

Longtime Studies and Field Experiences with Sulfate Attack

By Edward M. Harboe

Synopsis: Sulfate attack on concrete has long been studied and measures taken to combat sulfate attack. Therefore, damage due to sulfate attack is not prevalent today. Illustrations are given to show damage which results when preventive measures are not taken. Tests results are reviewed which led to preventive measures being taken, such as low C_3A cements, use of pozzolans, and low water to cement ratio concrete.

Keywords: aggregates; asbestos-cement products; concrete durability; concrete pipe; fly ash; long-time study; pozzolans; sulfate attack; sulfate resisting cements; tests; water cement ratio.

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INTRODUCTION

Sulfate attack on concrete has been studied almost as long as we have known portland cement. About 60 years ago, we learned that cements low in tricalcium aluminate resisted sulfate attack, and as a result in about 1940, ASTM developed a specification for sulfate resisting cement known as Type V. About the same time, we also learned that many pozzolans were beneficial in making concrete resistant to sulfate attack.

DETERIORATION OF STRUCTURES CAUSED BY SULFATE ATTACK

When I am asked to show someone a structure that has deteriorated due to sulfate attack, I am hard pressed to find good examples for them to see. For 40 years, we have been building our structures to resist sulfate attack, and the older structures that did deteriorate have now been replaced. When you add this to the fact that probably well over 90 percent of the concrete in the United States is not exposed to sulfate attack, it is not hard to understand why most people today have never seen sulfate attack. It is becoming very hard to convince people who have never seen sulfate attack that it is necessary to use premium-price, hard-to-get Type V cement. It is hard to justify why a particular pozzolan, which must be shipped 1,000 miles, should be used instead of a similar pozzolan available at a 50-mile distance.

A few examples from past years may serve to illustrate that sulfate attack on concrete is real and show what can happen when preventive measures are not taken because they cost a little more.

Figure 1 shows total loss of concrete from sulfate attack on White Wood Creek Bridge columns on our Belle Fourche Project in South Dakota. On this project, water samples have shown sulfate concentrations as high as 9,900 p/m.

Figure 2 shows a concrete-lined irrigation ditch on our San Luis Unit of the Central Valley Project in California. The concrete is in an extreme state of deterioration due to sulfate attack. The concrete was made with Type I cement and was 5 years old when the photograph was taken.

Figure 3 shows a test plot on our Uncompahgre Project in Colorado. Data are not available on this test plot, but the effect of sulfate on the concrete pipe specimens is quite obvious. The concrete was 20 years old at the time of photograph.

Figure 4 shows a slab on grade near our Coachella Project in southern California. Distress in the concrete caused by expansion due to sulfate attack caused abandonment of the project after about 3 years.

Figure 5 is a concrete drop structure on our Riverton project in Wyoming. In this location, the ground water is high so that seepage runs over the top of the concrete. The structure was 14 years old at the time of the photograph.

I hope these figures have served to illustrate that sulfate attack can be very severe and is also widespread throughout the western United States.

One difficulty in protecting against sulfate attack is locating the potential problem areas. Sulfates may be general over an area but more frequently appear as localized severe concentrations. Intermittent samples along the alignment of a pipeline, canal, or transmission line may not reveal localized areas of high concentrations of sulfates. Three choices are presented: (1) very extensive testing for sulfates; (2) construct the entire canal, pipeline, or all transmission tower footings of sulfate resistant concrete; or (3) construct for moderate resistance and take a calculated risk that isolated sections may have to be replaced at some future time.

TYPES OF STRUCTURES SUBJECT TO ATTACK

It is usually structures such as canals, pipelines, transmission tower footings, and highway pavements that are subjected to sulfate attack. One major structure of a different type that serves as an example is Alcova Dam (fig. 6). Alcova Dam is a 265-ft-high earthfill dam on the North Platte River in Wyoming. Construction of the dam was started in 1935 and completed in 1938. This dam has a concrete-lined open channel spillway in the left abutment. Over the years, progressive deterioration of the concrete in the spillway floor resulted in severe spalling and erosion. In 1967, steps were taken to repair the spillway. Because of the extent of the deterioration, cores were taken from the spillway for examination as to possible causes (1). The compressive strength of the concrete was still quite good with an average of 5,890 lb/in². However, the tensile strength was only 2.2 percent of the compressive strength and the modulus of elasticity (2.53 million lb/in²), only about one-half of the expected modulus. Under petrographic examination, the concrete showed alteration products of sulfate attack. White deposits of calcium sulfoaluminate (ettringite) were present in moderate amounts scattered throughout

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the broken surfaces of the samples and in some of the pebble sockets. Some deposits of silica gel were also visible but generally concentrated around only a few pebbles. In contrast, concrete from the spillway walls was sound and showed no evidence of sulfate attack. A spring originates from the hillside left of the spillway and flows toward the downstream end of the structure for a short distance and disappears into the ground. Chemical analysis of the spring water showed a soluble sulfate content of 1,370 p/m. Other ground water in the area had high enough soluble sulfates to exert a positive attack. It was concluded that the deterioration could be primarily attributed to sulfate attack.

