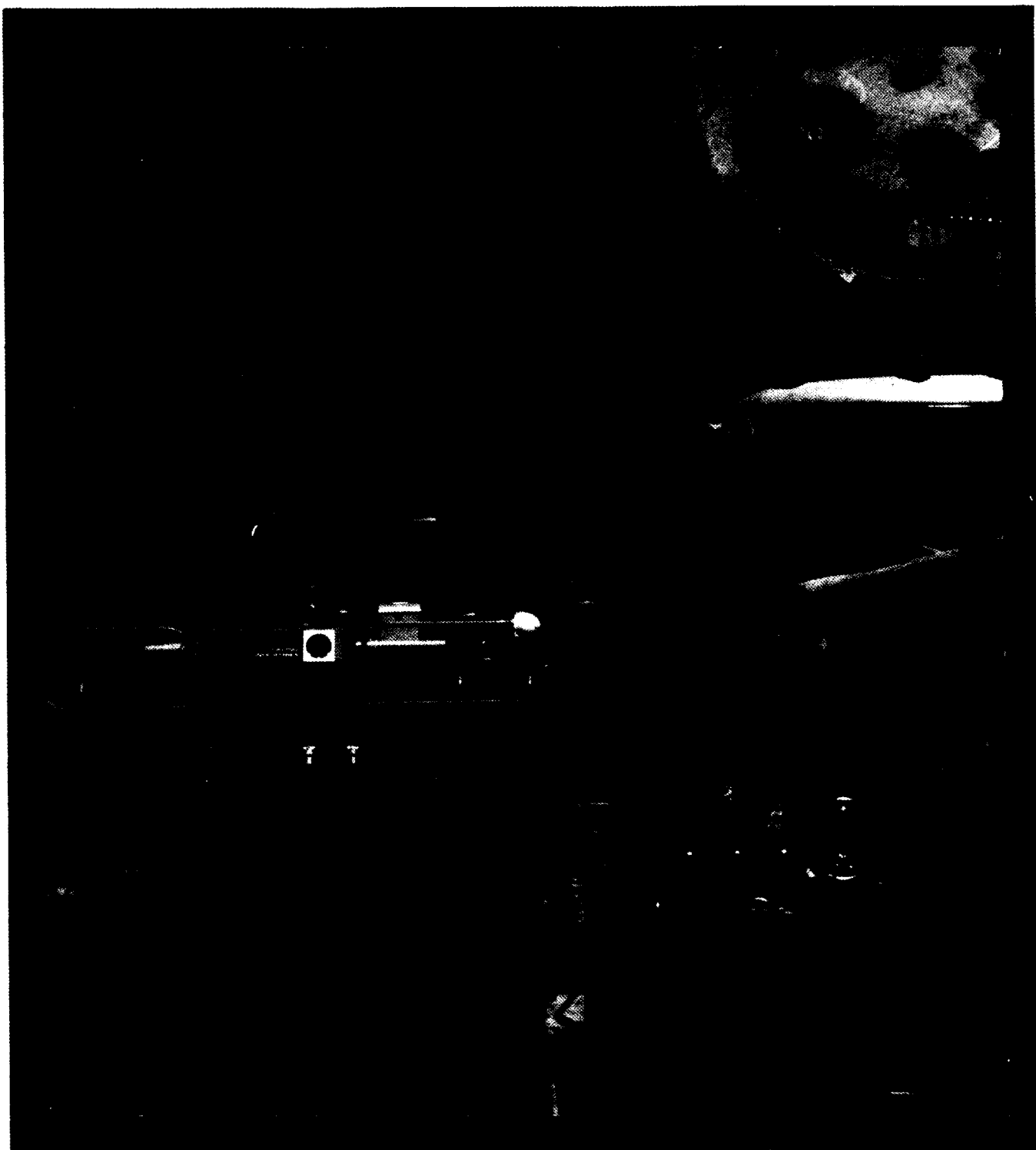


CHEMICAL ADMIXTURES



Compilation 23

American Concrete Institute

Chemical Admixtures

ACI Compilation 23

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Preface

ACI Compilations combine material previously published in Institute periodicals to provide compact and ready reference on specific topics. The Material in a compilation does not necessarily represent the opinion of an ACI technical committee — only the opinions of the individual authors. However, the information presented here is considered to be a valuable resource for readers interested in the subject.

William F. Perenchio
Chairman, ACI Committee 212
Chemical Admixtures

On The Cover: Fast-track concrete paving allows today's construction traffic to use pavement placed only 12 hours earlier. This new paving technique was recently introduced to Michigan when a non-reinforced unbonded concrete overlay was placed on the entrance road to the Dundee Cement Company plant. A large group of city, county, and state engineers, contractors, and other related industry personnel attended the demonstration. (Photo by Robert I. Pearson, engineering editor, *Concrete International*.)



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Admixtures — What's New on the Market

by John M. Scanlon

Concrete technology is changing rapidly. Industrial research has for the past 20 years taken the lead in developing new innovative materials, that, when used to their fullest potential, greatly enhance the properties of hydraulic cement concrete. Concrete is no longer a mixture of one, two, and three shovels of cement, sand, and coarse aggregate, respectively. It has matured. It is ready to lead us into the 21st century.

Many changes have resulted from the development of technology in new mineral admixtures (pozzolans) and chemical admixtures. The cement industry has finally discovered that not everyone desires to use a finely ground Type I/II combination, even though such cements may be more economical to manufacture, transport, and store. Concrete producers have become more sophisticated in their knowledge of concrete properties and the manufacture of concretes having various qualities.

About 15 years ago, mineral and chemical admixture companies had to produce admixtures that could be used successfully with whichever hydraulic cement happened to be available to the concrete producer. Now the knowledgeable concrete producer is requiring hydraulic cement that will permit his mineral and chemical admixtures to react the most efficiently.

The American Concrete Institute Committee 116 publication SP-19, "Cement and Concrete Terminology," defines concrete as "a composite material that consists essentially of a binding medium within which are embedded particles or fragments of aggregate, usually a combination of fine aggregate and coarse aggregate; in portland-cement concrete, the binder is a mixture of portland cement and water." It does not say that concrete will weigh 144 pounds per cubic foot (2306 kg/m³) or have a compressive strength of 3000 psi (21 MPa). It does not say that concrete will have an initial setting time of six hours

or a final setting time of nine hours. It does not say that the concrete must freeze below 32 F (0 C) or, for that matter, boil at 212 F (100 C). It does not say that the concrete shall have a modulus of elasticity of 3.0×10^6 psi. The point is, the industry has traditionally been placing additional requirements on hydraulic cement concrete so that the composite material will do what's required by the user and attain the particular hardened properties that are desired by the engineer or owner of the structure in question.

Based on the needs of the contractor in constructing concrete structures and the designer's requirements for specific hardened concrete properties, standard practices, sampling procedures, test methods, and specifications have been established to assist in ensuring that the concrete develops the desired properties. These standards have responded to the needs of the concrete industry for decades, but now technology demands more. Now the users and owners are demanding greater capabilities from their concrete. They need concrete that can:

- Gain strength, without freezing, down to and below 20 F (–7 C).
- Remain workable for hours or days without hardening, and then set on demand.
- Remain cohesive while being dropped through water, without the use of a tremie.
- Attain a modulus of elasticity of 7500 ksi (51 GPa) at age 28 days.
- Attain a strength of 20,000 psi (138 MPa) at age 56 days.
- Provide positive protection of embedded metals from corrosion.

Chemical admixtures²

Freeze protection admixture

ACI Technical Committee Report 306R-88, "Cold Weather Concreting," recommends that concrete placed in sections of 12 in. (300 mm) or less be placed at a temperature of at least 50 F (10 C) and be maintained at 50 F (10 C)

for the duration of the protection period.³ Such requirements actually cause many contractors to curtail concrete construction, especially when ambient temperatures fall below freezing. Only dedicated contractors, knowledgeable in cold weather construction, attempt concrete construction below 20 F (–7 C). In addition, ACI 306R recommends that a 12 in. (300 mm) section of concrete placed above ground, and containing 500 lb/yd³ (296 kg/m³) of cement, be protected with insulation having a thermal resistance (*R*) rating of 6 hr-ft²-F/Btu when the ambient temperature is expected to drop to 20 F (–7 C).

Curtailling concrete operations during low ambient temperatures is expensive and may not be cost-effective. Freeze-protection admixtures have been developed that can be used to prevent the concrete from freezing, down to an ambient temperature of approximately 20 F (–7 C), without insulation. In addition, these innovative freeze-protection admixtures comply with all requirements of ASTM C 494, "Standard Specification for Chemical Admixtures for Concrete,"⁴ for Type C accelerating, and for Type E water-reducing and accelerating admixtures. Typical test results are presented in Table 1.

The data in Table 2 illustrate that this admixture does not promote corrosion of steel in concrete, even at a dosage of 120 fl oz/cwt (78 cm³/kg) of cement.

Freeze-protection admixtures have been used in construction for approximately five winters with no known incidents of concrete freezing. Many specifiers are now requiring its use, so concrete construction will most likely continue throughout the winter months.

The parking garage of the Chrysler Technical Center, Detroit, Michigan, required 40,000 yd³ (30,600 m³) of concrete to be placed all year around. A

Presented at the 1992 National Concrete Engineering Conference, March 30 — April 1, Chicago, Illinois.



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Table 1 — Freeze-protection admixture laboratory evaluation results (ASTM C 494 requirements).

Parameter	Type C accelerator	Type E water reducing and accelerating	Freeze-protection admixture
Water content (maximum % of control)	—	95	90.8
Time of setting (hr:min)			
Initial	at least 1:00 earlier and not more than 3:30 earlier at least 1:00 earlier		2:02 earlier
Final			2:27 earlier
Compressive strength, (minimum % of control)			
3-day	125	125	136
7-day	100	110	126
28-day	100	100	116
6-month	90	100	119
1-year	90	100	121
Flexural strength, (minimum % of control)			
3-day	110	110	128
7-day	100	100	109
28-day	90	100	103
Length change (% increase over control)	0.010 max.	0.010	0.008
Relative durability factor (minimum)	80	80	96

Table 2 — Time-to-corrosion test results.

Mix ID	w/c	Admixture dosage (fl oz/cwt)	NaSCN concentration* (% by weight of cement)	Average time-to-corrosion (weeks)
1	0.57	0 ^a	—	1.5
2	0.57	20	0.045	5
3	0.55	60	0.135	11
4	0.52	90	0.203	7
5	0.52	120	0.271	12

*Thiocyanate ion (SCN⁻) is 71.6% of NaSCN
^aControl

freeze-protection admixture served as an all-temperature accelerator, in addition to protecting the concrete during the winter. In the summer, at ambient temperatures of 80 to 90 F (27 to 32 C), 5 fl oz/cwt (3 cm³/kg) of the freeze-protection admixture was used for the concrete to attain high early strength. All of this concrete attained compressive strengths exceeding 5,000 psi (34.5 MPa).

A 40 percent cost savings was realized in using a freeze-protection admixture on the Corning Glass Works, State College, Pennsylvania. At a dosage of 90 fl oz/cwt (59 cm³/kg), the admixture was used to protect the concrete from freezing and permit the slabs to be finished within 4 hours at ambient temperatures around 20 F (-7 C).

This particular freeze-protection admixture contains sodium thiocyanate

(NaSCN). Its effects on corrosion of steel in concrete when used at different dosages was evaluated by using the Southern Climate Accelerated Test Method.⁵ The results of this long-term test are shown in Table 2.

Extended set control admixture system

Conventional retarding and accelerating admixtures have been in use for many years. These admixtures are used to retard or accelerate the setting time of concrete by a few hours. According to ASTM C 494, the set alteration is limited to a minimum of 1 hour and a maximum of 3½ hours, whether it is retardation or acceleration.

Attempts have been made to extend the setting time of concrete beyond the typical retardation times achieved with conventional retarding admixtures.³ Al-

though the setting times were lengthened in these attempts, the workability of the concrete was compromised because of the inability to control the extended time of retardation. Recent developments in admixture technology have produced a two-part chemical system that, in effect, extends the setting time of concrete indefinitely. This is done by essentially stopping hydration of the cement, then stimulating resumption of hydration whenever it is desired, without loss of workability. The chemical that stops cement hydration will be referred to as the stabilizer and the reinitiator as an activator. The American Concrete Institute presently refers to these admixtures as "extended set-control admixtures."

Although the extended set-control admixture was primarily developed to reduce wasted concrete and wash water, additional innovative uses have been developed, such as:

- Extending cementitious grout workability from about 2 hours to 36 hours.
- Implementing long hauls of concrete, resulting in increased workability and reduced concrete temperature.
- Preventing cold joints in concrete caused by delayed delivery of concrete.

Anti-washout admixture

Experience has shown that the cost of dewatering hydraulic structures to place concrete averages about 50 percent of the construction cost. Therefore, the ability to place concrete without dewatering would result in significant savings. The primary procedure of placing concrete underwater has been by use of a tremie. This procedure is relatively slow, and maintaining embedment of the tremie in the fresh concrete is tedious but critical. If water gets into the tremie, cement is washed from the tremie concrete, resulting in cement-deficient layers of concrete in the placement. Many such weak areas go undetected during construction because detecting them requires unusually close inspection.

During the early 1980s, admixtures were developed that dramatically prevented cement from being removed from the concrete when falling through water. This concrete has excellent cohesion and can either be used by dropping directly through water, or as tremie concrete that assures the elimination of cement-deficient layers. The most successful of these anti-washout admixtures are composed primarily of derivatives of cellulose and water-reducing chemicals.

Washout and abrasion tests

The effects of the anti-washout admixture on setting time, on relative resistance to washout, and on underwater abrasion have been evaluated. The test program included evaluation of the effects of concrete temperature and the presence of fly ash. The washout test was conducted according to the procedure described in Appendix A of Technical Report REMR-CS-18, "Evaluation of Concrete Mixtures for Use in Underwater Repairs," U.S. Army Engineer Waterways Experiment Station. The underwater abrasion tests were conducted according to Corps of Engineers CRD-C 63-80,⁶ which was the basis for ASTM C 1138-89, "Standard Test Method for Abrasion Resistance of Concrete (Underwater Method)."

Freeze-thaw tests

The U.S. Bureau of Reclamation in Denver, Colorado, has conducted tests on concrete for the Coachella Canal In-Place Lining Project, containing the anti-washout admixture and Type II cement, with no air-entraining admixture.* The concrete contained 4.5 percent total air, but no air void parameters were determined. The results from tests on 3 x 6 in. (76 x 152 mm) cylinders, which went through freezing and thawing cycles at a rate of 3 per 24 hours, took 559 cycles to reach a 25 percent weight loss. The acceptable result is anything greater than 500 cycles before reaching the 25 percent loss.

