaSO₄·2H₂O) reacts with anhydrous calcium aluminate (C₃A) in a through-solution reaction and acts as a set retarder in Portland cement mixtures:

\[ \text{C₃A} + 3(\text{CaSO₄·2H₂O}) + 26 \text{H₂O} \rightarrow \text{C₃A·3C₅S·H₃₂} \]  

(1)

The retardation has been attributed to the early formation of an ettringite layer which acts as a coating over the surfaces of the cement grains soon after mixing [3]. This type of ettringite may also be called "primary" ettringite as opposite to "secondary" ettringite which will be defined later [1]. The formation of "primary" ettringite occurs in the plastic stage of the cement mixture and does not produce any significant harmful stress. Another example of harmless and useful EEF occurs when, under proper restraint, a calcium aluminate sulphate (C₄A₃S) hydrates within few days producing ettringite uniformly distributed and then homogeneous expansion throughout the hardened concrete (expansive cements):

\[ \text{C₄A₃S} + 6\text{Ca(OH)₂} + 8(\text{CaSO₄·2H₂O}) + 74 \text{H₂O} \rightarrow 3(\text{C₃A·3C₅S·H₃₂}) \]  

(2)

In such a case, the restrained expansion is advantageously transformed into a rather useful compressive stress (0.2 - 0.7 MPa) in shrinkage-compensated
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Concrete, or in a larger stress of 3 to 8 MPa in self-stressed reinforced concrete provided that a certain strength level and a corresponding modulus of elasticity are reached within few days.

Delayed Ettringite Formation: When ettringite forms later (after several months or years) - DEF - the related heterogeneous expansion in a very rigid hardened concrete can produce cracking and spalling. The disruptive effect is due to the non-uniform expansion localized only in the area of the concrete structure where ettringite forms. Therefore DEF, and not EEF, is associated with a damaging sulphate attack. There are two different types of DEF-related damage depending on the sulphate source, as shown in Table 1: external or internal sulphate attack. External sulphate attack (ESA) occurs when environmental sulphate (from water or soil) penetrates concrete structures. Internal sulphate attack (ISA) occurs in a sulphate-free environment when the sulphate source is inside the concrete and comes from either cement with high sulphate content or gypsum-contaminated aggregate.

According to the terminology currently used, "DEF" or "secondary ettringite" [5, 6] is related only to the ISA, particularly in heat-cured concrete structures where "primary" ettringite, responsible for setting regulation, is thermally decomposed and then forms again in an atmosphere that is saturated intermittently or continuously. However, correctly speaking the term delayed ettringite formation only means that ettringite forms later and therefore it should include both ESA and ISA as shown in Table 1. The following terms are used in the present paper: "ESA" or "ISA" to indicate DEF related to external or internal sulphate attack, respectively.

PURPOSE OF THE WORK

According to some previous studies of field concretes [7-10] delayed ettringite formation (DEF) could cause damage even in structures not experienced at high temperature. This was ascribed to the presence of excessive SO₃ in the clinker phases from which it would be only slowly released. From these field inquiries the exposure to moisture appeared to be very important in accelerating the DEF-related damage. Moreover, the DEF appeared to be accelerated by the presence of pre-existing cracks caused by the manufacturing process.

On the other hand, many other papers [11-17] indicated that both overheating of concrete (at temperatures higher than 70°C) and high SO₃ content in cement are needed to promote DEF-related expansion [6, 10-17].

The purpose of this work was to study the role played by the following parameters on the DEF-related concrete deterioration caused by ISA:

- sulfate content in the clinker phase and cement;
- curing temperature (20°C vs 80°C);
- pre-existing cracks.
EXPERIMENTAL

In the following paragraphs the raw materials and the proportions of concrete mixtures, as well as the curing process and length change measurement, will be examined.

Clinker and cements: Two clinkers were used with approximately the same mineralogical composition in terms of XRD patterns (Fig. 1). The main difference being the sulphate content: 1.05% in clinker 1 and 2.15% in clinker 2 (Table 2), both percentages in terms of SO₃.

Four different Portland cements (Table 3) were manufactured by grinding clinker 1 and 2 and different amounts of gypsum in order to obtain regular setting times (Table 4). Cement code C12 means that there is about 1% SO₃ in the clinker phase and about 2% as total SO₃ (really this is 2.70% as shown in Table 3).

On the basis of preliminary tests of steam-curing, it was found that for the cements shown in Table 3, the critical temperature causing the thermal decomposition of ettringite and its transformation into monosulphate (C₃A · 3C₅S · H₁₂) was 80°C [11]. Figure 2 shows the XRD patterns of the four anhydrous cements and of the corresponding hydrated products at 1 day with a curing at room temperature (20°C) or a steam-curing at a maximum temperature of 80°C.

Curing of concrete specimens and expansion measurements: On the basis of the above results on cement pastes, concrete mixtures were cured at room temperature (20°C) or steam-cured at T_max of 80°C, so that ettringite was respectively stable or transformed into monosulphate (C₃A · 3C₅S · H₁₂), at the end of the curing process (Fig. 2). For each concrete mixture (Table 5) two different types of specimens (80 x 80 x 280 mm) were prepared: sound specimens and cracked specimens obtained by localized compressive stress on the specimens under steel cutters. Table 6 shows the identification of the concrete specimens. For instance, C14S indicates sound (S) concrete manufactured with the cement C14, that is containing about 1% of SO₃ in the clinker phase and 4% in the cement. On the other hand, C14C indicates the same concrete in form of cracked (C) specimens. Both sound and cracked specimens with crack-opening width in the range of 0.2-1 mm, were cured at 20°C with R.H. of 95% for three weeks. Then they were permanently submerged under water and the length change was measured (over the length at the immersion time), as a function of the time under water at 20°C, for about 2 years.

Steam-cured concrete specimens (preliminary curing at 20°C for 3 hr; heating from 20°C to 80°C in 7 hr; curing regime at 80°C for 4 hr; cooling from 80°C to 20°C in 6 hr), were submerged in water; curing at 20°C with
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R.H. of 95% for two weeks. Then the length change, as a function of time under water at 20°C, was measured for about 2 years.

Other steam curing process at 90°C or high-pressure steam curing at 170°C were also adopted.

RESULTS AND DISCUSSION

Figures 3-8 show the length change results of the concrete specimens kept under water at 20°C. Similar results were also obtained in concrete specimens cured at 90°C or autoclaved at high-pressure steam curing at 170°C, and then only the results obtained on the 80°C-cured specimens will be discussed in the present paper.

There is no significant expansion in concrete specimens cured at 20°C (Fig. 3) independently of the pre-existing cracks or the SO₃ content in portland cement (2.60-4.20%) and in the clinker phase (1.02-2.15%); the expansion of about 200-300 \( \times 10^{-6} \) after some months of permanent immersion under water is normal and can be related to the swelling effect of the cement paste under water [18].

On the other hand, when concretes are steam-cured at temperature as high as 80°C (Fig. 4) there is a significant expansion (≈ 1500 \( \times 10^{-6} \) in less than 1 year) for the sound specimens C24S immersed under water.

The expansion is higher and quick in the concrete specimens with pre-existing cracks, C24C and C24C than in the corresponding crack-free specimens. C24S and C14S, (Fig. 5 and 6).

No significant length change was recorded for both sound and cracked steam-cured specimens when a relatively low sulfate content (< 2.70%) was adopted in the cement (Fig. 7 and 8).

Moreover, the expansion is accelerated by the higher sulphate content in the clinker phase (C24C > C14C; C24S > C14S). All these results could be related to the disappearance of ettringite caused by the steam-curing process at relatively high temperatures (≥ 80°C) as shown by the cement paste experiments (Fig. 2) and on its subsequent reformation at later ages (DEF) when kept under water.

In order to confirm this hypothesis concrete specimens were observed by optical microscope in order to assess the width change of the pre-existing cracks (Fig. 9) or the appearance of new microcracks on the surface of the originally sound specimens. The white material filling the pre-existing cracks (Fig. 10) or depositing within microcracks of the originally sound specimens (Fig. 11) was analyzed by X-Ray Diffraction (XRD) analysis. The XRD patterns (Fig. 12) indicate that ettringite (E), beside calcium hydroxide (CH), are the main products filling the pre-existing cracks or within the new microcracks of the originally sound specimens.

The SEM/EDS results of the material filling the pre-existing cracks or the new microcracks are shown in Fig. 13. The main difference in the morphology is in the better growth of the ettringite fibers filling the pre-
existing cracks of the $C24C$ specimen, with respect to the stubby ettringite crystals mixed with some C-S-H filling the new microcracks formed in the originally sound specimen ($C24S$).

CONCLUSIONS

1. Expansion related to DEF occurred only in some concrete specimens steam-cured at $80^\circ$C or at higher temperatures due to the thermal decomposition of the ettringite formed during the early stage of the portland cement hydration.

2. DEF-related expansion of concrete specimens steam-cured at $80^\circ$C occurred only when portland cements with about 4% of SO$_3$ were used independently of the SO$_3$ content (1 or 2%) in the clinker phases. These results agree with those obtained by Zhang et al. [16, 17]. However, the DEF-related expansion of steam-cured concrete specimens, at the same total SO$_3$ content of 4% in the cements, was quicker and higher when clinkers richer in the SO$_3$ content (2% vs 1%) were used. No DEF-related expansion occurred when cement with a total content of about 2% SO$_3$ was used independently of the curing temperature and SO$_3$ content in the clinker phases.

3. DEF-related expansion of concrete specimens manufactured with about 4% SO$_3$ content in Portland cement and steam-cured at $80^\circ$C is quicker in the presence of pre-existing cracks. However, it can occurs even in sound specimens although at much lower rate.

4. SEM and EDS studies combined with XRD analysis indicated the formation of well crystallized ettringite fibers (20 μm long and 0.5 μm thick) deposited into the pre-existing cracks or the new micro-cracks formed during the exposure to moist environment.

5. These results seem to agree with the expansion mechanism suggested by H.F.W. Taylor, C. Famy and K. Scrivener [14, 15] based on the growth of sub-micrometre ettringite crystals from monosulfate incorporated in the C-S-H gel.

6. These laboratory experiences under controlled conditions did not confirm studies of field concretes and the corresponding conclusions [8] that DEF could also occur in structures not experienced at high temperature.

7. From a practical point of view, with a curing at temperature lower than $80^\circ$C (preferably lower than $70^\circ$C) there is no thermal decomposition of ettringite and then no risk of DEF-related damage in concrete structures independently of the SO$_3$ content in the clinker phases (up to 2.7%) or portland cement (up to 4.2%). However if, for some reasons, a curing temperature higher than $80^\circ$C, preferably $70^\circ$C, cannot be excluded, then it would be better to limit the amount of SO$_3$ in the cement at percentage
lower than 4% by using, for instance, blended cements, as suggested by Lawrence [5].

REFERENCES


Table 1 - Delayed ettringite formation by external and internal sulphate attack.

FORMATION DELAYED ETTRINGITE

EXTERNAL SULPHATE ATTACK
- It occurs when environmental sulphate (from water or soil) penetrates concrete structures in service.
- It occurs in a permeable concrete.
- It occurs in a moist environment favouring diffusion of SO₄ through the aqueous phase of the capillary pores.

INTERNAL SULPHATE ATTACK
- It occurs in a sulphate-free environment for the late sulphate release from gypsum-contaminated aggregates or thermal decomposition of ettringite.
- It is favored by preliminary microcracks where deposition of ettringite crystals can occur.
- It occurs in a moist environment favoring diffusion of SO₄⁻ and other reacting ions (Ca⁺⁺ and aluminate through water-saturated capillary pores.

Table 2 - Chemical Analysis of Clinkers

<table>
<thead>
<tr>
<th>Component</th>
<th>Clinker 1</th>
<th>Clinker 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>21.42</td>
<td>21.37</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>6.18</td>
<td>5.81</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.36</td>
<td>2.07</td>
</tr>
<tr>
<td>CaO</td>
<td>65.07</td>
<td>64.99</td>
</tr>
<tr>
<td>MgO</td>
<td>1.04</td>
<td>1.43</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.15</td>
<td>1.20</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.10</td>
<td>0.09</td>
</tr>
<tr>
<td>SO₃</td>
<td>1.02</td>
<td>2.15</td>
</tr>
</tbody>
</table>
Table 3 – The SO₃ content in the clinker and the total SO₃ in the cement after gypsum addition.

<table>
<thead>
<tr>
<th>Cement Code</th>
<th>SO₃ (%) in the clinker phase</th>
<th>SO₃ (%) as gypsum addition</th>
<th>Total SO₃ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C12</td>
<td>1.02</td>
<td>1.68</td>
<td>2.70</td>
</tr>
<tr>
<td>C22</td>
<td>2.15</td>
<td>0.45</td>
<td>2.60</td>
</tr>
<tr>
<td>C14</td>
<td>1.02</td>
<td>2.98</td>
<td>4.00</td>
</tr>
<tr>
<td>C24</td>
<td>2.15</td>
<td>2.05</td>
<td>4.20</td>
</tr>
</tbody>
</table>

Table 4 – Setting time for the four Portland cements.

<table>
<thead>
<tr>
<th>Cement Code</th>
<th>Setting times (hr:min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>initial</td>
</tr>
<tr>
<td>C12</td>
<td>1:40</td>
</tr>
<tr>
<td>C22</td>
<td>1:55</td>
</tr>
<tr>
<td>C14</td>
<td>1:48</td>
</tr>
<tr>
<td>C24</td>
<td>2:05</td>
</tr>
</tbody>
</table>

Table 5 – Composition of concrete mixtures at a w/c=0.50 and slump of 250 mm.

<table>
<thead>
<tr>
<th>Cement Code</th>
<th>Composition (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cement</td>
</tr>
<tr>
<td>C12</td>
<td>450</td>
</tr>
<tr>
<td>C22</td>
<td>452</td>
</tr>
<tr>
<td>C14</td>
<td>448</td>
</tr>
<tr>
<td>C24</td>
<td>450</td>
</tr>
</tbody>
</table>

Table 6 – Identification of concrete specimens.

<table>
<thead>
<tr>
<th>Code Symbol</th>
<th>Approximate SO₃ (%) in: clinker</th>
<th>Type of concrete specimen</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cement</td>
<td>Sand 0-4 mm</td>
</tr>
<tr>
<td>C12S</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>C22S</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>C14S</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>C24S</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>C12C</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>C22C</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>C14C</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>C24C</td>
<td>2</td>
<td>4</td>
</tr>
</tbody>
</table>
Fig. 1 – XRD patterns of the two clinker with the SO₃ content of about 1% and 2%.

![XRD patterns of two clinker](image1)

Fig. 2 – XRD patterns of anhydrous or hydrated cements at 24 hrs cured at 20°C or steam-cured at 80°C: G=gypsum; CH=Calcium hydroxide; E=Ettringite; M=Monosulfate.

![XRD patterns of anhydrous and hydrated cements](image2)
Fig. 3 – Change length of concrete specimens cured at 20°C and then permanently submerged under water.

Fig. 4 - Change length of sound concrete specimens cured at 80°C and then permanently submerged under water.
Steam-curing at 80°C - Exposure under water

Fig. 5 - Change length of cracked and sound specimens cured at 80°C and then permanently submerged under water: concrete with \( \approx 2\% \) SO\(_3\) in the clinker phase and \( \approx 4\% \) SO\(_3\) in cement.

Steam-curing at 80°C - Exposure under water

Fig. 6 - Change length of cracked and sound specimens cured at 80°C and then permanently submerged under water: concrete with \( \approx 1\% \) SO\(_3\) in the clinker phase and \( \approx 4\% \) SO\(_3\) in cement.
Fig. 7 - Change length of cracked and sound specimens cured at 80°C and permanently submerged under water: concrete with $\approx 2\%$ SO$_3$ in the clinker phase and $\approx 2\%$ SO$_3$ in cement.

Fig. 8 - Change length of cracked and sound specimens cured at 80°C and permanently submerged under water: concrete with $\approx 1\%$ SO$_3$ in the clinker phase and $\approx 2\%$ SO$_3$ in cement.
Fig. 9 – Observation of the width-crack by optical microscope.

Fig. 10 – White material filling the pre-existing cracks.

Fig. 11 – White material filling the microcracks of the originally sound concrete specimens.
Fig. 12 – Typical XRD pattern of the white material filling the pre-existing cracks of the C14C concrete specimens.

Fig. 13 – SEM/SED of ettringite deposited into the pre-existing cracks (above) and within the new microcracks (below).
Lignosulphonate as Plasticizing Admixture on Cements of Different Chemical Composition

by B. G. Petersen, K. Reknes, and K. Olavesen

Synopsis:

Lignosulphonate is a widely used plasticizing admixture in concrete. It is well documented that different qualities of this material give different performance in concrete. Depending on what kind of concrete that is needed, workability can be controlled by adding different amounts or qualities of the lignosulphonate. This investigation compares the adsorption of lignosulphonate on three different portland cements, to the rheological properties of cement pastes made from the same cements.

The adsorption isotherms were calculated from depletion experiments. A rheometer with bob-cup geometry was used to measure the rheological properties of the cement pastes. The plasticizing effect of lignosulphonates in cement paste slurries was confirmed.

Recent advances have given a novel lignosulphonate with superplasticizer performance. This investigation demonstrates these improved properties achieved by this novel lignosulphonate by determining the differences in adsorption of the different lignosulphonates, on cements with different chemical characteristics.

Keywords: adsorption; concrete matrix; lignosulphonate; rheology; superplasticizer
INTRODUCTION

Lignosulphonate is a widely used plasticizing admixture in concrete. It is well documented that different qualities of this material give different performance in concrete. Depending on what kind of concrete that is needed, workability can be controlled by adding different amounts or qualities of the lignosulphonate. This investigation compares the adsorption of lignosulphonate on three different portland cements, to the rheological properties of cement pastes made from the same cements. Three cements were chosen to see how the performance of the admixtures are affected by the composition of the cements. The cements are all CEM I 42.5R. Cement H has a high aluminate content, cement C has high alkali content, while cement D is considered to be an average European cement.
The rheological properties of the matrix phase of a set of concretes are described. These concretes are reported by Reknes et al. [1]. The particle-matrix model was used as a tool for selecting the concrete mix proportions. The use of the particle-matrix model is described by Reknes [2]. The model explains the properties of concrete on the basis that the concrete consists of a matrix and a particle phase. The model is described in detail by Mørtsell [3].

This work was conducted as part of the project "Design and Function of Novel Polymeric Admixtures for More Durable High Performance Concrete, SUPERPLAST" that was funded by the 5th European Framework Program. The novel lignosulphonate superplasticizer (LS5) was developed during this project, and cements C, D and H were used by all the partners throughout this project.

Cement chemistry

The chemistry of cement and cementitious materials is described in detail by Taylor [4]. In short, cement consists of four main mineral phases and several minor minerals. Normal portland cement typically consists of 55-65% tricalcium silicate (C₃S), 15-25% dicalcium silicate (C₂S), 1-15% tricalcium aluminate (C₃A), 5-15% tetracalcium aluminoferrite (C₄AF) and small amounts of magnesium oxide, calcium oxide, alkali sulphates and gypsum.

Lignin chemistry

Lignosulphonate is a product made from sulphite pulping of wood. Lignin chemistry and properties of lignosulphonates has been described by Fredheim [5]. The molecules are non-uniform aromatic polyelectrolytes with varying molecular weight distribution.
Rheology

Rheology is the science of deformation and flow. All kinds of shear behaviour can be described as being in between two extremes: the flow of an ideal liquid and the deformation of an ideal solid. Concrete and cement paste will flow after a certain amount of deformation, and so they are normally considered to be viscoelastic materials [6].

Rheology can be an important tool in construction. Measurements of rheological properties like viscosity and shear stress can be used to control the quality of concrete, compare different mixes and understand interactions between ingredients in a concrete mix.

Struble [7] gives a review of the rheology of fresh cement paste and other dense particulate suspensions. The rheology of the matrix phase of concrete with lignosulphonate plasticizer is reported by Petersen and Reknes [8] and its corresponding concrete by Reknes and Petersen [9].

Adsorption

A review of cement-superplasticizer interactions are given by Mollah et al. [10], Ramachandran [11] and Young [12]. Adsorption of lignosulphonate on cement is discussed by Gustafsson and Reknes [13]. Flatt and Houst propose three categories to describe the interaction of superplasticizers with cement suspensions, and they stress that differentiating consumption from adsorption is essential for correct interpretation of experimentally obtained data [14]. Zhang et al. [15] and Gustafsson and Reknes [13] described the method of obtaining adsorption isotherms by measuring the adsorbance of the residue of polymer in the filtrate from a cement paste. This investigation also showed
that cement preferentially adsorbs the high molecular weight fraction of lignosulphonate. The same method was used by Myrvold et al. [16] when the cement adsorption isotherms was obtained for a high molecular weight lignosulphonate. This investigation also showed that lignosulphonate adsorbed differently on the different phases of the cement. This can help explain the differences in adsorption observed on cements with different chemical composition.

**EXPERIMENTAL**

**Admixtures and cements**

The plasticizing admixtures used in this investigation were two different sodium based lignosulphonate samples; Ultrazine NA, an ASTM class G plasticizer, and “LS5”, a new high quality lignosulphonate with superplasticizing properties made in a trial basis at Borregaard LignoTech R&D. The admixtures were added to the cement paste at 0.20, 0.40 or 0.60 % sbwc (solid by weight of cement).

The mix proportions, dosages, cements and plasticizing admixtures are corresponding to the concretes reported by Reknes et al. [1].

The cement paste was made at w/c = 0.41 or 0.47, using three different Portland cements CEM I 42.5R. the chemical compositions are given in Table 1. Norwegian limestone (d\text{max}= 0.200 \text{ mm}, d_{90}= 0.095 \text{ mm}) was added to simulate the fines in the concrete, i.e. filler and fines from the aggregates. The amount of fines was calculated from the sieving analysis of the aggregates used in the concrete. The ratio between fines and cement was 0.147 for w/c = 0.41 and 0.169 for w/c = 0.47.
Procedure

Rheological measurements
The cement paste was mixed in a Waring high-speed blender. The rheological measurements were carried out using Paar-Physica Controlled-stress Rheometer with bob-cup geometry. The bob has 1 mm deep slots, because smooth-walled concentric cylinders can suffer from wall slip according to Saak et al. [17] and Petersen og Reknes [18]. The measurements started 10 and 30 minutes after water addition. The measuring procedure was as follows:
1. Rotation at shear rate 100 1/s for 10 seconds.
2. Measuring at 10 ramps à 5 seconds, stepwise descending shear rate from 1000 to 0.1 1/s.

Adsorption measurements

Lignosulphonate solutions of different concentrations were made and the cement was added at w/c = 10. The paste was left shaking for 30 minutes before it was filtrated and the filtrate was collected. The filtrate was diluted with a weak NaOH solution to keep the absorbance below 1.0. The absorbance of the diluted filtrate was measured using UV spectroscopy at 280 – 283 nm. The extinction coefficient was calculated from measuring solutions of known concentration. The results were used to calculate the adsorption isotherms of LS5 for the three cements.

RESULTS AND DISCUSSION

Fig. 1 and 2 show how increasing dosage of lignosulphonate decreases both the viscosity and shear stress for normal portland cement. LS5 lowers these
properties more than Ultrazine Na (Ultr) at equal dosages does. As expected, the higher water to cement ratio gives lower viscosity and lower shear stress.

The workability does not change significantly in 30 minutes for w/c = 0.41 for all three cements. Figs 3 and 4 show that cements D and C behave almost the same, while cement H has a different behaviour. The adsorption isotherms in Fig. 5 shows that LS5 adsorbs more strongly to cement H than to C and D. This trend is expected to be the same for Ultrazine NA. The difference can be explained by the difference in phase composition. Cement H has a high aluminate content, while C have the highest alkali content. Cement D is considered an average European cement. This is in agreement with Myrvold et al. [16] who found that lignosulphonate adsorbs strongly to the aluminate phases, and that di-and trivalent metal ions had to be present if the lignosulphonate was to adsorb to the silicate phases. At low water to cement ratio, cement H is less workable because the lignosulphonate is consumed by the strong adsorption. At higher water content, less lignosulphonate is needed to give better workability. Since relatively more lignosulphonate is adsorbed, the effect is bigger and thus the viscosity decreases.

At high w/c and high dosage LS5, the pastes have a significantly different behaviour that is much less shear-thinning. The shear stress and viscosity are decades lower than at w/c = 0.41. Cement H also shows a remarkable different behaviour from C and D. The cement paste has become much less shear-thinning, and needs less force to exert almost Newtonian behaviour. Cement C and D show viscosity and shear stress within the same range at 10 and 30 minutes after mixing, while cement H has an increasingly decreasing viscosity and shear stress.

The adsorption isotherms are calculated from measurements in a slurry with w/c=10, while the cement paste slurries used for rheological measurements have w/c = 0.41 and 0.47. Since the mixing of these slurries are different, the plateau values for adsorbed amount of lignosulphonate will be different. However, it is safe to assume that the realive differences are similar, thus
making these isotherms a good base for discussing the amount adsorbed versus the rheological performance.

At the time this paper was written, the adsorption measurements of Ultrazine NA on these cements were on-going. Therefore no isotherms are reported for this lignosulphonate.

CONCLUSIONS

A novel lignosulphonate has been developed, and it shows very good plasticizing properties. Increasing dosage of lignosulphonate decreases both the viscosity and shear stress for normal portland cement. LS5 lowers these properties more than Ultrazine Na at equal dosages does. The viscosity and shear stress for the cement pastes with lignosulphonate does not change between 10 and 30 minutes after mixing. Cements C and D behave almost the same, while cement H has a different behaviour. This difference is also visible from comparing adsorption isotherms. LS5 adsorbs more strongly to cement H than to C and D. This difference can be explained by the difference in phase composition.

REFERENCES


Acknowledgement

This work was conducted as part of the project “Design and Function of Novel Polymeric Admixtures for More Durable High Performance Concrete, SUPERPLAST” that was funded by the 5th European Framework Program.
### TABLES AND FIGURES

Table 1: Chemical composition of the cements.

