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MINERAL ADMIXTURES

Compilation 22

American Concrete Institute

Mineral Admixtures

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Contents

Editors Note: The term "microsilica" as used above and elsewhere in this compilation can be considered interchangeable with "silica fume." See "Cement and Concrete Terminology," ACI Publication SP-19.

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.

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On The Cover: Roller compacted concrete with Class F fly ash was the primary material used to replace a failed dam in southwestern Utah. The completed dam is 75 ft high and will eventually impound over 40,000 acres. (Photo courtesy of Harry Roof, Western Ash Co., Denver, Colo.)

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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/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 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/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).

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 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

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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		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 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] 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.

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

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.

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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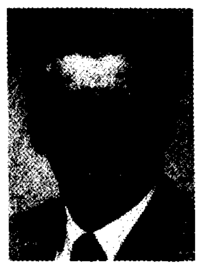
Selected for reader interest by the editors.



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Properties of Shrinkage-Compensating Silica-Fume Concrete Made with Type K Cement

by Ziad Bayasi and Rabih Abifaher

Within the need for rehabilitation of the aging infrastructure, repair and restoration of concrete pavements and bridges has a high priority. This situation is expected to continue into the future. An important consideration of any concrete repair project is the selection of proper repair material.[1,2] Among the important items to focus on in this selection are:

- Differential volume changes of the repair and original surface materials (substrate).
- Bond strength between the substrate and the repair material.
- Rapid strength development.
- High strength and durability.

This article describes an experimental investigation of the material properties of fresh and hardened shrinkage-compensating silica-fume concrete made with Type K cement. Those properties that pertain to repair applications are emphasized.

Shrinkage-compensating silica-fume concrete made with ASTM C 845 Type K cement has important properties for repair applications. Use of shrinkage-compensating concrete can help reducing shrinkage (or even generate expansion),[3,4] and it has been documented that adding silica fume to concrete decreases permeability, increases strength, enhances abrasion resistance, improves durability, and accelerates strength development at early ages.[5,6]

Shrinkage-compensating concrete basically differs from conventional concrete in two properties: workability and expansivity. Fresh Type K shrinkage-compensating concrete has a relatively high water demand compared to conventional concrete. The extra water is needed for the chemical reaction that generates expansion. Fig. 1 compares the dimensional change of shrinkage-compensating concrete with that of ASTM C 150 Type I portland cement concrete. The degree of expansion of shrinkage-compensating concrete is strongly linked to the efficiency and duration of curing, which is responsible for supplying the necessary water for the expansive reaction.[3,4]

Adding silica fume to conventional concrete reduces workability, decreases air content, significantly reduces permeability, and increases compressive strength (Fig. 2, 3, 4, 5). Silica fume also enhances flexural strength and accelerates early-age strength development.[5,6]

Experimental program

The silica fume used in this investigation contained 96.5 percent of SiO_2 and had an average particle size of 1.5 microns (6×10^{-5} in.).[8] An ASTM C 494 Type F naphthalene formaldehyde sulfonate-based high-range water-reducing admixture was used because of its reported effectiveness in silica-fume concrete.[9,10] Aggregates were a natural river sand and a pea gravel, (maximum size ⅜ in. [9 mm]).

Three mixes were tested (Table 1). The concrete was mixed in a laboratory drum mixer and consolidated by external vibration using a vibrating table. Slump was measured in accordance with ASTM C 143, and air content using the pressure method in accordance with ASTM C 231. After placement, the specimens were kept in their molds and covered with plastic sheets for 24 hours. The specimens were cured at 72 F (22 C) and 100 percent relative humidity for 7 days, then exposed to the laboratory environment (70 to 75 F [21 to 24 C]) and about 30 percent relative humidity) until testing at 35 days.

The dimensional change of the expansive silica-fume concrete during both fresh and hardened states was measured using two steel plates embedded in 3 x 3 x 10 in. (76 x 76 x 254 mm) concrete beams cast in flexible wooden molds (Fig. 6). Three beams were made for each mix. The plates were inserted during concrete vibration and the distance between them was measured immediately after placement and later during the curing period at ages of 1, 2, 3, 4, 5, 6, and 7 days using a micrometer. The average dimensional change of the three beams was considered to be representative of the pertinent mix. The flexible wooden molds were used so that expansion would be minimally restrained.

Measurement of expansion starting from the point of placement could help shed light on the behavior of silica fume in Type K concrete. Furthermore, as reported below, this method resulted in expansion values higher than those usually obtained for Type K concrete, since it measures the expansion in fresh and hardened states combined.

Compressive strength was measured in accordance with ASTM C 39 using three 6 x 12 in. (150 x 300 mm) cylinders. Flexural strength was measured in accordance with ASTM C 78 using three 4 x 4 x 14 in. (100 x 100 x 350 mm) beams loaded at ⅓ points over a span of 12 in. (300 mm). Rapid chloride permeability was measured in accordance with AASHTO T 277; two 4 x 8 in. (100 x 200 mm) cylinders were made from each mix and one 2 in. (50 mm) thick slice was sawed from the midheight of each specimen for the permeability test. Permeable void volume fraction was measured in accordance with ASTM C 642 using the remaining sections of the permeability specimens.