Sulfate resistance

Sulfate expansion tests were also performed, using 3 x 6 in. (72 x 152 mm) cylinders. The test procedure involved soaking of the test cylinders in a 2 percent sodium sulfate solution at room temperature for 16 hours, followed by air drying at 130 F (54 C) for 8 hours. This cycle was repeated until 0.5 percent expansion was achieved.

The test results indicate that after 600 cycles, considered to be equivalent to 16 to 20 years of service life, the expansion of concrete treated with the admixture is at 0.29 percent. The 0.5 percent expansion limit was never reached.

Corrosion inhibiting admixtures

Following the vast increase in highway construction starting in the late 1950s, and continuing to this day, much of the infrastructure has been found to be decaying due to corrosion of embedded

Table 3 — Chloride permeability based on charge passed.

Charge passed (coulombs)	Chloride permeability	Typical of
4000	High	High water-cement ratio (>0.6) Conventional PCC
2000 — 4000	Moderate	Moderate water-cement ratio (0.4 to 0.5) Conventional PCC
1000 — 2000	Low	Low water-cement ratio (<0.4) Conventional PCC
100 — 1000	Very Low	Latex modified concrete Internally sealed concrete
100	Negligible	Polymer impregnated concrete Polymer concrete

Table 4 — Concrete properties.

Mix proportions					Hardened concrete	
Mix ID	Portland cement	Silica fume	Fly ash	w/c	28-day compressive strength (psi)	28-day chloride permeability (coulombs)
1	497	—	74	0.52	4060	8356
5	497	37	—	0.52	5278	2201
17	507	38	152	0.52	5829	1112
4	505	76	75	0.52	6902	579
14	610	—	—	0.43	5699	4192
8	612	—	153	0.43	6221	3777
3	603	15	—	0.43	5612	4880
2	605	38	75	0.43	7439	456
7	605	38	76	0.43	7149	1035
12	610	38	76	0.43	7279	610
16	600	75	—	0.43	7265	301
9	608	76	152	0.43	8715	203
13	708	—	76	0.37	7265	2441
11	708	15	151	0.37	8294	1081
10	700	37	—	0.37	7120	816
15	703	38	150	0.37	8149	416
6	706	76	76	0.37	9077	283

metals in concrete. This is not only an American problem, it is a problem for all countries with concrete exposed to saline solutions of any sort, and especially for concrete treated with chlorides to remove ice and snow.

The first attempt at a solution to these corrosion problems was to reduce the water-cement ratio of the concrete and to increase the concrete cover over reinforcing steel. These measures primarily just slightly increased the time-to-corrosion and were not a permanent solution to the problem. Responding to this problem, the Federal Highway Administration developed a rapid test method for determining the apparent chloride permeability of various concretes. This method is described in the

report, FHWA /RD-81/119, "Rapid Determination of Chloride Permeability of Concrete," and is commonly referred to as the AASHTO T 277 test method. Table 3 shows the five chloride permeability categories that were created.⁷

Corrosion inhibitors, such as calcium nitrite, have been reported to delay the initiation of corrosion and control the rate of corrosion by stabilizing the passivating layer of iron oxide film on the embedded metal. These liquid admixtures have been around since the mid 1970s and have been successfully used in combination with condensed silica fume. Using data from research and field evaluations, the manufacturer of the calcium nitrite corrosion inhibitor has developed a system for predicting

*Bureau of Reclamation Tests on Anti-Washout Admixtures. Personal communication from James Pierce.

the service life of concrete containing various quantities of calcium nitrite, including various quantities of condensed silica fume. This service life is attained by varying the dosage rate of calcium nitrite.

Another manufacturer recently began marketing a liquid corrosion inhibitor which, unlike calcium nitrite, does not involve reactivity with chlorides and consequently can be used in a fixed dosage, and will not accelerate the time of setting.

Both of these admixtures are important developments. Their introduction has had a significant impact in extending the time-to-corrosion. Along with other mineral admixtures, they may improve the quality of our infrastructure for a long time.

Mineral admixtures Ground granulated blast-furnace slag

Ground granulated blast-furnace slag (GGBS) has been used as a cementitious material since the 18th century. GGBS is a mineral admixture that is currently being interground with portland cement to form portland blast-furnace slag cement (a blended cement). It is also batched separately at the concrete batch plant. Batching separately from the cement has two advantages: each material (cement, GGBS) is ground to its own optimum fineness; and the proportions of each ingredient can be varied. Such convenience provides more versatility to the concrete producer in developing specialty concretes. The quantity of GGBS used in comparison to the total cementitious materials (GGBS and portland cement) normally varies from 25 to 70 percent by mass. The following benefits are reported to be derived by using GGBS in concrete:

- Reduces temperature in mass concrete
- Greatly reduces permeability
- Improves sulfate resistance
- Reduces potential expansion due to alkali-aggregate reaction

Fly ash

Fly ash is "the finely divided residue resulting from the combustion of ground or powdered coal which is transported from the firebox through the boiler by flue gases" (ACI 116). Fly ash has been around for many years. It is generally classified as Class F or Class C. Class F is usually produced by burning anthracite or bituminous coal, and Class C is normally produced by burning sub-bituminous coal or lignite.

Fly ash provides many benefits in concrete, some of which are:

- Improved workability
- Reduced bleeding (which could be beneficial or not)
- Improved long-term strength
- Generally reduced generation of heat (Class C)
- Reduced permeability

Many benefits accrue from using fly ash in concrete. It is the author's opinion that unless there is an extraordinary reason that it shouldn't be used, all concrete should contain fly ash. Most 21st century concrete will most likely contain fly ash either as a blended cement or batched at the mixing plant. Many people in the concrete industry feel very strongly that concrete containing fly ash and a small quantity of condensed silica fume would have equal corrosion resistance to concrete containing larger quantities of condensed silica fume only as a mineral admixture. Extracting some data from Reference 7, we can see in Table 4 the effects fly ash, in combination with a small dosage of condensed silica fume, has on the 28-day chloride permeability of concrete.

In evaluating the test results in Table 4, the best results appear to have been obtained when condensed silica fume and fly ash were used together. Also, considering the cost of the various mixtures, obviously the use of fly ash with reduced quantities of condensed silica fume becomes the most cost-effective for equally low chloride permeabilities.

Conclusions

- Concrete can now be placed in freezing weather without freezing, gain strength rapidly, and remain durable by using a freeze-protection admixture.
- Concrete can be stopped from hydrating, then used when needed, by using an extended-set control admixture.
- Underwater structures can now be constructed and attain high quality without dewatering by using an anti-washout admixture.
- The use of both mineral and chemical admixtures can greatly increase the ability of concrete to resist the corrosion of embedded metals.
- Fly ash is a major contributing partner in developing cost-effective, corrosion-resistant concrete.
- Greater efforts need to be made to transfer such technology, so that more rapid implementation can occur.
- These innovations in chemical admixtures for use in concrete should greatly extend civil engineering capabilities by reducing wasted concrete and washwater from mixing trucks, allowing placement of concrete at relatively low (20 F [-7 C]) temperature, and placing concrete under water without the use of a tremie. Such capabilities reduce concrete construction costs, and the placement of concrete year around with reduced insulation during the winter.

• Innovations in mineral admixtures should provide the capability of obtaining exceptionally high strengths and moduli of elasticity, plus greater abilities to produce more impervious and corrosion-resistant concrete.

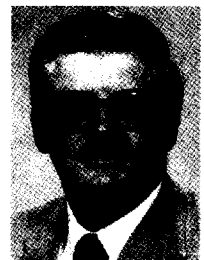
- Concrete technology is expanding rapidly. When further innovation is needed, an admixture will most likely be developed to respond to that need.

References

1. ACI Committee 116, "Cement and Concrete Terminology," SP-19(90), American Concrete Institute, Detroit, p. 15.
2. Senbetta, E. and Scanlon, J., "Effects of Three New Innovative Chemical Admixtures on Durability of Concrete," CANMET Second International Conference on Durability of Concrete.
3. ACI Committee 306, "Cold Weather Concreting," ACI 306R-88, American Concrete Institute, Detroit, p. 15.
4. "Standard Specification for Chemical Admixtures for Concrete," ASTM C 494, 1990 Annual Book of ASTM Standards, Section 4, V. 04.02, ASTM, Philadelphia, Pennsylvania, p. 250.
5. Gouda, V. K. and Monfore, G. E., "A Rapid Method for Studying Corrosion Inhibition of Steel in Concrete," *Journal of the Portland Cement Association Research and Development Libraries*, Sept. 1965, pp. 24-31.
6. *Handbook for Concrete and Cement*, Vol. 1, U.S. Army Corps of Engineers Waterways Experiment Station, Vicksburg.
7. Berke, Neal S.; Pfeifer, Donald W.; and Weil, Thomas G., "Protection Against Chloride-Induced Corrosion," *Concrete International*, V. 10, No. 12, Dec. 1988, pp. 45-55.

Selected for reader interest by the editors.

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REVISED!

The REVISED! ACI 318-89, Building Code Requirements for Reinforced Concrete, and Commentary

has been further edited to provide you with greater clarity and reduced ambiguity. The Code continues to provide engineers and designers with the minimum requirements for design and construction of reinforced concrete buildings. The Commentary presents background details, intent of various sections and suggestions for carrying out code requirements.

In an easy to use format, the revised Building Code combines the Code and Commentary under one cover, in parallel columns, with Commentary sections adjacent to the corresponding Code sections. Chapter 3 contains a newly updated list of ASTM standards. Revisions in Chapter 4 clarify the proper use of blended cement, slag, fly ash and other pozzolans. The term "water-cementitious materials ratio" is introduced to provide for the use of cementitious materials other than portland cement. All durability-related provisions remain in Chapter 4. Tables 4.2.2 and 4.3.1 addressing corrosion protection and sulfate resistance have been revised. All concrete quality, mixing and placing provisions are consolidated and remain in Chapter 5. Table 9.5(c) - Minimum Thickness of Slabs Without Interior Beams has been revised to include Grade 75 reinforcement. Chapter 12 includes an added factor for epoxy coated hook bars. A section has been added to Chapter 13 for lift-slab construction. A new Figure R13.14.8.6 - Location of Integrity Steel for Lift-Slab Construction has been added to Chapter 13. In Chapter 17, the computation of the horizontal shear strength, for prestressed members used in composite construction, has been simplified and made more consistent with the vertical shear computations in Chapter 11.

Chapter 21, Special Provisions for Seismic Design, has been completely reformatted into a more user friendly design sequence. Covered extensively within the revised Codes 21 chapters are the

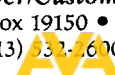
latest revisions on topics which include: minimum thickness of two-way slabs; requirements for skin reinforcement on large-size beams; two-way shear provisions around drop panels, shear capitals, and slab to column moment transfer. In addition, provisions for development length are expanded to account for concrete cover, spacing of reinforcement, and enclosing transverse reinforcement. The revised Code also sets limits on the $\sqrt{f_c}$ term in development length and shear unless higher minimum web reinforcement levels are used; and a revised section introduces provisions for general structural integrity.

Throughout the revised Code, permissive language has been removed. The relation of the ACI 318 Code to the legally adopted general building code is clarified.

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VAE Redispersible-Powder Hydraulic-Cement Admixtures

by D. Gerry Walters

Vinyl acetate-ethylene (VAE) copolymer redispersible powders are used as admixtures in hydraulic cement formulations.

Manufacturing VAE powders

VAE redispersible powders are manufactured by using two separate processes. The latex copolymer is made by emulsion polymerization which is then spray-dried to obtain the powder.

A typical composition for the emulsion polymerization of a suitable VAE copolymer is given in Table 1. After the polyvinyl alcohol is dissolved in hot water, a portion of the catalyst system and vinyl acetate monomer are added while the reactor is being heated. At the same time, the reactor is pressurized by the addition of liquid ethylene. When the required pressure and temperatures are obtained, the remainder of the monomers and catalyst system are added to the reactor at a constant rate over one to two hours.

When the reaction is complete, the latex is transferred to another vessel where additions are made to adjust the pH and viscosity. The resulting latex is formulated further by the addition of several ingredients such as bactericides, spray-drying aids, and application chemicals. The latter can include such materials as superplasticizers, anti-sag agents and defoamers which increase or decrease such parameters as workability or air content of the VAE powder-modified cement

Table 1 — VAE latex composition

Ingredient	Parts by Weight
Vinyl Acetate	80 - 90
Ethylene	20 - 10
Polyvinyl Alcohol	4 - 10
Catalyst System	<2
Water	80 - 100

Table 2 — Typical properties of VAE powders

Ash content, %	~9
Glass transition temperature, differential scanning calorimeter, inflexion, °C	-5 to +10
Moisture content, %	<1
Particle size, microns	~80

mixtures. At this time, only polyvinyl-alcohol-stabilized copolymers are used to make redispersible VAE powders.

A schematic of a typical spray-drying operation is given in Fig. 1. Prior to introduction into the system, the VAE latex is diluted to a suitable solids or nonvolatile content and is introduced into the spray-drying chamber via an atomizing device together with heated air. Air inlet temperatures are typically between 170 and 200 C (338 to 392 F). At this point, the water of the latex is vaporized leaving the copolymer as a fine powder. The flow of the powder through the system is controlled by the main fan which draws the powder into the cyclone where separation of the

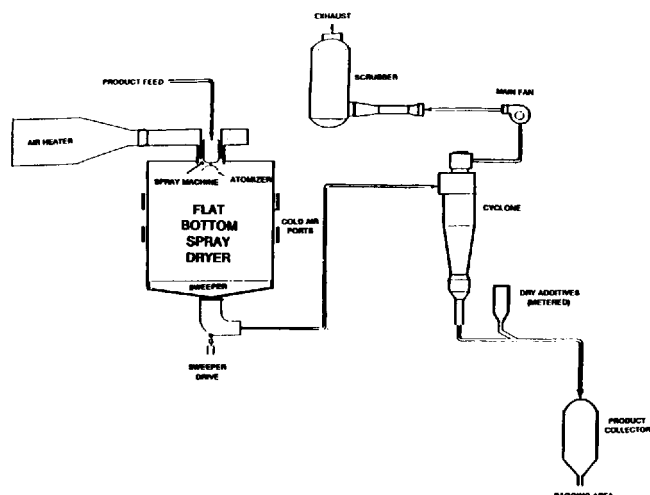


Fig. 1 — Spray-drying system.

