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Foreword

This symposium consists of two review papers, one research report, one case study of field deterioration and four discussions which treat the performance of concrete exposed to aggressive fluids. Portland cement concrete is stable in the vast majority of environments to which it is exposed in highway pavements and structures. There are, however, fluids to which concrete might accidentally or unknowingly be exposed that will chemically attack it and reduce or destroy its ability to perform the intended function.

The paper by Hansen presents a detailed critical review and evaluation of the published work on attack by alkali soils and waters, the major aggressive media in the case of inland pavements and structures. Mather, in like manner, presents the current state of knowledge of the effects of seawater on concrete. These papers, which cover almost 60 years of research, should serve as major reference works for research workers and other engineers concerned with the protection of concrete from aggressive attack under normal circumstances.

Idorn, in discussing Mather's paper, emphasizes the necessarily different approach to specifications for durability as contrasted with those for load-bearing capacity.

The aggressive environments discussed by Hansen and Mather comprise those normally encountered in nature. The paper by Keunning presents a progress report on a broad research study directed toward evaluating the resistance of portland cement mortar to attack by a variety of compounds. Although many of the compounds seem remote to concrete in highways, in today's highly complex society a highway pavement or structure might be exposed to a broad spectrum of materials resulting from industrial effluents, spillage from vehicles, and a variety of other causes.

Lossing presents a systematic study of concrete pavements in service which establishes sulfate attack as a cause of distress. This paper underscores the very practical ramifications of the concepts developed in the earlier papers. Newlon and Sherwood discuss an additional cause of probable sulfate attack and point out some difficulties in clearly establishing that such an attack has occurred.

Erlin and Stark give evidence of the occurrence of the mineral thaumasite in deteriorated field concrete. This represents the first such identification of this mineral and aids in a more complete understanding of the processes of sulfate attack.

The final general discussion by Neilsen indicates that, all other things being equal, the aggressiveness increases from sodium sulfate, to magnesium sulfate, to ferrous sulfate.

Taken together, the papers and discussions from this symposium present a summary and evaluation of the current state of knowledge on resistance of portland cement concrete to aggressive environments.

Sufficiently detailed for research workers and broad in coverage for the interested materials engineer, these papers furnish a reference which should be quite valuable and aid in providing durable concrete for use in highway pavements and structures.

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

W. C. HANSEN, Consulting Chemist, Valparaiso, Indiana

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.

*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:



and



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 $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{Mg(OH)}_2$. 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	C ₃ A (%) Min. Max.	Avg. Strength Ratio ^b		Mo. for 0.01% Expansion	
		1 Yr	5 Yr	1% MgSO ₄	1% Na ₂ SO ₄
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

^aFrom Miller and Manson.

^bCompressive 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

^aCylinders 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 magnesium and sodium, whereas sections of the same structure above groundline might show some sign of distress due to volume 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 percent 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 improved 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 MgSO_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

^aData from Ref. 31.

culated 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 similar 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

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 cal-

were similar 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:

S₁—burned in a batch kiln for 30 min, then allowed to cool slowly in the kiln;

S₂—reburn of S₁, burned and cooled as S₁;

Q₁—burned in laboratory rotary kiln and cooled quickly in air; and

Q₂—reburn of S₁ in laboratory rotary kiln and cooled quickly in air.

The clinkers were designed to give different ratios of C₃S to C₂S, to have variable free CaO and free MgO contents, to have low and high C₃A contents with low C₄AF contents, and to have low and high C₃A contents with high C₄AF 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 C₃S to C₂S 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 C₃A concentrations;

3. The effect of C₄AF on the sulfate resistance is usually masked by a much greater effect of C₃A but, in controlled experiments of constant C₃A concentration, increases in C₄AF 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 C₃A is less resistant to sulfate attack than a glass rich in C₃A, but crystalline C₄AF is more resistant than glass rich in C₄AF; 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 C₃A because the low C₃A 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. C ₃ A (%) ^c		Sugar Values ^d		Warping Test Failed 28 Days	Expansions (%) ^e		
	a	b	P	C		0.15M	0.15M	0.25M
						Na ₂ SO ₄ , 3 Wk	MgSO ₄ , 3 Wk	Na ₂ SO ₄ , MgSO ₄ , 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

^aData from Lerch and Ford (36).

^bFirst number of each number indicates type of cement.

^ca = corrected for minor oxides; b = uncorrected for minor oxides.

^dP = 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 1/2-in. slump with 4, 5 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 $Na_2SO_4 \cdot 10H_2O$ 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 $Na_2SO_4 \cdot MgSO_4 \cdot 2H_2O$ 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 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.	C ₃ A ^c	Rating, 18 Yr ^d	Expansions 1 (%)					
	a	b		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	-

^aData from Lerch (70).

^bFirst number indicates type of cement.

^ca = 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 1/2 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 ₃ A							
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 ₃ A							
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

^aData 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 ₂ SO 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 ₃ A							
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 ₃ A							
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

^aData from Budnikov and Gracheva (45).

hydroxide for 1 hr. The suspension was filtered and the SO₃ content of the filtrate was determined as a measure of the uncombined SO₃. 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 Na₂SO₄ solution, 1 percent MgSO₄ 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 C₃A cement had very poor resistance to attack by sodium and magnesium sulfates and that increasing the SO₃ content of the cement increased the resistance slightly. The results indicate that the low C₃A 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 SO₃ that can combine in 24 hr is about the optimum amount for low C₃A 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 "Ferropoortland" 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 C₃A 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 disintegration 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 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 unmolded 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 percent solution of sodium sulfate. The absorption of sulfate by the prisms with the simultaneous formation of sodium hydroxide in the solution is followed by daily titrations of the sulfate solution with 2N 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 specimens.

Wittekindt (4) criticizes 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 indications 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 underburned 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 resistance 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 mixture is then filtered and a 25-ml aliquot of the filtrate is titrated with 0.5N HCl, first to the phenolphthalein 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 $23 \pm 1.7^\circ\text{C}$, 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 C₃S 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 C₃S Mortar-0.15M MgSO₄ Solution

Consideration will now be given to what may happen when a C₃S mortar specimen is immersed in a relatively large volume of 0.15M MgSO₄ 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 SO₄ 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 MgSO₄ into this pocket would cause 31.6 cc of solid Ca(OH)₂ to dissolve and form 74.2 cc of solid CaSO₄ · 2H₂O and 24.5 cc of solid Mg(OH)₂. In this reaction, 36 cc of water have been converted into solid CaSO₄ · 2H₂O. 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 SO₄ 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 SO₄ 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 MgSO₄ would equal the final volume of the pocket. If the pocket had been smaller, less than 1 mole MgSO₄ 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 MgSO₄ 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 Na₂SO₄, 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 Na₂SO₄ to produce 74.2 cc of solid CaSO₄ · 2H₂O 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 MgSO₄ 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 C₂S Mortar-Na₂SO₄ Solution

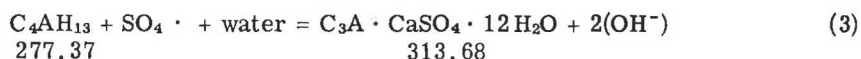
Thorvaldson (5) found that a 1:5 C₂S mortar expanded less than 0.01 percent when stored in a 2 percent solution of sodium sulfate for 22 yr, whereas when stored in an 8 percent solution this mortar began to expand slowly after 3 yr and reached an expansion of 0.9 percent at the end of 22 yr. It was pointed 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 C₃A

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 C₃A 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 similar 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 C₃A.

Recently Chatterji and Jeffery (79) suggested that the expansive reaction is a solid-state conversion of C₄AH₁₃ to the low-sulfate form of calcium sulfoaluminate, C₃A · CaSO₄ · 12H₂O. They point out that the crystal structure of C₄AH₁₃ is such that a sulfate ion can replace two hydroxyl ions by an ion exchange reaction as illustrated in Eq. 3:



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_{10} , 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 similar 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 (81, 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. Similar conclusions have previously been reached by Thorvaldson (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 (83) quotes Swayze as claiming that one such cement combined with about 2.5 percent SO_3 during the first 24 hr. Hansen (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 (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 (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:



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 similar 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, $C_3A \cdot 3CaSO_4 \cdot 32H_2O$;
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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Effects of Seawater on Concrete

BRYANT MATHER, Supervisory Research Civil Engineer, Chief, Engineering Sciences Branch, Concrete Division, U. S. Army Engineer Waterways Experiment Station, Jackson, Mississippi

Concrete exposed to seawater is wetted by a solution of salts—principally sodium chloride and magnesium sulfate. Damage to concrete, if it occurs, usually results from failure to use good practices in concrete construction, and often is the result of freezing and thawing or wetting and drying, as much as or more than the results of the effects of seawater as such. Magnesium sulfate may attack most, if not all, of the constituents of hardened portland cement paste, especially the aluminate constituent; chlorides may promote corrosion of steel; alkalis may participate in alkali-aggregate reaction. Thus, concrete exposed to seawater should be made with cement of controlled aluminate content and with nonreactive aggregate, embedded steel should be well covered by concrete of low permeability, and good construction practices should be followed.

•FOR AS LONG as concrete has been used, it has been employed in construction exposed to the action of seawater. Examples of concrete used by the Romans 2,000 years ago in structures exposed to seawater on the shores of the Mediterranean Sea are still intact. When concrete is to be employed under conditions in which it will be exposed to the effects of seawater, cognizance should be taken of these effects and appropriate precautions taken. Generally, these precautions are not drastic and do not involve the selection and use of unusual materials or procedures nor cause any significant increase in cost of production (12).

The effects of seawater on concrete may conveniently be examined by considering: (a) the factors characteristic of the seawater exposure that can affect concrete; (b) the elements of the specific concrete involved that may be affected by these factors; (c) the consequences of the interaction of seawater with the concrete; and (d) the precautions that should be taken to avoid undesirable performance of the concrete due to its interaction with seawater.

PERTINENT FACTORS IN A SEAWATER EXPOSURE

Concrete exposed to seawater will be subjected to wetting by an aqueous solution containing principally dissolved sodium chloride and magnesium sulfate. The oceans contain, on the average, about 35 parts per thousand (3.5 percent) dissolved salts. The major cations, Ca^{++} , Mg^{++} , Na^+ , and K^+ , exist in seawater largely as uncomplexed species. The major anions include Cl^- , which is also not strongly complexed, and $\text{CO}_3^{=}$, HCO_3^- , and $\text{SO}_4^{=}$, which are. Expressed as milligrams per liter of seawater, the principal elements present in solution are chlorine, 19,000; sodium, 10,600; magnesium, 1,300; sulfur, 900; calcium, 400; and potassium, 380. All other elements are probably present, but no others make up more than 65 mg/l. The six elements mentioned make up 99 percent of the dissolved salts in seawater. Although the concentration of dissolved solids has been found to vary from place to place, the ratio of any one of the major constituents to the total dissolved solids is nearly constant everywhere. The foregoing information, taken from a recent report (2), can be compared with an analysis (Table 1) of a specific sample reported by Forrest and Worthley (4).

TABLE 1
ANALYSIS OF SEAWATER FROM
ST. VINCENT GULF,
SOUTH AUSTRALIA^a

Ion	Concentration (g/100 ml)	Ion	Concentration (g/100 ml)
Na ⁺	1.22	Cl ⁻	2.19
Mg ⁺⁺	0.145	SO ₄ ⁼	0.32
Ca ⁺⁺	0.056	HCO ₃ ⁻	0.014
K ⁺	0.044	Br ⁻	0.008

^aSpecific gravity of seawater (25°C), 1.03.

Thus, the factors inherent in seawater exposure that should be considered for their effects on concrete are wetting and drying and chemical reaction of chlorides, sulfates, alkalies (sodium and potassium), and, in some instances, dissolved carbon dioxide.

The elements of concrete that may be affected by wetting or by chemical reaction with chlorides, sulfates, or alkalies include the cement, the aggregates, and reinforcing steel or other metal, if present.

EFFECTS OF CONTINUOUS IMMERSION OF CONCRETE IN SEAWATER

Concrete that is totally and continuously immersed in water, even if the water contains dissolved salts such as are found in seawater, generally may be regarded as being in a protected exposure. Continuous immersion usually provides a uniformity of environment with respect to temperature and moisture content that prevents the immersed concrete from being subjected to such deteriorating influences as frost action, volume change due to wetting and drying, and differential volume change due to moisture content differences between the surface and the interior. Continuous immersion also tends to reduce the potential for chemical reaction by removing changes in the degree of saturation as a mechanism for the flow into and out of the concrete of solutions containing ions capable of attacking constituents of the concrete, and leaving only concentration gradients as the means of ingress of such ions. Locher and Pisters (11) note that, under equal conditions of exposure, the aggressiveness of water increases with increasing concentration of the relevant substances, but that aggressiveness is also increased by higher temperatures, higher pressures, wetting and drying, or mechanical abrasion by fast-flowing or turbulent waters.

EFFECTS OF INTERMITTENT IMMERSION OF CONCRETE IN SEAWATER

Most concrete structures exposed to seawater are partially or wholly situated so that they are sometimes immersed in seawater and sometimes exposed to the air. If the structure is located where the temperatures fall below freezing, the concrete exposed to the air with falling tide is probably subjected to as severe frost action as is any concrete in natural exposure. The realization that concrete exposed in the tidal zone in a region of low winter temperatures would be subjected to very severe frost action resulted in the selection of the mean-tide elevation at Treat Island, Cobscook Bay, Me., as the location for the U. S. Army Corps of Engineers severe natural weathering station. This location has been used since 1936 by the Corps of Engineers to develop information rapidly on the relative resistance of concretes to frost action (8). Since effects of frost action on concrete are not within the scope of this symposium, this subject is not developed further here.

The second important effect on concrete related to wetting and drying is the volume change relations due to changes in, or changes in uniformity of, moisture content. These phenomena, often referred to as drying shrinkage effects, are also not within the scope of this symposium, and hence are not discussed further here.

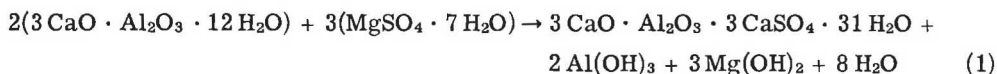
In localities such as Treat Island, the mean temperature of the seawater is low and chemical reactions take place relatively slowly. Concretes relatively deficient in resistance to frost action seldom survive long enough to manifest any readily observable effects of chemical attack; hence, it can be argued that there is a general tendency for the severity of chemical attack to be reduced when that of physical attack increases, and vice versa (8).

CHEMICAL ATTACK OF SEAWATER ON CONCRETE

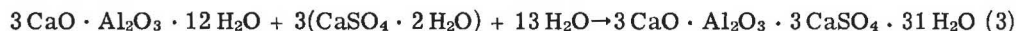
The potentially aggressive constituents of seawater with respect to concrete are the sulfate, chloride, carbonate, bicarbonate, alkali metal, and magnesium ions. The aggressive action of the sulfate ion on concrete is discussed by other contributors to this symposium (22). However, since in seawater the sulfate component is magnesium sulfate rather than sodium or calcium sulfate, as is more often the case in sulfate-attack situations not involving seawater, the various chemical reactions of magnesium sulfate with several of the constituents of hydrated portland cement are noted subsequently. These comments are based on the discussion by F. M. Lea (9) who pointed out that, initially, magnesium sulfate has a similar action to that of other sulfates in attacking calcium aluminate hydrate, but that later it can induce a significantly different and more far-reaching effect because of its ability—as distinguished from other sulfates—to attack and decompose the calcium silicate hydrate. This reaction (Eq. 4) proceeds to completion because of the low solubility of magnesium hydroxide.

Magnesium Sulfate

Magnesium sulfate initially reacts with calcium aluminate hydrate ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 12\text{H}_2\text{O}$) to form calcium aluminum sulfate hydrate (ettringite, $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O}$) magnesium hydroxide, and aluminum hydroxide:



Magnesium sulfate also reacts with calcium hydroxide to form calcium sulfate (gypsum) which, in turn, reacts with calcium aluminate hydrate to form additional calcium aluminum sulfate hydrate (ettringite):

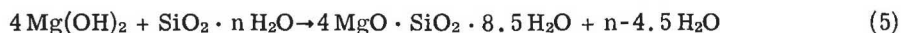


Magnesium sulfate also can react with calcium silicate hydrate ($3\text{CaO} \cdot 2\text{SiO}_2 \cdot n\text{H}_2\text{O}$) to form calcium sulfate, magnesium hydroxide, and silica gel ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$).



The calcium sulfate formed in Eq. 4 may then react with calcium aluminate hydrate according to Eq. 3.

Finally, the magnesium hydroxide formed in the reactions indicated by either Eqs. 1 or 4 can react with silica gel, as produced by the reaction indicated in Eq. 4 or otherwise, to form a magnesium silicate hydrate ($4\text{MgO} \cdot \text{SiO}_2 \cdot 8.5\text{H}_2\text{O}$):



A soft white material having the approximate composition $4\text{MgO} \cdot \text{SiO}_2 \cdot 8.5\text{H}_2\text{O}$ was found by Cole and Hueber (3) in a deteriorated concrete seawall.

Carbonate and Bicarbonate

The carbonate and bicarbonate ions may participate in the reaction of carbonation of calcium ion or calcium hydroxide formed during hydration of cement. In a discussion (16) of deterioration of concrete in the shipways at Newport News, Va., in 1948, Mrs. Terzaghi concluded that two processes were at work, one involving sulfate attack that caused internal expansion and cracking, and the other involving carbon dioxide dissolved in the water as carbonic acid that caused local softening and disintegration. The water samples taken from relief wells in these shipways were regarded as containing from 30 to 60 percent seawater, based on chloride content, and had free CO_2

contents of 7 to 99 mg/l; the highest CO_2 content was found in the sample of lowest seawater content which had 57 mg/l aggressive CO_2 and a pH of 6.9.

Alkalies

The alkali metal ions may participate in any of several reactions with reactive silica or reactive carbonate constituents of the aggregates. Stanton (15) in 1937 listed among structures adversely affected by alkali-silica reaction, sections of seawalls in Ventura and Santa Barbara Counties in California. Recently it was suggested that expansion of concrete in certain dry docks in New York had resulted from the alkali-carbonate reaction. The available data, however, indicated that the aggregates in these structures are natural siliceous sand and gravel. Hence, as far as is known, there have as yet been no documented cases of alkali-carbonate reaction which have caused deterioration of concrete structures exposed to seawater. Kennedy and Mather (8) found that in concrete containing a crushed limestone aggregate that had been exposed to seawater at Treat Island, there was evidence of the formation of reaction rims on certain limestone coarse-aggregate particles. The particular limestone studied contained about 4 percent of a montmorillonitic clay which undergoes greater swelling when wetted with a solution containing sodium ion than when sodium ion is not present. They showed that this material, processed as manufactured fine aggregate, exhibited two to three times as much increase in volume when immersed in seawater as when immersed in fresh water or in a saturated solution of calcium hydroxide.

Chlorides

The chloride ion may participate either in chemical reactions similar to those involving the sulfate ion—so as to yield such products as chloraluminates that are analogous to sulfoaluminates—or in reactions involving the corrosion of reinforcing or other embedded metal. In this latter connection, Halstead and Woodworth (6) reported that reinforced concrete structures exposed under coastal conditions (within 10 mi of the seacoast) in South Africa have, in some cases, shown deterioration believed caused by electrochemical corrosion of the steel. In the discussion of their paper, it was noted that the South African Railway Administration has adopted the policy of using reinforced concrete structures in preference to steel because of difficulties in maintaining steel structures. This agency also has attempted to design structures for a minimum of reinforcing steel. The performance of such structures has generally been good, and such deterioration as has occurred is believed related to insufficient concrete cover over reinforcing steel that permitted corrosion to occur.

The role of chlorides in seawater in chemical interaction with concrete is twofold. Chlorides act independently to do those things that chlorides are capable of doing, and they also tend to retard or inhibit the action of sulfates. The presence of chlorides, as in seawater, retards or inhibits the expansion of concrete by sulfate solutions, but not the degree of reaction. Lea (9) cited the work of Batta, who attributed this effect to the greater solubility of gypsum and calcium aluminum sulfate in chloride solutions, and it is the reason why failure arising from chemical attack by seawater is not preceded by swelling to the same degree as in solutions of sodium or magnesium sulfate.

Griffin and Henry (5) studied, separately, the effects of sodium chloride and seawater salts in concrete. Their purpose was to determine the effect of sea-salt spray on concrete and the permissible amounts of salt in concrete when it is mixed. They found that the optimum salinity of mixing water for maximum compressive strength was from 18 to 36 g/kg when sodium chloride was used and up to 88 g/kg when sea salt was used. They also found that, when sodium chloride was used, the rate of moisture migration through concrete from a region of higher to one of lower relative humidity decreased with increasing salinity of mixing water to a salinity of about 70 g/kg and then remained relatively constant with further increases in salinity. When sea salt was used, the rate of moisture migration also decreased with increase in salinity, but leveled off at about 25 g/kg.

They concluded that some salt may be beneficial to concrete in some respects. With a mixing water salinity of about 25 g/kg, strength was improved, the rate of moisture

movement was reduced, and corrosion of mild steel in the low-strength concrete used in their investigation was negligible. With sodium chloride, the maximum corrosion of mild steel appeared to take place at a salinity of about 70 g/kg. It should perhaps be emphasized that Griffin and Henry were studying the "permissible amounts of salt" that could be tolerated; it is not, I believe, their intent to suggest that one would deliberately add salt to reinforced concrete if it could readily be avoided.

Work done in connection with studies of the action of chloride salts used to remove ice from concrete pavements, insofar as it concerns the effect of chloride ion, may be considered relevant to the action of seawater. Hartmann (7) has noted that the reaction of sodium chloride solutions with tricalcium aluminate or tricalcium aluminate hydrates produces either or both the calcium chloraluminates, $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$ or $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCl}_2 \cdot 18\text{H}_2\text{O}$. However, she concluded that, although chemical effect of chloride de-icing salts on concrete was a possible cause of damage, it did not seem to be a probable cause.

FACTORS AFFECTING RESISTANCE OF CONCRETE TO CHEMICAL ATTACK

Results of experiments in which mortars and concrete specimens have been exposed to seawater are in general agreement that the attack occurs to the extent that hydrated calcium aluminate is available and accessible to the sulfates in the seawater. The more permeable the concrete and the higher the C_3A content of the cement, the sooner will evidence of sulfate attack be manifested and the greater will be the degree of attack.

The use of pozzolans in concrete to be exposed to seawater has long been advocated because of observations that their use increases the resistance of the concrete to chemical attack of the seawater. Lea (9) reviewed the various explanations that have been offered for this effect, and concluded that many or all of them sound reasonable. However, he also concluded that no one by itself provides an adequate explanation, and that all of them taken together fail to give the complete story. The explanations include: (a) reduction in amount of free calcium hydroxide by reaction with pozzolan, thus reducing the degree to which the reaction of sulfates and calcium hydroxide can occur; (b) increased solubility of hydrated calcium aluminates with decreased concentration of calcium hydroxide, and hence greater likelihood that the sulfate-aluminate reaction will take place through solution rather than in the solid state and thus produce less expansion; (c) decreased tendency of the low-sulfate calcium aluminum sulfate to convert to the high-sulfate form (ettringite) as the concentration of calcium hydroxide in solution decreases, due to the higher sulfate concentration required to effect the conversion as such decrease occurs; (d) decreased permeability of the concrete with reduced rate of entry of sulfate solution; (e) formation of lime-pozzolan reaction product films that protect the hydrated calcium aluminate; and (f) decomposition of lime-pozzolan reaction products by seawater to leave silica and alumina gel which are more stable products.

Satisfactory concrete for exposure to seawater will be obtained if reasonable precautions are followed in the selection and use of the materials of which it is composed. The 1963 ACI Standard Building Code (1) requires that concrete to be exposed to freezing while wet have a water-cement ratio not exceeding 6 gal/sk and contain entrained air. It references ACI 613-54 (1) for requirements for seawater exposure, Table 4 of which requires that water-cement ratios not exceed $4\frac{1}{2}$ gal/sk for thin members and 5 gal/sk for thicker members in contact with seawater. The cement should meet the requirements for Type II, specifically in that it should not contain more than 8.0 percent tricalcium aluminate (C_3A) as calculated from the chemical analysis. Reinforced concrete members should be designed and inspected continuously during construction to ensure that no steel is closer than 3 in. from the exposed faces and 4 in. from corners, unless special precautions are taken to prevent corrosion.

Special treatments and materials may, in certain cases, prove advantageous. Wakeman et al. have described (17) the successful use of asphalt impregnation of precast concrete piling to improve resistance to seawater exposure. Li (10) has called attention recently to the potential benefits of expansive cements for concrete construction in marine exposures. Portions of his statement indicate that concretes

made with expansive cement may be controlled to achieve shrinkage compensation, resistance to cracking, reduced permeability, and wear resistance. Such properties may help to render wharf decks crackproof, waterproof and, hence, more wear-resistant. Expansive-cement concrete should further enhance the resistance to seawater of both reinforced and prestressed concrete piles for waterfront applications.

Neville (14) notes that portland blast-furnace slag cement is frequently used in seawater construction because of the fairly high sulfate resistance of concrete made with it. He also notes that concrete made with aluminous cement stands up extremely well in seawater, but points out that seawater should not be used as mixing water when aluminous cements are used.

The performance of portland cement concrete when used in service involving exposure to seawater has often been excellent, usually adequate, but sometimes exceedingly poor. It is believed that, when poor performance has occurred, the cause was poor concrete, the inferior nature of which was perhaps revealed more rapidly by the somewhat more severe exposure than might have been the case in a less severe situation. Mention was made earlier of concrete which has been exposed to Mediterranean Sea water for 2,000 years and is in rather good shape.

EXAMPLES OF PERFORMANCE OF REINFORCED CONCRETE IN MARITIME EXPOSURES

Wentworth-Shields (21) described the first maritime reinforced concrete structure in Great Britain, constructed at Southampton in 1899, and noted that very few failures have occurred. The 1899 structure was a jetty consisting of a 100- by 40-ft deck on piles. In 1902, Town Quay, a reinforced concrete structure 360 by 20 by 34 ft high, was built at Southampton. A few years later longitudinal cracks appeared above the mean-tide level along lines of reinforcement, due to rusting of steel. Repairs were made with pneumatically applied mortar. The rusting of the steel has been ascribed to the permeability of the concrete, but in the case of Town Quay electrolytic action was, if not the sole cause, a very important contributory cause. The 1899 structure, which is still in excellent condition, was made with dry, low water-cement ratio concrete; the 1902 one was made with a "rather wet" mixture.

