Attack on Portland Cement Concrete by Alkali Soils and Waters—A Critical Review

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The literature pertaining to the development of sulfate-resistant portland cement is reviewed. The field and laboratory studies carried out by such organizations as the National Bureau of Standards, University of Minnesota, Portland Cement Association, Engineering Institute and National Research Council of Canada are reviewed and discussed. The accelerated tests proposed for acceptance and specification purposes are reviewed as are hypotheses advanced to explain the mechanism by which sulfate destroys concrete. Data obtained in accordance with ASTM Designation: C 452-64 are correlated with 18-yr data for concrete beams exposed to sulfate soils in the field at Sacramento, Calif.

•THE OBJECT of this paper is to review and discuss the results of the principal investigations pertaining to the development of portland cements suitable for use in alkali soils and waters. According to Burke and Pinckney (1), alkali, in the popular sense, is a term used to designate the soluble salts that accumulate in regions of little rainfall. Such salts are formed by the disintegration of rocks and are present in soils when they are formed. With sufficient rainfall and drainage, these salts are leached and removed by the drainage water. They accumulate wherever such alkali-laden waters collect and evaporate, as in the ocean, salt lakes or soils.

The salts usually present in greatest amounts in the soil and drain waters of the arid and semiarid West are the sulfates, carbonates and chlorides of sodium and magnesium and, in smaller amounts, calcium. The sodium sulfate makes up the larger part of the deposits generally known as white alkali; usually also there is more or less of the magnesium sulfate.

The so-called black alkali is largely sodium carbonate. It is called black from its property of dissolving organic matter from the soil to form dark-colored solutions. This property is not shared with the sulfates, though they are usually present with the sodium carbonate in black alkali.

According to Lea and Desch (2), the commercial development of calcium aluminate cement by Bied arose from the serious troubles experienced in France owing to the decomposition of mortars and concretes in ground containing large amounts of sulfates, notably gypsum. The problem of sulfate attack had become important by 1890 because of failures on a railway in southern France. Bied investigated some of these failures and concluded that they were caused by gypsum in the soil and groundwaters. The disintegration of the concrete was attributed to the formation of calcium sulfoaluminate (3) and the crystallization of gypsum in the pores of the concrete. In 1900 and 1902 further troubles from gypsum were experienced in tunnels in France and from magnesium and sodium sulfates in structures in southern Algeria. Wittekindt (4), in reviewing early research on this subject, points out that Klaudy discovered in 1903 that sodium sulfate constituted a much greater danger than gypsum water.

Lea and Desch (2) point out that in many parts of Great Britain and in many extensive regions outside of England, clay and soils are found containing considerable quantities of mineral sulfates, notably those of magnesium, calcium, sodium and potas-

sium. As much as several percent pyrites may be present in clays. When exposed to the air the pyrites undergo oxidation leading to the formation of other mineral sulfates. The free sulfuric acid initially produced is neutralized by bases, usually calcium and magnesium carbonates present in the clay. Across large areas of the United States and Canada occur the so-called alkali soils. Gypsiferous territories and sulfate-bearing soils occur also in France, other parts of Europe, and elsewhere. The problem of the resistance of concrete to sulfate salts is therefore of widespread interest.

Thorvaldson (5) reports that many attempts were made to produce commercial cements which combined the desirable properties of the portland type with resistance to the action of sulfate waters. In the German iron ore or Erz cement, ferric oxide and sand were substituted for clay in the raw mix. Originally this cement contained very little alumina so that a binary calcium ferrite phase took the place of the ternary calcium aluminoferrite phase of portland cement. The Erz cement was more resistant to sulfates, set and hardened more slowly and had a higher density than normal portland cements. By 1925 the composition had already been altered by the use of raw materials containing alumina to give a ratio of A* to F of about 0.7. This would yield a cement with a calculated C_3A content of zero and the calcium aluminoferrite phase would be a solid solution (6) of C_6A_2F and C_2F.

About 1920, Ferrari produced a calcareous cement (5) in which the proportion between the F and A was supposed to be between 1 and 1.563. The object was to obtain a cement free of the binary calcium compounds of alumina and iron. Ferrari reported that this cement known as "ferroportland" possessed a high degree of resistance to sulfate waters when used with pozzolans. A recent patent (7) for a sulfate-resisting cement calls for an A:F ratio of 0.50 to 0.55, a S:F ratio greater than 1.8:1, and 1.5 times as much C_3A as Fe_2O_3 in the mixed crystal (solid solution) phase.

Following the report by Hansen, Brownmiller and Bogue (8) of the existence of the compound C_4AF in portland cement, Fleming (9) made experimental plant runs at Port Colborne, Ontario, in 1930 in which the plant kiln feed was modified to reduce the calculated potential C_3A contents with a corresponding increase in the calculated C_4AF contents of the clinkers. On the basis of the iron phase being C_4AF, the regular plant cement contained 11 percent C_3A and two experimental cements contained 7 and 5 percent C_3A. These were tested by Thorvaldson (5) and these reductions in the calculated C_3A contents markedly improved the resistance of the cements to sulfates.

Early in the present century, work on the destruction of concrete in alkali soils and waters was begun in the United States and Canada. Among the leaders in this work in the United States were the National Bureau of Standards (NBS), the Department of Agriculture, and the Portland Cement Association (PCA) and, in Canada, the Engineering Institute and the National Research Council.

MAJOR INVESTIGATIONS ON SULFATE RESISTANCE

Western States

At about the beginning of the century, Montana (1, 10), Colorado (11, 12) and other western states (13, 14) became aware of the destruction of concrete by sulfates in soils. The following statement (10) was made regarding the failure of a sewer in Great Falls, Mont.:

> This sewer, which was constructed in 1890, after a comparatively short service showed defects of so serious a character as to necessitate rebuilding of portions of it. The remaining portions of the sewer have disintegrated in many places and occasionally portions of the pipe are gone; the cement in places has the appearance and consistency of fresh lime mortar.
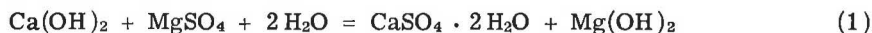
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*The usual procedure in the literature on portland cements of using C, A, S, F and H instead of CaO, Al_2O_3, SiO_2, Fe_2O_3 and H_2O, respectively is followed in this paper.

Investigations of this and other structures led to the conclusion that sulfates from the soils were carried by rainwater into the backfill of the structures and that this water was attacking the concrete. This led to an investigation by Burke and Pinckney (1) of the chemical reactions involved in this destruction.

Burke and Pinckney immersed pats of hardened cement pastes in solutions of sulfate and found that they expanded and cracked. They then crushed pats of hardened pastes to pass a No. 100 sieve and treated these powders with solutions of salts. From the results of chemical analyses of the filtrates and of the residues from these tests, they formulated the following hypothesis to explain the harmful effects of alkali waters on concrete:

> The chemical reaction of alkali that is destructive to cement work is double decomposition between the various alkali salts and calcium hydroxide, which is an unavoidable constituent, and probably the binding constituent, of all set cement, whether the cement is classed as portland, natural, or slag. This reaction removes greater or lesser amounts of the calcium hydroxide, the amount depending upon the salts present, the concentration of the solution, the cement, and the solubility of the reaction products, and deposits in its place, in most cases, a molecular equivalent amount of other compounds, which have good cementing properties but occupy more space than calcium hydroxide. This increase in space occupied disrupts the cement, causing it to bulge, crack and crumble.

The double decompositions were illustrated by the following equations:

$$Ca(OH)_2 + MgSO_4 + 2H_2O = CaSO_4 \cdot 2H_2O + Mg(OH)_2 \tag{1}$$

and

$$Ca(OH)_2 + Na_2SO_4 + 2H_2O = CaSO_4 \ 2H_2O + NaOH \tag{2}$$

As is well known, the volumes of the reactants and reaction products in such reactions are obtained by dividing the molecular weights by the specific gravities of the compounds. By such calculations (15), Burke and Pinckney (1) found that in the reaction of Eq. 1, 1 cc of solid $Ca(OH)_2$ yielded 3.13 cc of solid $CaSO_4 \cdot 2H_2O + Mg(OH)_2$. They assumed that these reaction products tended to be deposited in the space originally occupied by the $Ca(OH)_2$ and accordingly caused the cement paste to expand. This would be true if these were solid-liquid reactions of the type discussed by Hansen (16). This hypothesis and the mechanisms of the reactions are discussed in more detail later.

National Bureau of Standards

Work (17) was begun at NBS in about 1910 primarily to study the resistance of concrete to destruction by seawater. However, the program developed into a study of the destruction of concrete by sulfate waters. In the first study, 1:2, 1:3 and 1:4 hollow cement-sand mortar cylinders were filled with salt solutions, sometimes under a hydrostatic pressure, and the solutions were permitted to evaporate through the walls of the cylinders. One conclusion from this study was

> portland cement mortar or concrete if porous enough can be disintegrated by the mechanical forces exerted by the crystallization of almost any salt in its pores, if a sufficient amount of it is permitted to accumulate and a rapid formation of crystals is brought about by drying. Porous stone, brick and other structural materials are disintegrated in the same manner. Therefore, in alkali regions where a concentration of salts is possible, a dense nonporous surface is essential.

Tannat and Burke (10) observed that sandstone foundations were disintegrated in the soils that destroyed concrete and recommended that nonporous stone be used in place of the porous sandstone that was commonly used. The mechanism of the destruction of porous materials by the growth of salt crystals has been studied in detail and the literature was recently reviewed and discussed (18).

This preliminary investigation at NBS was followed by a cooperative study (19) in 1914 with the U. S. Department of Agriculture, U. S. Bureau of Reclamation and the American Portland Cement Manufacturers Association. In this study, drain tile, made with only one portland cement, was exposed to alkali soils in Iowa, Missouri, Minnesota, Arizona, New Mexico, Washington, Colorado and South Dakota. In 1915 the program (20) was expanded to include 10- by 10- by 30-in. concrete blocks containing reinforcing steel. These were placed in alkali soils so as to extend some distance into the soil to observe the effect of the mechanical forces exerted by frost action and by the crystallization of alkali salts absorbed by capillarity into the pores of the concrete above the groundwater surface. Several different brands of cement and some new exposure sites were used. The tiles broken periodically in the strength tests during the exposure program were replaced with tiles manufactured from a different brand of cement.

Progress reports (19, 20) were made on this work in 1917, 1922 and 1926. Some of the conclusions from these studies were as follows:

1. Disintegration may be manifested in sulfate water by physical disruption by expansion resulting from crystallization of salts in pores, but it is primarily due to chemical action between salts in solution and the constituents of the cement. In the case of dense drain tile of low permeability exposed to sulfate water, disintegration may occur at or just inside the surface skin and progress into the wall of the tile.

2. The use of tile in soils containing alkali salts of the sulfate type in considerable quantities is hazardous, since some specimens of the best quality have been disintegrated during an exposure of less than 6 years.

3. Porous or permeable tile, due to use of lean mixtures or relatively dry consistencies, are subject to disintegration in sulfate waters of relatively low concentrations.

4. In sulfate waters with a concrete or mortar of given quality, the disintegration effect seems to vary with the concentration of the solution.

5. The strength of the tile after being subjected to the action of the sulfate salts is not a true measure of the extent of the attack. Apparently the salts crystallized in the pores give a considerable amount of compressive strength to specimens even when disintegration is very marked.

These conclusions have, in general, been verified by all investigators in this field. However, when investigators used cements from a large number of sources, they found big differences among the performances of some brands. This was particularly demonstrated in the work of Miller and associates discussed below.

University of Minnesota

In the spring of 1919, the attention of the U. S. Department of Agriculture was called to a number of failures of drain tile in the ground in southwestern Minnesota. This resulted in the establishment of a laboratory at the University of Minnesota for the purpose of studying the problems associated with the deterioration of concrete in alkali soils. An extensive investigation was undertaken under the direction of Dalton G. Miller and a number of publications resulted from those studies. Two papers by Miller and Manson (21, 22) contain most of the data and discuss the findings of the laboratory studies. In addition, Miller, Manson and Chen (23) prepared a comprehensive annotated bibliography of the literature published on this subject before 1952.