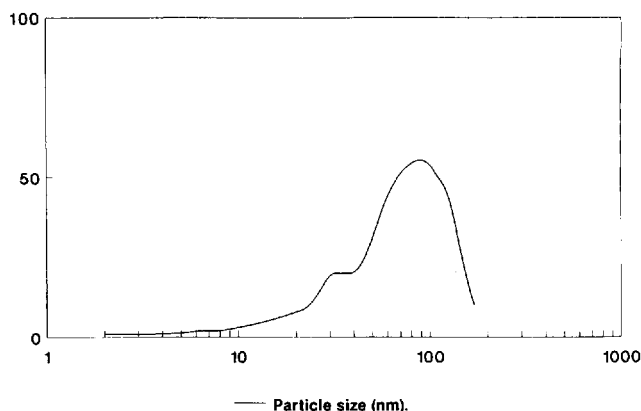


Fig. 2 — Particle size of Vinyl Acetate-Ethylene Copolymer.

powder from the hot air and other vaporized materials occurs. The latter are sent to a scrubbing system for odor and particulate discharge control. Outlet temperatures are typically between 65 and 85 C (149 to 185 F). The powdered latex flows from the cyclone to the product collector where the material is packaged into bags, drums, or totes. Anti-blocking aids can be introduced into the powder at the spray-drying chamber or downstream after the cyclone. These aids are required to prevent "caking" of the VAE powder on storage. Clays, silicas and calcium carbonates are used for this purpose. Application chemicals may also be added downstream.

Properties of VAE powders

VAE redispersible powders are usually free-flowing, white powders. Table 2 gives typical physical properties of some VAE powders. The ash content, which primarily comes from the anti-blocking aid, will vary depending on the type of material. Calcium carbonates and clays will give lower ash contents than equivalent amounts of silicas. The bulk density of the powder is quite low — less than 25 percent that of portland cement.

The particle size distribution of the powder is described in Fig. 2 and usually averages about 80 microns. However, these particles are agglomerates that break up on redispersing in water to give typical VAE latex-particle sizes of one to five microns. The glass-transition temperatures (T_g) of VAE powders

Table 3 — Redispersed properties

Particle size, micron	1 - 5
Film properties:	
tensile strength, psi	≈ 1,000
elongation at break, %	≈ 400

will vary depending on the ratio of vinyl acetate to ethylene in the copolymer. Most commercial VAE powders have a T_g between -5 and +10 C (+23 to +50 F). The VAE powders used in the experimental work described here have T_g values of approximately 1 C (+34 F).

If these powders are stored improperly (at high temperature, at high humidity, and under load), the VAE powder will tend to "cake" and form lumps. These VAE powders easily redisperse when mixed with water or water dispersions, but unless the viscosity of the redispersed latex is raised the VAE particles will tend to settle because their specific gravity is higher than that of water. Some typical properties of the redispersed polymer are given in Table 3.

Test methods

Flow of the unhardened mortars was measured by one of two procedures. The first used an ASTM C 230 flow table and flow was measured after 25 drops. An alternative procedure was used for mortars with too great a flow to be measured using the flow table. This method involved placing a open-ended cylinder vertically on a flat

Table 4 — Self-leveling floor overlay

	parts by weight
portland cement	70.0
alumina cement	25.0
gypsum	5.0
fine silica sand	70.0
calcium carbonate	20.0
superplasticizer (powder)	1.0
rheology modifier	0.1
VAE redispersible powder	10.0
water	≈ 50.0

surface. The cylinder, which measured 5.7 cm (2.2 in.) high and 3.7 cm (1.5 in.) in diameter, was filled with the mortar and the top surface was floated with a spatula so that it was level with the top of the cylinder. The cylinder was immediately lifted vertically in a swift motion. After the resultant mortar "patty" had hardened, its diameter was measured in four places, about 45 degrees apart, and the average was calculated. Density of the unhardened mortars was calculated by measuring the mass required to fill a 400 ml Vicat cup.

Unless stated otherwise, the VAE-modified mortars were cured for 16 to 24 hours in the mold, followed by storage in laboratory air at about 75 F (24 C) and 50 percent relative humidity until test time.

The hardened mortars were measured for flexural strength using ASTM C 78 with beams of 5 x 1 x 1 in. (12.7 x 2.5 x 2.5 cm), compressive strength using ASTM C 109, chloride permeability using

Table 5 — VAE latex and powder PMC

Mixture proportioning	Mortar (parts by weight)	
	A	B
portland cement	100	100
graded silica sand	300	300
VAE latex (55% solids)	18	0
VAE powder (9% ash)	0	11
water	39	49
Mortar properties		
water-cement ratio	0.47	0.49
flow, ASTM C 230, 25 drops	110	110
flexural strength, psi	1590	1320
compressive strength, psi	5140	5040
permeability, coulombs	1130	1370
adhesion, psi	300	260

Table 6 — Comparison of UMC and VAE-PMCs

	Mortar		
	C	D	E
VAE powder-cement ratio	0.00	0.10	0.15
Water-cement ratio	0.40	0.40	0.40
Dry density, g/ml	2.11	2.09	2.10
Compressive strength, psi			
3 days	5480	4340	3910
7 days	5700	5290	4940
28 days	6620	6380	6010
Flexural strength, psi			
7 days	760	1280	1420
28 days	850	1380	1530
Adhesion, 7 days, psi	180	260	250
Permeability, 28 days coulombs	6420	2080	1560

AASHTO T 277, adhesion using a tensile bond method developed by Kuhlmann¹ and for dry density by measuring the mass of the various specimens and dividing by their relative volumes.

Experimental

Two VAE polymer-modified mortars were made using a 3 to 1 graded silica sand-portland cement Type I ratio with a VAE polymer-cement ratio of 0.10. In mortar A, the VAE polymer was added in the form of a latex; in mortar B, the VAE polymer was added as a powder. The VAE latex was the same as that used to make the VAE powder, but the latter did contain the extra ingredients required to make a redispersible powder. Consequently, the level of VAE powder was increased to allow for the anti-blocking aid, which in this case was about 10 percent clay. The water-cement ratio was adjusted so that both mortars gave a flow of 110 percent (C 230).

Mortars C, D, and E compared an unmodified portland cement mortar (UMC) with portland cement mortars modified with VAE redispersible powder (PMC). The mixture proportioning was a 2.5:1 ratio of graded silica sand to portland cement with a water-cement ratio of 0.40. The PMCs used VAE powder-cement ratios of 0.10 and 0.15. The VAE powder used in this study was formulated prior to spray-drying with a small quantity

of a retarding superplasticizer (RSP). The UMC was cured for 16 to 24 hours in the mold, followed by immersion in saturated lime-water at about 75 F (24 C) until testing time.

Mortars F, G, and H compared three VAE powders that were made with: a retarding superplasticizer (RSP), a superplasticizer (SP), and no additive. The mortars used a 2.5:1 graded silica sand-portland cement ratio with a VAE powder-cement ratio of 0.15. The water-cement ratio was adjusted to give a flow of 110 to 115 percent (ASTM C 230).

Mortars I and J also contained VAE powders; one was formulated with a defoamer prior to spray drying, while the other was not. These mortars were measured for flow (ASTM C 230) and wet and dry densities. Mixture proportioning was a 3:1 graded silica sand-portland cement Type I ratio with VAE polymer-cement and water-cement ratios of 0.15 and 0.45, respectively.

Mortars K through O were made using a basic self-leveling mortar proportioning (Table 4). The five VAE powders were formulated prior to spray drying with no application chemicals (K), a superplasticizer (L), a retarding superplasticizer (M), extra surfactant (N), and an anti-sag agent (O). These mortars were assessed for flow by measuring the diameter of the hardened patty formed when the mortar

was released from the cylinder whose diameter was about 3.7 cm (1.5 in).

Results & discussion

Coefficients of variation (COVs) were determined for flexural strength, compressive strength, tensile bond adhesion, and permeability by dividing the standard deviation by the average value and expressing that value as a percentage. The following COVs were obtained: flexural strength — 9.1 percent, compressive strength — 2.9 percent, tensile bond adhesion — 8.4 percent, and chloride permeability — 12.5 percent.

Table 5 summarizes the data obtained from mortars A and B. The VAE powder PMC gives flexural strength, adhesion, and permeability values which are 15 to 20 percent lower than those obtained with the VAE latex. Although these differences are barely significant (being between two and three COVs) it is believed that the differences are real. At this time the reason for this loss in properties of the powder PMC is not fully understood. It may be a combination of the additives required for spray drying, together with less than 100 percent redispersibility of the powder in the cementitious mixture.

Table 6 summarizes the data obtained from mortars E, F, and G. Like other polymer-modified mortars, the VAE powder PMC gives higher flexural strength, better ten-

Table 7 — Effect of superplasticizers

	Mortar (parts by weight)		
	F	G	H
portland cement	100	100	100
graded silica sand	250	250	250
VAE powder - no SP*	15	0	0
VAE powder - RSP*	0	15	0
VAE powder - SP	0	0	15
water	37	32	31
	F	G	H
flow, ASTM C 230, 25 drops	110	111	111
compressive strength, psi			
3 days	5460	5120	6230
7 days	6500	6580	7290

*SP = superplasticizer, RSP = retarding superplasticizer

Table 9 — Effect of additives on flow

	Mortar (parts by weight)				
	K	L	M	N	O
Mortar Masterbatch	190	190	190	190	190
VAE powder - no add	10	0	0	0	0
VAE powder - SP*	0	10	0	0	0
VAE powder - RSP	0	0	10	0	0
VAE powder - ESF	0	0	0	10	0
VAE powder - ASG	0	0	0	0	10
water	50	50	50	50	50
flow, diameter, cm	11.0	12.3	13.4	14.4	<7

*SP = superplasticizer, RSP = retarding superplasticizer
ESF = extra surfactant, ASG = anti-sag agent

Table 8 — Effect of defoamer

	Mortar (parts by weight)	
	I	J
portland cement	100	100
graded silica sand	300	300
VAE powder	15	0
VAE* powder	0	15
water	45	45
	I	J
flow, ASTM C 230, 25 drops	113	110
wet density, g/ml	1.86	2.23
dry density	1.80	2.11

*VAE powder contained defoamer which was added prior to spray drying.

sile bond adhesion, and lower permeability than the UMC. As expected, these differences increase with the higher VAE powder-cement ratio, except for adhesion, which appears to reach its maximum at a lower ratio. Compressive strength of the PMC is significantly lower than that of the UMC at earlier stages of cure, but is less so after 28 days cure. The greater initial difference is probably due to the retarding superplasticizer. The lower compressive strength, obtained when 0.15 polymer-cement ratio is used compared to that of 0.10, is believed to be caused by the co-matrix of polymer and hydrated cement being softer or more flexible at the higher ratio.

Table 7 gives a summary of the data of the properties of mortars F, G, and H. The effect of the use of the superplasticizers in the VAE powder is very evident by the lower water contents of mortars G and H required to give similar flows. Also, the effect of the retarding superplasticizer is evident from the lower compressive strengths of mortar G.

Table 8 shows the differences in flow and wet and dry densities of mortars I and J. The lack of defoamer in the VAE powder used to make mortar I gives higher flow but lower densities. These data indicate that if the VAE powder does not contain a defoamer, the user must add one to obtain low air contents in the cementitious mixture.

Table 9 gives the flow values obtained with mortars K through O. The flow illustrates the increase in flow obtained by the addition of either superplasticizers or surfactants. Conversely, the addition of an anti-sag agent appears to cause a decrease in flow. Further work is required to assess the effect of the addition of these chemicals on other properties of the mortars such as compressive strength.

Conclusions and suggested applications

The data indicate that these VAE redispersible powders give similar properties in portland-cement mortars to those of the VAE latexes, with some slight reduction in the properties typically improved by the

polymer. The data also indicate that the VAE powders can be modified by the addition of various chemicals, causing significant differences in the properties of the resultant cementitious mixture.

The obvious advantage that the VAE powders have over their latex counterparts is the convenience of handling. This advantage has two facets: one is that it is easier for most people to store a powder rather than a latex; the other is that packaging costs are usually lower for powders than liquids.

But the greatest advantages are in the production, sale, and use of pre-packaged, polymer-modified, cementitious mixtures. One problem with the use of latex-modified cementitious mixtures in the field is that it is a two-part system with a limited pot-life, which involves proportioning of the two parts prior to use. Pre-proportioning of the VAE powder with the hydraulic cement and aggregates gives:

- better control of the polymer-cement ratio,
- only requires addition of water to obtain a suitable mixture,
- gives less loss of material since it is easier to make smaller sized mixtures, and
- means the contractor only has to take one material to the job site (assuming potable water is available).

The major applications of VAE powders in cementitious mixtures

Table 10 — Ceramic Tile Adhesive

parts by weight	
portland cement	100.0
fine silica sand	100.0
cellulosic thickener	0.2
VAE redispersible powder	10.0
water	≈ 45.0

are those where the convenience of pre-packaged mixtures is paramount. Three such applications are indicated:

Ceramic tile adhesives and grouts

Table 10 gives a starting mixture proportioning for a ceramic tile adhesive or grout. The cement, sand, cellulosic thickener, and VAE powder are premixed and sold by a formulator to contractors or homeowners. Such mixtures usually comply with the application property requirements of the American National Standard Specification for Latex-Portland Cement Mortar, A 118.4.

Table 11 — Patching Mortar

parts by weight	
portland cement	100.0
graded silica sand (ASTM C 33)	250.0
VAE redispersible powder	10.0
water	≈ 38.0

Self-leveling floor overlays

Table 4 gives a very basic mixture proportioning for a self-leveling floor overlay. The application will not be discussed here because Alexanderson² has described this application in detail.

Pre-packaged patching mortars

Table 11 gives a basic mixture proportioning for a prepackaged patching mortar. Again the cement, sand, and VAE powder is proportioned and packaged by a formulator for sales to contractors and homeowners. The latter completes the proportioning by the simple addition of water.

References

1. Kuhlmann, L. A., "Measuring Bond Strength of Latex-Modified Concrete and Mortar," *ACI Materials Journal*, V. 87, No. 4, July-Aug., 1990, pp. 387-394.
2. Alexanderson, J., "Self-Smoothing Floors Based on Polymer Cement Concrete," *Concrete International: Design and Construction*, V. 12, No. 1, Jan. 1990, pp. 49-51.

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Organic-Based Corrosion-Inhibiting Admixture for Reinforced Concrete

by Charles K. Nmai, Stephen A. Farrington, and Gregory S. Bobrowski

Each year, more and more reinforced concrete structures undergo deterioration that is mainly due to chloride-induced corrosion of embedded steel reinforcement. The high cost of maintenance and rehabilitation required to preserve the structural integrity and overall safety of these structures is radically changing design procedures and material selection in the concrete industry. Some structural designers now offer owners a tiered choice of protection systems with varying degrees of cost.