Not only is the first maritime reinforced concrete structure built in Great Britain still in excellent condition, but most concrete structures in seawater exposures are in good condition when good practice was used and care was taken in their design and construction. For example, the concrete ship "Atlantus," the first constructed by the United States Government, was launched in 1918. It was brought to Cape May, N. J., to serve as a terminal for a ferry line and in 1927 became stranded on a sandbar. It was inspected at various times between 1918 and 1930. A report on its trial run in 1919 from Brunswick, Ga., to Charleston, S. C., states that the concrete was "in a practically perfect state of preservation with no important rust stains visible, although there could be traced in certain places on the hull the faint markings of hairline cracks which paralleled the system of reinforcing closest to the outer surface." Walter in 1929 (18) published a photograph of a specimen of concrete taken from the ship in 1928 showing the imprint of a square bar $\frac{13}{16}$ in. and a round bar $\frac{5}{16}$ in. from the outer exposed surface of the concrete, and stated that the steel was not corroded. After an examination of the ship in 1928, it was reported that a very pronounced rust stain had developed in the bulkhead enclosing the afterquarters, and in one spot the bars parallel to the deck were clearly outlined for a space of 2 or 3 ft each way. A close inspection of this area showed that there was almost no concrete coverage. In some places the intended depth of coverage was $\frac{1}{4}$ in.; in some cases the actual coverage was less than $\frac{1}{16}$ in. A disc of concrete 3 in. in diameter and 0.7 in. thick was cut from a fragment collected in 1928, tested in the laboratory, and found to have very low water permeability (13).

Similar inspection reports have been recorded on other concrete ships built during World War I. The "Selma," now stranded near Galveston, Texas, was inspected and reported on by Rogers at the 1953 Regional Meeting of the American Concrete Institute. The "Selma" was a tanker built in Mobile in 1918 and sunk at Galveston in about 1923.

Samples of the concrete tested in 1953 showed a compressive strength of about 10,000 psi. No corrosion of steel was observed, even though less than 1 in. of cover was provided. Another of these vessels, the "Palo Alto," is exposed on the Pacific coast at Seacliff Beach State Park, 6 mi south of Santa Cruz, Calif., where it is used as a fishing pier. It was built as a tanker during World War I and is 435 ft long. It remained anchored in the Oakland Estuary, where it was built, until 1930 when the Cal-Nevada Stock Company purchased it and had it towed to Seacliff on Monterey Bay, about 100 mi to the south. The sea cocks were opened and it now rests on a sandstone shelf. It was later acquired by California when the state park was created. The ship has broken its back, but a gangway across the fracture permits both parts to be used. It is probably the most accessible of the remaining World War I concrete ships (20).

CONCLUDING STATEMENT

The conclusions of the 18th Congress of the Permanent International Association of Navigation Congresses* as summarized by Warren (19) are quoted as a closing statement:

It was agreed that the deterioration of concrete in warm sea-water is mainly due to chemical action, namely, the change in composition of the cement caused by the chlorides and sulphates present in the water. Little can be done to protect poor concrete, the remedy being to select a suitable type of cement and good sound aggregates in the first place, and to take steps to ensure that the finished product is as dense and impermeable as possible. In colder water, chemical action is less severe and the main damage is done by temperature changes. There are other causes of deterioration, such as abrasion and acids deposited by lithofagous organisms.

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*Much useful data on performance of structures exposed to seawater are contained in the publications of the Permanent International Association of Navigation Congresses (General Secretary, 155 Rue de la Loi, Brussels, Belgium) (23).

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Discussion

G. M. IDORN, Concrete Research Laboratory, Karlstrup, Karlslunde, Denmark—For about the last 250 years it has been possible to calculate structures, with due regard to their safety, by the development of static methods. The absolute basis for this was Newton's Principia, published in 1687, which brought about acknowledgment of universal gravitation, the fact that the force of gravity is constant. The immeasurable value of this acknowledgment to static and other calculations is possibly one reason why civil engineers so often tend to tabulate, and reckon on, and introduce constant values or ratios, even when a design problem calls for consideration of chemical or physical processes. Another reason for this tendency to tabulate is perhaps that many structural engineers are not educated to apply chemistry and physics.

However, unlike the situation with respect to static calculations, it is gradients and accumulations that characterize the conditions under which chemical and physical forces can have a deleterious effect on concrete. One is tempted to recall the words of Leonardo da Vinci: "To understand motion is to understand the universe." For example, it is sometimes considered probable that the climate on the coast of Denmark is more severe for concrete than the climate inland. However, in the moor regions or post-glacial sands of Jutland, for instance, the climate has a definite continental character, with 100 to 200 days of frost per year against only 70 to 80 on the west coast of Jutland. Similarly, frost starts about 1 month earlier and ends about 1 month later than on the west coast. The rate of freezing must vary correspondingly inland, and this factor is decisive in controlling the degree to which deleterious hydraulic pressures develop during the formation of ice in the capillary system of hardened con-

crete. In seawater and near the coast, the temperature variations generally are relatively slight. Even in the case of shallow water there is hardly any place in the world with a greater variation per 24 hr than 5 C, and the annual variation in Denmark is at any rate between -1 C and +20 C (and considerably less in both polar and tropical zones). The relative humidity of the air also generally varies less at the coast than inland. However, topographical, geological, and industrial conditions, for example, may cause considerable variations from place to place, frequently of such a magnitude as to render a broad geographical classification quite illusory. Discussion of these matters is in any case difficult because no comprehensive compilation and treatment of observations seem to exist.

A further illustration of the mistake in tabulating chemical conditions in standard specifications is the requirement that when groundwater contains more than 300 mg/l sulfate, precautions must be taken against sulfate reactions, for instance by the use of special cements for concrete exposed to the action of groundwater.

This requirement or a similar one is known from a number of countries and is considered useful in regions of completely uniform and constant geochemical conditions. Considering Denmark, however, it must not be forgotten that the aggressive action of sulfates on concrete is dependent on many other conditions than the concentration determined by chemical analysis of samples of water. It depends, for instance, on the cations with which the sulfates are able to combine, on the possibility of oxidation or reduction in the milieu in question, on the presence of suitable conditions for the accumulation of sulfates whereby the concentrations might locally or temporarily increase, and on whether the surroundings are such that a future increase in sulfate production must be expected. Industrial and urban development is thus frequently a source of considerable increase in the sulfate content of the soil and groundwater. Dewatering of bogs or marshes is another important source of sulfates.

The physical and chemical conditions touched on here can be denoted a part of the "milieu description" of a concrete structure or building area. The provision of data for such descriptions, their interpretation and an evaluation of their effect on the characteristics of concrete, especially its durability, will in future years become an important, although at the same time a difficult, field of research.

The statistical nature of the phenomenon of deterioration is also insufficiently recognized, and methods have not, therefore, been developed for quantitative treatment of the problems of durability touched on here for guidance in practice. For example, up to the present time, the main stress has been laid on describing and analyzing "average" results from laboratory tests, whereas stress should, in reality, be laid on the extremes encountered in practice. Therefore, correlations can rarely be established between test data and practical precautions. The data most often collected cannot be used for this purpose and they are, moreover, from a statistical point of view, encumbered with much greater uncertainty than usually dealt with in concrete technology. These remarks tend to support the opinion that attempts should not be made to govern the durability of concrete by standard specifications. Moreover, as experience has shown that the deterioration of concrete is not a problem of safety but a question of choice between initial and maintenance expenditure, the choice must juridically remain a private matter, and socially lead to the most economical practice by distributing the responsibility rather than centralizing it.

Many of those responsible for the practical production of concrete will perhaps be shaken by the consequences of these comments. Is one not being deprived of vital, unambiguous rules of law that one has been accustomed to having or assumed to have in previous standards? Will it not be necessary, for each individual project, to carry out a much more thorough analysis of the problems of concrete technology (as is traditionally done with the problems of stress calculation and design) before stipulating special conditions? Does not the average engineer lack the necessary technological insight?

The answer to the first question is a clear NO. Standard specifications have never been the only juridical basis in contracts. Both ordinary and special conditions are also included. The latter may refer to any supplementary requirement and instructions on which the contractual parties may agree.

The answer to the next question is also NO provided we invest not only in research but also in the preparation of the results of such research for the purposes of practical guidance. This is probably the point where there have not been sufficient advances in recent years, especially in certain fields in which an overwhelming quantity of research results are being produced. In this work there is still a need both for the more theoretical instructions, which also give assumptions for and explanations of the recommended methods and modes of execution, and for the highly condensed tabular form, which gives short and unambiguous instructions on methods. The former category of recommendations and directions provides a valuable contribution to the practical training of engineers, and the latter has proved a powerful instrument in forced production.

The answer to the third question is undoubtedly YES. There is a very great need for new concepts, especially in the training of engineers.

There is thus quite definitely a very great social task to be undertaken in the critical preparation of the results of research for instruction purposes and in the continued revision of technological training with special reference to the advances made in research and the main trends of the coming development in concrete construction practice.

BRYANT MATHER, Closure—Mr. Idorn's discussion of the necessarily different approach to durability as contrasted with that that is taken with respect to load-bearing capacity in specifications for concrete structures is very welcome and a very important addition to the remarks contained in my paper. Mr. Idorn speaks of the choice between initial and maintenance expenditures as an important concept employed in dealing with the problems of durability in specifications for concrete work. In many instances, the degree to which precautions are properly required to be taken in the selection of materials, dimensions, and construction practices will depend on the degree to which the owner desires to provide himself with assurance of freedom from deterioration and the degree to which he is willing to pay for such assurance. If the structure is to be a monument where aesthetic considerations are of great importance and cost need not be kept to a minimum, it may well be that the use of precautions is justified, even though the eventualities that they are intended to preclude are extremely remote. In other cases, where initial cost is the dominant consideration and anticipated service need is relatively shorter in duration, precautions may be not taken, even though the phenomena whose effects might be mitigated by the taking thereof are quite likely to manifest their effects. In any case, the desirability of greater understanding of these considerations by all concerned is a goal that should be sought far more diligently than it often is at present.

Resistance of Portland Cement Mortar to Chemical Attack—A Progress Report

WILLIAM H. KUENNING, Principal Engineer, Technical Information Department, Research and Development Laboratories, Portland Cement Association

An extensive study to furnish information about the resistance of concrete to chemical attack by various inorganic and organic compounds has been undertaken using 1.5- by 1.5- by 10-cm mortar bars. Changes in length, weight and sonic modulus are measured periodically. The study is designed to determine relative resistance to chemical attack of various special type mortars ("microconcretes") at water-cement ratios representative of full-scale concretes. It also furnishes information which may help explain the mechanisms of attack by specific agents.

About 1,200 specimens have been placed under test; many have been exposed for more than 2 years. Most are still in satisfactory condition. Those failures which have occurred represent one of two main kinds of attack, or sometimes both. The first is removal of soluble compounds from cement by acid, sequestering agent, or exchangeable ion. The second is the deposition of new compounds within the paste. Rates of attack are compared and the nature of the attack by various groups of substances is discussed.

•MOST PORTLAND cement concrete is sufficiently resistant to its chemical environment not to suffer deterioration. Even when subjected to aggressive chemical exposure, much concrete is of sufficiently high quality to withstand some kinds of attack for substantial periods of time. The length of time that a particular quality of concrete can resist a specific chemical environment is sometimes of primary concern to the architect-engineer and to the maintenance man.

Several sources of information offer valuable guidance. Lea (1) devotes 83 pages to the discussion of resistance of concrete to organic and inorganic chemicals, natural waters, and sulfate soils. He relates performance of concrete to its physical and chemical properties. Kleinlogel (2) offers considerable information organized alphabetically for easy reference, drawing primarily on field experience. Biczok (3) gives perhaps the most extensive treatment of the relationship of attack to the properties of the concrete, citing the results of both laboratory investigations and field experience. Rabald (4) tabulates the resistance of concrete to a broad range of agents, giving resistance in four categories ranging from "practically resistant" to "unusable." Nelson (5) gives data for resistance of concrete to a similarly large group of agents. He classifies attack in terms of four categories of "corrosion rate," each representing a range of dimensional change, based on reports of many investigators. Since most of his materials are metals and other relatively nonporous materials, this change undoubtedly represents pitting or dissolving of the surface. For concrete and other relatively porous materials, however, it sometimes indicates expansion. Data for more than one concentration or for temperatures above 75 F are occasionally provided. Kleinlogel (2) gives only a limited number of references, although the original German edition gives many. Both Rabald (4) and Nelson (5) give bibliographic references but do not indicate specifically the sources of the individual values published. All of these

compilations offer extensive information in convenient form, and Lea, Kleinlogel and Biczok give helpful interpretive comment.

More detailed information can be obtained from primary sources giving detailed descriptions of field observations or laboratory tests on more limited subjects. Such reports have discussed measurements and results of attack by acids (6-14), by inorganic chemicals (6, 7, 9), by organic chemicals (8, 13-16), by sulfates, sulfate soils and sulfate waters (6, 7, 9, 17, 18, 19), by seawater (20-22), by river and groundwaters (20, 23-25), and by atmospheric gases (26-28).

When these and similar references have been searched, there may be unanswered questions. These questions may pertain to the severity with which a material attacks concrete or the existence of a limiting concentration below which, or even above which, attack will not occur. (Such information may be available for some materials; for example Locher and Pisters (25) have reported on the problem of safe concentrations.) There may be questions whether there is a type of cement which will not be attacked or if there is a water-cement ratio which will sufficiently reduce permeability and increase strength to make a concrete adequately resistant to a given agent. The effect of curing time may be of interest. There may be a need to select a less deleterious compound that can be substituted for the aggressive agent.

For a given chemical agent, some of these questions may be adequately answered, but this is likely to be the exception. Comparison of the rate or extent of chemical attack as a function of the identity of the chemical, the quality of the concrete, the type of cement, or some other variable may be adequate within a single published investigation. However, such comparisons are difficult among separate investigations because of the effects of different sizes of specimens, different proportions of concrete or mortar, different exposures, and different methods of evaluation.

CONCEPT AND PLAN

Nature of Present Study

There is, therefore, a need for a comprehensive study. Such a study should show not only the resistance of concrete to inorganic chemicals, organic chemicals and complex materials, but also broader comparisons of the effects of solution concentrations, cement type, water-cement ratio and cure time. The study could also help to form a new basis of comparison of the many existing reports at present only vaguely related to one another.

To fulfill this need for a comprehensive investigation, a long-time study of the resistance to chemical attack of portland cement mortar (proportioned as microconcrete) was undertaken. Chemicals, most of them inorganic, are added to the program as time and space allow. The program is intended to be open-end and to continue for an indefinite time. Some specimens have been under test for more than 2 years, with no definite termination yet scheduled, and some may be left under test for 5, 10 or more years.

The test method permits exposure of the same kind of specimen to all kinds of aggressive agents, regardless of the kind of attack anticipated. To provide adequate information, the study requires measurement of more than one physical property on the same specimen. If the reaction mechanism is not known, the variety of diagnostic evidence obtained from the several kinds of measurement is more likely to help explain the mechanism than the evidence from a single kind of measurement.

In addition, the test method is considered to be applicable to (a) conditions of high or low temperature, (b) cycling between wet and dry exposures, (c) cycling between two temperatures, or (d) exposure to gaseous agents. It may also be as readily adaptable to evaluation of protective coatings or other protective treatments as to a study of the substrate. (A limited number of tests at temperatures up to 200 F are reported here. Other tests not reported are in progress to evaluate the effect of surface treatment by silicon tetrafluoride gas to improve resistance to chemical attack.)

Substances to Be Studied

The study of resistance of portland cement concrete to chemical attack is potentially

the study of its resistance to attack by all other forms of matter, yet the existing knowledge of the properties of these forms permits elimination of large groups which are not aggressive. It would be impossible to study all of those remaining substances of possibly deleterious nature which might at some time come into contact with concrete. A judicious choice must be made so that the number of substances studied is small enough to fall within the scope of one investigation, but large enough to represent many broad classes of aggressive agents.

Accordingly, many of the substances in this study were chosen to be representative of a class of chemicals, one or more of which might be expected to come into contact with concrete; for example, sodium chromate was chosen to represent all chromate salts. Other compounds were chosen simply because they are known to come into frequent contact with concrete, even though they may belong to a class of compounds already represented. Some anions, such as chlorides, nitrates and sulfates, are represented in the salts of several metals. Most of the inorganic compounds were salts, but acids were also included and alkalis will be included later. When the intent was to determine the effect of the anion, the sodium salt was usually, but not always, the most convenient or appropriate salt for investigation. Substances known to be deleterious to concrete have been included whether they are complex materials or have simple and known chemical identities. Such complex materials as molasses, urine, blood, paper mill waste, and other naturally occurring, refined, or waste products will eventually be included. Two such materials already under test are linseed oil and seawater.

Specimen Size

Small mortar specimens were used to economize on storage space (Fig. 1), minimize the cost of chemicals (frequently replaced), simplify handling and measuring, and reduce the time required to attain significant effects. Prisms, 1.5- by 1.5- by 10-cm, which contain no reference points, similar to those used to determine sulfate resistance in Canadian Standard A5-1961 (29), were used. Measurements were made

of changes in length, weight, or Young's modulus of elasticity, all useful in quantitative evaluation of specimen exposure to the test solutions (6, 7, 8, 27, 28, 30).

TABLE I
CHARACTERISTICS OF CEMENTS USED

Composition	ASTM Type I	ASTM Type V	0-C ₃ A
SiO ₂ , %	20.9	24.4	20.9
Al ₂ O ₃ , %	5.7	3.1	2.8
Fe ₂ O ₃ , %	3.0	3.3	4.5
CaO, %	63.8	63.8	66.1
MgO, %	2.4	1.6	2.0
SO ₃ , %	2.6	1.4	3.0
Na ₂ O, %	0.25	0.08	0.08
K ₂ O, %	0.46	0.22	0.16
Loss on ignition, %	0.67	0.8	0.68
Insol. residue, %	0.09	0.09	0.03
Free CaO	0.18	0.5	0.85
Mn ₂ O ₃	0.28	0.09	0.12
Sp. gr. (kerosene)	3.20	3.210	3.179
Passing No. 325 sieve, %	91.04	98.0	-
Fineness, sq cm/gm ²	3,070	3,483	4,620
Compound composition:			
C ₂ S, %:			
Potential, calc.	51	41 ^b	76
Quantitative ^c	51.0	45.5	67.9
C ₃ S, %:			
Potential, calc.	21	39 ^b	2
Quantitative ^c	24.9	39.6	13.4
C ₃ A, %:			
Potential, calc.	9.9	3.7 ^b	0.0
Quantitative ^c	5.7	0.2	0.0
C ₄ AF, %:			
Potential, calc.	9.2	10.0 ^b	-
Quantitative ^c	10.3	9.0	10.0
Pot. ss C ₄ AF + C ₂ F, Calc., %	-	-	13.5

^aAir permeability.

^bLTS-51, composition as reported by Lerch and Ford (34).

^cCalculated from x-ray diffraction data as described by Kantroet al. (35).

^dSolid solution of calcium aluminoferrite and calcium ferrite.

Qualities of Concrete to Be Studied by Means of Mortar

The choice of specimen size required the use of mortar instead of concrete. While the rate of attack on small specimens is high, because of their high surface-to-volume ratio, mortar specimens are nevertheless acceptable alternatives to concrete if they can be successfully made as microconcrete at water-cement ratios representative of full-scale concrete. Two water-cement ratios were chosen, 0.60 to represent paste in acceptable concrete of ordinary quality, and 0.40 to represent the paste in a high-quality concrete.

Since the primary concern was the resistance of the hydrated paste to chemical attack, silica sand, an aggregate immune to attack by most agents, was selected. The sand had the following

grading: passing No. 20 sieve, 97 to 100 percent; passing No. 30 sieve, 78 to 81 percent; passing No. 50 sieve, 34 to 40 percent; passing No. 100 sieve, 20 to 22 percent; and passing No. 200 sieve, 4 to 5 percent.

Three portland cements were used. The first was a Type I portland cement, the only one used at both water-cement ratios. Mortars of Type V portland cement were included in the study because of their low tricalcium aluminate (C_3A) content. Portland cements of low C_3A content are commonly used to reduce or prevent attack by some chemicals, notably sulfates, which react with C_3A . A portland cement containing no C_3A was also used. Mortars made with Type V and zero- C_3A cements were prepared at a water-cement ratio of 0.40. The chemical compositions of the three cements are given in Table 1, including both the potential compound compositions and the quantitative X-ray diffraction compositions.*

Specimens of each kind of mortar were cured for either 3 or 28 days before they were exposed to chemical attack. Mortar compositions and curing times of the eight different qualities of mortar tested are given in Table 2. For agents which attack C_3A in hydrated cement, the resistance of these mortars was expected to increase progressively from top to bottom of the table. Within each of the four major classifications, the mortars cured 28 days were expected to have better resistance than those cured 3 days.

Solution Concentrations

The more concentrated solutions can usually be expected to be more aggressive than dilute solutions. It was desirable to design the tests to be representative of the possible range of concentration for any given chemical. This range varies widely from one chemical to another. The solubility of sodium fluoride, for example, is

TABLE 2
COMPOSITION AND QUALITY OF MORTARS USED

Cement Type	C_3A (%)	W/C (by wt)	Cement/Agg. (by wt)	Moist Cure, 73 F (days)	Typical Dynamic Mod. ^a (psi × 10 ⁶)	Avg. Unit Wt. at End of Cure, (lb per sq ft)
I	9.9	0.60	0.25	3	1.6 × 10 ⁶	140
	9.9	0.60	0.25	28	2.1	140
	9.9	0.40	0.40	3	2.2	144
	9.9	0.40	0.40	28	2.5	146
V	3.7	0.40	0.40	3	1.9	144
	3.7	0.40	0.40	28	2.5	145
0- C_3A	0	0.40	0.40	3	2.5	145
	0	0.40	0.40	28	2.7	146

^aAt end of cure.

*For the purposes of this report interpretations are based primarily on the potential compound compositions. This approach is justified by the existence of a large body of experience correlating potential compound composition with field performance. The quantitative X-ray diffraction data are presented as additional information. Interpretation of chemical resistance on the basis of these data is beyond the scope of this paper. As field experience develops, and supplements the data on resistance to chemical attack presented here, the quantitative X-ray data will be useful in making new correlations.

TABLE 3
COMPOSITION OF SYNTHETIC
SEAWATER SOLUTIONS

Ion	Weight (gm/1 solution)	
	Conc. Syn. Solution ^a	Syn. Solution ^b
Na ⁺	54.64	10.93
K ⁺	1.98	0.40
Mg ⁺⁺	6.72	1.34
Ca ⁺⁺	2.14	0.43
CO ₃ ⁻⁻	0.36	0.07
SO ₄ ⁻⁻	13.72	2.74
Cl ⁻	98.74	19.75
Br ⁻	0.34	0.07
Total	178.64	35.73

^aMade with following quantities of salt per liter of solution: NaCl, 138.9 gm; MgCl₂ · 6 H₂O, 41.50 gm; MgSO₄, 8.75 gm; CaSO₄, 6.45 gm; K₂SO₄, 4.00 gm; KBr, 0.50 gm; and CaCO₃, 0.60 gm.

^bEquivalent to the analysis given by Challenger Expedition (31), which also reported mean density to be 1.027 gm/ml.

discrepancies may result from differences in analytical techniques or may indicate differences in disproportionation in compounds which are not entirely stable.

Dilute solutions were prepared for the twofold purpose of (a) comparing low concentrations and (b) making this comparison on the basis of chemically equivalent concentration rather than equal weight. Solutions were prepared at 0.1 normal concentration, and normalities were calculated from potential ion exchange with respect to the anion, assuming no oxidation or reduction. The weights of solute used to make these solutions are given in Tables 9 through 11. Because some of the chemicals used were not of the highest purity, and because the solutions were not assayed nor adjusted in concentration, the "0.1N" concentrations are only closely approximated.

Mineral acids, purchased as solutions, were tested at the concentrations purchased as well as at nominally 0.1N.

Synthetic seawater was made to the composition (Table 3) reported by the Challenger Expedition (31), except for dissolved gases. The synthetic seawater was also used at 5 times normal concentration in exploratory tests at temperatures of 160 and 200 F, using 28-day-cured Type V mortar. Such results would help to evaluate the potential performance of concrete in evaporators for desalination of seawater.

The various organic chemicals to which mortar prisms are exposed are reported in Table 13 (Appendix). The concentrations chosen for study depend largely on the agent. Some are used on a 0.1M basis; others are made at somewhat arbitrary concentrations, thought to be of interest, in water or in benzene. Some are liquids used without dilution or solids which can be made into solutions with negligible amounts of water.

Physical Conditions of Tests

Complete continuous immersion of the specimen, the easiest exposure to maintain,

about 42 gm/l of water; that of ammonium bisulfate is about 3,350. Therefore, it was desirable to study the upper end of the possible range of concentration for each chemical agent.

Saturated solutions were not used because of possible adherence of the crystals of the solute, which might have obscured observation of any new deposits formed on the prisms or the container walls during test and measurement. Solutions at 90 percent of saturation were used for the inorganic solids. These were conveniently prepared by dilution of 360 ml of stock saturated solutions with 40 ml of water before introduction into test containers. The amounts of solute in these solutions, calculated from published solubilities of the test chemicals, are listed to the right of the chemical names in Tables 9 through 11 of the Appendix. There is some uncertainty in such calculated values for two reasons:

1. Not all of the chemicals used were pure substances, and the presence of other dissolved substances affects solubility; and

2. Published solubility data are not always reliable and are sometimes in disagreement from one source to another;

was used in these tests. To date most tests have been conducted at room temperature. However, other conditions or combinations, such as partial immersion, intermittent immersion, or temperature cycles, may be included in subsequent tests.

SPECIMEN PREPARATION AND TESTING

Preparation and Exposure

Mortars were made in a room at 73 F and 50 percent R. H., following the mixing procedure specified in ASTM Method C 305-59T, but using a modified paddle with rubber wipers. Specimens were cast in two layers, tamped with a hard rubber tamper of $\frac{1}{2}$ - by 1-in. cross-section, cut off level, and lightly steel troweled. Although the zero-C₃A mortar had greater flow than the other two mortars at the same water-cement ratio, the unit weights determined on hardened prisms were about the same (Table 2). After being cured 1 day in the moist room, the prisms were stripped from the molds and capped on the ends with a neat paste of the same cement used in making the mortar. The caps served as the surfaces on which the anvil and the spindle of the length comparator bore when making measurements. Metal gage plugs were not used because of the possibility of corrosion. The capped specimens were returned to the moist room until the 3-day or 28-day curing was complete. At the end of the curing period, measurements were made of length, weight, and fundamental transverse frequency. The specimens were then placed in the test liquids.

The capping of prisms was abandoned in January 1965 because a significant number of caps had been lost during the course of the test, destroying the continuity of length change measurements. It was found that good measurements could be made on uncapped specimens. However, no data on uncapped specimens are included in this report.

Prisms were exposed to various chemical agents by storage of duplicate specimens from the same batch in 400 ml of liquid in a covered container. Specimens in aqueous inorganic solutions were stored in polystyrene boxes with internal polystyrene supports for the specimens (Fig. 1). A bead of vaseline was placed around the top edge of each plastic container to minimize evaporation and prevent creep of crystals onto the exterior surface. Specimens in organic liquids or hot liquids were stored in 16-oz wide-mouth clear flint glass bottles with plastic screw caps and paper or metal foil gaskets (Fig. 1).

The pH was determined for each inorganic solution at the start of test and occasionally at later ages. A glass electrode was used for most measurements, but an antimony electrode was used for sodium salts. Additional determinations were made with Hydrion paper; these did not always agree closely with the electrometric values. The initial pH for each solution is given in Tables 9 through 11 of the Appendix.

