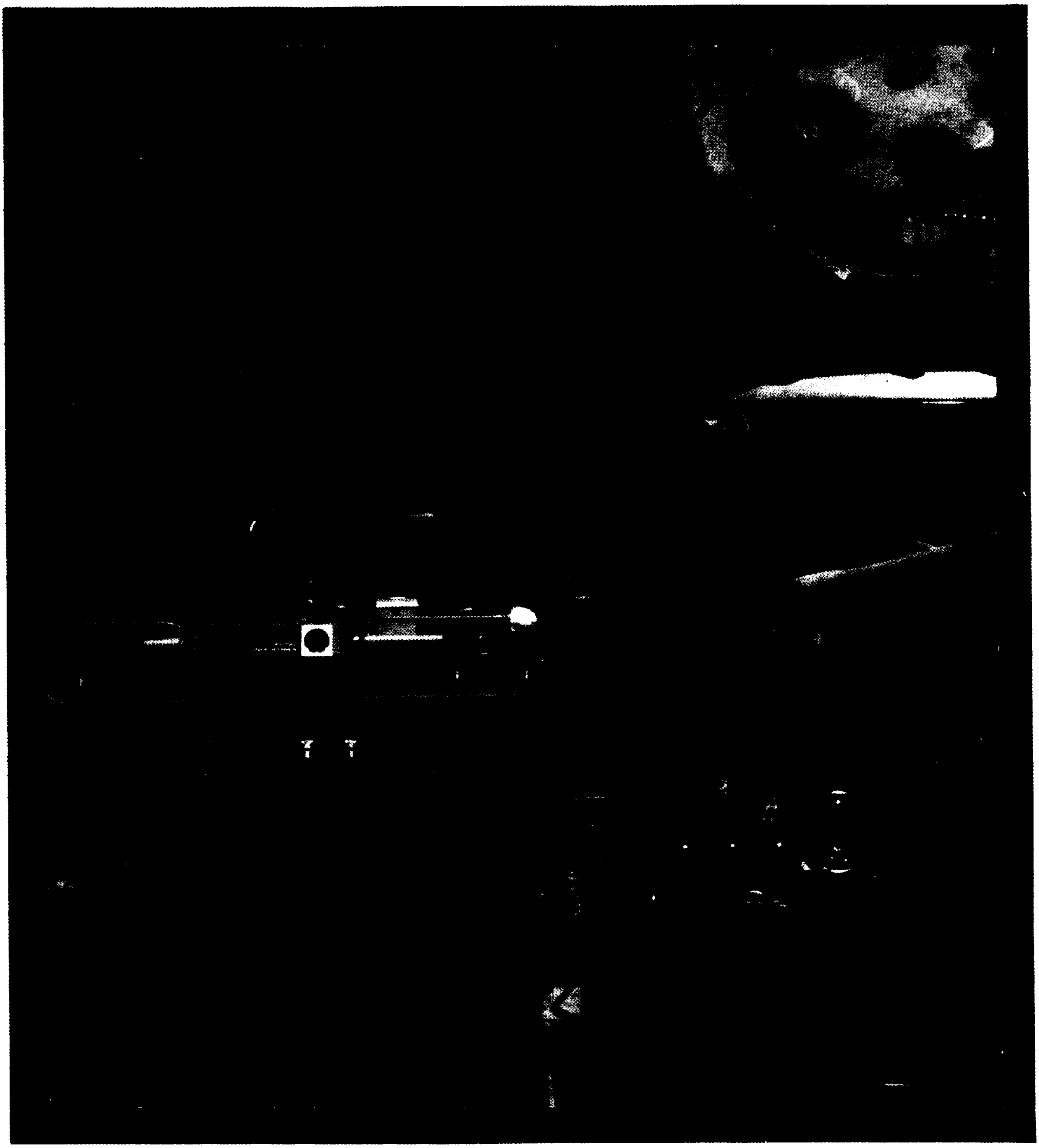
CHEMICAL ADMIXTURES



Compilation 23

American Concrete Institute

Chemical Admixtures

ACI Compilation 23

Contents

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."[1] It does not say that concrete will weigh 144 pounds per cubic foot (2306 kg/m^3) 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 x 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 admixtures[2]

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/yd^3 (296 kg/m^3) of cement, be protected with insulation having a thermal resistance (*R*) rating of 6 hr·ft^2·F/Btu when the ambient temperature is expected to drop to 20 F (−7 C).

Curtailing 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 cm^3/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 yd^3 (30,600 m^3) of concrete to be placed all year around. A

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

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		2:02 earlier
Final	at least 1:00 earlier		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†	—	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
†Control

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 cm^3/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 cm^3/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] Although 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 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.

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

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.

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Selected for reader interest by the editors.

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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 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

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