These protection systems include the use of epoxy-coated reinforcement, protective coatings and membranes, cathodic protection, low water-cementitious ratio concrete, silica fume concrete, and corrosion-inhibiting admixtures. In some cases, combinations of protection systems have been recommended.

So far, silica fume concrete has been shown to provide the highest level of protection for reinforcing steel,¹ but a novel organic corrosion-inhibiting admixture (OCIA) has been introduced that shows promise. It offers protection by forming a protective film at the steel surface and by reducing the ingress of chloride ions into the concrete matrix.

The basic objective of all of these corrosion-protection systems is to prevent aggressive agents, mainly chlorides, from attacking the surface of the reinforcing steel. Some systems function either by providing a physical barrier to the ingress of aggressive agents or by chemically stabilizing the steel surface. A commercially available inorganic

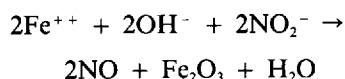
corrosion-inhibiting admixture is an example of the latter. When it is used, the ratio of chloride ions to that of the inhibiting agent is critical to preventing an imbalance that can result in accelerated corrosion and pitting of the steel.²

Existing corrosion-inhibiting admixtures for reinforcing steel

By definition, a corrosion inhibitor is a substance that will prevent or minimize corrosion. They may be classified as inorganic, organic, or vapor-phase inhibitor;³ however, corrosion-inhibiting admixtures for reinforced concrete typically are classified as anodic, cathodic, or mixed (anodic and cathodic), depending how they affect the corrosion process.²

Prior to the introduction of OCIA, only one corrosion-inhibiting admixture was commercially available. It is calcium nitrite-based and generally is considered to be an anodic inhibitor. As with other anodic inhibitors, it functions by minimizing the anodic reaction in the corrosion process.

It has been proposed that calcium nitrite inhibits corrosion by reacting with ferrous ions to form a film of ferric oxide, Fe_2O_3 , around the anode according to the following⁴



It is believed that nitrite and chloride ions engage in competing reactions, both of which influence

the corrosion process.^{4,5} In contrast to the inhibiting action of the nitrite ion, the chloride ion promotes corrosion. Therefore, the amount of nitrite ions present relative to the amount of chloride ions in the vicinity of the steel surface will determine whether or not corrosion inhibition is achieved. Accordingly, an apparent limitation of this nitrite-based corrosion-inhibiting admixture in particular, and other anodic inhibitors in general, is obvious.

The performance of anodic inhibitors has been investigated in various studies, ranging from anodic polarization tests^{6,7} to macrocell corrosion evaluations.^{1,8-10} The data presented in the literature indicate that anodic inhibitors generally are effective when present in sufficient quantities.

Corrosion performance of OCIA

A unique organic-based corrosion-inhibiting admixture (OCIA), a combination of amines and esters in a water medium, has been developed as an alternative approach for protecting steel reinforcement. Organic compounds belonging to the same class as those used in formulating OCIA are used extensively in industries such as oil and gas production/transmission, refineries and petrochemical processes, and boiler-water return lines. OCIA represents a successful transfer of the organic corrosion-inhibitor technology used in these industries to the concrete industry. The recommended dosage for OCIA is 1 gal/yd³ (5.0 l/m³) of concrete.

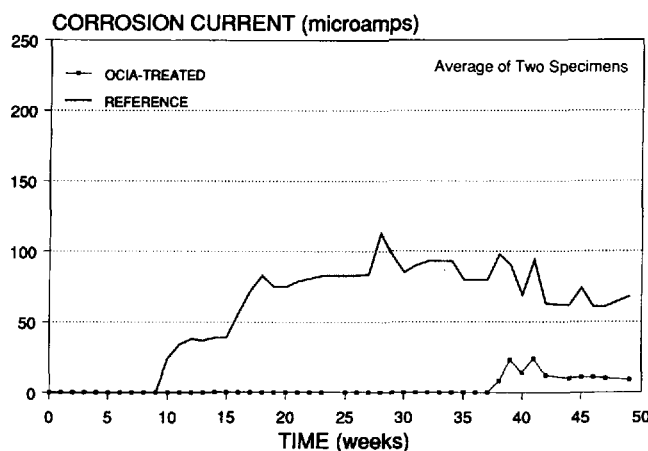


Fig. 1 — Macrocell corrosion current data.

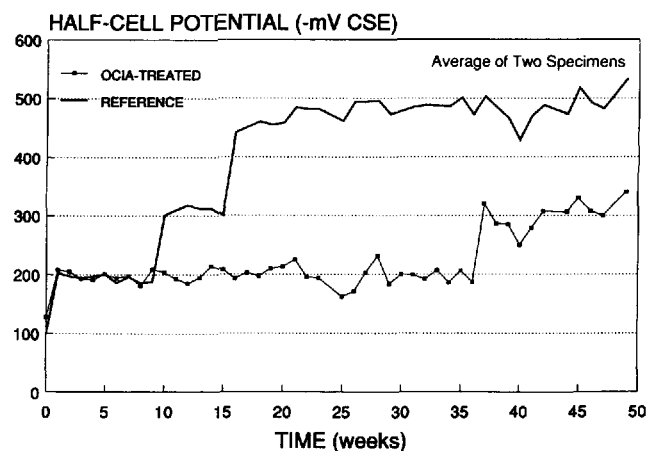


Fig. 2 — Half-cell potential data.

Table 1 — Nominal concrete mixture data (time-to-corrosion evaluation)

	lb/yd ³
Type I cement	450
Fine aggregate	1540
Coarse aggregate	1890
Water	225
	gal/yd ³
OCIA	0; 1.0

The corrosion-inhibiting characteristics of OCIA were evaluated using two different time-to-corrosion tests. The first test was similar to the Southern Climate Accelerated Corrosion Test,¹ which provides a measure of the corrosion resistance of concrete subjected to prolonged chloride exposure. The test specimen configuration enables measurement of (a) the half-cell potential of the top layer of reinforcing bars with respect to a copper-copper sulfate electrode (CSE), (b) any macrocell corrosion current that is developed, and (c) the mat-to-mat resistance of the concrete. The nominal mix proportions for the reference and OCIA-treated concretes are given in Table 1.

Macrocell corrosion current data obtained from this evaluation for the reference and OCIA-treated concretes are presented in Fig. 1, which shows that measurable corrosion current was obtained for the reference concrete after 9 weeks, as compared to 36 weeks for the OCIA-treated concrete. In addition, the magnitude of corrosion

activity, which is directly proportional to the areas under the curves, was significantly lower for the OCIA-treated concrete. The onset of corrosion activity as indicated by the corrosion current measurements is supported by the half-cell potential data for the reference and OCIA-treated concretes shown in Fig. 2. Using a potential of -240 mV CSE to indicate the onset of corrosion activity,¹ the times-to-corrosion determined from the half-cell potentials are in agreement with those determined from the macrocell corrosion current data. These results show that significant corrosion inhibition is provided by OCIA.

The second time-to-corrosion test, using precracked reinforced concrete beams, was undertaken for two reasons: to determine the corrosion-inhibiting effectiveness of OCIA for reinforcing steel in cracked concrete, and to obtain information about OCIA's corrosion protection mechanism. For comparison purposes, a calcium nitrite-based admixture (CNA) also was evaluated at a dosage equivalent to 4 gal/yd³ (20.0 l/m³).

Initially, test specimens consisted of 3 x 4 x 14 in. (76 x 102 x 356 mm) concrete beams reinforced with single sandblasted #4 steel reinforcing bars. Clear concrete cover over the reinforcement was approximately 1.5 in. (38 mm). Concrete mix proportions similar to those given in Table 1 were used. After casting, the test specimens were moist-cured for 14 days, notched across the top width at half-length,

then stressed flexurally under center-point loading to induce cracks through the concrete to the level of the reinforcing bar.

The top surfaces of the specimens were then diked and continuously ponded with a 6 percent sodium chloride solution to allow for the ingress of chloride ions through the cracks directly to the steel. Ponding began at an age of 28 days. The half-cell potentials of the embedded reinforcing bars were then measured periodically with copper-copper sulfate electrodes.

The measured half-cell potentials for the reference, CNA-treated, and OCIA-treated concretes are presented in Fig. 3. Again using -240 mV CSE as the potential beyond which active corrosion occurs, the onset of corrosion in the reference concrete specimens occurred after about 5 days of exposure to the sodium chloride solution. The CNA-treated concrete specimens showed signs of corrosion after approximately 30 days of continuous ponding. After 180 days there was no sign of corrosion activity in the OCIA-treated specimens, indicating that OCIA is effective in delaying the onset of corrosion of reinforcing steel in cracked concrete.

The specimen configuration used in the initial precracked-beam corrosion evaluations enabled measurement of only the half-cell potential of the reinforcing steel from which the time to corrosion was determined. In subsequent evaluations to obtain further information after corrosion initiation, three sandblasted reinforcing bars were

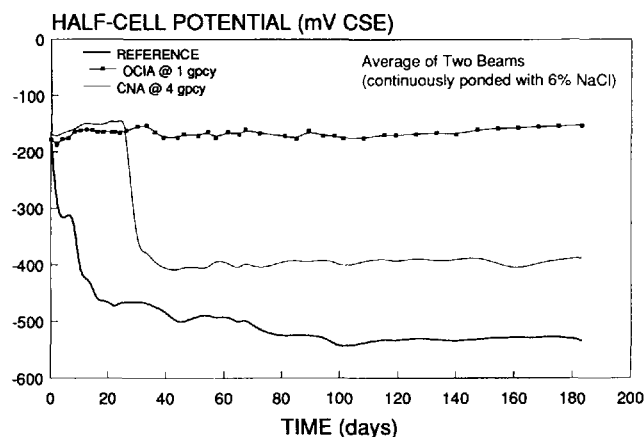


Fig. 3 — Half-cell potential data for reinforcing steel in precracked concrete beams subjected to chloride ponding (single rebar configuration).

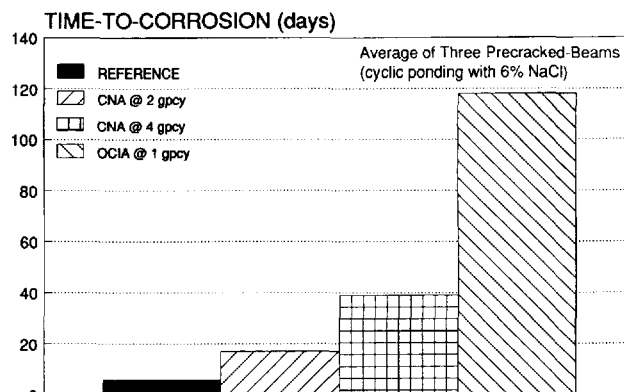


Fig. 4 — Time-to-corrosion data for precracked concrete beams subjected to chloride ponding (three-bar configuration).

used, one at the top and two at the bottom. The top and bottom bars were externally connected via a 10-ohm resistor. This configuration enabled measurement of both the half-cell potential of the top steel bar and the macrocell corrosion current.

The beams were notched as before and loaded in flexure until the crack extended just past the level of the top steel bar. Cyclic ponding with a 6 percent sodium chloride solution then followed. Each cycle consisted of four days of ponding and three days of air drying at 70 ± 5 F (21 ± 2.8 C).

Fig. 4 shows data obtained from one such evaluation, which included concrete treated with the calcium nitrite-based corrosion-inhibiting admixture (CNA) at dosages of 2 and 4 gal/yd³ (10.0 and 20.0 l/m³). The data indicate that, on average, corrosion was initiated in the untreated reference concrete at 6 days, and at 17 and 39 days in the concrete treated with the CNA at 2 and 4 gal/yd³ (10.0 and 20.0 l/m³), respectively. The average time-to-corrosion for the concrete treated with OCIA at the recommended dosage of 1 gal/yd³ (5.0 l/m³) was 118 days.

As stated earlier, OCIA inhibits corrosion by a twofold mechanism that includes reducing chloride-ion ingress. Chloride ions will penetrate into untreated concrete and concrete treated with the calcium-nitrite inhibitor at faster rates than into concrete treated with OCIA. To substantiate this, powder samples were obtained from all the pre-

cracked-beam specimens for chloride analysis at the onset of corrosion in OCIA-treated specimens. The powder samples were obtained from holes drilled 0.25 in. (6.25 mm) on either side of the crack at the level of the top reinforcing bar. The analysis indicated that the average chloride-ion concentration in OCIA-treated specimens was approximately 5.0 lb/yd³ (2.96 kg/m³) compared to 12.0 lb/yd³ (7.10 kg/m³) for the untreated specimens. The companion precracked-beam specimens treated with 2 and 4 gal/yd³ (10.0 and 20.0 l/m³) of CNA had average chloride-ion contents of 13.0 and 14.7 lb/yd³ (7.70 and 8.70 kg/m³), respectively. The slight increase in chloride-ion concentration in the calcium nitrite-treated specimens compared to the untreated specimens is consistent with the accelerating effect of calcium nitrite on concrete and, consequently, its effect on concrete permeability.

Despite its apparent lower chloride threshold, OCIA-treated concrete delayed the onset of corrosion longer than CNA-treated concretes. This can be attributed to the reduction in chloride-ion ingress provided by OCIA-treated concrete and, as discussed later, the fact that actual chloride limits for CNA appear to be lower than those published in the literature.¹¹ The significant protection provided by silica fume concrete, which has a chloride threshold approximately equal to that of untreated concrete, is also largely due to its effectiveness in reducing chloride-ion ingress.

Using untreated concrete as a basis, the test data suggest that the chloride threshold for OCIA-treated concrete is approximately 12.0 lb/yd³ (7.10 kg/m³). Therefore, it is important that concretes with different permeabilities be considered on a common basis when comparing their corrosion-inhibiting performances. A logical basis is the time that it takes to build up to the chloride threshold.

Chloride limits for CNA

It has been reported in the literature that the CNA provides protection at chloride-to-nitrite ratios exceeding 1.5 to 1 by weight,^{10,11} but less than 2.5 to 1 by weight.¹⁰ However, analyzing half-cell potential and chloride-content data from concrete deck specimens subjected to daily salting indicated that chloride-to-nitrite ratios greater than 1.611 to 1 by weight will result in corrosion.¹⁰ This ratio was determined by using a potential of -350 mV and using the copper-copper sulfate half-cell electrode (CSE) to indicate the onset of active corrosion. By industry standards at the time,¹² half-cell potentials more negative than -350 mV CSE indicated a greater than 90 percent probability of corrosion activity; however, some studies have shown that the onset of active corrosion occurs at half-cell potentials of about -240 mV CSE.¹ Analyzing the half-cell potential-versus-chloride data provided¹⁰ using -240 instead of -350 mV CSE indicates that corrosion will occur at chloride-to-nitrite ratios exceeding 0.92

to 1 by weight, and not 1.611 to 1 as published.¹⁰

Published literature¹¹ indicates that 1 gal/yd³ (5.0 l/m³) of CNA contains approximately 2.2 lb (1.0 kg) of nitrite ions; therefore, chloride-to-nitrite ratios at current recommended dosage rates of CNA¹¹ range from 1.2-1.5 to 1 by weight. Using a critical chloride-to-nitrite ratio of 0.92 to 1 by weight, the current recommended dosage rates of this admixture will offer protection against smaller amounts of chloride ions than indicated in the literature.¹¹ Therefore, at the maximum recommended dosage of 6 gal/yd³ (30.0 l/m³), CNA will offer protection against approximately 12.1 lb (5.5 kg) of chloride ions, and not 16.0 lb (7.3 kg) as published (see Table 2). This implies that the recommended dosages of CNA will have to be increased by 33 to 67 percent to offer adequate protection against the quantities of chloride ions indicated in current literature.