The 0.1 N solutions were changed every 3 mo* and 90 percent saturated solutions every 6 mo, except as noted for acids. Organic liquids (other than acids) at concentrations greater than 100 gm/1,000 ml solvent were changed every 6 mo. Those at lower concentrations were changed every 3 mo.

Testing

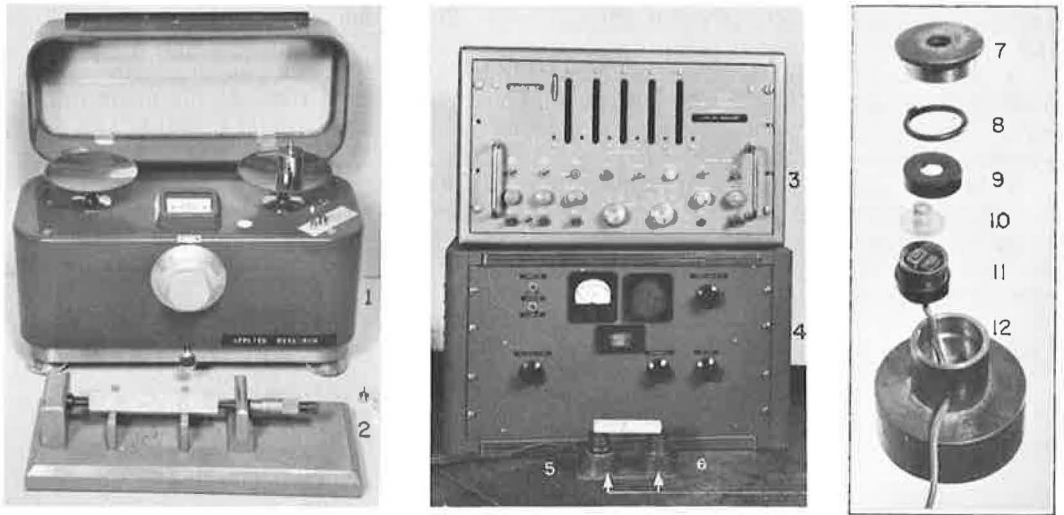
After the initial measurements, periodic measurements of length, weight and fundamental transverse frequency were made at ages measured from time of immersion of 1, 3, 7, 14, 21, and 28 days. Measurements were then made monthly until age 6 mo and every 3 mo thereafter.

Length measurements were made in the comparator, readable to 0.01 mm, which conforms to Canadian Standard A5-1961 (29) (Fig. 2). Specimens were always placed in the comparator in the same way to avoid error. Weights were measured to the nearest 0.01 gm on the 120-gm capacity torsion balance also shown. Fundamental transverse frequency was determined by a procedure similar to that of ASTM Method

*For some solutions this was longer than required to exhaust the solution, but the period was adopted in the interest of uniformity of procedure.



Figure 1. Storage of specimens in limited space, using polystyrene boxes and glass bottles.



- | | | |
|----------------------------|------------------|--------------------------------|
| 1 Torsion Balance | 5 Driver | 9 Cap |
| 2 Length Comparator | 6 Pick up | 10 Diaphragm and Prism Support |
| 3 Frequency Display Meter | 7 Housing Cap | 11 Transducer |
| 4 Oscillator and Amplifier | 8 Retaining Ring | 12 Housing |

Figure 2. Equipment used for physical measurements.

C 215-60, except that the specimen is supported by the driver and pickup, positioned just below the two ends (Fig. 2).

The main body of test is given in the Appendix—for inorganic compounds in Tables 8 through 11, for seawater in Table 12, and for organic compounds in Tables 13 and 14.

NATURE OF TEST RESULTS

The test results may be used for at least partial diagnosis of the mechanism of the attack observed on the specimens. They may also serve to evaluate resistance to attack relative to other mortar compositions and qualities. In addition, they may be used to evaluate resistance to other chemicals and to another concentration of the same chemical.

Use in Diagnosis

Diagnosis depends on inferences which may be drawn from each of the measurements. The evidence from several measurements may provide a set of inferences which together are of considerable help in picturing the nature of the attack.

Increase in weight may mean that water is being absorbed by a specimen that is less than saturated. A larger increase may mean that the specimen is being penetrated by a liquid which is more dense than water and is being absorbed. It may mean that crystals are being formed within the specimen. These are usually more dense than the liquid and add more weight. If the crystals cause expansion they may open cracks, creating new paths for ingress of liquid and new space in which additional crystals can deposit and increase the weight further. Crystals sometimes also deposit on the surface and add to the weight but do not penetrate significantly. It is not always possible, however, to determine visually whether the crystals are on the surface only.

A decrease in weight may mean that water is being replaced by a less dense liquid. It usually means that hydrated cement compounds are being leached from the mortar and the binder material is dissolving. As this process progresses, sand grains, insoluble reaction products, or other debris may deposit on the bottom of the container.

An increase in length is likely to indicate deposition of crystals either on the surface of the prism or in the interior. When small cracks begin to open within the specimen, the process is likely to be accelerated.

A decrease in length is likely to mean that compounds are being leached from the cement. However, in the present study a large, abrupt decrease may have meant that one or both caps had broken free of the specimen.

An early increase in fundamental harmonic frequency usually means continued hydration of portland cement, and continued slow increase may indicate the same thing. An increase in fundamental harmonic frequency may also mean that crystals are being deposited within the specimen.

If continuing deposition of crystals within the specimen causes microcracking, the fundamental harmonic frequency will eventually decrease. When the rate of microcracking becomes high, the fundamental harmonic frequency will decrease rapidly. Another cause of decrease in fundamental harmonic frequency is the loss of binder or mortar by solution.

Use of Data for Evaluation

In many aqueous solutions, the specimens increased in strength during the early part of the test, as indicated by increase in dynamic modulus of elasticity. The dynamic modulus of elasticity is given by

$$E = CWN^2 \quad (1)$$

where E is the dynamic Young's modulus of elasticity, W is the weight of the specimen, N is the fundamental transverse frequency, and C is a constant which depends on the dimensions of the specimen and Poisson's ratio. It has the dimensions of strength and is related to it. Independently it is not a reliable index of strength, but it can indicate whether the strength of a given specimen is increasing or decreasing.

TABLE 4

CHANGE IN LENGTH AND WEIGHT OF PRISMS DURING STORAGE IN MAGNESIUM NITRATE SOLUTIONS COMPARED TO SATURATED LIMEWATER^a

Cement Type	W/C	Cure (days)	Length Change ^b (%)								Weight Change ^c (%)							
			3 Mo	6 Mo	9 Mo	12 Mo	15 Mo	18 Mo	21 Mo	24 Mo	3 Mo	6 Mo	9 Mo	12 Mo	15 Mo	18 Mo	21 Mo	24 Mo
(a) Immersion in 0.1 N Magnesium Nitrate																		
I	0.6	3	0.24	0.28	0.29	0.32	0.31	0.34	0.35	0.34	2.74	2.95	2.99	3.33	3.41	3.52	3.60	3.52
	0.6	28	-0.08	-0.08	-0.08	-0.10	-0.08	-0.06	-0.05	-0.06	0.65	1.27	1.46	1.54	1.77	1.92	2.04	2.23
	0.4	3	0.24	0.38	0.42	0.42	0.42	0.48	0.46	0.53	2.99	3.40	3.62	3.62	3.58	3.70	3.64	3.77
V	0.4	28	0.00	0.00	0.00	0.02	0.04	0.04	0.04	0.07	0.37	0.56	0.59	0.82	1.09	1.37	1.48	1.56
	0.4	3	0.30	0.34	0.41	0.46	0.50	0.50	0.51	0.50	4.26	4.79	5.15	5.13	5.17	5.34	5.39	—
	0.4	28	0.20	0.00	-0.01	-0.02	0.00	0.03	0.04	0.10	0.34	0.74	1.13	1.38	1.49	1.60	1.88	2.26
0-C ₃ A	0.4	3	0.12	0.22	0.24	0.27	0.26	0.40	0.29	0.26	2.41	3.28	3.83	3.76	4.01	—	4.12	4.16
	0.4	28	0.00	0.04	0.06	0.07	0.05	0.06	0.07	0.08	1.22	1.98	2.22	2.07	2.19	2.30	2.40	2.56
(b) Immersion in 90% Saturated Magnesium Nitrate																		
I	0.6	3	0.75	1.74	—	—	—	—	—	—	4.43	5.28	—	—	—	—	—	—
	0.6	28	-0.02	0.22	0.72	1.48	1.86	2.24	2.42	—	-0.04	2.85	3.54	4.25	4.67	4.75	4.17	—
	0.4	3	0.04	0.23	0.60	0.92	1.27	1.62	1.94	—	0.15	1.59	2.31	3.15	3.66	4.21	3.71	—
V	0.4	28	0.02	0.10	0.45	1.02	1.37	1.67	2.16	2.84	0.56	0.74	1.64	2.53	3.67	4.09	4.39	4.84
	0.4	3	0.05	0.10	0.18	0.28	0.37	0.42	0.48	0.45	0.57	2.01	2.99	4.43	4.88	5.22	5.42	4.75
	0.4	28	0.00	0.10	0.22	0.34	0.40	0.48	0.11	0.16	0.42	2.08	2.59	3.09	3.25	3.13	10.66	7.42
0-C ₃ A	0.4	3	0.09	0.40	0.62	1.02	1.57	2.08	2.56	—	0.61	2.12	2.12	2.86	3.92	—	5.56	8.40
	0.4	28	0.09	0.32	0.46	0.84	1.21	1.95	2.88	—	1.73	2.18	2.13	2.73	3.20	3.20	3.18	—
(c) Immersion in Saturated Limewater																		
I	0.6	3	0.02	0.00	0.00	0.00	0.02	-0.02	-0.01	-0.01	1.16	1.36	1.56	1.80	1.92	1.98	2.04	2.18
	0.6	28	0.00	-0.01	-0.02	-0.02	—	-0.02	-0.02	-0.04	0.88	1.18	1.45	1.36	—	1.89	1.96	1.91
	0.4	3	0.02	0.00	0.00	-0.02	-0.04	-0.06	-0.03	-0.03	1.44	1.52	1.56	1.64	1.74	1.84	1.76	1.97
V	0.4	28	0.01	0.00	0.00	0.00	—	-0.01	0.00	0.00	0.78	0.96	1.30	1.16	—	1.31	1.36	1.35
	0.4	3	0.00	0.00	0.00	0.00	-0.02	-0.01	0.00	-0.01	0.84	1.06	1.16	1.21	1.30	1.30	1.33	1.36
	0.4	28	0.00	-0.01	-0.01	—	-0.03	-0.03	-0.03	-0.03	0.20	0.44	0.56	—	0.67	0.73	0.72	0.71
0-C ₃ A	0.4	3	0.02	0.02	-0.01	0.00	-0.02	-0.02	0.00	0.00	0.47	0.56	0.48	0.42	0.16	0.40	0.54	0.62
	0.4	28	0.02	0.02	0.02	0.05	—	0.02	0.02	0.02	0.24	0.10	0.34	0.51	—	0.55	0.54	0.55

^aEach value average of two prisms.^bAll values positive (expansion) unless otherwise indicated.^cAll values positive (increase in weight) unless otherwise indicated.

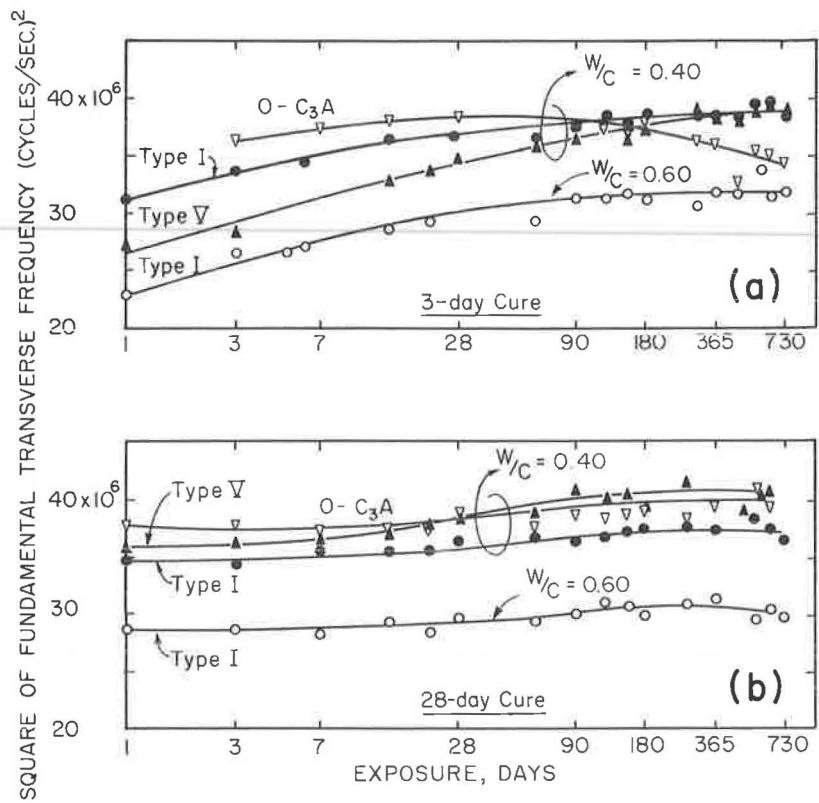


Figure 3. Effect on dynamic modulus of prisms of 2-yr immersion in saturated limewater (modulus expressed as square of fundamental transverse frequency).

TABLE 5
COMPARISON OF POSSIBLE CRITERIA OF FAILURE BASED
ON LOSS OF SONIC MODULUS^a

Criterion	Time to Failure (days)					
	Type I, W/C 0.60		Type I, W/C 0.40		O-C ₃ A, W/C 0.40	
	3 Days	28 Days	3 Days	28 Days	3 Days	28 Days
Loss of 50% of initial modulus	100	260	620	550	560	320
Decrease in modulus						
To 20 × 10 ⁶ cycles ² /sec ²	18	190	450	500	280	350
To 18 × 10 ⁶ cycles ² /sec ²	26	220	520	520	350	420
To 15 × 10 ⁶ cycles ² /sec ²	42	270	660	610	500	540
To 10 × 10 ⁶ cycles ² /sec ²	92	375	—	—	—	—

^aExpressed in terms of square of fundamental frequency; specimens stored in 90% saturated magnesium nitrate solution.

In these tests, the increase was attributed to continuing cement hydration. Specimens cured only 3 days before storage in the test solutions showed greater increase in strength, indicating more continuing hydration than those cured 28 days. The rate of change in saturated limewater is shown in Figure 3. Most of the mortars stored in saturated limewater increased considerably in modulus and, hence, in strength. Specimens cured 28 days and then stored in saturated limewater gained strength more slowly (Fig. 3b) Table 2 gives typical values of initial dynamic modulus of each of these mortars. Changes in length and weight of these same specimens were not large during the first 24 mo. Data for 15, 21 and 24 mo are given at the ends of Tables 11, 10, and 9, respectively.

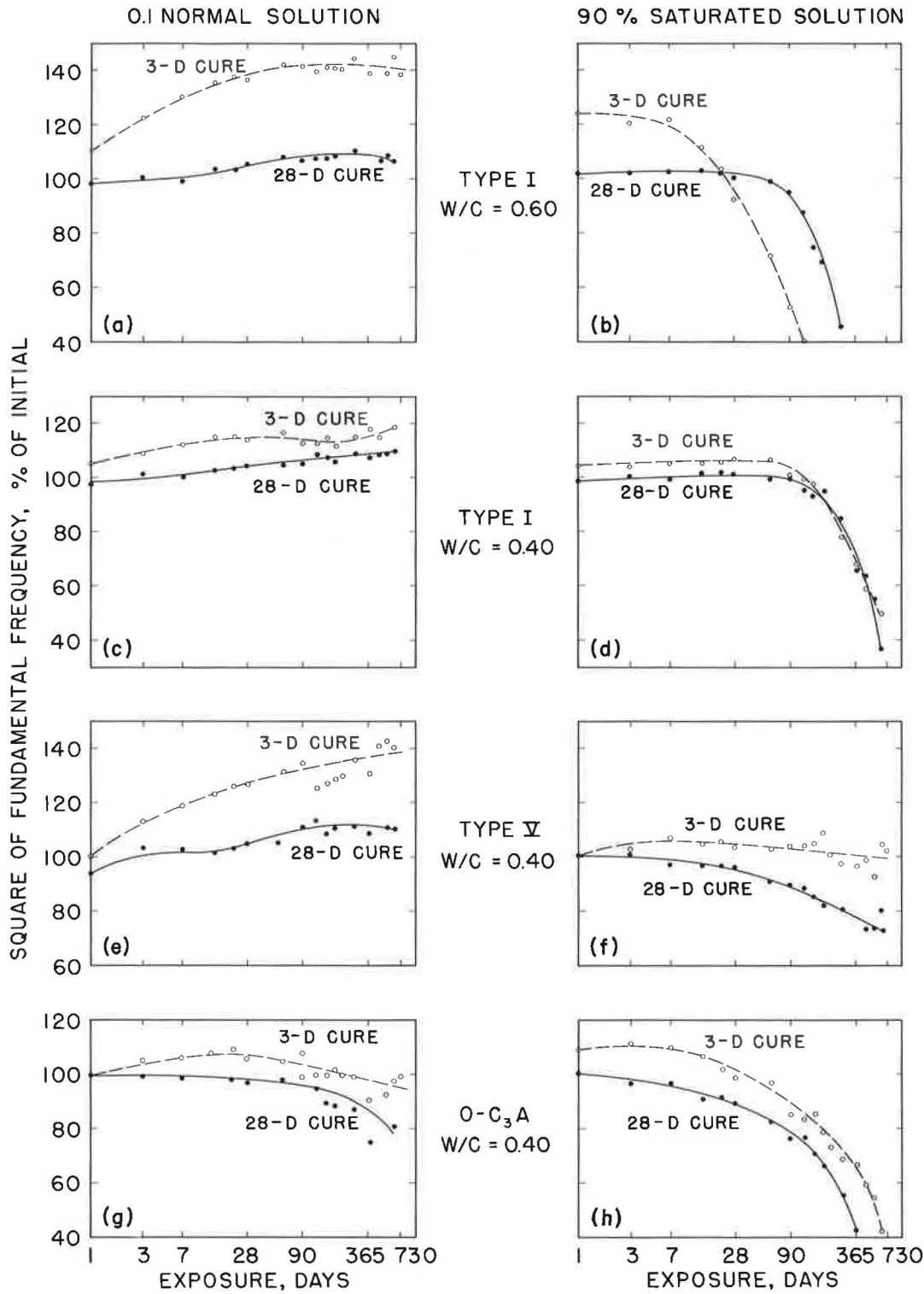


Figure 4. Change in modulus of prisms used to determine rate of deterioration (specimens in magnesium nitrate solutions).

Criteria of Failure.—The criteria of failure selected were a change in length of ± 0.20 percent, a change in weight of ± 10 percent, or a loss in sonic modulus of 50 percent. The change in sonic modulus may usually be calculated with sufficient accuracy by comparing the squares of the fundamental transverse frequency. For additional information, the tests were continued beyond the point of failure indicated by any single criterion.

Change in Length and Weight.—For some chemicals, measurements of change in length are demonstrably useful in revealing considerable differences among the various mortars in the two-solution concentrations. For example, data for specimens immersed in magnesium nitrate solutions for periods up to 24 mo are given in Table 4. Several reached the arbitrarily chosen criterion of failure at early ages, and the magnitudes vary considerably at any age. Changes in weight of the mortars in the same solutions during the same period also differentiated among them (Table 4).

Change in Dynamic Modulus.—The criterion of failure in terms of dynamic modulus was chosen to be a reduction of modulus to 50 percent of initial (expressed as the square of the fundamental frequency, as previously noted). This criterion, commonly used in durability studies, gives an indication of how far microcracking has progressed.

An alternative criterion could have been adopted, setting failure in terms of some absolute value of modulus. Any of the various possible end points, such as those given in the last four lines of Table 5, might have been chosen. Of these, a decrease in the square of the fundamental frequency to 15×10^6 (or a decrease in the frequency to 3,800, rounding to the next lower value) might seem to be the most suitable. However, this criterion could easily result in equating the strengths of two mortars, one having high initial strength and much ultimate microcracking and the other having low initial strength but also little microcracking. The criterion would put more emphasis on residual strength than on integrity of the specimen. Consequently, this criterion was not chosen for this program.

In using the criterion which was chosen, however, the reader should be aware of its limitations. He could be misled while trying to draw conclusions about the relative strengths of mortars of different initial quality. For example, in looking at Figure 4h, he would note that the mortar cured 3 days did not reach the failure criterion until about 560 days, compared to only 320 days for 28-day-cured mortar, as also recorded in Table 5. He would next observe that the curve for the mortar cured 3 days was higher; in the absence of additional information he might conclude that this mortar had higher strength throughout the test.

A different impression is obtained when the moduli are compared as absolute values, rather than as percentages of initial. Such a comparison has been made for the same specimens in Figure 5d. Here the reader would draw a different impression; i.e., that the mortar cured 28 days was stronger at all ages shown. Figures 5a, b, and c also convey impressions somewhat different from Figures 4b, d, and f, which are based, respectively, on the same original data.

Thus, the reader must be careful not to infer too much about the strengths of prisms from the squares of fundamental frequency, N^2 , which are given in terms of percent of initial. These are recorded in Tables 9 through 12 and 14. He may find it possible, however, to make very rough comparisons between mortars by using the absolute values of N , in cycles per second, which are recorded in the same tables.

There are 16 sets of test data for any given inorganic chemical, representing 8 mortars (Table 2), each immersed in two different concentrations of solution. Examples of the manner in which these sonic data were utilized are the 16 typical curves for solutions of magnesium nitrate shown in Figure 4. These curves should be studied in conjunction with Figure 3, which shows the effect of control specimens immersed in limewater where chemical attack is presumably not involved.

Most of the specimens immersed in 0.1N solutions of magnesium nitrate gained in strength; those cured 28 days gained at a rate about equivalent to that of similar specimens in saturated limewater. The specimens in 90 percent saturated solutions of magnesium nitrate gained little or no strength and eventually weakened.

The test was effective in sorting out the relative resistances of eight mortars in magnesium nitrate solutions of two different concentrations. The poorest quality of

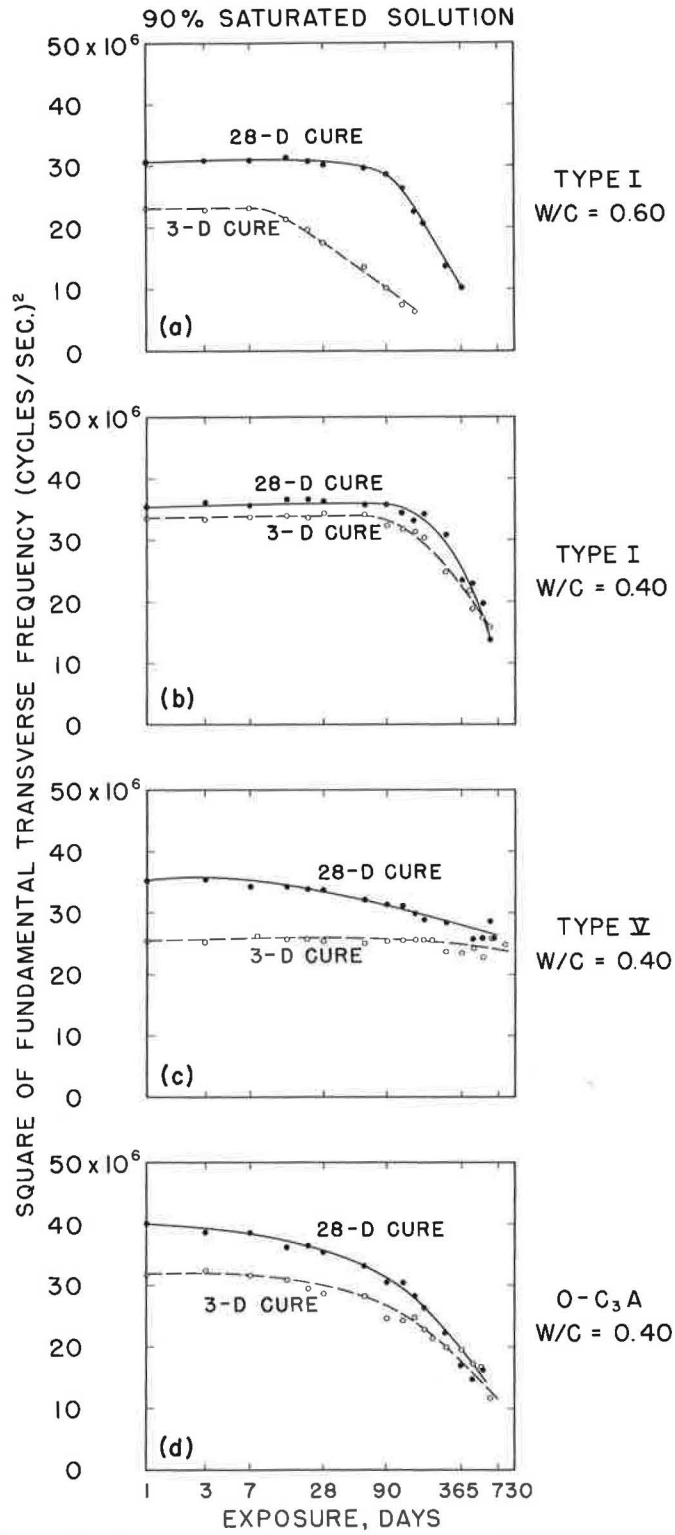


Figure 5. Modulus of prisms compared to that of other specimens forms measure of relative quality (specimens in magnesium nitrate).

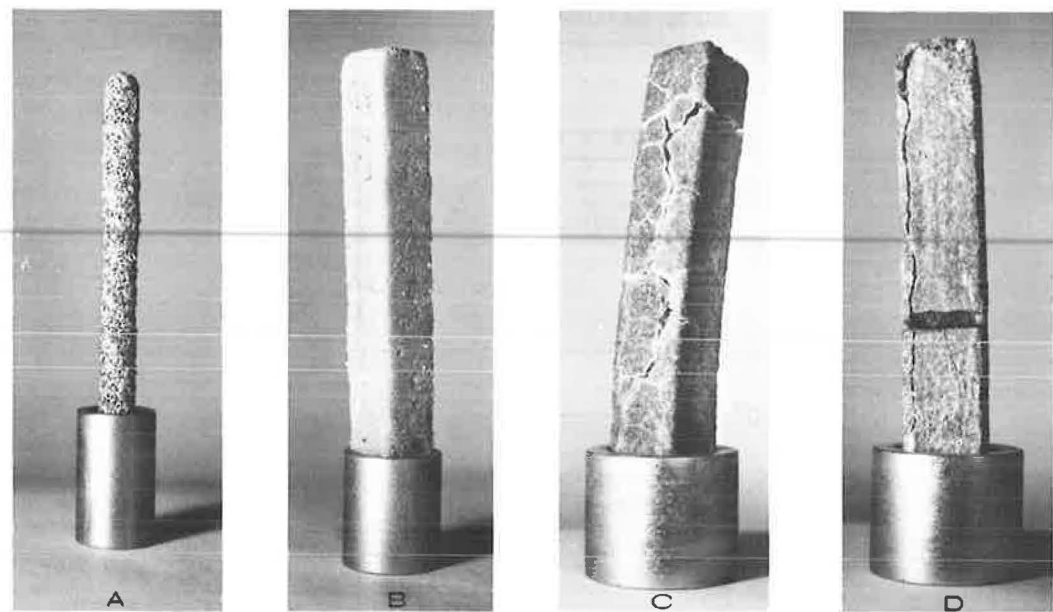


Figure 6. Examples of various kinds of deterioration.