<table>
<thead>
<tr>
<th>Chemical analysis</th>
<th>H</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂ %</td>
<td>20.5</td>
<td>20.7</td>
<td>20.1</td>
</tr>
<tr>
<td>Al₂O₃ %</td>
<td>5.8</td>
<td>4.9</td>
<td>5.2</td>
</tr>
<tr>
<td>Fe₂O₃ %</td>
<td>2.1</td>
<td>3.0</td>
<td>3.4</td>
</tr>
<tr>
<td>CaO %</td>
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<td>63.8</td>
</tr>
<tr>
<td>MgO %</td>
<td>0.9</td>
<td>1.7</td>
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</tr>
<tr>
<td>SO₃ (total) %</td>
<td>3.0</td>
<td>2.9</td>
<td>3.1</td>
</tr>
<tr>
<td>Clinker SO₃ %</td>
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<td>1.9</td>
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<td>1.6</td>
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<td>C₄AF (Bogue) %</td>
<td>6.5</td>
<td>9.0</td>
<td>10.5</td>
</tr>
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</table>
Fig. 1: Apparent viscosity of cement C with increasing dosages of lignosulphonate at a) w/c = 0.41 and b) w/c = 0.47
Fig. 2: Shear stress of cement C with increasing dosage of lignosulphonate at a) w/c = 0.41 and b) w/c = 0.47.
Fig. 3: Workability life. w/c = 0.41 with 0.60%sbwc LS5.
Fig. 4: Workability life, w/c = 0.47, 0.60 %sbwc LS5.
Fig. 5: Adsorption isotherms of LS5 on three different cements.
Properties of Geopolymer Concrete with Fly Ash as Source Material: Effect of Mixture Composition

by D. Hardjito, S. E. Wallah, D. M. J. Sumajouw, and B. V. Rangan

Synopsis:

This paper presents the effect of mixture composition on the compressive strength of fly ash-based geopolymer concrete. Test results show that water-to-sodium oxide (H₂O-to-Na₂O) molar ratio and the water-to-geopolymer solids ratio by mass influence the compressive strength of fly ash-based geopolymer concrete. The compressive strength decreases when these ratios increase. However, the sodium oxide-to-silicon oxide (Na₂O-to-SiO₂) molar ratio of the geopolymer mixture does not have any significant effect on the compressive strength within the range of 0.095 and of 0.120 of this ratio.

Keywords: compressive strength; fly ash; geopolymer concrete; mixture composition
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Steenie E. Wallah and Dody M.J. Sumajouw are lecturers at Sam Ratulangi University, Manado, Indonesia, and currently PhD students at Curtin University of Technology, Perth, Australia.

ACI Fellow B. Vijaya Rangan is Professor and Dean of Faculty of Engineering and Computing, Curtin University of Technology, Perth, Australia. He was a recipient of numerous awards, including ACI’s Raymond C. Reese Structural Research Award.

INTRODUCTION

Geopolymer is an inorganic alumino-silicate polymer synthesized from predominantly silicon and aluminium materials of geological origin or by-product materials such as fly ash. The term geopolymer was introduced by Davidovits to represent the mineral polymers resulting from geochemistry. The polymerisation process involves a chemical reaction under highly alkaline conditions on Al-Si minerals, yielding polymeric Si-O-Al-O bonds, as described by [1]:

\[ M_n (\text{Si-O}_2 \text{Al-O})_z \cdot wH_2O \]  

where M is the alkaline element, the symbol \(-\) indicates the presence of a bond, z is 1, 2, or 3, and n is the degree of polymerisation. The chemical composition of geopolymer materials is similar to zeolite, but they reveal an amorphous microstructure [1]. The polymerisation process may be assisted by applied heat, followed by drying. The chemical reaction period is fast and the required curing period may be within 24 to 48 hours.

Geopolymer-based materials are environmentally friendly, and need only moderate energy to produce. They can be made using industrial by-products, such as fly ash, as the source material. In geopolymer concrete, the geopolymer paste serves to bind the coarse and fine aggregates, and any un-reacted material. Geopolymer concrete can be utilised to manufacture precast concrete structural and non-structural elements, to make concrete pavements, to immobilize toxic wastes, and to produce concrete products that are resistant to heat and aggressive environments.
Davidovits proposed that the ranges of the oxide molar ratios suitable to produce geopolymeric materials may be as follows: 0.2<Na₂O/SiO₂<0.28, 3.5<SiO₂/Al₂O₃<4.5, and 15<H₂O/Na₂O<17.5, where Na₂O, SiO₂, Al₂O₃ are respectively the sodium, silicon and aluminium oxides, and H₂O is the water [2]. Based on tests performed on geopolymer pastes using calcined kaolin as the source material, Barbosa et al [3] found that the optimum composition occurred when the ratio of Na₂O/SiO₂ was 0.25 and the ratio of H₂O/Na₂O was 10.0. This paper presents the results of experimental work on the effect of the molar ratio of H₂O/Na₂O and Na₂O/SiO₂ of the mixture composition on the compressive strength of fly ash-based geopolymer concrete.

PREVIOUS RESEARCH

In our previous papers, we have reported that curing time, curing temperature, and sodium silicate-to-sodium hydroxide (liquid) by mass ratio significantly influenced the compressive strength of fly ash-based geopolymer concrete [4]. We also observed that for specimens cured at 60°C for 24 hours, the compressive strength did not depend on age, unlike Portland cement based concrete [5]. With regard to resistance to chemical attack, we found that specimens soaked in 5% sodium sulfate solution for three months did not show any significant change in properties [6]. Other researchers have reported that geopolymeric materials did not suffer from alkali-aggregate reaction even in presence of high alkalinity [1], and possessed excellent fire resistance [7].

EXPERIMENTAL PROGRAM

Materials

Locally available low calcium (ASTM class F) fly ash, with a specific surface area of 1.29 m²/mm³, was used as the source material. The chemical composition of the fly ash as determined by XRF test is given in Table 1. Analytical grade sodium hydroxide in flake form (98% purity), and sodium silicate solutions (Na₂O=14.7%, SiO₂=29.4% by mass) were used as the alkaline activators. Distilled water was used to dissolve the sodium hydroxide flakes. The alkaline activators were prepared and mixed together at least one day prior to use.

The nature of the fresh geopolymer concrete is stiff with high viscosity [8]: hence it tends to have low workability. In order to improve the workability of the fresh concrete, a sulphonated-naphthalene based superplasticiser was added. Four types of locally available aggregates, i.e. 20 mm, 14 mm, and 7 mm aggregates, and fine sand, in saturated surface dry condition, were mixed together. The fineness modulus of the combined aggregates was 5.0.
Specimen Preparation

The aggregates and the fly ash were mixed dry in a pan mixer for 3 minutes. The alkaline solutions, the superplasticiser, and the extra water, if any, were mixed together, then added to the solid particles in the mixer, and mixed for another 4 minutes. The mixture was cast in 100x200 mm cylinder steel moulds in three layers. Each layer received 60 manual strokes, and was vibrated for 10 seconds on a vibrating table. Five cylinders were prepared for each of the test variables selected.

Immediately after casting, the specimens were covered by a film to avoid the loss of water due to evaporation during curing at elevated temperatures. The specimens were left in room temperature for about 30 minutes, and then were placed in the oven for curing at a specified temperature for 24 hours. At the end of the curing period, the specimens were removed from the oven, and kept in the moulds for another six hours to avoid drastic change of the environment. The specimens were then left to air dry in room temperature until tested in compression at the age of 7 days in a universal test machine. The loading rate and the other test procedures used were in accordance with the details specified in the relevant Australian Standard for testing concrete.

Mixture Proportions

The combined aggregates occupied about 77% by mass of the mixture, while the alkaline solution-to-fly ash ratio by mass was about 0.35 for the basic mixture when no extra water was added. The percentage of superplasticiser to the mass of fly ash was 1.5%.

The mixture proportions were derived from many trial mixes. The test variables for this series of experiments were $\text{H}_2\text{O}$-to-$\text{Na}_2\text{O}$ molar ratio and the $\text{Na}_2\text{O}$-to-$\text{SiO}_2$ molar ratio. With regard to $\text{H}_2\text{O}$-to-$\text{Na}_2\text{O}$ molar ratio, only the range from 10.0 to 14.0 was found to be feasible. For $\text{H}_2\text{O}$-to-$\text{Na}_2\text{O}$ molar ratio less than 10.0, the concrete mixtures were not easily workable; on the other hand, for values of this ratio greater than about 14.0, considerable segregation of mixture ingredients occurred due to the presence of excess water.

No suitable concrete mixture could be prepared within the range of $\text{Na}_2\text{O}$-to-$\text{SiO}_2$ molar ratio as proposed by Davidovits [2]. This might be due to the different in the type of source material and the aggregates used in the manufacture of concrete. For the source material, Davidovits used pure calcined kaolinite, named KANDOXI (KAolinite, Nacrite, Dickite OXide), by calcining kaolin clay at 750°C for 6 hours [1], while fly ash was used as the source material in our laboratory work. Also, the mixtures used by Davidovits were geopolymer pastes with no aggregates. To suit the solid materials and the activator liquids used, we limited the range of $\text{Na}_2\text{O}$-to-$\text{SiO}_2$ ratio between 0.095 and 0.120 in the present series of tests.
In order to investigate the influence of the $H_2O$-to-$Na_2O$ molar ratio on the compressive strength, $14\ \text{M (Molar, i.e. moles per litre)}$ sodium hydroxide solution was used; the sodium silicate-to-sodium hydroxide solution ratio by mass was $2.5$. The $H_2O$-to-$Na_2O$ molar ratio of this basic mixture was $10.0$. By adding $10.6\ \text{kg/m}^3$ of extra water to the basic mixture, the $H_2O$-to-$Na_2O$ molar ratio became $11.25$, and by adding $21.2\ \text{kg/m}^3$ of extra water, this ratio became $12.50$. However, the molar ratios of $Na_2O$-to-$SiO_2$ and $SiO_2$-to-$Al_2O_3$ were kept constant at $0.11$ and $3.89$ respectively.

The influence of the $Na_2O$-to-$SiO_2$ ratio on the compressive strength was studied by performing tests on specimens made using mixtures 1 to 5 given in Table 2. For all these mixtures, the molar ratios of $SiO_2$-to-$Al_2O_3$ and $H_2O$-to-$Na_2O$ were kept constant at $3.89$ and $12.43$ respectively. The sodium silicate-to-sodium hydroxide solution ratio by mass was $2.5$.

**RESULTS AND DISCUSSION**

Each of the test data points plotted in various graphs corresponds to the mean value of the compressive strengths of five cylinders in a series. The standard deviations are plotted on the test data points as the error bar.

**Influence of $H_2O$-to-$Na_2O$ molar ratio on compressive strength**

Figure 1 shows the effect of $H_2O$-to-$Na_2O$ molar ratio on the compressive strength of geopolymer concrete for various curing temperatures. An increase in this ratio decreased the compressive strength of concrete. These test trends confirm those observed by Barbosa et al [3], obtained from tests performed on geopolymer pastes made using materials of pure geological origin. Obviously, as the $H_2O$-to-$Na_2O$ molar ratio increased, the mixtures contained more water and became more workable.

Figure 2 illustrates the effect of water-to-geopolymer solids ratio by mass on the compressive strength. The total mass of water is the sum of the mass of water contained in the sodium silicate solution, the mass of water in the sodium hydroxide solution, and the mass of extra water, if any, added to the mixture. The mass of geopolymer solids is the sum of the mass of fly ash, the mass of sodium hydroxide flakes, and the mass of solids in sodium silicate solution (i.e. the mass of $Na_2O$ and $SiO_2$). The test data presented in Figure 2 show that the compressive strength of geopolymer concrete decreased as the ratio of water-to-geopolymer solids by mass increased. This test trend is analogous to the well-known effect of water-to-cement ratio on compressive strength of cement-based concrete.
Influence of Na$_2$O-to-SiO$_2$ molar ratio on compressive strength

Figure 3 shows the influence of Na$_2$O-to-SiO$_2$ molar ratio on the compressive strength of geopolymer concrete. It can be seen that the compressive strength varied very little when the Na$_2$O-to-SiO$_2$ molar ratio increased from 0.097 to 0.120. In the experimental work, as can be observed from the data given in Table 2, the required Na$_2$O-to-SiO$_2$ molar ratio was achieved by increasing the sodium hydroxide concentration and by adding extra water to keep the H$_2$O-to-Na$_2$O molar ratio constant. Therefore, mixture 2 contained more water than mixture 1, and so on. Any change in the water content alone does not affect the compressive strength of geopolymer concrete, provided that the H$_2$O-to-Na$_2$O molar ratio is kept constant. However, the presence of extra water in the mixture improved the workability (Fig. 4).

CONCLUSIONS

A series of tests were performed on geopolymer concrete made using fly ash as the source material. Based on the results of these tests the following conclusions are drawn:

1. The H$_2$O-to-Na$_2$O molar ratio or the water-to-geopolymer solids ratio by mass influences the compressive strength of fly ash-based geopolymer concrete. As these ratios increased, the compressive strength decreased (Figs. 1 and 2).

2. The Na$_2$O-to-SiO$_2$ molar ratio of the geopolymer mixture does not have any significant effect on the compressive strength of fly ash-based geopolymer concrete for the range of values of this ratio between 0.095 and 0.120.

3. Extra water improved the workability of the concrete mixture (Fig. 4). However, water content alone did not have any significant influence on the compressive strength, provided that either the H$_2$O-to-Na$_2$O molar ratio or the water-to-geopolymer solids ratio by mass remained constant.

ACKNOWLEDGMENTS

The authors are grateful to Dr. Terry Gourley and Mr. Chris Busck for introducing them to the fascinating topic of Geopolymers and for their advice and encouragement. The first and second authors are recipients of the Australian Development Scholarships. The third author is supported by the TPSDP – Asian Development Bank.
REFERENCES


Table 1: Composition of fly ash as determined by XRF (mass %)

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<thead>
<tr>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>TiO₂</th>
<th>MgO</th>
<th>P₂O₅</th>
<th>SO₃</th>
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<td>53.36</td>
<td>26.49</td>
<td>10.86</td>
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<td>0.37</td>
<td>0.80</td>
<td>1.47</td>
<td>0.77</td>
<td>1.43</td>
<td>1.70</td>
<td>1.39</td>
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</table>

*) LOI = Loss on ignition

Table 2: Influence of Na₂O-to-SiO₂ molar ratio: mixture composition for binder

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Concentration of sodium hydroxide solution</th>
<th>Added Water (kg/m³)</th>
<th>Na₂O/SiO₂</th>
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<td>0.097</td>
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<tr>
<td>Mixture 2</td>
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<td>Mixture 3</td>
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Recent Advances in Concrete Technology

Fig. 1. Effect of the $\text{H}_2\text{O}$-to-$\text{Na}_2\text{O}$ molar ratio on Compressive Strength

Fig. 2. Effect of the Water-to-Geopolymer Solids ratio by mass on Compressive Strength
Fig. 3. Effect of the molar Na$_2$O-to-SiO$_2$ ratio on Compressive Strength

Fig. 4. Slump values for mixtures 1 to 5
Effectiveness of Anti-Corrosion Products for Reinforced Concrete Exposed to United Arab Emirates Environmental Conditions

by A. Qasimi and S. M. K. Chetty

Synopsis:

A long-term research study on anti-corrosion products for reinforced concrete exposed to aggressive environmental conditions was initiated in 1990. The performance of products was evaluated through accelerated laboratory testing and natural site exposure conditions as tidal zone, above ground and below ground. An exposure site on the Dubai creek shore is designated for long term performance testing at different ages extending up to ten years. A series of physical and electrochemical testing were performed in three phases. The prime objective of the first phase was to assess the performance of the various products, and to assess the practical value of different electrochemical test methods. The focus of the second phase testing shifted towards a more comprehensive evaluation of the test methods. The interim results have been presented at different international conferences. The focus of third phase, which was performed in early 2000, was to observe the actual extent of corrosion sustained by the rebar. This paper presents the final data to substantiate conclusions relating to ingress of chlorides for the various exposure conditions (threshold values), provides recommendations for corrosion monitoring for new structures and test methods for evaluating products and future research requirements.

Keywords: chloride ingress; concrete; corrosion; electrochemical test; inhibitor; threshold
Dr. Abdulghafoor Qasimi: Assistant Director and Head of Research and Standardization Management Office at Dubai Central Laboratory Department (DCLD) of Dubai Municipality. He received his Ph.D. in civil engineering from University of South Carolina. His major field of interest is in research activities in different areas of civil engineering and presented several papers on researches performed at DCLD in international conferences. His current research interests are in the areas of durability of concrete and in particular corrosion of reinforcement in concrete.

Dr. S.M.K. Chetty: Specialist in standards and specifications - Research and Standardization Management Office at Dubai Central Laboratory of Dubai Municipality. He is a former UN Expert in Iran and U.A.E. and served as member of several ISI committees. His current interest is in the field of technical approval of non-standard materials and in standardization. He has authored numerous papers on various aspects of construction materials and technology.

**INTRODUCTION**

Dubai Municipality had a long-term research programme since December 1990 involving reinforced concrete specimens placed at an exposure site on the Dubai creek shore at the Al Jaddaf area. A series of physical and electrochemical testing on selected specimens, which were not in a state of structural stress, were performed to establish the effectiveness of anti-corrosion products.

**Products Characteristics**

The characteristics of these products as declared by their manufactures are as follows:

- **Product 1**: A pure inorganic soluble silicate in powder form
- **Product 2**: An aqueous suspension of polymerglobules with a hydrophobic pore-blocking ingredient
- **Product 3**: An aqueous suspension of ammonium stearate and hydrocarbon resins.
- **Product 4**: A product of about 92% amorphous silicon dioxide
- **Product 5**: A penetrating surface coating which becomes part of the concrete chemistry.
- **Product 6**: An amalgam of different chemicals in powder form.

The identification of the products are replaced by numbers to protect their commercial name.
PARAMETERS

Considering the site practices prevalent in the local construction industry with regard to quality control on site and workmanship skill levels, the performance of the proposed products are evaluated by using the following parameters:

1. Exposure - environment
   - tidal zone (lying on beach -- submerged at high tide)
   - below ground (covered with 300 mm of soil)
   - above ground (on racks in air)

2. Mixtures - concrete water cement ratio
   - Mixture A -- 0.44 W/C (high quality mixture)
   - Mixture B -- 0.60 W/C (low quality mixture)

3. Electrochemical testing by specialist laboratories
   - A specialist laboratory performed a series of physical and electrochemical testing on selected specimens.

PROGRAMME

The testing consisted of three phases

The First Phase

The first phase of testing was performed in 1995 and reported in January 1996. The prime objectives of that testing were to assess the performance of the various corrosion control 'products' incorporated in the specimens, and to assess the practical value of different electrochemical test methods:

i) Cover measurements
ii) Continuity measurements
iii) Half-cell potential measurements
iv) Linear polarisation resistance testing (corrosion rate measurements)
v) AC impedance measurements
vi) Corrosion current measurements
vii) Resistivity measurements

The results of the studies have been published in four research papers [1-4] contributed at regional and international conferences. Test results produced were used to assess the effectiveness of various products for inhibiting the corrosion of reinforcing steel in concrete. Among the six products used in the study, two were found to be totally ineffective (products 1 & 6) and they were discontinued.
The Second Phase

The second phase of testing was performed in late 1997 and early 1998. The focus of this test phase shifted towards a more comprehensive evaluation of the test methods, by evaluating the correlation between them. As such, it was necessary to evaluate the extent of corrosion actually sustained by the rebar and compare these observations with the electrochemical test data.

i) Half-cell potential measurements
ii) Resistivity measurements
iii) Corrosion rate measurements (linear polarisation resistance testing)

The Third Phase

The third phase of testing was performed in early 2000. The testing programme was applied to the reinforced concrete specimens Fig. 1. The specimens were taken from the same group of specimens tested during Phases 1 and 2. Non-destructive testing was followed by removal of reinforcement and examination of the rebar. The focus of this testing was to collect a final set of measurement data, followed by destructive testing to observe the actual extent of corrosion sustained by the rebars. Each specimen consisted of four longitudinal rebars tied together with rebar links near each end of the specimen such that the concrete cover varied on each rebar. A significant aspect of the specimen construction was that the longitudinal rebar were positioned on the inside of the link bars which meant that the links had substantially less cover. This significantly affected the results of the exposure, particularly for the uncoated rebar. Two specimens were selected from each of the above Exposure / Mixture / Product combinations and, once prepared, a series of electrochemical tests were applied, consisting of the following:

i) Continuity verification
ii) Half-cell potential profiles
iii) Chloride ingress tests

For each specimen tested, the rebar having 'Most' / 'Least' concrete cover was individually tested. For “least cover” the range was from 15 mm to 30 mm while for “most cover” the range was from 30 mm to 65 mm as shown in Fig. 2.

OBSERVATIONS OF SPECIMEN AND REBAR CONDITION

Classification System

Insofar as the electrochemical testing is concerned, the purpose of the condition survey was to ‘classify’ the extent of corrosion damage sustained and study its correlation to the electrochemical test data. Following a detailed study of
the condition survey data obtained, a classification system was developed as follows:

- **Class 1 - Negligible**: Specimens exhibiting limited concrete surface discoloration by corrosion of the rebar (i.e. <20%) and no visible signs of corrosion of the rebar deterioration.
- **Class 2 - Superficial**: Specimens exhibiting corrosion but no apparent metal loss. The limits of the rebar surface area corrosion were 20% to 40%.
- **Class 3 - Moderate**: Specimens exhibiting 40% to 60% rebar surface corrosion, but no significant metal loss.
- **Class 4 - High**: Specimens exhibiting 60% to 80% rebar surface corrosion and/or metal loss.
- **Class 5 - Severe**: Specimens exhibiting >80% rebar surface corrosion and/or metal loss causing large cracks and delaminations in the concrete.

Whilst the classification system above was developed specifically for the main rebar in the specimens, variations of it were also applied to the Concrete. Table 1 shows the extent of metal loss from the rebar and links. This was measured via the reduction in diameter in the bars. Initially the rebar, and links diameter were 12 mm and 10 mm respectively. The $D_{\text{Reduction}}$ columns in Table 1 show the smallest diameter along the length of the rebar as per the following calculation method used to calculate the reduction in the bar diameter.

The calculation assume that the metal loss is evenly distributed around the diameter of the bar.

Length to weight ratio:
$L/W$ ratio (kg/m) = weight of rebar specimen / Length of rebar specimen

For any given two specimens:

\[
\frac{\text{Area}_1 (m^2)}{\text{Area}_2 (m^2)} = \frac{(L/W \text{ratio}_1)}{(L/W \text{ratio}_2)} \cdot \frac{\rho_{\text{steel}}}{\rho_{\text{recl}}} = \frac{L/W \text{ratio}_1}{L/W \text{ratio}_2}
\]

Hence: $r_2 = \frac{r_1}{[(L/W \text{ratio}_1)/(L/W \text{ratio}_2)]^{1/2}}$

Where: $r_1 = $ Initial radius $r_2 = $ Final radius

Therefore reduction in nominal diameter:

\[
(r_1 - r_2) = r_1 \left[1 - \frac{1}{[(L/W \text{ratio}_1)/(L/W \text{ratio}_2)]^{1/2}} \right]
\]
DISCUSSION OF TEST RESULTS

General Comment

The parameters considered in the study are compressive strength, water absorption, water penetration, and chloride ingress. Among these, chloride ingress is the prime deciding factor influencing the corrosion of reinforcing steel in concrete. This ingress is dependent on the water absorption and water penetration of concrete. These parameters are functions of the characteristics of the pores in the concrete such as their volume, size, distribution and continuity. Water absorption measures the volume of pore space in concrete, while water penetration depends on the permeability of concrete which is not only a function of its porosity but also depends on the size, distribution and continuity of pores. So, introduction of pore blockers into the concrete mixture would affect both water absorption and water penetration. From this, it is to be expected that the lower the absorption and penetration, the less chloride penetration should be. However, comparison of the test results published in [1–4] shows that this is not the case.

Possible explanations could be due to variation in the salinity concentration levels surrounding the specimens in the below ground exposure and variation in the salinity deposition on the specimens due to alternate wetting and drying of specimens subjected to inter-tidal movements. With respect to above ground exposure conditions, the permeability may be high but there is not much chloride in the environment available for penetration. Thus results do not follow expected trends, and we find no rational basis for deriving co-relations.

All corrosion prevention products / techniques mentioned above are intended as a supplement – and are not intended to be a substitute – for concrete quality. Proper mixture, cover depth, compaction and curing are equally important and effective in halting rebar corrosion.

Environments

The potentials measured in the specimens above ground are much less ‘active’ than those of the tidal zone & below ground specimens. The specimens above ground exhibited potentials (-380 to + 40) mV Ag/AgCl range, while those of the tidal zone and below ground typically fell in the (-200 to -650) mV Ag/AgCl range. The more ‘active’ potentials in the tidal zone & below ground specimens are attributed to higher chloride concentration owing to direct exposure to salt water / saline soil, and to the water saturation of these specimens which would reduce oxygen availability in these exposures.
Exposure

The tidal zone and below ground exposures yielded similar results both in terms of electrochemical testing and sustained corrosion. Owing to their direct immersion in highly saline water / soil, the extent of corrosion in these exposures was high. In contrast to the tidal zone and below ground specimens, the specimens exposed above ground are not affected as yet. This difference clearly illustrates the need to consider exposure when designing reinforced concrete structures.

Potential Measurements

The potential measurement data correlated well and consistently with the corrosion classification data. It is a relatively easy test method to implement, is well understood and should definitely be applied in assessing the condition of reinforced concretes structures. Referring specifically to corrosion potential over 1995, 1998 & 20000 test programs, there is a direct correlation to the guidelines provided in ASTM C876-91. The limitation of the method is that rebars will not exhibit active potentials until the chloride has ingressed through the cover.

Chloride Penetration Measurements and Mixtures

The study included the correlation of the electrochemical test results with chloride ingress tests. These tests were performed on the same specimens as were employed for the electrochemical testing. The test data indicates the chloride levels at three depths (i.e. 0-15 mm, 15-30 mm & 30-45 mm). The results in most cases indicated that generally the chloride content diminished with depth consistent with ingress from the outside environment.

With the mixture A results, products 2, 4 & 5 had noticeably lower chloride ingress. The difference in the mixture B results is less distinct which highlights the importance of concrete quality. For the purpose of correlation, the average chloride concentration at the 30-45 mm depth was employed. The data provided by this operation correlated well with the corrosion classification and potential data.