CONCRETES RESISTANT TO SULFATE ATTACK

A test program conducted in the 1950's (2) evaluating the effect of sulfate exposure on the mechanical properties of concrete developed the same basic conclusion of previous investigations; namely, that the lower the percentage of tricalcium aluminate (C_3A) in the cement, the better would be the concrete resistance to sulfate attack (fig. 7). The exposure condition for the test data shown in figure 7 was a laboratory accelerated test in which concrete specimens were alternately soaked 16 hours in a 2.1 percent solution of sodium sulfate at approximately 73 °F and dried 8 hours in air, under forced draft, at 130 °F. This program also reflected that an increase in cement content increased the sulfate resistance of the concrete for all types of cements. This is perhaps better illustrated by these curves (fig. 8) from a different test program (3). Concretes with water to cement ratios of 0.45 require about twice the time to produce failure as comparable concretes at 0.65 water to cement ratios.

There is one limiting factor in the use of figures 7 and 8. Cements with zero C_3A have not shown greater resistance to sulfate attack than cements having around 3 percent C_3A . Therefore, any extrapolation of these curves below 3 percent C_3A is not valid.

Calcium chloride is frequently added to concrete during cold weather concreting to accelerate early strength. However, our test data indicate that calcium chloride added to concretes containing Types II and V cements reduces their ability to resist sulfate attack (4). Our specifications at the present time do not permit the use of calcium chloride with Type V cement.

Many pozzolans have been found that can effectively double the service life of a concrete when exposed to sulfate attack (fig. 9) (5). The composition of the pozzolan that causes it to increase or decrease the resistance of the concrete to sulfate attack is not fully understood, but in general terms it appears that low calcium pozzolans perform best in sulfate environments. Most natural pozzolans meeting the requirements of ASTM specification C 618 for class N pozzolans are effective in res

sulfate attack as are most fly ashes meeting ASTM C 618 class F requirements. Fly ashes meeting class C requirements should be individually evaluated if subjected to sulfate exposures.

SULFATE RESISTANCE OF ASBESTOS-CEMENT PIPE

The failure of an asbestos-cement pipeline near Ordway, Colorado, due to sulfate attack after only 13 years of service led to studies of asbestos-cement pipe products. It was found that asbestos-cement pipe which had been water cured followed the same resistance pattern of other concretes. However, asbestos-cement pipe which had been autoclave cured (high-pressure steam cured) showed good resistance to sulfate attack regardless of the type of cement used in the pipe. Therefore, a specification requirement that the pipe shall have less than 1 percent uncombined calcium hydroxide will assure an autoclave cure and a sulfate resistant pipe. Tests on specimens from asbestos-cement pipe are difficult to conduct and evaluate. Sawed specimens tend to delaminate when placed in sulfate solutions. Expansion measurements, therefore, reflect any expansion due to delamination as well as the expansion that results from sulfate attack.

EFFECT OF AGGREGATES CONTAINING SULFATES

Occasionally aggregates are proposed for use that contain significant quantities of sulfate in various forms. Some of these produce a self-contained type of sulfate attack when the concrete is exposed to moisture. Mortar bar tests using the mineral alunite (a hydrous potassium aluminum sulfate) as aggregate suffered extensively from sulfate attack when kept moist (6). On the other hand, a jarositic (potassium iron sulfate hydrate) sandstone did not show significant expansion during 24 months of moist sealed storage at 100 °F. At this time, we have no criteria for acceptance of sulfate bearing aggregates. When they occur, each one must be evaluated individually in moist storage for self-induced sulfate expansion.

TESTS OF CONCRETE PIPE

Perhaps our biggest disappointment in sulfate testing occurred in a joint testing program with the American Concrete Pipe Association. The test pipes were made at a pipe production plant and specimens sawed or drilled from the pipe were shipped to our laboratory in Denver for testing and evaluation. Test variables included 5- and 7-bag cement contents; 0 and 20 percent pozzolan using both a fly ash and a natural pozzolan; concrete of low, medium, and high absorption, and pipe made by packerhead and spinning processes. All of the pipe tested showed poor resistance to sulfate attack, regardless of the method of manufacture or combination of cementitious materials used. Instead of having all the answers as to how to make concrete pipe that will withstand sulfate attack, we were left with the conclusion that no matter how we made it or what materials were used, we could not make a concrete pipe with any degree of resistance.

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to sulfate attack. We were not willing to accept this conclusion and since any explanation was purely speculative, a report was never published.

TYPE OF SULFATE EXPOSURE

Soil samples taken from areas around our convention site here in Las Vegas show very high soluble sulfate contents. Therefore, our construction specifications in this area require not only a Type V cement but also a good sulfate resistant pozzolan. There is some question as to whether this degree of protection is necessary because the sulfates encountered in this area are calcium sulfates. The calcium sulfates have a solubility of only 2,000 and 3,000 p/m. Even though the total sulfates available from soil samples are very high, will the low solubility of these calcium sulfates ever expose the concrete to the same severity level as the more soluble sodium sulfates? Until we have a more conclusive answer, we will probably continue to specify a Type V cement plus a sulfate resistant pozzolan.