Effect of OCIA on plastic properties

OCIA has very little effect on the plastic properties of concrete. Test data on time of setting, slump, air content, and temperature development of concrete containing OCIA and those of a reference concrete obtained from a field evaluation are presented in the following sections. The mix proportions are presented in Table 3. OCIA was used at a dosage equivalent to 1 gal/yd³ (5.0 l/m³).

Slump and time of setting

OCIA does not accelerate the hydration of portland cement and has little effect on concrete slump.

The effect of OCIA on the setting time of concrete was evaluated at ambient temperatures of 50, 72, and 90 F (10, 22, and 32 C). Initial and final set times were obtained at each temperature, but, because the trends are similar, only the initial setting time data are presented here (Fig. 5). The data indicate that OCIA does not have a significant

effect on initial set time at ambient temperatures of 72 and 90 F (22, and 32 C). At 50 F (10 C), OCIA retarded the concrete slightly; however, the amount of retardation is less than that specified in ASTM C 494 for classification as a Type B, or retarding, admixture.¹²

Air content

Adding OCIA to a concrete mixture may require increasing the amount of air-entraining admixture used and extending mixing to achieve a given air content. OCIA is compatible with vinsol resin-based and synthetic air-entraining admixtures.

Temperature development profile

As shown in Fig. 6, OCIA will not affect the peak exotherm or temperature development profile of concrete. The data shown in this figure were obtained from thermocouples placed in the center of insulated 1-ft³ (0.028-m³) concrete-filled wooden boxes that were insulated to simulate a mass concrete placement. The temperature development profiles are consistent with the time-of-setting data already discussed.

Effect of OCIA on hardened properties

The hardened properties of concrete are not affected significantly by the use of OCIA. The strength and durability properties of concrete containing OCIA that were evaluated in a field test program are presented here. The mix proportions for the reference and OCIA-treated concretes used in this evaluation are presented in Table 3. As stated earlier, OCIA was used at a dosage equivalent to 1 gal/yd³ (5.0 l/m³).

Compressive and flexural strengths

The compressive and flexural strengths of concrete treated with OCIA were evaluated in accordance with ASTM C 192 and C 39, and C 78, respectively.¹² Test data ob-

tained through one year indicate that OCIA has a marginal effect on compressive strength, as shown in Fig. 7. A similar trend was observed for flexural strength through 180 days. The strength differences between the reference and treated concretes are less than 10 percent. However, analysis of stress-strain data indicate that OCIA will not affect modulus of elasticity or other stress-strain properties of concrete. A 28-day modulus of elasticity of 4.90 million psi (33.8 GPa) was obtained for OCIA-treated concrete, as compared to 4.65 million psi (32.1 GPa) for untreated concrete.

Concrete-steel bond strength

The bond strength developed between concrete and steel is not affected by OCIA. In an independent evaluation,* a normalized bond strength of 5920 lb/in. (1040 N/mm) was obtained for untreated concrete, with corresponding values of 6280 and 5750 lb/in. (1100 and 1010 N/mm) for concrete treated with OCIA at dosages equivalent to 1 and 2 gal/yd³ (5.0 and 10.0 l/m³), respectively. On the basis of equal compressive strength, it was concluded that, there is no difference in bond strength between the reference and OCIA-treated concretes, even at a dosage rate twice that recommended for corrosion inhibition.

Rapid chloride permeability

OCIA has no effect on the coulomb rating of concrete tested in the Rapid Chloride Permeability Test (AASHTO T 277¹³), as shown in Fig. 8. This indicates that OCIA does not decrease the electrical resistivity of concrete, and was confirmed by data obtained from the Southern Climate Accelerated Corrosion time-to-corrosion test. At the end of the 48-week test period, the mat-to-mat resistance of the concrete specimens containing OCIA

*Darwin, D., and Hadje-Ghaffari, H., "Effects of PE-271 on Steel-Concrete Bond Strength," report on research sponsored by Master Builders, Inc., University of Kansas, Lawrence, Sept. 1990, 10 pp.

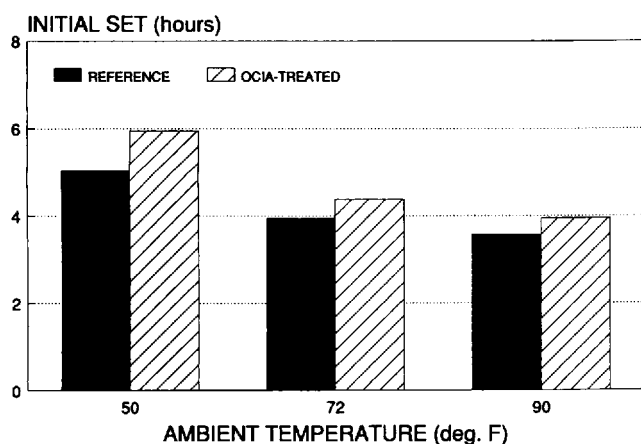


Fig. 5 — Effect of OCIA on initial set of concrete.

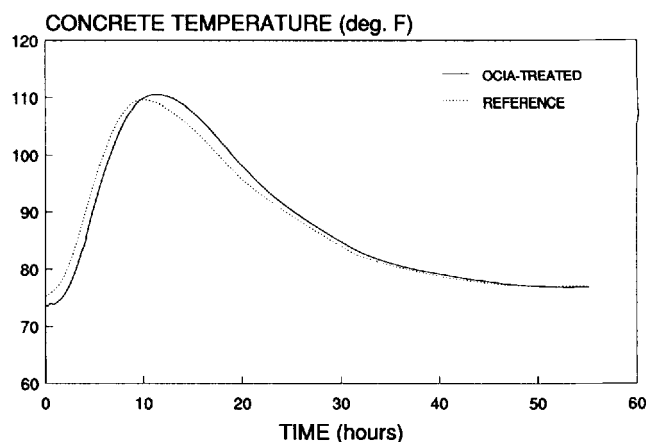


Fig. 6 — Effect of OCIA on temperature development of concrete.

was marginally higher than that of the reference specimens, 405 ohms versus 350 ohms.

90-day chloride ponding

The susceptibility of concrete containing OCIA to chloride-ion penetration was evaluated in accordance with the AASHTO T 259 test method.¹³ Data obtained from analyzing powder samples indicate a decrease in chloride-ion content in the OCIA-treated concrete, as compared to the reference concrete, particularly in the 0.5 to 1 in. (12 to 25 mm) depth (Fig. 9). The trend is consistent with chloride-ion data obtained from time-to-corrosion tests, and further confirms that OCIA is effective in reducing chloride-ion ingress into concrete.

Freezing and thawing resistance

The effect of OCIA on the freezing and thawing resistance of concrete was evaluated in accordance with ASTM C 666, Procedure A.¹² At the end of 300 freeze-thaw cycles, a durability factor of 96 percent was obtained for the OCIA-treated concrete relative to the reference concrete. This indicates that OCIA will not affect the freezing and thawing resistance of concrete.

Air-void system parameters

The effect of OCIA on the air-void system parameters of concrete was evaluated extensively using truck-mixed and central-mixed concretes. Vinsol resin-based and synthetic air-entraining admixtures were used at dosages ranging from 1.5 to 3.0 fl oz/cwt (98 to 196 ml/100 kg). The

Table 2 — Chloride-to-nitrite ratios for calcium nitrite-based inhibitor (CNA)

CNA dosage, gal/yd ³	Current chloride/nitrite ratio	Chloride limit, lb/yd ³	Revised chloride limit @ 0.92 ratio, lb/yd ³
2	1.36	6.0	4.1
3	1.50	9.9	6.1
4	1.48	13.0	8.1
5	1.36	15.0	10.1
6	1.21	16.0	12.1

results of the air-void system analysis, performed in accordance with ASTM C 457,¹² are summarized in Table 4 for the truck-mixed and central-mixed concretes. The data show excellent correlation between the plastic and hardened air contents, indicating that OCIA will not affect the stability of air voids during the hardening process. The calculated spacing factors are less than or equal to the maximum value of 0.008 in. (0.20 mm) recommended by ACI¹⁴ for adequate freeze-thaw durability of concrete.

Abrasion resistance

The effect of OCIA on the abrasion resistance of concrete was determined in accordance with ASTM C 779, Procedure A.¹² The average depth of wear after 60 minutes of abrasion was 0.049 and 0.050 in. (1.24 and 1.27 mm) for the reference and OCIA-treated concretes, respectively. This indicates that OCIA will not affect the abrasion resistance of concrete.

Length change

The shrinkage characteristics of concrete are not affected by the use

of OCIA, as shown in Fig. 10. The data shown were obtained from a length-change evaluation performed in accordance with ASTM C 157.¹²

Corrosion protection mechanism

OCIA inhibits the corrosion of steel in concrete by a twofold mechanism that involves forming a protective film on the steel surface and reducing the susceptibility of concrete to chloride-ion penetration, or, simply stated, by "chloride screening."

OCIA functions to inhibit corrosion by the same mechanism as that of other organic corrosion inhibitors — by adsorption on the metal surface. It is generally accepted that organic corrosion inhibitors bond to metals by adsorption, physically and/or chemically, due to the polar or weakly polar characteristic of the organic compounds typically used in their formulation. The following excerpt from Reference 15 gives a basic understanding of organic corrosion inhibitor or filming inhibitor technology:

Table 3 — Concrete mixture data, field evaluation

	Reference	OCIA
Cement, lb/yd ³	650	650
Fine aggregate, lb/yd ³	1250	1250
Coarse aggregate, lb/yd ³	1800	1800
Water, lb/yd ³	260	260
w/c	0.40	0.40
AEA - air-entraining admixture, fl oz/cwt	1.4	1.5
HRWRA - high-range water reducing admixture, fl oz/cwt	10.0	12.0
OCIA, gal/yd ³	—	1.0
Slump, in.	7.0	6.5
Air Content, percent	6.2	5.7
Unit Weight, lb/ft ³	145.1	147.5
Concrete Temperature, F	73	72

Table 4 — Air-void system analysis data

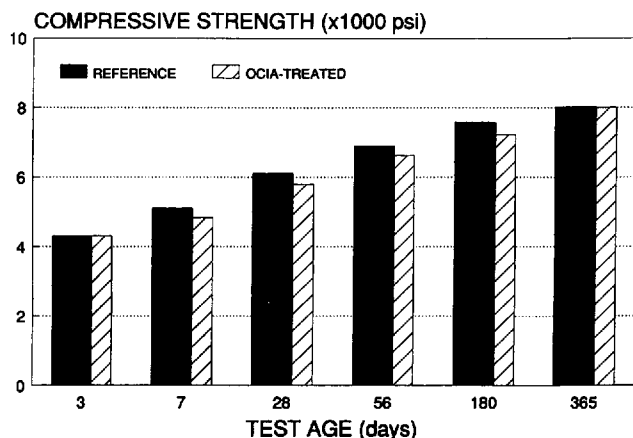
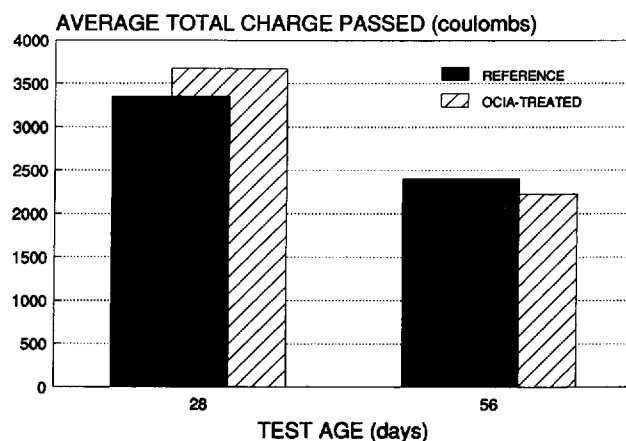
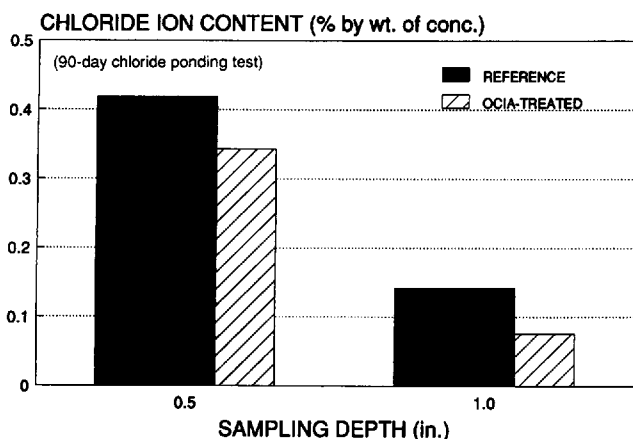
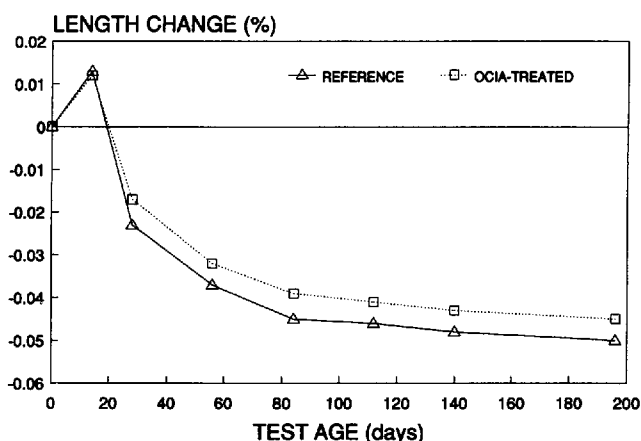
Evaluation No.	AEA*/Dosage fl oz/cwt	Air content percent		Specific surface, in. ⁻¹	Spacing factor, in.
		Fresh	Hardened		
Truck-mixed					
1	VR ¹ /3.5	8.1	8.2	741	0.004
2	VR ¹ /3.5	11.3	13.7	571	0.002
3	VR ¹ /1.5	9.0	6.0	667	0.006
4	VR ¹ /1.5	7.5	7.1	645	0.006
5 [†]	VR ¹ /2.0	7.9	7.1	678	0.005
6 [†]	VR ¹ /2.0	6.8	6.1	571	0.008
7	VR ¹ /1.5	5.7	5.5	571	0.008
Central-mixed					
8	VR ¹ /2.25	7.7	8.7	615	0.005
9	VR ¹ /2.25	7.7	6.9	615	0.007
10	VR ¹ /2.25	7.1	7.2	727	0.004
11 [‡]	VR ¹ /3.0	6.8	7.9	548	0.006
12 [‡]	VR ¹ /3.0	6.8	6.6	615	0.006
13	VR ¹ /2.25	5.3	5.8	625	0.007
14 [§]	VR ¹ /2.5	5.7	5.7	769	0.006
15	SYN [§] /2.0	7.8	8.9	580	0.006

* Air-entraining admixture.