TABLE 6
COMPARISON OF RATE OF pH CHANGE
WITH CONCENTRATION

Solution	Concentration (gm/l)	pH		Elapsed Time (mo)
		Init.	Later	
Sodium bisulfate:				
0.1 N	6.00	1.4	9.6	2.6
90% sat.	387	0.0	0.5	2.8
Potassium persulfate:				
0.1 N	13.57	1.8	9.0	2.6
90% sat.	180	1.6	8.9	2.7
Sodium dichromate:				
0.1 N	14.90	3.9	9.4	2.8
90% sat.	1,845	3.2	4.9	2.8

mortar had failed in 90 percent saturated solution after 3 mo (Table 10). At the other extreme, neither of the Type V mortars had failed by this criterion even after 2 yr (3 mo later than the comparative data given in Table 10), although they had weakened. There were indications of strength loss, or lack of strength gain, among mortars in 0.1 N solutions, and some at least are expected to fail eventually.

Degree of Concordance Between Specimens

For each exposure the two companion specimens were made from the same batch of mortar. Individual specimens of each pair were in fair agreement with each other initially. Of all the specimens used in the program, 98 percent of the pairs had differences in initial fundamental frequency of 300 or less. At failure the agreement in

fundamental frequency between specimens tended to spread out greatly, so that only 75 percent of them had differences of 300 or less. This is understandable, since the values were decreasing rapidly in the period just preceding failure. When the age at failure by the criterion of dynamic modulus was calculated, 80 percent of those which failed by dissolving had differences in age at failure of 30 days or less. Among those which failed by expansion the differences in age at failure were considerably greater.

In general, on a percentage basis, agreement between specimens with respect to change in length or weight was as good as with respect to change in fundamental frequency, or better.

Visual Evidence of Deterioration

In badly deteriorated specimens, several kinds of change in outward appearance may be seen. Several typical examples are shown in Figure 6. Specimen A shows the kind of attack that may be observed with acids. In specimen B, much hydrated portland cement has been dissolved away by acid, leaving loosely bound silica sand in almost the original shape and size of the specimen. The expansion cracking and warping seen in specimen C are typical of sulfate attack. Expansion sometimes causes cracking parallel to each of the 12 edges of the prism, as shown in specimen D, which has been cut in two for examination.

RESISTANCE TO ATTACK BY INORGANIC SUBSTANCES

The following descriptions of resistance to attack are based on chemical classification; discussions of acids, hydroxides, various cations and anions, and seawater are taken up in alphabetic sequence. Quantitative comparisons, if significant, are made between types of cement, water-cement ratios, amount of cure of the mortar, concentration of the solution, or kinds of ions. Where possible, comments are made on the mechanism of attack as understood from the literature or as inferred from the tests and supplementary observations described here.

Acids and Acidity

Acids attack concrete by dissolving both hydrated and unhydrated cement compounds, as well as carbonate aggregate. Such aggregate was not used in these tests. Many of the salts tested are also acidic through either ionization or hydrolysis, or both, and have pH below 7.0, as indicated in Tables 8-10. Many such salts thus tend to react like acids and dissolve concrete.

Acidity is commonly expressed in terms of pH; values progressively lower than 7 represent progressively higher acidity, and progressively higher potential for reaction with concrete. Yet pH values by themselves must be interpreted with caution. The extent of reaction will depend upon the total amount of acid present, and not simply on pH. For example, a dilute, strong acid might have the same pH as a concentrated, weak acid, and an equal volume of the two might consequently attack concrete at the same initial rate. However, since there is less of the strong acid present, it would not react to the same extent, and would not finally dissolve as much concrete.

During the reaction, the change in pH may be large. In the tests reported here, two test specimens totaling either about 18 or 28 gm of cement before hydration would, when even partially hydrated, impart a pH of 12 or more to 400 ml of water containing no solute, or react ultimately with roughly 0.4 or 0.7 gm-eq. wt of acid. Consequently, for dilute solutions, including some 90 percent saturated solutions of low concentration, the pH rose rapidly, in some instances above 7.0. For example, a Type I cement mortar at 0.4 water-cement ratio cured 3 days was immersed in 0.1 N ammonium chloride solution. After 1.3 mo immersion, the pH had changed from 5.6 to 10.2. The concentration was initially 5.35 gm/l.

Solutions of higher concentration usually changed pH more slowly than those of low concentration, as indicated by Table 6. The test was performed in contact with static liquids; flowing liquids in the same concentrations would be expected to maintain lower pH, as though the test solution were being continually renewed. In these tests the

effect of pH is obscured to varying degrees by the changing concentration of the solution.

However, no simple correlation was found, as indicated by Figure 7, between the rate of change in weight of the mortar and the initial pH of the solution. In this figure the change in weight between 3 and 28 days is plotted against the initial pH for a Type V cement mortar made at a water-cement ratio of 0.4 and cured 3 days. The distribution was similarly diffuse for the remaining mortars. The rate of weight loss was not predictable on the basis of pH alone, no matter whether any particular group of solutions is considered or all are considered together. Yet it may be noted that, among these compounds, when very large losses did occur it was when the initial pH was 5.3 or lower.

A limited number of tests have been completed using mineral acids; results are reported in Table 8 (Appendix) on specimens made with Type I cement. The rapid rate of reaction quickly depleted the acid in 0.1N solutions, and for the first 3 wk, these solutions were renewed daily except on weekends. They were renewed weekly for 2 wk and less frequently thereafter. The data indicated a fairly constant loss of weight per change of 0.1N solution.

Specimens failed in 0.1N hydrochloric acid and 0.1N nitric acid after about the same amount of exposure, but attack by 0.1N sulfuric or phosphoric acid was considerably slower.

The concentrated mineral acid solutions were not renewed during the period of test, which was usually brief. The first measurements of the specimens after immersion were made at 6 hr; failures earlier than 6 hr were estimated by interpolation. Failures came early in concentrated hydrochloric and nitric acids. Concentrated phosphoric acid caused early failure as judged by expansion, but did not cause so rapid decline in strength as hydrochloric and nitric acids. Concentrated sulfuric acid was least aggressive by all criteria, probably because of the very small amount of water present. When an amount of water was present equivalent to that in solutions of other acids (note the 0.1N solutions), the sulfuric acid was slightly more aggressive than the phosphoric acid. Calcium sulfate and calcium orthophosphate, reaction products, have such limited solubilities that they undoubtedly deposit on the surface and reduce the rate of attack of sulfuric and phosphoric acids.

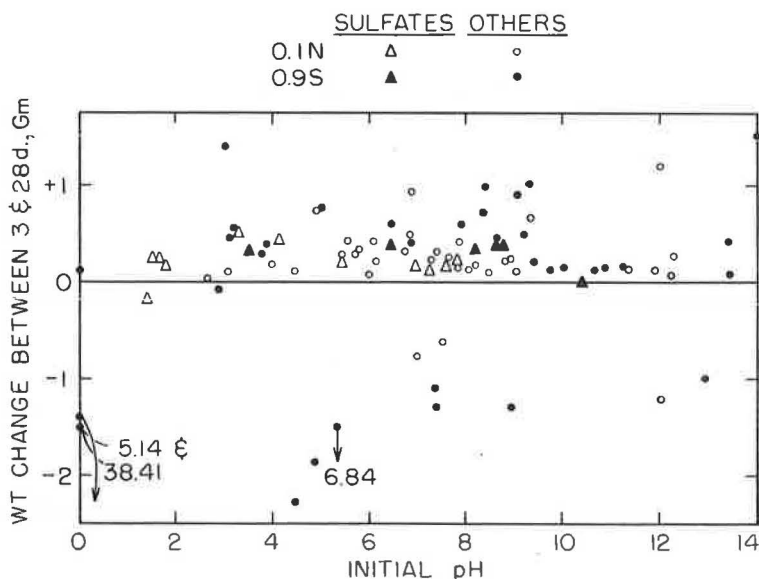


Figure 7. No correlation found between initial pH of solutions and weight loss of mortar bars in test used (Type V cement, W/C = 0.40, 28-day cure).

Aluminates

Sodium aluminate is a highly soluble aluminate of high alkalinity. The pH of the 0.1N solution before immersing specimens in it was 12.3. Changes in specimens immersed in 0.1N solutions were not large after 24 mo (Table 9). In the saturated solution, specimens made with Type I cement at a water-cement ratio of 0.60 and cured 28 days increased in length and considerably in weight, presumably because of crystal buildup on the prisms. The crystals were identified by X-ray analysis as gibbsite, a form of hydrated alumina.

Ammonium Salts

Many ammonium salts attack concrete. Water dissolves calcium, sodium and potassium hydroxides from hydrated portland cement. In the presence of these hydroxyl ions, ammonia gas is released. The calcium, sodium and potassium then replace it in solution, allowing more of the hydroxides to dissolve (1, 3).

The effects of specific ammonium salts are discussed in the sections dealing with the anions.

Borates

Sodium perborate has a relatively low solubility and produces alkaline solutions. No serious changes in length or weight were measured during a period of 24 mo, and all mortars gained strength during immersion (Table 9). Sodium tetraborate (borax) also has a relatively low solubility and produces slightly less alkaline solutions. All of the mortars gained in length and weight, some of them substantially, during 24 mo of immersion. However, most of the change was perhaps caused by the deposition of crystals on the ends and sides of the prisms. Almost all gained in strength during 24 mo.

Carbonates and Bicarbonates

Neither the so-called ammonium carbonate solution nor the ammonium bicarbonate had caused distress in any of the specimens up to age 21 mo. This result may be related to the very limited solubilities of calcium carbonate and bicarbonate. Not all mortars are yet under test (Table 10). The changes in length, weight, and sonic modulus of any given mortar were roughly comparable, whether the mortar was immersed in ammonium carbonate, ammonium bicarbonate, sodium carbonate, or sodium bicarbonate.

Ammonium carbonate solutions have an ambiguous nature (thought to be an equimolar mixture of NH_4HCO_3 and $\text{NH}_4\text{CO}_2\text{NH}_2$) and are known to change composition with age. The solution used in these tests was made from "ammonium carbonate" with a minimum ammonia content of 33 percent. After being stirred for several hours, the saturated solution contained only about 360 gm of salt per liter, though the salt is said to have a solubility of 1,000 gm/l at 59 F. However, ammonia volatilized throughout the stirring operation, so the solution was deficient in ammonia (molar ratio of ammonia to carbon dioxide analyzed at 1.93) and higher in ammonium bicarbonate content. Ammonium bicarbonate is only soluble to the extent of 212 gm/l, so the production of this salt would tend to drive salt out of solution.

It seems likely that the so-called 90 percent saturated ammonium carbonate solution used in these tests began at a maximum concentration of about 0.90×360 gm/l or less. During the test the solution would lose more ammonia and partially convert further to the bicarbonate, reducing the solubility further toward the limiting value of 212 gm/l, the estimated solubility of ammonium bicarbonate.

Chlorates

Several mortars failed by the length criterion in 90 percent saturated sodium chlorate (Table 9) at relatively early ages. Two failed in 0.1N solution also. No failures were observed in the perchlorate, which was considerably more concentrated in the

90 percent saturated solution. The specimens, left under test, still presented a good visual appearance after 24 mo. The changes in length, weight, and sonic modulus during 24 mo are given in Table 9. Some specimens suffered loss of modulus in 90 percent sodium chlorate; the losses were smaller in sodium perchlorate. The Type V specimens cured 3 days were in the best condition with respect to sonic modulus in 90 percent saturated solutions of both salts.

Chlorides and Other Halides

Data are available only on specimens cured 3 days. After 15 mo of immersion in ammonium chloride, all specimens had lost weight significantly and had undergone large changes in sonic modulus (Table 11). Specimens of all four kinds of mortar failed by the modulus criterion in 3 to 12 days when immersed in 90 percent saturated solution. Failures in some of the same specimens were indicated at later ages by other criteria. In 0.1N solution, the zero-C₃A mortar had failed by the modulus criterion after 6.5 mo. Others were approaching failure at 15 mo.

Specimens were in generally good condition after 15 mo in sodium chloride solutions (Table 11), although failure by increase in length was indicated after 12.5 mo for the Type I cement at 0.4 water-cement ratio in 90 percent saturated solution. The test is continuing.

Sodium bromide can be more deleterious. Its solubility is higher than that of sodium chloride. In 90 percent saturated solutions, the Type I portland cement mortars suffered severe loss in modulus, large increase in length, and considerable increase in weight; unexpectedly, the Type I mortar with the lower water-cement ratio was the more severely affected of the two, and failed earlier (Table 11). The zero-C₃A cement mortar had suffered considerable loss in strength by the end of 15 mo. The Type V cement was still in good condition, though the square of the frequency had decreased to 106 percent of initial from the maximum of 120 percent reached at 3 mo. Specimen D of Figure 6 was disrupted by sodium bromide.

The 90 percent saturated solution of sodium fluoride was much less aggressive than that of sodium bromide, as one might expect from its much higher pH and lower concentration and the precipitation of calcium fluoride. Biczok (3) says that sodium fluoride hardens concrete by changing lime to the hard calcium fluoride. It nevertheless caused some reduction in modulus in the Type I mortar made at 0.6 water-cement ratio and in the zero-C₃A mortar (Table 11).

Of the cements tested, Type V appeared to be the most resistant to 90 percent saturated solutions of sodium halides. All cements withstood 0.1N solutions quite well during the first 15 mo of test.

Chromates and Dichromates

All specimens tested were in good condition after 15 mo of immersion in the sodium chromate solutions. However, most of those in sodium dichromate were not (Table 11). In 0.1N solutions, all specimens suffered severe loss in modulus, and most of them failed before the 15 mo had elapsed. The initial pH of the solution had been 3.9. Although this increased to between 8 and 10 during continued immersion, the losses in weight recorded for most specimens indicated that there had been a considerable amount of cement dissolved.

In 90 percent saturated solutions of sodium dichromate, the losses in sonic modulus and in weight were less than in the dilute solutions, even though the pH rose only to 4 or 5 during test. However, the high concentration of the solution, 1,845 gm/l, may have reduced the solubility of the reaction products. At intermediate concentrations the solution might be considerably more destructive. Biczok (3) notes that potassium dichromate is highly aggressive.

Ferrocyanides

Among the specimens tested for a period of 21 mo, none was significantly damaged by the sodium ferrocyanide solutions. Data are given in Table 10.

Fluosilicates

All specimens immersed in magnesium fluosilicate had good strength after a period of 15 mo, even though most of those in 90 percent saturated solutions had undergone a slight loss in weight. The small weight loss perhaps represents some dissolving of cement hydration products, since the 90 percent saturated solution is strongly acidic. The reaction products, however, are compounds of very low solubility—calcium fluoride, magnesium fluoride and silica. These are generally believed to deposit in the pores, making the hydrated cement harder and less permeable. Magnesium and zinc fluosilicates have long been used for this purpose.

Hydroxides

Any limited volume of water in contact with hydrated portland cement soon becomes saturated with calcium hydroxide, because there is more than enough calcium hydroxide present to exceed its very low solubility. When solutions of distilled water in contact with the specimens were not disturbed, the calcium hydroxide diffused slowly enough so that the total solution was less than half saturated after a week. However, measurements of pH indicate that in the vicinity of the specimens the solutions probably became saturated with calcium hydroxide within about a day.

Saturated calcium hydroxide (saturated limewater) was accordingly used as the control for the tests in this program; the data are given in Table 4, and in Tables 9, 10, and 11 of the Appendix, and are plotted in Figure 3. This is the only hydroxide which has yet been tested in this program.

Solutions of sodium and potassium hydroxide at high concentrations are reported to be deleterious to concrete (1, 3), depending on its quality. These will be investigated as the program continues.

Magnesium Salts

Magnesium salts tested included the nitrate (Tables 4 and 10, and Figures 4 and 5), the fluosilicates and the sulfate (Table 11). Most magnesium salts are destructive to concrete. They leach out calcium hydroxide to form the soluble calcium salt and deposit magnesium hydroxide, which is far less soluble than calcium hydroxide. They are also said to react with the other cement hydration products to form such compounds as magnesium hydroxide, soluble calcium salts, silica and alumina; the latter two possibly react with the magnesium hydroxide to form hydrated magnesium silicates and magnesium aluminate (1, 25, 36, 37).

The 90 percent saturated magnesium nitrate solution had the highest magnesium concentration of the three magnesium salts tested:

Mg in $\text{Mg}(\text{MO}_3)_2 \cdot 6 \text{H}_2\text{O} = 109 \text{ gm/l}$;

Mg in $\text{MgSO}_4 = 63 \text{ gm/l}$; and

Mg in $\text{MgSiF}_6 = 53 \text{ gm/l}$.

This may be one reason that magnesium nitrate was the most destructive. Length changes at 15 mo caused by magnesium nitrate solutions may be found in Table 4 and compared with those caused by fluosilicate and sulfate and recorded in Table 11. Type V cement was more resistant to increase in length when immersed in magnesium nitrate than the other cements. Magnesium fluosilicate had not caused any distress by the end of 15 mo; its hardening effect has been previously discussed under fluosilicates.

When magnesium nitrate and magnesium sulfate are compared on the basis of equivalent concentrations, in 0.1N solutions, the differences are not nearly as great. (The 15-mo data from Table 4 may again be compared with the data of Table 11.) However, the length changes of all specimens cured only 3 days are excessive when immersed in magnesium nitrate for 15 mo, but the Type V cement and zero- C_3A cement specimens cured 3 days were still in good condition after 15 mo in magnesium sulfate.

Manganates

Potassium permanganate (Table 11) was the only salt studied in this group. No

distress has been shown during 15 mo of immersion by any of the specimens tested, although not all specimens have yet been put under test.

Molybdates

The specimens made with Type I cement at a water-cement ratio of 0.60 and cured 28 days had gained 10.60 percent in weight after 15 mo of immersion in 90 percent saturated sodium molybdate of specific gravity 1.395 (Table 11). It seems likely that some kind of solid has been deposited within the prisms. For these particular prisms, the increase was 5.48 gm per prism. If there were no solids deposited and no change in volume of the prism, this weight change would have required replacement of 13.9 ml of water in the prism by an equal amount of the denser solution. However, 13.9 ml is far more than the total amount of liquid which can be accommodated by the prism, as approximately equal to the volume of mixing water (5.6 ml). The specific gravity of sodium molybdate salt, however, is 2.59. The observed weight increase would require replacement of only 3.44 ml of water per prism by salt crystals. The deposition of solids thus comes much closer to satisfying the volume limitations of the material which has caused the weight increase. All of the specimens immersed in 90 percent saturated sodium molybdate had considerably increased in weight. The zero-C₃A specimens increased the least.

None of the specimens in any of the solutions underwent excessive length change in 15 mo. All had fundamental sonic frequencies higher than the original. The Type I specimens with water-cement ratio of 0.60, cured 28 days, began to decline in sonic frequency after this time, however, whether they were immersed in 0.1N or 90 percent saturated solutions.

Nitrates and Nitrites

Of the nitrates, ammonium nitrate was by far the most destructive. No specimens withstood the attack of 90 percent saturated ammonium nitrate for more than about 2 wk, and many of them failed much earlier (Table 10). Even a 0.1N solution was destructive to most specimens; only the Type V specimens cured 3 days survived after 21 mo. The rapidity of the attack by ammonium nitrate can be attributed to the ammonium cation.

Magnesium nitrate is next to ammonium nitrate in severity of attack. Here again the cation (magnesium) is responsible. Although the pH of the 90 percent saturated solution was initially only 3.8, and although a large amount of salt was present (1,152 gm/l of water), the pH did not remain low. When measured after one set of Type I specimens had been immersed for 3 wk, the pH had risen to 7.5; similar measurements were obtained on solutions containing other mortars. Specimens suffered from changes in weight, length and sonic modulus. The weight changes of all specimens were positive (Table 10), indicating that if there was any acid attack it was less significant than deposition or absorption of additional substances in the mortar.

The Type V cement was the most resistant to attack by 90 percent saturated magnesium nitrate, although it does not sustain continuous attack indefinitely (Table 10, Fig. 4f). The zero-C₃A cement mortar was less resistant to attack in this solution than Type I cement made at the same water-cement ratio. In 0.1N solutions, all specimens cured only 3 days had excessive increases in length during 21 mo of immersion, but all specimens cured 28 days still had acceptable length changes after 21 mo. Figures 4a and g indicate that two of the mortars may have been starting to deteriorate in 0.1N solution, although they were still in good condition at that time.

In some specimens immersed in 90 percent saturated solutions of potassium or sodium nitrates, excessive expansions were measured; one was 0.86 percent at 21 mo (Table 10). In potassium nitrate, acceptable expansions were measured only with mortars made of Type V cement; in sodium nitrate, expansions were acceptably low in mortars made with either Type V or zero-C₃A cement. The reasons for the excessive expansions are not yet known. A qualitative test of the stock saturated solution of sodium nitrate showed that the solution contained a small amount of sulfate. However, 90 percent saturated potassium nitrate, which produced more expansion in every instance than sodium nitrate, contained essentially no sulfate.

The apparent expansion and increase in weight of specimens immersed in lead nitrate may have been only the heavy crystal buildup on the surfaces of the specimens. The X-ray diffraction pattern of this precipitate indicated the possible presence of lead silicates, lead aluminosilicate, lead phosphates, and lead sulfates. Qualitative analysis shows that there has been some ion exchange, which can only mean that the hardened cement paste has been altered.

Most specimens in sodium nitrite appeared to be in good condition after 21 mo immersion, although the sonic modulus was beginning to decrease in some (Table 10). Two specimens indicated excessive expansion; this was probably because the caps had begun to crack and were perhaps coming loose.

Phosphates

Monobasic sodium orthophosphate was the only one of the three orthophosphates which had damaged specimens seriously by the end of 15 mo. The deterioration occurred only in specimens immersed in 90 percent saturated solutions. The acidity of these solutions remained strong, and the pH typically rose no higher than 3.6 during 6 mo of immersion. Visual examination showed that all specimens in 90 percent saturated solutions had become white from deposition of insoluble reaction products and had been eroded along the edges. Caps also became whitened, eroded along the edges, and expanded at the center. Measured length changes, usually large (Table 11), may have been partially the result of these changes in the caps. At later ages, longitudinal cracks formed along the edges and caused failure. No failures had occurred by age 15 mo, but sonic moduli were decreasing significantly, as indicated by the value of N^2 in Table 11. Specimens made of zero- C_3A cement had larger increases in weight than other cements.

Specimens in sodium hexametaphosphate gave evidence of slight surface erosion, although they were in good condition as far as changes in length, weight and sonic modulus indicated (Table 11). Specimens in sodium pyrophosphate, however, were in good condition in all respects.

Seawater

Mather (32) has discussed the mechanism of deterioration of concrete by seawater, which may involve attack by sulfate, chloride, carbonate, bicarbonate, alkali metal and magnesium ions. The actions of some of these ions are discussed individually elsewhere in this paper. The condition of specimens of the various mortars after immersion for 6 mo in synthetic seawater is given in Table 12 of the Appendix. Type I specimens and zero- C_3A specimens cured 3 days had already exceeded the expansion limit of 0.20 percent before 6 mo had elapsed, and the time required for failure is given in the table. The mortar made with Type V cement was superior to the others in resisting seawater attack.

The Type V mortar cured 3 days was also tested at temperatures of 160 and 200 F in solutions of synthetic seawater and of seawater at 5 times this concentration (Table 12). All such specimens were in good condition after 6 mo.

Stannates

Only one stannate, sodium stannate, was tested; this produced highly alkaline solutions (Table 11) and did not harm the mortars during 15 mo of immersion. Some gained a considerable amount of weight.

Sulfates and Bisulfates

Sulfate Attack.—The destructive action of sulfates on concrete is primarily the result of their reaction with either C_3A or the C_3A hydration products to form the high-sulfate form of calcium sulfoaluminate (ettringite, $C_3A \cdot 3CaSO_4 \cdot 32H_2O$). The crystalline reaction product is of larger volume than the original aluminate constituent, and expansion results. The concrete or mortar increases in compressive strength at first, because of the increase in solid matter, even though it is changing chemically. As the process continues the concrete or mortar expands, cracks, becomes progres-

TABLE 7
ADDITIONAL IONS PRESENT IN
SULFATE SOLUTIONS

Solution	Addition Ion	
	0.1 N	90 Percent Sat.
Sodium bisulfate	H ⁺ ^a	H ⁺ ^a
Ammonium sulfate	NH ₄ ⁺ , H ⁺ ^b	NH ₄ ⁺ , H ⁺ ^b
Ammonium bisulfate	NH ₄ ⁺ , H ⁺ ^a	NH ₄ ⁺ ^c , H ⁺
Copper sulfate	H ⁺	H ⁺
Manganese sulfate	H ⁺ ^d	H ⁺
Magnesium sulfate	Mg ⁺⁺	Mg ⁺⁺

^aAcidity did not persist, since pH rose to more than 9 during test.

^bAcidity did not persist, since pH quickly rose to more than 7.

^cAmmonium ion was probably not aggressive at low pH of solution, which remained at a measured value of 0.

^dAcidity did not persist, since pH rose above 7 in about 1 mo.

in Table 7. Hydrogen ion was present in copper and manganese sulfates because of hydrolysis. Both the 0.1 N and 90 percent saturated solutions of copper sulfate remained distinctly acid throughout the test, but only the 90 percent saturated manganese sulfate remained acid, as indicated in Table 7. The 90 percent saturated ammonium bisulfate, which had the unusually high concentration of 3,015 gm/l (Table 11), remained at a measured pH of 0 throughout the test, whereas the 0.1 N solutions rose to pH values between 9 and 10. Ammonium sulfate solutions, both 0.1 N and 90 percent saturated, were initially acidic (Table 11) but quickly rose in pH.

Sodium bisulfate had an unusually low initial pH (Table 11) which remained persistently low in the 90 percent saturated solutions throughout the test, never rising above 1. The 0.1 N solutions, however, reached pH values of about 10. In the 90 percent saturated solutions one would naturally expect the dissolving action of the acid to open the structure to rapid penetration and attack by sulfate. The dissolving action was the predominant mode of attack. Deterioration by sodium bisulfate was faster than by any other sulfate salt tested. All mortars tested failed in a very short time in the 90 percent saturated solution, and none lasted longer than 7 mo in 0.1 N solution.