LABORATORY RESULTS CONFIRMED BY FIELD EXPOSURE

From 1951 to 1971, Interpace Corporation maintained a field exposure test plot near Fort Collins, Colorado (7). This site was selected because of severe sulfate attack on a concrete pipeline in this area. We had a great interest in this test plot and, since it was convenient to our laboratory and remote from Interpace's laboratory, it was to our mutual benefit that we participate in all the evaluations. Figure 10 shows the beginning of excavation to retrieve test specimens. The ground water in this area is high so that at all times there was enough moisture present to sustain sulfate attack. Figure 11 shows some of the test specimens removed from the pit after they were washed and brushed. Test specimens included cast cylinders, concrete pipe sections, irregular pieces of larger diameter concrete pipe, and even a few pieces of metal pipe. Figure 12 shows mortar lining and coating specimens from the test plot.

I believe it is significant that results from this test plot tend to verify our laboratory tests. Concretes made with Type I cements and concretes with very high absorptions are reduced to rubble in the same length of time in actual field exposure as in laboratory tests. It is also noted that nearly all specimens in the plot showed some signs of attack. On this basis our present requirements for sulfate resistant concrete are not considered to be excessively conservative. A disturbing result is the degree of attack shown by the mortar coating samples. The cement content of mortar coatings was expected to make them more resistant than indicated in these tests.

SUMMARY

I hope these illustrations show that sulfate attack is real. However, procedures have been developed and used that make concrete resistant to sulfate attack. Primarily these procedures are the use of cements with low tricalcium aluminate content, concrete made with low water to cement ratio, and the addition of certain pozzolans to the concrete. Much of this testing was being performed during the same time period George Verbeck was conducting investigations into the sulfate resistance of concrete and these data support the conclusions set forth by him (8).

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REFERENCES

1. Good, R. E., "Deterioration of Spillway Concrete in Alcova Dam, Kendrick Project, Wyoming." USBR Report No. REC-OCE-70-50, September 1970.
2. Smith, F. L., "Effect of Cement Type on the Resistance of Concrete to Sulfate Attack." USBR Report No. C-828, November 1958.
3. Tuthill, L. H., "Resistance to Chemical Attack." ASTM Special Technical Publication No. 169, 1955.
4. Smith, F. L., "Effect of Calcium Chloride Additions on Sulfate Resistance of Concretes." USBR Report No. C-900, July 1959.
5. Elfert, R. J., Jr., "Bureau of Reclamation Experiences With Fly Ash and Other Pozzolans in Concrete." A paper presented at the Third International Ash Utilization Symposium, March 1973.
6. Failor, S. V., "Mortar Bar Expansion Tests for Chemical Reactivity Between Sulfate Bearing Rocks in Aggregate and Portland Cements." USBR Report No. C-931, February 1960.
7. Gebler, S. H., "Study of Sulfate Attack on Greeley, Colorado, Pipeline." Wharton Technical Center Report No. D-5, September 1971.
8. G. J. Verbeck, "Field and Laboratory Studies of the Sulfate Resistance of Concrete." Portland Cement Association Research Department Bulletin 227.



Fig. 1--Sulfate attack on bridge columns. White Wood Creek, Belle Fourche Project, South Dakota



Fig. 2--Sulfate attack on concrete canal lining. San Luis Unit, Central Valley Project, California





Figure test plot. Uncompahgre Project, Colorado





Fig. 5--Sulfate attack from ground water on canal drop structure. Riverton Project, Wyoming