The difficulty with this test is the need to drill holes in the concrete surface to collect dust for analysis. It is therefore a destructive test and the analysis can be costly. It is not a practical test to repeat in a close grid on the surface of reinforced concrete structures.

The advantage of the data provided by this test is that it provides a measure of chloride ingress before it reaches the steel. Therefore, the results of this test at a limited number of locations and in conjunction with potential measurement data can provide a very meaningful picture for corrosion assessment. The potentials of both
mixture A & mixture B specimens were in similar ranges for each condition due to the fact that they have reached the same level of corrosion.

**Pore-Blocking Products**

The efficiency of these products is best tested by their response to the most severe environment, namely the tidal zone. All the products showed less-electronegative potential readings than the control specimen. Overall, Product # 4 showed the lowest active potential readings [3 - 4] The differences in potential were not sufficient to provide product rankings.

**Visual Inspection**

Visual inspection was performed from time to time to check the physical conditions of the specimens at exposure site. This consisted of noting of rust stains, cracking, spalling, etc. Some of the specimens which did not show any signs of distress in the first year of exposure did so in the second and third year. This applies to all specimens with pore blocking products, and the control specimens placed in below ground and tidal zones. At the end of ten years of exposure, the above ground specimens containing pore blockers and the control were found to be in satisfactory condition with no signs of corrosion activity for both mixtures. Only in some specimens of mixture B, rust stains were noticed at random positions.

**THRESHOLD CHLORIDE CONTENT**

The threshold chloride content for reinforced concrete structures can be briefly described as the chloride ion concentration for which the rebar surface is de-passivated and actively corroding, thus resulting in metal loss of the rebar and eventually deterioration of the given structure. From the data obtained in phase three testing, there are three approaches by which threshold chloride levels may be determined. Some of the products (particularly the admixtures) can affect the properties of the concrete and these must be investigated separately.

The above ground specimens provide the best conditions (electrical and physical) for determining the threshold chloride content levels for the following reasons:

i) The above ground specimens were atmospherically exposed specimens. The specimens were not saturated with chlorides, as in the tidal zone specimens.

ii) Other factors that could cause ‘active’ steel potentials were minimized.
iii) Initiation of corrosion can be seen in some specimens which can be used to indicate the chloride levels required for initiation of corrosion. Most of the specimens in the below ground and tidal zone environments had already undergone deterioration due to corrosion.

**Approach I**

The first approach is dependent on the ASTM C 876 values for indicating corrosion activity. It is not indicative of the rate of corrosion, which is of key importance in determining the extent of damage. This approach is to use ASTM value of $-350 \text{ mV CSE}$ as the electrochemical potential at which steel is activated. By applying this criteria to electrochemical data of the specimens, the chloride concentration at which corrosion is occurring can be determined. The specimens with rebar potentials closest to $-300 \text{ mV Ag/AgCl}$ being more 'active' may be experiencing corrosion activity and therefore may have likely attained chloride threshold levels. Product # 2, in both mixture A and mixture B had recorded potentials closest to $-300 \text{ mV Ag/AgCl}$ with a chloride level of 0.028% for mixture A and 0.014% for mixture B by mass of concrete.

**Approach II**

The second approach used the physical condition of the above ground specimens as indicative of the initiation of corrosion. Corrosion of rebars eventually physically manifests itself as deterioration of the specimen. The specimens that exhibit any signs of deterioration have experienced corrosion activity induced by chloride ingress, and therefore may contain threshold concentration levels of chlorides. The specimens of product 4 show main bar and link bar with more than 60% of the rebar as being affected by corrosion. The data indicate that chloride content of 0.021% by mass of concrete is sufficient to cause physical deterioration of the specimen.

This method is more pragmatic approach in that it indicates the minimum chloride concentration level at which physical deterioration may occur in the specimens. However, it addresses the chloride content issue after the damage becomes visible rather than at the exact moment at which corrosion begins. This approach is to use the physical condition of the specimens as indicative of the initial and progression of corrosion. Any physical indication of corrosion in the form of staining, cracking or spalling or rebar cage condition, in an otherwise sound specimen, is indicative of the threshold chloride concentration having been reached.
Approach III

The third approach is to use electrochemical potential data of the above ground specimens where the stepped increase in potential in the negative direction is indicative of initiation of corrosion activity. Consequently, it may be assumed that the chloride threshold concentration has been reached. The above ground specimens in Phase III testing is a direct result of the presence of threshold concentration levels of chlorides at the rebar surface. It does not consider that the higher rebar potential activity may be due to other factors.

The different approaches all indicate different chloride threshold levels for the specimens. The threshold chloride value expressed in percent by mass of concrete of the different methods are as follows:

- ASTM C 876: 0.007%
- Physical Condition: 0.021%
- Potential Data: 0.007%

The values of the threshold content vary among themselves, with the first and third method showing similarity, but each of the methods are indicative of corrosion in some form.

The above three approaches are however useful in providing a range of chloride threshold values that can be used as a guideline.

CORROSION MONITORING FOR NEW STRUCTURES

To date, most approaches to concrete deterioration due to rebar corrosion have been reactive, occurring after much deterioration has already been sustained — and requiring major remedial actions. A proactive approach that would enable strategic and economic mitigation of further deterioration is preferred.

The objective of the following approach is to provide the Owner of a structure with the actual performance data required for him to make timely & informed decisions regarding the long-term integrity of his structure — in a cost-effective manner.

The general approach is to take advantage of the opportunity to position probes during construction that will provide consistent and easily obtained measurements of corrosion potential and corrosion rate at strategically selected locations in a structure.

The parameters to be measured are:
- Rebar Potential: Requires an embedded reference electrode
- Corrosion Current: Requires a calibrated steel coupon
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- Cumulative Corrosion Rate: Requires an 'Electrical resistance' type corrosion rate probe

The advantages of cast-in probes include:
- their ability to provide corrosion data in actual in-situ conditions.
- comparative data over time at exact positions
- may be placed at locations that would be inaccessible using portable equipment
- avoidance of complications / errors and difficulties related to access that are associated with measurements obtained using portable equipment on the concrete surface

Implementation of corrosion monitoring for new structures includes the following steps:
i) Choose locations on structure to be monitored
ii) Design cable layouts and test point locations
iii) Install and Commission
iv) Determine test measurement frequency (e.g. monthly, quarterly, annually)
v) Establish required data base and analysis / reporting tools
vi) Implementation should be performed by an experienced corrosion engineer working in conjunction with a structural engineer familiar with the structure being monitored.

TEST METHODS FOR EVALUATING PRODUCTS

The following outlines a philosophy and specific approach to the evaluation of various classes of 'products' that are employed to reduce rebar corrosion, based on the results of this research testing.

Evaluation of Product Performance

A complete evaluation of products requires long-term performance testing in-situ. This is not always practical – and certainly requires a very long evaluation period. The other consideration is that often a combination of products and techniques are employed which may have synergistic effects in the long term.

The disadvantage of most accelerated testing vis-a-vis rebar corrosion, is that the simulated test conditions often do not accurately represent site conditions; the corrosion process may be quite different under these conditions and extrapolation of the results may be misleading.

For example, accelerated tests where concrete specimens are continuously exposed to humid environment or immersed in salt water may 'saturate' the
specimen and thereby have a limited oxygen availability. The rebar corrosion rate in such a test will likely be much less than at a longer test involving alternate wet / dry phases. Similarly, tests involving specimens of 'isolated' rebar with a homogenous exposure do not include 'macro-cell' effects that often exist in the field. Also, accelerated tests typically do not provide an accurate reflection of the long-term performance / degradation of some inhibiting products. At best, accelerated testing should be limited to comparative evaluations of products within a specific category, as discussed in subsequent sections. Semi-accelerated testing (e.g. 3 to 5 year) period under conditions that closely represent severe site conditions is recommended for a fuller product evaluation.

**Product Categories and Test Methods**

The products employed for mitigating rebar corrosion tend to fall into one of the following categories:

- Pore-blocking admixtures
- Concrete Surface Coatings
- Inhibitors

The basis of operation and proposed applicable test methods for each of these are discussed below.

**Pore-Blocking Admixtures**

The intent of Pore-Blocking admixtures (e.g. microsilica) is to reduce the rate of chloride ingress to rebar depth and thereby extend the time to the initiation of rebar corrosion.

**Concrete surface coatings**

The intent of Concrete Surface Coatings are to provide a barrier on the concrete surface that will stop / slow chloride ingress into the concrete from the outside environment.

Other tests, not directly corrosion related, should be performed to evaluate the coatings:

- Adhesion to concrete surface
- Weatherability
- UV resistance
- Breathability (ability to pass vapour without disbonding)
Accelerated testing of different anode materials can be performed to determine their capacity. Consideration must be given to different anodic reactions that may occur under accelerated testing, as well as any inherent self-consumption rates.

**Inhibitors**

Most concrete inhibitors (e.g. calcium nitrite) are chemical admixtures that effect the oxidation and/or reduction reactions at the rebar surface. There are different types of inhibitors (e.g. anodic, cathodic, combination anodic/cathodic), and there tends to be a critical limit of inhibitor concentration required to halt corrosion (particularly for anodic inhibitors).

Most inhibitor applications require monitoring of critical concentrations and re-dosing as required. There is no option for re-dosing in reinforced concrete applications. Therefore, the maintenance of critical concentrations over the long-term service life of a structure is a great concern. The only way to evaluate this is by long term testing.

Corrosion rate (Resistance type) probes can give accurate results. However, the low corrosion rates in concrete require long periods for detection and evaluation. Sensitive probes are available, but these tend to have short service life.

**CONCLUSIONS**

The performance of various products considered in the study at the end of ten years of exposure for concrete specimens not in a state of stress were as follows:

1. The tidal zone and below ground exposure conditions tended to yield similar results which would indicate that chloride and moisture ingress levels would also be similar.
2. The above ground test results indicated that the corrosion activity/rates in these samples were very low.
3. The concrete specimens placed above ground including control specimens were found to be in a satisfactory condition.
4. Among the six products used in the study, two were found to be ineffective (products 1 & 6) while the effectiveness of other products trends had been changed with time and none of the products was found to be effective in the long term.

**ACKNOWLEDGEMENT** - It is acknowledged with thanks the assistance and the support extended by M.I. Jasar as co-worker in conducting the testing and collating the data for the presentation of this paper.
REFERENCES


Table 1. Summary of Results for the Classification System.

<table>
<thead>
<tr>
<th>Rebar Condition</th>
<th>Concrete Condition</th>
<th>Link Condition</th>
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</thead>
<tbody>
<tr>
<td><strong>Above Ground</strong></td>
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<table>
<thead>
<tr>
<th>Admixtures</th>
<th>Classification</th>
<th>$D_{\text{reduction}}$ (mm)</th>
<th>Cracks</th>
<th>Classification</th>
<th>$D_{\text{reduction}}$ (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>Class 1</td>
<td>0.043</td>
<td>Nil</td>
<td>Class 1</td>
<td>na</td>
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<tr>
<td>Pro#2</td>
<td>Class 1</td>
<td>0.053</td>
<td>Nil</td>
<td>Class 1</td>
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<tr>
<td>Pro#3</td>
<td>Class 1</td>
<td>0.068</td>
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</tr>
<tr>
<td>Pro#4</td>
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<td>-0.082</td>
<td>Nil</td>
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<td>na</td>
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<tr>
<td>Pro#5</td>
<td>Class 1</td>
<td>-0.040</td>
<td>Nil</td>
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<td>na</td>
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</table>

| **Below Ground**|                |

<table>
<thead>
<tr>
<th>Admixtures</th>
<th>Classification</th>
<th>$D_{\text{reduction}}$ (mm)</th>
<th>Cracks</th>
<th>Classification</th>
<th>$D_{\text{reduction}}$ (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Pro#2</td>
<td>Class 2</td>
<td>0.068</td>
<td>Severe</td>
<td>Class 5</td>
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<tr>
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<td>Class 5</td>
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<td>Class 2</td>
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</tr>
<tr>
<td>Pro#5</td>
<td>Class 3</td>
<td>0.002</td>
<td>Severe</td>
<td>Class 4</td>
<td>--</td>
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</table>

| **Tidal Zone**|                |

<table>
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<tr>
<th>Admixtures</th>
<th>Classification</th>
<th>$D_{\text{reduction}}$ (mm)</th>
<th>Cracks</th>
<th>Classification</th>
<th>$D_{\text{reduction}}$ (mm)</th>
</tr>
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<tbody>
<tr>
<td>Control</td>
<td>Class 3</td>
<td>0.604</td>
<td>Moderate</td>
<td>Class 3</td>
<td>--</td>
</tr>
<tr>
<td>Pro#2</td>
<td>Class 4</td>
<td>0.089</td>
<td>Moderate</td>
<td>Class 5</td>
<td>--</td>
</tr>
<tr>
<td>Pro#3</td>
<td>Class 4</td>
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<td>Moderate</td>
<td>Class 5</td>
<td>--</td>
</tr>
<tr>
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<td>Class 2</td>
<td>-0.004</td>
<td>Moderate</td>
<td>Class 5</td>
<td>--</td>
</tr>
<tr>
<td>Pro#5</td>
<td>Class 5</td>
<td>0.121</td>
<td>Moderate</td>
<td>Class 5</td>
<td>--</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Classification</th>
<th>Degree of Corrosion of Rebar</th>
<th>Surface cracks on specimen</th>
<th>General Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class 1</td>
<td>&lt;20%</td>
<td>No cracks</td>
<td>Negligible</td>
</tr>
<tr>
<td>Class 2</td>
<td>21 - 40%</td>
<td>---</td>
<td>Superficial</td>
</tr>
<tr>
<td>Class 3</td>
<td>41 - 60%</td>
<td>Minor cracks</td>
<td>Moderate</td>
</tr>
<tr>
<td>Class 4</td>
<td>61 - 80%</td>
<td>---</td>
<td>High</td>
</tr>
<tr>
<td>Class 5</td>
<td>&gt;81%</td>
<td>Deep extensive cracks</td>
<td>Severe</td>
</tr>
</tbody>
</table>

Note: Classification system was developed specifically for the main rebar in the specimens, variations of it were also applied to the concrete
Fig. 1 Test specimen 360 mm x 150 mm x 150mm

Fig. 2 Cross-section of the test specimen
Autogenous Healing; Ingress of Chloride and Sulfate through Cracks in Concrete Under Marine Environment

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

Synopsis:

Autogenous healing of cracks; and ingress of chloride and sulfate through the cracks in concrete were investigated utilizing 15 years old precracked prism specimens. The size of the specimens was 100x100x600 mm. The specimens were made with ordinary portland, slag (Types A, B and C), and fly ash (Type B) cements. A round steel bar of diameter 9 mm was embedded in each specimen. W/C were 0.45 and 0.55. Crack widths were varied from 0.1 to 5 mm. The specimens were exposed to the tidal and submerged zones. Deposits along the path of the healed cracks as well as the de-bonded areas over the steel bars located at the root of the crack were investigated by scanning electron microscope (SEM) and X-ray diffraction (XRD). Mappings for chloride, sulfate, and magnesium oxide through the cracks in concrete were carried out by electron probe micro analyzer (EPMA).

Autogenous healing is observed for narrower cracks (≤ 0.5 mm) irrespective of the cement types and exposure zones. Healing continues along the crack path. It extends to the debonded area over the steel bars at the cracked region. The deposits are confirmed as calcium carbonate, ettringite, magnesium hydroxide, and rust. Accumulation of more chloride is found in the vicinity of the unhealed wider cracks (> 0.5 mm), especially for slag cements with a high amount of slag content. Sulfate ingress was limited over a very thin region from the crack plane. Interestingly, chloride concentration at the sulfate rich region is remarkably low. It indicates dissolution of chemically adsorbed chloride as well as the loss of ability of adsorption of chloride in the pore structures with the presence of sulfate.

Keywords: chloride; concrete; crack; healing; marine environment; sulfate
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INTRODUCTION

The autogenous healing of cracks in concrete was realized several decades before. Most of the laboratory studies on this subject were carried out with simulated solution (1,2). In a recent review of autogenous healing by Adam Neville, it was emphasized that there remains a gap between the laboratory-based knowledge and the behavior of concrete and mortar in the field (3). In the author’s laboratory, an experimental investigation was started on pre-cracked concrete specimens in a tidal pool 15 years ago. A significant number of pre-cracked specimens were made. Crack widths were varied from 0.1 to 5 mm. Cement types were ordinary portland (OPC), slag cements of type A, B, and C (SCA, SCB, SCC), and fly ash cement of type B (FACB). Exposure conditions were tidal and submerged. Recently, the authors investigated the specimens after 15 years of marine tidal and submerged exposure. The results related to the corrosion of steel bars and chloride concentrations were reported separately (4,5). In this report, results of investigation on deposits at the cracks by SEM, XRD, and EPMA are summarized. The deposits in the crack, onto the crack plane, as well as near the steel bars were carefully examined. In addition to the healing, ingress of sulfate and chloride through the cracks were also examined. The results will be very useful as it was carried out in a tidal pool using seawater directly from the sea for a period of 15 years. The results can also be used to compare with the same kind of study in the laboratory. To clarify the formation of macro corrosion cell, extent of micro-cell corrosion, and the degree of passivity of steel bars at healed and unhealed cracks, an extended study was carried out. The results were reported separately (6).
SCOPE

Pre-cracked prism specimens of size 100x100x600 mm were used. The specimens were made with different types of cement, such as ordinary portland cement (OPC), slag cement of Type A (SCA), B (SCB) and C (SCC), and fly ash cement of Type B (FACB). Water-to-cement ratios were 0.45 and 0.55. Both tap and seawater were used as mixing water. The cases and the number of the specimens investigated are listed in Table 1. In total 87 specimens were examined. Crack widths on the surface of the specimens varied from 0.1 to 5 mm. The specimens were exposed in the tidal and submerged zones of a tidal pool for 15 years. Mapping for chloride, sulfate, magnesium oxide, and calcium oxide were carried out by EPMA at the vicinity of the crack. Deposits in the cracks as well as the debonded areas (over concrete and steel bars) were examined by SEM. The deposits in the cracked region were also confirmed by XRD. All of these data are summarized in this report. The results of electrochemical and physical evaluations of corrosion of steel bars and the chloride concentrations at the cracked and the uncracked regions were reported separately (5,6).

MATERIALS

Ordinary portland cement (OPC), slag cement of Type A, B and C (SCA, SCB and SCC according to JIS R5211) and fly ash cement of Type B (FACB according to JIS R5213) were used. Physical properties and chemical analysis are listed in Table 2. The classifications of the cements on its blended content are given in Table 3. Crushed river gravel and sand were used as coarse and fine aggregates, respectively. The properties of the aggregates are given in Table 4. Japanese Industrial Standard steel bar (JIS SR 24) of diameter 9 mm was used. The yield strength of the steel bars was 230 MPa. The chemical compositions of the steel bar are summarized in Table 5. The chemical compositions satisfied JIS G3112.

MIXTURE PROPORTIONS

Mixture proportions of concrete are summarized in Table 6. W/C were 0.45 and 0.55. The slump of the fresh concrete was 80±10 mm and air content 4±1 %. Mixing waters were tap and seawater. Physical properties and chemical compositions of seawater are summarized in Table 7. The chemical composition was tested in several years before. The chloride level in seawater was found at around 19000 ppm based on the recent laboratory analysis.
SPECIMENS

The layout of the specimens is shown in Fig. 1. The size of the specimens was 100×100×600 mm. In each specimen, a round steel bar of diameter 9 mm and length 500 mm were embedded at a cover depth of 45.5 mm i.e., at the center of the specimen. After 28 days of standard curing, the specimens were cracked in the laboratory by applying a load at the center of the specimens. For this, each beam was supported on two rollers at the ends and a load was applied at the center of the specimens. The load was gradually increased till crack width became the pre-specified value. The strain of the steel bars was not monitored, however expected that the stress will not reach to the level of yield strength, as plain steel bars were used and the ends of the bars were not anchored. After cracking, the specimens were exposed to the tidal and submerged zones of a tidal pool located beside the sea at latitude about 35° N and longitude about 138° E. Seawater was automatically pumped into and drained out at six hours interval from the tidal pool. Tidal specimens were subjected to two cycles of wetting and drying a day (wetting for 7 hours and air drying for 5 hours). The submerged specimens were placed at 1 m below the low water level. The specimens were free from freezing and thawing effect.

METHOD OF EVALUATION

After 15 years of exposure, the specimens were transferred from the exposure site to the laboratory and cleaned. Crack widths on the surface were measured using an optical microscope. For SEM investigation of the deposit at the cracked and the debonded area over the steel bars, split open surface or cut surfaces were collected from the required locations. If necessary, the samples were coated with epoxy before cutting to avoid fracture along the crack. All SEM samples were carbon coated before observations. The white deposit over the steel bars (for narrow crack widths) at the cracked region was checked by SEM. Deposits onto the split open healed crack plane were also collected. The deposits were scratched from the split open crack surface and their crystalline morphology was determined by using a diffractometer, i.e. XRD method. EPMA mappings for chloride, sulfate, magnesium oxide, and calcium oxide from the crack plane to the inner region were also carried out. During cutting, the samples were epoxy coated to avoid breakdown of the samples along the crack, if necessary.

For physical evaluation, the specimens were fractured longitudinally by compression under a loading machine with a sharp edge placed along the mid of the specimens. Each fractured region was split opened along the crack by applying impact with a steel hammer. The split open crack planes and the concrete surface surrounding the steel bars at the cracked region were checked for the deposits. A 1% phenolphthalein solution was sprayed on the freshly
opened crack planes to check the alkalinity, i.e. existence of carbonation.

Visual investigation of the deposit was carried out for all specimens. SEM, XRD, and EPMA investigations were carried out for the selected cases.

**EXPERIMENTAL RESULTS AND DISCUSSION**

A series of plain cylindrical specimens made with OPC, SCA, SCB, SCC, and FACB was tested for compressive strength of concrete after 15 years of exposure. These data were reported in the last CANMET/ACI conference in India (4). Electro-chemical and physical evaluation of corrosion of steel bars in cracked concrete were evaluated and reported separately (5,6).

**General Observations**

Based on the visual observation on 87 specimens, it was found that the narrower cracks (≤ 0.5 mm) were healed with white deposit irrespective of the cement types (OPC, SCA, SCB, and FACB) and exposure zones (tidal submerged). Deposits were also protruded from the surface of the specimens in some cases. Typical views of the concrete surface and the split open crack planes are shown in Fig. 2. Simple observation by optical microscope is also shown in the same figure. The color of the split open concrete surface turned to pink after spraying phenolphthalein solution. Therefore, it was understood that the deposit is highly alkaline. Wider cracks (>0.5 mm) were not healed. The split open crack planes were brownish in color, the surface of the crack was carbonated but just limited to 1-2 mm from the crack plane. No attempt was made to measure the tensile strength of the healed cracks, as no specimens were made without steel bars. However, during breaking the specimens, it was found that the specimens were easily split opened along the crack plane with impact by a steel hammer. Therefore, the tensile strength of healed plane is expected to be much lower than the tensile strength of concrete.

In this investigation, the maximum possible crack width that can be healed was found at 0.5 mm. Healed cracks shows no corrosion or little trace of corrosion, if any. But, severe loss of bar diameter was found for the unhealed cracks. The results clearly indicate that to achieve sustainable marine concrete structures, healing can play a leading role. It can be considered as self repair process of cracks in concrete. The data related to the pit depths and their locations were explained in Reference (5).

**SEM Investigation Across the Cracks and Onto the Crack Plane**

SEM investigations were carried out on the deposit from the surface region to the inner region along the crack. Healing observed throughout the crack
path. SEM micrographs taken on a crack path (surface width = 0.1 mm) located at 5, 13, 25, and 40 mm from the surface are shown in Figs. 3-6. Ettringite needles are clearly seen in the deposit. It is also mixed with other deposits, which were confirmed as calcium carbonate (in the form of calcite, vaterite, aragonite), magnesium hydroxide, and rust. Presence of very random CH crystals was also found. Typical SEM micrographs onto a split open crack plane are shown in Fig. 7. Ettringite needles are densely populated onto the crack plane.

**SEM Investigation Near the Debonded Area**

After splitting the specimens, a white cover was found over the steel bars in the vicinity of the crack that ceased the progress of corrosion. The condition of the steel bars at the cracked region is schematically explained in Fig. 8 for healed and unhealed cracks. The rust formed at the early age of exposure was generally covered by the white deposit. In many cases, the deposit was mixed with rust. The white deposit was also clearly seen on the split open concrete surfaces surrounding the steel bar at the cracks. Typical SEM micrographs of these deposits are shown in Fig. 9. Densely populated ettringite needles are clearly seen.

The results clearly indicate that healing exists throughout the crack path. To see the deposit near the steel bars, the specimens were cut along the steel bar by a slow speed diamond cutter. The condition of the crack near the steel bar is shown in Fig. 10. The presence of the deposit was also confirmed near the steel bars as well as the vicinity of debonded area.

The cracks in concrete cannot be avoided for many reasons. Therefore, the occurrence of healing should be a great advantage for making long-term durable marine concrete structures. Studies on the progress of healing in the natural marine exposure at the early stage of exposure are still necessary. The authors were also carried out an investigation to clarify the progress of macro- and micro-cell corrosion of steel bars in cracked concrete under marine environment. It was found that soon after the marine exposure, a remarkably high amount of macro-cell current was developed at the cracked region, but it gradually drops to a negligible level due to the progress of healing. The preliminary results of this study can be obtained in Reference 7.

It is worth noting that the deeper corrosion pits were observed at the uncracked regions due to the voids at the steel-concrete interface, which were not subjected to the beneficial effect of healing. The data related to the depth of corrosion pits and their locations can be obtained in Reference 5. Extensive study on the passivity of the steel bars at the healed and unhealed cracks was also carried out in an extended study and reported in Reference 6. It was found that the healing generally improves the passivity of the steel bars. The results strongly support that healing will play a beneficial role to make long-term durable concrete structures under marine environment.
**Investigation of the Deposit at the Cracked Region by XRD**

The crystalline phases of the deposit collected from the healed cracks were examined by XRD for a wider and narrower cracks for FACB. The results are shown in Fig. 11 for crack widths of 0.1 mm and 0.5 mm. Peaks for three types of calcium carbonate crystals, in the form of calcite, aragonite, and vaterite were found. However, in many cases, the peak was limited to the calcite only. The peaks for brucite are also found. The presence of carbonate in the form of calcite matched well with the laboratory investigations carried out by many authors as explained in the review report of Adam Neville (3). The presence of carbonate in the form of aragonite and vaterite is explained due to existence of other ions in seawater (8). Ettringite peaks are not detected by XRD. However, SEM investigations showed abandoned ettringite onto the split open crack plane. Based on the EPMA mapping, trace of rust was confirmed in the deposit. The rust was diffused or entrapped into the deposit at the beginning stage of healing.