The stated objectives of the research program were to investigate the causes of failure of agricultural drain tile, the means of obviating such failures and the mapping of areas where extra precautions are necessary. The chemical analyses, made by the U. S. Bureau of Soils, of 1,062 samples of water and 150 samples of soil collected in southwestern Minnesota revealed that, in all cases, the failures were closely associated with the presence in the subsoils, adjacent to the tiles, of sodium and magnesium sulfates. Other laboratory work included the preparation and studying of 75,000 2- by

4-in. concrete and mortar cylinders, 10,140 lean mortar bars of standard Ottawa sand, and 5,000 standard sand briquets. Many of the specimens were stored in tap water and in solutions of sodium and magnesium sulfate in the laboratory. About 25,000 specimens, mostly cylinders, were stored in Medicine Lake, S. D. The water of this lake averaged about 5 percent total sulfates during the exposure period of many years. Both cylinders and mortar bars were used for length change measurements.

The variables studied included the quantity of water in the mix, quantity of cement in the mix, length of time of mixing, long-time water curing, long-time air hardening, curing in water vapor at several temperatures, and the possible effects of integral waterproofing and siliceous admixtures. A total of 122 portland cements from 85 mills were used in these studies. Also a few aluminous, pozzolan, natural and air-entrained cements were studied.

Early in the studies, it was observed that cylinders made with commercial cements from different mills displayed striking differences in sulfate resistance even though there did not appear to be marked differences in the cements as indicated by chemical analyses. In 1934, arrangements were made with NBS to make complete chemical analyses, including FeO, Na_2O, K_2O, Mn_2O_3 and TiO_2 on 100 samples of cement. Later this number was increased to 122. Before this, as will be discussed later, Torvaldson and associates had been studying the behaviors of the individual cement minerals in sulfate solutions and had observed that C_3A was the compound most readily affected by sulfate solutions. Many European investigators had, as pointed out in the introduction, concluded that C_3A was the point of attack by sulfates. Also Hansen, Brownmiller and Bogue (8) had reported in 1928 that a ternary compound of the composition C_4AF was one of the portland cement minerals. Since C, A, S and F usually make up about 98 percent of the clinker, the potential composition of a cement could be calculated in terms of its principal mineral components, i. e., C_3S, C_2S, C_3A and C_4AF, and the behaviors of cements could be related to these components.

When Miller and associates compared the resistance of their cements to sulfate solutions in terms of these calculated compositions, they found that generally the resistance increased as the calculated C_3A decreased. They arranged for 19 mills to modify their cements by raising the F:A ratio from an average of about 0.45 to 0.96. These modified cements were studied in the same manner as the unmodified cements. The number of months for the expansions for these 38 modified and unmodified cements in either sodium or magnesium sulfate solution to reach 0.01 percent correlated very well with the calculated C_3A contents of the cements. For example, the specimen of one unmodified cement with a calculated C_3A content of 11.4 percent attained this expansion in 23 mo, whereas the specimen of the modified cement with a calculated C_3A content of 3.3 percent required 220 mo to attain this amount of expansion.

Specimens of each of the 122 cements were studied for sulfate resistance by determining the compressive strengths of 2- by 4-in. cylinders stored in Medicine Lake and by determining the number of months required for similar cylinders to expand 0.01 percent when stored in 1 percent solutions of Na_2SO_4 and $MgSO_4$(0.071 and 0.084 M) solutions. To obtain an "average strength ratio," the strengths of the cylinders stored in Medicine Lake were divided by the strengths of companion cylinders stored for equal periods of time in tap water in the laboratory. The 122 cements were divided into 12 groups, 10 cements in each of 11 groups and 12 cements in group 12 on the basis of the "average strength ratio" and on the basis of the average number of months required for 0.01 percent expansion in each of the two sulfate solutions. Table 1 gives the range in C_3A contents for each of these groups, the 1- and 5-yr average ratios and the number of months required for 0.01 percent expansion in each of the sulfate solutions. This method of arranging the cements in groups on the basis of the average sulfate resistance divided the cements into groups with rather narrow ranges of C_3A contents.

From these long-time tests, Miller and Manson concluded that there was a definite correlation between sulfate resistance of portland cement and the percentage of C_3A as calculated. With but few exceptions, this relationship held without giving any consideration whatever to variables of manufacturing practices at the different mills. It appears that the extreme upper limit of C_3A permissible for a cement of high sulfate

TABLE 1

DATA ON 2- BY 4-IN. CYLINDERS[a]

Cement Group	C₃A (%) Min. Max.		Avg. Strength Ratio[b]		Mo. for 0.01% Expansion	
	Min.	Max.	1 Yr	5 Yr	1% MgSO₄	1% Na₂SO₄
1	4.4-	5.4	92	82	220	260
2	4.1-	6.7	92	69	160	190
3	5.9-	9.7	90	56	130	150
4	7.4-	9.5	87	45	97	122
5	8.1-10.3		83	29	79	106
6	8.7-	9.7	85	28	68	71
7	9.2-10.9		85	8	58	55
8	9.0-11.6		79	0	46	51
9	9.9-13.5		76	0	36	29
10	10.6-14.1		72	0	29	24
11	11.1-13.4		62	0	29	20
12	11.9-14.2		50	0	18	13

[a] From Miller and Manson.
[b] Compressive strength—Medicine Lake storage/laboratory water storage.

TABLE 2

DATA ON 2- BY 4-IN. CYLINDERS CURED AT 350 F[a]

Days in Water	Hr in Steam	Compressive Strength (psi)			
		Tap Water, 5 Yr	Medicine Lake		
			1 Yr	5 Yr	17-20 Yr
20	-	6,560	4,070	0	0
-	6	5,700	4,130	5,660	6,740
-	12	4,390	3,760	4,730	5,620
-	96	5,850	4,530	5,620	6,750

[a] Cylinders cured initially for 24 hr in moist room.

resistance is 5.5 percent. In general, this will mean a cement with an aluminum oxide content between 4 and 5 percent and an iron-alumina ratio of about 1.0. If the calculated C₃A content is to be truly significant, it must be based either on the direct determination of aluminum oxide or on corrected values which do not include such minor oxides as titanium, phosphorous, and manganese. Unless this is done, the C₃A value, as calculated, will be too high, in many cases by as much as 2 or 3 percent.

Miller and Manson cured some of their specimens in water vapor at temperatures of 100, 155, 212, 260, 315 and 350 F. Curing at 212 F or over produced marked improvement in sulfate resistance of the specimens. This type of curing is now known as high-pressure steam curing or autoclave curing. At the time of their work, Menzel (24) had not published his work which showed marked improvements in the strengths of autoclaved products when some finely divided silica was used to replace a part of the cement. Hence, with modern practices, even better results than those obtained by Miller and Manson might be expected from autoclaved products.

Several cements were used in making cylinders that were cured at these temperatures. Some of the cylinders were stored in tap water and others were stored in Medicine Lake. Curing at temperatures below 212 F showed no significant improvement in the sulfate resistance of the specimens. Curing at 212 F showed some improvement and curing at the other higher temperatures showed marked improvement in the sulfate resistance as measured by the compressive strengths. Cylinders cured at 350 F had strengths after curing for 6, 24 and 96 hr that averaged higher than those cured at 212, 260 and 315 F. Some data for one cement are given in Table 2 which indicates that the normal cured specimens had disintegrated in Medicine Lake before the 5-yr inspection, whereas the high-pressure steam-cured cylinders had greater strengths after 17 to 20 yr in Medicine Lake than did companion specimens cured for 5 yr in tap water in the laboratory. The authors made the following statement regarding this type of steam curing:

> High-temperature steam curing proved to be an extremely effective means of increasing the sulfate resistance of portland cement concrete and mortar specimens. The best results followed curing at 350 for 6 hours or more.

As pointed out earlier, this investigation also included studies with other cements and the use of integral waterproofing and siliceous admixtures. Drain tiles were made with two aluminous cements and exposed in three soils and in Medicine Lake. The tile with one cement had an initial strength of 1,180 lb/lin ft and after 19 to 22 yr in Medicine Lake the strength was 1,370 lb/lin ft. The strengths for specimens of the other cement were 1,540 lb/lin ft initially and 1,750 lb/lin ft after 19 to 22 yr in Medicine Lake. The authors point out that aluminous cement specimens are not always completely stable at temperatures higher than ordinary room temperature, 70 to 100 F. However, they state,

it appears that concrete made with aluminous cements will give
highly satisfactory service in structures well below groundline
almost regardless of the concentration of the sulfates of mag-
nesium and sodium, whereas sections of the same structure
above groundline might show some sign of distress due to vol-
ume increase by summer temperatures.

Few of the 40 admixtures used markedly increased sulfate resistance; many had
little or no effect and others were deleterious. Five of the siliceous materials slightly
increased the resistance of the cylinders of some series. Some other materials showed
slight improvements with some cements. The authors state in summary that "results
with admixtures were largely disappointing. About the only exceptions were certain
oils emulsified as they were added to the batch."

Some commercial asbestos-cement pipe were included in the Minnesota tests (25).
A few sections of normal cured 2- and 3-in. diameter pipe were placed in Medicine
Lake in June 1931 and removed finally in 1946. The 3-in. pipe began to show effects
of sulfate expansion after 3 yr of exposure and the 2-in. pipe after 7 yr of exposure.
After 11 yr, both sets of pipe had failed completely.

In June 1936, 100 sections of 4-in. autoclaved pipe were put under test. Thirty
were stored in Medicine Lake and 30 were stored in tap water in the laboratory. Five
specimens were removed from each type of storage after 1, 4, 10 and 24 yr. The
average crushing strengths for laboratory storage were 7,370, 8,220 and 11,870 lb/ft,
respectively, for 1-, 10- and 24-yr storage. The average strengths for the lake storage
were 8,320, 8,520, 9,880 and 12,940, respectively, for 1-, 4-, 10- and 24-yr storage.

Microscopic and X-ray examinations were conducted on the autoclaved pipe after
24 yr in Medicine Lake. There was a slight tendency for surface swelling, but 95 per-
cent of the pipe appeared to be sound. A coating of solid calcium carbonate, 0.1 to
0.7 mm thick, was noted on the outer and inner surfaces. The hydrated cement paste
in the walls of the pipe appeared normal, and some grains of unhydrated cement were
present.

In summary, it may be said that the extensive work at the University of Minnesota
clearly established that normal cured concrete of low permeability had good resistance
to sulfates when the cement contained not more than about 5.5 percent calculated C_3A.
Concretes with high sulfate resistance can be prepared by curing in high-pressure
steam and composition of the cement, with respect to calculated C_3A, does not appear
to be important in this type of curing.

Canadian Studies

In 1921 the Council of the Engineering Institute of Canada formed the Committee on
the Deterioration of Concrete in Alkali Soils (26) to study the problems associated with
the deterioration of concrete in alkali soils which had become acute in western Canada.
The work of the committee was supported financially (27) by the Research Council of
Canada, the Canada Cement Company, the Canadian Pacific Railroad and the three
Prairie Provinces of Canada. The committee decided that no extensive program of
field exposure tests would be undertaken because other investigations in Canada and
the United States had demonstrated that portland cement concrete of good quality would
be disintegrated when exposed to high concentrations of alkali soils and water consisting
mainly of sodium and magnesium sulfates. However, a limited program was undertaken to

provide a basis for comparison of the durability of plain portland
cement concretes with concretes treated with numerous alkali and
waterproofing compounds on the market, as well as modified or im-
proved cements which might be developed in the chemical laboratory.

The field program consisted of making specimens in the laboratory and exposing
them at sites in Manitoba, Saskatchewan and Alberta. The specimens were 7- by 21-
in. cylinders made from the aggregates available in the areas of the exposure sites
and having two strength levels, 1,200 to 1,500 and 2,500 to 2,800 psi at 28 days. Inte-

gral compounds and surface coatings were used with one brand of cement which was used for all the specimens in the program. Some tests were made with a natural cement, an aluminous cement and a portland classified as "Super Cement."

After the 1927 inspection (28), it was stated:

> The results obtained from the field exposure tests are quite in accord with those obtained in other field investigations, as well as with the objectives which the Committee had in mind when the field work was planned. That the main effort should be centered upon research in the chemical laboratory was the original decision of the Committee, and this has proven sound. Few new data or ideas have been brought by the field, but the chemical research has greatly extended our knowledge of the behaviors of cements when exposed to sulfate solutions.