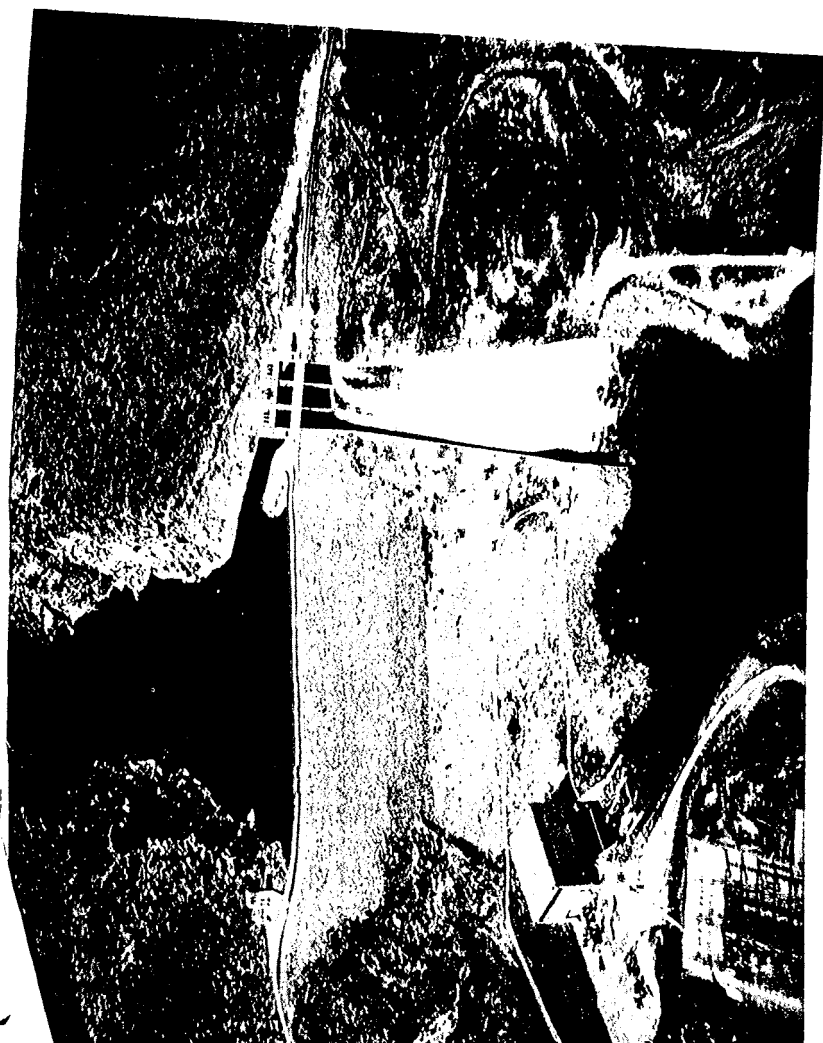


Fig. 6--Concrete spillway attacked by sulfate ground water. Alcova Dam, Wyoming

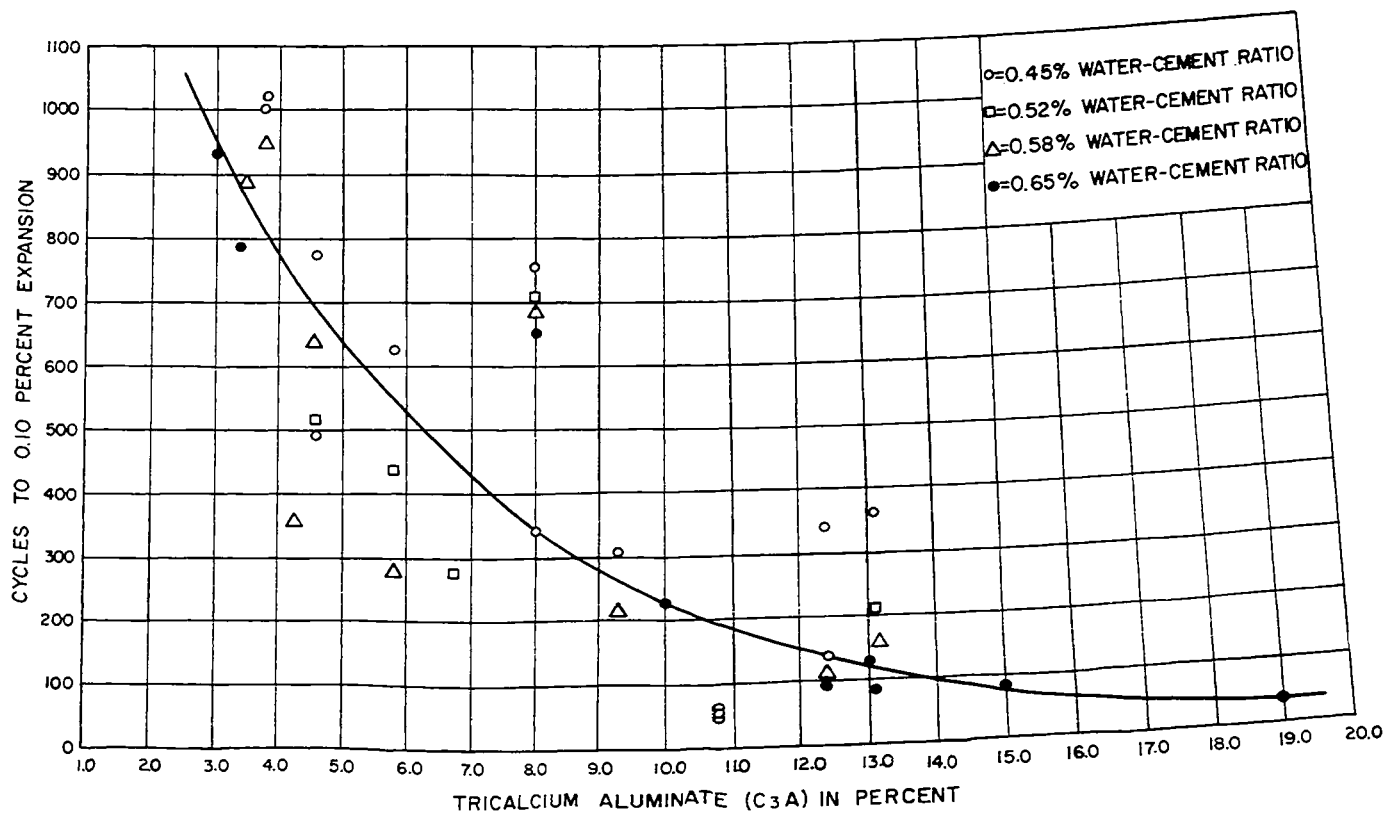


Fig. 7--The lower the percent of C₃A in the cement, the better the resistance of concrete to sulfate attack

EXPANSION OF 3x3x16-INCH CONCRETE BARS DURING 7-YEARS IN SOAP LAKE WATER (4.6%-Na₂SO₄)
COLUMBIA BASIN PROJECT, WASHINGTON