**EPMA Mapping for Chloride, Sulfate, Magnesium Oxide, and Calcium Oxide: Narrower and Wider Cracks**

EPMA mapping for chloride, sulfate, magnesium oxide, and calcium oxide from the crack region to the inner region of the specimens was carried out. Schematic distribution of chloride, sulfate and magnesium oxide are shown in Fig. 12 based on the results of EPMA mapping. As the original mappings were done in color, therefore schematic sketches were presented. Generally no significant difference in chloride concentration is found for a healed and an unhealed cracks for the concrete made with ordinary portland cement (OPC) or fly ash cement of type B (FACB) or slag cement of Type A (SCA). Concrete made with these cements have relatively a poor microstructure compared to SCB and SCC. Microstructure of these concretes was also examined utilizing 15 years old cylinder specimens and reported in Reference 9. For concrete made with a high amount of slag content, such as slag cement of Type B and C (SCB, SCC), chlorides are highly concentrated at the unhealed wider cracks due to the dense microstructure of concrete. Also, prolonged exposure will improve microstructure further. The high slag concretes tend to screen chloride and restrict them to the surface region. The concentration of chloride was low for the healed cracks near to the steel surface. This suggests that the healing results in the reduction of chloride ingress into concretes made with SCB and SCC cements that contain from 30 to 70% slag. Corrosion of steel bars with a large amount of chloride at the vicinity of the cracked region for a dense concrete was explained separately and will not be covered here (6).

Concentrated sulfate rich region was found at the vicinity of both the unhealed and healed cracks. However, the depth was relatively narrower for SCB and SCC. The depth of sulfate ingress was much lower than the same for chloride. Concentrated magnesium oxide was found in the healed region. The trace of magnesium oxide was also found onto the split open crack planes of
unhealed wider cracks. Interestingly, the sulfate rich region shows remarkably low chloride concentration irrespective of the cement mass. It is understood that the presence of sulfate may cause the dissolution of the Friedel’s salt. It also reduces the affinity to adsorb chloride in the hardened matrix as the chloride concentration was very low at the sulfate rich region.

No significant traceable leaching of calcium was found from the cracked region for healed or unhealed cracks when compared to the inner regions of the specimens. A very thin surface region of less than 1 mm is seen with less calcium oxide by EPMA mapping. This indicates that the leached Ca from the very vicinity of the crack was recharged by the calcium ions from the inner region and thereby maintained a uniformity of calcium ions in the matrix. Further study of the ion migration is necessary to confirm this.

Reactions Involved

The following reactions are supposed to be responsible for the formation of calcite at the cracked regions (2):

\[ Ca^{\text{(II)}} + CO_3^{\text{(-)}} \Leftrightarrow CaCO_3 \ (pH > 8.0) \]

\[ Ca^{\text{(II)}} + HCO_3^- \Leftrightarrow CaCO_3 + H^+ \ (7.5 < pH < 8.0) \]

The pH of seawater was 7.7. In the cracked region, it can be raised further due to the leaching of calcium ions from the concrete. With the presence of carbonate or bicarbonate ions in seawater, the above-mentioned reactions are anticipated at the cracked region.

It is expected that the monosulfate hydrates at the vicinity of the cracks or onto the fractured surface are transferred to ettringite due to the ingress of sulfate from seawater as shown below (7):

\[
\text{MgSO}_4 + [Ca(OH)_2 + 3CaO.Al_2O_3.CaSO_4.18H_2O] \rightarrow \\
\text{Mg(OH)}_2 + 3CaO.Al_2O_3.3CaSO_4.32H_2O
\]

Due to the absence of chloride at the sulfate rich region, but the presence of the abandoned ettringite indicate that the following conversion reactions take place at the vicinity of the crack. At the initial stage, Friedel’s salt is expected to transform into monosulfate caused by the replacement of chloride in Friedel’s salt by sulfate. With the gradual build-up of sulfate at the surface region, the monosulfate is finally transformed to the ettringite. This process causes the liberation of chloride and also movement of chloride from sulfate rich region.

\[ \text{Friedel’s Salt (3CaO.Al}_2\text{O}_3.CaCl}_2.10\text{H}_2\text{O)} \rightarrow \text{Monosulfate (3CaO.Al}_2\text{O}_3.CaSO}_4.12\text{H}_2\text{O) } \rightarrow \text{Ettringite (3CaO.Al}_2\text{O}_3.3CaSO}_4.32\text{H}_2\text{O) } \]
The presence of magnesium hydroxide is due to the following reactions (7):

\[ MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaCl_2 \]

\[ MgSO_4 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaSO_4 \cdot 2H_2O \]

CONCLUSIONS

From the scope of this study, the following conclusions are drawn:

1. Healing observed at the narrower cracks irrespective of the cement types, such as ordinary portland cement, slag cement of types A, B, and C, and fly ash cement of type B. Wider cracks larger than 0.5 mm were not healed. Healing continues to the steel bars as well as the debonded area along the steel bars. The deposits were confirmed as calcite, ettringite, magnesium oxide, and rust.

2. Healing causes a reduction in chloride ingress through the cracks, especially for the cases with a large amount of slag, such as SCB and SCC. Accumulation of more chloride was found at unhealed cracks for these cements.

3. Sulfate rich region was observed on a thin region from the crack plane. This region shows a very low chloride concentration. It indicates that Friedel’s salt diminishes with the presence of sulfate. Also the affinity to adsorb chloride in the cement matrix reduces with the presence of sulfate.

4. Sulfate ingress is much lower than chloride ingress.

5. Magnesium oxide rich region was observed in the healed crack path only.

6. Healing is found to be an effective way for making sustainable concrete structures in the marine environment.

ACKNOWLEDGEMENTS

The authors wish to express their gratitude and sincere appreciation to the authority of Port and Airport Research Institute, Yokosuka, Japan for financing several on-going research projects related to the durability of concrete structures. The authors also express their sincere thanks to the previous members of the materials laboratory for planning several long-term experimental plans.
REFERENCES


### Table 1 Plan of the Specimens

<table>
<thead>
<tr>
<th>Specimen's Title</th>
<th>Tidal Zone</th>
<th>Submerged Zone</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(OPC-T-45)</td>
<td>3 (0.2,0.1,0.1)</td>
<td>1 (0.1)</td>
</tr>
<tr>
<td>2(OPC-T-55)</td>
<td>3 (0.1,0.1,0.1)</td>
<td>1 (0.1)</td>
</tr>
<tr>
<td>3(OPC-S-45)</td>
<td>3 (0.1,2.0,0.1)</td>
<td>3 (0.1,0.1,0.1)</td>
</tr>
<tr>
<td>4(OPC-S-55)</td>
<td>3 (0.1,0.1,0.1)</td>
<td>1 (0.1)</td>
</tr>
<tr>
<td>5(SCA-T-45)</td>
<td>3 (0.1,0.3,0.2)</td>
<td>1 (0.1)</td>
</tr>
<tr>
<td>6(SCA-T-55)</td>
<td>3 (0.2,0.3,0.2)</td>
<td>1 (0.1)</td>
</tr>
<tr>
<td>7(SCA-S-45)</td>
<td>3 (0.15,0.2,0.3)</td>
<td>-</td>
</tr>
<tr>
<td>8(SCA-S-55)</td>
<td>3 (0.2,1.0,2.0)</td>
<td>1 (0.1)</td>
</tr>
<tr>
<td>9(SCB-T-45)</td>
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<td>2 (0.1,0.1)</td>
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<tr>
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<td>3 (0.1,0.1,0.8)</td>
</tr>
<tr>
<td>11(SCB-S-45)</td>
<td>3 (0.3,0.2,0.1)</td>
<td>2 (0.1,0.1)</td>
</tr>
<tr>
<td>12(SCB-S-55)</td>
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<td>3 (1.5,0.6,0.9)</td>
</tr>
<tr>
<td>13(SCC-T-45)</td>
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<td>2 (1.5,1.5)</td>
</tr>
<tr>
<td>14(SCC-T-55)</td>
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<td>3 (0.3,0.1,1.0)</td>
</tr>
<tr>
<td>15(SCC-S-45)</td>
<td>2 (0.8,0.7)</td>
<td>-</td>
</tr>
<tr>
<td>16(SCC-S-55)</td>
<td>3 (1.5,2.5,5.0)</td>
<td>1 (0.1)</td>
</tr>
<tr>
<td>17(FACB-T-45)</td>
<td>3 (0.1,0.3,0.5)</td>
<td>-</td>
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<td>18(FACB-T-55)</td>
<td>2 (0.1,0.3)</td>
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<td>19(FACB-S-45)</td>
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</tr>
<tr>
<td>20(FACB-S-55)</td>
<td>3 (0.3,0.2,0.1)</td>
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</table>

*OPC - ordinary portland cement, SCA - slag cement of Type A, SCB - slag cement of Type B, SCC - slag cement of Type C, FACB - fly ash cement of Type B, T - tap water (mixing water), S - seawater (mixing water), 45 and 55 are % of W/C.

*The figures in the bracket indicate crack width in mm.*
Table 2 Physical Properties and Chemical Compositions of Cements (OPC, SCA, SCB, SCC and FACB)

<table>
<thead>
<tr>
<th>Items</th>
<th>OPC</th>
<th>SCA</th>
<th>SCB</th>
<th>SCC</th>
<th>FACB</th>
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<tr>
<td>Specific Gravity</td>
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<td>3.07</td>
<td>3.03</td>
<td>2.97</td>
<td>2.97</td>
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<tr>
<td>Blaine Fineness, cm²/g</td>
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<td>3610</td>
<td>3700</td>
<td>3980</td>
<td>3190</td>
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<tr>
<td>Ignition Loss, %</td>
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<td>0.9</td>
<td>0.7</td>
<td>0.9</td>
<td>0.6</td>
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<tr>
<td>SiO₂, %</td>
<td>21.3</td>
<td>24.9</td>
<td>26.5</td>
<td>28.9</td>
<td>20.4</td>
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<tr>
<td>Al₂O₃, %</td>
<td>5.3</td>
<td>7.8</td>
<td>9.2</td>
<td>11.3</td>
<td>4.7</td>
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<tr>
<td>CaO, %</td>
<td>64.4</td>
<td>56.8</td>
<td>53.4</td>
<td>47.9</td>
<td>54.2</td>
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<tr>
<td>MgO, %</td>
<td>2.2</td>
<td>3.8</td>
<td>4.3</td>
<td>5.2</td>
<td>1.3</td>
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<td>SO₃, %</td>
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<td>2</td>
<td>2</td>
<td>1.9</td>
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<td>Na₂O, %</td>
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<td>K₂O, %</td>
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<td>-</td>
<td>-</td>
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<td>TiO₂, %</td>
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<td>MnO, %</td>
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<td>-</td>
<td>-</td>
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<td>Fe₂O₃, %</td>
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<td>1.8</td>
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<td>P₂O₅, %</td>
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<td>-</td>
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<tr>
<td>C, %</td>
<td>0.01</td>
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<tr>
<td>S, %</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
<td>-</td>
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- Indicate unknown items. OPC satisfied JIS R5210: SCA, SCB and SCC satisfied JIS R5211; and FACB satisfied JIS R5213.

Table 3 Classifications of Slag and Fly Ash Cements (JIS R5211-1992, JIS R5213-1992)

<table>
<thead>
<tr>
<th>Type</th>
<th>Slag or Fly Ash Content (Weight %)</th>
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<tr>
<td>Slag Cement A</td>
<td>5 – 30</td>
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<tr>
<td>Slag Cement B</td>
<td>30 – 60</td>
</tr>
<tr>
<td>Slag Cement C</td>
<td>60 – 70</td>
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<td>Fly Ash Cement B</td>
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Table 4 Aggregate Properties

<table>
<thead>
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<th>Specific Gravity</th>
<th>Absorption (%)</th>
<th>Fineness Modulus</th>
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<tr>
<td>Sand</td>
<td>2.64</td>
<td>1.82</td>
<td>2.89</td>
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<tr>
<td>Gravel</td>
<td>2.76</td>
<td>1.10</td>
<td>6.66</td>
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</table>
Table 5 Chemical Compositions of Steel Bar

<table>
<thead>
<tr>
<th>C (%)</th>
<th>Si (%)</th>
<th>Mn (%)</th>
<th>P (%)</th>
<th>S (%)</th>
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</thead>
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<tr>
<td>0.1</td>
<td>0.21</td>
<td>0.66</td>
<td>0.02</td>
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</table>

Table 6 Mixture Proportions

<table>
<thead>
<tr>
<th>Case</th>
<th>W/C</th>
<th>S/(S+G)</th>
<th>W</th>
<th>C</th>
<th>S</th>
<th>G</th>
<th>AEWRA</th>
<th>AEA</th>
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<tbody>
<tr>
<td>1,3  OPC-T or S-45 0.45</td>
<td>41</td>
<td>162</td>
<td>360</td>
<td>738</td>
<td>1110</td>
<td>3.60</td>
<td>360</td>
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<td>2,4  OPC-T or S-55 0.55</td>
<td>45</td>
<td>166</td>
<td>302</td>
<td>826</td>
<td>1056</td>
<td>3.02</td>
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<tr>
<td>5,7  SCA-T or S-45 0.45</td>
<td>42</td>
<td>160</td>
<td>356</td>
<td>756</td>
<td>1091</td>
<td>3.56</td>
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<td>6,8  SCA-T or S-55 0.55</td>
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<td>9,11 SCB-T or S-45 0.45</td>
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<td>160</td>
<td>355</td>
<td>736</td>
<td>1108</td>
<td>3.55</td>
<td>355</td>
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<tr>
<td>10,12 SCB-T or S-55 0.55</td>
<td>43</td>
<td>162</td>
<td>295</td>
<td>793</td>
<td>1099</td>
<td>2.95</td>
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<tr>
<td>13,15 SCC-T or S-45 0.45</td>
<td>41</td>
<td>162</td>
<td>360</td>
<td>714</td>
<td>1120</td>
<td>3.60</td>
<td>360</td>
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<tr>
<td>14,16 SCC-T or S-55 0.55</td>
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<td>164</td>
<td>298</td>
<td>789</td>
<td>1094</td>
<td>2.98</td>
<td>298</td>
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<tr>
<td>17,19 FACB-T or S-45 0.45</td>
<td>41</td>
<td>160</td>
<td>356</td>
<td>733</td>
<td>1103</td>
<td>3.56</td>
<td>356</td>
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<td>18,20 FACB-T or S-55 0.55</td>
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<td>295</td>
<td>790</td>
<td>1096</td>
<td>2.95</td>
<td>295</td>
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All notations are explained in Table 2.

Table 7 Physical Properties and Chemical Composition of Seawater

<table>
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<tr>
<th>Specific Gravity</th>
<th>pH</th>
<th>Na</th>
<th>K</th>
<th>Ca</th>
<th>Mg</th>
<th>Cl</th>
<th>SO_4</th>
<th>CO_3</th>
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<tbody>
<tr>
<td>1.022</td>
<td>7.77</td>
<td>9290</td>
<td>346</td>
<td>356</td>
<td>1167</td>
<td>17087</td>
<td>2378</td>
<td>110</td>
</tr>
</tbody>
</table>
The specimens were cracked in the laboratory at the age of 28 days and then exposed to the tidal environment.

Cover Concrete = 45.5 mm

The beams were cracked by bending. For this, the ends of the beam were supported on rollers and a load was gradually applied until the crack width became a pre-specified value.

Fig. 1. Layout of the Specimens

W/C=0.55, Crack Width =0.5 mm
Deposit on Concrete Surface and in Crack

W/C=0.55, Crack Width =0.1 mm
Healed Crack

Optical Microscopic View

Photographs of Concrete Surface and Crack Plane

Fig. 2. Deposit in Crack
Fig. 3. SEM Micrograph of the Deposit in Crack (5 mm from the surface)

Fig. 4. SEM Micrograph of the Deposit in Crack (13 mm from the surface)
SCB-T-45(2), Crack Width = 0.1 mm

Fig. 5. SEM Micrograph of the Deposit in Crack (25 mm from the surface)

Fig. 6. SEM Micrograph of the Deposit in Crack (40 mm from the surface)
Recent Advances in Concrete Technology

SCB-T-45(2), Crack Width = 0.1 mm

Fig. 7. SEM Micrograph onto the Split Open Crack Plane

Narrow cracks
< 0.5 mm

Wide cracks
> 0.5 mm

White Deposit (ettringite, CaCO3)

Loss of bar diameter around the perimeter

Fig. 8. Schematic Diagram of the Condition of the Steel Bars in Crack
Fig. 9. SEM Micrograph of the Deposit on the Steel Bar at and Near Crack
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**Fig. 10. Healing Over the Steel Bar in Crack**

**Fig. 11. XRD Chart of Deposit in Crack**

C: Calcite; V: Vaterite, Ar: Aragonite, Br: Brucite, Others: Different Rocks
Fig. 12. Schematic Diagram of the Distribution of Chloride, Sulfate, and Magnesium Oxide from Crack
Corrosion Study of Stainless Steel Bars in Cracked Concrete

by T. Yamaji, T. Hirasaki, R. Takahashi, S. Mizuma, and M. Yamakawa

Synopsis:

Corrosion of stainless steel bars in concrete was investigated using sound and pre-cracked concrete specimens. Three types of stainless steel were investigated, such as 18Cr, 18Cr-8Ni and 18Cr-12Ni-2.5Mo. Concrete specimens were exposed to two environments, where wetting and drying alternately repeated. One was in the outdoor with atmospheric temperature, and the other was in a controlled chamber, where the temperature was 60°C during wetting and 15°C during drying.

The detail investigation was carried out after two years. No corrosion was observed on stainless steel bar in both sound and pre-cracked concrete exposed to outdoor. The maximum chloride ion concentration was 7.0 kg/m^3 for 18Cr-8Ni, 8.0 kg/m^3 for 18Cr-12Ni-2.5Mo and 6.0 kg/m^3 for 18Cr at the crack region of concrete. This result indicated that the chloride ion threshold level for stainless steel was larger than these values under marine environment with atmospheric temperature.

No corrosion was observed on both 18Cr-12Ni-2.5Mo and 18Cr in both sound and pre-cracked concrete exposed to controlled chamber. However, corrosion was observed only for 18Cr-8Ni at the crack region, even when the chloride ion concentration at the crack region was 6.0 kg/m^3. This was considered to be due to the effect of a high temperature.

Keywords: chloride; corrosion; cracked concrete; stainless steel
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**INTRODUCTION**

The durability of reinforced concrete structures largely depends on the corrosion of steel bars. This indicates that their durability will be much improved if replaced by the steel reinforcement with corrosion-resistant alloy, such as stainless steels [1]. In the sound concrete without crack, stainless steel in concrete was not corroded at high chloride ion concentration [1], and it was
reported that no corrosion occurred for a widely used austenitic stainless steel (18Cr-8Ni), even when a chloride ion concentration was 24 kg/m³ of concrete [2]. However, when concrete is cracked, the chloride ion concentration is high and pH is decreased around stainless steel bar. Also, stainless steels tend to corrode at the crevice, such as a crack region, where the difference of oxygen concentration occurs (this type of corrosion is called ‘crevice corrosion’). Therefore, it is considered that the corrosion threshold level may be decreased at the crack region compared to the uncracked region.

In this study, to investigate the corrosion property of stainless steel in cracked concrete, pre-cracked concrete specimens with stainless steel were exposed under two marine environments. Also, pitting potential of the stainless steels in simulated concrete pore solution with different chloride concentrations was measured by using electrochemical method.

**EXPERIMENTAL**

**Property of Stainless Steel Used in This Study**

Table 1 shows the chemical composition of three types of stainless steel (two types of austenitic stainless steel and one type of ferritic stainless steel) and carbon steel used in this study. Corrosion-resistant property is enhanced by increasing the amount of Cr and Mo contents. Therefore, steel type SUS316 (18Cr-12Ni-2.5Mo) has the best corrosion-resistant property among the three stainless steels, followed by steel type SUS304 (18Cr-8Ni) and SUS 430 (18Cr). Fig. 1 shows the pitting potential [3], which represents corrosion-resistant property. The relationships are the same as mentioned above for all kinds of stainless steels. Table 2 shows the mechanical and physical properties. Steel types SUS 304 and 316 have almost the same property as carbon steel, except higher elongation than carbon steel.

**Exposure Test**

Normal portland cement was used. Crushed gravels (relative density: 2.64, fineness modulus: 6.71) and sand (relative density: 2.61, fineness modulus: 2.65) were used as coarse aggregate and fine aggregate. Table 3 shows the mixture proportion. It was determined to satisfy that the slump was between 80 ± 25 mm and the air content was between 4 ± 1.5 %. Here, the W/C was set at a
comparatively higher value, to make chloride ingress faster. The compressive strength of concrete at 28 days was 33.1 MPa. Fig. 2 shows the scheme of specimens. The size of specimen for corrosion study was 100x100x400 mm. Reinforcement bars of diameters 13 mm were embedded at 20 and 43.5 mm of cover depth. Some specimens were cracked by bending in the laboratory before exposure. Table 4 shows the list of specimens. Here, ‘0’ means carbon steel, ‘1’ means SUS304, ‘2’ means SUS316 and ‘3’ means SUS430. ‘N’ means sound concrete without crack and ‘C’ means pre-cracked concrete. Crack widths varied between 0.1 and 0.4 mm. Specimens were exposed to two environments with wetting and drying alternately repeated. In one environment, wetting was carried out by spraying natural seawater in the outdoor for about three hours, and drying was carried out by exposing in the outdoor for about nine hours. This wetting and drying cycle repeated two times per day. In the other environment, wetting was carried out by soaking in a 60 °C natural seawater for three days, and drying was carried out by exposing for four days in the chamber at temperature 15 °C and humidity 40 ~ 70 %. This drying and wetting cycle was decided as per the standard of Japan Concrete Institute, JCI-SC3 [4]. Hereafter, the former environment is described as ‘splash environment’, and the latter environment is described as ‘accelerated environment’. Exposure term to the splash environment was 2.2 years, and that to the accelerated environment was 110 cycles (almost 2.1 years). Half-cell potentials were measured by putting the reference electrode (saturated KCl-Ag/AgCl electrode: SSE) on the concrete surface, after soaking in a 20 °C natural seawater for one or two days. Total (acid soluble) chloride ion concentration in concrete was measured based on JCI-SC4 [4]. Samples were cut from both the specimen for corrosion study and the specimen for measuring the chloride ion profile, as shown in Figure 2. Corrosion of steel bar was estimated after tracing the corroded area on a transparent plastic film.

**Measurement of Pitting Potential**

Pitting potential of stainless steels was measured, in order to carry out the corrosion study of stainless steel in concrete. The measurement was carried out just after soaking the metal specimens (20x20x2 mm) in the simulated concrete pore solution. Here, any surface treatment was not carried out before measurement. The room temperature was about 20 °C, however, the
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temperature in the solution was not controlled. The pitting potential was defined as the potential when current density reached at $1.00 \times 10^{-3}$ A/m$^2$ with sweeping at the rate of 20 mV/min, forward to anodic direction, based on Japanese Industrial Standard. JIS G 0579. The concentration of chloride ion in the simulated concrete pore solution was done at 4 levels (1.9, 5.0, 8.3 and 12.7 %), and then the concentration of Ca(OH)$_2$ was at 2 levels (0% and saturated). Saturated Ca(OH)$_2$ solution means sound concrete. and 0 % Ca(OH)$_2$ solution means cracked concrete.

TEST RESULTS AND DISCUSSIONS

Results of Visual Observation

The specimen 0-N, which was sound concrete with carbon steels, cracked due to steel corrosion around 30 cycles under the accelerated environment. The other specimens did not crack, under both splash and accelerated environment.

Behavior of Half-Cell Potential

Fig. 3 shows the time-dependent change of half-cell potentials of each bar at 20 mm of cover depth in concrete exposed to the splash environment, and Fig. 4 shows the time-dependent change of half-cell potentials of each bar at 20 mm of cover depth in concrete exposed to the accelerated environment. Here, -230mV shown in Figs. 3, 4 means the corrosion threshold value for carbon steel, based on ASTM C 876 [5]. In Figs. 3, 4, the half-cell potentials of carbon steels in sound and pre-cracked concrete (0-N, 0-C) fell below -230 mV. These carbon steels were considered to be corroded. The half-cell potentials of austenitic stainless steels (1-N, 1-C, 2-N, 2-C) varied between -150 and -50 mV. Reference [6] indicated that austenitic stainless steel (SUS 304) in concrete did not corrode when the half-cell potentials varied between +45 and -155 mV vs. SSE (0 and -200 mV vs. SCE). Therefore, these austenitic steels were not considered to be corroded. The half-cell potentials of ferritic stainless steels (3-N, 3-C) were around -200mV at initial in Fig. 3, 4. The half-cell potentials of ferritic stainless steel in concrete seemed to become more negative than that of austenitic stainless steels. The tendency of change in half-cell potential was similar to austenitic stainless steels in Figs. 3, 4.
Chloride Ion Concentrations

Fig. 5 shows the profiles of total chloride ion concentration in concrete exposed to both splash and accelerated environment. The chloride ion concentration around the surface of concrete exposed to the accelerated environment was smaller than that in concrete exposed to the splash environment. However, the chloride ion concentration in internal part of concrete exposed to the accelerated environment was larger than that in concrete exposed to the splash environment.