Ammonium Sulfates.—Ammonium sulfate and bisulfate solutions were highly aggressive, causing failures in all mortars tested whether immersed in 0.1 N or 90 percent saturated solutions (Table 11). In 90 percent saturated solutions of ammonium bisulfate, acid attack predominated over sulfate attack much like sodium bisulfate, and caused failures almost as rapidly with all of the mortars tested. Specimen A of Figure 6 shows a specimen which failed in less than a month in ammonium bisulfate but which was photographed after 15 months storage in the original solution. In 0.1 N solution the nature of the attack differed somewhat because the rise in pH from 1.6 to more than 9 had the effect of replacing acid attack by ammonium ion attack. The passage of calcium ions from the hydrated cement into solution to replace ammonium ions which were breaking down by volatilization of ammonia (see Ammonium Salts) would make the cement more porous and more subject to attack by sulfate ions. All of the mortars tested succumbed to this attack by 0.1 N solution (Table 11). Type V cement and zero-C₃A cement were not immune.

The action of ammonium sulfate was similar, except that the hydrogen ion concentration in the 90 percent saturated solution was initially lower and decreased more quickly. Thus, ammonium ion was the effective agent, with sulfate ion, in both the 90 percent saturated solution and the 0.1 N solution and produced more solid matter of a different kind in the bottom of the container. The rate of attack by ammonium sulfate was not greatly different from that of the bisulfate; apparently it was faster for some mortars and slower for others.

sively weaker, and finally disintegrates. Specimen C of Figure 6 has undergone sulfate attack.

Sodium Sulfate.—Sulfate attack is well illustrated by the effect of 90 percent saturated sodium sulfate, which caused early failure of Type I cement mortars by one or more of the three criteria (Table 11). Of all the mortars tested, Type V cement mortar was most resistant to attack. None of the mortars yet tested in 0.1 N solutions had failed by the end of 15 mo, but even in such a dilute solution the Type I cement mortar made at 0.40 water-cement ratio and cured 3 days had undergone a serious loss in dynamic modulus.

Association of Other Aggressive Ions with Sulfate.—In each of the other sulfate solutions tested, there was an additional aggressive ion or two present, as indicated

Copper Sulfate.—Copper sulfate remained acidic even in the 0.1 N solutions, where the pH rose to less than 5. Here the deposition of calcium sulfate on the surface perhaps slowed the rate of attack by acid and prevented the depletion of a small amount of acid present. Prisms had relatively uneroded surfaces with sharp edges after 15 mo. Sulfate attack proceeded, however, as indicated by the increases in weight and length and, in one set of specimens (Table 11), serious decrease in dynamic modulus of elasticity.

Acid attack is obvious in the weight losses and erosion of specimens in the 90 percent saturated solutions. However, these changes were accompanied by internal deposits formed by sulfate action, as evidenced by the expansions of all specimens and the decrease in dynamic modulus of many of them.

Type V cement mortars appeared to be the most resistant of all the mortars tested in both 0.1 N and 90 percent saturated solutions of copper sulfate, but they also failed.

Manganese Sulfate.—Manganese sulfate is more acidic than copper sulfate, as indicated by the initial pH (Table 11), but during a $\frac{1}{2}$ -mo immersion of specimens in 0.1 N solutions, the pH rose above 7. The action seems to be much like that of copper sulfate, with some differences in magnitude of changes in length, weight and dynamic modulus of elasticity. Specimens made with Type V cement were still resistant after 15 mo, when all others had failed.

In the 90 percent saturated solutions of manganese sulfate, however, acid attack was far more pronounced than in copper sulfate, as shown by the considerably larger weight losses. The initial pH was lower than that of copper sulfate (Table 11), but the final pH was higher (about 6 for manganese sulfate compared to about 3.5 for copper sulfate). This indicates more depletion of hydrogen ion, perhaps through more extensive chemical reaction. The changes in specimen length were always negative, showing the predominance of acid attack over sulfate attack at this concentration.

Magnesium Sulfate.—At the equivalent concentrations represented by the 0.1 N solutions, magnesium sulfate was more severe than sodium sulfate in its attack on specimens of all kinds (Table 11). The difference is perhaps in the aggressive effect of magnesium ion (see Magnesium Salts). Magnesium sulfate was less aggressive than the salts of ammonia, copper and manganese and the acid salts of ammonia and sodium, discussed previously. In 0.1 N solutions, only the Type I cement mortar made at a water-cement ratio of 0.60 and cured 3 days suffered changes in length and dynamic modulus at all comparable to those in solutions of the other cations. The Type I mortar at a water-cement ratio of 0.40 cured 3 days suffered failure by the expansion criterion in 14.5 mo. All other specimens were in satisfactory condition after 15 mo.

In 90 percent saturated solutions, magnesium sulfate was less aggressive than sodium sulfate, although the concentration was higher in the magnesium sulfate solution and although two kinds of aggressive ions were present in the solution. Some specimens in magnesium sulfate increased in weight because of the deposition of new crystalline material within them. As the process proceeded, however, debris began to slough off and deposit on the bottom of the container, causing losses in weight to the prisms (Table 11). Type V cement did not appear to be noticeably more resistant than Type I in this solution.

Other Sulfur-Containing Anions

Sodium sulfide (Table 11) was the only sulfide tested. The solutions were highly alkaline in both concentrations, and no deterioration of the mortar was measured. For a period of 15 mo, in the absence of oxidizing agents, sodium sulfide appears to have been harmless.

In 0.1 N solution, sodium sulfite was at least as aggressive to the mortars tested as sodium sulfate of the same concentration, or more so (Table 11). Sodium bisulfite appeared to be more aggressive to some mortars than sodium bisulfate but not to others. All mortars withstood 0.1 N sodium bisulfite for 15 mo except Type I cement mortar made at a water-cement ratio of 0.60 and cured 3 days; this failed in expansion in 9.5 mo. Of those tested in sodium bisulfite, only Type V cement mortar cured 3 days survived 15 mo.

Both Type V and zero-C₃A cement mortars were resistant for 15 mo to attack by 90 percent saturated sodium sulfite (Table 11). Failures occurred in all Type I cement mortars except the one made at 0.40 water-cement ratio cured 3 days, which, for unknown reasons, far outlasted the mortar cured 28 days.

Sodium bisulfite in 90 percent saturated solution was less concentrated, but more acidic and more destructive than sodium sulfite, and failures occurred earlier.

Sodium thiosulfate was about as aggressive in 0.1 N solution as in 90 percent saturated (Table 11). Failures were indicated by excessive changes in length. Type V cement mortar and zero-C₃A cement mortar were resistant to expansion, but in the 0.1 N solution, the zero-C₃A cement mortar cured 3 days failed by expansion in 10 mo. The mortar of ostensibly lowest quality, on the other hand, with Type I cement at 0.60 water-cement ratio cured 3 days did not fail in 15 mo in 0.1 N solution in these tests.

In 0.1 N solution potassium persulfate caused large expansions and failures in those specimens made of Type I cement mortar (Specimen C, Fig. 6), but not of either the Type V or zero-C₃A (Table 11). It was highly destructive in 90 percent saturated solutions, causing failures in Type V and zero-C₃A mortars as well as Type I, though at later ages. The solutions were strongly acid initially, but the pH rose to about 9 or 10 in both the 0.1 N and 90 percent saturated solutions during test.

RESISTANCE TO ATTACK BY ORGANIC SUBSTANCES

The tests conducted so far with organic substances have been limited to mortars made with Type I cement, at water-cement ratios of 0.60 and 0.40, moist cured 28 days. The other mortars will be tested as the program continues. Data are available only up to 6 mo of immersion.

Acids

One schedule for renewal of organic acid solutions was planned for those less concentrated than 100 gm/l, and another for more concentrated solutions. Both schedules were interrupted, but the history of each pair of specimens may be seen in a general way from the number of solution changes and the length of exposure recorded in Table 13 in the Appendix.

The four acids tested were concentrated lactic acid, 0.1 M lactic acid, a mixture containing 2 percent lactic plus 2 percent acetic acid in a single solution and a solution of 200 gm stearic acid per liter of benzene. Specimen B, of Figure 6 is shown after 3 mo of immersion in the lactic-acetic acid mixture, which had been renewed twice during that time. All four solutions were highly destructive (Table 13), including the two in contact with very little water. One of these was concentrated lactic acid which contained only sufficient water to liquefy, and the other was stearic acid dissolved in benzene with no water present. The prisms themselves, however, contained some absorbed water initially.

Alcohols

Specimens were immersed in methyl alcohol, tertiary butyl alcohol, ethylene glycol and glycerol made to the concentrations given in Table 14. The changes in weight and length which occurred in 6 mo were acceptably low at all concentrations tested. Strength appeared to be diminishing in the concentrated liquids at 6 mo, but the specimens were still in good condition at that time.

Amino Acid Salts

The disodium salt of ethylenediamine tetraacetic acid (EDTA) was dissolved in water to concentrations of 34.42 gm/l of solution (0.1 M), and 125 gm/l of water. EDTA is a sequestering agent for calcium, and the solutions used had initial pH values of about 6.

As with the organic acids, the schedule for renewal of solutions was interrupted, but the number of exposures to fresh solution and the total exposure time are given in Table 13. As indicated in the table, EDTA is as aggressive as a weak acid.

The more concentrated solution was changed monthly, like the more concentrated acid solutions, and the total elapsed time before failure was recorded. The time to failure recorded by this method was somewhat longer.

Drying Oils

Specimens were immersed in a pure grade of boiled linseed oil, undiluted. After 6 mo of immersion, the specimens were still in good condition (Table 4).

Esters

Specimens immersed in undiluted butyl stearate were in good condition after 6 mo (Table 4), as were specimens immersed in a solution of 30 gm technical grade glyceryl tristearate per liter of benzene (Table 14).

Hydrocarbons

Benzene caused no great change in the specimens in 6 mo (Table 14).

Sugars

Sucrose was made to two concentrations (Table 14), neither of which damaged the specimens in 6 mo.

RELATIVE RESISTANCE OF THE MORTARS

Type V cement mortar was more resistant to sulfate attack than either Type I or zero- C_3A , as indicated by its greater durability in sodium sulfate, sodium sulfite, and sodium thiosulfate. However, in acid salts or other salts with low pH, such as ammonium bisulfate, sodium bisulfate, copper sulfate, manganous sulfate, and potassium persulfate, Type V was not significantly more resistant, if at all. Nor was it very resistant in ammonium sulfate or magnesium sulfate, salts in which the cation is also aggressive.

The resistance of zero- C_3A cement mortar was inferior to that of Type V with respect to many of the chemicals studied so far. Insofar as this observation is dependent on the change in dynamic modulus, it may partly reflect the lower modulus of the zero- C_3A cement as measured at later ages (Fig. 3), particularly for specimens cured 3 days. In addition to the absence of potential C_3A , the zero- C_3A cement also differed from the Type V cement in that it contained considerably more C_3S , a factor which may influence chemical resistance.

Type I cement mortar made with a water-cement ratio of 0.40 was usually more resistant than that made with a water-cement ratio of 0.60. Longer cure time usually increased resistance. Exceptions to either of these observations may have been the result of experimental error.

PRODUCTS OF ATTACK

Efforts have been made to detect and identify products of reaction between hydrated portland cement and some of the chemicals studied in this investigation. Petrographic examination showed that various foreign crystalline materials were present in the interior of some mortar bars. These were usually so finely crystallized, so small in quantity, or so embedded in other materials that they could not be positively identified. Amorphous materials were sometimes seen. X-ray diffraction measurements on powders or on polished surfaces from the mortar bars also did not lead to positive identification.

However, some auxiliary tests were performed which produced some helpful information. The Type I cement was hydrated at a water-cement ratio of 2.0 in a polyethylene bottle while agitating for 7 days by keeping the bottle clamped to a rotating wheel. The agitation continually exposes fresh surface and permits the hydration to approach completion in this period of time without binding the products into a mass. After 7 days, the excess water was filtered off and the solids were vacuum dried and bottled.

Samples of this powder were then weighed and exposed to solutions in plastic boxes in approximately the same proportions involved when mortar bars were immersed. Additional samples were exposed to solutions in polyethylene bottles stoppered to exclude carbon dioxide. The purpose was to increase the amount of surface area immediately accessible to the solution, in the hope that if any reaction occurred it might go more nearly to completion than in the prisms, and produce larger identifiable crystals. Solutions used were 90 percent saturated sodium chlorate, lead nitrate, potassium nitrate, sodium nitrate, sodium nitrite, sodium bromide, sodium chloride, and sodium fluoride. After a month or more of exposure, samples withdrawn from the top surface of the solid layer were examined by X-ray diffraction. At the present time only some general conclusions can be drawn.

After exposure to the solutions, the hydrated pastes no longer showed the presence of calcium sulfate, but sulfate was present in each of the solutions, showing that calcium sulfate had come out of the solid into solution. However, there was evidence of new compounds formed by reaction with the various solutions. These were deposited in the paste and appeared to be bromoaluminates, chloroaluminates, or nitroaluminates, depending on the solution used. Several kinds of anions are known to combine with calcium aluminate (1), possibly producing compounds which cause expansion.

Calcium fluoroaluminate did not form by reaction with the sodium fluoride solution; calcium fluoride, which was identified, has a low solubility and forms preferentially. The reaction of lead nitrate with paste is perhaps also more complex than reaction with other nitrates; the sample had many diffraction peaks.

There was no X-ray evidence of addition compounds with calcium silicate hydrates, but evidence from other work indicates that these hydrates can take up quantities of other anions without noticeable modification of the broad peaks of their diffraction patterns. Hence, it is uncertain whether compounds other than calcium aluminate hydrate also react with aggressive solutions to form compounds which may cause expansion. It should be noted that the zero-C₃A mortar underwent some expansion when in contact with sodium chlorate, lead nitrate, and potassium nitrate (Tables 9 and 10), but it is not known whether this expansion was caused by formation and deposition of new compounds.

SUMMARY

The resistance of portland cement concrete to chemical attack is being studied by using small mortar (microconcrete) specimens immersed in aggressive liquids and measuring changes in length, weight and dynamic modulus of elasticity. The specimens are 1.5- by 1.5- by 10-cm mortar prisms. The mortar is made with well-graded fine silica sand, which is (for all purposes of the study) inert to the chemicals to be studied. Mortars were made to water-cement ratios such as those which are attainable in concrete so that the hydrated paste is representative of the paste fraction of concrete in permeability and strength.

Because the method uses three measurements—length, weight and fundamental harmonic frequency—it provides more information for explaining the mechanism of attack than if only one or two measurements were used. When it is necessary to draw additional conclusions about the mechanism of attack, these measurements can be supplemented by chemical, X-ray, and petrographic studies of the deteriorated mortars, solutions, precipitates, and residues.

The study confirms the observations of other investigators about some liquids that are detrimental or may be detrimental to concrete. Among these are seawater and solutions of ammonium salts, magnesium salts, organic and inorganic acids, sulfates, sulfites, thiosulfate, and salts producing low pH. Some other chemicals have also been found to be detrimental to some concretes at rates of attack that depend on exposure conditions. These include solutions of lead nitrate, potassium nitrate, sodium bromide, sodium dichromate, sodium chlorate, and EDTA (ethylenediamine tetraacetic acid, disodium salt—a sequestering agent for calcium). During the reported times of exposure, other chemicals have appeared to be less aggressive. More information about these will be obtained as the tests continue.

Resistance of mortar was increased by longer cure time and by decrease in water-cement ratio. The Type V cement mortar was more resistant to sulfate attack than the other mortars, but not to acidic sulfates or those which contained ammonium or magnesium. The zero- C_3A cement mortar was generally lower in resistance to chemical attack than Type V.

The rate of attack may be directly related to the activity of the aggressive ion. Solutions of high concentration were generally more aggressive than those of low concentration. In sulfuric acid, however, a Type I cement mortar had only about the same resistance in a solution of 9.81 gm/l, replenished 5 times a week, as in a solution of 960 gm/kg which was not replenished.

Another striking exception to the increase in rate of attack with increase in concentration of the aggressive chemical was shown consistently in the data for sodium dichromate solutions. Solutions containing 14.90 gm/l of solution were more deleterious than those containing 1,845 gm/l of solvent.

The rate of attack may sometimes be affected by the solubility of the reaction products in the particular concentration of the aggressive solution. For example, the weight loss from the mortar after each change of 0.1 N sulfuric acid was not sufficient to provide enough calcium sulfate to saturate the solution. This would prevent calcium sulfate from depositing on the prisms. The solubility of calcium sulfate in the concentrated acid solution is much lower, however, and was exceeded within a few hours. Furthermore, this solution was not renewed and for almost the entire period of immersion in concentrated H_2SO_4 , calcium sulfate was being deposited on the surfaces of the prisms, impeding the reactions.

Mortars of Type V cement immersed in hot seawater for 6 mo appeared to be more resistant to attack than those immersed in seawater at 73 F. The same may be true for mortars immersed in seawater at 5 times its natural concentration. Ettringite crystals apparently do not form at the temperatures utilized, 160 and 200 F; therefore, in this exposure the increase in temperature appears to have been beneficial. Freedom from formation of ettringite and consequent expansion may be of considerable importance to the future use of concrete in this kind of application.

It is well known that lowering of pH decreases the resistance of mortar by increasing the rate of solution. However, the chemical composition of an aggressive liquid was at least as important as pH in influencing the rate at which a mortar prism lost weight. When the pH of many chemicals was compared with weight loss of mortar bars, no correlation was found.

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Appendix

DATA FROM EXPOSURE TESTS

Explanatory Notes

Following each name and chemical formula in the tables are letters in parentheses to indicate the grade (purity) of chemical used according to the following code:

ACS = American Chemical Society,

NF = National Formulary,

P = Purified,

PI = Pure Industrial,

Pr = Practical,

R = Reagent,

T = Technical, and

USP = U. S. Pharmacopoeia.

Data indicating concentrations of solutions are indicated as shown below. The initial pH, where applicable, follows immediately after the solution concentration.

Table	Kind of Solution	Units Used to Express Concentration	Location of Concentration Data with Respect to Chemical Name
8	0.1 N	Grams per liter of solution	Below, left
8	Concentrated	Grams per kilogram of solution	Below, right
9-11	0.1 N	Grams per liter of solution	Left
9-11	90% saturated	Grams per liter of water	Right
13, 14	0.1 M	Grams per liter of solution	Below, left
13, 14	Intermediate concentrations	Grams per liter of solvent	Below, center
13, 14	Concentrated liquid	Grams per liter of solvent (except as noted)	Below, right

TABLE 8
AGES AT FAILURE IN MINERAL ACIDS

All specimens were made with Type I cement, with $W/C = 0.60$, cured 3 days. The 0.1-normal solutions were renewed 5 times per week for three weeks, weekly for two weeks, and less frequently thereafter.

The concentrated solutions were used as received and the concentration recorded below is the average given on the label of the bottle. These were not renewed during the period of test.

Three criteria of failure are used:

$$\Delta L = \pm 0.20\%$$

$$\Delta W = \pm 10.0\%$$

$$N^2 = 50\% \text{ of initial}$$

Criterion	Time to Failure by Various Criteria		
	0.1 N Solutions		Concentrated Solutions
	No. of Fresh Solutions	Total Exposure Time	Total Exposure Time
	3.65 g./l.	Hydrochloric Acid, HCl (ACS)	370 g./kg.
ΔL	2	3d.	2h.
ΔW	9	14d.	- ^a
N^2	10	15d.	5h.
	6.30 g./l.	Nitric Acid, HNO ₃ (ACS)	700 g./kg.
ΔL	3	4d.	2h. ^a
ΔW	9	14d.	-
N^2	11	16d.	5h.
	9.80 g./l.	Phosphoric Acid, H ₃ PO ₄ (ACS)	850 g./kg.
ΔL	22	127d.	6h.
ΔW	20	106d.	1.5d.
N^2	- ^a	- ^a	15d.
	9.81 g./l.	Sulfuric Acid, H ₂ SO ₄ (ACS)	960 g./kg.
ΔL	10 ^b	15d. ^b	24h. ^c
ΔW	15	39d.	18d.
N^2	16	56d.	- ^a

^aDiscontinued before failure was indicated by this criterion.

^bOne specimen only. Increase in length.

^cDecrease in length.

TABLE 9
CONDITION OF SPECIMENS STORED IN INORGANIC AQUEOUS SOLUTIONS FOR
24 MONTHS

The change in length (ΔL), the change in weight (ΔW), and the square of the frequency (N^2) are all expressed as percent of initial readings.

Criteria of failure are:

$$\begin{aligned}\Delta L &= + 0.20\% \\ \Delta W &= + 10.0\% \\ N^2 &= 50\% \text{ of initial}\end{aligned}$$

Ages at failure are interpolated to nearest 0.1 month up to 3 months and nearest 0.5 month above 3 months.

Note: Where no failure has occurred for a particular agent, the "age at failure" lines have been omitted.

Cement Curing Period	In 0.1 Normal Solutions								In 90% Saturated Solutions											
	W/C=0.6		W/C = 0.4						W/C=0.6		W/C = 0.4									
	Type I	Type I	Type I	Type V	O-C ₃ A	Type I	Type I	Type V	O-C ₃ A	Type I	Type I	Type V	O-C ₃ A	Type I	Type I	Type V	O-C ₃ A			
3d.	28d.	3d.	28d.	3d.	28d.	3d.	28d.	3d.	28d.	3d.	28d.	3d.	28d.	3d.	28d.	3d.	28d.			
ALUMINATE:	8.20 g./l., pH = 12.30								Sodium Aluminate NaAlO ₂ , (T)								1156 g./l., pH = 14.15			
ΔL	+0.08	-.06	+0.03	-.06	-.03	-.12	+0.04	-.03		+0.96 _a							+0.34 _a			
ΔW	+2.3	+9	+1.6	+1.6	+3.7 ^u	+7	+1.6	+1.1												
N ²	154	115	136	112	151	112	112	104		63							129			
N, cycles/sec.	5750	6010	6330	6310	6240	6280	6380	6480		4190							6890			
Age at Failure, Mo.	ΔL	-	-	-	-	-	-	-		4.5 _a							11.0 _a			
	ΔW	-	-	-	-	-	-	-												
	N ²	-	-	-	-	-	-	-												
BORATE:	9.98 g./l., pH = 10.43								Sodium Perborate, NaBO ₃ ·H ₂ O, (T)								40 g./l., pH = 10.78			
ΔL	+0.06	-.09	+0.08	+0.04	+0.02	-.06	+0.02	.00	+0.08	-.05	.00	-.04	.00	-.04	-.02	-.02	-.02			
ΔW	+1.1	+1	+1.1	+4	+8	+5	+8	+5	+1.5	+2	+1.2	+4	+1.2	+7	+1.0	+5	+5			
N ²	150	110	140	106	150	115	116	106	164	130	136	108	150	116	156	112				
N, cycles/sec.	5790	5780	6370	6330	6320	6340	6460	6640	5950	5920	6380	6230	6420	6340	6550	6400				

19.07 g./l., pH = 9.22																
Sodium Tetraborate, Na ₂ B ₄ O ₇ ·10H ₂ O, (NF)																
44 g./l., pH = 9.39																
ΔL	+4.2 ^b	+3.4 ^b	+3.3 ^{b,c}	+4.8 ^b	+3.6 ^b	+1.4 ^b	+1.6 ^b	+0.9 ^b	+0.8 ^b	+1.0 ^b	+1.0 ^b	+1.1 ^b	+0.8 ^b	+1.16 ^b	+1.0 ^b	+1.2 ^b
ΔW	+8.2	+10.2 ^a	+6.6 ^c	+5.2	+6.6	+8.1	+5.5	+7	+6.7	+10.2	+4.2	+4.5	+4.6	+4.5	+4.4	+4.8
N ²	155	97	124 ^c	106	148	107	105	98	171	112	135	113	157	113	115	118
N, cycles/sec.	5720	5280	5960 ^c	6140	6100	5760	6220	6080	6140	5620	6460	6410	6470	6080	6420	6450
Age at	ΔL	1.6 ^b	4.5 ^b	-	4.5 ^b	8 ^b	7.5 ^b	-	-	-	-	-	-	-	-	-
Failure	ΔW	-	22.5 ^a	-	-	-	-	-	-	-	-	-	-	-	-	-
Mo.	N ²	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CHLORATE: 10.64 g./l., pH = 7.35 Sodium Chlorate, NaClO ₃ , (T) 891 g./l., pH = 7.55																
ΔL	+0.3	-.02	+1.7	+2.7	+0.4	+0.4	+2.0	+1.0	+2.8	+6.1	+8.2	+1.22	+1.16	+1.14	+4.6	+2.4
ΔW	+3.1	+2.0	+1.9	+1.8	+2.3	+9	+2.0	+1.1	+4.6	+3.6	+5.2	+4.8	+4.6	+4.3	+2.8	+3.4
N ²	146	112	129	101	151	117	111	96	108	75	92	62	117	98	86	88
N, cycles/sec.	5720	5820	6340	6160	6150	6280	6120	6030	4860	4860	5400	4880	5400	5760	5400	5930
Aged at	ΔL	-	-	-	22 ^d	-	-	20 ^d	-	4	0.9	1.5	1.5	-	-	2.5
Failure,	ΔW	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Mo.	N ²	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
12.24 g./l., pH = 7.70 Sodium Perchlorate, NaClO ₄ , (R) 1724 g./l., pH = 5.95																
ΔL	-.02	+1.2	+1.8	-.11	+0.6	+0.7	+0.6	-.02	+0.4	+0.1	+0.4	+0.1	.00	-.04	-.01	-.01
ΔW	+3.4	+1.9	+2.0	+1.6	+2.1	+2.2	+2.2	+1.4	+5.5	+4.8	+2.8	+3.9	+2.3	+3.4	+3.3	+2.3
N ²	143	104	128	105	154	108	105	100	105	102	99	89	110	93	105	94
N, cycles/sec.	5570	5560	6290	6230	6200	6080	6000	6280	4900	5410	5610	5800	5360	5810	6070	5990
CONTROL: Saturated Limewater, Ca(OH) ₂ , (R) 1.5 g./l., pH = 12.20																
ΔL									-.01	-.04	-.03	.00	-.01	-.03	.00	+0.2
ΔW									+2.2	+1.9	+2.0	+1.4	+1.4	+7	+6	+6
N ²									140	103	128	104	156	109	98	112
N, cycles/sec.									5660	5410	6240	6020	6240	6230	5870	6150

- a/ Some uncertainty in wt., or time of failure based on change in wt., because of dense crust of crystals on exterior.
- b/ Some uncertainty in length, or time of failure based on change in length, because of crust of crystals on ends.
- c/ Measurement on one specimen only.
- d/ Failure indicated by only one of two specimens under test.

The change in length (ΔL), the change in weight (ΔW), and the square of the frequency (N^2) are all expressed as percent of initial readings.

$$\begin{aligned}\Delta L &= + 0.20\% \\ \Delta W &= + 10.0\% \\ N^2 &= 50\% \text{ of initial}\end{aligned}$$

See also "Explanatory Notes for Tables 7-10, 12 and 13."

Note: Where no failure has occurred for a particular agent, the "age at failure" lines have been omitted.