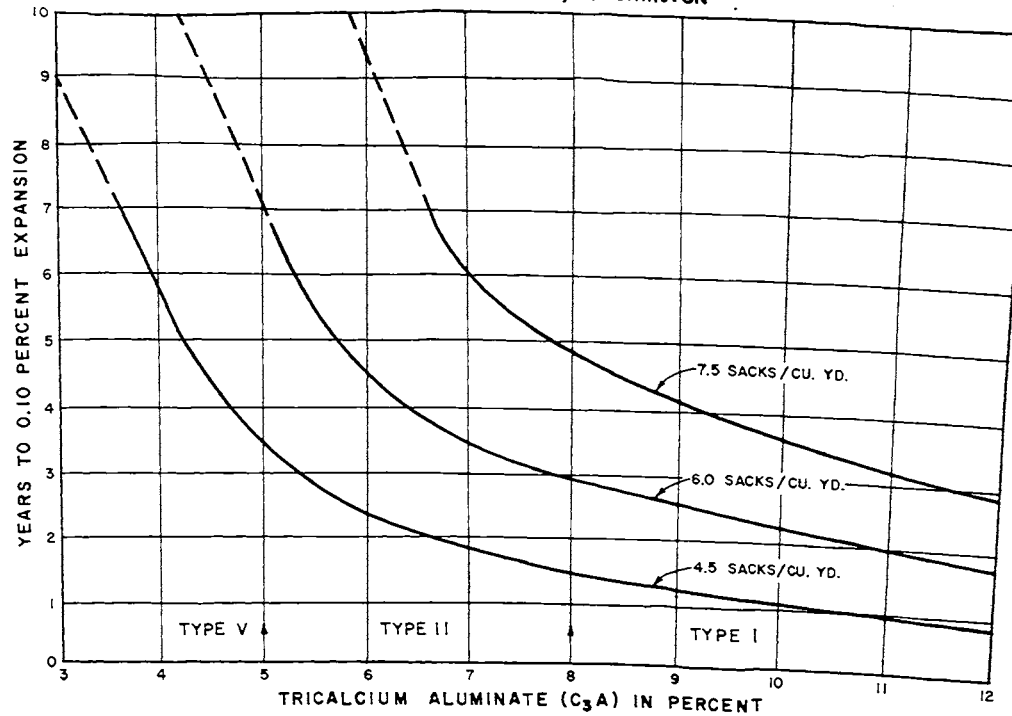


Fig. 8--The lower the percent of C₃A in the cement, and the richer the mix, the better will be the resistance of concrete to sulfate attack

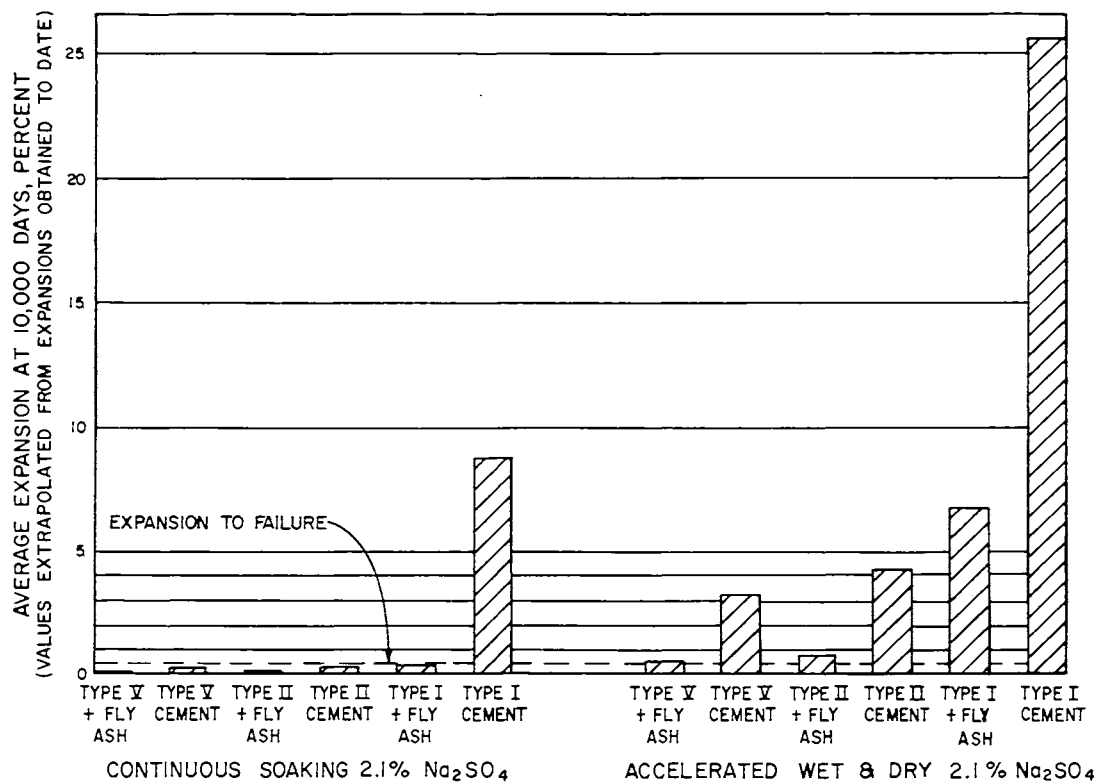


Fig. 9--Many pozzolans have been found that can effectively double the service life of a concrete when exposed to sulfate attack