Fig. 6 shows the total chloride ion concentration at 20 and 43.5 mm of cover depth in concrete exposed to the splash environment. The total chloride ion concentrations in sound concrete were between 5.0 and 6.0 kg/m$^3$ at 20 mm of cover depth, and between 0.5 and 1.0 kg/m$^3$ at 43.5 mm of cover depth. On the other hand, the total chloride ion concentrations in pre-cracked concrete were between 6.0 and 9.0 kg/m$^3$ at 20 mm of cover depth, and between 5.0 and 6.0 kg/m$^3$ at 43.5 mm of cover depth. The values at both cover depth in pre-cracked concrete and at 20 mm of cover depth in sound concrete exceeded the chloride threshold value for carbon steel, which is set at 1.2 kg/m$^3$ in Concrete Standard Specification in Japan [7].

Fig. 7 shows the total chloride ion concentration at 20 and 43.5 mm of cover depth in concrete exposed to the accelerated environment. The total chloride ion concentrations in sound concrete were between 1.0 and 2.5 kg/m$^3$ at 20 mm of cover depth, and between 0.5 and 1.0 kg/m$^3$ at 43.5 mm of cover depth. On the other hand, the total chloride ion concentrations in pre-cracked concrete were between 5.5 and 7.0 kg/m$^3$ at 20 mm of cover depth, and between 5.0 and 6.0 kg/m$^3$ at 43.5 mm of cover depth. The values at both cover depth in pre-cracked concrete much exceeded 1.2 kg/m$^3$.

Corroded Area of Each Bar

Fig. 8 shows the corroded area ratio of each bar in concrete exposed to the splash environment. Carbon steel in sound and pre-cracked concrete (0-N, 0-C) clearly corroded, except at 20 mm of cover depth in sound concrete when the chloride ion concentration was less than 1.0 kg/m$^3$. All stainless steels did not corrode in sound and pre-cracked concrete. The maximum chloride ion concentration was 7.0 kg/m$^3$ for 1-C, 8.0 kg/m$^3$ for 2-C and 6.0 kg/m$^3$ for 3-C, at 20 mm of cover depth in pre-cracked concrete. Therefore, it is considered that
the chloride threshold level for stainless steel was larger than these values under marine environment with atmospheric temperature.

Fig. 9 shows the corroded area ratio of each bar in concrete exposed to the accelerated environment. Carbon steel in sound concrete corroded, and also SUS304 at 20 mm of cover depth in pre-cracked concrete (1-C) corroded at the crack region. However, the corroded area ratio was only 0.2%. Other stainless steels did not corrode in sound and pre-cracked concrete.

**Corrosion Study of Stainless Steels in Cracked Concrete**

SUS304 corroded at the chloride ion concentration of 6.13 kg/m³ in pre-cracked concrete under the accelerated environment where the temperature was 60 °C during wetting. In order to carry out the corrosion study of stainless steels, it is effective to compare the pitting potential of stainless steel in concrete with the half-cell potentials of stainless steel. In this study, the pitting potential was estimated based on the results of simulated concrete pore solution, and it was compared with the half-cell potential shown in Fig. 4.

Fig. 10 shows the pitting potential in the simulated concrete pore solution with different chloride ion concentrations. Here, simulated conditions were two kinds. One simulated a sound concrete, which Ca(OH)₂ was saturated in the solution. The other simulated a cracked concrete, which Ca(OH)₂ was not added in the solution. Pitting potential decreased when chloride ion concentration increased, and decreased when Ca(OH)₂ was not added in the simulated concrete pore solution, that is, when pH around bars in concrete was lower. Also, pitting potential was affected by temperature as shown in Fig. 1, which was the result of 3% NaCl solution without Ca(OH)₂.

The pitting potential of stainless steel at the crack region in concrete exposed to the accelerated environment was estimated as shown in the Fig. 11. First, the pitting potential, at the temperature of 60 °C and at NaCl concentration of 3% without Ca(OH)₂ which simulated lower pH concrete, was estimated as the point A in Fig. 11 (a). Second, the difference of pitting potential (ΔEₚ), between the chloride ion concentration of 3% NaCl (2.90 kg/m³) of concrete and each chloride ion concentration of concrete (x kg/m³) at the temperature of 20 °C, was estimated as shown in Fig. 11 (b). Finally, the pitting potential, at the temperature of 60 °C and at each chloride ion concentration of concrete under lower pH in concrete, was estimated as the point D in Fig. 11 (a),
by subtracting $\Delta E_p$ from the point A. Here, it was assumed that the gradient of line in Fig. 11 (a) was independent of the chloride ion concentration, and the gradient of line in Fig. 11 (b) was independent of the temperature. Table 5 shows the pitting potentials at 60 °C without Ca(OH)$_2$, estimated by the procedure mentioned above. The pitting potential at each chloride ion concentration were estimated as -41.1 mV for SUS316, -130.4 mV for SUS304 and -232.8 mV for SUS430.

Fig. 12 shows the comparison of the half-cell potentials in pre-cracked concrete exposed to accelerated environment with the pitting potential in Table 5. The half-cell potentials of SUS316, on which no corrosion was observed, were almost below the pitting potential. This indicated that pitting corrosion did not occur. The half-cell potentials of SUS304, on which corrosion was observed, were above the pitting potential by 40 to 90 mV until 80 cycles, and fell suddenly around 110 cycles. This indicated that pitting corrosion occurred around 110 cycles. The half-cell potentials of SUS430, on which no corrosion was observed, were above the pitting potential by 20 to 50 mV from 50 to 110 cycles. This difference in SUS430 between the half-cell and pitting potential was smaller than that in SUS304. Also, the half-cell potential of SUS430 did not fall below the pitting potentials all the time. These indicated that pitting corrosion did not occur at 110 cycles. However, the possibility of pitting corrosion was high.

**CONCLUSIONS**

In order to study the corrosion property of stainless steel in cracked concrete, pre-cracked concrete specimens with three kinds of stainless steel bars (18Cr-8Ni, 18Cr-12Ni-2.5Mo and 18Cr) were exposed under two marine environments. The conclusions obtained as the result of this study are shown below:

1) No corrosion was observed on each stainless steel bar in both sound and cracked concrete exposed to the marine environment, where wetting and drying alternately repeated for 2 years in the outdoor. The maximum chloride ion concentration became 7.0 kg/m$^3$ for 18Cr-8Ni, 8.0 kg/m$^3$ for 18Cr-12Ni-2.5Mo and 6.0 kg/m$^3$ for 18Cr at the crack region. The result indicated that the chloride ion threshold level for stainless steel was larger
than these values under marine environment with atmospheric temperature.

2) No corrosion was observed on both 18Cr and 18Cr-12Ni-2.5Mo stainless steel bars in both sound and pre-cracked concrete exposed to the marine environment, where wetting and drying alternately repeated for 2 years in the chamber. Here, the temperature was 60°C during wetting. The maximum chloride ion concentration became about 6.0 kg/m³ for 18Cr-12Ni-2.5Mo and 7.0 kg/m³ for 18Cr at the crack region. On the other hand, corrosion was observed only for 18Cr-8Ni stainless steel bar at the crack region for chloride ion concentration of 6.0 kg/m³. This was considered to be due to the effect of a high temperature.

REFERENCES

Table 1. Chemical Composition

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<td>SUS304 (18Cr-8Ni)</td>
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<td>SUS430 (18Cr)</td>
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Table 2. Mechanical and Physical Property

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<th>Tensile strength (N/mm²)</th>
<th>Proof stress (N/mm²)</th>
<th>Elongation (%)</th>
<th>Elastic modulus (x10⁵N/mm²)</th>
<th>Coefficient of thermal expansion (x10⁻⁵)</th>
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<td>7.84</td>
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<td>386</td>
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<td>244</td>
<td>30.3</td>
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*Yield stress

Table 3. Mixture Proportion

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Table 4. List of Specimens

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<th>Type of concrete</th>
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<th>Crack width (mm)</th>
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<td>Splash Accelerated</td>
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<td>0-N</td>
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Table 5. Pitting Potential at 60°C without Ca(OH)$_2$

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<th>Chloride ion concentration (kg/m$^3$)</th>
<th>Δ$E_p$: Decrease in pitting potential from 2.90 to $x$ kg/m$^3$</th>
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<tr>
<td>2.90 (3%NaCl)*</td>
<td>5.56**</td>
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<td>5.56**</td>
<td>6.13**</td>
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<td>6.13**</td>
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<td>-232.9</td>
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*: At 60°C in Fig. 1  **: Fig. 7  ***: Fig. 10
Fig. 1. The Relationship between Temperature and Pitting Potential [3]

Fig. 2. The Scheme of Specimens
Fig. 3. Time-Dependent Change of Half-Cell Potentials in Concrete Exposed to the Splash Environment

Fig. 4. Time-Dependent Change of Half-Cell Potentials in Concrete Exposed to the Accelerated Environment

Fig. 5. The profiles of Total Chloride Ion Concentration in Concrete
Fig. 6. Total Chloride Ion Concentration in Concrete Exposed to the Splash Environment

Fig. 7. Total Chloride Ion Concentration in Concrete Exposed to the Accelerated Environment

Fig. 8. Corroded Area Ratio of Each Bar in Concrete Exposed to the Splash Environment
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Fig. 9. Corroded Area Ratio of Each Bar in Concrete Exposed to the Accelerated Environment

Fig. 10. The Dependence of Chloride Ion Concentration for Pitting Potential of Various Stainless Steels in the Simulated Concrete pore solution
Fig. 11. Estimation of Pitting Potential at Each Chloride Ion Concentration

Fig. 12. Comparison of Half-Cell Potential with Pitting Potential
Working Mechanism of a Shrinkage-Reducing Superplasticizer of New Generation

by K. Yamada, H. Nakanishi, S. Tamaki, M. Yaguchi, M. Kinoshita, and S. Okazawa

Synopsis:

The working mechanism of a polycarboxylate superplasticizer (PC) which is a new generation of superplasticizer (NSP) is investigated. This NSP shows a shrinkage reducing effect as well as a water reducing effect with adequate slump retention in a wide range of water cement ratio by introducing a shrinkage-reducing component (SRC) into the molecular structure. Superplasticizers have been thought to be adsorbed on cement hydrates and to show their particle dispersing effects by modifying the inter-particle potentials. On the other hand, shrinkage reducing agents of the organic type have been thought to exist at the interface between the aqueous and the pore phases in hardened cement paste and to show their shrinkage reducing effects by reducing the surface tension, which occasionally results in the degradation of freezing and thawing (F/T) resistance. In this study, the mechanisms of NSP are discussed. By building a SRC into the molecular structure, the entrained air system is expected to be controlled successfully compared to traditional shrinkage-reducing agents (SRA) and so the degradation of F/T resistance can be avoided. With the progress of hydration, SRC is released from NSP and the surface tensions decreases, which results in the reduction of drying shrinkage.

Keywords: freezing and thawing; polycarboxylate; shrinkage reducing admixture; superplasticizers
INTRODUCTION

In the field of chemical admixtures, the 1st generation was air-entraining (AE) agent, which enhances freezing and thawing (F/T) resistance. The 2nd generation was AE water-reducing agent. The 3rd was poly-beta-naphthalene sulfonate condensate (PNS) and poly-melamine sulfonate condensate (PMS) called as a superplasticizer, which enabled to obtain high strength concrete. The 4th was polycarboxylate with polyether graft chain (PC). Although PC enabled very high water reduction and its fluidity retention, it is necessary to prepare several kinds of PC in order to make concrete with wide range of a water cement ratios (W/C).

As the concrete technology advances, users expect better performance in terms of durability as well as high strength or high flowability and also good fluidity retention. In order to realize a concrete structure with high durability, it is required to develop effective methodology for the mitigation of cracks. One of major causes of cracking in concrete are due to volumetric changes resulted from shrinkage, for example drying shrinkage in general concrete and autogenous shrinkage in high strength concrete.

In recent years, studies of concrete shrinkage have proposed several mitigative methodologies. Above all, the Capillary Tension Mechanism is regarded as the most useful (1), (2), (3), (4). Commercial products of shrinkage reducing admixtures (SRA) can reduce concrete volumetric changes. However, the dosage is very high around 2 % by
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mass of cement. One problem of SRA is occasional degradations of freezing/thawing resistance. By keeping an appropriate entrained air system, durable concrete can be obtained. Besides, additional equipment to supply SRA is needed to be installed in concrete plants.

In order to satisfy these various requirements, one new category of chemical admixture can be proposed as the 5th generation. That is NSP with multifunction performance for multipurposes. Sugiyama et al, (5) found that by introducing a drying shrinkage-reducing component (SRC) into the molecular structure of PC, NSP can reduce drying shrinkage and still keep the performance of superplasticizer as well. The authors have shown that this type of NSP can be applied to wide range of W/C from 55 % to 20 % (6).

PC is thought to work as a dispersant by modifying the surface potential of fine particles by its steric hindrance effect (7). This becomes effective only after their adsorptions to the cement grains. SRA is thought to reduce the shrinkage by reducing the surface tension of pore solution. This can be achieved by their being present at the interface between the pore solution and the empty pore. Therefore, SRA must exist in solution phase. NSP realizes these contradicting requirements simultaneously. This study aims to investigate the working mechanism of this NSP.

EXPERIMENTS

Materials

The materials used in experiments are summarized in Table 1. The cement used was Japanese normal portland cement. The aggregates used were crushed sand as fine aggregate and crushed hard sandstone as coarse aggregate.

As organic admixtures, two kinds of commercial PC, SP1 and SP2 and two kinds of NSP, NSP1 and NSP2 were used. SP1 is suitable for higher W/C from 55 % to 40 % and SP2 is for that lower than 30 %. NSP1 is designed to show a high water reducing performance as well as a shrinkage reducing performance. NSP2 is designed to show a higher shrinkage reducing performance. Estimated molecular structures of SP1, SP2, and NSP are shown in Fig. 1. Solid contents of these admixtures are around 20 – 25 mass%. SRC used was diethylene glycol dipropylene glycol monobutyl ether. The major difference between NSP1 and NSP2 is the ratio of SRC in a molecule. NSP2 has more number of SRC in a molecule.

A kind of commercial SRA, which is composed of ethylene glycol tetrapropylene glycol monomethyl ether was also tested as comparison.

Mixture Proportion of Concrete

PC is used in a wide range of W/C. Therefore, W/C of concrete test was set at
52.5, 47.1 and 22%. The dosage of SRA was fixed as 2.0 mass% of cement.

The target slump was set as 18 cm for the mixtures 1 and 2, and as 60 cm of slump flow for the mixture 3. The workability was adjusted by changing the dosage of SP. The target air content was set as 4.5% for the mixtures 1 and 2 and as less than 2.0% for the mixture 3. The mixture proportions are shown in Table 2.

In some cases, the performances of PC and NSP were evaluated in mortar mixtures, the mixture 4 in Table 2. W/C was set as 47.1% and sand/cement ratio was 3.0.

Sample Preparation

The concrete of mixtures 1 and 2 was mixed in a pan-type forced mixer of 50-litter capacity for 90 s. The mixing time of mixture 3 was prolonged to 180 s. The mortar mixture 4 was mixed by a Hobart mixer for 5 min.

Evaluation of Basic Performances

The properties of concrete were evaluated by the following methods. Slump and air was measured in accordance with JIS A 1101 and 1128 respectively. The compressive strength was measured in accordance with JIS A 1108. The setting time was measured in accordance with JIS A 1147. The length change was measured in accordance with JIS A 1129. Specimens were kept in a room at 20°C and 60%RH for the evaluation of drying shrinkage. F/T resistance was measured in accordance with JIS A 1148. Specimens were cured in water for 2 weeks before testing. F/T was carried out in water. The autogenous shrinkage was measured in accordance with “Test method for autogenous shrinkage and autogenous expansion of cement paste, mortar and concrete” by JCI. Rectangular specimens of 100x100x400 mm were used, and all specimens were sealed and stored in a room at temperature of 20°C.

Characterization

In order to characterize the hardened concrete, the following analyses were carried out. The microstructure of concrete was observed by a scanning electron microscope. Pore solution was extracted by using a high-pressure vessel. The surface tension of pore solution was measured by a surface tension meter using a platinum plate. The chemicals in pore solution were measured by a size exclusion chromatograph (SEC).

RESULTS AND DISCUSSIONS

Basic performance of NSP1

Results of concrete tests are summarized in Table 3 (6). In every W/C, NSP1 shows equivalent fluidity compared with SP1. NSP1 shows the better slump retention in W/C =
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47.1% than SP1. Setting time is slightly delayed when NSP1 is used in low W/C. Compressive strength is almost the same in every range of W/C. Drying shrinkage can be reduced around 10% by using NSP1 compared with SP1.

Performance of NSP2

By changing the ratio of SRC in the molecular structure, the performance of shrinkage reducing can be modified. SRC occupies several sites of the carboxylic group and this results in the reduction of adsorption site for cement hydrates. The relationship between the dosage of admixtures and mortar flows are shown in Fig. 2. Although SP1, SP1 with SRA, and NSP1 show a similar flow, NSP2 requires double dosage for the equivalent flow. However, as shown in Fig. 3, the performance of shrinkage reduction is improved. At the same dosage of 0.8 mass% of NSP2 with SP1, the drying shrinkage was reduced as much as 25% at 12 weeks. With 2 mass% of SRA, the reduction of drying shrinkage was 35%. Significant reduction of drying shrinkage can be obtained by the limited amount of admixture by using NSP2.

Freezing/thawing resistance

One problem of SRA is occasional degradations of F/T resistance. With special cautions to keep the entrained air system, this problem can be avoided. However, for more safety, it is desirable to improve the F/T resistance.

The test results of concrete of W/C = 47.1% are shown in Fig. 4. In this case, SRA degrades the F/T resistance whereas NSP1 shows good F/T resistance. In order to study the mechanism of poor F/T resistance of SRA, various characteristics of hardened concrete were evaluated. The chemical composition of pore solution extracted under high pressure and the pore size distribution by mercury intrusion porosimetry were evaluated. However, no significant relationship with the F/T resistance was found in this study. SEM observation of the surface of entrained air bubbles indicated the different textures. The bubble surface of specimens with SP1 and NSP1 are relatively smooth and had a small number of crystal hydrates. However, the bubble surface of that with SRA is perfectly covered by many larger crystals of hydrates. This suggests that the bubble is occupied with water instead of air and this lack of air is thought to reduce the F/T resistance of SRA.

Mechanism of the reduction of shrinkage

In order to study the mechanism of the reduction of drying shrinkage, the pore solutions in hardened mortar were evaluated. For better precision a relatively large amounts of expressed solution is required for the measurement of surface tension and so mortar specimens at young ages were used as well as concrete specimens.

The measurement results by SEC are shown in Fig. 6. The component of dispersant appears around 14 min. This component disappears after hydration and is thought to be adsorbed on the cement hydrates. Peaks from 17 to 27 min are noise. The
SRC in mixing water is limited as shown in Fig. 6 and the concentration increases with the progress of hydration. This increase is thought to be caused by the release of SRC from NSP1 by debonding from the site of carboxylic group. By building SRC into the molecular structure, it is possible to avoid the effect of SRC on the entrained air system and to obtain the shrinkage reducing effect after hardening.

The relationships between surface tension and the length change by drying are shown in Fig. 7. The data of concrete, wet-screened (WS) mortar, and separately mixed (SM) mortar are shown. In each case, linear relationships are observed and the reduction of surface tension is judged to be the reason of the reduction of the drying shrinkage.

CONCLUSIONS

The working mechanism of a new PC with multifunction capabilities were investigated.

1) NSP1 shows equivalent performances with conventional PC in general. Besides, NSP1 reduces drying and autogenous shrinkage around 10%.
2) By modifying the chemical composition of NSP, the shrinkage-reducing performance can be enhanced. NSP2 shows 25% reduction of drying shrinkage with the dosage of 0.8 mass% whereas 2.0 mass% of SRA with 0.8 mass% of SPI reduces 35% of shrinkage.
3) By building SRC into the molecular structure, the degradation of freezing and thawing resistance can be avoided. The degradation is thought to be caused by the existence of water in entrained air bubbles.
4) The mechanism of drying-shrinkage reduction of NSP is thought to be the reduction of surface tension by SRC released with the progress of hydration.

ACKNOWLEDGMENTS

The authors express their appreciations to Dr. Y. Tanaka, Mr. K. Umezawa, Dr. A. Ohta, NMB Co., Ltd, Mr. H. Ozu of R&D center, Taiheiyo Cement Corp. and the staffs of Cement & Concrete Technology Center, Taiheiyo Cement Corp, Central research laboratory of NMB Co., Ltd, and Chemical Admixture Division of Takemoto Oil&Fat Co., Ltd, who assisted this study.

REFERENCES

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<table>
<thead>
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</thead>
<tbody>
<tr>
<td><strong>Cement (C)</strong></td>
<td>Normal Portland cement. Density = 3.16 g/cm³</td>
</tr>
<tr>
<td><strong>Water (W)</strong></td>
<td>Tap water</td>
</tr>
<tr>
<td><strong>Fine aggregate (S)</strong></td>
<td>Crushed sand. Density = 2.60 g/cm³</td>
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<tr>
<td><strong>Coarse aggregate (G)</strong></td>
<td>Crushed hard sandstone, Density = 2.64 g/cm³</td>
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<tr>
<td><strong>Organic Admixture</strong></td>
<td>SP1: Polycarboxylate Superplasticizer (commercial product)</td>
</tr>
<tr>
<td></td>
<td>SP2: Polycarboxylate Superplasticizer (commercial product)</td>
</tr>
<tr>
<td></td>
<td>NSP1: Polycarboxylate New Superplasticizer (Highly water reducing type)</td>
</tr>
<tr>
<td></td>
<td>NSP2: Polycarboxylate New Superplasticizer (Highly shrinkage reducing type)</td>
</tr>
<tr>
<td></td>
<td>SRA: Shrinkage reducing agent</td>
</tr>
<tr>
<td><strong>Inorganic additive</strong></td>
<td>Silica fume (SF)</td>
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### Table 2 Mixture proportions of concrete/mortar

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Type of admixture</th>
<th>W/C (%)</th>
<th>W/B (%)</th>
<th>SF/B (%)</th>
<th>s/a (%)</th>
<th>Target slump (cm)</th>
<th>Target air content (%)</th>
<th>Unit mass (kg/m³)</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. High W/C range</td>
<td>SP1 + SRA(C × 2%)</td>
<td>52.5</td>
<td>-</td>
<td>-</td>
<td>48.3</td>
<td>18</td>
<td>4.5</td>
<td>163 310 871 948</td>
</tr>
<tr>
<td></td>
<td>SP1</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>NSP1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>2. Mid W/C range</td>
<td>SP1</td>
<td>47.1</td>
<td>-</td>
<td>-</td>
<td>47.0</td>
<td>18</td>
<td>4.5</td>
<td>164 348 832 953</td>
</tr>
<tr>
<td></td>
<td>NSP1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. Low W/B range</td>
<td>SP2</td>
<td>-</td>
<td>22.0</td>
<td>10</td>
<td>41.9</td>
<td>60 *1</td>
<td>2.0&gt;</td>
<td>175 715 80 591 832</td>
</tr>
<tr>
<td></td>
<td>NSP1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. Mid W/C range-</td>
<td>SP1 + SRA(C × 2%)</td>
<td>47.1</td>
<td>-</td>
<td>-</td>
<td>S/C=3.0</td>
<td>-</td>
<td>2.0&gt;</td>
<td>243 515 1545 -</td>
</tr>
<tr>
<td>mortar</td>
<td>NSP1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NSP2</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</table>

*1: The target workability of concrete was set as 60cm of slump flow. B=C+SF.
Table 3 General performances of NSP1

<table>
<thead>
<tr>
<th>W/C</th>
<th>SP</th>
<th>W</th>
<th>C</th>
<th>Dosage</th>
<th>Slump (flow) / cm</th>
<th>F. Setting</th>
<th>Comp. Strength</th>
<th>Shrinkage (26w)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>mass%</td>
<td>0 hr</td>
<td>1 hr</td>
<td>hr:mm</td>
<td>MPa / 28d</td>
</tr>
<tr>
<td>52.5</td>
<td>SP1</td>
<td>163</td>
<td>310</td>
<td>1.0</td>
<td>18.0</td>
<td>-</td>
<td>8:20</td>
<td>48.5</td>
</tr>
<tr>
<td></td>
<td>SP1+SRA</td>
<td>163</td>
<td>310</td>
<td>1.0+2.0</td>
<td>19.5</td>
<td>-</td>
<td>9:35</td>
<td>45.1</td>
</tr>
<tr>
<td></td>
<td>NSPI</td>
<td></td>
<td></td>
<td>0.8</td>
<td>19.0</td>
<td>-</td>
<td>8:25</td>
<td>44.2</td>
</tr>
<tr>
<td>47.1</td>
<td>SP1</td>
<td>164</td>
<td>348</td>
<td>0.75</td>
<td>17.9</td>
<td>12.5</td>
<td>7:20</td>
<td>49.6</td>
</tr>
<tr>
<td></td>
<td>NSPI</td>
<td></td>
<td></td>
<td>0.6</td>
<td>19.2</td>
<td>18.1</td>
<td>8:50</td>
<td>51.9</td>
</tr>
<tr>
<td>22.0</td>
<td>SP2</td>
<td>175</td>
<td>715</td>
<td>1.8</td>
<td>68.0</td>
<td>-</td>
<td>8:05</td>
<td>133</td>
</tr>
<tr>
<td></td>
<td>NSPI</td>
<td></td>
<td></td>
<td>1.8</td>
<td>64.5</td>
<td>-</td>
<td>10:25</td>
<td>127</td>
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*Autogeneous shrinkage / Total shrinkage
M: Metal, Me: Methyl, EO: Ethylene oxide
EP: Diethylene glycol dipropylene glycol monobutyl ether

Fig. 1. Molecular structures of polycarboxylate superplasticizer.

Fig. 2. Dispersing performance of superplasticizers.
Fig. 3. The performance of shrinkage reduction of NSP2.

Fig. 4. Freezing and thawing resistance of superplasticizers.
Fig. 5. SEM micrographs of the surface of entrained air bubbles. (a) SP1, (b) SP1+SRA, (c) NSP1. Scale bars are 750 μm, 60 μm, and 30 μm from lower to higher magnifications. In higher magnifications, the central position is enlarged.
Fig. 6. Analysis of the pore solutions by SEC.