† Vinsol resin-based.

‡ Silica fume concrete mixture; 8 percent compacted silica fume addition by weight of cement.

§ Synthetic.

Note: All concrete mixtures contained 650 lb/yd³ of cement, OCIA at 1.0 gal/yd³, and a high-range water-reducing admixture for workability.**Fig. 7 — Effect of OCIA on compressive strength development of concrete.****Fig. 8 — Effect of OCIA on rapid chloride permeability of concrete.****Fig. 9 — Effect of OCIA on the susceptibility of concrete to chloride ion penetration.****Fig. 10 — Effect of OCIA on the shrinkage characteristics of concrete.**

The mechanism by which all materials function is the same and requires their adsorption onto the metal through their polar group or head. The nonpolar tail of the inhibitor molecule is oriented in a direction generally vertical to the metal surface. It is believed that the hydrocarbon tails mesh with each other in a sort of "zipper" effect to form a tight film which repels aqueous fluids, establishing a barrier to the chemical and electrochemical attack of fluids on the base metal. A secondary effect is the physical sorption of hydrocarbon molecules from the process fluids by the hydrocarbon tails of the adsorbed inhibitor molecules. This increases both the thickness and effectiveness of the hydrophobic barrier to corrosion.

This process also is applicable to OCIA. During the mixing operation, the admixture is distributed uniformly throughout the concrete mixture where it becomes a part of the paste fraction. After concrete is placed, key components of the admixture are adsorbed onto the reinforcing steel surface, forming a protective film. The presence of this film on steel samples that were removed from OCIA-treated concrete test specimens has been detected by surface analytical techniques that used ultraviolet spectroscopy and gas chromatography. The film enhances the naturally occurring passive layer on the steel surface and offers significant resistance to the detrimental effect of chloride ions.

OCIA also inhibits corrosion of steel by reducing chloride-ion ingress into concrete. Data obtained from the 90-day chloride-ponding test showed a decrease in chloride-ion concentration in OCIA-treated concrete compared to the plain concrete (Fig. 9). Lower chloride-ion concentrations in OCIA-treated concretes relative to plain concrete also have been obtained from analyzing various corrosion test specimens subjected to cyclic ponding with chloride solutions. In effect, this implies that the rate of chloride-ion ingress is significantly lower for concrete treated with OCIA compared to untreated concrete.

The longer time-to-corrosion obtained with OCIA-treated concrete,

particularly in the precracked-beam corrosion evaluations (Fig. 3 and 4), can be attributed to the combined effects of the protective film and reduction in chloride-ion ingress. This is because, even though a crack will provide chlorides with direct access into the concrete matrix, the chloride-screening process will delay their diffusion laterally along the reinforcing steel. Thus, a buildup of chlorides in concrete adjacent to the crack will occur at a slower rate in OCIA-treated concrete compared to untreated concrete or concretes with similar chloride permeabilities.

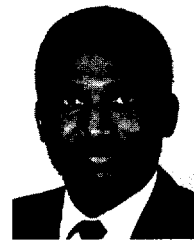
References

1. "Protective Systems for New Prestressed and Substructure Concrete," Report No. FHWA/RD-86/193, U.S. Department of Transportation, Federal Highway Administration, Apr. 1987, 126 pp.
2. *Concrete Admixtures Handbook — Properties, Science, and Technology*, V.S. Ramachandran, ed., Noyes Publications, 1984, 626 pp.
3. *Encyclopedia of Chemical Technology*, 3rd edition, V. 7, Kirk-Othmer, 1978, 891 pp.
4. Rosenberg, A. M., and Gaidis, J. M., "Mechanism of Nitrite Inhibition of Chloride Attack on Reinforcing Steel in Alkaline Aqueous Environments," *Materials Performance*, V. 18, No. 11, Nov. 1979, pp. 45-48.
5. Berke, N. S., and Rosenberg, A., "Technical Review of Calcium Nitrite Corrosion Inhibitor in Concrete," *Concrete Bridge Design and Maintenance: Steel Corrosion in Concrete*, Transportation Research Record 1211, 1989, pp. 18-27.
6. Gouda, V. K., and Monfore, G. E., "Rapid Method for Studying Corrosion Inhibition of Steel in Concrete," *PCA Journal*, V. 7, No. 3, Sept. 1965, pp. 24-31.
7. Rosenberg, A. M.; Gaidis, J. M.; Kosivas, T. G.; and Previte, R. W., "Corrosion Inhibitor Formulated with Calcium Nitrite for Use in Reinforced Concrete," *Chloride Corrosion of Steel in Concrete*, STP 629, ASTMm 1977, pp. 89-99.
8. Holm, J., "Comparison of the Corrosion Potential of Calcium Chloride and a Calcium Nitrite Based Non-Chloride Accelerator — A Macrocell Corrosion Approach," *Corrosion, Concrete, and Chlorides*, SP-102, American Concrete Institute, Detroit, 1987, pp. 35-48.
9. *Time-to-Corrosion of Reinforcing Steel in Concrete Slabs — Calcium Nitrite Admixture or Epoxy-Coated Reinforcing Bars as Corrosion Protection Systems*, V. 5, U.S. Department of Transportation, Federal Highway Administration, Publication No. FHWA/RD-83/012, Sept. 1983, 71 pp.
10. Gaidis, J. M., and Rosenberg, A. M., "Inhibition of Chloride-Induced Corrosion in Reinforced Concrete by Calcium Nitrite," *Cement, Concrete, and Aggregates*, V. 9, No. 1, Summer 1987, pp. 30-33.
11. Berke, N. S., "Effects of Calcium Nitrite and Mix Design on the Corrosion Resistance of Steel in Concrete (Part 2, Long-Term)," *Corrosion of Metals in Concrete*, Proceedings of the Corrosion/87 Symposium, National Association of Corrosion Engineers, 1987, pp. 134-144.
12. *Annual Book of ASTM Standards*, V. 04.02, Concrete and Aggregates, ASTM, 1990, 804 pp.
13. *Standard Specifications for Transportation Materials and Methods of Sampling and Testing, Part II — Methods of Sampling and Testing*, 14th ed., AASHTO, Aug. 1986, 1275 pp.
14. ACI Committee 201, "Guide to Durable Concrete," (ACI 201.2R-77), ACI JOURNAL, Proceedings V. 74, No. 12, Dec. 1977, pp. 573-609.
15. *Corrosion Inhibitors*, C. C. Nathan, ed., National Association of Corrosion Engineers, 1973, 279 pp.

Received and reviewed under Institute publication policies.

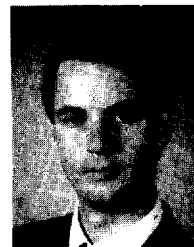
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Non-chloride, non-alkaline admixture
effectively prevents freezing of fresh concrete

Antifreeze Admixture Developed in Japan

by K. Sakai, H. Watanabe, H. Nomachi, and K. Hamabe

Concrete placement in cold weather is necessary for a variety of reasons. For example, construction may be limited to certain periods so as not to inconvenience tourists; the water supply in irrigation canals in need of improvement may have to be maintained until fall; in revetment works, temporary coffering is needed; and cold weather concreting may be necessary when urgent completion of a project is required. Furthermore, year-round construction in cold regions is preferable because it minimizes the variation in use of construction materials and facilities and the number of workers employed.

The rate of hydration of cement in concrete depends on the ambient temperature. When fresh concrete is exposed to low temperatures, strength development may be delayed and the concrete may suffer from damage due to freezing. In such an environment, special considerations must be made to prevent early freezing of concrete, and materials, mix proportions, mixing, transporting, placing, curing, formwork, and shoring must be carefully evaluated to ensure development of required strength.

In the Japan Society of Civil Engineering (JSCE) standard specification for design and construction of concrete structures,¹ cold weather concreting must be conducted when the average daily air temperature is forecast to be below 4 C (39 F). Cold weather concreting is usually

expensive because of the need for equipment to protect the fresh concrete from frost damage. A technologically simple and economically beneficial alternative is to use antifreeze admixtures to lower the freezing point of the fresh concrete.

There are a few antifreeze admixtures for concrete on the market in Japan. They lower the freezing point of the pore water in concrete with compounds containing chloride or sodium ions, which may cause the corrosion of reinforcing steel or alkali-aggregate reactions.

A non-chloride cold weather admixture was recently developed in the United States.² An antifreeze admixture that is both non-chloride and non-alkaline has been developed in Japan. This admixture contains polyglycolester derivatives and calcium nitrite-nitrate. In the usual dosage of this admixture there are approximately 10g/m³ (0.27 oz/yd³) of alkali and less than 10g/m³ (0.27 oz/yd³) of chloride ions.

Laboratory tests

Freezing temperature of pore water

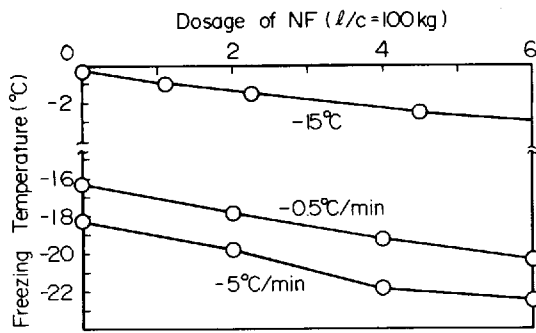
The temperature of ice formation in mortar with different amounts of antifreeze admixture (NF) was determined using two methods. Method A used a differential scanning calorimeter and tested 30mg (0.001 oz) of mortar with a water-cement ratio of 0.50, sealed in an aluminum cell. Aluminum powder

was used as the standard material. The temperature was decreased from 10 C (50 F) at 0.5 C/min (0.9 F/min) and 5 C/min (9 F/min). In method B, a polyethylene container with 1 l (0.26 gal) mortar with a water-cement ratio of 0.45 was immersed in a -15 C (5 F) unfrozen liquid (a 75 percent solution of ethylene glycol). The freezing temperature of the pore water was measured with a copper-constantan wire at the center of the container. It took about thirty minutes until the test was terminated. The freezing temperatures of the pore water varied with the test method used (Fig. 1), although the water-cement ratio also had some effect. However, at all three freezing rates the difference in freezing temperatures between zero and maximum NF addition is 3 to 4 C (5.4 to 7.2 F).

Heat evolution

The rate of heat evolution was measured with a conduction calorimeter at 5 C (41 F). Water with 4 l (1.1 gal) NF per 100kg (220 lb) cement was added to 20g (0.7 oz) of cement. The paste was stirred for 3 minutes. The water-cement ratios were 0.50 and 0.40. The heat evolution of both these mixtures and plain cement were measured.

Fig. 2 shows the rate of heat evolution for 12 hours. From the test results, it is obvious that the NF accelerates the early rate of hydration. The heat evolution of the NF and plain mixes became almost the same after 6 hours. After 12 hours



Clockwise from above:

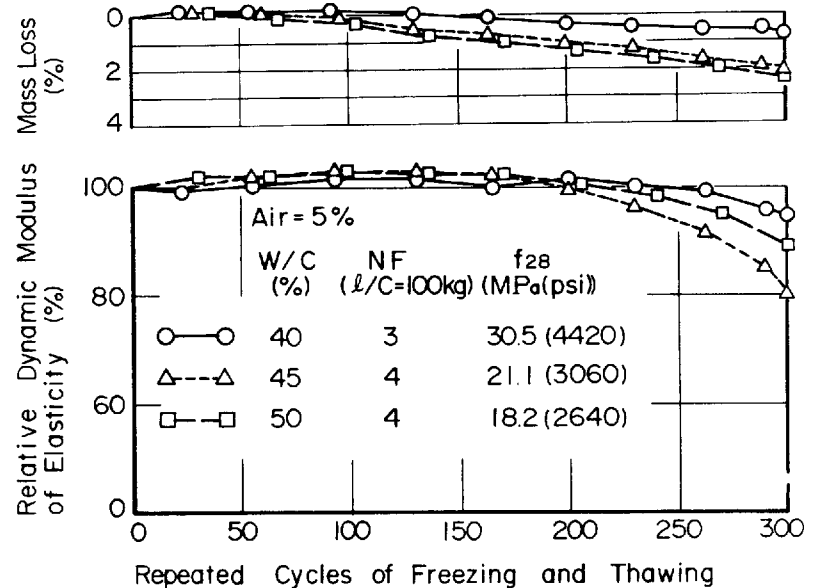
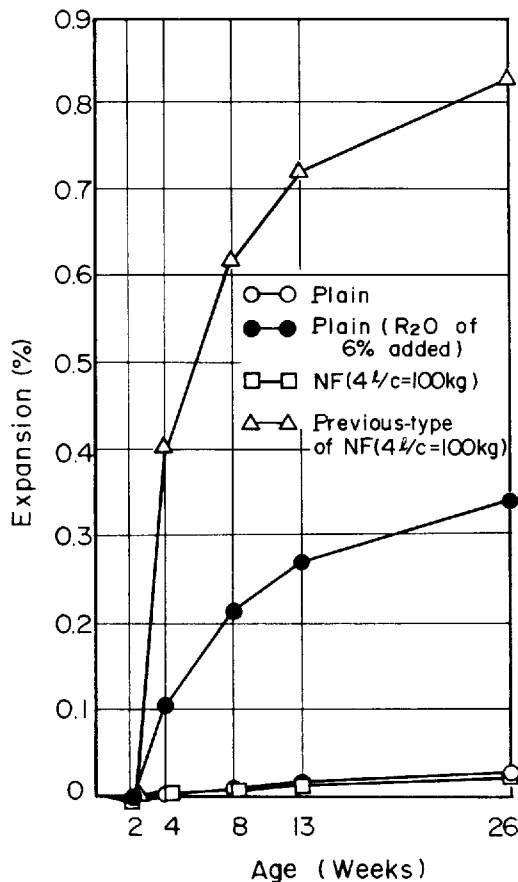
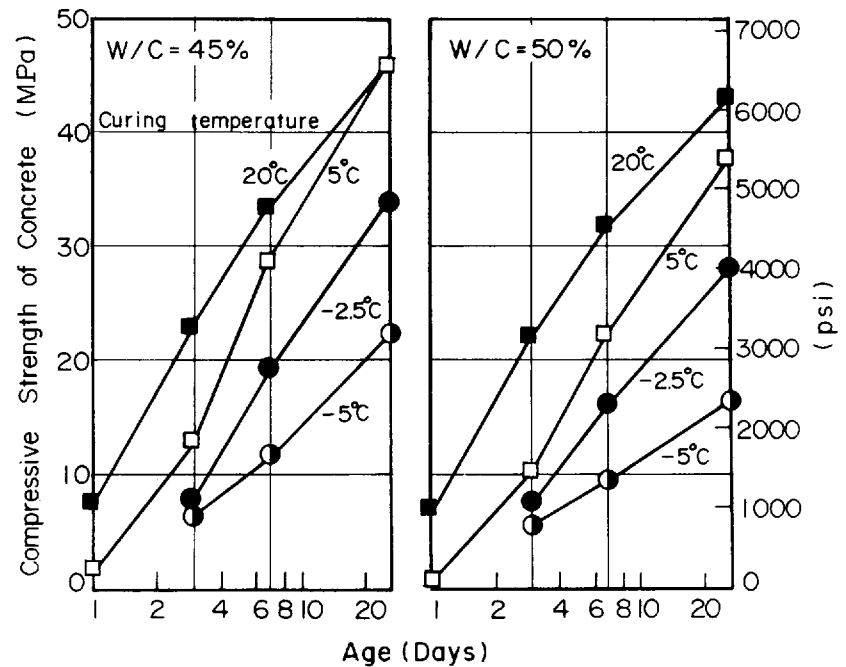
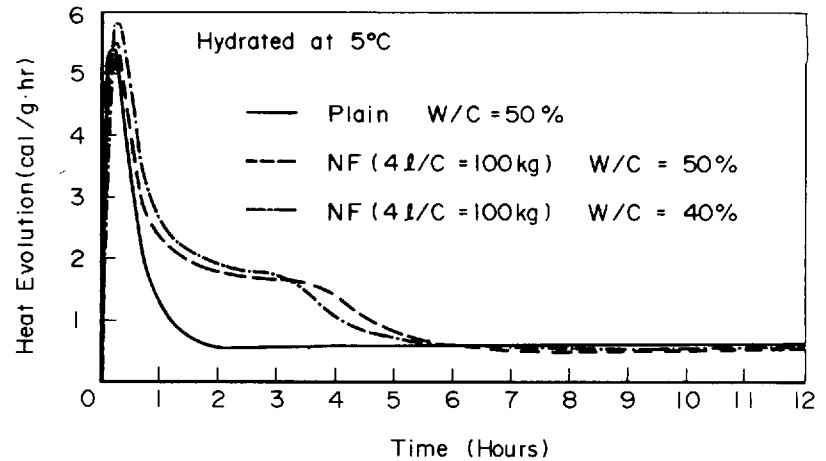
Fig. 1 — Effect of admixture on freezing temperature of pore water in mortar.

Fig. 2 — Rate of heat evolution of plain cement paste and cement paste with admixture.

Fig. 3 — Effect of curing temperature on compressive strength of concrete with 4 l admixture per 100kg cement.

Fig. 4 — Results of rapid freezing and thawing tests in water.

Fig. 5 — Mortar bar test results.



the total heat evolution was 13.8 cal/g (24.8 Btu/lb) for the NF mix with a water-cement ratio of 0.50, and 9.7 cal/g (17.5 Btu/lb) for the plain mix. The tests were stopped at 72 hours where the total heat evolution was 44.3 cal/g (79.7 Btu/lb) with NF and 40.4 cal/g (72.7 Btu/lb) without. There were no significant differences in the total heat evolution until 12 hours in the NF mixes with 3 or 5 l (0.8 or 1.3 gal) NF per 100 kg (220 lb) cement.

Strength development

Tests were carried out to examine the relationship between the curing temperature and compressive strength of concrete using NF. The concrete was placed in 10 x 20 cm (4 x 8 in.) cylindrical molds and cured at 5 C (41 F) for 24 hours after mixing, and then at set temperature conditions. The concrete specimens were wrapped in vinyl to prevent evaporation. The temperature of concrete after mixing was approximately 20 C (68 F).

Fig. 3 shows examples of the effect of curing temperatures on compressive strength with 4 l (1.1 gal) NF per 100 kg (220 lb) cement. The amount of cement that corresponds to water-cement ratios of 0.45 and 0.50 was 373 kg/m³ (629 lb/yd³) and 336 kg/m³ (566 lb/yd³) respectively. When the water-cement ratio is 0.45 and the curing temperature -5 C (23 F) the compressive strength at 28 days is 22.3 MPa (3235 psi). From Fig. 3, it can be seen that the compressive strength gain decreases with decreases in curing temperatures. When the NF dosage increased from 4 l (1.1 gal) per 100 kg (220 lb) cement to 5 l (1.3 gal), the compressive strength at 28 days increased from 22.3 MPa (3235 psi) to 30.1 MPa (4367 psi) with a 0.45 water cement ratio and a curing temperature of -5 C (23 F). This means that the amount of the NF plays an important role in the strength gain of concrete. The cor-

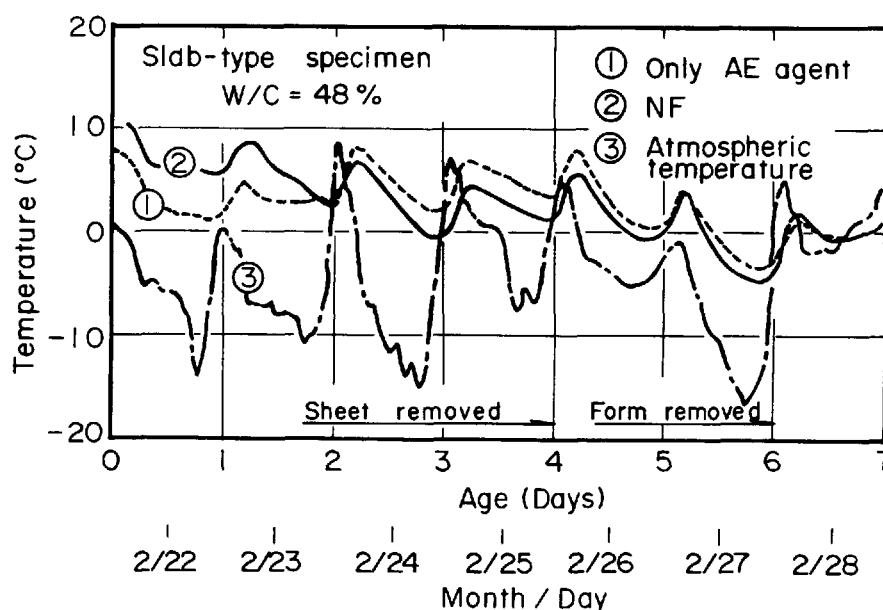


Fig. 6 — Temperature history at central part of slab-type field-cured specimens with admixture and air entraining agent alone.

responding strength gain at 3 days was 6.5 MPa (938 psi) and 7.6 MPa (1109 psi), respectively.

Freeze-thaw resistance

The resistance to repeated cycles of freezing and thawing of concrete with NF was examined. Rapid freezing and thawing tests were carried out using concrete at 28 days. The concrete was cured at -5 C (23 F) after being kept at 5 C (41 F) for 24 hrs. In this test, rectangular 10 x 10 x 40 cm (4 x 4 x 16 in.) prisms of concrete were frozen and thawed in water. In one half-cycle, the temperature of the test specimens was changed from 5 C (41 F) to -18 C (-0.4 F) over 1.7 hours. The variables considered in the tests were the water cement ratio (0.40, 0.45, and 0.50) and the amount of NF (3 l [0.8 gal] and 4 l [1.1 gal] per 100 kg [220 lb] cement). The dynamic modulus of elasticity and the mass loss were periodically measured.

Fig. 4 shows the results of freezing and thawing tests until 300 cycles. The mass losses were a few percent after 300 cycles. A relative dynamic modulus of elasticity of more than 80 percent after 300 cycles was obtained. From these results, it seems that the concrete can withstand freezing and thawing with

appropriate amounts of NF in the field. The relative dynamic modulus of elasticity of more than 100 in Fig. 3 means that the strength of concrete increased during the freezing and thawing tests.

Alkali-aggregate reaction

Tests were carried out to examine alkali-aggregate reactions of mortar with NF. Two kinds of fine aggregate, one shown to be potentially deleterious in chemical methods and deleterious in mortar bar tests and the other innocuous in both methods, were mixed fifty-fifty. The cement had 0.6 percent alkali (R_2O). Four mortar bar tests were carried out: (a) plain; (b) plain (0.6 percent R_2O added to mortar); (c) previous NF,³ which is an alkaline type anti-freezing admixture (4 l [1.1 gal] per 100 kg [220 lb] cement); and (d) new NF (4 l [1.1 gal] per 100 kg [220 lb] cement). The water-cement ratio of test specimens was 0.50.

Fig. 5 shows the relationship between mortar expansion and age. The test results indicate that the mortar expansion with the previous NF is greater than plain mortar with 0.6 percent R_2O . This means that the previous NF promotes alkali-aggregate reactions of aggregate because of the large amount of alkali.

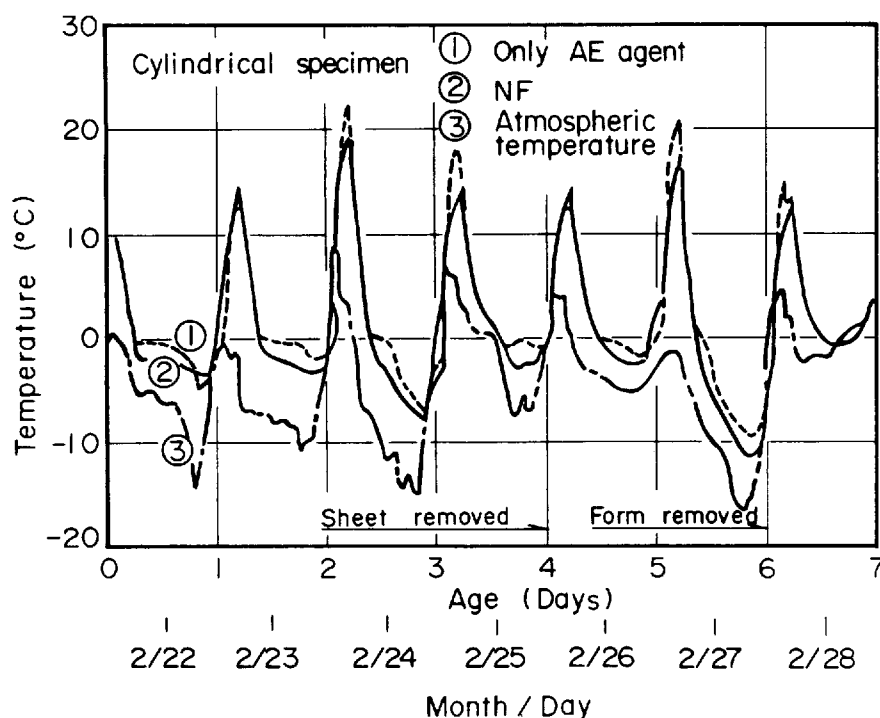


Fig. 7 — Temperature history at central part of cylindrical field-cured specimens with admixture and air entraining agent alone.

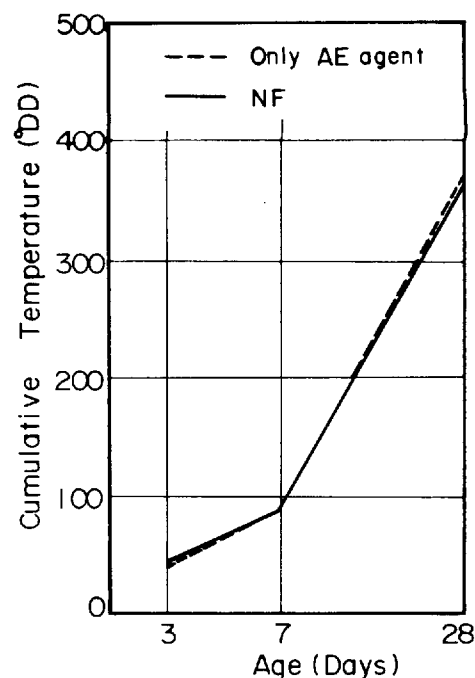


Fig. 8 — Relationship between age and cumulative temperature of slab-type specimens with admixture and air entraining agent alone.

The expansion of plain mortar where the amount of R_2O was not adjusted was almost the same as that using the new NF. These results show that the new NF does not affect the alkali-aggregate reaction of aggregate.

Field tests

Test specimens and methods

Field tests were conducted to ascertain the effectiveness of NF in cold weather. Slab specimens, 1.0 m (3.3 ft) wide, 0.2 m (0.66 ft) thick, and 2.0 m (6.6 ft) long were manufactured. The concrete for the slab specimens was placed directly on the ground and covered with a 0.192 mm (0.008 in.) thick polyethylene sheet. The water cement ratio was 0.48. The amount of NF used in the concrete was 4 l (1.1 gal) per 100 kg (220 lb) cement. A slab specimen with air-entraining (AE) agent alone was also tested. The AE agent was also used in concrete with NF. The air content was 4.5 ± 1 percent. From the slab specimens, 10 x 20 cm (4 x 8 in.) cylinders for compressive strength tests were made by coring. Cylindrical test specimens were also made in lightweight metal molds.

The sheets were removed 4 days after concreting and the formwork

after 6 days. In the cylindrical specimens for standard curing, the molds were removed one day after placing the concrete and cured in 20°C (68°F) water until the test. The cylindrical field-cured specimens were kept sealed in vinyl sacks together with the slab specimens.

The temperature of concrete was measured with copper-constantan wire. Data was recorded and processed by a personal computer.