Fig. 11--Test specimens after removal from test plot and washing



Longtime Study of Concrete Durability in Sulfate Soils

by David Stark

Synopsis: Eleven year performance data are presented for concrete beams stored in sulfate bearing soil in Sacramento, California. Concrete variables include ASTM cement type, cement factor, air entrainment, pozzolanic replacements for cement, portland blast-furnace slag cement, and steam curing. Results reaffirm the importance of cement type, that is, the tricalcium aluminate content of the cement and, more significantly, cement factor with attendant change in water-cement ratio on resistance to sulfate attack. In this study, the use of 40% replacements of cement by high alumina granulated blast-furnace slags had a generally detrimental effect on concrete durability. Twenty percent fly ash replacements were beneficial in the leaner mixes but generally of little or no value in the richer mixes. Forty percent fly ash replacements were generally detrimental to sulfate resistance, particularly where Types II and V cement were used in richer mixes. Calcined Monterey shale showed similar trends but with a greater dropoff in durability in the richer mixes. Air entrainment and steam curing were beneficial to varying degrees.

Keywords: air entrainment; beams (supports); blast furnace slag ; cement factor; cement types; concrete durability; concretes; long-time study; permeability; pozzolans; shales; steam curing; sulfate soils; tricalcium aluminates; water cement ratio.

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INTRODUCTION

For nearly forty years the Portland Cement Association (PCA) has been evaluating the durability of concrete beams stored in sulfate soils in an outdoor test facility in Sacramento, California. Following the initial installation of test specimens in 1941, additional sets of beams were placed into test in 1949 and 1958. Several reports (1-4) have been published on these test programs, the latest being Verbeck's report in the Thorvaldson Symposium held in 1967. That report concentrated on the 1941 and 1949 installations, for which 25 and 16 year data, respectively, were available, while only a partial analysis of seven year data was made for the 1958 installation. This report will summarize the most recent data for the 1958 program, for which 11 year test data are now available.

SCOPE OF PROGRAM

The 1958 program was designed to evaluate the relative performance of concretes containing selected ASTM Types I, IS, II, IIS, III, and V cements, cement content and water-cement ratio, air entrainment, two pozzolanic admixtures, and steam curing. Three PCA Long Time Study (LTS) cements, Nos. 12 (Type I), 21 (Type II), and 51 (Type V), were included, together with four other cements, identified as P1 (Type I), P2 (Type I), P3 (Type II), and LS (Type III), the latter calculated to have 0% C₃A. Clinkers for P1, P2, and P3 cements were combined with granulated blast-furnace slags, with calculated alumina contents of 11 to 12%, to produce three portland blast-furnace slag cements, PS1, PS2, and PS3, respectively. Each contained approximately 40% slag by weight, which is considerably less than maximum slag contents now suggested in the literature for adequate sulfate resistance. (5) Two pozzolans, Type F fly ash from Chicago Fly Ash Co., with a specific gravity of 2.39, and calcined Monterey shale, with a specific gravity of 2.52, were used as 20 and 40% replacements by weight for cement in the air-entrained concretes. Three cement contents, 223, 307, and 390 kilograms per cubic meter, (kg/m³) (4.0, 5.5, and 7.0 U.S. bags per cubic yard) were used for the moist cured concretes, while only the 307 kg mix was used for the steam-cured specimens. Pertinent compositional data for the various cements are given in Tables 1 and 2. Compositional data for the two pozzolanic materials were not



available. Sand and gravel from Elgin, Illinois, with a maximum particle size of 3.8 cm, (1.5 in.) was used for all concretes. Slumps for all concretes were held at 50 to 90 mm, (2-3.5 in.) thereby permitting progressive reductions in water-cement ratio with increase in cement factor. Four companion 150x150x760 mm (6x6x30 in.) beams, three for test and one for control, were cast at the PCA Laboratories. Most were moist cured at 23°C for 28 days, then stored in laboratory air until shipment to Sacramento. Steam curing consisted of four hours autogenous curing at 23°C, followed by 16 hours at 71°C with a temperature rise of 12°C per hour to 71°C. Cooling to 23°C was completed in 4 hours, at which time the specimens were stripped from their molds and stored in laboratory air until shipment. Specimens cured at room temperature were placed into test in late 1958, while the steam cured specimens were placed into test in late 1959.

All test beams were stored horizontally half depth (76 mm) in a basin with soil containing approximately 10% sodium sulfate, as shown in Fig. 1. Exposure then consisted of flooding the basin with water so as to totally immerse the beams. Atmospheric drying was then permitted to drop the moisture level to the soil surface, at which time the basin was again flooded. About six to eight such cycles were completed per year. Following drying, the beams were rated visually at least every two years.