Fig. 7. The surface tension of pore solution and the shrinkage.
Steel Fiber Product Introduction through Pre-Cast Reinforced Concrete Pipe

by C. N. MacDonald and J. Trangsrud

Synopsis:

This paper presents the introduction of a steel fiber made by a pre-cast manufacturer suitable for plant-produced products and transit-supplied concrete. The fiber configuration allows fiber manufacturing to be done in-house as are the other concrete products. Toughness test results indicate equivalent or improved performance with lab mixtures compared with other steel fibers available and tested. Tests were conducted with both wet (laboratory and transit mixture) and dry cast techniques for testing samples and full-scale three-edge bearing tests for dry cast pipe. Performance issues were identifiable for the sample casting techniques, compression strength, maturity, and toughness tests with fiber reinforcement. Pipe tests were conducted for the first visible crack, the first 0.25 mm crack, and the ultimate load with fabric reinforcement only, fiber reinforcement only, and then with both fabric and fiber reinforcements. Concrete mixture proportions for the pipe were constant with three dosages of fiber used: 0.25, 0.50, and 0.75 percent by volume.

Keywords: average residual strength tests; pre-cast concrete pipe; steel fiber reinforced concrete
INTRODUCTION

The primary role of fibers in hardened concrete is to modify the cracking mechanism. By modifying the cracking mechanism, the macro cracking becomes micro cracking. The cracks are smaller in width; thus reducing the permeability of concrete and the ultimate cracking strain of the concrete is enhanced. The fibers are capable of carrying a load across the crack. A major advantage of using fiber reinforced concrete (FRC) besides reducing permeability and increasing fatigue strength is that fiber addition improves the toughness or residual load carrying ability after the first crack (1). Additionally, a number of studies have shown that the impact resistance of concrete can also improve dramatically with the addition of fibers.

Combining the technical benefits and in place costs, FRC has been found to meet the prerequisites of Value Engineering for use, particularly in airport and highway pavements, in bridge deck overlays, curtain walls, sewer pipes and precast concrete products. Fibers have also been used in shotcrete for rockfill stabilization, tunnel linings and dome structures (2, 3). FRC has also been used extensively in overlays and repairs of airport pavements and bridge decks. FRC composites are almost ideal materials for repair, rehabilitation, retrofit and renovation of the world’s deteriorating infrastructure (4, 5). Concrete fiber composites technology has grown over the last three decades into a mature industry.

A new steel fiber has been developed for the fiber reinforced concrete market. This study held concrete material properties equal and varied the fiber type and amounts. This paper summarizes three investigations comparing the new fiber with 1) six other steel fibers from four other suppliers on the market in laboratory mixtures, 2) pipe pre-casting operations and welded wire fabric, and 3) another fiber in transit mixtures.
Table 1 describes fibers tested in this study. All the concrete was mixed or tested according to ASTM Standards. Fiber 5 is the new fiber, and it was as easy or easier to mix this fiber than the other fibers in both the laboratory and field transit mixtures.

The three investigations used four different mixture proportions as described in Table 2. The W/C and other mixture attributes were kept constant for each mixture proportion and the fiber dosage or type was changed for an easier comparison or understanding of the fiber influence. The aggregates were tested for moistures, and the mixture proportions adjusted to make consistent and reproducible concrete. The FRC samples were tested according to ASTM C 1399 Test Method for Average Residual Strength (6). This test measures material toughness and the strength results can be used to compare the effects from fiber dosage and fiber type.

Control or non-fiber mixtures are used for comparing the concrete properties with those of the fiber mixtures. The laboratory mixture proportions were chosen based on experience with proportions that typically worked satisfactorily with other fiber mixtures. The two pipe mixture proportions were from previous pipe manufacturing experience without using fibers. The transit mixture proportions were from a previous mixture that used fibers. None of the mixture proportions used were an attempt to optimize fiber performance but to allow consistency in comparing the fiber effects.

**COMPARISON OF LABORATORY MADE SPECIMEN**

The 28-day average compressive strength was 46.2 MPa, with a plus 12% and minus 8% range. The 28-day beam flexural strengths (Modulus of Rupture) for the non-fiber mixtures were 11 percent of the non-fiber concrete compressive strengths. This percentage would be considered typical. Refer to Table 3.

The Average Residual Strengths (ARS) are grouped and ordered from the highest to the lowest. Fiber 1 and 5: 2.80 MPa plus; Fiber 2B, 4, and 3A: 2.10 MPa plus, and Fiber 3B and 2A: 1.40 MPa plus. Refer to Table 4.

The performance groupings are not unusual in an analysis of this type. Other researchers have described similar groupings of behavior when discussing ASTM C 1018, which is similar to these tests. The resultant range of values for similar fiber amounts is typical of the test and added to the justification for the comparison investigation.

Many factors can influence ARS results; however, these tests are very useful for comparison between fiber types (7).
Tests of Fiber 5 indicate comparable or better ARS strength and other attributes when compared with the performance of other fibers. The ARS values and the ease of mixing with Fiber 5 provide comparable performance with the other highest ARS value fiber tested.

Further testing of Fiber 5 was warranted because these successful laboratory test results generally indicated the fiber had comparable or better ARS values than the other fibers tested. Further investigation of any new fiber performance should include incorporation into other mixture proportions and characterization of the behavior for different dosages and for different applications. Since the Fiber 5 manufacturer was already in the concrete business, the next tests were done with pre-cast pipe.

**PRE-CAST PIPE TESTING**

Concrete for pipe was mixed and dry-cast in a pre-cast concrete facility. Fiber 5 was used in manufacturing some of the pipe tested. The Fiber 5 and pipe manufacturer tested the pipe as part of normal operations for making pipe. Other concrete samples from the same mixtures were tested in an independent laboratory.

**Pre-Cast Pipe Mixture Proportions**

Mixture proportion 1 was used for 9 batches and mixture proportion 2 was used for 3 batches. The difference between the two mixture proportions is that proportion 2 has the same cementitious total but portland cement was replaced with 15 kg of fly ash and had a greater proportion of coarse aggregate. Mixture proportion 2 was used for making pipes with fibers and without any welded wire fabric. Mixture proportion 1 was used for making pipes with welded wire fabric without fibers, and pipes with welded wire fabric and fibers. Mixture proportion 2 was used to gain strength faster and in order to move the pipes while they are still green. Previously, pipes with only fibers were made with mixture proportion 1, but they crumbled when moved due to insufficient strength.

Both mixture proportions were not adjusted volumetrically for the different fiber additions; rather, the fibers were just added over and above the basic mixture proportions. The mixture proportions were not optimized for the fiber additions, but were standard mixtures used for normal pipe production. The fiber volume percentages used were 0.25, 0.50, and 0.75, which are equivalent to 20, 39, and 59 kg/cu.metre. Refer to Table 2.
The fibers were added by sprinkling onto the conveyer in front of the guide tire on the mixing chamber side from the discharge of the weigh hopper. Additional mixing time was not necessary to adequately disperse the fibers due to the high shearing action of the machine. Vibration helps eliminate voids in the manufactured pipe. The time was increased slightly with the increasing fiber content to ensure consolidation of the dry fiber mixture even though there were no apparent problems with the fiber mixtures. The added time was minimal. The operator viewing the end consolidation appearance in the mold controlled the amount of vibration, and the non-fiber mixture vibration amounts are controlled the same way.

All of the pipe and laboratory test specimens were cured the same way during the first 24 hours, which included an initial factory floor time, about 8 hours of steam cure, and then more factory floor time. About 24 hours from initial casting, the laboratory specimens were tested or ambient cured (not moist cured) for later testing and the pipe was load tested or stored outside until load tested.

**Compressive Strength Tests for Pre-Cast Pipe**

There was no appreciable trend showing an increase in compressive strength with increasing fiber volume. This is consistent with other reported experiences, as fibers are added for toughness strength purposes. For a given mixture, maturity was the major influence for compressive strength.

The 1-day mixtures are within 10 percent of one another and the 7-day mixtures are within 2 percent of one another. This difference in the one-day strengths could be attributed to the sample casting method. Three mixtures were three-lift cast with a plunger between lifts on a vibrating table and not rodded. Three mixtures were one-lift cast with a plunger on top on a vibrating table and not rodded. Comparing the 7-day tests, the sample strengths could be considered the same regardless of casting method. When compared for compression, the casting method by three lifts gives slightly higher 1-day strengths. Refer to Table 5.

**Average Residual Strength Tests for Pre-Cast Pipe**

Beams were tested at 1 and 6 days. There is a definite correlation as shown in Table 5 between the ARS and the fiber volume percent. Other factors can influence ARS results but these results emphasized fiber dosages as the most significant strength influence.
In some cases, outside breaks occurred in the end thirds of the beam length and a correction factor was applied for 3 beams. (A correction factor for this type break is not specifically addressed in ASTM C 1399, as it is in ASTM C 78. However, ASTM C 1399 does direct “measure the beam and crack locations as in test method C 78.”) Six test values were discarded in the analysis due to testing errors.

Table 5 analyzes ARS by casting lifts, fiber volume, and age. The casting by single lift shows significant increased strength over the two-lift castings. Like the compression test comparisons for casting lifts, the beams were cast using a plunger on a vibrating table with two lifts and one lift. Even though the beams are rotated 90 degrees from cast position for testing, the data indicates the two-lift method introduces a weak plane in the beam, that is, with minimal fibers across lifts. The single lift beam is more homogeneous and has fibers randomly oriented throughout the beam. Recommended future testing would include casting fiber beams with a single lift when compacted with a plunger on a vibrating table.

Table 5 shows that the ARS values are more dependent on fiber volume and less dependent on age. This appears consistent with the testing method, which pre-cracks the specimen to remove the concrete influence. However, the concrete needs to be strong enough so that there is adequate bond between the fibers and the concrete. The testing then indicates the influence of the fibers only.

Since the flexural strength of the concrete is removed by the test, the fiber contents are only tested. The test results are also affected by casting method, orientation of fibers, configuration of fibers, consolidation, etc. This is why more beams are tested to establish a statistically acceptable value. The ARS values do not show an expected linear correlation between fiber dosages and ARS results. As an example, ARS values for fiber volume percentages 0.25-0.50-0.75 are approximately 0.85-1.25-2.75 MPa. The 0.25 % by volume of fibers should be more homogeneous in the mixture because there are fewer fibers and tend to be more easily distributed. The higher amounts of fibers can clog the mixture because there are too many fibers to coat or lock into the concrete. Based on previous experience with wet mixture concrete and with the same fiber at 0.50 % by volume, these dry casts at 0.50 and 0.75 % by volume of fibers would have given higher test values. Mixture proportions and methods for making dry cast FRC have not been fully investigated to optimize fiber performance.
Reinforced Concrete Pipe Three-Edge Bearing Test Results

All the pipes tested were size 0.53 m diameter, Class 5, length 2.44 m, wall type C, and wall thickness 89 mm. Correlations existed between the lab results and pipe strengths. The pipes were tested according to ASTM C 497 Test Method for Concrete Pipe (8).

The reinforced concrete pipe three-edge bearing test data are summarized in Table 6 and shows the pipe strength test results in total load and per metre. Table 6 also shows the pipe strengths by maturity or test day for reinforcement effect. Since there are many single or two pipe values for a maturity or reinforcement condition, trends are easier to identify than individual comparisons. With similar maturities, the fibers have an increasing strength benefit at lower maturities and a greater improvement between fiber dosages at higher maturities. This seems intuitively consistent with the fibers’ inherent stiffness and configuration, and also with the amount of fiber in the weaker and in the stronger concrete.

Increases in age (maturity) did not contribute significantly to the ARS values as discussed earlier in this paper about fiber bond and the concrete influence removed. The fiber-only pipe has 8 percent or less change in strength due to the increased maturity between a 5 and 15-day test.

These changes in strength due to maturity would indicate the fiber-only pipe strength values have a consistency with the strength gain of concrete. The change in compressive strength is greater from 1 to 7 days than from 5 to 15 days. Also, the welded wire fabric seems to work with the compressive strength. In general, the addition of fiber or welded wire fabric would increase the pipe strength. Higher compressive strength would also benefit the pipe by increasing the pipe strength. There is also a strength benefit by using fibers and welded wire fabric together in pipe rather than individually as each contributes to pipe strength differently.

In Table 6, there are 3 types of pipe strengths reported as load and load per metre. The 3 strengths are from first crack, 0.25 mm crack width, and ultimate load for each pipe tested. These strengths are normally used evaluating pre-cast pipe performance. The pipes were tested with Mixture Pipe 1 at 1 and 7 days and with Mixture Pipe 2 at 2 and 5 days. Table 6 also shows the difference in strengths between the days tested and the percentage change of this difference over the first day’s test.

With Mixture Pipe 1, the combination of fibers and welded wire fabric reduced the range of strength measurements at first crack, 0.25 mm crack width, and ultimate load. Increasing fiber dosage with welded wire fabric increased strength but also increased the range of strength measurements. With Mixture
Pipe 2, the fibers only and no welded wire fabric reduced the range of strength measurements with increasing fiber dosage.

**Pre-Cast Pipe Testing Summary and Recommendations**

FRC sample specimen can be cast or consolidated differently for anticipated test age and strengths. However, this would be more complicated in practice due to holding some specimen for later testing. Therefore, one method of casting and consolidation should be used regardless of anticipated test age and strength. These fiber dosages did not significantly influence sample specimen compressive strength, but significantly influenced sample specimen average residual strengths.

Reinforcement types, fiber dosages, and the strength of concrete influence pipe strengths. Fiber dosages could be optimized for different mixture proportions and casting operations to obtain the maximum fiber effect on the pipe. Changes in mixture proportions, especially portland cement content, would seem to be the most sensitive to the economics of how much fiber can be used. Fiber dosages could also be optimized for the type of strength needed (compression or ARS) at different maturities.

**TRANSIT MIXTURE COMPARISON**

Concrete was mixed and cast from truck transit mixers at a local transit mix plant. The procedure involved adding the fibers after concrete was normally mixed. The fibers were added from a platform, by hand, into the rear chute of the trucks.

About five minutes of additional mixing time was used to thoroughly mix both fiber types. The trucks used were not the same. The same 0.50 % by volume of fiber was added from paper bags or cardboard boxes to 8.0 and 6.1 cubic meter volumes of concrete respectively.

The two seven-day flexural strengths or modulus of rupture are consistent and as expected for a designed concrete with a 28-day compressive strength of 27.56 MPa. Refer to Table 3.
Average Residual Strength Tests for Transit Mixture

The Average Residual Strength (ARS) data are in Table 4. One ARS value was deleted due to a testing error and two ARS values were corrected because the breaks occurred outside the middle third of the beams during testing.

The range of values is not unusual for these tests. Due to some breaks outside the middle third of the beam and range of values, using five beams for a sample value proved to be a prudent testing practice.

Beam samples were consolidated in two lifts and externally tapped with a rubber mallet. A 16 mm diameter rod was used 25 times for each lift. The beams were rocked and also dropped two or three times about 25 mm from an end to improve the consolidation. This consolidation procedure is significantly different from the external vibration used in the previous cases. ASTM allows both consolidation methods, but there were no means for external vibration in the field.

The ARS values of the transit mixture FRC are about 25 percent less than the samples cast in the pre-cast plant and 45 percent less than the samples cast in the laboratory. Though the same fiber dosages were used, there are significant differences in the mixture proportions and sample casting methods. Also, during testing, the FRC beams were not rotated 90 degrees from casting when placed in the test rig. However, the FRC beams were tested in the same way for comparison.

There is a significant difference in the fiber size and configuration as shown in Table 2. There are twice as many Fiber 5 fibers per kilogram compared to Fiber 2C. The longer length of the Fiber 2C could have produced a higher ARS.

Field observations were made of the placement and finishing operations for the two types of FRC slab on ground. No significant differences were noted in placement or finishing operations and subsequent appearance five days later.

Transit Mixture Summary

The Fiber 5 gives an equivalent ARS value compared to Fiber 2C with this Ready-Mix concrete mixture. Fiber type 5 and 2C performed equally when mixed with concrete in a transit mixture; the ARS values were not significantly different for these two fiber concretes when tested at the same age.
SUMMARY CONCLUSION

Fiber type 5 behaved as expected compared to other steel fibers in laboratory and transit concrete mixtures. Fiber type 5 ARS tests were equal or exceeded other steel fibers tested. Consolidation of dry-cast FRC beam samples is dependent on one plunger lift to avoid incorporating a weakened plane. Fiber reinforcing adds strength and improves strength behaviors in dry-cast pipe when tested by the three-edge bearing test method. Fiber reinforcement in concrete mixture proportions should be optimized for dosage in relation to the application, strength, and other desired properties or behavior of the concrete.

REFERENCES


(2) MacDonald, C. N., (1984), "Plastic and Steel Fiber-Reinforced Concrete Applications", Transportation Research Record 1003, TRB, Washington, DC.


(6) ASTM C 1399 Test Method for Average Residual Strength


(8) ASTM C 497 Test Method for Concrete Pipe
Table 1 Fiber Descriptions

<table>
<thead>
<tr>
<th>Fiber Type</th>
<th>Cross-section</th>
<th>Deformation Description</th>
<th>Length mm</th>
<th>Dimension</th>
<th>mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>round ends have one hook</td>
<td>30.0</td>
<td>diameter</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>2A</td>
<td>crescent</td>
<td>corrugated along length</td>
<td>41.0</td>
<td>largest width</td>
<td>3.0</td>
</tr>
<tr>
<td>2B</td>
<td>round ends are flattened</td>
<td>30.0</td>
<td>diameter</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>3A</td>
<td>round ends have two hooks</td>
<td>31.0</td>
<td>diameter</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>3B</td>
<td>round ends have two hooks</td>
<td>31.0</td>
<td>diameter</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>rectangular</td>
<td>six edge indents along length</td>
<td>38.0</td>
<td>largest width</td>
<td>2.0</td>
</tr>
<tr>
<td>5</td>
<td>rectangular</td>
<td>ends enlarged and bent</td>
<td>40.0</td>
<td>largest width</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Table 2 Mixture Proportions

<table>
<thead>
<tr>
<th>Mixture Designations</th>
<th>Units</th>
<th>Laboratory</th>
<th>Pipe 1</th>
<th>Pipe 2</th>
<th>Transit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
<td>kg/m3</td>
<td>384</td>
<td>326</td>
<td>341</td>
<td>279</td>
</tr>
<tr>
<td>Fly ash</td>
<td>kg/m3</td>
<td>89</td>
<td>74</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>Cementitious content</td>
<td>kg/m3</td>
<td>384</td>
<td>415</td>
<td>415</td>
<td>349</td>
</tr>
<tr>
<td>Admixture weight</td>
<td>kg/m3</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Coarse Aggregate</td>
<td>kg/m3</td>
<td>897</td>
<td>681</td>
<td>984</td>
<td>996</td>
</tr>
<tr>
<td>Fine Aggregate</td>
<td>kg/m3</td>
<td>901</td>
<td>1,369</td>
<td>1,067</td>
<td>800</td>
</tr>
<tr>
<td>Moisture Content</td>
<td>kg/m3</td>
<td>174</td>
<td>199</td>
<td>158</td>
<td>157</td>
</tr>
<tr>
<td>W/C</td>
<td></td>
<td>0.45</td>
<td>0.48</td>
<td>0.38</td>
<td>0.45</td>
</tr>
</tbody>
</table>

| Number of Mixes | 3 | 1 |
| Fiber Type      | 5 | 5 |
| fiber           | 20 | 20 |
| volume %        | 0.25 | 0.25 |

| Number of Mixes | 11 | 3 | 1 | 2 |
| Fiber Type      | 1, 2A, 2B, 3A, 3B, 4, 5 | 5 | 5 | 2C, 5 |
| fiber           | 39 | 39 | 39 | 44 |
| volume %        | 0.50 | 0.50 | 0.50 | 0.57 |

| Number of Mixes | 3 | 1 |
| Fiber Type      | 5 | 5 |
| fiber           | 59 | 59 |
| volume %        | 0.75 | 0.75 |
## Table 3 Compressive and Flexural Strength Summary

<table>
<thead>
<tr>
<th>Fiber Type</th>
<th>Compressive (CS)</th>
<th>% of the Average</th>
<th>Flexural (MOR)</th>
<th>%</th>
<th>Compressive (DCS)</th>
<th>Flexural (MOR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>51.8</td>
<td>112%</td>
<td>5.39</td>
<td>10%</td>
<td>27.6</td>
<td>3.36</td>
</tr>
<tr>
<td>none</td>
<td>46.5</td>
<td>101%</td>
<td>5.50</td>
<td>12%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>48.0</td>
<td>96%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2A</td>
<td>45.7</td>
<td>97%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2B</td>
<td>49.3</td>
<td>107%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3A</td>
<td>42.5</td>
<td>92%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3B</td>
<td>44.2</td>
<td>96%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>44.7</td>
<td>97%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>42.5</td>
<td>92%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>46.1</td>
<td>5.44</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

## Table 4 Average Residual Strength Summary (ARS)

<table>
<thead>
<tr>
<th>Fiber Type</th>
<th>ARS, MPa</th>
<th>Number of Beams</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
<td>Laboratory Comparison, 28 day</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>3.15</td>
<td>4</td>
<td>These ARS values are within 9% of the highest value and greater than 2.80 MPa.</td>
</tr>
<tr>
<td>5</td>
<td>2.85</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>2B</td>
<td>2.46</td>
<td>4</td>
<td>These ARS values are within 11% of the highest value and greater than 2.10 MPa.</td>
</tr>
<tr>
<td>4</td>
<td>2.33</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>3A</td>
<td>2.19</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>3B</td>
<td>1.86</td>
<td>4</td>
<td>These ARS values are within 22% of the highest value and greater than 1.40 MPa.</td>
</tr>
<tr>
<td>2A</td>
<td>1.45</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Transit Comparison, 7 day</td>
<td></td>
<td></td>
<td>Average</td>
</tr>
<tr>
<td>2C</td>
<td>1.91</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1.97</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>1.94</td>
<td>Average</td>
<td></td>
<td></td>
</tr>
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</table>
Table 5 Pipe Compressive Strength and Average Residual Strength Summary

<table>
<thead>
<tr>
<th>Fiber Type 5</th>
<th>Volume %</th>
<th>Compressive Strength, MPa (average of 6 per day or lift)</th>
<th>Lift Relationship</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Age Relationship</td>
<td>Lift Relationship</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Age 1 day</td>
<td>Age 7 day</td>
</tr>
<tr>
<td>0.25</td>
<td>28.0</td>
<td>45.2</td>
<td>1.61</td>
</tr>
<tr>
<td>0.50</td>
<td>31.0</td>
<td>45.9</td>
<td>1.48</td>
</tr>
<tr>
<td>0.75</td>
<td>29.3</td>
<td>45.6</td>
<td>1.56</td>
</tr>
<tr>
<td>Average</td>
<td>29.4</td>
<td>45.6</td>
<td>1.55</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fiber Type 5</th>
<th>Volume %</th>
<th>Average Residual Strength, MPa (average of 6 per day or lift)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Age 1 day</td>
</tr>
<tr>
<td>0.25</td>
<td>0.82</td>
<td>0.86</td>
</tr>
<tr>
<td>0.50</td>
<td>1.11</td>
<td>1.34</td>
</tr>
<tr>
<td>0.75</td>
<td>2.79</td>
<td>2.67</td>
</tr>
<tr>
<td>Fiber Type 5 Volume %</td>
<td>Load (1 000 kg)</td>
<td>Load (1 000 kg) per Metre</td>
</tr>
<tr>
<td>-----------------------</td>
<td>----------------</td>
<td>---------------------------</td>
</tr>
<tr>
<td></td>
<td>First Crack</td>
<td>0.25 mm Crack</td>
</tr>
<tr>
<td>Mixture proportion Pipe 1 with welded wire fabric, 2 pipes per Test Day</td>
<td></td>
<td></td>
</tr>
<tr>
<td>none</td>
<td>14.6</td>
<td>17.7</td>
</tr>
<tr>
<td>none</td>
<td>17.8</td>
<td>19.8</td>
</tr>
<tr>
<td>3.2</td>
<td>2.1</td>
<td>7.6</td>
</tr>
<tr>
<td>22%</td>
<td>12%</td>
<td>25%</td>
</tr>
<tr>
<td>0.25</td>
<td>16.3</td>
<td>20.4</td>
</tr>
<tr>
<td>0.25</td>
<td>17.7</td>
<td>19.1</td>
</tr>
<tr>
<td>1.4</td>
<td>(1.4)</td>
<td>3.1</td>
</tr>
<tr>
<td>8%</td>
<td>-7%</td>
<td>9%</td>
</tr>
<tr>
<td>0.50</td>
<td>18.3</td>
<td>22.9</td>
</tr>
<tr>
<td>0.50</td>
<td>20.6</td>
<td>25.2</td>
</tr>
<tr>
<td>2.4</td>
<td>2.3</td>
<td>4.8</td>
</tr>
<tr>
<td>13%</td>
<td>10%</td>
<td>13%</td>
</tr>
<tr>
<td>Mixture proportion Pipe 2 without welded wire fabric, 1 pipe per Test Day</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.75</td>
<td>20.0</td>
<td>25.2</td>
</tr>
<tr>
<td>0.75</td>
<td>23.1</td>
<td>29.7</td>
</tr>
<tr>
<td>3.2</td>
<td>4.5</td>
<td>4.8</td>
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<td>16%</td>
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</tr>
<tr>
<td></td>
<td>20.4</td>
<td>22.0</td>
</tr>
<tr>
<td></td>
<td>22.0</td>
<td>22.0</td>
</tr>
<tr>
<td>1.6</td>
<td>1.6</td>
<td>1.6</td>
</tr>
<tr>
<td>8%</td>
<td>8%</td>
<td>8%</td>
</tr>
<tr>
<td>0.50</td>
<td>22.7</td>
<td>22.7</td>
</tr>
<tr>
<td>0.50</td>
<td>23.4</td>
<td>23.4</td>
</tr>
<tr>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>3%</td>
<td>3%</td>
<td>3%</td>
</tr>
<tr>
<td>0.75</td>
<td>27.0</td>
<td>27.0</td>
</tr>
<tr>
<td>0.75</td>
<td>27.7</td>
<td>27.7</td>
</tr>
<tr>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>3%</td>
<td>3%</td>
<td>3%</td>
</tr>
</tbody>
</table>
Autogenous Shrinkage of Cementitious Paste—State-of-the-Art

by H. Justnes

Synopsis:

This state-of-the-art starts out with a short discussion of the methods for measuring autogenous deformation of cementitious paste and how influence of artifacts (e.g. segregation forming bleed water) can be avoided. The influence of all components of cementitious paste on autogenous shrinkage is reviewed; water-cement ratio, cement type, additives like silica fume and fly ash (including the pozzolanic reaction itself), and admixtures like lignosulphonate and super-plasticizers. The mechanism of autogenous shrinkage is discussed, with emphasis on it’s relation to setting time and pore pressure. Finally, remedies to reduce the amount of autogenous shrinkage are briefly mentioned in terms of mechanisms and effects.