Test results

Fig. 6 shows the temperature history at the central part of the slab specimens with the NF and the AE agent alone. Fig. 6 also includes the ambient temperature. The temperature of concrete with NF is higher than that with the AE agent alone for the first two days after which the order changes. This result indicates that NF promotes hydration and generates more heat at the early stage than the AE agent alone. When the ambient temperature dropped to -13.7°C (7.3°F) the lowest temperature at the center of the specimens with NF was -0.6°C (30.9°F) and with the AE agent alone 2.2°C (36.0°F). The temperature 1 cm (0.4 in.) above the lower surface was higher and 1 cm (0.4 in.) below the upper surface lower than the center. This may be ex-

plained by the foundation below the specimens preserving hydration heat and radiating it as the ambient temperature dropped. In the daytime, however, the temperature distribution was the opposite. The lowest temperature 1 cm (0.4 in.) below the upper surface was -2.4°C (27.7°F) in the slab specimen with NF.

Fig. 7 shows the temperature history of the cylindrical field-cured specimen. After placing the concrete, the temperature dropped below zero, and reached -2.5°C (27.5°F) with the NF and -0.9°C (30.4°F) with AE agent alone after 8 hours. The concrete with the AE agent alone may have frozen during this time. The temperature of the specimen continued falling and within one day reached -5.0°C (23°F) with the AE agent alone and -3.6°C (25.5°F) with the NF. Since the specimen was sealed in a vinyl sack, the temperature increased during the day and fell below zero at night.

The relationship between age and cumulative temperature at the center of the slab specimen is shown in Fig. 8. There were no differences between the specimens with AE agent alone and with NF.

From the laboratory test results, it was expected that NF promotes the strength development at the early stage in addition to lowering

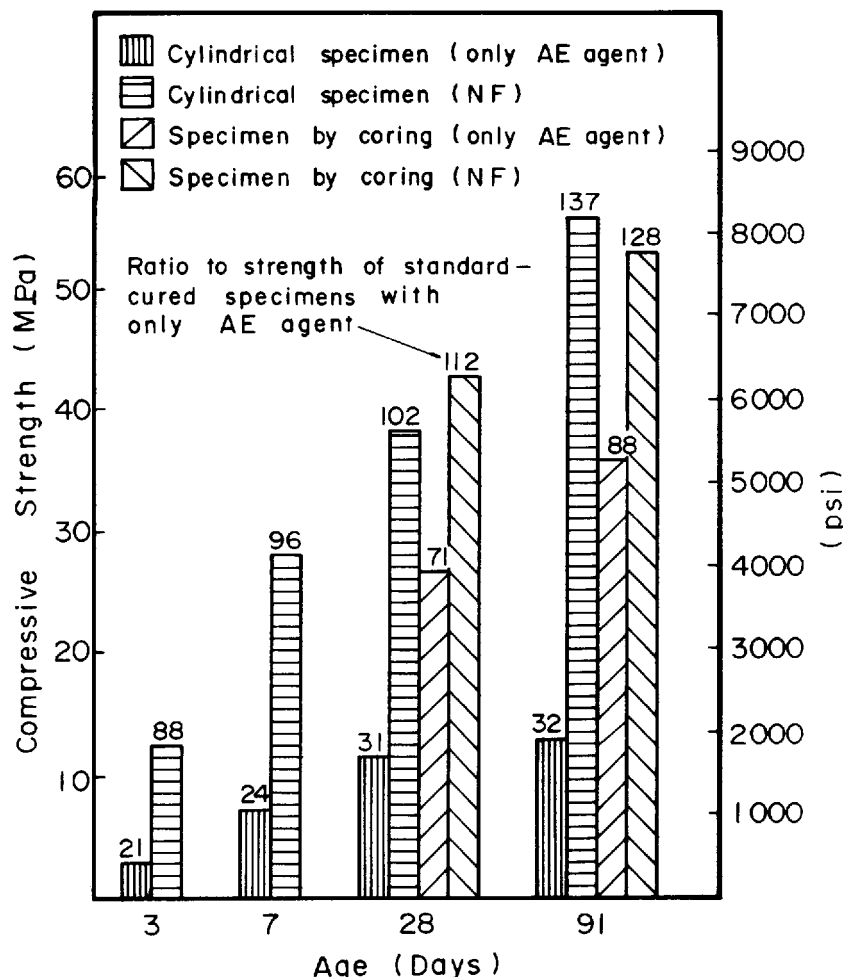


Fig. 9 — Compressive strength of field-cured concrete.

the freezing point, and consequently the concrete is protected from freezing. Fig. 9 shows the compressive strength of different concretes. The strength of cylindrical specimens with NF increased remarkably with age and reached more than 100 percent of the strength of standard-cured specimens at 28 days. However, the corresponding strength of cylindrical specimens with the AE agent alone was only 31 percent. This suggests that the cylindrical specimen suffered frost damage within one day. In the core specimens taken from the slab specimen with NF, the strength was 112 percent of standard-cured specimen at 28 days and 128 percent at 91 days. This is because the slab specimen with AE agent alone did not suffer early frost damage. The strength of the core specimen was rather lower than that of the standard-cured specimen at 28 days, possibly because the specimen was cured at low temperatures.

The slab specimen with AE agent alone was not subjected to frost damage because of the hydration heat and the accumulation of heat on the ground. However, the test results with the cylindrical specimens show clearly that the newly-developed antifreezing admixture, NF, is effective in cold weather.

Conclusion

The non-chloride non-alkaline antifreezing admixture containing polyglycolester derivatives and calcium nitrite-nitrate performed well in laboratory and field tests. The test results showed that the admixture lowered the freezing point of pore water and promoted strength development and is an excellent antifreezing admixture for cold weather concreting.

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References

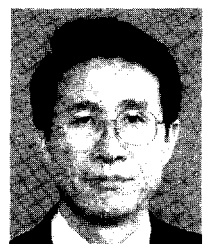
1. "Standard Specification for Design and Construction of Concrete Structures," Japan Society of Civil Engineers, 1986, 306 pp.
2. Brook, John W.; Factor, David F.; Kinney, Frederick D.; and Sarkar, Asok K., "Cold Weather Admixture," *Concrete International*, V. 10, No. 10, Oct. 1988, pp. 44-49.
3. Watanabe, Hiroshi; Sakai, Koji; Takada, Makoto; and Umezawa, Kenichi, "Use of Antifreezing Admixtures for Concrete," *Proceedings, '88 Cold Region Technology Conference*, Nov. 1988, pp. 512-517.

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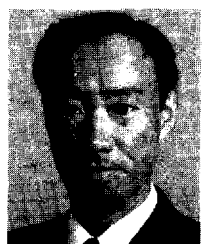
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Freezing weather admixture can reduce plastic shrinkage cracking by reducing temperature differential between concrete and air

Control of Plastic Shrinkage Cracking in Cold Weather

by Ephraim Senbetta and Mark A. Bury

Low temperatures reduce the rate of cement hydration. During cold weather, various approaches are used to compensate for this and obtain desirable setting times for concrete. Use of accelerating admixtures is one common practice; heating the mix water and aggregates is another. Both approaches have limitations, particularly at temperatures below freezing: conventional accelerating admixtures may not be effective because the concrete can freeze before it reaches initial set; heating the mix water and aggregates can aggravate the plastic shrinkage cracking problem by increasing the temperature differential between the concrete and the surrounding air.

Plastic shrinkage cracking

The most commonly mentioned cause for plastic shrinkage cracking is rapid evaporation of water from a concrete surface before it sets. The rate of evaporation that results in plastic shrinkage cracking has often been related to the rate of bleeding. According to ACI Committee 305,¹ plastic shrinkage cracks are likely to appear when the rate of evaporation is greater than the bleeding rate of the concrete, and particularly when ambient conditions are such that the rate of evaporation of water exceeds 0.2 lb/ft²/h (1 kg/m²/h).

However, a recent study by Shaeles and Hover² suggests that other factors such as the paste content of concrete, the screeding, and

the finishing operations may also have a significant influence on plastic shrinkage cracking. Differential settlement of fresh concrete due to interference to uniform settlement by coarse aggregate pieces or reinforcing steel has also been identified as one possible cause of cracking in plastic concrete.³

Evaporation of water

The rate of evaporation of water from fresh concrete surfaces is affected by three factors:

- Everything else being equal, the higher the temperature and wind velocity, and the lower the relative humidity, the greater the rate of evaporation. A monogram which relates these factors to evaporation rates is often cited in publications dealing with hot-weather concreting and curing of concrete.^{1,4}
- The ingredients and proportions of the concrete mixture, which affect the bleeding characteristics of concrete. For example, everything else being equal, air entrainment reduces bleeding (reference 3, p. 485). Water-reducing admixtures that entrain air have a similar effect, but there are also water-reducing admixtures that increase the rate of bleeding.⁵ Cement fineness and composition also have an effect on bleeding: bleeding decreases as fineness increases and as the alkali and C₃A contents increase. And the addition of pozzolans also reduces bleeding (reference 3, p. 225).
- The difference between the ambient and the concrete temperatures. Vapor pressure of water increases

with temperature, and water vapor moves from a higher vapor pressure zone to a lower. When the concrete temperature is greater than the air temperature, the vapor pressure adjacent to the concrete surface is greater than the vapor pressure in the surrounding air, and there is a higher rate of evaporation of water from the surface of the concrete.

The study described in this article was carried out to determine if, in fact, an increase in the difference between the ambient temperature and that of the concrete can result in a greater rate of evaporation and an increase in shrinkage cracking.

Laboratory study

The laboratory study of the plastic shrinkage cracking of fresh mortar at low temperatures was designed to simulate typical cold weather concreting conditions where a heated mix placed at low temperatures produces a situation where evaporation is likely to occur. The objective was to see if keeping the concrete temperature low by using a freezing weather admixture (FWA) instead of hot water reduces plastic shrinkage cracking.

Test program

The test method used in this study was the same as described by Kraai⁶ and Shaeles and Hover,² with one exception: the mortar test panels used were slightly larger, with dimensions of approximately 36 x 36 x ¾ in. (9140 x 9140 x 190 mm). To monitor the evaporation of mois-

Table 1 — FWA dosage and mix temperature for test mortars.

Mix No.	FWA dosage (oz/cwt)	Mix Temp. (F)
1	—	65
2	—	40
3	20	40
4	60	40
5	90	40

Table 2 — Area of plastic shrinkage cracking (in.²) on mortar test panels.

FWA dosage (oz/cwt)	—	—	20	60	90
Mix Temp.	65 F	40 F			
Round					
1	0.076*	0.111*	0.006	—	—
2	0.355*	0.043*	—	—	—
3	0.288*	*	—	—	—
4	*	*	—	—	—
5	0.181*	*	—	—	—

* Mortar frozen at 24 hours.

ture, mortar specimens for the moisture loss test accompanied each panel. Both the mortar test panels and the moisture loss test specimens were simultaneously exposed to environmental conditions that were expected to cause plastic shrinkage cracking of the panels.

In the test environment, the ambient temperature was 30 ± 2 F (-1 ± 1 C), the relative humidity was 67 percent, and the wind velocity was 5 to 6 mile/hr (8 to 10 km/hr). The wind was produced by five identical fans set up so that each mortar panel had the same amount of breeze blowing across it. Plywood panels were erected between each test panel to direct the wind in one direction across each test specimen. A wind velometer was used to measure the wind speed adjacent to the surface of each panel.

The study focused on observations of cracks in the test panels and moisture loss after 24 hours of exposure. Five different mixes were tested (Table 1). Mix 1 represents a typical cold weather concreting scenario: warm concrete placed at a cold ambient temperature. Mixes 2,3,4, and 5 have a much lower mix temperature to more closely match the ambient temperature. For each of the five rounds of experimentation (Table 2), the mixes were randomly placed in one of five test sites in the environmental chamber to prevent bias.

Materials

Ten 94 lb (42.6 kg) bags of ASTM C 150 Type I portland cement were hand blended to ensure a uniform representative cement sample for each round of experimentation.

An angular, well graded concrete sand with a fineness modulus of 2.98 was used. It also was mixed and blended to ensure uniformity for each round of experimentation, and placed into waterproof containers.

The FWA was the same as described by Factor, et al.⁷ It is a multi-component formulated admixture that not only prevents freezing of fresh concrete at temperatures as low as 20 F (-7 C) but also has water reducing and accelerating characteristics.

A vinsol resin air-entraining admixture was used.

Mortar

For each round of experimentation, the mortar mixes consisted of 778 lb/yd³ (462 kg/m³) of cement, 2486 lb/yd³ (1475 kg/m³) of sand, an air-entraining admixture at a dosage of 0.7 oz/cwt (46 ml/100 kg) (air contents between 6 and 8 percent), and enough water to produce a uniform consistency of 90 to 110 percent flow. The flow for each mix was measured following the procedures in ASTM C 109.⁸ Three of the five mortar mixes for each round of testing contained the FWA (Table 1). The mortar was mixed in a 3.0 ft³ (0.08 m³) mortar paddle mixer following procedures in ASTM C 305.⁹

Sample preparation

The test panels were cast from each mix by placing the mortar in wooden forms treated with a waterproof coating to ensure that no moisture from the mortar was absorbed into the mold. In this way water was permitted to escape only through evaporation from the surface. The mortar was consolidated and leveled using a damp wooden

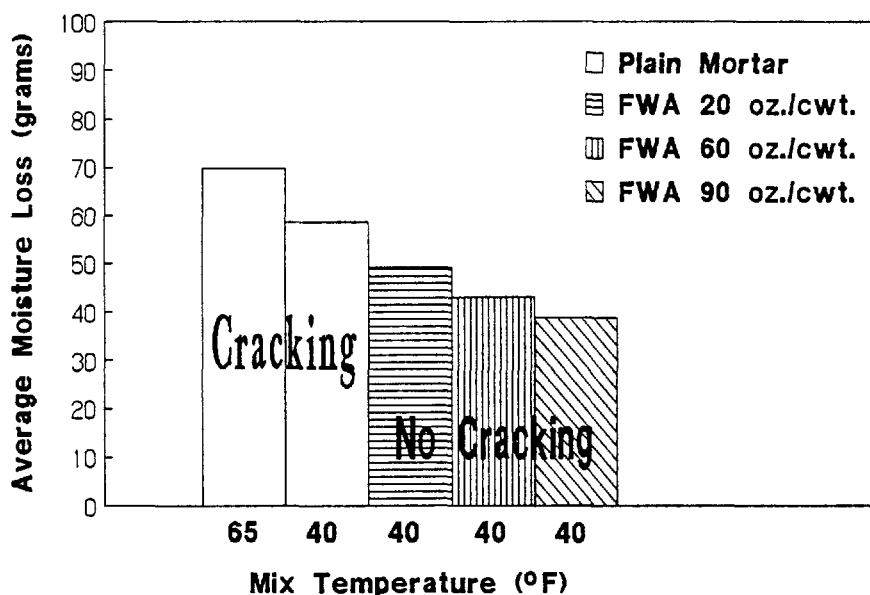


Fig. 2 — Effect of total moisture loss on cracking of mortar panels.