	In 0.1 Normal Solutions								In 90% Saturated Solutions									
Cement Curing Period	W/C=0.6		Type I		W/C = 0.4		Type V		O-C ₂ A	W/C=0.6		Type I		W/C = 0.4		Type V		O-C ₂ A
	3d.	28d.	3d.	28d.	3d.	28d.	3d.	28d.		3d.	28d.	3d.	28d.	3d.	28d.	3d.	28d.	
CARBONATES:	4.80 g./l., pH = 9.04				Ammonium Carbonate, (NH ₄) ₂ CO ₃ , (ACS)					< 325 g./l. ^a , pH = 9.09								
ΔL		-.02		-.03		-.04		-.05		-.05		-.04		-.08		-.08		
ΔW		+.2		+.2		+1.		+2.		+4.5		+2.2		+2.5		+2.1		
N ^b		120		106		113		103		104		107		124		108		
H,cycles/sec.		5650		6400		6380		6430		5400		6400		6760		6650		
	3.95 g./l., pH = 8.06				Ammonium Bicarbonate, NH ₄ HCO ₃ , (R)					191g./l., pH = 8.38								
ΔL	+.02	-.04	+.02	-.07	-.03	-.02	-.01	-.06	-.04	-.04	-.02	-.04		-.02	.00	-.02		
ΔW	+1.1	-.2	+1.1	+2.	+1.5	+9	+1.2	+8	+5	+2.4	+2.3	+3		+1.5	+1.2	+5		
N ^b	145	111	125	106	153	114	112	101	134	107	136	107		120	112	106		
H,cycles/sec.	5490	5850	6200	6380	6350	6230	6450	6260	5310	5750	6360	6340		6300	6380	6400		
	5.30 g./l., pH = 11.30				Sodium Carbonate, Na ₂ CO ₃ , (R)					200 g./l., pH = 11.63								
ΔL	.00	-.06	-.02	-.02	-.04	-.02	-.02	-.03	+16	+06	+10	+12	+02	.00	+06	+02		
ΔW	+5	-.2	+6	.0	+6	+3	.4	+1	+6.1	+5.4	+4.2	+4.4	+3.4	+2.5	+2.6	+2.4		
N ^b	150	113	132	112	140	114	114	102	121	95	128	107	147	111	105	99		
H,cycles/sec.	5610	5650	6250	6350	6090	6370	6370	6400	5020	5120	6240	6220	6250	6300	6200	6150		
	4.20 g./l., pH = 8.15				Sodium Bicarbonate, NaHCO ₃ , (R)					86 g./l., pH = 8.35								
ΔL	-.02	-.04	.00	-.08	-.01 ^c	-.05	+01	-.06	-.02	-.06	-.02	-.05	-.04	-.06	-.05	-.06		
ΔW	+6	+2	+8	+1	+6 ^d	+3	+5	+2	+5.5	+2.3	+2.6	+1.2	+2.2	+7	+8	+4		
N ^b	156	111	130	110	155 ^e	114	116	102	108	103	130	105	149	115	113	102		
H,cycles/sec.	5570	5630	6350	6320	6370 ^f	6310	6440	6260	4770	5720	6180	6160	6300	6310	6420	6330		
FERROCYNAMINE:	12.10 g./l., pH = 8.23				Sodium Ferrocyanide, Na ₄ [Fe(CN) ₆]·10H ₂ O, (T)					286 g./l., pH = 9.60								
ΔL	+06	+06	+10		+14	+15			+18	+11	+14		+16	-.01				
ΔW	+9	+2	+1.1		+6	+2			+1.4	+5	+1.2		+1.2	+2				
N ^b	143	102	123		149	110			142	97	124		142	110				
H,cycles/sec.	5580	5460	5840		6210	6250			5500	5430	5720		6030	6340				
NITRATES:	8.00 g./l., pH = 6.03				Ammonium Nitrate, NH ₄ NO ₃ , (ACS)					1692 g./l., pH = 4.88								
ΔL	+04	+01	+24	+45	-.16	+12	+13	+07	c	-.19	-.16	-.17	c	-.16	c	c		
ΔW	-4.8	-4.1	-5.3	-5.2	-3.0	-4.00	-5.9	-4.8	c	-5.9	-8.1	-9.1	c	-9.0	c	c		
N ^b	23	22	20	14	57	44	26	43	c	d	9	d	c	d	c	c		
H,cycles/sec.	2160	2640	2520	2290	3820	3960	2990	4060	c	d	1770	c	c	d	c	c		
Age at ΔL	-	-	18	-	-	-	-	-	-	-	-	-	-	-	-	-		
Failure ΔW	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-		
Mo. N ^b	11	8	11.5	9.5	-	15	11.5	14	0.07	0.2	0.2	0.4	0.2	0.5	0.1	0.1		
	15.56 g./l., pH = 4.96				Lead Nitrate, Pb(NO ₃) ₂ , (P)					495 g./l., pH = 2.98								

ΔL	+4.1	+4.30	+3.59	+3.56	+4.12	+3.34	+3.06	+3.16	+3.19	+3.11 ^b	+3.25	+3.58	+3.20	+3.15	+3.58	+3.23
ΔW	+5.3	+6.9	+4.6	+6.6	+4.6	+3.7	+5.9	+6.8	+17.7	+11.9 ^b	+18.2	+15.1	+21.1	+7.0	+16.0	+24.7
N^2	121	90	100	75	123	87	79	69	113	80 ^b	87	72	104	70	80	58
N, cycles/sec.	4920	5230	5660	5800	5470	5590	5270	5360	4710	5020 ^a	5320	5130	5090	4970	5180	4760
Age at ΔL	0.5	1.0	5	1.4	-	7	-	-	3	11.5	2.7	2.2	5.5	-	2.8	4
Failure, ΔW	-	-	-	-	-	-	-	-	5.5	10	8	7	5	-	4	3.5
Mo. N^2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
12.82 g./l., pH = 6.90 Magnesium Nitrate, $Mg(NO_3)_2 \cdot 6H_2O$, (T) 1152 g./l., pH = 3.75																
ΔL	+3.5	-0.5	+4.6	+0.4	+5.1	+0.4	+2.9	+0.7	c	+2.42	+1.94	+2.16	+4.8	+4.5 ^b	+2.56	+2.88
ΔW	+3.6	+2.0	+3.6	+1.5	+5.4	+1.9	+4.1	+2.4	c	+4.2	+3.7	+4.4	+5.4	+10.7	+5.6	+3.2
N^2	145	107	119	110	140	110	98	81	c	21	50	37	106	81	42	d
N, cycles/sec.	5520	5710	6140	6290	5960	6280	5810	5810	c	2490	4000	3660	5080	5350	3410	d
Age at ΔL	2.1	-	2.2	-	0.4	-	5.5	-	0.8	6	5.5	7	9.5	8.5 ^b	3.5	4.5
Failure, ΔW	-	-	-	-	-	-	-	-	-	-	-	-	-	20.5 ^b	-	-
Mo. N^2	-	-	-	-	-	-	-	-	3	9.0	-	19	-	-	18	12
10.11 g./l., pH = 6.81 Potassium Nitrate, KNO_3 , (T) 284 g./l., pH = 6.89																
ΔL	+0.5	+1.0	+1.1	+1.0	+1.1	-0.6	+0.6	+0.5	+3.4	+3.3	+6.2	+8.6	+2.9	+1.9	+2.8	+2.6
ΔW	+2.8	+1.8	+2.4	+1.0	+3.6	+1.3	+2.6	+1.4	+3.2	+3.5	+4.8	+3.8	+6.2	+2.7	+3.6	+2.4
N^2	161	107	129	107	123	117	122	98	126	98	106	89	138	103	95	85
N, cycles/sec.	5700	5790	6470	6220	6160	6380	6270	6280	5140	5430	5900	5700	5940	6090	5630	5900
Age at ΔL	-	-	-	-	-	-	-	-	3.5	6	3	2.5	7.5	-	8	15.5
Failure, ΔW	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Mo. N^2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
8.50 g./l., pH = 7.70 Sodium Nitrate, $NaNO_3$, (T) 788 g./l., pH = 7.52																
ΔL	+0.2	+0.8	+1.9	.00	.00	-0.2	+0.7	.00	+2.0	+2.8	+5.7	+2.4	+1.2	.00	+1.9	+0.3
ΔW	+2.8	+1.8	+2.6	+1.5	+2.0	+1.5	+1.8	+1.2	+4.5	+3.5	+4.1	+2.9	+4.2	+2.5	+3.2	+2
N^2	152	117	128	110	153	114	108	93	124	93	98	91	127	95	85	96
N, cycles/sec.	5940	5740	6290	6380	6340	6270	6290	6260	5310	5300	5560	5800	5780	5830	5600	6080
Age at ΔL	-	-	4	-	-	-	-	-	21	16.5	3	21	-	-	-	-
Failure, ΔW	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Mo. N^2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NITRITE: 6.90 g./l., pH = 7.70 Sodium Nitrite, $NaNO_2$, (ACS) 765 g./l., pH = 8.00																
ΔL	+0.2	+0.4	+0.9	.00	+0.2	-0.2	+1.0	-0.4	+1.8	+5.6 ^b	.00	+2.8	+0.5	e	f	-1.4
ΔW	+2.6	+1.9	+2.1	+1.8	+1.8	+1.2	+1.5	+1.0	+3.1	+2.3	+3.5	+1.9	+1.9	+2.0	+1.2	-1.6
N^2	145	105	126	103	151	115	107	97	119	96	109	92	126	84	103	78
N, cycles/sec.	5850	5740	6220	6260	6240	6350	6350	6320	5210	5480	5800	5840	5870	5450	6150	5560
Age at ΔL	-	-	-	-	-	-	-	-	-	7.5 ^b	-	16	-	-	-	-
Failure, ΔW	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Mo. N^2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CONTROL: Saturated Limewater, $Ca(OH)_2$, (R) 1.5 g./l., pH = 12.20																
ΔL	-	-	-	-	-	-	-	-	-	-0.1	-0.2	-0.3	.00	.00	-0.3	+0.2
ΔW	-	-	-	-	-	-	-	-	-	+2.0	+2.0	+1.8	+1.4	+1.3	+7	+5
N^2	-	-	-	-	-	-	-	-	-	138	106	132	108	160	115	105
N, cycles/sec.	-	-	-	-	-	-	-	-	-	5610	5490	6310	6120	6300	6380	6260

a/ See text.
b/ Measurement on one specimen only.
c/ Test terminated at earlier age.

d/ Accurate reading not obtainable.
e/ Caps of prisms are loose.
f/ Caps of prisms are gone.

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	ΔL	+1.05	+1.31	+1.57	+1.42	+1.26	+1.22	+1.29	+1.45	+1.84	+1.46	+1.64	+1.54	+1.31	+1.30	+1.37
	ΔW	+6.0	+5.0	+4.1	+2.9	+4.4	+3.2	+4.9	+4.0	-4.9	-4.3	-6.0	-7.9	-7.5	-8.6	-13.4
	N^2	110	58	116	100	153	115	110	105	83	71	93	80	123	90	82
N, cycles/sec.		5000	4180	6000	6100	6400	6380	6460	6540	4340	4680	5290	5500	5630	5750	5820
Age at	ΔL	5.5	7.5	7	11	10	13.5	11	4.5	4.5	6.5	8	10	11.5	5	4
Failure, ΔW		-	-	-	-	-	-	-	-	-	-	-	-	-	-	12.5
Mo.	N^2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
6.02 g./l., pH = 6.95 Magnesium Sulfate, $MgSO_4$, (ACS) 311 g./l., pH = 8.16																
	ΔL	+1.07	+1.13	+1.22	+1.02	+1.03	+1.02	+1.02	.00	f	+1.23	e	+1.40	+1.08	+1.30	e
	ΔW	+3.3	+1.8	+2.1	+1.4	+1.2	+1.3	+1.3	+1.4	f	+1.5	-4.0 ^e	-1.2	-2.6	+1.5	-3.4
	N^2	50	102	112	105	147	119	112	103	f	118	129 ^e	107	130	112	106 ^e
N, cycles/sec.		3470	5600	5880	6260	6260	6370	6360	6470	f	5900		6250	5910	6290	6270 ^e
Age at	ΔL	7.45	-	14.5	-	-	-	-	-	7	13	-	8.5	-	11	8 ^e
Failure, ΔW		-	-	-	-	-	-	-	-	(9) ^g	-	-	-	-	-	14 ^e
Mo.	N^2	16.5	-	-	-	-	-	-	-	(9) ^g	-	-	-	-	-	-
8.45 g./l., pH = 3.22 Manganese Sulfate, $MnSO_4 \cdot H_2O$, (ACS) 646 g./l., pH = 1.26																
	ΔL	+2.31	+1.64	+1.67	+1.03	+1.19		+1.40		-1.38	-2.40	-1.32	-1.02	-1.93		-1.36
	ΔW	+6.1	+2.6	+4.7	+1.6	+3.2		+3.8		-5.4	-38.1	-3.0	-9.8	-17.9		-5.1
	N^2	111	87	52	105	190		120		141	86	62	101	156		108
N, cycles/sec.		4790	4970	4080	6380	6990		6530		5660	5220	4570	6140	6360		6360
Age at	ΔL	4	8	5.5	-	-		7.5		10.5	2.0	10.5	4	7		6
Failure, ΔW		-	-	-	-	-		-		-	0.8	-	-	8		-
Mo.	N^2	-	-	-	-	-		-		-	-	-	-	-		-
7.10 g./l., pH = 8.15 Sodium Sulfate, Na_2SO_4 , (R) 175 g./l., pH = 7.00																
	ΔL	+1.06	+1.05	+1.02	.00	+1.02		.00		+3.46	+5.55	+5.04	f	+1.28		+1.48
	ΔW	+1.1	+1.5	+1.9	-1	+1.9		+1.8		+11.8	+12.6	+13.4	f	+4.0		+5.6
	N^2	138	105	64	108	193		118		73	26	39	f	194		80
N, cycles/sec.		5520	5560	4620	6470	7090		6480		4040	2790	3540	f	6780		5460
Age at	ΔL	-	-	-	-	-		-		0.3	1.0	2.4	3.5	12 ^b		8.5
Failure, ΔW		-	-	-	-	-		-		10.5	5.5	11	(6) ^g	-		-
Mo.	N^2	-	-	-	-	-		-		-	2.1	12	(6) ^g	-		-
6.00 g./l., pH = 1.42 Sodium Bisulfate, $NaHSO_4$, (T) 387 g./l., pH = 0 ¹																
	ΔL	e		+1.76	+1.84	+1.69		+1.74		f		f	f	f		f
	ΔW	e		-1.5	+1.9	-2.2		-1.8		f		f	f	f		f
	N^2	e		47	72	117		76		f		f	f	f		f
N, cycles/sec.		e		3910	5220	5560		5260		f		f	f	f		f
Age at	ΔL	2.5		3.5	7	4.5		4.5		0.07		0.07	0.03	.07		0.07
Failure, ΔW		-		-	-	-		-		0.03		0.07	0.07	.07		0.1
Mo.	N^2	-		14.5	-	-		-		(0.1) ^g		0.6 ^c	0.6	.6		0.6
SULFIDE: 12.01 g./l., pH = 12 to 12.5 ^h Sodium Sulfide, $Na_2S \cdot 9H_2O$, (T) 507 g./l., pH = 13 to 14 ^h																
	ΔL	+1.02	+1.02	+1.05 ^c	+1.01	-1.01	.00	.00	-1.01	+1.16	+1.07	+1.07	+1.03 ^c	+1.06	+1.04	+1.04
	ΔW	+1.6	-1.2	+1.4 ^c	.0	+1.5	+1.1	+1.5	.0	+1.2	+1.1	+1.0	+1.6 ^c	+1.2	+1.0	+1.4
	N^2	149	116	118 ^c	104	148	110	115	102	141	111	114	104 ^c	132	113	111
N, cycles/sec.		5730	5800	5980 ^c	6370	6450	6390	6450	6470	5520	5590	5960	6320 ^c	6000	6430	6260

TABLE 11 (Cont.)

Cement Curing Period	In 0.1 Normal Solutions								In 90% Saturated Solutions							
	W/C=0.6		W/C = 0.4						W/C=0.6		W/C = 0.4					
	Type I		Type I	Type V		O-C ₃ A			Type I		Type I	Type V		O-C ₃ A		
	3d.	28d.	3d.	28d.	3d.	28d.	3d.	28d.	3d.	28d.	3d.	28d.	3d.	28d.	3d.	28d.
SULFITES:	12.61 g./l., pH = 9.00				Sodium Sulfite, Na ₂ SO ₃ ·7H ₂ O, (ACS)				472 g./l., pH = 9.48							
ΔL	+1.34	+0.07	+1.15	+0.02	+1.10	+0.02	+0.06	-.02	f	-	+0.02	+6.46	-.04	+1.10	-.03	-.04
ΔW	+1.2	+1.1	+1.0	.0	+1.2	+1.5	+1.4	-.1	f	-	+1.6	+12.5	+1.8	+2.8	+1.4	+1.0
N ²	122	115	126	108	154	114	113	104	f	-	112	14	150	106	110	98
N, cycles/sec.	5280	5910	6320	6390	6540	6550	6430	6640	f	-	5940	2300	6310	6100	6360	6350
Age at Failure, Mo.	ΔL 9.5	-	-	-	-	-	-	-	7.5	-	-	8.5	-	-	-	-
	ΔW -	-	-	-	-	-	-	-	-	-	-	13.5	-	-	-	-
	N ² -	-	-	-	-	-	-	-	<15 ⁱ	<12 ⁱ	-	12	-	-	-	-
	5.20 g./l., pH = 2.20				Sodium Bisulfite, NaHSO ₃ , (ACS)				90 g./l., pH = 2.45							
ΔL	e	+4.48 ^c	+1.76	+1.38	+2.4		+1.90		f	+0.08 ^c	+3.66	.00	e		e	
ΔW	e	+1.3 ^c	+2.6	+2.0	-2.3		-5.9		f	-1.4 ^c	-10.9	-11.0	-27.0 ^e		-26.5 ^e	
N ²	e	12 ^c	84	47	133		48		f	92 ^c	23	89	127 ^e		73 ^e	
N, cycles/sec.	e	1880 ^c	5170	4240	5810		4080		f	5290 ^c	2260	5890	5710 ^e		5200 ^e	
Age at Failure, Mo.	ΔL 3	3	7	5.5	13		6		2.0	2.7 ^c	2.8	-	5 ^c		2.7 ^c	
	ΔW (6) ^g	-	-	-	-		-		4.5	-	5.5	4.5	5		4.5	
	N ² 6	5	-	-	-		-		2.8	-	5.5	-	-		-	
THIOSULFATE:	12.41 g./l., pH = 7.28				Sodium Thiosulfate, Na ₂ S ₂ O ₃ ·5H ₂ O, (T)				958 g./l., pH = 8.70							
ΔL	+1.12		+1.28	+1.40	+1.10		+1.36		+1.14		+1.38	+1.13	+1.12		+1.12	
ΔW	+1.6		+2.3	+2.0	+1.8		+1.8		+3.6		+4.2	+1.2	+3.8		+2.3	
N ²	129		110	84	145		93		125		107	92	128		101	

N, cycles/sec.	5400		6010	5630	6240		5810	5430	5860	5850	5920		6150
Age at ΔL	-		13	11.5	-		10	-	9	-	-		-
Failure, ΔW	-		-	-	-		-	-	-	-	-		-
Mo. N^2	-		-	-	-		-	-	-	-	-		-
PERSULFATE:													
			13.57 g./l., pH = 1.79				Potassium Persulfate, $K_2S_2O_8$, (ACS)				180 g./l., pH = 1.55		
ΔL	k		+41	+34	+08		+13	+2.61	+2.63	+4.44	+32		+1.86
ΔW	+6.3		+1.4	+9	+9		+1.3	+6.1	+4.7	+6.7	+2.0		+6.8
N^2	52		117	92	154		105	124	69	34	137		67
N, cycles/sec.	3500		6120	5980	6270		6350	5400	4690	3550	5980		5050
Age at ΔL	4		9.5	13	-		-	0.4	6	0.9	9.5		6.5
Failure, ΔW	-		-	-	-		-	-	-	-	-		-
Mo. N^2	-		-	-	-		-	-	-	13	-		-
CONTROL:													
			Saturated Limewater, $Ca(OH)_2$, (R)							1.5 g./l., pH = 12.20			
ΔL								-0.02	-0.02	-0.03	.00	-0.02	-0.03
ΔW								+1.9	+1.6	+1.8	+1.2	+1.3	+0.7
N^2								140	106	132	108	153	116
N, cycles/sec.								5650	5500	6310	6130	6170	6410
													5700
													6110

- a/ Accurate reading not obtainable.
b/ Failure indicated by only one of two specimens under test.
c/ Measurement on one specimen only.
d/ Some uncertainty in weight, because of crystals on exterior.
e/ Caps of prisms are gone.
f/ Test terminated earlier than 15 months.
g/ Failure not indicated by this criterion, but test terminated at age shown.
h/ By Hydrion paper. Not readily measurable electrometrically.
i/ Age of failure unknown (incomplete data), but specimen too weak to handle at age indicated.
k/ Too warped to measure.
l/ As read on pH meter, which has lower limit of 0.

TABLE 12
CONDITION OF SPECIMENS STORED IN SYNTHETIC
SEAWATER FOR 6 MONTHS

The change in length (ΔL), the change in weight (ΔW), and the square of the frequency (N^2) are all expressed as percent of initial readings.

Composition of synthetic sea water is given in Table 3.

Criteria of failure are:

$\Delta L = \pm 0.20\%$
 $\Delta W = \pm 10.0\%$
 $N^2 = 50\%$ of initial

However, no failures had occurred in the first six months, with the possible exception noted in the footnote for specimens stored at 73 F.

Synthetic Seawater										Concen- trated Synthetic Sea- water ^a
Cement Type	W/C = 0.6		W/C = 0.4						W/C = 0.4	
	Type I		Type I		Type V		0-C ₃ A		Type V	
Curing Period	3d.	28d.	3d.	28d.	3d.	28d.	3d.	28d.	3d.	
Stored at 73 F ^b										
ΔW N ²	% of Initial	+3.0 118	1.2 111	+3.0 111	+ .7 109	+3.2 ^c +126 ^c	+ .7 109	+1.8 91	+1.0 98	+4.6 139
N		5190	5580	5980	6110	5540 ^c	6240	5640	6200	5650
Stored at 160 F										
ΔL ΔW N ²	% of Initial					+ .19 +2.2 149				+ .18 +3.8 149
N						5720				5740
Stored at 200 F										
ΔL ΔW N ²	% of Initial					+ .16 +2.3 153				+ .13 +3.7 147
N						5860				5900

^aConcentration is 5 times that of synthetic seawater.

^bSome uncertainty in length, or time of possible failure based on length, because of crust of crystals on ends. When such crystals were removed from crystals by gentle scraping, no increase in length was any longer measured.

^cAverage of 2 sets of two specimens each.

TABLE 13
AGES AT FAILURE IN ORGANIC ACIDS AND "EDTA"

All specimens were made with Type I cement and moist cured 28 days.

Solutions of less than 100 g./1000 ml. were renewed more frequently than those of higher concentrations, but both schedules were interrupted and were somewhat irregular. The number of fresh solutions used for each pair of specimens is recorded below.

The change in length (ΔL), the change in weight (ΔW), and the square of the frequency (N^2) are all expressed as percent of initial readings.

Criteria of failure are:

$$\Delta L = \pm 0.20\%$$

$$\Delta W = \pm 10.0\%$$

$$N^2 = 50\% \text{ of initial}$$

Age at Failure by Various Criteria, Months											
In 0.1 Molar Solutions				In Intermediate Concentrations				In Concentrated Liquids			
W/C = 0.6		W/C = 0.4		W/C = 0.6		W/C = 0.4		W/C = 0.6		W/C = 0.4	
No. of Fresh Solu-tions	Total Expo-sure Time	No. of Fresh Solu-tions	Total Expo-sure Time	No. of Fresh Solu-tions	Total Expo-sure Time	No. of Fresh Solu-tions	Total Expo-sure Time	No. of Fresh Solu-tions	Total Expo-sure Time	No. of Fresh Solu-tions	Total Expo-sure Time
ACIDS:											
Lactic Acid, $\text{CH}_3\text{CHOHCOOH}$, (USP)											
9.01 g./l. solution						a					
ΔL	5	61d.	9	105d.				0	12d.	0	10d.
ΔW	9	104d.	7	100d.				0	24d.	1	79d.
N^2	11	110d.	14	124d.				-	-	-	-
Stearic Acid, $\text{CH}_3(\text{CH}_2)_{15}\text{COOH}$, (USP)											
200 g./l. benzene											
ΔL				0	4d.	0	4d.				
ΔW				0	2d.	0	4d.				
N^2				-	-	-	-				
Lactic Acid, $\text{CH}_3\text{CHOHCOOH}$, (USP) Acetic Acid, CH_3COOH , (Pr)											
20 g. lactic + 20 g. acetic/0.960 l. water											
ΔL				0	5h.	0	12d.				
ΔW				4	7d.	2	84d.				
N^2				1	4d.	0	72d.				
AMINO ACID SALT: "EDTA" - Ethylenediamine tetraacetic acid (disodium salt), $\text{NH}_2\text{CH}_2\text{N}(\text{CH}_2\text{COOH})_2(\text{CH}_2\text{COONa})_2$, (R)											
34.42 g./l. solution				125 g./l. water							
ΔL	0	5h.	0	66d.b/	0	62d.	1	72d.			
ΔW	4	104d.	5	94d.	1	106d.	2	120d.			
N^2	5	109d.	10	112d.	0	12d.	1	94d.			

^a100% of grade received, used without dilution.

^bOne specimen only.

TABLE 14

CONDITION OF SPECIMENS STORED IN ORGANIC CHEMICALS FOR 6 MONTHS

All specimens made with Type I cement and moist cured 28 days.							
The change in length (ΔL), the change in weight (ΔW), and the square of the frequency (N^2) are all expressed as percent of initial readings.							
		In 0.1 M Solutions		In Intermediate Concentrations		In Concentrated Solutions or Liquids	
		W/C = 0.6	W/C = 0.4	W/C = 0.6	W/C = 0.4	W/C = 0.6	W/C = 0.4
ALCOHOLS:		Methyl Alcohol, Absolute, CH_3OH , (Pr)					
		3.20 g./l. solution		500 g./500 ml. water		a	
ΔL		-.02	-.04	-.02	-.04	-.02	-.01
ΔW	% of	+.6	+.2	-.2	-.5	-.5	-1.0
N^2	Initial	101	106	98	98	86	94
N		5270	6120	5090	5770	4760	5700
		t-Butyl Alcohol, $(\text{CH}_3)_3\text{COH}$, (R)					
		7.41 g./l. solution		500 g./500 ml. water		a	
ΔL		.00	.00	+.02	+.02	-.04	-.05
ΔW	% of	+.8	+.6	-.4	-.8	-1.4	-1.5
N^2	Initial	107	100	102	100	97	90
N		5280	5820	5160	5800	4980	5600
		Ethylene Glycol, $(\text{CH}_2\text{OH})_2$, (T)					
		6.21 g./l. solution		500 g./500 ml. water		a	
ΔL		-.01	.00	.00	.00	-.15	-.03
ΔW	% of	-.0	+.6	+.8	+.1	+.5	-1.2
N^2	Initial	108	100	94	96	85	87
N		5420	5780	5090	5670	4700	5440
		Glycerol, $\text{CH}_2\text{OHCHOHCH}_2\text{OH}$, (ACS)					
		9.21 g./l. solution		500 g./500 ml. water		a	
ΔL		.00	.00	.00	.00	.09	-.10
ΔW	% of	+.9	+.6	+.8	-.4	-1.1	-3.5
N^2	Initial	105	101	95	102	97	92
N		5260	6020	5080	5850	5070	5700
SUGAR:		Sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, (USP)					
		34.23 g./l. solution		500 g./500 ml. water			
ΔL		-.10	.00	-.01	.00		
ΔW	% of	+1.8	-.2	-.5	-.5		
N^2	Initial	101	101	102	99		
N		5230	5820	5080	5780		

TABLE 14 (Cont.)