Keywords: additives; admixtures; autogenous shrinkage; cement paste
INTRODUCTION

Early-age cracking of concrete is a well known phenomenon that may seriously affect the service life of structures. High-performance concrete, in particular on horizontal surfaces such as bridge decks, is prone to cracking (Sellevold et al. (1)) even less than 12 hours after placing in spite of efforts to avoid drying. Kompen (2) has summarized field experience in early-age cracking of high-performance concrete. Such observations indicate that the importance of autogenous shrinkage as a driving force may have been underestimated in the past. This state-of-the-art is an effort to summarize the research on autogenous shrinkage over the last 10 years or so, while other mechanisms like drying shrinkage (i.e., water evaporation) and thermal deformations due to heat of hydration are omitted. Likewise, the review focuses on paste matrix measurements, excluding mortars and concrete with a few exceptions. Autogenous shrinkage of concrete and mortar will normally be less than predicted from their volume of paste due to restraint caused by the embedded aggregate and the release of absorbed water from the aggregate.

DEFINITIONS

RILEM Technical Committee 181-EAS (3) recently (2002) issued a comprehensive report on early-age cracking in cementitious systems, where some terminology has been agreed upon:

Chemical shrinkage is the internal-microscopic volume reduction which is the result of the fact that the absolute volume of hydration products is smaller than that of the reacting constituents (cement and water). It is roughly proportional to the degree of hydration beyond the very early stage.

Autogenous shrinkage is the external-macroscopic (bulk) dimensional reduction of the cementitious system which occurs under isothermal conditions.
without exchange of moisture or any other substance with the surroundings (i.e., sealed curing). Autogenous shrinkage is usually driven by chemical shrinkage and the magnitudes of the two are roughly equal as long as the paste matrix is fluid-like. The autogenous shrinkage becomes smaller than the chemical shrinkage when the paste matrix has developed a self-supporting skeleton and the difference between them is manifested as internal contraction pores. (roughly at the time of setting as shown by Justnes et al. (4) and reproduced in Fig. 1).

_Self-desiccation_ is the reduction of internal relative humidity in a sealed system when empty contraction pores are generated.

Chemical shrinkage is sometimes denoted as _total chemical shrinkage_, while autogenous shrinkage is denoted as _external chemical shrinkage_ in line with the above definitions (e.g. Justnes et al. (5)).

METHODOLOGY

The methods for measuring chemical shrinkage all have in common that the specimen has to be kept water saturated and that the water needed to replace the volume decrease is measured. The common methods for measurement of autogenous shrinkage are characterized by sealed curing of the paste. There are mainly 3 techniques for measuring chemical and autogeneous shrinkage; 1) dilatometry, 2) gravimetry and 3) pycnometry.

Dilatometry is based on direct measurement of length or volume change. The most common dilatometry technique for total chemical shrinkage measurement is to put the paste in a receptacle (e.g. glass tube), filling the rest of the receptacle with water and plugging the receptacle with a water filled pipette stuck through. Reading the fall of the water level in the pipette versus time gives the total volume change. Knudsen and Geiker (6) have pioneered a variety of applications for this method since the 1980s. The practical arrangement of this technique was also evaluated by Justnes et al. (5). A dilatometer technique for autogenous shrinkage was developed by Jensen and Hansen (7) based on measurement by inductive sensors of the uniaxial length change of a flexible, sealed tube filled with paste.

Gravimetry is based on indirect measurement of volume change by recording the reduced buoyancy under water by submerged weighing (i.e., the law of Archimedes). If the mass change is recorded for a container filled with paste and excess water having at least one flexible wall (e.g. Paulini (8)), the chemical shrinkage is measured. If the mass change of an elastic bag filled with paste only is registered, autogenous shrinkage is measured. The latter method was evaluated by Justnes et al. ((5) and (9)) and the major draw-back of the method is the sensitivity to bleeding. Bleed water sucked into the paste after
setting will lead to erroneously high measurement of autogenous shrinkage and static sample (i.e. no sample rotation) measurements are only suitable for pastes of w/c < 0.3. The bleeding effect can be avoided by rotating the specimen until past setting (Justnes et al. (9)) and weighing it in a separate water bath.

Pycnometry is only applicable for chemical shrinkage measurements, and is carried out by filling a pycnometer with paste and topping it with water. Water is added to refill the pycnometer at different ages, and the weight increase relates to the total volume change.

MECHANISMS

The basic mechanisms of autogenous shrinkage were recently evaluated by Lura et al. (10). Other contributions to understanding the mechanisms have been given by Wittmann (11), Mitani et al. (12), and Thomas and Jennings (13). The basic mechanisms are actually more or less outlined in the preceding definitions of chemical shrinkage, autogenous shrinkage, and self-desiccation.

Before setting, when chemical shrinkage and autogenous shrinkage is equal, the external volume change will be followed by a stretched, elastic rubber membrane if used. In a uni-axial, horizontal dilatometry set-up, this external volume reduction would be manifested as subsidence and usually not recorded, or the measurement starts after setting and demolding.

After setting there will be a formation of empty contraction pores that initially are empty and that are forming an under-pressure. At this stage, the pore connectivity is quite high, so the water will re-distribute so the coarsest pores will be empty first. Koenders and de Rooji (14) discussed internal moisture flow by microstructural contraction. The empty pores will have a minimum pressure equal to the partial pressure of water in equilibrium with the pore water and some dissolved air going into the gas phase when the pressure is reduced (i.e., solubility of gas is proportional to the pressure). The magnitude of this under-pressure is governed by the amount of solute in the water according to Raoult's law;

\[
P/P_0 = X \quad (= \text{relative humidity in case of water}) \]

where \(P\) = is partial pressure over the solution, \(P_0\) = the pressure over pure solvent, and \(X\) is the molar fraction of free solvent in the solution. Note that in the case of water, water molecules coordinating around the ions also have to be subtracted in calculations. Water in fresh paste contains in general about 0.1 M alkali hydroxides and some sulphates that will ion-exchange to hydroxides rather quickly. Lura et al. (10) measured an initial RH of 0.98 due to this effect, while Page and Vennesland (15) measured 0.967 for the composition of the pore solution extracted from a w/c = 0.45 paste after 2 months. However, the
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effect of Raoult's law will first become an important factor when solutions are getting concentrated (achievable for w/c < 0.4) where RH on the order of 0.4 may be obtained easily. This is the same principle used to obtain constant humidity by saturated salt solutions. Concentrated KOH gives, for instance, 9% RH at 20°C.

However, at the stage of concentrated salt solutions, the pore refinement has progressed for a while and the equilibrium pressure of water over the meniscus in the coarsest pore filled with water (i.e., assuming that water will redistribute easily) will dominate in the period before that in accordance with the Kelvin equation for cylindrical pores:

\[ \ln \left( \frac{P}{P_0} \right) = -\frac{2 \cdot \gamma \cdot M \cdot \cos \theta}{\rho \cdot r \cdot R \cdot T} \]  

[2]

where \( \gamma \) = surface tension of water (0.073 N/m in pure water and 0.055 N/m for a pore fluid according to Jensen (16)), M = molar mass of water (18.02 g/mol), \( \theta \) = the contact angle between water and solids (close to 0°), \( \rho \) = density of water (approx. 1,000 kg/m³), \( r \) = the radius of the meniscus (m), R = the ideal gas constant (8.314 J/mol·K), and T = the absolute temperature (K).

If the contribution to reduction of relative humidity by dissolved salts according to Raoult’s law in Eq. 1 could be isolated from the contribution due to water meniscii according to the Kelvin equation (Eq. 2), the radius, \( r \), of the coarsest pore filled with water could be calculated from simple RH measurements. This could be used to calculate the tensile stress in the pore fluid according to the Laplace law for cylindrical pores:

\[ \sigma_{\text{Cap}} = \frac{2 \cdot \gamma}{r} \]  

[3]

This tension stress of capillary water, \( \sigma_{\text{Cap}} \), is generally thought to be the major driving force of autogenous shrinkage. Jensen (16) claimed that the measured relative humidity could be approximated by the product of the contributions from Eqs. 1 and 2. This was also used by Lura et al. (10) who also claimed that the contribution of dissolved salts in accordance with Raoult’s law (Eq. 1) was constant to 2% RH reduction throughout hydration. The present author will argue that these assumptions are not correct, and the fit between observed and calculated linear shrinkage by Lura et al. (10) showed a large deviation when RH caused by meniscus formation fell below 97%.

There will be an under-pressure in the empty pores, which for a sealed case without air bubbles and dissolved air can not exceed the pressure of water vapour above free water (23 torr at 25 °C), but will be much less due to the effects described by Eqs. 1 and 2.
The pressure drop in the paste can also be measured directly by a method developed by Radochea (17), using a water filled tube attached to a pressure transducer. The tension recorded in the water in the tube is believed to reflect the tensile stress of the pore water ($\sigma_{\text{cap}}$ in Eq. 3), which in turn is transferred to the hydration products and creating shrinkage. Examples of pressure drop in pastes of cements of different fineness are shown by Sellevold et al. (1) and the device was later used by Hammer (18). At first, the pressure equals the hydrostatic pressure of the suspended paste (i.e. a column of cement paste) in such an experiment according to

$$P = \rho \cdot g \cdot h$$

where $\rho = $ the density of the paste (kg/m$^3$), $g = $ gravitational constant and $h = $ depth of measurement below surface (m). The pressure drops slowly as a function of time to a level corresponding to a column of same height of water percolating through the network of selfsupporting particles (i.e., only $\rho$ changes from about 1,900 to 1,000 kg/m$^3$ in this “segregation” process of hydrating particles). Thereafter, there is a plateau until the first water menisci and vapour filled pores are formed roughly at the point of setting, followed by a gradually capillary water tension increase at first, which is rapidly accelerating. As seen in Fig. 2, the time from setting to achieve a pore water tension of 100 mm “hanging” (i.e., negative) water column is in the order of 1 hour, and from there it may take only half an hour to increase pore water tension further to a 500 mm negative water column, and even less. Note that at such a low tension, the water vapour pressure is not affected much, so water may evaporate from coarser pores, be transported as vapour, and condensate in smaller pores. For comparison, it will take a pore water tension build up corresponding to a $10^6$ mm water column (i.e., 1 km water column or 100 atm) before the relative humidity is reduced to 93% (according to Eqs. 2 and 3).

Charron et al. (19) compared autogenous shrinkage by a volumetric method with that of a linear dilatometric method for mortars. They found, like many others, that there is a large discrepancy between the two methods, where the dilatometry method gives an order of magnitude less shrinkage after setting, even when they are made comparable by multiplying the linear measurements by a factor of 3 to take into account all principal directions. The authors did not find any good arguments for this observation.

According to the present author, one cannot rule out that the samples for linear measurements are not sealed properly, even when they are covered by wraps to avoid evaporation (with the exception of the corrugated tubes used by Jensen (16)). The pressure in the pores will then soon approach atmospheric by air being sucked in. The contribution to shrinkage by vacuum will then be removed, although the capillary tension due to menisci still will be in place. If
evaporation is hindered by placing the sample in a chamber of high humidity, also the capillary tension can be lowered due to capillary condensation. This could be an important contribution to explaining the discrepancy between volumetric and linear shrinkage.

The smaller autogenous shrinkage observed by linear methods relative to volumetric methods was discussed in detail by Hammer et al. (18). They mentioned factors like 1) friction between sample and substrate, 2) bleeding and re-suction of bleed water creating expansion and 3) thermal expansion effects as the three important factors. In particular the 3rd effect, since temperature rise due to heat of hydration in non-submersed samples is difficult to avoid, and it may reach as much as 10°C above the surroundings. This effect may actually be the reason for the difference (factor of 10) observed by Charron et al. (19) since they compared the residual shrinkage after the temperature and thermal expansion peak for the sample in the linear experiment. Since hydration rate is roughly increased by a factor of 2 per 10°C increase, the sample for the linear measurement would have been more mature at the point of comparison.

EFFECT OF WATER-CEMENT RATIO

Justnes et al. (20) measured the effect of w/c on chemical and autogenous shrinkage of two different cement pastes. Chemical shrinkage (water saturated curing) was largely independent of w/c over the investigated w/c range (0.3 to 0.50) and time (0 to 48 h). Autogenous shrinkage (sealed curing) against time curves matched the chemical shrinkage curves until a flattening out level, or relatively constant value, is reached (see Fig. 1). This level is largely independent of w/c when shrinkage is expressed as mL/100 g cement, meaning that the volumetric autogenous shrinkage increases with decreasing w/c (since there is more cement per unit volume). There was also a tendency towards a more rapid fluid to solid skeleton transition at higher w/c and a slower more gradual transition at lower w/c.

Justnes et al. (21) investigated the effect of w/c in addition to the effect of admixtures on autogenous shrinkage. It was confirmed that the magnitude of autogenous shrinkage was only marginally (within 0.1 mL/100 g cement) influenced by w/c (0.3, 0.4 and 0.5) when measured as mL/100 g cement. A similar conclusion was drawn from an independent study by Justnes et al. (4).

Charron et al. (19) measured the linear autogenous deformation on mortar with w/c = 0.45 and 0.35 and found a larger shrinkage for the lower w/c.
EFFECT OF CEMENT TYPE

Justnes et al. (22) studied the effect of the characteristics of 10 different Portland cements on chemical and autogenous shrinkage for paste of w/c = 0.30 (not all combinations were made). Unfortunately, samples were not rotated prior to setting. Autogenous shrinkage was identical for 4 out of 6 cement samples up to 48 h, while two coarse cement types with very low C_{3}A content had nearly the double magnitude of autogenous shrinkage. However, minor bleeding effects cannot be ruled out. There was also substantial autogenous shrinkage measured between 10 min (earliest possible) and 1 h prior to setting, with a magnitude increasing from 0 to 0.25 mL/100 g cement with increasing fineness and content of the most reactive phases, that is, C_{3}A, C_{3}S, alkalis, and sulphates. However, autogenous shrinkage prior to setting will result in subsidence in practice.

Justnes et al. (4) investigated the setting and shrinkage behaviour of pastes for 2 different cements with various techniques. Autogenous shrinkage was somewhat lower for the cement with the highest Blaine value and C_{3}A content.

EFFECT OF MINERAL ADDITIVES

Justnes et al. (23) tested the effect of 10% precipitated calcium carbonate and silica fume on the chemical and autogenous shrinkage of pastes with different cements. The influence of the mineral additives on chemical shrinkage rate was dependent on cement type; sometimes accelerating and sometimes equal to the reference. The effect of mineral additives on autogenous shrinkage was also dependent on the cement type; sometimes increasing the flattening out level and sometimes leaving it equal relative to the reference. A higher flattening out level for pastes with fine mineral additives can be explained by pore refinement and menisci formed by initial contraction pores leading to stronger forces. Thus, more hydration is required to create stronger network to resist them.

Justnes et al. (24) tested the effect of silica fume (SF) replacing cement at dosages of 0.0, 2.6, 5.3, 11, 20 and 25% on chemical and autogenous shrinkage up to 7 days. Deformation was reported as mL/100 g cement, which means that a lower, equal or higher value correspond to a pozzolanic reaction that expands, has no volume change, or shrinks, respectively. Chemical shrinkage increased with increasing SF dosage, showing that the pozzolanic reaction leads to shrinkage, as expected. The autogenous shrinkage showed (see Fig. 3) equal flattening out levels for SF replacements up to 11%, while 20 and 25% SF successively increased the autogenous shrinkage. This observation was explained by the particle packing of the system; up to 11% SF replacement of cement (about 0.15 μm size) fills in the gaps formed between the irregular cement grains (average size 15 μm), maintaining close contact between individual
cement grains, and about the same amount of hydration is required to form a hydrate network strong enough to resist the contracting forces. With greater SF replacements, cement grains are dispersed in excess silica fume and a higher degree of hydration is required to form such a network.

Justnes et al. (24) also studied 20% replacement of cement by Class F fly ash ground to cement fineness in a lab mill. The chemical shrinkage was higher than for pure cement, but lower than for 20% SF replacement, indicating that the pozzolanic reaction of fly ash leads to shrinkage and that the reaction probably is slower than for SF (or alternatively that it shrinks less). Autogenous shrinkage was between that of neat paste and that of paste with 20% SF replacement.

Justnes et al. (24) investigated the chemical shrinkage of the pozzolanic reaction between lime and silica fume and between lime and class F fly ash without cement. The effects of lime/silica ratio, pH, and water content of these pastes were investigated. The rate of chemical shrinkage decreased with increasing pH of SF with lime, in spite of the catalytic necessity of alkalis for rapid pozzolanic reaction. This was explained by the fact that increasing pH (12.5, 13.0, and 13.5) decreases the solubility of calcium hydroxide (CH) due to the common ion effect assuming dissolution of CH is followed by the precipitation of CSH as the rate limiting step. The chemical shrinkage was relatively unaffected by the mass ratio w/cm in the range 0.8 to 1.2 and by the molar C/S ratio in the range 0.7 to 1.5. On the other hand, the rate of chemical shrinkage increased with increasing pH for the lime-fly ash mixture indicating that the dissolution of the glassy aluminosilicate phase by alkalis is rate determining for this pozzolanic reaction. The chemical shrinkage of the pozzolanic reactions was crudely estimated to be 8.8 mL/100 g of reacted SF and 10.0 mL/100 g of reacted fly ash, as compared to 6.3 mL/100 g for hydrated cement. However, taking into account density differences (2,200 kg/m³ for silica fume and 3,150 kg/m³ for cement), the chemical shrinkage is roughly equal when expressed per unit volume of cementing material.

Jensen and Hansen (25) studied the influence of SF on linear autogenous shrinkage of cementitious paste (w/c = 0.30) in horizontal corrugated plastic tubes for two different cement types and 0, 5, 10, and 20% SF addition. Note that with addition, rather than replacement, w/cm is reduced from 0.30 to 0.25 for 20% SF addition. The effect of silica fume was increased linear autogenous deformation with increasing addition rate. Particularly surprising was the large increase in autogenous shrinkage from 0 to 5% SF addition, while the effect from 10 to 20% was minor. Note that any minor bleeding by the reference paste would hamper the results, since suction of bleed water will counteract shrinkage and even may lead to swelling. However, both the effective lowering of w/cm and refinement of the pores by improved particle packing will lead to earlier meniscus formation in finer pores and thereby create higher tensile stresses.
Reduced tensile strain capacity of the paste with SF relative to the magnitude of the tensile stress build-up may explain the results.

**EFFECT OF PLASTICIZERS**

Justnes et al. (26) investigated the effect of the three types of plasticizers (lignosulphonate, naphtalene sulphonate-formaldehyde condensate and sulphonated melamine-formaldehyde condensate) in 3 different dosages on chemical and autogenous shrinkage of cement paste made from 5 types of portland cement. They concluded that the flattening out level of autogenous shrinkage was independent of admixture type, and was the same as for the reference paste without admixtures, as long as the specimens were rotated (i.e., undisturbed by bleeding). Furthermore, the admixtures did not directly influence the chemical shrinkage in a way that should indicate a higher risk of cracking. However, the retardation of early hydration and setting of cement by lignosulphonate could allow a longer period of evaporation of water from floors and bridge decks in practice. For this reason mixtures with lignosulphonates might be more prone to form drying shrinkage cracks. The conclusions were confirmed by Justnes et al. (21).

**MITIGATION OF AUTOGENOUS SHRINKAGE**

There are two principle measures for mitigating autogenous shrinkage functioning in accordance with its mechanisms. One is to supply the cement paste with water from internal sources when it self-dessicates, and the second is to modify the surface tension of water to reduce the stresses formed by menisci in partially emptied capillary pores. Jensen and Lura (27) recently reviewed techniques for so called internal water curing of concrete, ranging from inclusion of super-absorbant polymers (SAP) to water filled porosity in lightweight aggregate (LWA). Berke and Li (28) evaluated the effect of a shrinkage-reducing admixture (SRA) based on glycol-ether and found that it reduced the autogenous as well as drying shrinkage.

Hammer (29) investigated the effect of water content in LWA on the uniaxial shrinkage of sealed LWA concrete (8% SF and nominal \( w/cm = 0.30 \)) prisms by dilatometry from 1 to 180 days. Some results are replotted in Fig. 4. LWAC with dried and impregnated (prevents water suction) LWA shows high shrinkage, while LWAC with oven dried (105°C) LWA shows no shrinkage and late expansion since water absorbed by the LWA in the fresh state is released back to the matrix when pore water tension has become high enough. LWAC made with untreated LWA stored outdoors (moist) exhibit an expansion for the whole period due to the reservoir of extra water (i.e., absorbed during periods of rain) released to matrix.
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Fig. 1 Chemical (●) and autogenous (○) shrinkage of cement paste (w/c = 0.40) compared with initial (left vertical line) and final (right vertical line) setting time by Vicat Needle. The gap between the two curves is the volume of contraction pores. (from Justnes et al. (4)).

Fig. 2 Principle for interpretation of the development of pore water pressure and tension in cement paste after Hammer (18).
Fig. 3 Autogenous shrinkage of cement pastes as a function of silica fume replacement (after Justnes (24)).

Fig. 4 Uniaxial length change of sealed LWA concrete prisms with LWA treated in different ways. Legends dry, imp. and moist refer to LWA dried at 105°C, dried LWA impregnated with stearic acid, and untreated LWA stored outdoors, respectively. Replotted from Hammer (29).
Evaluation of Bond Strength between Ultra-High Performance Reactive Powder Composite Materials and Fiber-Reinforced Concrete by Slant Shear Test

by A. Hassan, M. Kawakami, S. Matsuoka, and H. Tanaka

Synopsis:

The use of precast panels made of new ultra-high performance reactive powder composite materials (RPCM) in civil construction as permanent formwork for concrete structures and buried forms for bridge slabs is a new application that has great applicability prospects due to the high strength and durability of these new materials. The bond at the interface between RPCM and fiber-reinforced ordinary cement concrete is studied in this paper using slant shear tests. The program aimed at testing the bond between a substrate of RPCM with different surface treatments and an overlay of ordinary concrete with different fiber contents. This study concluded that casting the bonding surface of the substrate on air-cell plastic sheets produces a rough surface with concavities and thus provides an easy and effective way to increase the bonding strength. The results of this method of surface preparation are comparable to conventional methods like sandblasting or grinder treatment. Increasing the fiber content of the concrete overlay increases the bond strength with the RPCM substrate if the surface of RPCM is not treated. When the surface of RPCM is roughened to obtain mechanical interlock, the high fiber content of the concrete overlay negatively affects the bond strength. A volumetric fiber content of 0.1% in the concrete overlay is found to be adequate in all surface types.

Keywords: bond strength; concrete; fibers; reactive powder composites; slant shear; ultra-high performance materials
INTRODUCTION

Mechanical and durability properties of ultra-high performance reactive powder composite materials (RPCM) surpass those of ordinary concrete [1]. The cost of such materials is very high, however, and ranges between 8 to 15 times that of ordinary or high-strength concrete. This high cost precludes these materials from completely substituting for ordinary cement concrete. While few structures have been built using only RPCM [2,3], combining RPCM with ordinary concrete may be, however, an economically feasible application at present when the long-term life-cycle cost is considered. An example of this combination is precast panels made of RPCM and used as permanent formwork for concrete structures and buried forms for bridge slabs [4]. This new application has great potential because it provides economy and ease of construction compared with conventional formwork. The high strength of the RPCM panels reduces the need for falsework during construction, and their high durability provides a protective layer to the concrete. Cost saving can be further achieved from the reduction of the cover concrete around the reinforcing bars. Examples of RPCM panels are shown in Fig.1. The contribution of the RPCM panels to the strength of the composite structure might also be considered, leading to the possible elimination of the reinforcement in the concrete especially when using fiber-reinforced concrete.

Whether or not full composite action is considered in design, the application of RPCM panels requires a strong bond between the panels and the concrete which is to be cast later. The bond at the interface between RPCM and ordinary concrete has not been studied so far, and the present paper reports the results of an experimental program of slant-shear tests to fill a part of this knowledge gap. Because the subsequent part of the authors research was using RPCM panels in bridge slabs application, slant-shear method was chosen for the evaluation of bond strength between RPCM and concrete in this study. Slant-shear tests, which subject the interface to a combination of compression and shear, were thought to be more suitable for this particular application than different tests such as direct tensile tests. The slant-shear test method was also proven to have lower degree of
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results variability than other methods when evaluating bond strength between new and old concretes [5,6].

MATERIALS

Ultra-High Performance Reactive Powder Composite Materials

A fiber-reinforced ultra-high performance reactive powder composite material was used as a substrate for the slant-shear tests. The material was supplied as a premixed powder consisting of approximately 32% cement, 11% silica fume, 10% crushed quartz, and 47% sand by mass. The premixed powder was mixed with water and a special water-reducing agent according to the mixture proportions shown in Table 1. The ratio of water to the premixed powder was about 0.08 by mass. The fiber-reinforced RPCM was supplied with two different types of monofilament (smooth and round) fibers: steel fibers and organic fibers. The properties of these two types of fibers are given in Table 2 as provided by the manufacturer. The RPCM with steel fiber has higher strength after hardening of the material. The RPCM specimens were submerged in water of 20°C for 48 hours, then the molds were removed and the specimens were steam-cured at 90°C for 48 hours as specified by the manufacturer. After this curing, the RPCM is supposed to reach its design strength with little change thereafter. Table 3 presents the strength properties of the hardened RPCM compression test cylinders (50 mm x 100 mm) tested at 56 days which was the age at time of the slant-shear tests. Stress strain relationships were obtained for these compression test cylinders as illustrated in Fig. 2, which also shows the failure modes of the tested cylinders. Testing was in conformance with JIS A 1108 [7] in which the modulus of elasticity is determined from the line between the two points of 50 micro strain and 1/3 ultimate stress.