In a report in 1922, G. M. Williams (26) told of the decision of the committee to have Dr. Thorvaldson direct chemical research in the laboratories of the University of Saskatchewan. This work resulted in a great many papers that have contributed greatly to an understanding of the reactions of the cement minerals with sulfate solutions. One phase of this work was to prepare and study the reactions with water and sulfate solutions of the three compounds which Rankin and Wright (29) had shown to be the principal minerals in portland cement clinkers, i.e., C_3S, C_2S, and C_3A. Later C_4AF, C_2F, C_5A_3, C_3A_5 and CA were included in these studies. The studies with the pure compounds included the following:

1. Microscopical studies of dilute suspensions of each mineral after exposure in water and salt solutions for various periods of time;

2. Extraction studies in which each mineral was extracted repeatedly with a large volume of water for a period of several weeks; and

3. Strength and length changes of lean mortar bars made with pure compounds and blends of the compounds and stored for long periods of time in water and in solutions of salts.

An extensive review of this work is beyond the scope of this paper. Accordingly only results that have a direct bearing on the problem of the deterioration of concretes are discussed. These data are further discussed under the heading of mechanisms of the destructive reactions. Thorvaldson, Vigfusson and Larmour (30) studied mortar bars of the following compositions:

    I. 1 part C_3S + 5 parts sand;
   II. 1 part C_2S + 5 parts sand;
  III. 1 part C_3S + 0.25 parts C_3A + 5 parts sand;
  IV. 1 part C_2S + 0.25 parts C_3A + 5 parts sand; and
   V. 0.53 parts C_3S + 0.26 parts C_2S + 0.21 parts C_3A + 7.5 parts sand.

In 2 and 8 percent solutions of Na_2SO_4, mortars I and II expanded no more than those stored in water. However, in $MgSO_4$ solutions of about the same concentrations, both mortars expanded gradually. The incorporation of C_3A with the silicates, III, IV and V, destroyed the high resistance to sulfate observed for mortars I and II. The increased rate of expansion was more marked for mortars III and V containing C_3S than for mortar IV containing C_2S.

In 1928, bars containing C_4AF and C_2F were introduced into the studies. The results of those studies showed that substitution of either C_4AF or C_2F for C_3A in the mortars markedly increased their resistance to sulfate solutions. This is indicated by the results for 1:10 mortars (30) given in Table 3.

The results of these studies with the pure compounds clearly indicated that portland cements with relatively high resistance to sulfate could be prepared either by decreasing the alumina content of the kiln feed or adding some ferric oxide to it. Either of these changes should decrease the C_3A content of the clinker. As mentioned earlier, Fleming (9), in 1930, made two experimental plant runs in which the composition of the kiln

TABLE 3

EXPANSIONS OF 1:10 MORTAR BARS IN 0.15 M Mg_2SO_4[a]

Cement Composition (%)					Expansion (%)	Exposure (days)
C_3S	C_2S	C_3A	C_2A	C_4AF		
100	-	-	-	-	1.12	200
-	100	-	-	-	1.26	200
50	50	-	-	-	1.05	325
80	-	20	-	-	4.86	26
80	-	-	20	-	1.48	200
80	-	-	-	20	2.04	160
40	40	20	-	-	3.08	11
40	40	-	20	-	1.11	450
40	40	-	-	20	+1.22	200
-	80	20	-	-	3.05	35
80	-	-	-	20	0.85	1,100

[a] Data from Ref. 31.

feed was modified to yield clinkers with increased C_4AF and decreased C_3A contents. The unmodified and the two modified cements were tested in Thorvaldson's (5) laboratory by exposure as 1:5 mortars to various solutions. The calculated C_3A contents of the three cements were 11, 7 and 5 percent, respectively, for cements A, B and C. The expansions in 4 wk in 0.15 M Na_2SO_4 were 1.5+, 0.17 and 0.01, respectively, for cements A, B and C; at 6 mo the expansion for B was 1.10, whereas that for C was only 0.84 percent in 14 yr.

The expansions in 4 wk in 0.15 M $MgSO_4$ were 0.91, 0.60 and 0.17 percent, respectively, for cements A, B, and C. At 12 mo the expansion for B exceeded 1.0 percent and that for cement C was 1.0 percent in 6 mo.

The results of these tests demonstrated the feasibility of improving the sulfate resistance of cements by limiting the calculated C_3A content of the clinker. Fleming (9) reported these results in 1933 and, as stated earlier, Miller and Manson had their 122 cements analyzed in 1934 to permit correlation of the sulfate resistance data with the calculated compound compositions of the cements.

Another phase of the work of Thorvaldson and his associates was a study of the reactions with water of the pure compounds alone and in blends when cured with high-pressure steam. Thorvaldson, Vigfusson and Wolochow (31) studied different temperatures of curing and found that the temperature should be somewhat above 100 C or 212 F. Very good results were obtained at temperatures of 150 and 175 C. A 1:10 mortar bar which was cured for 21 days in the moist closet expanded 1.0 percent in 8.5 days in 0.15 M Na_2SO_4, whereas a similiar bar autoclaved at either 150 or 175 expanded 0.02 percent at 12 mo. A bar cured for 21 days in the moist cabinet expanded 1.0 percent in 11.5 days in 0.15 M $MgSO_4$. Similar bars autoclaved at 150 and 175 expanded 0.24 and 0.14 percent, respectively, in 12 mo.

Thorvaldson, Harris and Wolochow (32) prepared neat cement briquets with distilled water and, after curing for 28 days in the moist closet, powdered them for use in extraction tests with various salt solutions. In one test 20-gm portions were shaken with (a) 1 liter of distilled water and (b) with a solution of sodium sulfate. At first, the water and sulfate solution were replaced every 2 or 3 days with fresh water and solution and then at weekly intervals. The extracts were analyzed for C, A and S. After 32 1-liter extractions, during a period of 1 yr, 72 percent of the C in the cement had been extracted by the water and 84 percent by the sulfate solution. At first, only C was found in the extracts, but later A and S were also present. This shows that the sulfates can react with not only the C present as calcium hydroxide when the specimen is immersed in the sulfate water but also with all of the C in the cement. Also when the C has been reduced to some low level, the NaOH formed by the reaction illustrated in Eq. 2 can dissolve A and S. This is discussed under mechanisms of the reactions.

Portland Cement Association

In a large-scale program (33) begun in 1921 by PCA, about 2,000 concrete cylinders, 10 by 24 in., were made in the laboratory and, after 2 to 3 mo of curing, were shipped to the field and stored in sulfate soils and waters at Montrose, Colo., and Medicine Lake, S. D. Parallel tests were carried out in a laboratory program in which 4- by 8-in. cylinders were stored in water and in salt solutions. The results of these studies

were similiar to those of the studies carried out by NBS and the University of Minnesota and showed serious deterioration of the concrete in short periods of time. It was concluded that an intimate relation existed between the 28-day compressive strength of plastic workable concretes and their ability to withstand sulfate attack; the stronger the concrete, the higher was the resistance to attack.

When the PCA Fellowship was established at NBS in 1924, one of the cooperative programs of the Fellowship's and Bureau's staffs was a comprehensive investigation of the properties of cements as influenced by the composition and heat treatment of the clinkers. Portions of this study were published in various reports, and Bogue (34) published a complete report in 1929 on the portions pertaining to the volume stability of portland cement pastes.

Over 400 cements were used in these investigations; some were commercial cements but most were prepared in laboratory kilns and were ground in laboratory mills to permit close control of composition and heat treatment. The clinkers were prepared in the laboratory as follows:

S_1—burned in a batch kiln for 30 min, then allowed to cool slowly in the kiln;
S_2—reburn of S_1, burned and cooled as S_1;
Q_1—burned in laboratory rotary kiln and cooled quickly in air; and
Q_2—reburn of S_1 in laboratory rotary kiln and cooled quickly in air.

The clinkers were designed to give different ratios of C_3S to C_2S, to have variable free CaO and free MgO contents, to have low and high C_3A contents with low C_4AF contents, and to have low and high C_3A contents with high C_4AF contents. The slow cooling and quenching gave cements of identical compositions with different glass contents. Neat 1- by 1- by 6-in. bars were used for storage in water and 1- by 1- by 6-in. 1:2 sand mortar bars were used for storage in 2 percent solutions of sodium and magnesium sulfates. Some of the specimens were cured in high-pressure steam at 177 C. The principal findings with respect to sulfate were as follows:

1. Changes in the ratio of C_3S to C_2S result in little observable effect on expansion in water or sulfate solutions;

2. Expansions of specimens in 2 percent solutions of sodium and magnesium sulfates increase rapidly with increases in C_3A concentrations;

3. The effect of C_4AF on the sulfate resistance is usually masked by a much greater effect of C_3A but, in controlled experiments of constant C_3A concentration, increases in C_4AF to high values (20 to 27 percent) may result in marked acceleration in the rate of length increase of specimens;

4. Steam treatment of specimens for 6 hr at 177 C may prevent excessive expansion in sulfate solutions;

5. Crystalline C_3A is less resistant to sulfate attack than a glass rich in C_3A, but crystalline C_4AF is more resistant than glass rich in C_4AF; hence, in high A/F clinkers, sulfate resistance is benefited by rapid cooling (high glass), whereas in low A/F clinkers sulfate resistance is benefited by slow cooling (low glass);

6. Glasses of low A/F ratios are more resistant to sulfate action than are those of higher A/F ratios; and

7. Incorporation of precipitated silica in amounts of 5 to 10 percent improved the resistance of specimens stored in sulfate solutions. This was most noticeable with cements of intermediate (about 11 percent) concentrations of C_3A because the low C_3A cements were all resistant regardless of the presence or absence of this admixture.

Long-Time Study

In 1940, PCA began an investigation (35) known as the Long-Time Study of Cement Performance in Concrete. The object of this study was to evaluate, in field structures and with laboratory specimens, the influence of the physical and chemical properties of portland cement clinkers, variations in types of raw materials, and variations in the manufacturing operations on the performance of cements in concrete. Twenty-one clinkers (eight of Type I composition, five of Type II, three of Type III, four of Type IV and one of Type V) were obtained from commercial mills. Six of the clinkers, in addition to being ground as normal cements, were ground with Vinsol resin as air-

TABLE 4

RELATIONSHIP BETWEEN CALCULATED C₃A AND
DATA FROM SEVERAL TESTS[a]

Cement No.[b]	Calc. C₃A (%)[c]		Sugar Values[d]		Warping Test Failed 28 Days	Expansions (%)[e]		
	a	b	P	C		0.15 M Na₂SO₄, 3 Wk	0.15 M MgSO₄, 3 Wk	0.25 M Na₂SO₄, MgSO₄, 1 Wk
(a) Non-Air-Entraining Cement								
23	2.1	3.8	2.6	2.6	No	0.078	0.190	0.510
51	2.2	3.8	7.5	8.4	No	0.069	0.298	0.242
42	2.7	3.4	2.1	2.1	No	0.024	0.074	0.048
41	3.4	4.7	3.4	3.4	No	0.037	0.096	0.124
25	3.8	4.8	2.6	2.6	No	0.027	0.064	0.228
43A	3.9	5.3	23.2	31.7	No	0.054	0.196	0.266
24	4.4	5.4	5.8	6.4	No	0.074	0.182	0.436
43	4.8	6.2	2.9	2.9	No	0.078	0.053	0.039
21	5.1	6.3	8.0	9.2	No	0.056	0.126	0.428
34	5.2	5.6	46.1	60.1	Yes	0.806	0.495	0.798
22	5.4	6.6	2.3	2.3	No	0.116	0.204	0.316
16	6.4	7.4	29.3	41.9	No	0.280	0.416	0.686
14	7.1	8.2	4.2	4.4	No	0.446	0.442	0.698
13	8.9	10.0	43.2	59.8	No	0.240	0.497	0.772
17	9.1	10.4	6.2	6.7	No	0.525	0.642	1.055
33	9.2	10.4	52.4	71.7	Yes	0.585	0.775	1.032
31	9.6	10.7	48.9	68.0	No	0.838	0.532	0.638
15	9.9	12.0	7.1	7.4	No	0.524	0.502	0.676
11	10.9	12.1	30.3	42.8	No	0.398	0.316	0.323
12	11.2	12.6	15.0	23.0	Yes	1.000	0.618	0.314
18	12.2	13.0	25.6	40.5	Yes	0.590	0.783	0.692
(b) Air-Entraining Cements								
21T	5.4	6.6	6.3	7.1	No	0.018	0.022	0.040
16T	6.8	7.9	32.7	46.2	No	0.058	0.043	0.163
33T	9.3	10.4	51.4	71.0	Yes	0.141	0.047	0.018
11T	11.0	12.2	30.1	42.8	No	0.398	0.060	0.132
12T	11.1	12.5	14.7	24.0	Yes	0.301	0.095	0.160
18T	12.2	13.2	31.2	48.3	Yes	0.597	0.228	0.190

[a]Data from Lerch and Ford (36).
[b]First number of each number indicates type of cement.
[c]a = corrected for minor oxides; b = uncorrected for minor oxides.
[d]P = phenolphthalein end point; C = clear point.

entraining cements, giving a total of 27 cements for the performance studies. With respect to sulfate resistance, these were tested in the laboratory for performance in the following tests (36):

1. Sugar solubility test (37),
2. Neat slab test (38), and
3. Expansion of 1:6 mortar bars in 0.15 M Na₂SO₄, in 0.15 M MgSO₄ and in a mixed solution of 0.25 M Na₂SO₄ and 0.25 M MgSO₄.