		In 0.1 M Solutions		In Intermediate Concentrations		In Concentrated Solutions or Liquids	
		W/C = 0.6	W/C = 0.4	W/C = 0.6	W/C = 0.4	W/C = 0.6	W/C = 0.4
ESTERS:		Butyl Stearate, $C_{17}H_{35}COOC_4H_9$, (P)					
		a					
ΔL						-.02	+.02
ΔW	% of					-1.1	-.9
N^2	Initial					107	102
N						5730	5910
		Glyceryl Tristearate, $(C_{17}H_{35}COO)_3C_3H_5$, (T)					
		30 g./l. benzene					
ΔL				-.09	-.09		
ΔW	% of			-.9	-1.0b		
N^2	Initial			101	97		
N				5170	5730		
HYDROCARBON:		Benzene, C_6H_6 , (PI)					
		a					
ΔL						-.08	-.06
ΔW	% of					-.8	-.8
N^2	Initial					105	97
N						5060	5770
DRYING OIL:		Linseed Oil, (P)					
		a					
ΔL						+.01	+.02
ΔW	% of					-1.3	-.8
N^2	Initial					100	100
N						5060	5920

^a100% of grade received, used without dilution.

^bOne specimen only.

Sulfate Attack on Concrete Pavements in Mississippi

FAY A. LOSSING, Assistant Testing Engineer, Mississippi State Highway Department

During the past 15 years, the Testing Division of the Mississippi State Highway Department has observed and attempted to determine the causes of deterioration of concrete on some sections of highways within the state. Originally, it was believed that the deterioration was the result of physical causes, such as excessive finishing, overstressing, and lack of or improper placing of load transfer devices at joints. The deterioration consists of a gradual development of map cracking, discoloration in the area of the cracks, later scaling of the top surface, and eventual disintegration of the entire depth of the concrete in some cases. The phenomenon normally appears at joints and cracks.

Recently it was suspected that sulfate reaction may be a contributing factor in this deterioration. Suspicion was aroused when a concrete pavement was removed during new construction in an area where the presence of large amounts of sulfates was known to exist in the native surrounding soil. Tests and investigations confirmed the belief that these sulfates, transported by surface water, combined with the tricalcium aluminate in the portland cement used in the concrete to produce calcium sulfoaluminate crystals (ettringite). These crystals then grow in volume, resulting in overstressing and disintegration of the concrete.

As a result of this finding, the Testing Division has intensified its efforts toward an investigation of concrete deterioration resulting from sulfate attack. Various concrete pavements and some concrete parking lots in widely separated areas of the state have been and are being examined for evidence of sulfate attack. Results of these studies are reported in this paper.

•FOR THE PAST 15 yr, the Testing Division of the Mississippi State Highway Department has been observing concrete pavements which have developed a condition now well established as being at least partially due to a reaction of waterborne sulfates with portland cement. The theory of this reaction, in simplest terms, is that waterborne sulfates from surrounding and possibly underlying soils, react with the tricalcium aluminate (C_3A) in the cement to form calcium sulfoaluminate (ettringite). On evaporation of the water, this chemical deposits crystals which grow in volume with repeated depositions, eventually disrupting the concrete by overstressing. The attack always begins at a joint or at a crack in the concrete and, generally, at the intersection of a longitudinal and a transverse joint.

Disruption of the concrete in the form of surface crazing or map cracking usually appears within 7 or 8 yr after construction. The concrete adjacent to these cracks becomes discolored with a dark-colored exudation which gradually turns light gray (Fig. 1). The cracking increases and spreads until the upper portion of the concrete

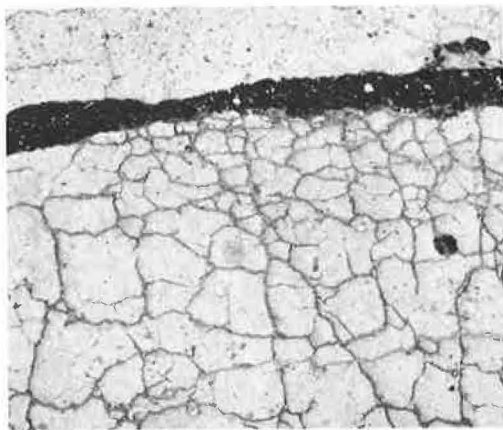


Figure 1. Typical appearance of intermediate stage of sulfate reaction in concrete.

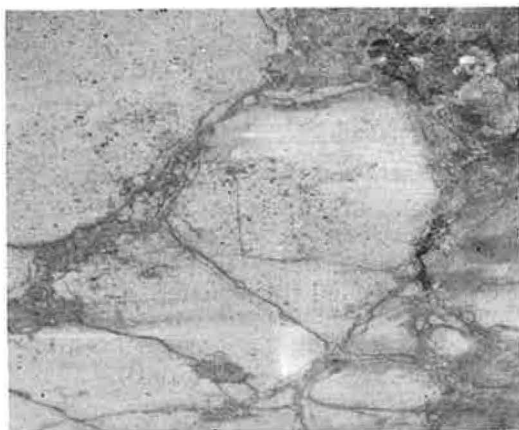


Figure 2. Close-up of cracking and spalling of concrete subjected to sulfate reaction.

separates from the lower portion and eventually spalls off (Fig. 2). It is believed that the original disruption occurs at the surface due to the more rapid evaporation of moisture from this area. The disintegration apparently progresses downward with time, finally resulting in disruption of the entire depth of concrete.

This phenomenon at first was believed to be caused by one or more of the following: excess finishing, improperly placed reinforcing steel or dowel bars, and concentrations of stresses due to other faulty joint construction. Before our first observation of the phenomenon, other states and agencies were experiencing alkali-silica reaction in concrete. At that time, the Testing Division explored this possibility in connection with our concretes and determined that, with one or two exceptions in the extreme northeastern portion of the state, concrete made with Mississippi aggregates is not susceptible to serious alkali-silica reaction. Aggregates used in the pavements discussed in this paper did not originate in the northeastern part of the state. It is our belief, therefore, that the deterioration of these pavements is not due to alkali-silica reaction.

These conditions first appeared on US 49, just north of Jackson, Miss. Cracking and discoloration were noted but were not considered serious at that time. The pavement was partly removed due to new construction and a portion was covered with asphalt for use as a service road before the conditions had progressed to an advanced stage. No investigations were made, therefore, but the same early conditions prevailed as on pavements later investigated.

It was only recently that Mr. and Mrs. Bryant Mather, on being consulted by the Testing Division and furnished samples of concrete in the process of disintegration, advised that the phenomenon appeared to be caused by sulfate reaction. With their cooperation, investigations were intensified, resulting in a tentative conclusion that waterborne sulfates, combined with a high C_3A content in the cement, constitute the primary contributing cause of the disintegration.

GENERAL DATA

Four sections of Mississippi highways exhibiting the foregoing conditions have been investigated and are discussed here. These four sections were constructed with the following common features: normal steel wire mesh reinforcement, formed longitudinal and transverse joints, load transfer dowels at all transverse joints, Type I cement, and a cement factor of 1.45 barrels/cu yd of concrete. Features not common to the four sections are given in Table 1.

At the time of construction of the projects studied, there were no specified requirements for aluminum oxide (Al_2O_3) or ferric oxide (Fe_2O_3) in Type I cement and no requirement for C_3A , a function of the two oxides. Consequently, the commercial laboratories testing the cement did not determine these values. Fortunately, however, for the purpose of this study, the cement companies did make such determinations and maintained complete records. During the investigation into possible sulfate reaction, the companies that produced cement for the four projects furnished, at our request, the analyses of the cement (Table 2). The values shown for each project and used in the following discussion are pertinent for the year during which shipments of cement were made.

PWA 75 AND PWA 327A,
CHICKASAW COUNTY

During 1950, the author and A. R. Brickler of the Portland Cement Association made a detailed survey of this project, located in Chickasaw County, on Miss. 15, south of Houston. At the time of this survey, a large number of the interior corners (intersection of longitudinal and transverse joints) in the central portion of this project displayed distinct signs of distress in the form of broken and spalled concrete. There was some indication of distress at a number of transverse joints between the center and the edge of the slab. Tentatively, it was concluded from this survey that the distress was caused by either excess finishing, improper alignment of the steel dowels, otherwise faulty joint construction, or a combination of some or all of these factors. Since 1950, the disruption has advanced greatly.

As will be noted from Table 1, this 25-yr-old pavement was paved with two brands of cement: the south 2.75 mi and the north 3.57 mi with Brand B, the center 4.72 mi with Brand A(1). All other factors were the same (Fig. 3). According to the data furnished by the cement companies (Table 2), at the time of production for this project Brand A(1) contained an average of 17.2 percent C_3A ; Brand B, an average of 11.3 percent. (Whenever a value for C_3A is stated here it is the calculated value.)

TABLE 1
CONSTRUCTION FEATURES FOR FOUR SECTIONS OF MISSISSIPPI HIGHWAYS INVESTIGATED FOR SULFATE REACTIONS

Project	County	Highway	Year Paved	Cross-Section	Length (mi)	Subgrade	Base Under Pavement	Curing Method	Location of Aggregate Source	Brand Cement Used	Joint Spacing (ft)		Wt Wire Mesh Reinforcing (lb/100 sq ft)	Avg. Strength	
											Expansion	Contr.		Beam ^a	Core ^b
PWA 75, 327A	Chickasaw	Miss. 15	1939	9, 6, 9 in. x 20 ft.	11.04	Porters Creek	15 in. A2	Cotton mats	Near Columbus	A(1), B	40	None	53	872	6,304
F1(5), F32(4)	Lee, Itawamba	US 78	1948	8, 6, 8 in. x 22 ft.	13.68	Coffee sand and Mooreville chalk	15 in. A2	Paper	Columbus	A(1), B, C, D, E	-c	20 1/2	59	815	6,007
U32(5)	Lauderdale	US 80	1949	8 in. uni-form x 24 ft.	6.16	Zilpha, Winona, Tallabatta formations	12 in. A2	Paper	Hattiesburg	A(1)	-c	31 1/2	39	886	5,325
PWS 50A	Issaquena	US 61	1938	9, 6, 9 in. x 20 ft.	6.99	Sharkey clay	None	Cotton mats	Clabornne	A(2)	90	30	53	821	6,323

^aFlexural, at 28 days.

^bCompressive, at variable ages, all more than 28 days.

^cExpansion joints spaced according to air temperature; none placed if temperature was 70 deg or above.

TABLE 2
VALUES FOR CEMENT USED IN PAVING MISSISSIPPI HIGHWAYS
INCLUDED IN STUDY

Brand Symbol	Year	Yearly Avg. Percentage				Project Furnished
		Al ₂ O ₃	Fe ₂ O ₃	C ₃ A	C ₄ AF	
A(1)	1938	8.4	3.3	16.7	10.0	—
	1939	8.4	3.0	17.2	9.1	PWA 75, 327A
	1948	7.5	3.8	13.5	11.6	F1(5), F32(4), U32(5)
	1949	7.2	3.9	12.5	11.9	UI-251(7)
A(2)	1938	6.3	2.6	12.3	7.9	PWS 50A
B	1939	5.8	2.4	11.3	7.3	PWA 75, 327A
	1948	5.2	2.4	9.7	7.3	F1(5), F32(4), U32(5)
C	1948	5.7	2.3	11.2	7.0	F1(5), F32(4), U32(5)
D	1948	5.8	3.3	9.8	10.0	F1(5), F32(4), U32(5)
E	1948	6.3	2.4	12.6	7.3	F1(5), F32(4), U32(5)

In August 1964, a second detailed survey was made; in the section paved with Brand A(1) cement, it was noted that almost every transverse joint was seriously broken and spalled with the spalled area in most cases extending several feet from the joint. In numerous places the area adjacent to the longitudinal joint, between transverse joints, was badly spalled. Figure 4 is a typical example of the conditions existing on this section of highway.

In the two sections paved with Brand B cement, these conditions do not exist; the concrete shows only the normal signs of age, with one exception between stations 455 and 470 (approximate), a distance of about 1,500 ft or a normal day's run at that time. The conditions here are the same as in the Brand A(1) section. The reason for this exception has not been determined. At the time of paving the project, cement was in somewhat short supply and a different cement may have been used on the day that this section was paved, though records do not reveal such change.

Cores were drilled recently from this pavement, in both good and bad areas. Figure 5 shows typical examples of the condition of the concrete. An examination of the cores obtained shows the following:

1. Station 463 + 55 (in the 1,500-ft section of distressed concrete made from Brand B cement, according to our records)—concrete contains an abundance of ettringite, some gel and indication of frost damage, all suggesting the possibility of minor alkali-silica reaction as a result of previous cracking of the concrete;
2. Station 518 + 75 (Brand B cement, concrete in good condition)—concrete contains some gel and ettringite; and
3. Station 364 + 09 (Brand A(1) cement, concrete spalled and broken badly)—concrete contains a considerable amount of ettringite and some gel; a large amount of calcite is present in surface cracks.

This project lies in the Porters Creek formation, with all embankments and cuts consisting of this type of soil. Porters Creek clay is a dark gray, blocky, shaly clay, slightly glauconitic and micaceous, containing gypsum crystals (calcium sulfate) and some marcasite nodules which weather rapidly to hydrated iron sulfate (melanterite). A sample of the soil from a typical cut contained 1.88 percent soluble sulfate (as determined by U. S. Army Corps of Engineers Test Method CRD-C403-59) and had a pH of 3.1 (Table 3). Approximately 15 in. of fair quality sand clay were placed as a base under the concrete pavement.

F1(5), F32(4), U32(5)—LEE AND ITAWAMBA COUNTIES

In Lee and Itawamba Counties, on US 78, east of Tupelo, is a concrete highway paved in 1948. Several years after the highway was paved, the concrete in various parts of the project was showing signs of deterioration. Alkali-silica reaction was again suspected. However, the aggregates were obtained from the Columbus, Miss. area and these are definitely not alkali-reactive aggregates.

This pavement was placed during a time period when portland cement was in short

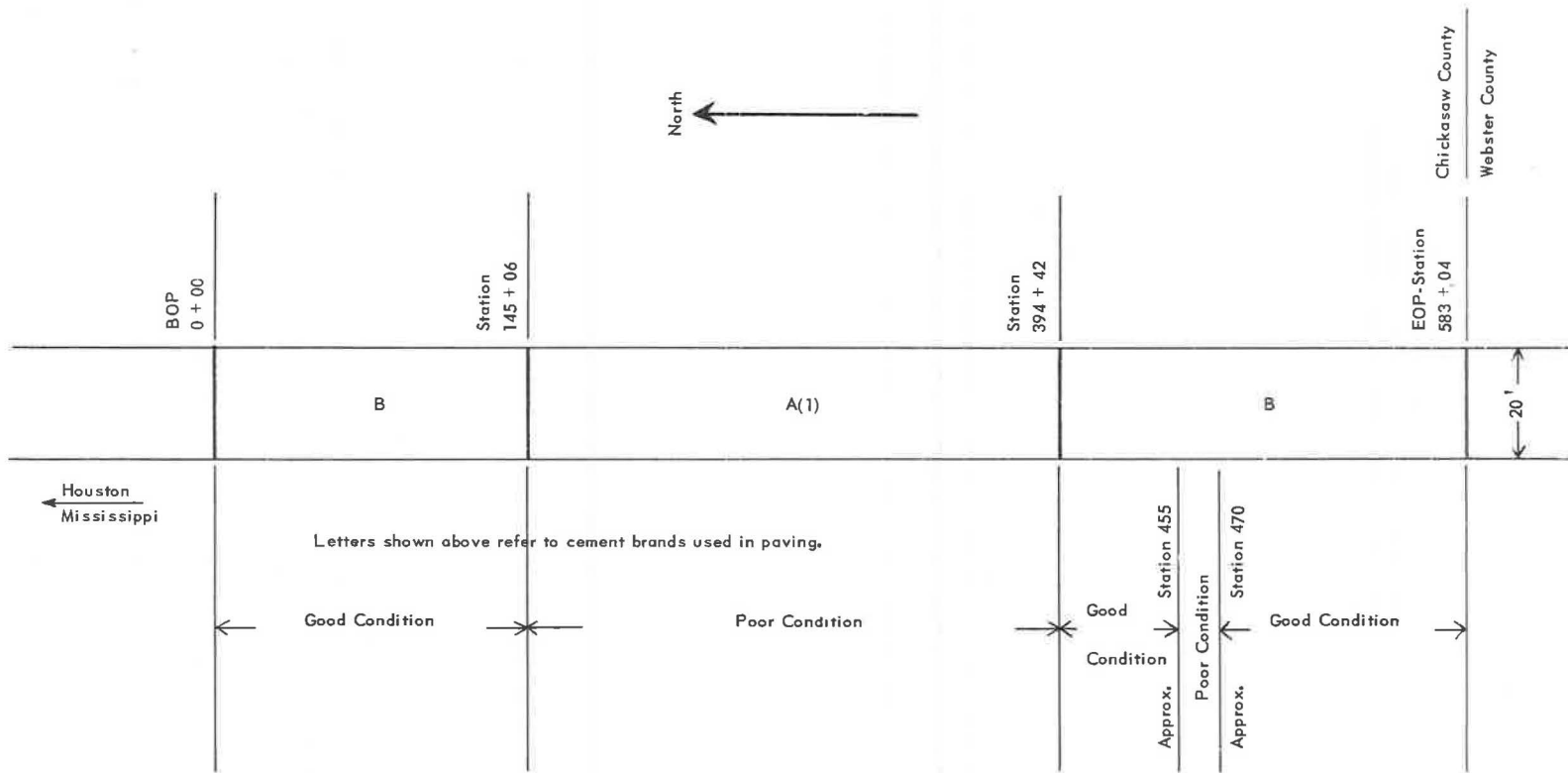


Figure 3. Project FWA 75 and 327A, Chickasaw County, Miss. 15.

TABLE 3
SOLUBLE SULFATES AND pH IN SOILS
ADJACENT TO SECTIONS OF
MISSISSIPPI HIGHWAYS INVESTIGATED

Project	County	Sol. Sulfates ^a (%)	pH
PWA 75, 327A F1(5), F32(4), U32(5)	Chickasaw	1.88	3.1
	Lee, Itawamba	0.55 ^b 0.33 ^c	2.9 7.2
PWS 50A	Issaquena	0.43	5.0
UI-251(7)	Lauderdale	0.45	4.6

^aCorps of Engineers Method CRD-C403-59.

^bMooreville chalk in eastern portion.

^cCoffee sand in western portion.



Figure 4. Typical view of 25-yr-old concrete pavement on project PWA 75 and 327A, Miss. 15, showing patching at transverse joint and spalling at left; two cores previously drilled from area.

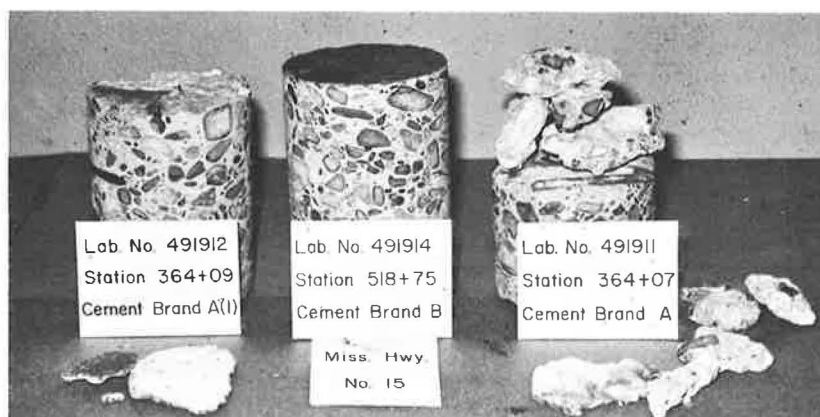


Figure 5. Cores drilled from Project 75 and 327A, Miss. 15; concrete in cores on left and right made from cement Brand A(1), center core from Brand B.

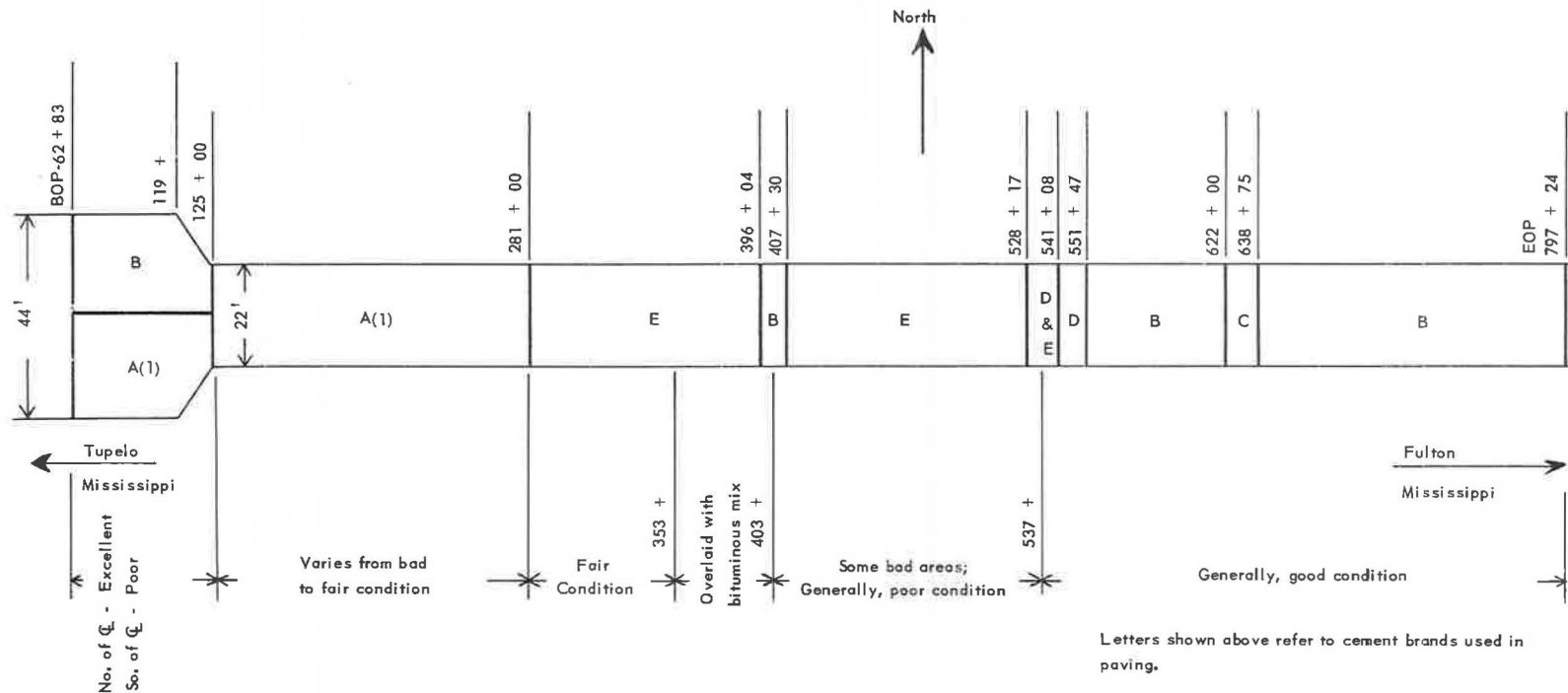


Figure 6. Project F1(5), F32(4), U32(5), Lee and Itawamba Counties, US 78.



Figure 7. Project Fl(5), 32(4), U32(5), US 78, facing west; concrete on right of centerline made from Brand B cement, on left from Brand A(1) cement; pavement age 16 yrs.

supply and, consequently, several brands of cement were used intermittently in the construction as shown in Figure 6.

Recently, it was discovered that in those sections in which Brands A(1) and E were used, the concrete is in bad condition, generally, with the same symptoms described earlier in this paper. It will be noted that cement Brand A(1) had an average C_3A content of 13.5 percent; Brand B, 9.7 percent; Brand C, 11.2 percent; Brand D, 9.8 percent; and Brand E, 12.6 percent. The cements in the concrete now showing distress were the two with the highest C_3A content, both in excess of 12 percent.

A spectacular example of contrasting conditions exists from station 62 + 83 to station 125. In this section, as shown in Figure 6, Brand B cement was used in the westbound lane and Brand A(1) in the eastbound lane. The former shows no deterioration, whereas every transverse joint in the eastbound lane exhibits advanced symptoms of sulfate reaction (Figs. 7 and 8). The difference cannot be attributed to traffic since reliable information indicates that the westbound lane has been subjected to very much heavier wheel loads by the hauling of gravel to Tupelo and projects to the west. Where Brand E was used, the distressed areas are somewhat intermittent; Figure 6 indicates that nearly 1 mi of Brand E cement concrete has been covered with a bituminous overlay because of the poor condition of the concrete.

Cores were drilled recently from the



Figure 8. Project Fl(5), 32(4), U32(5), US 78; view of transverse joint, facing north; concrete in foreground from Brand A(1) cement, beyond centerline from Brand B; typical of joints in widened portion of project; pavement age 16 yrs.