RATING SYSTEM

Performance of the test specimens was evaluated visually using a numerical rating system of 1.0 to 6.0, with 1.0 indicating no evidence of deterioration, and 6.0 indicating failure. During evaluation, reference was made to states of deterioration representative of each rating, as indicated in photographs adopted in the 1940's. Consensus interpolation by the rating team was used to determine intermediate ratings to 0.1 increments. Two or three man teams, with overlapping membership from year to year, were used for each rating. Typical degrees of deterioration, with ratings of 1.1, 3.7, and 5.8, are shown in Fig. 2. In two previous reports (1,2), results were given in terms of the average numerical rating of a given concrete mix. However, Verbeck (3) attempted to interpret these ratings in terms of percent deterioration per year, whereby it was assumed that differences between successive whole number ratings represented equal increments of deterioration. In reality, they represent progressively greater increments, thus, deterioration rates for 7, 16, and 25 year data in that report are not necessarily on equivalent bases. To avoid these uncertainties, this paper reports results in terms of the original visual rating scale.

TEST RESULTS

A summary of performance data is given in Tables 3-5, while significant comparisons among the various concrete mixes are shown graphically in Figs. 3-10. Following are analyses of performance as affected by concrete variables.

C₃A Content of Cement

Figure 3 summarizes the performance of the air entrained 223, 307, and 390 kg mixes made with cements 12, 21, and 51, which are ASTM Types I, II, and V, respectively, and the 0% C₃A cement, LS, which is a Type III cement. Here it is seen that, with the 223 and 307 kg mixes, cements with progressively lesser C₃A contents produced corresponding increases in durability, with the greater increases occurring with the 223 kg mixes. For the 390 kg mix, cements 21, 51, and LS, with 6.3, 3.8, and 0% calculated C₃A contents, respectively, showed similar performance, with all having produced a 1.1 rating, or practically no evidence of deterioration. Only concrete containing cement 12, with 12.6% C₃A, provided lesser durability in this mix. It is also seen that all 390 kg mixes provided durability equal to or greater than the 223 and 307 kg mixes, regardless of the C₃A content of the cement. This is due primarily to progressively lower water-cement ratios, which decrease permeabilities, with increasing cement factors - the ratios decreasing from 0.49 to 0.37 and 0.32.

Air Entrainment

The effect of air entrainment on sulfate resistance is shown in Tables 3 and 4, and in Fig. 4, where data are again plotted for concretes containing cements 12, 21, and 51. Here, entrained air contents range from 4.8 to 6.3%, while the air contents of non-air-entrained concretes range from 1.2 to 1.8%. In all cases, the air-entrained mixes showed measurably greater durability than their non-air-entrained counterparts in the 223 and 307 kg mixes, with the greater improvement occurring in the 223 kg mixes. This improvement is again due to reductions in water-cement ratio and permeabilities, wherein the water-cement ratio reductions averaged 0.11 and 0.04, respectively, in the 223 and 307 kg mixes. Among the 390 kg mixes, essentially no deterioration was evident, thus leaving essentially no margin for improved durability among the various concretes. Both the air-entrained and non-air-entrained mixes containing cement 51, and the air-entrained mix containing cement 21, showed equally the highest durability, wherein water-cement ratio reductions averaged only 0.01. Among the three cements, air entrainment in the 223 and 307 kg mixes had the greatest beneficial effect with cement 21, followed in order by cements 51 and 12. Overall, the effects of air entrainment with its attendant reduction in water-cement ratio are most significant in the leaner, higher water-cement ratio concretes, and become progressively less important

with increasing cement factor and its attendant reduction in water-cement ratio.

Portland Blast-Furnace Slag Cement

The visual ratings for concretes containing the portland blast-furnace slag cements, PS1, PS2, and PS3, show generally lesser durability than their counterparts containing straight portland cements P1, P2, and P3. The exception was in the 223 kg mix for cements P1 and PS1, although advanced degrees of deterioration developed in both concretes. Data plotted in Fig. 5 indicate that greater durability was provided for any even mix containing cements P3 and PS3 made from Type II clinker containing 7.0% C_3A , compared with concretes containing cements P2 and PS2 made with Type I clinker containing 10.2% C_3A . Among the three cement factors, similar durability was provided with each pair of cements in the 223 kg mixes, with slightly greater durability being provided in the straight portland cement concretes. In the 307 and 390 kg mixes, the straight portland cement concretes showed still greater increases in durability.

Pozzolanic Replacements

The effects on sulfate resistance of 20 and 40% fly ash replacements of portland cement are shown in Figs. 6 through 8. Comparison of data reveals that 20% replacements provided greater sulfate resistance in the 223 and 307 kg mixes for cements 12, 21, and 51, which are ASTM Types I, II, and V, respectively, but had no measurable effect in the 390 kg mixes. As would be expected, the effects were greater in the 223 than in the 307 kg mixes. The 40% replacements produced equal or slightly increased durability, compared with 0 and 20% replacements, only for cement 12. While, in the other mixes, the 40% replacement resulted in lesser durability than both the 0 and 20% replacements. In the other mixes with already lower water-cement ratios, high resistance to sulfate attack already is present, thus leaving little or no margin for improved durability.

Among individual cements, the greatest differences in durability occurred with cement 12, which has the highest C_3A content, followed in order by cements 21 and 51, which have progressively lower C_3A contents. Results for cement 12 parallel those for cement 51.