Fiber-Reinforced Ordinary Concrete

Ordinary cement concrete was prepared for the overlay portion of the slant-shear specimens. In addition to plain concrete, concretes with polypropylene fibers added at two different percentages were prepared. The first percentage of added fibers was 0.1% by volume, an amount recommended by the manufacturer to provide effective plastic shrinkage cracking resistance. The second percentage of added fibers was 0.5% by volume, as recommended for the concrete used in steel-free slabs with no internal reinforcement [8]. Fiber contents greater than 0.5% by volume were found to negatively affect the workability and pumpability of concrete. Mixture proportions of the three types of overlay concrete are given in Table 4. The fibers added to the concrete were fibrillated net-like polypropylene fibers that disperse within the concrete matrix during the mixing process. Their properties are shown in Table 5 as provided by the manufacturer. After casting the concrete overlays on top of the RPCM substrates, the slant-shear specimens, together with the overlay concrete compression test cylinders (100 mm x 200 mm), were cured at 20°C and 60% relative humidity for 28 days. The results of the compressive strength tests [7] are given in Table 6, where each value represents the mean
value of all the compression test cylinders of the same concrete type (See table 7 for number of replicate specimens). The stress strain relationships of the concretes are illustrated in Fig. 2, from which the effect of fiber content on increasing the ductility before failure is easily recognized. The curves in Fig. 2 and the values in Table 3 refer to the third cycle of loading after two cycles of loading and unloading to approximately 40% ~ 45% of the ultimate load.

TEST SPECIMENS AND PROCEDURES

Surface Treatment

The RPCM half-cylinder substrates were prepared to obtain the following four types of surface textures shown in Fig. 3:

1) **Smooth surface**—Obtained by casting the RPCM in a cylinder mold with a dummy half-cylinder as an insert within. This dummy half-cylinder had an acrylic plate as an upper surface (the slant surface) that gives a very smooth surface to the RPCM half-cylinder substrate.

2) **As-cast surface**—Obtained by casting RPCM in a cylinder mold that was tilted 30° from the horizontal by fixing it to a specially prepared inclined stand. The RPCM was placed to fill half of the cylinder and the upper surface was left as cast without treatment.

3) **Grinder-roughened surface**—Specimens were cast using the “as-cast surface” procedure. Shallow grooves were then made on the slant surface in two directions using a grinder. The grooves were approximately 2 mm wide, 2 mm deep, and spaced 10 mm apart. The resulting checkerboard pattern surface can be seen in Fig. 3(c). This treatment was chosen to represent sandblasting treatment, which would be more economical to perform than the grinder method when manufacturing actual RPCM panels. In the case of slant-shear specimens, however, sandblasting was difficult to control due to the small size of the treated surface. Using high power sandblasting destroyed the shape and scraped away pieces of the surface while low power sandblasting did not affect the surface because of the high toughness of the RPCM.

4) **Air-cell surface**—Air-cell is a common packaging material used for wrapping and cushioning products. Specimens were made as in the smooth-surface specimens. The acrylic plate, however, was covered with an elliptical shaped air-cell plastic sheet of similar size. The resulting surface of the RPCM half-cylinder specimens is a negative print of the air-cell plastic sheet with circular concavities spaced 12 mm apart from center to center. The air-cell diameter was 9 mm and the depth varied between 1 mm to 4 mm because some of the air-cells were inevitably warped or torn during casting. This method offers an inexpensive and easy-to-perform surface treatment that would eliminate the need for sandblasting or other time-consuming methods.
Slant-Shear Test Specimens

The tests specimens were made according to ASTM C 882 [9] with larger cylinders (100 mm x 200 mm) to accommodate the aggregates of the concrete because the cylinders in the ASTM C 882 (75 mm x 150 mm) are mainly for mortar use. After making the RPCM half-cylinders and preparing the surfaces as described in the previous paragraph, the overlay concrete was placed and a vibration table was used for compaction (50 Hz, 2 layers, 10 s each layer). The final combinations of the different types of concretes, RPCM, and surface treatments and the number of specimens are shown in Table 7. A schematic of the slant-shear specimen is shown in Fig. 4.

Test Procedures

Specimens were tested on the 28th day after casting the concrete overlay using an Amsler-type testing machine. A free joint was placed between the upper platen of the testing machine and the top of the specimen to reduce any eccentricity during loading. The specimen was placed on a custom-made roller pad with stainless-steel balls to reduce the influence of the platen restraint in the horizontal direction and encourage joint failures. Clinaco and Regan [10] showed that tests without rollers bellow the specimens had a 10% increase in slant-shear strength as compared with specimens with rollers. The upper joint and the roller ball pad are shown in Fig. 5. Loading speed was varied within the range specified for compressive strength tests [7] so that the loading period was almost similar for all specimens.

TEST RESULTS AND DISCUSSIONS

Test results are expressed as bond strength which was calculated as specified in ASTM C 882 [9] by dividing the failure load by the elliptical bond surface area (the slant plane). These surface areas were measured for each individual specimen before casting the concrete overlay. The results of all the specimens are presented in Fig. 6.

The failure stress was calculated by dividing the failure load by the cross-sectional area of the cylinder in order to compare the strength of the slant-shear specimen with the compressive strength of the cylinders of the concrete overlay. The averages of each similar group of slant-shear specimens are given in Fig. 7.

Failure Patterns

Due to the high strength of the RPCM substrate, the substrate part of all specimens did not incur any damage during testing. Failure occurred primarily as a clean break of the bond plane, or within a thin layer of the concrete overlay parallel to the joint as explained hereafter:

1) For the specimens with smooth surface and as-cast surface—Failure occurred at the bond plane without any damage to either the substrate or the overlay. A thin layer
of cement paste was adhered to the RPCM surface and could be noticed visually on parts of the substrate joint surface. This layer indicated the area where the concrete overlay was bonded strongly to the substrate. The specimens where this area was larger failed under higher loads. Figure 8 shows an example of two RPCM substrates with smooth surface (the case of concrete with 0.5% polypropylene fibers on steel-fiber RPCM) where the difference in the bond strength was due to the difference of this size of the adhesion area. This later difference is thought to be due to the free water that was not completely removed after wetting the joint surface prior to casting the concrete overlay. Free water may have prevented the concrete from completely adhering to the substrate causing a clean break. Climaco and Regan [10] reported that dry surfaces had better bond strength than the wet surfaces even when free water was removed.

2) For the specimens with grinder-roughened surface and air-cell surface--The failure was a shear failure of the concrete overlay above the RPCM substrate parallel to the joint. Examples of these specimens are shown in Fig. 9. The grooves of the grinder-roughened surface that were parallel to the shear force on the bond plane (the vertical grooves in Fig. 3(c)) were not as effective as the perpendicular grooves.

Effect of Test Parameters

In order to compare the different parameters, the failure stresses were normalized by calculating the ratio of the failure strength of the slant-shear specimens to the compressive strength of the corresponding overlay concrete. The relationship between this ratio and the fiber content of the concrete overlay is illustrated for the different RPCM substrates and the different surface treatments in Fig. 10.

1) RPCM type--Compressive strength of the RPCM substrate is 4 to 5 times higher than that of the concrete overlay (Tables 3 and 6 and Fig. 2). Therefore, changing the type of RPCM did not yield markedly different results because all failures occurred at the bond surface. The results from Figs. 6 and 10 show, however, that slant-shear specimens of the organic-fiber RPCM had higher bond strength than those of the steel-fiber RPCM especially for the specimens with an as-cast surface. This could be attributed to the smoother finish surfaces of the steel-fiber RPCM due to the lesser amount of fiber (2% Vol.) compared with the organic-fiber RPCM (3% Vol.).

2) Fiber content of concrete--For smooth and as-cast joint surfaces, higher fiber content of the concrete overlay resulted in much higher bond strength with the substrate as can be clearly seen in Fig. 10. Even when mechanical interlock was present, that is, the grinder-roughened surface and the air-cell surface, adding 0.1% by volume of fibers to the concrete increased the bond strength compared with the plain concrete. This observation was reported previously by Chen et al. [11] whose direct-push bond strength tests, with a vertical joint surface, showed that adding fibers (0.35% by volume in their study) resulted in mortars that bond strongly to old mortars.

The bond strength of the specimens with grinder-roughened surfaces and air-cell surfaces tended to decrease, however, when adding high volume of fibers (0.5% Vol.), as can be seen from the upper two lines in Fig. 10. A high volume of fibers may have
negatively affected the bond strength because it may have hindered the mechanical interlock in the grooves or concavities of the RPCM substrate surface. This is clearly visible in Fig. 9 by comparing the failure surfaces of a specimen with no fiber (middle) with a specimen with 0.5% Vol. fibers (right).

3) **Surface treatment**—The as-cast surface had good bond that provided up to 50% of the strength of the overlay concrete when using a high volume of fibers. The improvement in bond strength was between 2.5 to 3 times compared with smooth surfaces. The improvement was even higher for overlay concretes without fibers (10 times) because the smooth surface specimens without fibers in the concrete overlay had very low bond strength. The air-cell surface gave higher bond strength than the grinder-roughened surface (between 1.2 to 1.6 times). The preparation of the air-cell surface texture was much easier and less time/effort consuming than grinding or other similar machine-treatments like sandblasting. It also resulted in failure stresses that were up to 80% of the strength of the concrete overlay.

**CONCLUSIONS**

Based on the results of this study, the following recommendations are suggested when bond is required between reactive powder composite materials (RPCM) and ordinary concrete. A practical example is the case when using RPCM precast panels as permanent formwork for concrete structures. These recommendations are applicable equally when the substrate is concrete of higher strength than the overlay concrete because the tests were related to the failure at the joint plane, not in the substrate or the overlay materials.

1) If the surface of the RPCM (or concrete substrate) is not roughened, i.e., smooth or left as-cast, use a high volume of fiber in the overlay concrete because it improves the bonding considerably. Up to 0.5% by volume of fibers or higher, if workability is not a problem, can improve the bonding further.

2) If the surface of the RPCM (or concrete substrate) is roughened to have a mechanical interlock with the concrete overlay, do not use a very high fiber content because there may be a negative effect on the interlock mechanism. Fiber content of 0.1% by volume was found to increase the bond strength, but a value of 0.5% was found to decrease it. The numerical results for 0.1% and 0.5% fiber volumes were close, suggesting that values between 0.1% and 0.5% would not provide considerable improvement over using 0.1%.

3) Cast concrete on dry surfaces of RPCM (or concrete substrate), or remove the free water completely before casting when wetting is required for cleaning.

4) As a substitute for grinding or sandblasting treatments, casting the joint surface of the RPCM (or concrete substrate) on an air-cell plastic gives a surface with salt-shear bond strength comparable to these conventional methods. This method is easier, less time/effort consuming than machine-treatments, and is effective even if some of the air-cells warp or tear during casting.
ACKNOWLEDGMENTS

The authors would like to acknowledge Taiheio Cement Corporation for supplying the reactive powder composite material marketed under the trademark DUCTAL®.

REFERENCES


Table 1. Mixture proportions of the reactive powder composite material

<table>
<thead>
<tr>
<th>Type of RPCM</th>
<th>W / P (%)</th>
<th>Quantity (kg / m³)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Water</td>
<td>Premixed powder</td>
</tr>
<tr>
<td>RPCM with Steel Fiber</td>
<td>7.99</td>
<td>180</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>RPCM with Organic Fiber</td>
<td>7.99</td>
<td>180</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Properties of the fibers included in RPCM

<table>
<thead>
<tr>
<th>Type of fiber</th>
<th>Material</th>
<th>Length</th>
<th>Diameter</th>
<th>Density</th>
<th>Tensile Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monofilament</td>
<td>Ultra high strength steel wire</td>
<td>15</td>
<td>0.20</td>
<td>7.87</td>
<td>3000</td>
</tr>
<tr>
<td>Steel Fiber</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monofilament</td>
<td>Polyvinyl-acetate fibers</td>
<td>12~15</td>
<td>0.20~0.40</td>
<td>1.30</td>
<td>882</td>
</tr>
<tr>
<td>Organic Fiber</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3. Strength properties of RPCM

<table>
<thead>
<tr>
<th>Type of RPCM</th>
<th>Compressive Strength</th>
<th>Modulus of Elasticity</th>
<th>Poisson’s ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>RPCM with Steel Fiber</td>
<td>189.4</td>
<td>49.2</td>
<td>0.21</td>
</tr>
<tr>
<td>RPCM with Organic Fiber</td>
<td>137.4</td>
<td>44.6</td>
<td>0.21</td>
</tr>
</tbody>
</table>

Table 4. Mixture proportions of ordinary cement concrete used as overlays

<table>
<thead>
<tr>
<th>Type of Concrete</th>
<th>w / c</th>
<th>Quantity (kg / m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Water</td>
</tr>
<tr>
<td>Concrete without fibers</td>
<td>0.55</td>
<td>192.5</td>
</tr>
<tr>
<td>Concrete with 0.1% Vol. fibers</td>
<td>0.55</td>
<td>192.5</td>
</tr>
<tr>
<td>Concrete with 0.5% Vol. fibers</td>
<td>0.55</td>
<td>192.5</td>
</tr>
</tbody>
</table>
Table 5. Properties of the fibers added to the overlay concrete

<table>
<thead>
<tr>
<th>Type of fiber</th>
<th>Material</th>
<th>Length (mm)</th>
<th>Section (mm x mm)</th>
<th>Density (g/cm³)</th>
<th>Tensile Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fibrillated (net-like) PP fiber</td>
<td>Homopolymer Polypropylene</td>
<td>19</td>
<td>1.5 x 0.05</td>
<td>0.91</td>
<td>600 ~ 700</td>
</tr>
</tbody>
</table>

Table 6. Strength properties of the overlay concrete

<table>
<thead>
<tr>
<th>Type of Concrete</th>
<th>Compressive Strength (MPa)</th>
<th>Modulus of Elasticity (GPa)</th>
<th>Poisson’s ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concrete without fibers</td>
<td>37.4</td>
<td>31.9</td>
<td>0.2</td>
</tr>
<tr>
<td>Concrete with 0.1% Vol. fibers</td>
<td>37.1</td>
<td>29.3</td>
<td>0.2</td>
</tr>
<tr>
<td>Concrete with 0.5% Vol. fibers</td>
<td>36.2</td>
<td>27.2</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Table 7. Number of specimens and parameters of the slant-shear tests

<table>
<thead>
<tr>
<th>Overlay Substrate</th>
<th>Slant-shear test specimens joint surface</th>
<th>Compressive strength specimens</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Smooth surface</td>
<td>As-cast surface</td>
</tr>
<tr>
<td>Concrete with no fiber</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>RPCM with Organic-fiber</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Concrete with 0.1% Vol. fiber</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>RPCM with Organic-fiber</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Concrete with 0.5% Vol. fiber</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>RPCM with Organic-fiber</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Concrete with 0.1% Vol. fiber</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>RPCM with Steel-fiber</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Concrete with 0.5% Vol. fiber</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>RPCM with Steel-fiber</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>71</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 1. Examples of permanent formwork made of ultra-high performance reactive powder composite material

Fig. 2. Stress-strain relationships and failure modes for materials used
Fig. 3. Surface treatment of the RPCM substrate

Fig. 4. Schematic of the slant-shear test specimen

Fig. 5. The upper joint and the lower roller pad
Fig. 6. Bond strength results for all specimens based on the elliptical bond surface area.
Fig. 7. Failure stress results of the composite specimens based on the cylinder cross-sectional loading compared with the compressive strength of cylinders of the overlay concrete.
Fig. 8. Comparison between the bonding area of two specimens with smooth surface

Fig. 9. Examples of the failure surfaces

Fig. 10. Normalized results of the failure stress of the slant specimens and their relationships to the fiber content of the concrete overlay, the surface treatment, and the type of RPCM
A Magnetic Resonance Imaging Technique to Determine Lithium Distribution in Mortar

by J. J. Young, B. J. Balcom, T. W. Bremner, M. D. A. Thomas, and K. Deka

Synopsis:

Magnetic Resonance Imaging (MRI) is a nondestructive technique that can be used to spatially resolve distributions of certain nuclei. Lithium is a relatively sensitive nucleus for MRI. Therefore, it is possible to directly measure the distribution of lithium in cement-based materials. Lithium salts are used in concrete to suppress alkali-silica reaction.

The MRI relaxation parameters associated with lithium in cement-based materials are relatively short by traditional MRI standards. Due to the short relaxation parameters, special MRI measurement techniques and hardware considerations had to be developed in order to quantify lithium distributions in cement-based materials.

MRI has the potential to play an important role in concrete technology. While this method has been developed for laboratory studies, measurements could be made on cores extracted from existing concrete structures.

Keywords: alkali-silica reaction; lithium; magnetic resonance imaging; nondestructive testing
J.J. Young is a PhD candidate in the Department of Civil Engineering at the University of New Brunswick. His current research interest is the application of MRI to concrete durability problems.

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ACI Fellow T.W. Bremner, P.Eng., PhD, is an Honorary Research Professor of Civil Engineering at the University of New Brunswick and is Past President of the Atlantic Chapter of ACI. He received the ACI Cedric Wilson Award for Research on Lightweight concrete and is past chairman of ACI 213-Lightweight Aggregate Concrete and ACI 122-Energy Conservation.

Michael Thomas is a professor of civil engineering at the University of New Brunswick in Canada. He has been active in the field of cement and concrete research for 20 years previously working at the University of Toronto and Ontario Hydro in Canada, and the Building Research Establishment in the U.K. He is a previous winner of ACI's Wason Medal and the ACI Construction Practice Award, and is a member of numerous ACI committees.

K. Deka is a PhD candidate in the Department of Physics at the University of New Brunswick. His current research interest is density weighted MRI for short NMR signal lifetimes.

INTRODUCTION

Alkali-silica reaction (ASR) is a major problem in some concrete structures. The expansive nature of ASR leads to cracking of concrete. The expansions produced by ASR can lead to serviceability problems of concrete structures and accelerate other processes such as the ingress of chloride ions leading to the corrosion of embedded steel reinforcement and freezing and thawing damage.

McCoy and Caldwell (1) found that lithium can be used to prevent ASR expansion. Current commercial lithium formulations may be either incorporated into concrete at the time of mixing or be applied to existing concrete suffering from ASR. Treating a concrete structure with lithium salts and suppressing ASR expansions will potentially increase the service life of a structure. However, to successfully treat ASR-affected concrete, lithium salts
must penetrate to a critical depth and be of sufficient quantity in the pore solution to suppress expansion. It is therefore desirable to have a technique to identify spatially the distribution of lithium salts in portland cement based materials.

Pore solution extraction provides reliable information about the quantity of lithium salts held in the pore solution, as well as other ionic species (2). However, one limitation of this technique is that it is very difficult to identify spatially the distribution of ionic species that exist in a sample. To determine a lithium profile, the specimen has to be physically sectioned and each section tested individually. The spatial resolution of this technique is very low due to the large size of specimen needed to extract a sufficient quantity of pore solution for analysis.

In this study magnetic resonance imaging (MRI) is evaluated as a nondestructive technique, to identify spatially and quantify the distribution of lithium held in a portland cement based material. There are many nuclei sensitive to magnetic resonance (MR). Balcom, et al. (3) have successfully used MRI to identify spatially the distribution of hydrogen (water), sodium, and chlorine in portland cement based systems. Lithium, similar to hydrogen, sodium, and chlorine is an MR active nucleus.

MAGNETIC RESONANCE IMAGING

SPRITE is an MRI technique that is well suited for imaging nuclei with short signal lifetimes (4). This study used a modified version of the technique known as double half k SPRITE (DHK-SPRITE). The signal equation for DHK-SPRITE is given by Eq. 1, where \( S \) is the signal intensity at any point, \( \rho \) is nuclei density, \( t_p \) is the phase encoding time, \( T_2^* \) is effective spin relaxation time, and \( \alpha \) is the flip angle. \( \alpha \) and \( t_p \) are parameters that can be adjusted in the measurement.

\[
S = \rho \cdot e^{\frac{t_p}{T_2^*}} \cdot \sin \alpha \tag{1}
\]

Fig. 1 schematically outlines the DHK-SPRITE technique. It is desirable to use DHK-SPRITE because of the short relaxation times associated with lithium in mortar. Additionally, this technique is advantageous if \( T_2^* \) is known or is constant. The signal becomes proportional to the quantity of lithium at any point.

MATERIALS AND METHODS

Quartz fine aggregate and Type 1 portland cement were used to prepare mortar with a W/C of 0.5. The mortar was prepared in accordance with ASTM
Two cylindrical specimens, 43-mm in diameter and 50-mm long, were cast and cured under sealed conditions for 3 days at 23 °C. Specimen 1 was then oven dried at 105 °C for 1 day and Specimen 2 for two days prior to exposure to lithium nitrate solution. Teflon tape was applied to the curved surface of the specimen. Each specimen was then placed such that the bottom of the cylinder was submerged approximately 1-2 mm into a lithium nitrate solution as shown in Fig. 2.

Mass and MR measurements were performed at different times for each specimen. Specimen 1 had measurements performed after approximately 1, 2, 3, and 24 hours of contact with the LiNO$_3$ solution. Specimen 2 had measurements performed after 3, 6, 9, and 22 hours of contact with the LiNO$_3$ solution. MR measurements included free induction decay (FID), inversion recovery, and DHK-SPRITE profiles. FID measurements were made to estimate the bulk $T_2^*$ of lithium in mortar. Additionally, FID measurements were used to develop the relation between MR signal and the change in mass of the specimen due to lithium penetration. Inversion recovery measurements were made to estimate the bulk $T_1$, an additional MR parameter, of lithium in mortar. DHK-SPRITE profiles were obtained to determine the depth and relative quantity of lithium present in the sample. It should be noted that it is $^7$Li that is detected. It has a natural abundance of 92.58% and has 27% of the sensitivity of $^1$H (5).

MR measurements were acquired using a 2.4-T, 32 cm bore, superconducting magnet with a water cooled gradient insert. A birdcage type probe was used for signal detection. The radio frequency amplifier was 2 kW. At this magnetic field, the resonance frequency of lithium is 38.54 MHz. MRI parameters $a$ and $t_p$ were 5° and 30 μs respectively.

RESULTS AND DISCUSSION

Bulk $T_1$ and $T_2^*$ relaxation times for Li were on average measured to be 10 ms and 120 μs. The relatively short relaxation times for Li in portland cement materials requires special consideration for the selection of a suitable MRI technique. The SPRITE technique has been shown to be very well suited for imaging materials with short signal life times (4). Traditional MRI techniques, such as those readily used for clinical purposes would be unsuitable to measure the distribution of Li in cement based materials, due to the fact that they have been designed to image relatively long signal life time species.

Prior to MRI profiles, the increase in mass of the specimens to the nearest 0.01 g was determined using a balance. The amplitude of the FID was also measured at each time period. The initial FID amplitude is generally a bulk measure of the mass of the MR sensitive nucleus. Both the FID amplitude and gravimetric results were normalized and plotted in Fig. 3. Results of linear regression analysis indicate a linear relation between MR signal and mass gain.
The short time scale of lithium penetration and the direct relation between MR signal and mass suggests that the signal observed is only of lithium held in the pore solution of the paste phase. MR excites all the lithium nuclei; however, relaxation times of the individual nuclei will determine how much signal is detected relative to the MRI method. The location of the nuclei, for example if it is physically or, chemically bound, or free in solution, will affect the relaxation times. Chemically combined hydrogen in cement paste will have relaxation times such that the signal component from this form of hydrogen will not be detected and only water held in the pore structure will be observed (4). It is believed that this method only detects lithium in the pore solution of the cement paste phase. Currently a program is underway to look at the effects of hydration on lithium MR signal.

One-dimensional DHK-SPRITE profiles, with a nominal resolution of 1.56 mm were measured for the two samples at various times as shown in Figs. 4 and 5. A reference is present in both figures and used to permit scaling of profiles to compensate for variations in the sensitivity of the instrument. For these measurements, no scaling was necessary. As expected, the penetration depth increased with contact time. At penetration times 1.2, and 3 hours, the rate of penetration decreases. After 22 and 24 hours, lithium had penetrated approximately 35 mm and 40 mm, respectively. At these times lithium had not penetrated the full depth of the specimen. In addition, the signal intensity at a given point within the penetration region increased with time. Assuming negligible effects of T2* weighting, some pores become filled much slower than others.

CONCLUSIONS

The DHK-SPRITE technique was used successfully to measure the penetration, with millimeter resolution, of lithium into mortar. The cement used was a Type 10 portland cement. The measurement time is rapid which will permit time resolved studies.

The MR signal and mass are directly related. On short time scales, the MR signal observed is directly proportional to the mass of Li held in the pore structure of the cement paste phase.

Work is in progress to understand the effects of hydration and binding of Li on the observed MR signal and resulting images.

ACKNOWLEDGEMENTS

This work was supported by equipment and operating grants awarded to BJB by NSERC of Canada. The UNB MRI Centre is supported by an NSERC major facilities access grant (BJB, MDAT, TWB). BJB thanks the Canada
Chairs program for a Tier 1 Canada Research Chair. JJY thanks NSERC for a Canada Graduate Scholarship.

REFERENCES


Fig. 1. One-dimensional DHK-SPRITE technique. The magnetic field gradient (Gz) is ramped in 64 steps. A single data point is acquired at each gradient step at the time t₀ after the application of a radio frequency (RF) pulse, with flip angle α. The center point is acquired after a 5T₁ time delay.
Fig. 2. Unidirectional LiNO₃ uptake by portland cement mortar.

Fig. 3. Normalized FID intensity versus normalized mass gain.
Fig. 4. Lithium distribution at times 1 h (●), 2 h (■), 3 h (▲), and 24 h (○) immersion in LiNO₃ for mortar Specimen 1. DHK-SPRITE measurement parameters: FOV=100 mm, 64 points, t =30 μs, α=5°, 5T =100 ms, scans=1024, and acquisition time 6 min. The specimen extended from 35 mm to 85 mm on the x-axis scale.

Fig. 5. Lithium distribution at times 3 h (●), 6 h (■), 9 h (▲), and 22 h (○) immersion in LiNO₃ for mortar Specimen 2. DHK-SPRITE measurement parameters: FOV=100 mm, 64 points, t =30 μs, α=5°, 5T =100 ms, scans=1024, and acquisition time 6 min. The specimen extended from 35 mm to 85 mm on the x-axis scale.