The results of these tests (36) compared to the calculated C₃A contents of the cements are shown in Table 4. These test data are discussed in more detail later under the subject of test methods. Generally the results of these tests show that per-

formance is a function of the calculated C_3A content of the cement. Miller and Manson (21) pointed out that the values for calculated C_3A content, to be meaningful with respect to sulfate resistance, should be based on values of Al_2O_3 corrected for minor oxides. Both corrected and uncorrected values are given in Table 4.

In addition to these laboratory tests, 6- by 6- by 30-in. concrete beams were exposed in sulfate soils in Sacramento, Calif. (39). The aggregates used in the concrete were siliceous sand and gravel from a deposit close to Sacramento. Three mixes designed to have $1\frac{1}{2}$-in. slump with 4, $5\frac{1}{2}$ and 7 sk/cu yd of cement were used in making the beams; these were designated as mixes 1, 2 and 3, respectively. Two basins were built to hold the specimens and the soil which was a natural alkali soil from Willows, Calif. The soil in basin 1 contained about 10 percent soluble material, mostly Na_2SO_4. Magnesium sulfate and alkali-free soil were added to the Willows' soil to give a soil for basin 2 with about the same salt content as that of basin 1 but in which the ratio of sodium to magnesium sulfate was about 2:1. The specimens were placed in the basins and the soil was added to a depth of about 3 in., leaving about half of the beam specimen exposed above the soil. Tap water was added to a level just above the surfaces of the beams; this was the standard level to which the basins were filled whenever water was added to them. Winter rains caused the basins to overflow; therefore, the water was analyzed each spring and salts were added as required to give approximately the original salt contents. During the summer and fall, water was added to the basins when the soil began to appear dry.

At approximately 1-yr intervals, the beams were examined visually and rated for extent of deterioration. A rating of 1 indicated a perfect beam, 2 indicated slight rounding of the edges and corners, 3, 4 and 5 indicated greater and greater deterioration and 6 indicated complete failure. It was expected that the rate of deterioration would be greater in the mixed sulfate soil, basin 2, than in the primarily sodium sulfate soil of basin 1. However, the reverse was found to be the case. Close examination revealed that the salts deposited on the surfaces of the beams in basin 1 turned into a powdery solid when the surfaces became dry, whereas the salts on the surfaces of the beams in basin 2 assumed a glass-like appearance when the surfaces became dry. It seemed evident that the glass-like deposit was sealing the specimens against evaporation of water from them. A study of the properties of the salts showed that $Na_2SO_4 \cdot 10 H_2O$ was the salt deposited on the beams in basin 1 as the water evaporated. This salt dissociates into Na_2SO_4 and water vapor at the temperatures and humidities of the atmosphere in Sacramento during the summer and fall.

On the other hand, the salt deposited on the beams in basin 2 during evaporation of the water was $Na_2SO_4 \cdot MgSO_4 \cdot 2 H_2O$ which does not dehydrate at those temperatures and humidities. Evaporation of the water deposited this salt as a glass-like deposit which formed a continuous layer over the surface of a beam. This protected the beams from the deterioration to be expected from the exposure to the solution in basin 2. Hence, all conclusions from this phase of the study with respect to the durability of the concretes in sulfate soils have been limited to the data from basin 1.

The specimens of mixes 1 and 2 (4- and $5\frac{1}{2}$-sk concrete) deteriorated rather rapidly and the data do not provide a very sound basis for judging the long-time performance of the cements in higher quality concrete. However, the data substantiate one conclusion of all investigators in this field, i.e., that concrete must be highly impermeable if it is to perform satisfactorily in alkali soils and waters.

The specimens of mix 3 (7-sk concrete) are deteriorating at a relatively slow rate and the data from them are useful in showing the long-time performance. Table 5 compares the values calculated for the C_3A contents of the cements with the ratings of the beams in basin 1, after 18 yr of exposure (39). This table also contains data for the expansions of mortar bars of these cements tested in accordance with ASTM Method C 452, which is discussed later.

As pointed out previously, a rating of 2 indicates slight rounding of edges and corners. Miller and Manson (21) concluded that cements with not more than about 5.5 percent calculated C_3A would give good service in well-made concrete in alkali soils. Table 5 indicates that, with two exceptions, all the normal cements with not more than 5.4

TABLE 5

RELATIONSHIP OF CALCULATED C₃A, 18-YR RATINGS AND
DATA BY ASTM METHOD C 452[a]

Cement No.[b]	Calc. C₃A[c] a	Calc. C₃A[c] b	Rating, 18 Yr[d]	Expansions 1 (%)					
				7 Days	14 Days	21 Days	28 Days	84 Days	365 Days
(a) Non-Air-Entraining Cements									
23	2.1	3.8	1.2	0.020	0.027	0.033	0.038	0.059	0.093
51	2.2	3.8	1.3	0.018	0.025	0.030	0.033	0.049	0.086
42	2.7	3.4	1.4	0.022	0.030	0.035	0.040	0.057	0.089
41	3.4	4.7	1.4	0.025	0.033	0.038	0.042	0.063	0.114
25	3.8	4.8	1.2	0.030	0.040	0.047	0.052	0.075	0.121
43A	3.9	5.3	1.2	0.026	0.037	0.044	0.049	0.071	0.112
24	4.4	5.4	1.3	0.017	0.023	0.027	0.030	0.100	0.081
43	4.8	6.2	2.7	0.038	0.051	0.068	0.068	0.083	0.124
21	5.1	6.3	1.4	0.027	0.038	0.046	0.052	0.083	0.144
34	5.2	5.6	2.7	0.025	0.033	0.038	0.045	0.066	0.167
22	5.4	6.6	1.6	0.036	0.048	0.058	0.066	0.107	0.225
16	6.4	7.4	3.1	0.030	0.044	0.054	0.062	0.103	0.216
14	7.1	8.2	2.2	0.028	0.039	0.048	0.054	0.091	0.166
13	8.9	10.0	2.0	0.027	0.042	0.052	0.060	0.104	0.375
17	9.1	10.4	3.2	0.039	0.048	0.062	0.072	0.137	0.325
33	9.2	10.4	3.1	0.039	0.060	0.076	0.093	0.240	0.253
31	9.6	10.7	3.3	0.039	0.060	0.076	0.092	0.353	0.353
15	9.9	12.0	3.4	0.043	0.066	0.090	0.117	0.177	0.216
11	10.9	12.1	2.1	0.045	0.067	0.085	0.102	0.222	0.645
12	11.2	12.6	3.5	0.058	0.088	0.114	0.135	0.329	0.733
18	12.2	13.0	4.1	0.085	0.135	0.180	0.224	0.741	-
(b) Air-Entraining Cements									
21T	5.4	6.6	1.2	0.035	0.049	0.058	0.065	0.093	0.162
16T	6.8	7.9	1.3	0.033	0.047	0.057	0.065	0.106	0.192
33T	9.3	10.4	2.0	0.051	0.075	0.096	0.116	0.258	0.255
11T	11.0	12.2	1.6	0.055	0.081	0.103	0.123	0.338	0.359
12T	11.1	12.5	3.4	0.070	0.108	0.139	0.166	0.425	1.15
18T	12.2	13.2	3.9	0.093	0.146	0.191	0.235	1.295	-

[a]Data from Lerch (70).
[b]First number indicates type of cement.
[c]a = corrected for minor oxides; b = uncorrected for minor oxides.

percent calculated C₃A contents had ratings well below 2 after 18 yr of exposure. Air entrainment appeared to be beneficial when used with cements of low calculated C₃A.

This phase of the Long-Time Study program was extended in 1949 to include specimens made with eight additional Type II and V cements, and again in 1958 to include specimens made with portland blast-furnace slag cements and with cements containing pozzolan admixtures (40). It is likely to be some years before significant data will be available from these studies.

California Studies

The Metropolitan Water District of Southern California (41) tested available cements for sulfate resistance by immersing the ends of 1:3 standard mortar briquets broken for strength tests in a 1 percent solution of sodium sulfate. Since some specimens were unaffected by this treatment for periods up to 2 to 3 ½ yr, the procedure was changed to the use of 2- by 4-in. mortar cylinders, made with a regraded natural sand,

stored in a 10 percent solution of sodium sulfate at 160 F. It was concluded that the test in the 10 percent solution was a true acceleration of the test in the 1 percent solution because no anomalies appeared when the results of the two tests were compared. The results also substantiated the generally accepted conclusion that, other things being equal, the resistance of a cement is closely related to its calculated C_3A content.

Investigations were being made at the University of California into the possibility of producing a low-heat cement for use in the construction of Boulder Dam (42, 43). The work of Lerch and Bogue (44) had shown that the heat of hydration of C_3A was 207 cal/gm compared to 100 for C_4AF, and that for C_3S was 120 cal/gm compared to 62 for C_2S. Obviously the way to produce a low-heat cement was to limit the C_3A and C_3S contents. A number of laboratory cements were prepared at the University of California to test out the feasibility of producing a low-heat cement by control of the composition. Samples of these cements were supplied to the Metropolitan District laboratory for studies in the sulfate resistance program.

It was decided from the results of this program that up to that time no test studied gave results in a short enough period of time to be used as an acceptance test. However, it was decided that a satisfactory cement could be obtained by specifying the chemical composition and certain physical properties, as follows:

C_3A, not more than 4 percent;
$C_3A + C_4AF$, not more than 12 percent;
C_3S, not more than 50 nor less than 30 percent;
7-day tensile strength, not less than 225 psi; and
Specific surface, Wagner turbidimeter, not less than 2,000 sq cm/gm.

Russian Studies

Budnikov and Grachera (45) studied two cements, I and II, with 5.0 and 10.9 percent calculated C_3A and 16.0 and 10.2 percent calculated C_4AF, respectively. These were studied with three levels of SO_3 contents for rate of reaction with SO_3 and for resistance to sulfates. Three types of calcium sulfate, i.e., anhydrite and alpha and beta hemihydrate, were added in amounts of 3, 5 and 10 percent to the clinkers. The method used to study the rate of combination of SO_3 was to make neat specimens with 50 percent water by weight and store in molds for 24 hr. The specimens were then removed from the molds and stored in the moist cabinet until tested by crushing to a powder and shaking 2 gm of this powder with 200 ml of a saturated solution of calcium

TABLE 6

RATE OF COMBINATION OF SO_3 FROM ANHYDRITE WITH TWO CEMENTS[a]

Added Anhydrite		Total SO_3 in Cement ($\%$)	Uncombined SO_3 in Hydrated Paste ($\%$)				
Percent	As Percent SO_3		6 Hr	1 Day	3 Days	7 Days	28 Days
(a) Clinker I—5.0 $\%$ C_3A							
3.0	1.76	2.05	0.780	0.170	0	—	—
5.0	2.95	3.24	1.390	0.083	—	—	—
10.0	5.88	6.17	3.07	2.22	1.38	1.17	0.308
(b) Clinker II—10.9 $\%$ C_3A							
3.0	1.76	2.18	0.041	0	—	—	—
5.0	2.95	3.37	0.632	0	—	—	—
10.0	5.88	6.30	1.66	1.310	1.545	0.222	0

[a]Data from Budnikov and Gracheva (45).