Performance data for the mixes with 20 and 40% cement replacements by calcined Monterey shale are shown in Figs. 9 and 10 for cements 12 and 21. For both cements, a 20% replacement in the 223 kg mixes provided greater durability while a 40% replacement provided equivalent or reduced durability. In the 307 and 390 kg mixes, both the 20 and 40% replacements produced increased resistance to sulfate attack. For all cement 51 mixes, both the 20 and 40% replacements decreased resistance to sulfate attack. Among comparable mixes, the fly ash as a pozzolanic

replacement provided for greater durability than the calcined Monterey shale.

Steam Curing

Test data for the steam cured concretes, which were made only in the air entrained 307 kg mixes, are shown in Table 5. Here it is seen that, compared with the normal moist cure, steam curing provided for greater durability where the straight Type I, II, and V cements were used, together with the Type I cement with the 20% fly ash replacement. However, steam curing reduced durability where the portland blast-furnace slag cement and the 20% calcined Monterey shale replacement for Type I cement were used.

As a final observation, it was noted that certain coarse aggregate particles showed vulnerability to sulfate attack, as evidenced by the development of popouts. These were particularly evident in the lean mixes and probably are related to cyclic crystallization, hydration, and dissolution of the salt solutions contained in the pores of the vulnerable aggregate particles.

SUMMARY

Eleven year data indicate that cement factor, with attendant changes in water-cement ratio, was the most significant factor affecting the resistance of concrete to sulfate attack. Cement type, reflecting particularly the C_3A content, also greatly affected durability, as was expected. Their significances are revealed in the wide range of performance among the 223 kg mixes, and the progressively higher and more similar performance with change to the 307 and 390 kg mixes. Air entrainment was beneficial by allowing reductions in water-cement ratio (thus permeability) among concretes of similar workability. Concretes made with portland blast-furnace slag cements generally showed lesser durability than concretes made with straight portland cement manufactured from the same clinker as that used in the blended cement. In these cases, however, relatively high alumina slags were used in much less than recommended cement replacements, thus partially accounting, perhaps, for the observed performance. Twenty percent replacement of cement with fly ash provided greater durability among the 223 kg mixes regardless of cement type, while providing little or no improvement, or lesser durability, among the 307 and 390 kg mixes, depending on cement type (C_3A content). In contrast, 40% fly ash replacements provided improved sulfate resistance in the 223 and 307 kg mixes using Type I cement, but resulted in lesser durability in all mixes containing Types II and V cement. Calcined Monterey shale replacements were less effective than fly ash in combating sulfate attack, and generally resulted in lesser durability in 307 and 390 kg mixes with each cement type. Steam curing generally improved sulfate resistance. In addition, certain types of coarse aggregates in concrete may be vulnerable to destruction when exposed to sulfate soils.

REFERENCES

1. McMillan, F. R., Stanton, T. E., Tyler, I. L., and Hansen, W. C., "Long Time Study of Cement Performance in Concrete, Chapter 5, Concrete Exposed to Sulfate Soils," ACI special publication, published in cooperation with the Portland Cement Association, 64 pp, December 1949. Reprinted as PCA Res. Dept. Bull. 30.
2. "Twenty Year Report on the Long-Time Study of Cement Performance in Concrete," Advisory Committee, W. C. Hansen, Chairman, PCA Res. Dept. Bull. 175, May 1965.
3. Verbeck, G. J., "Field and Laboratory Studies of the Sulfate Resistance of Concrete," Performance of Concrete. Resistance of Concrete to Sulfate and Other Environmental Conditions, A Symposium in Honour of Thorbergur Thorvaldson, held in Toronto, Ontario, April 1967 by the Division of Building Research, National Research Council of Canada, and ACI, pp. 113-124. Reprinted as PCA Res. Dept. Bull. 227.
4. Klieger, Paul, "Extensions to the Long-Time Study of Cement Performance in Concrete," Journal, PCA Research and Development Laboratories, Vol. 5, No. 1, January 1963, pp. 2-14.
5. Locher, F. W., "The Problems of the Sulfate Resistance of Slag Cements," Zement-Kalk-Gips, New Series, Vol. 19, No. 9, September 1966, pp. 395-401.

TABLE 1
Summary of Oxide Analyses of Cements

Cement	ASTM Type	Oxide Analysis, %							
		SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O
LTS 12	I	21.5	6.3	2.4	63.6	3.1	1.6	0.28	0.40
LTS 21	II	24.0	4.4	3.2	64.6	1.3	1.2	0.22	0.40
LTS 51	V	24.5	3.5	3.3	64.3	1.7	1.4	0.08	0.22
LS	III	22.4	2.14	5.20	66.5	0.60	2.53	0.03	0.09
P1	I	21.4	6.39	2.62	63.0	2.04	2.24	0.08	0.52
P2	I	21.1	5.13	2.03	64.0	2.57	2.36	0.07	0.63
P3	II	22.9	4.86	3.45	63.8	1.34	1.52	0.21	0.72
PS1	IS	26.0	8.63	2.30	54.3	3.44	2.08	0.10	0.47
PS2	IS	26.0	7.66	1.68	58.3	2.12	1.55	0.07	0.97
PS3	IIS	27.3	6.74	2.55	55.3	2.49	2.36	0.46	0.75