TABLE 7

FLEXURAL STRENGTHS OF 1- BY 1- BY 3-CM BARS
AFTER STORAGE IN SOLUTIONS[a]

Anhydrite Added (%)	Flexural Strengths (kg/sq cm)							
	Water 28 Days	5 % Na_2SO_4		1 % $MgSO_4$		Sat. $CaSO_4$	
		28 Days	3 Mo	28 Days	3 Mo	28 Days	3 Mo
(a) Clinker I—5.0 % C_3A							
3.0	53.0	42.0	45.0	42.8	39.8	62.6	54.6
5.0	48.0	47.8	47.0	52.0	33.6	55.8	50.0
10.0	28.8	32.4	35.0	34.0	36.4	32.4	30.6
(b) Clinker II—10.9 % C_3A							
3.0	46.2	36.6	0	37.0	5.6	50.2	45.4
5.0	50.6	50.0	12.2	57.0	23.8	54.8	57.0
10.0	30.0	26.8	26.4	40.4	24.0	46.0	37.5

[a]Data from Budnikov and Gracheva (45).

hydroxide for 1 hr. The suspension was filtered and the SO_3 content of the filtrate was determined as a measure of the uncombined SO_3. The rates of combination were nearly alike for the three types of calcium sulfate. The data for the anhydrite are given in Table 6.

The cements were also made into 1- by 1- by 3-cm 1:3 mortar bars which after storage for 28 days in water were tested for sulfate resistance by being stored in 5 percent Na_2SO_4 solution, 1 percent $MgSO_4$ solution, and a saturated solution of calcium sulfate. The flexural strengths of the specimens were tested after 28 days in water and after 28 days and 3 mo in the solutions. Here again, the results for the three types of calcium sulfate were very much alike. The results for the anhydrite are given in Table 7.

The results show that the high C_3A cement had very poor resistance to attack by sodium and magnesium sulfates and that increasing the SO_3 content of the cement increased the resistance slightly. The results indicate that the low C_3A cement was being slowly attacked by the sodium and magnesium sulfates and that the specimens with 3 and 5 percent anhydrite were superior to those with 10 percent. The data indicate that the amount of SO_3 that can combine in 24 hr is about the optimum amount for low C_3A cements for maximum sulfate resistance.

STUDIES WITH POZZOLANS

Before the discovery that a cement with high resistance to attack by sulfates could be produced by controlling the composition of the cement clinker, considerable effort was made to find a pozzolan that could be used with any portland cement to increase the resistance to attack by sulfates. As pointed out in the introduction, Ferrari (5) claimed that his "Ferroportland" cement possessed a high degree of resistance to sulfate waters when used with a pozzolan. Most of the investigators of sulfate resistance included pozzolans in their studies. The results of these studies usually showed that some pozzolans markedly increased the sulfate resistance of cements that showed poor resistance without them but had little, if any, effect with cements that showed relatively high sulfate resistance. In some cases the pozzolan had an adverse effect with all cements. It is beyond the scope of this paper to review the extensive literature on this subject in detail, but it seems desirable to review briefly a few of the more recent investigations.

Tuthill (41) found that diatomaceous silica used either alone or with hydrated lime increased the resistance of certain cements but was ineffective with others. His conclusion was that great care would have to be exercised in the selection of portland-pozzolan cement as a sulfate-resistant cement.

Davis and coworkers (46) used clinkers in which the calculated C_3A varied between 8 and 11 percent and found that diatomaceous silica, waste asbestos rock and pumicite

increased the sulfate resistance of cements made from those clinkers. In another investigation (47), they found that fly ashes from certain sources improved the sulfate resistance of these cements, whereas fly ashes from other sources were either ineffective or decreased the resistance slightly. In still another investigation (48) with these cements with various pozzolans, 1:3 standard sand briquets stored in either 2 or 10 percent solutions of sodium sulfate were badly disintegrated within 1 yr.

Polivka and Brown (49) studied the behaviors of concrete made with two cements, one with a high and the other with a low calculated C_3A content, in which 25 percent of the cementing ingredient was one of the following pozzolans: (a) calcined opaline shale, (b) low carbon fly ash, and (c) pumicite or volcanic ash. The high C_3A cement contained 11.7 and 8.2 percent C_3A and C_4AF, respectively. The low C_3A cement contained 2.8 and 9.5 percent C_3A and C_4AF, respectively.

The specimens were 3- by 6-in. cylinders made with local sand and gravel aggregate in a mix designed to contain 5 sk/cu yd of concrete. The solutions used were a mixed solution of 5 percent each magnesium and sodium sulfate and a 2.1 percent solution of sodium sulfate. Three types of exposure were used: (a) continuous complete immersion, (b) continuous partial immersion, and (c) cyclic wetting and drying. The deterioration was determined by loss in weight, length change, change in compressive strength, visual observations and photographic records.

Loss in weight appeared to be the best criterion of the degree of deterioration and continuous immersion appeared to be the best test condition. The tests indicated that a pozzolan of high quality used as partial replacement of high C_3A cement will produce concrete having greater resistance than plain high C_3A cement. The use of a very low C_3A cement results in concrete having superior resistance to sulfate action, with practically no disintegration under any of these test conditions. A partial replacement of very low C_3A cement with pozzolan produces no improvement in sulfate resistance.

Davis (50) summarized the experience with pozzolans as follows:

> In general where pozzolans are used to replace Type I or Type II cement, the resistance to sulfate water (sodium and magnesium sulfate) is improved, and for cements which are high in C_3A this improvement is large. The finely divided diatomites and other pozzolans high in opal are most effective in preventing disintegration of concrete due to sulfate action. Next in line appear to be some of those high in glass, such as pumicite and fly ash. About 10 to 12 percent of finely ground diatomaceous earth, for example, may be as effective as 25 to 30 percent of pumicite. The use of some of the calcined clays leads to no improvement whatever. Generally speaking the higher the percentage of replacement the greater the resistance to sulfate action.

Wittekindt (4), in a review of the literature on methods used in testing portland cements and portland blast-furnace slag cements for sulfate resistance, points out that there is need for an accurate definition of cement with high sulfate resistance in terms of calculated compound composition. He also points out that in the case of slag and other cements it is necessary to give a "verifiable definition of the interground constituent."

Tashpulstov and Glekel (51) studied calcined clayey rocks and tripoli as admixtures in sulfate resistance tests. They judged the resistance by determining the ratio of the strengths for 6-mo storage in water and in sulfate solutions. They concluded that 40 percent of either of these admixtures with a cement containing 9 percent calculated C_3A produced sulfate-resistant cements regardless of the strength of the sulfate solution.

The experience of all investigators of pozzolans can be summarized with a statement about as follows: the use of certain pozzolans will very likely improve appreciably the sulfate resistance of concrete made with cements of relatively high calculated C_3A contents but is not likely to produce a significant improvement of the sulfate resistance of concrete made with cements of low calculated C_3A contents.

TEST METHODS AND SPECIFICATIONS

Field tests such as those carried out by the University of Minnesota and PCA are expensive and require relatively long periods of time for definitive results. For these reasons many efforts have been made to develop tests which can be performed in the laboratory with relatively small amounts of materials and in relatively short periods of time and can provide results for acceptance and specification purposes. It seems to be generally agreed that a test used for acceptance of materials for construction purposes should yield the desired results within a few weeks. It is not possible to review in this paper the large number of the papers published in this field; however, an attempt is made to review briefly all methods that have been seriously considered as suitable test methods for estimating the sulfate resistance of cements.

Le Chatelier-Anstett Method

According to Blondiau (52), a test method known as the Le Chatelier-Anstett test was developed by Le Chatelier in 1903 to study the resistance of cement products to decomposition in seawater. This was probably the first effort to develop an accelerated test for evaluating the sulfate resistance of cements.

Blondiau reports that Le Chatelier arrived at the general conclusion that the disingegration of cements in seawater—or sulfate waters—was caused primarily by the reactions of calcium sulfate in solution with solid C_3A to form solid calcium sulfoaluminate (ettringite—$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$). That is, in this reaction the C_3A does not dissolve in the water but reacts directly as a solid with the dissolved $CaSO_4$ to yield a solid product; the solid-liquid reactions are discussed by Hansen (16). Apparently Le Chatelier also reasoned that C_3AH_6 could also undergo this solid-liquid reaction because he decided that the most effective test procedure would be to measure expansions of specimens prepared from fully hydrated cement pastes.

In the Le Chatelier method as modified by Anstett, the cement which is ground to pass a sieve having 4,900 openings per sq cm is mixed with 50 percent by weight of distilled water and cast in a sealed container. At age of 24 hr the specimen is removed from the container and stored in distilled water for 14 days. It is then powdered and dried at 40 C. In some cases it may be desirable to repeat the process of hydration and again dry and grind. The dried powder plus an equal amount of gypsum is ground to minus 200 mesh, mixed with 6 percent distilled water, and molded under a pressure of 5 kg/sq cm into a pat 80 mm in diameter and 30 mm high. The specimen is then removed from the mold, placed on a rack covered with filter paper extending down into distilled water, in a container and tightly in closed to prevent free exposure to carbon dioxide of the air. The specimen is measured, in place, daily for change in diameter.

Blondiau reasons that to resist the disintegration action of calcium sulfate, the cement used in a structure where it will be exposed to sulfates should satisfy the condition of not being able to give rise to the formation of ettringite with its accompanying destructive expansion. According to his data, the only cement tested that did not show significant expansions in this test was a sursulfate cement, i.e., a cement consisting principally of blast-furnace slag and anhydrous calcium sulfate. His tests show that a specimen of a Type II cement with 7.33 and 10.55 percent calculated C_3A and C_4AF, respectively, expanded 93 percent in 60 days. A specimen of a Type V cement with 0.5 and 20.2 percent calculated C_3A and C_4AF, respectively, expanded 152 percent in 1 yr and one made with a cement with 0 and 19.6 percent calculated C_3A and C_4AF, respectively, expanded 1.5 percent in 44 days and 78 percent in 90 days.

Blondiau points out that Lerch and Bogue (53) found that C_4AF reacts with water to form hydrated C_3A and an amorphous hydrated calcium ferrite. He argues that it is conceivable that this hydrated C_3A will react without prior solution with calcium sulfate and accordingly produce expansion. According to Jones (54), improved X-ray techniques have shown that C_4AF in cement pastes reacts with water in the presence of calcium hydroxide to form solid solutions of C_4AF (aq) and C_4A (aq). These compounds are unstable and convert to hydrogarnets, i.e., C_3AH_6 and C_3FH_6 and solid solutions of the two. These compounds and their solid solutions take up silica from the calcium silicates. Flint and Wells (55) prepared C_3AH_6 and the hydrogarnets in which F and S

replaced A and tested their stability in a solution of sodium sulfate. They found that C_3AH_6 was readily converted to ettringite, but that the substitution of F and S for A produced crystals that were stable in the solution of sodium sulfate.

Wittekindt (4), in discussing the Le Chatelier-Anstett test, points out that Flint and Wells established that hydrated C_4AF is not attacked by sulfate solutions. He also pointed out that Bogue (34) reported the following expansions of portland cement mortar bars in a 2 percent solution of sodium sulfate for periods of 1, 2, 3 and 4 yr: with 0 percent C_3A, 0.15 percent for all periods; and with 1 to 3 percent C_3A, 0.09, 0.11, 0.25 and 2.73 percent, respectively.

Wittekindt argues that although the Le Chatelier-Anstett test is very severe, it may have real merit. He points out that this test is criticized because some blast-furnace slag cements cannot pass it in spite of their good sulfate resistance. He cites work by Lieber and Bleher (56) in which conventional blast-furnace slag was mixed with portland cement. The mixture with about equal parts of slag and cement showed the greatest expansion in the Le Chatelier-Anstett test. Also, when a cement without C_3A was used, the greatest expansion was obtained with 70 to 80 percent slag. He concludes that these results are of great importance because they show that slag additions will improve the sulfate resistance of normal portland cements but will not improve the resistance of cements without C_3A.

Small Prism Test

Lieber and Bleher (56), from their studies of combinations of slags with portland cements, concluded that the Le Chatelier-Anstett method was not a suitable test for sulfate resistance because it could not be used with all cements. That is, some cements showing good resistance when exposed to sulfate solutions showed expansion in this test. They felt, however, that a "small prism" test developed by Koch and Steinegger (57) was suitable.

In this test, 1- by 1- by 6-cm prisms, made from a mix of 15 gm cement, 15 gm fine standard sand and 30 gm coarser sand (1:1:2) with a water-cement ratio of 0.6 by weight, are suspended by copper wires molded into one end in a 10 percent solution of sodium sulfate. The prisms are cured for 24 hr under wet filter paper and then un-molded and suspended in distilled water. Some are allowed to remain in water until tested for flexural strength. Others at the age of 21 days are suspended in the 10 per-cent solution of sodium sulfate. The absorption of sulfate by the prisms with the simul-taneous formation of sodium hydroxide in the solution is followed by daily titrations of the sulfate solution with 2 N sulfuric acid for a period of 56 days. The sulfate resistance of the cement is defined in terms of the rate and amount of sulfate absorption and on the basis of visual examinations and changes in length and flexural strength of the spec-imens.

Wittekindt (4) critizes this test on the basis of the extreme sensitivity of the small prism which must be prepared with utmost precision for meaningful results in the flexural strength test, as well as on the basis that the sulfate absorption does not yield the desired relation to sulfate attack, does not make possible an objective comparison based on the difference in compositions of the cements used, and does not give indica-tions of durability under practical conditions.

From the standpoint of an accelerated test, the use of a 21-day curing period with a 56-day test period seems to involve an excessive amount of time. Most users would prefer to have results at the end of either 14 or 28 days.

Sugar Solubility Test

Merriman (37) proposed a "sugar solubility test" as a means of detecting under-burned clinker and clinker that had been harmed by exposure to water. This was studied by Merriman (58) and Carlson and Bates (59) as a measure of the sulfate re-sistance of a cement. In this test, 7.5 gm of cement are shaken with 100 ml of a sugar solution (15 gm sugar dissolved in 100 ml of saturated lime water) for 2 hr. The mix-ture is then filtered and a 25-ml aliquot of the filtrate is titrated with 0.5 N HCl, first to the phenophthalein and then to the methyl orange end point. It was assumed that the

first end point was reached when lime alone was neutralized and that the difference between the amounts of acid required for the two titrations represented the amount of acid required to react with iron, alumina and silica in solution. This difference was called the index of disintegration. Merriman (58) studied 32 cements for this index and for the performance of neat slabs (38) in 10 percent solution of sodium sulfate. Generally low C_3A cements behaved best in both tests, but the correlation between this index and C_3A content was not good. The reason for this is discussed later.

Carlson and Bates (59) studied 138 samples of 24 brands of cement for the index of disintegration and for sulfate resistance as measured by the behavior of 1:3 standard sand briquets stored in a 10 percent solution of sodium sulfate. The solution was renewed monthly. They tried to relate calculated C_3A content with this index and with resistance to sulfate. Generally, the cements with high C_3A contents disintegrated first. However, the authors concluded that the results varied so much as to be of little value except as indicating a trend.

Lerch (60) studied the sugar solubility test as influenced by the SO_3 content of the cement. He found that the gypsum in the cement dissolves in the sugar solution and reacts with the C_3A in the cement to give insoluble calcium sulfoaluminate. As long as gypsum is present in the solution, the solution does not contain significant amounts of silicates and aluminates and the titration values are low. When the sulfate is depleted, the solution dissolves calcium aluminates and silicates and the titration values increase. For example, a cement with a calculated C_3A content of 9.8 percent and an SO_3 content of 1.08 percent gave titrations of 31.9 and 48.5, respectively, for the phenolphthalein and clear end points. These values dropped to 10.0 and 11.0, respectively, when the SO_3 content was increased to 3.8 percent.

Since the rate of reaction of sulfate with C_3A in the cement generally increases as the C_3A content of the cement increases, the sugar solubility test might be expected to show increasing titration values as the C_3A content of the cement increases. Accordingly the titration values should be related to some extent to the sulfate resistance of the cement. However, as may be seen from Tables 4 and 5, no good correlation was found between the sugar solubility titrations and either the sulfate resistance or the C_3A contents of the Long-Time Study cements. Perhaps a better correlation would have been found if the cements had all contained the optimum amounts of gypsum as defined by Lerch (61).

Neat Slab Tests

Merriman proposed a neat slab test as a means of determining the qualities of cements. According to Bogue (38), in this test neat 2- by 4- by $\frac{1}{4}$-in. slabs are cured for 1 day in the molds and 2 days in water and then are suspended in a 10 percent solution of sodium sulfate. The sulfate solution is titrated daily with sulfuric acid. Specifications based on this test required that the slabs should be unwarped and free of cracks after immersion for 28 days in the sulfate solution. Table 4 indicates that most of the Long-Time Study cements would have passed such a specification, although there were marked differences in the expansions of mortar bars in sulfate solutions.

Stenzel (62), working with Tuthill, attempted to develop a rapid acceptance test by the use of neat slabs. In this test, 100 gm cement were mixed with 40 cc distilled water and cast as a 2- by 4.5- by 1.25-in. slab. After this had attained final set in the moist cabinet, the top was scraped off, and the slab was removed from the mold and placed in distilled water to age for 7 days. The bottom of the slab was then coated with an impervious material and the specimen was placed in a 10 percent solution of sodium sulfate. Because the attack was from one side, the specimens warped. The warpage was measured at 21 days with a spherometer. The difference between the 21- and 7-day readings was called the index of warping, and a fair correlation was obtained between this index and the calculated C_3A content of the cement.

Concrete Cylinder Tests

Larmour, McMaster and Frei (63) proposed a test based on cylinders. In this test a series of cylinders is stored in water for 14 days, dried for 24 hr at 205 F, cooled,

and immersed in a 5 percent solution of sodium sulfate. At an age of 21 days, two cylinders are tested for compressive strength and the remainder are subjected to drying and reimmersion in the sulfate solution. This cycle is repeated at 7-day intervals until the specimens fail or reach the age of 42 days. As expected, the most rapid failure occurred with cements of high C_3A contents.

The Bureau of Reclamation (64) uses 3- by 6-in. cylinders made with graded aggregate with a top size of $\frac{3}{4}$-in., water-cement ratio of 0.51 by weight, 3-in. slump and an air content of 5 ± 1 percent. The cylinders are cured 14 days in the moist cabinet and 14 days in laboratory air at 50 percent R. H. and 73.4 ± 3 F. They are then immersed in a 2.1 percent solution of sodium sulfate for 28 days, dried for 24 hr in laboratory air and measured for length change. An increase in length of 0.2 percent over the length at time of immersion is considered failure. The laboratory test results are being correlated with results of field tests started in 1945. Eighteen Type I, II and V cements in a total of 96 different concrete mixes are exposed as 6- by 12-in. cylinders, 3- by 3- by $16\frac{1}{4}$-in. bars and 6- by 6- by 48-in. posts in a 4 to 5 percent solution of sodium sulfate in tanks in the field. The cylinders and bars are immersed, and the posts are partially immersed. The plan is to continue the test for 50 yr. At 6 yr, the 7.5 sk concrete made with cements with less than 5 percent calculated C_3A had not expanded 0.05 percent. Neither had the bars of the 6-sk concrete made with cements having less than 4 percent calculated C_3A. Type V concrete with 4.5 sk of cement was equal to 6.5-sk concrete made with Type II cement. This work indicated that cements low in C_3A contents should be used in concrete structures which may be in contact with sulfate-bearing water. If the concentrations are 0.1 to 0.2 percent water-soluble sulfates in the soil or 150 to 1,000 ppm sulfates in the water, Type II cement with a C_3A content of 8 percent or less may be used. If, however, the sulfate content is greater, the use of a type cement, which by definition has a C_3A content of 5 percent or less, is recommended.

Lean Mortar Bar Tests

Miller and Manson (21) first used one-half of each of three briquets used in the standard 7-day tensile test stored in a 5 percent solution of sodium sulfate to distinguish between cements of low and high sulfate resistance. They then changed to measuring length changes of concrete and mortar cylinders stored in solutions of sodium and magnesium sulfates.

Thorvaldson, Larmour and Vigfusson (65) made a study of the use of mortar bars for studying the sulfate resistance of cements. They used 1:7.5, 1:5 and 1:3 cement: standard Ottawa sand mortars and studied the influence of various factors on the results obtained for the expansions. Their conclusion was that a method based on the expansion of a lean mortar in a sulfate solution was suitable for evaluating the relative sulfate resistance of cements.

In 1940, ASTM Committee C-1 organized the Working Committee on Sulfate Resistance of Portland Cement. The first effort of this committee was one in which Miller and Synder (66) studied 12 cements as 1:5 and 1:6 cement:standard Ottawa sand mortars exposed in 0.15, 0.050 and 0.78 M solutions of sodium and magnesium sulfates. They decided that the 1:5 mortar appeared to give the most reliable results. The working committee then undertook a cooperative study in which six laboratories studied this method. There was fair agreement between the results of the six laboratories, but the committee did not recommend the adoption by Committee C-1 of this method as a standard method of test (67).

The committee then carried out two cooperative tests in which 17 laboratories worked with 11 cements in one series and with 13 cements in another. In these series, the expansions of lean mortar bars stored in sodium sulfate were compared with the "sulfate reaction value" as determined by a sulfate susceptibility test (68). In this test a sample of cement equal to 5.4 gm/percent SO_3 in the cement is agitated with 30 gm standard Ottawa sand for 6 hr. The suspension is filtered and the precipitate is washed. The filtrate is analyzed for SO_3 content to determine the amount of SO_3 combined, the sulfate reaction value. The results of these tests were promising and the committee

(69) recommended that the two methods be studied by others to accumulate data for further evaluation of the methods. It was proposed that 0.352 and 0.5 percent solutions of sodium sulfate be used with 1:4 standard Ottawa sand mortar bars. It should be mentioned that the sulfate susceptibility test had the same weakness as the sugar solubility test; i.e., the experimental values depended on the SO_3 content of the cement.

The committee (70) started a new cooperative series of tests in 1953 with a new method. In this method, sufficient powdered gypsum is added to the cement to give an SO_3 content of 7.0 percent. The specimens are 1:2.75 graded Ottawa sand mortar bars which, after curing for 24 hr in a moist cabinet, are removed from the molds, measured for length, immersed in distilled water at 23 ± 1.7 C, and measured periodically for change in length. Thirteen laboratories cooperated in these tests and the agreement between the laboratories was considered good enough to warrant recommending to Committee C-1 the adoption of this method as a standard method of test. This was adopted in 1960 as ASTM Designation: C 452-60T, "Tentative Method of Test for Potential Sulfate Resistance of Portland Cement." Table 8 gives the average, maximum and minimum expansions at 14 days obtained by the 13 laboratories and the calculated C_3A contents for ten cements. Data obtained by this method on 27 cements are given in Table 5.

Specifications

According to Moreell (71), the Technical Committee on Cement, Lime and Plaster of the Federal Executive Committee, under the leadership of P. H. Bates, undertook in the fall of 1935 the preparation and revision of the then current specifications for normal portland cement. The Committee decided on five separate specifications as follows: (a) normal portland cement, (b) high early-strength cement, (c) moderate heat of hardening cement, (d) low-heat cement, and (e) sulfate-resisting cement. Later the Committee found no need for both moderate heat of hardening and low-heat cements, and on Sept. 30, 1936, specifications for four cements were adopted. The chemical requirements for the sulfate-resisting cement were as follows:

Loss on ignition (max.), 3.0 percent;
Al_2O_3 (max.), 4.0 percent;
MgO (max.), 4.0 percent;
SO_3 (max.), 2.0 percent;
Fe_2O_3 (max.), 4.0 percent;
SiO_2 (min.), 24.0 percent;
C_3A (max.), 5.0 percent; and
A/F, 0.7 to 2.0.

TABLE 8

EXPANSION DATA FROM
13 LABORATORIES

Cement No.	C_3A (%)	Expansion at 14 Days (%)		
		Avg.	Min.	Max.
15	9.9	0.066	0.053	0.082
31	9.6	0.060	0.049	0.086
14	7.1	0.039	0.031	0.046
22	5.4	0.046	0.038	0.056
21	5.1	0.038	0.031	0.046
43	4.8	0.051	0.040	0.060
43A	3.9	0.037	0.037	0.043
41	3.4	0.023	0.030	0.037
51	2.2	0.025	0.018	0.029
23	2.1	0.027	0.019	0.033

Moreell made the following statement regarding the specification for the sulfate-resisting cement: "It is evident that the Committee intends this to be a 'de luxe' cement of great durability."

In 1939, a Subcommittee of ASTM Committee C-1, under the chairmanship of C. H. Scholer (72), recommended the adoption of specifications for five types of portland cement. It was recommended that the chemical limitations for Type V-sulfate resistant cement be identical with those of Federal Specification SS-C-211, which were given previously. These specifications were accepted as tentative in 1940 and adopted as standard by ASTM in 1941.

MECHANISM OF DESTRUCTIVE REACTIONS IN ALKALI WATERS

Structure of Hardened Cement Paste

To discuss the reactions in the hardened paste, it will be necessary to define certain expressions that will be used. Powers and Brownyard (73), from their extensive studies of cement pastes, proposed a structure for the paste in terms of cement gel, which consists of colloidal-sized reaction products and gel pores, and capillary pores. Powers, Copeland and Mann (74), from permeability studies, concluded that after a period of time depending on the initial water-cement ratio of the paste, the capillary pores cease to be channels and become isolated holes or pockets. In pastes saturated with water, these pockets are filled with a solution, largely of calcium and alkali hydroxides.

Hansen (18) has pictured gel pores as layers of adsorbed water on the colloidal particles of the reaction products. These adsorbed layers, gel pores, separate the particles from one another and provide a path through which ions and molecules of water and dissolved substances, such as alkali and calcium hydroxide, can diffuse from one capillary pocket to another. Also salts in solutions in which the specimen of concrete is immersed can diffuse through these gel pores into the capillary pores. The thickness of these layers of water and the size of the capillary pockets depend on the water-cement ratio of the original paste.

Verbeck and Gramlich (75) present data that show the effect of water-cement ratio on the permeability of hardened cement pastes. They used osmotic cells which consisted of two chambers fitted with capillary tubes and separated from each other by a membrane consisting of hardened neat cement paste. The cells were filled with a solution of alkali hydroxide containing some solid calcium hydroxide. One cell also contained some particles of opal which, on reacting with the alkali hydroxide, increased the concentration of salts and decreased the concentration of alkali hydroxide in that cell. This caused alkali hydroxide and water to flow into this cell from the other cell through the portland cement membrane. The rate of flow of solution, measured by the capillary tube, was almost zero for a membrane with a water-cement ratio of 0.3 by weight. The rate gradually increased with increasing water-cement ratio of the membrane and became approximately 7×10^{-3} cm/day for a membrane with a water-cement ratio of 0.8.

Diffusion in Hardened Cement Pastes

Spinks, Baldwin and Thorvaldson (76) measured the diffusion coefficients for the sulfate ion in aqueous solutions by use of radioactive sulfur (S-35) as a tracer. They found at 25 C for a 1:3, a 1:2 mortar and a neat cement paste that D_{SO_4} was, respectively, 30×10^{-10}; 12×10^{-10} and 2×10^{-10} sq cm/sec.

In discussing the migration of seawater in concrete, Thorvaldson (5) suggested the following mechanisms:

1. Transportation of seawater by hydrostatic pressure through interconnecting capillaries across walls;

2. Capillary movement of liquid as evaporation occurs above the water level on the opposite side of a wall; and

3. (a) Diffusion of sulfate through the liquid in capillaries, (b) diffusion through the gel formed by the hydration of the cement, and (c) diffusion along interphase boundaries through the crystalline materials present.

If one substitutes gel pores for capillaries in these statements, the statements would agree with the present concept that the capillary pores, in the terminology of Powers and Brownyard, are not continuous channels but that the gel pores provide a continuous path by which diffusion is possible in hardened cement paste. For specimens that are continuously immersed, as was the case for the specimens in most of the investigations discussed earlier in this paper, the movement of water and salt molecules and ions would be by mechanism 3a and possibly to some degree by mecha-

nisms 3b and 3c. When a specimen containing hardened cement paste is cured in saturated water vapor or in water, the capillary pockets are probably filled with a solution consisting principally of calcium and alkali hydroxides. According to the previous picture, these pockets are connected to one another by gel pores and the solution in the pockets must be in equilibrium with the liquid in the gel pores. It seems that one has to postulate that the adsorbed layers of water, gel pores, contain some molecules and ions of the substances dissolved in the capillary pockets.

When such a specimen is immersed (for example, in a solution of sodium sulfate), water molecules either diffuse into or out of the specimen, depending on whether the solution is more or less concentrated than the solution in the capillary pores. If water diffuses into the capillary pores, the specimen should expand; if the flow is reversed, it should contract. Thorvaldson, Wolochow and Vigfusson (31) found that 1:10 mortar bars of C_3S shrunk 0.02 percent in 5 yr in 0.15M sodium sulfate.

For simplicity in these discussions, it will be assumed that only ions of the dissolved salts and water molecules diffuse into and out of the specimens. If the solution in the specimen is less concentrated than the immersion solution, both sodium and sulfate ions should diffuse in at faster rates than ions diffuse out of the specimen. As pointed out earlier, it has often been assumed that this diffusion of sulfate ion into the capillary pores of the paste precipitates gypsum crystals which destroy the specimen through expansion. It seems desirable to examine this assumption in some detail.

System C_3S Mortar-0.15M $MgSO_4$ Solution

Consideration will now be given to what may happen when a C_3S mortar specimen is immersed in a relatively large volume of 0.15M $MgSO_4$ solution. It will be assumed that no reaction occurs in the gel pores but that the reaction of Eq. 1 occurs in a capillary pocket.

For reasons that will be obvious later, it will be assumed that this pocket has a volume of 67 cc. When Mg and SO_4 ions diffuse into this pocket, they cause the solution of $Ca(OH)_2$ from its walls, thereby enlarging it. Information (15) required for the following calculations is given in Table 9.

From the data given in Table 9, it may be seen that the diffusion of one mole of $MgSO_4$ into this pocket would cause 31.6 cc of solid $Ca(OH)_2$ to dissolve and form 74.2 cc of solid $CaSO_4 \cdot 2H_2O$ and 24.5 cc of solid $Mg(OH)_2$. In this reaction, 36 cc of water have been converted into solid $CaSO_4 \cdot 2H_2O$. The original pocket was enlarged from 67 cc to 67 + 31.6 or 98.6 cc. The new solids occupy a volume of 74.2 + 24.5 or 98.7 cc. Since the volumes of these solids equal the volume of the enlarged pocket, it is apparent that 67 - 36 or 31 cc of water had to diffuse from this pocket during this reaction if the walls of the pocket were not to be subjected to hydraulic pressure. There appears to be no reason to believe that water molecules will not leave such a pocket as Mg and SO_4 ions are diffusing into it because the immersion liquid is much more concentrated than the liquid in the pocket. Also, it seems obvious that this reaction will have to stop when there is no longer water in the pocket to receive the Mg and SO_4 ions and to dissolve $Ca(OH)_2$ for reaction with them.

The size of the capillary pocket was given a value of 67 cc so that the volume of the solid reaction products from 1 mole of $MgSO_4$ would equal the final volume of the pocket. If the pocket had been smaller, less than 1 mole $MgSO_4$ would have taken part in the reaction by the time all of the water had either been used up or driven from the pocket. If the pocket had been larger, more than 1 mole of $MgSO_4$ would have been required to fill it with solids by the time the pocket no longer contained free water. That is, the volume of the pocket has no bearing on the final result. Hence, what has been said for large pockets would apply to the very small capillary pockets in hardened cement pastes.

In the case of Na_2SO_4, the suggested reaction follows Eq. 2. If the pocket has a volume of 43.6 cc, 31.6 cc of $Ca(OH)_2$ will react with 36 cc of water and 1 mole of Na_2SO_4 to produce 74.2 cc of solid $CaSO_4 \cdot 2H_2O$ and 80 gm of highly soluble NaOH. The new volume of the pocket will be 43.6 + 31.6 or 74.2 cc and the volume of the new solids will be 74.2 cc. In this reaction, the NaOH as formed would be dissolved in the water and should diffuse with it in the immersion liquid. Here as with $MgSO_4$ there

TABLE 9

Compound	Mol. Wt.	Sp. Gr.	Cc/Mole
Ca(OH)$_2$	74.10	2.34	31.6
MgSO$_4$	120.39	2.66	45.2
CaSO$_4$ 2 H$_2$O	172.18	2.32	74.2
Mg(OH)$_2$	58.34	2.38	24.5
H$_2$O	18.0	1.0	18.0

does not appear to be any possibility of the reaction in the pocket causing expansion of the specimen.

It seems from these calculations that it is impossible for a through-solution reaction as represented by either Eq. 1 or 2 to form solid reaction products, in a capillary pocket, that occupy a greater volume than the volume of the pocket plus the volume of the solid calcium hydroxide that dissolves and takes part in the reaction. This conclusion is based on the seemingly sound assumptions that water and solute ions and molecules can diffuse from the pocket and that the reaction stops when there is no longer free water in the pocket.

Thorvaldson (5) in closing a discussion of theories of sulfate resistance made the following statement:

> Many observations such as these suggest that volume changes in mortars are controlled by osmotic forces concerned with the swelling of gels, that the chemical reactions condition the gel system and destroy cementing substances while the formation of crystalline material is incidental to these chemical reactions, and that the increased resistance to volume changes with increased richness of mix may not be primarily due to decreased permeability but rather to the more prolonged maintenance of conditions within the mortar unfavorable to the swelling of the gels.

In addition to the capillary pockets, some unreacted grains of cement, and some noncolloidal crystals, the gel system consists of gel pores and colloidal products of the reaction of the cement minerals with water. A colloidal product formed in an aqueous solution, because of its surface energy, is surrounded by a shell of adsorbed water. The outside surface of this shell is in equilibrium with what might be classed as the free water of the ambient solution, which in this discussion will be considered a saturated solution of calcium hydroxide. The saturated cement gel is made up of these particles with their shells of adsorbed water and some capillary pockets filled with solution or free water. In keeping with this picture, two particles are separated from each other by their shells of adsorbed water or what might be visualized as a column of adsorbed water which at its center is in equilibrium with the free water of the solution in the capillary pocket. It has been suggested (18) that these columns are the gel pores of Powers and Brownyard (73). The loss or gain of water by this pore or column of water causes the cement gel to undergo changes in volume. It seems reasonable to postulate that this column of water contains calcium and hydroxyl ions just as the water in the capillary pocket does. If this is true, then when a specimen of hardened cement paste is immersed in a solution of magnesium sulfate, magnesium ions and sulfate ions will diffuse into the gel pore and calcium and hydroxyl ions will diffuse from it into the immersion solution. Since the solubility of magnesium hydroxide is much lower than that of calcium hydroxide, magnesium hydroxide should precipitate as a colloidal solid in the gel pore. The water in this pore is in equilibrium with the surface energy of the particles composing the walls of the pore and the addition of new solids to this water disturbs this equilibrium. The equilibrium can be restored by additional water entering the pore from the immersion solution to furnish the newly formed solid particles with their shells of adsorbed water. This entrance of water causes the gel system to expand. This appears to be a mechanism by which the reaction illustrated in Eq. 1 can cause concrete to expand. The pressure causing the swelling is hydraulic pressure just as is osmotic pressure; however, it may not be correct to classify this as osmotic pressure. Contrary to the reasoning of Thorvaldson,

the formation of the new solid is responsible for the swelling, but Thorvaldson is correct in that the formation of the solid products did not produce the swelling because of requiring greater space than was available in the pores of the paste.

It might be argued in opposition to this hypothesis that the calcium hydroxide taking part in this reaction dissolves from the walls of the pore and accordingly the surface is destroyed as a new surface in the form of magnesium hydroxide is being created. However, magnesium hydroxide, because of its low solubility, usually precipitates as a gelatinous mass composed of very small particles. Hence, if the calcium hydroxide is derived from relatively coarse crystals of calcium hydroxide, the new surface created by the formation of magnesium hydroxide might greatly exceed the surface destroyed by the solution of calcium hydroxide.

The solubility of gypsum is only slightly less than that of calcium hydroxide; therefore, any crystals of gypsum formed in the gel pores may not create appreciably more surface than is lost by the solution of calcium hydroxide crystals. Accordingly, precipitation of gypsum in the gel pores may not cause much, if any, swelling of the pore by imbibition of water. This is discussed again later.

System C_2S Mortar-Na_2SO_4 Solution

Thorvaldson (5) found that a 1:5 C_2S mortar expanded less than 0.01 percent when stored in a 2 percent solution of sodium sulfate for 22 yr, whereas when stored in an 8 percent solution this mortar began to expand slowly after 3 yr and reached an expansion of 0.9 percent at the end of 22 yr. It was pointed out earlier that Thorvaldson, Harris and Wolochow (32) found that most of the calcium oxide could be removed from the hardened portland cement paste by leaching with solutions of sodium sulfate. From Eq. 2, it is seen that, as the calcium hydroxide reacts with sulfate to form gypsum, sodium hydroxide is formed. As this reaction proceeds, the solution in the capillary pockets and gel pores tends to become a solution of sodium hydroxide.

As pointed out previously, the formation of gypsum in the gel pores may not add new surface at a greater rate than the surface is destroyed by the solution of calcium hydroxide that takes part in the reactions when specimens of mortar are immersed in sulfate solutions. If this is true, the mechanism outlined for swelling produced by the formation of magnesium hydroxide in gel pores would not be operative when only gypsum is formed in the pore. This could explain the lack of expansion of calcium silicate mortars in solutions of sodium sulfate. However, as the concentration of sodium hydroxide increases because of the reaction of Eq. 2, this hydroxide might slowly attack the quartz crystals of the aggregate and cause an expansion because of an alkali-silica (77) reaction. This reaction might account for the delayed and slow expansion observed in the 8 percent solution of sodium sulfate over the period of 22 yr.

Systems Containing C_3A

As pointed out in the introduction, the formation of ettringite has long been claimed to be the cause of the expansion and destruction of portland cement concrete. Candlot (78), who was the first to prepare a calcium sulfoaluminate, called the compound "cement bacillus" because of the manner in which sulfates destroyed portland cement products. Hansen (16), in a review of the literature on solid-liquid reactions, points out that Le Chatelier appears to have been the first to suggest that C_3A reacts directly as a solid with calcium and sulfate ions and molecules of water to form solid ettringite and that this solid-liquid or topochemical reaction is responsible for the destruction of portland cement products when exposed to sulfates. One can go through calculations similiar to those given for sodium and magnesium sulfates with calcium hydroxide and show that the formation of ettringite by a through-solution reaction will not explain the expansions obtained from portland cements containing C_3A.

Recently Chatterji and Jeffery (79) suggested that the expansive reaction is a solid-state conversion of C_4AH_{13} to the low-sulfate form of calcium sulfoaluminate, $C_3A \cdot CaSO_4 \cdot 12H_2O$. They point out that the crystal structure of C_4AH_{13} is such that a sulfate ion can replace two hydroxyl ions by an ion exchange reaction as illustrated in Eq. 3:

$$C_4AH_{13} + SO_4 \cdot \ + water = C_3A \cdot CaSO_4 \cdot 12\,H_2O + 2(OH^-) \qquad (3)$$
$$\phantom{C_4AH_{13} +} 277.37 313.68$$

The values 277.37 and 312.68, the volumes of the two solid compounds, show that the volume of the solids increases about 14 percent if this reaction occurs. There appears to be no reason why this reaction should not occur as a solid-liquid reaction and cause expansion in concrete. However, there are difficulties in discarding the hypothesis that the formation of ettringite from C_3A and sulfate is a solid-liquid reaction and is responsible for some, if not most, of the expansion in portland cement products caused by reactions of the C_3A.

There appears to be no evidence to show that, while the liquid phase contains sulfate ions in excess of those from the normal dissociation of ettringite, C_3A reacts with water to form C_4AH_{19}, which later converts to C_4AH_{13}. In fact, it appears that the sulfate in ettringite reacts with C_3A to form the low-sulfate form of calcium sulfoaluminate after the gypsum in the cement has been converted to ettringite. Chatterji and Jeffery observed this to take place between 14 days and 3 mo in neat cement pastes with a water-cement ratio of 0.6. These authors postulate that the C_3A first forms C_4AH_{13} and that this then reacts with sulfate furnished by ettringite in accordance with the reaction of Eq. 3.

The data in Table 5 show that a mortar made with a cement containing 9.9 percent calculated C_3A and 7.0 percent SO_3 expanded 0.043 percent in 7 days and 0.066 percent in 14 days of storage in water. The data of Table 6 show that a paste made with a cement containing 10.0 percent calculated C_3A and 5.88 percent SO_3 contained 0.2 percent uncombined SO_3 at the end of 7 days. Data such as these lead to the conclusion that considerable expansion occurs while the liquid phase of a cement paste contains dissolved gypsum and while the C_3A and $CaSO_4$ are reacting to form ettringite. Hence, it appears to be established that the formation of ettringite can cause expansion. When concrete is immersed in solutions of sulfates, the amount of sulfate available is generally far in excess of that required to form ettringite. Also, investigators have identified ettringite in concrete that has deteriorated in sulfate waters.

These discussions have been primarily concerned with explanations of the expansions in concrete caused by reactions with sulfates. It should, of course, be recognized that the reactions of Eqs. 1 and 2 can destroy concrete by converting the cementing constituents into products that, under those conditions of formation, have little, if any, cementing properties.

Studies by Heller and Ben-Yair

Heller and Ben-Yair (80) made a rather extensive study with a Type I and a Type V cement in an effort to add to the information regarding the mechanisms by which sulfates attack hardened cement paste. Neat and mortar bars were exposed to solutions of sodium and magnesium sulfates and to such solutions containing sodium chloride and sodium hydroxide. Four identical bars were immersed in a given solution. Periodically, two bars were measured for length changes and portions of the other bars, at those periods, were studied for phase compositions by X-ray diffraction (XRD) and differential thermal analysis (DTA) methods. These samples were called bulk samples to distinguish them from samples of salt deposits on the surfaces of some of the specimens also studied by these methods. Some of their findings with the bulk samples were as follows:

1. Low-sulfate calcium sulfoaluminate occurred only in small amounts and could not be detected in the presence of magnesium ions;

2. Gypsum in minor amounts was detected in some specimens but there was no indication of an appreciable increase in its concentration on prolonged exposure;

3. In the presence of chloride ions, calcium chloraluminate was invariably found;

4. No magnesium hydroxide or magnesium silicate hydrate were detected in any of the bulk samples but were found in some of the salt deposits;

5. The XRD and DTA data indicated that although strong expansion was usually associated with the presence of considerable amounts of calcium sulfoaluminate, there was no steady increase in the concentration of this compound with time of exposure;

6. Addition of 5 percent sodium hydroxide to 10 percent sodium sulfate solution greatly reduced the expansion, although the XRD data indicated similiar amounts of calcium sulfoaluminate in the specimens.

The results of their study show that expansion is not directly related to the amounts of crystalline sulfoaluminate present. This does not accumulate with time, nor is it transformed into another crystalline phase; it seems probable, therefore, that it changes into a gel which may either constitute a separate phase or form a part of a solid solution series with hydrated calcium silicate, resembling "phase X" described by Kalousek for set portland cement ($\underline{81}$, $\underline{82}$). Initial expansion of cements on sulfate attack may, therefore, be attributed to the formation of calcium sulfoaluminate; subsequent volume change, however, depends also on other factors, e.g., moisture movement in the gel phase. This would explain the irreproducibility of some of the results quoted in the literature. Similiar conclusions have previously been reached by Thorvaldson ($\underline{5}$). The surprising similarity in the concentration of the calcium sulfoaluminate in specimens of Type I and V cements remains to be explained.

The data by Heller and Ben-Yair show that the high-sulfate calcium sulfoaluminate, ettringite, is formed in pastes made from cements of zero calculated C_3A contents. This has been assumed because such cements combine with sulfate at least during the early reaction periods. Hansen ($\underline{83}$) quotes Swayze as claiming that one such cement combined with about 2.5 percent SO_3 during the first 24 hr. Hansen ($\underline{84}$) made the following statement regarding aluminoferrites:

> The aluminoferrites appear to form sulfoaluminates during hydration of the cement because cements that theoretically contain no tricalcium aluminate combine with calcium sulfate in pastes as they set and harden. However, the aluminoferrites do not appear to cause expansion in sulfate solutions. Since these compounds are dibasic compounds, they may not be able to chemisorb calcium sulfate and water for a direct transformation to solid sulfoaluminoferrites

The results by Heller and Ben-Yair with respect to the low-sulfate calcium sulfoaluminate are in agreement with the results of others which show that this compound is not formed in cement pastes until most, if not all, calcium sulfate has been converted to the high-sulfate calcium sulfoaluminate. For example, Green ($\underline{85}$) gives DTA data for a cement paste which show the presence of the high-sulfate compound at 5 min, the absence of gypsum at 24 hr, and the presence of the low-sulfate compound at 7 days. These results by Heller and Ben-Yair do not support the hypothesis of Chatterji and Jeffery that expansion is the result of the conversion of C_4AH_{13} to the low-sulfate compound because they found little, if any, of this compound in highly expanded specimens, whereas they found relatively large amounts of the high-sulfate compound.

It seems that the results of Heller and Ben-Yair support the conclusions that (a) the direct reaction of solid C_3A with calcium sulfate and water to form solid calcium sulfoaluminate causes expansions, and (b) the aluminoferrites do not react as solids with calcium sulfate and water to form solid sulfoaluminoferrites. Their results also indicate that, in the presence of relatively large amounts of sodium hydroxide, C_3A is converted to calcium sulfoaluminate without producing expansion.

It is known that the addition of alkali hydroxides to the mixing water with some cement pastes causes flash set. Also it seems unquestionable that flash set occurs with some cements unless the liquid phase of the paste contains a relatively high concentration of calcium hydroxide. The prevention of flash set by calcium hydroxide has been attributed to the formation of hydrated tetracalcium aluminate on the crystals of C_3A. Hansen ($\underline{83}$) has suggested that, when the calcium hydroxide concentration in the liquid phase is reduced to a low value by the presence of alkali hydroxides, C_3A reacts as follows before reacting with calcium sulfate:

$$C_3A + water = C_2AH_x + CH \qquad (4)$$

The data by Heller and Ben-Yair support the conclusion that C_3A reacts differently with water and calcium sulfate in relatively concentrated solutions of alkali hydroxides than it does in the normal liquid phase of portland cement pastes. It seems that in the highly alkaline solutions, the calcium sulfoaluminate is formed by a through-solution reaction and, accordingly, does not cause expansion.

These authors concluded that the amount of calcium sulfoaluminate does not increase with time of exposure of the specimens and suggest that it changes into "a gel which may constitute a separate phase or form part of a solid solution series with the hydrated calcium silicates resembling 'phase X' described by Kalousek." It seems that the sulfoaluminate might become a part of this phase. However, it seems just as reasonable to assume that the reactions of the aluminates in the hardened paste, when the supply of water is limited, may produce amorphous products that do not respond as the crystalline products do to XRD and DTA methods. That is, instead of concluding that sulfoaluminate changes into a gel, it might be concluded that it formed a gel composed of more or less amorphous particles. Actually it seems that the authors may be offering either of these conclusions when they say "it therefore seems probable that it changes into a gel which may either constitute a separate phase or ...." If only the calcium sulfoaluminate produced while there was a relatively large amount of water available formed crystals responding in a given manner to XRD or DTA methods, it probably should not be surprising that similiar concentrations of this compound are found in pastes of Type I and V cements.

Concrete Partially Immersed in Sulfate Waters

In certain structures the concrete is partially exposed to air and partially immersed in sulfate-bearing water, i. e., either water or water-bearing soil. This concrete often deteriorates by what is classified as progressive scaling. Studies pertaining to the mechanism causing this type of scaling were reviewed recently (18). In this mechanism, as water evaporates from the surface exposed to air, the salt solution in the concrete becomes concentrated near the surface sufficiently to cause crystals to form in the larger capillary pockets. Such a crystal, being in contact with solution in smaller pores in which crystals will not nucleate at that concentration, grows because salt molecules from this solution attach themselves to the base of the crystal. As the crystal grows, it exerts sufficient pressure to spall off a thin layer of paste or mortar that covers the pocket. One conclusion of the early work at NBS (17) was that "concrete if porous enough can be disintegrated by the mechanical forces exerted by crystallization of almost any salt in its pores."

SUMMARY

This review of the literature on studies pertaining to the mechanisms by which portland cement concrete may be caused to expand by the actions of sulfate waters suggests that the following mechanisms may be involved:

1. A solid-liquid reaction by which C_3A is transformed into a high-sulfate calcium sulfoaluminate such as ettringite, $C_3A \cdot 3\,CaSO_4 \cdot 32\,H_2O$;

2. Precipitation of magnesium hydroxide, and possibly gypsum, in gel pores which increases the surface energy of the solids in those pores; and

3. The mechanical pressure created by salt crystals growing in pores close to surface of concrete exposed partially in air and partially in water.

Probably all three actions occur more or less simultaneously in some structures. For example, the beams, referred to earlier, stored in the soil at Sacramento, Calif., were allowed to become dry on the surfaces before being re-covered with water. It seems likely that scaling and rounding of the edges and corners were the result of crystallization of salt and that the expansions and cracking of the specimens were the result of the reaction taking place in accordance with mechanisms of Eqs. 1 and 2.

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