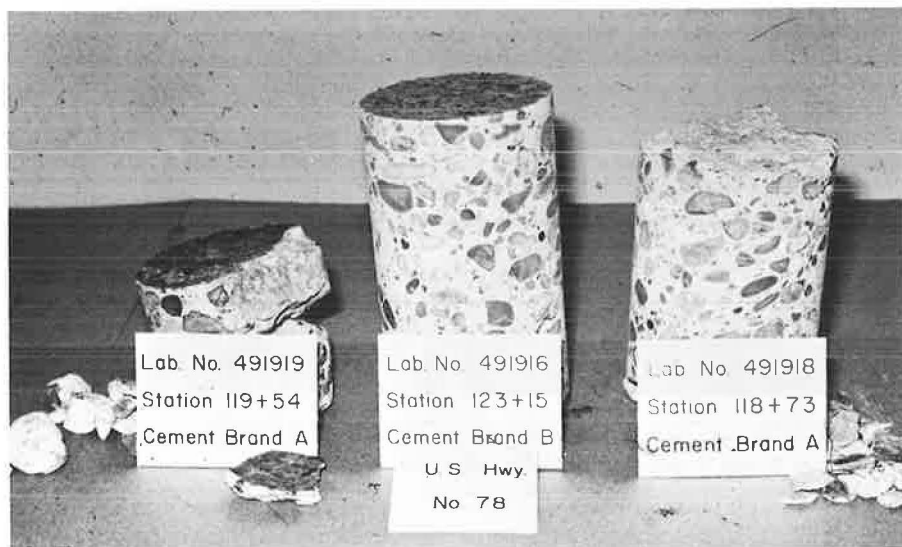


Figure 9. Project F1(5), F32(4), U32(5), US 78; cores on right and left represent concrete made from Brand A(1) cement, in middle from Brand B.

concrete at various locations. Figure 9 shows typical examples of the condition of the concrete at this time. Examinations of these cores reveal the following:

1. Station 123 + 15 (Brand B cement; pavement in good condition)—concrete contains a very small amount of gel and ettringite;
2. Station 118 + 73 (Brand A(1) cement, pavement badly broken)—concrete contains a large amount of ettringite and shows cracking, top and bottom of the core, parallel to the surface; and
3. Station 407 + 57 (Brand E cement, concrete in a short section of distressed pavement)—concrete contains more ettringite than that at station 123 + 15, but less than that at station 118 + 73.

Most of the natural soils within the limits of the project have a very high sulfate content. Predominantly, these soils are Coffee sands and Mooreville chalk. The Coffee sand formation is a light gray color, crossbedded to massive glauconitic sand and sandy clay, containing some calcareous sandstone. Numerous nodules of marcasite are present in this soil in the Tupelo area. Mooreville chalk is a marly chalk and calcareous clay. In some areas this is a dark, shaly type of clay, containing considerable quantities of melanterite.

Samples of the natural soils were obtained from cutbanks, source of the embankment materials. The west end of the project is in the Coffee sand formation, which contains 0.33 percent soluble sulfates; the east end is in the Mooreville chalk series, which contains 0.55 percent soluble sulfates; pH values are 7.2 and 2.9, respectively (Table 3). It is our belief that the sulfates in these soils, combined with the high C_3A content of cement Brands A(1) and E, have been the primary cause of the deterioration of this pavement.

Figure 10 is a photograph of the Mooreville chalk taken at the base of a ditch back-slope, after more than 16 yrs. of exposure.

The concrete pavement from the east end of this project to the Alabama state line is several years older than the preceding project. It is showing advanced deterioration also, but the appearance and type of disruption is entirely different from that caused by sulfates. Aggregates were from an area which has been excluded for several years by the Mississippi State Highway Department from use in concrete due to

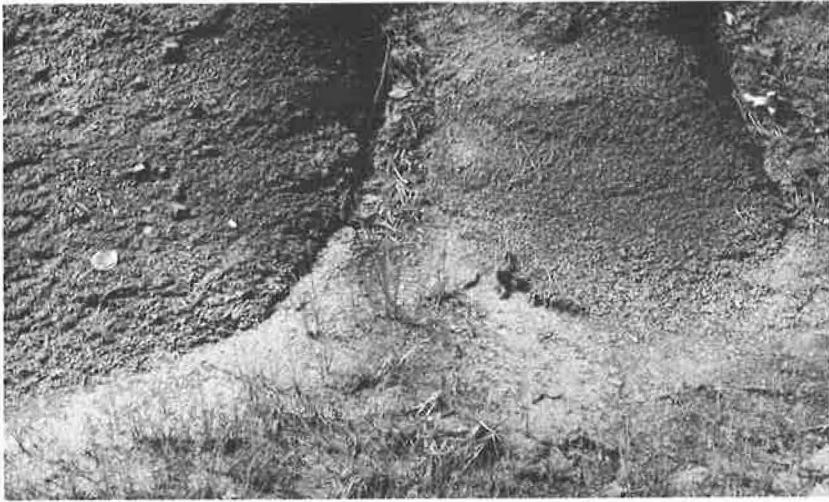


Figure 10. Project Fl(5), 32(4), U32(5), US 78; typical appearance of Mooreville chalk in backslope of ditch after 16 yr of exposure (note scant vegetation).



Figure 11. Project PWS 50A, US 61; close-up of concrete attacked by sulfates showing patched and spalled areas, typical of transverse joints on this project; pavement age 26 yr.

the presence of opal, as determined by petrographic examination. The concrete contains an abundance of gel but little or no ettringite. This is probably one of the few cases of alkali-silica reaction in Mississippi.

PWS 50A, ISSAQUENA COUNTY

This pavement, in Issaquena County on US 61, was constructed in the summer of 1938. During the study of sulfate reaction, it was reported that the pavement exhibited the same conditions as the other pavements studied. An inspection revealed that this is apparently another case of sulfates reacting with the cement. Figure 11 shows a typical condition of this pavement. Cement Brand A(2) was used on this project; the cement contained an average of 12.3 percent C_3A .

Samples of the surface concrete were obtained from a spalled area. Examination of these samples shows thorough deterioration and the presence of large amounts of ettringite. This project lies in the floodplains of the Mississippi River, in an area containing soils usually referred to as "delta gumbo." The water table in the area is high. The soils contain considerable organic material and a large percentage of soluble sulfates; a sample of the soil from beneath the edge of the slab contained 0.43 percent with a pH value of 5.0 (Table 3). Cores of the soil, taken at depths of 3 to 20 ft, were found to contain a very large quantity of gypsum and iron sulfate. The greatest concentration of these chemicals is in the upper 3 to 5 ft.

UI-251(7), LAUDERDALE COUNTY

In 1949, US 80 was relocated west of Meridian, Miss. The original concrete paved highway, a narrow, winding road traversing the higher ridges in this area, has exhibited no symptoms of any reaction. The pavement on the relocation, however, began to show signs of deterioration at the age of about 7 yr. As this deterioration was rapidly becoming worse, an investigation was started in 1957 to determine the cause. Later, in 1962, it was necessary to remove a badly disrupted portion of the pavement to make a connection with I-20 then under construction. It was possible, therefore, to examine the concrete without being limited to small samplings as with cores.

It was in connection with this project that Bryant and Katherine Mather were first consulted. After examination of several pieces of concrete, they tentatively concluded that the conditions were caused by sulfate reaction. However, they more probably result from a combination of causes and an acceleration of effect; the areas surrounding this project have a very high acid content, as well as a high sulfate content. A sample of soil obtained from a cut on this project contained 0.45 percent of soluble sulfate and a pH value of 4.6 (Table 3). Figures 12 and 13 show typical conditions of the pavement on this project. Cement Brand A(1) used in the concrete contained an average of 12.5 percent C_3A .

Figure 14 shows the typical condition of cores drilled from this pavement. Examination of the cores and the samples obtained during the removal of the pavement indicates the presence of large amounts of ettringite. The cores were badly broken with numerous cracks parallel to the surface at various depths. Some of these cracks extended almost entirely around the periphery of the core.

This project lies principally in the Zilpha and Tallahatta formations. Zilpha clay is a chocolate color and contains some glauconite, large amounts of marcasite and considerable gypsum, which weathers very rapidly to melanterite. Tallahatta clay is a glauconitic clay and siltstone with lenses of sand and some sandstone, highly cross-bedded, blocky, with numerous joints throughout. Tallahatta clay also contains considerable lenses of marcasite, as well as elemental sulfur. Figure 15 is a typical view of a cutbank in the vicinity of this project.

Mineralogy studies of soils submitted to and examined by Katherine Mather confirm the presence of varying amounts of gypsum, unstable pyrite, jarosite ($KFe_3(SO_4)_2(OH)_6$) and siderotil ($FeSO_4 \cdot 4H_2O$) (1). These are probably the immediate sources of sulfates.

Three samples of deteriorated concrete obtained from this project by the Testing Division were submitted to the U.S. Army Engineer Waterways Experiment Station at Jackson, Miss. These included a fragment of concrete (Sample A) and two drilled cores (Samples 7 and 8).

The samples of concrete were analyzed chemically to determine whether the sulfate content of the concrete (and, therefore, of the cement) had increased over the amount previously present. These analyses were made in accordance with a test method currently being considered by ASTM Committee C-9, Subcommittee III-1, and described in the Appendix. Calculated results of the tests are given in Table 4.

It was the original intention to confine this study principally to the physical and geological aspects. The limited chemistry on the concrete (Table 4) is admittedly far from adequate; the need is recognized for considerably more chemistry before more confidence can be placed in the results. In addition, one should take into account the variations inherent in field proportioning of concrete and the normal errors of testing.



Figure 12. General view of US 80; project UI-251(7), showing effects of sulfate reaction; pavement age 15 yr.



Figure 13. Close-up of transverse joint on project UI-251(7), US 80; pavement age 15 yr.

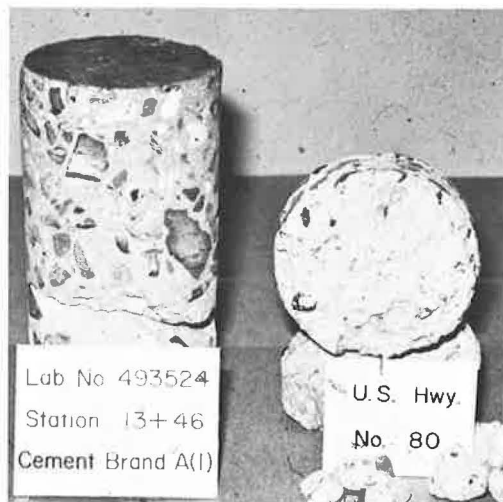


Figure 14. Two cores drilled from concrete pavement on US 80, project UI-251(7); concrete in both cores made from Brand A(1) cement.

Although the three specimens tested were obtained from distressed concrete on the same project, the test results are at considerable variance. Sample A shows a significant increase in SO_3 from that in the original cement but little or no decrease in cement content; Samples 7 and 8 show the opposite, i. e., little or no



Figure 15. Project UI-251(7), US 80; typical appearance of Zilpha clay in cutbank, showing lack of vegetation and light-colored areas with covering of melanterite.

TABLE 4
CALCULATED RESULTS OF DETERMINATIONS OF CEMENT AND
SULFATE CONTENT OF SAMPLES OF
DETERIORATED CONCRETE^a

Determination	Value		
	Sample A	Sample 7	Sample 8
Type of sample	Fragment	Core	Core
Condition of concrete	Fair	_b	_b
Cement content (oven-dried wt, (550 C))	14. 43	12. 44	13. 53
% SO ₃			
In cement in concrete	2. 14	2. 04	1. 97
In original cement ^c	1. 98	1. 98	1. 98
Increase in SO ₃ (%)	0. 16	0. 06	-0. 01
Cement as received			
% in concrete	13. 75	11. 91	13. 03
Lb. /cu yd	531. 0	460. 7	500. 1
Sk/cu yd	5. 6	4. 9	5. 3
Sk/cu yd cement originally incorporated, theoretical	5. 8	5. 8	5. 8
Loss cement from original (sk/cu yd)	0. 2	0. 9	0. 5

^aBrand A(1) cement used; from project UI-251(7) in Lauderdale County; results as reported by Leonard Pepper, Chief Chemist, U.S. Army Waterways Experiment Station, Jackson, Miss.
^bExtremely poor condition, broken, and cracked on top and bottom of core parallel to pavement surface.
^cFrom average cement analysis during period between May 27 and Sept. 17, 1949.

increase in SO₃ but a possible decrease in cement content. There are no apparent reasons for these variations; however, they possibly occurred because the test method requires a minimum sample of 10 lb; the samples as submitted each weighed approximately this amount and, therefore, the whole sample was tested, the results representing the average analysis of all the concrete in the sample. The amount of affected and deteriorated concrete represented a very small portion of the whole sample, and it was realized after completion of the tests that the analysis should have been made only on this small portion. This procedure probably would have given a more accurate indication of chemical changes in the concrete.

Samples 7 and 8, it will be noted, indicate decreases of 0.9 and 0.5 sk/cu yd, respectively, in cement content from that theoretically in the original concrete. These decreases are considered to indicate losses of cement which resulted from leaching of the calcium in the cement; this would, in turn, indicate the movement of foreign water through the concrete.

The chemical results tend to support the theory that the deterioration of the concrete pavement, on this project in particular, is due to a combination of chemical reactions, with two probable reactors being the acids and sulfates from the surrounding soils reacting with certain components in the cement.

SUMMARY AND CONCLUSION

For sulfate reaction to take place, certain factors must be present; namely, soluble sulfates, water to dissolve and transport the sulfates, C_3A in the cement, and evaporation of water from the surface of the concrete. It is believed that a reaction takes place if these factors exist to any degree but that the speed and intensity of the reaction varies directly with an increase in any factor; that is, if either is limited, the reaction can be delayed or rendered innocuous.

It is impractical to cover a new concrete pavement to reduce evaporation of water; however, this appears to be a possible deterrent to further reaction on old concrete under sulfate attack. Limitation of C_3A to a low percentage appears to be the most practical means of preventing or delaying the reaction.

AASHTO Standard Specification M 85-60 limits C_3A content for Type I cement to 15 percent; before 1960 there was no such limitation. In Type II cement it is limited to 8 percent; in Type III to 15 percent, except that the engineer may specify a maximum of 8 percent for moderate sulfate resistance or a maximum of 5 percent when high sulfate resistance is required; Type V cement is limited to 5 percent C_3A . Thus, there are safeguards provided by AASHTO standards, and it becomes the responsibility of the engineer to determine the type of cement best suited to the existing conditions.

An interesting observation from this limited study has been that concretes containing cement with C_3A content less than 12 percent have exhibited to date no serious sulfate reaction, whereas those with more than 12 percent have deteriorated, apparently as a result of sulfate reaction. Cook, in commenting on a research project on which, in 1940, concrete specimens were cast from 51 different cements and exposed to seawater at Salt Run, St. Augustine, Fla., states (2): "After nine years a total of only nine of the specimens had failed; eight of these specimens contained one or the other of the only three cements among the fifty-one used that had a calculated tricalcium aluminate content greater than 12 per cent."

On the projects in Chickasaw, Lee and Itawamba Counties, we obtained samples of the underlying soils through the core holes drilled in the pavement. In all cases, chemical analysis showed that these soils contained only a trace (0.01 percent or less) of soluble sulfate, although the subgrade soils contained from 0.33 to 1.88 percent. A somewhat granular topping material was placed under these pavements. On the Issaquena County project, the soil directly under the pavement consisted of Sharkey clay with 0.43 percent soluble sulfate; no granular material was placed under the concrete.

As an explanation of the reason for the low sulfate content of the granular subsoils, it has been suggested that the water, carrying sulfates obtained from the surrounding soils, loses only a minute amount of sulfate in traveling through granular soils under the pavement due to the chemically inert nature of these soils, and that the greater portion of the sulfates is deposited in the concrete because of the chemical nature of the concrete. Another suggestion has been made that some of the sulfates are carried by surface water and deposited in cracks by gravity, a small amount gravitating into the underlying soils. Either suggestion may be an explanation of the low sulfate content of the soils under the pavement.

A cement-treated base, whether under an asphaltic or a concrete pavement, is effectively sealed by the pavement, and evaporation of water from the surface of the base is eliminated. Since surface drainage is today recognized as a major design factor, the possible problem of surface water delivering sulfates to the surface of the

pavement should be minimized. Therefore, now that we are aware of the existing problem, we feel that steps have been and are being taken to prevent any major recurrence of the disruption of pavements described in this paper.

Mississippi is, and has been for some time, cement treating all bases under asphalt or concrete pavements and usually places a granular subbase under the treated base. These two insulating layers should effectively reduce any reaction from sulfates except in those areas of abnormally high acidity or sulfate-bearing soils. In such areas, Type II cement, or Type I with a maximum C_3A content of 8 percent, is being required both in the cement-treated base and in the paving concrete.

Although results of our studies indicate that cement Brands A(1), A(2) or E have been used in the affected areas, it is not the purpose of this paper to condemn these or any other brand or any source of portland cement. The cement furnished the projects described was tested and inspected by reputable commercial laboratories and the cement complied with the specifications prevailing at the time of construction.

In addition to the sections of pavement described, there are other areas in Mississippi in which the concrete pavements exhibit symptoms of possible sulfate reaction. This paper includes only those actually studied and investigated. However, it is not the intent to convey the impression that all concrete pavements in Mississippi are defective. Actually, the sections noticeably affected by what appears to be sulfate reaction constitute only a small percentage of Mississippi concrete highways. Each section described in this paper has served, or will continue to serve, satisfactorily during a normal and expected life-span. Some sections have been overlaid with an asphaltic pavement; such an overlay, maintained properly and sealed from time to time to prevent or reduce evaporation of water, will act as a deterrent to further deterioration of the concrete.

A word of caution may be appropriate. After studying the sections of concrete pavement, we have perhaps become sulfate reactivity conscious. Recently, a few small areas were noticed in a new concrete pavement that resembled the beginning of sulfate reaction deterioration. Samples of the concrete showed the presence of a small amount of ettringite and immediately it was concluded that perhaps we had a case of accelerated sulfate reaction. On removal of the defective concrete and a study of the placing records, however, it was determined that the trouble resulted from physical causes. Sulfate reaction, therefore, is not always the cause of trouble.

ACKNOWLEDGMENTS

The author wishes to acknowledge with gratitude the assistance received from Bryant and Katherine Mather, Leonard Pepper, I. B. Kelly, and Clyde V. Clark in the investigation and in the preparation of this paper.

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Appendix

METHOD FOR DETERMINATION OF CEMENT AND SULFATE CONTENT IN HARDENED CONCRETE

This method follows the procedures in a test method under consideration by the ASTM Committee C-9, Subcommittee III-1:

1. Sample is broken into 2- to 3-in. particles and allowed to dry to constant weight at 105 C.
2. The particles are then heated for 3 hr at 550 C.
3. The aggregates in the heat-treated sample are cleaned by hand and by scraping with a spatula; the sample is separated into three sieve fractions—retained on the No. 4, passing the No. 4 and retained on the No. 20; passing the No. 20.
4. The individual fractions are weighed; the plus No. 4 and the No. 4 to No. 20 sieve fractions are washed with dilute HCl to remove adhering cement and reweighed.
5. A representative portion of the minus No. 20 sieve material is ground in a mortar and pestle to pass a No. 200 sieve; this material is used for all chemical determinations.
6. Weight losses at 105 and 550 C are recorded.

Before the samples are prepared in this manner for analysis, they are stored in water for 96 hr, weighed in water, and then weighed in air in a saturated surface-dry condition. These weights are obtained to convert cement content from percentage by weight to sacks per cubic yard.

Discussion

HOWARD NEWLON, Jr., and W. CULLEN SHERWOOD, Virginia Council of Highway Investigation and Research, Charlottesville, Va.—The interesting paper by Mr. Lossing focuses attention on the importance of providing proper safeguards against chemical attack of paving concrete in certain geographical areas and also points up the need to consider the inherent interrelationships between structural and materials behaviors. The cases cited by the author are similar in many respects to an 18-yr-old pavement near Fredericksburg, Va., that the writers have studied intermittently for several years in an attempt to explain its relatively poor performance.

Although no general problem of sulfate attack is known to exist in Virginia, there are sizable areas in which soluble sulfates are found. In addition to extensive seawater exposures, jarosite (4) and other soluble sulfates have been reported in the Coastal Plain area. In the Piedmont and Ridge and Valley portions of the state, sulfate sources include oxidation products of sulfides brought to the surface by mining of coal and metallic ores and the weathering of disseminated sulfides from schists and black shales. Sulfates from some limestones and from rather extensive evaporite deposits in the Saltville area of southwest Virginia might also be of local concern. Because of these areas, Type II cement has been required by the Virginia Department of Highways for all structural and paving concrete since its introduction. This requirement has tended to alleviate or strongly reduce problems of chemical durability which might otherwise exist.

The project that the writers have studied, although small, is of particular interest since it was an experimental pavement embodying different structural designs of varying joint spacing and reinforcement. Thus, it is important in diagnosing the observed

TABLE 5
VARIATIONS OF CEMENT COMPOSITION FROM
PROJECT TEST REPORTS

Cement	C ₃ A (%)	C ₃ S (%)	SO ₃ (%)	MgO (%)
A	6-8	38-49	1.28-1.75	1.29-1.56
B	7	39-47	1.50-1.82	2.51-2.65
C	5-8	39-44	1.81-2.00	2.91-3.20



Figure 16. Views of project showing type of distress associated with concrete (cement C), with lane on far side of median showing no distress (cement A).

failures to isolate as much as possible the effects of structural design from other factors such as chemical attack. In the interest of brevity, details of the project will be omitted here, although they are available in several unpublished reports (e.g., 6, 7). It is sufficient to say that normal materials and construction procedures were used.

During the progress of the work three different cements were used; some of the important characteristics are given in Table 5. It will be noted that the cements were all similar Type II's, except for the MgO content which was relatively high in cement C.

Although the performance of the concrete was obviously influenced by the variations in structural design and conditions of drainage, there were also differences in performance that appear to be related to the cements used. Performance was generally poor in concrete made with cement C, intermediate for that with cement B, and good with cement A. Poor performance became extensive in portions of the concrete made with cement C when the pavement was 3 to 5 yr old. The concrete containing cement C has been resurfaced twice, that with cement B once, and that with cement A is still performing without resurfacing.

The behavior of the most affected concrete at an age of 6 yr is shown in Figures 16 and 17. The similarity to the behavior described by Mr. Lossing is apparent.

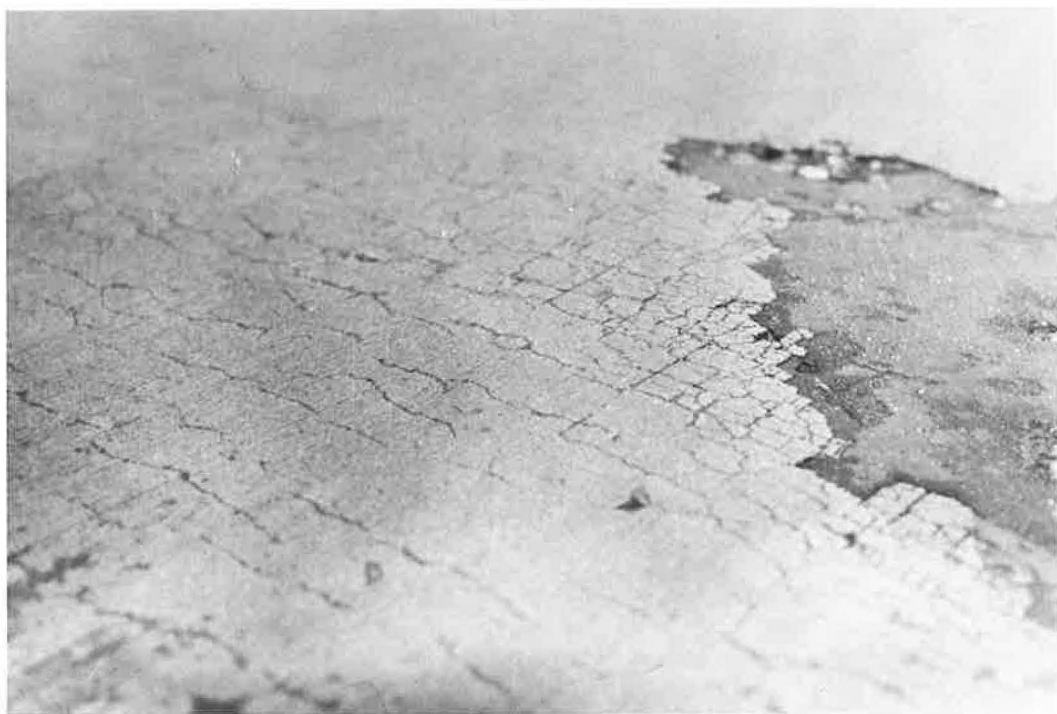


Figure 17. Close-up of distressed concrete from Figure 16.

Since the characteristics of the concrete suggested a mechanism other than structural failure, samples of the various concretes were taken for laboratory analysis. These samples showed extensive secondary deposits in voids and aggregate sockets. Figure 18 is a close-up of a fracture surface. Ettringite ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O}$) was found to constitute the major portion of the secondary deposits with measurable amounts of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and brucite ($\text{Mg}(\text{OH})_2$) present. Although the finding of ettringite in deteriorated concrete is not uncommon, the presence of uncombined gypsum in the concrete was of particular interest as a possible indication of sulfate in excess of that attributable to the cement.

Uncombined gypsum of undetermined origin was reported by Mather and Mielenz in concrete from the McPherson Test Road (3). They concluded, however, that no sulfate attack had occurred since there was no addition of sulfate from the subgrade. On the basis of such literature and discussions with other workers in the field, the writers believed that it was necessary to demonstrate an amount of SO_3 in the concrete greater than would be attributed to the cement. Accordingly, samples of the concrete and the base material directly below the pavement were selected for analysis. Some analyses have been completed and more are in progress. On the basis of the results to date, it can be stated with reasonable certainty that the sulfate content of the distressed concrete is neither significantly greater than would be expected from the original cement nor higher than that found for the sound concrete. In fact, the reverse appears to be true. It is interesting to note that Mr. Lossing found essentially the same thing, including no sulfate in the base material, even though considerable sulfate existed in the surrounding soil.

To date it appears that study of the Fredericksburg pavement has brought forth evidence which may be interpreted both for and against sulfate attack. At the present time, the evidence indicative of sulfate attack may be summarized as follows:

1. Observed distress is the type expected from a chemical breakdown of the concrete as opposed to structural failure;



Figure 18. View of fractured concrete removed from the pavement shown in Figure 16, showing the white secondary deposits coating aggregate particle and socket and forming two small nodules shown in upper center.

2. Soluble sulfate minerals are known to occur in the area;
3. Soluble sulfates in amounts as great as 0.09 percent were indicated for the base material under the pavement and from the project borrow pit;
4. Large amounts of ettringite were found to be concentrated in voids and cracks and at the aggregate-mortar interface in the deteriorated concrete;
5. Small, but measurable, amounts of gypsum and brucite were detected in the ettringite by X-ray diffraction and microscopic examination;
6. Deterioration of the concrete appears to be related to the three brands of cement utilized in the project; and
7. Deteriorated concrete was limited to low areas of poor drainage where sulfate-bearing waters, if present, have ready access to the pavement.

Evidence indicating that sulfate attack may not have occurred is as follows:

1. Percentages of soluble sulfate in base material used immediately below the pavement (ranging from 0.024 to 0.093) are below 0.10 percent, often considered the minimum necessary for deleterious attack;
2. Sulfate contents of the concrete samples are generally lower than that added with the cement alone;
3. Sulfate contents in the deteriorated concrete were slightly lower than those in the sound concrete;
4. Sulfate contents in the base material under the distressed concrete are generally lower than those for material under sound concrete;
5. From project test reports and mill analysis, the average C_3A content of the concrete used in the deteriorated areas was lower (thus more resistant to attack) than that of the adjacent unaffected concrete;

6. X-ray diffraction patterns of the distressed concrete showed normal calcium aluminate hydrates that are usually broken down during sulfate attack to form calcium sulfoaluminate; and

7. Type II cement was used throughout the project.

Despite the seemingly conflicting evidence for and against sulfate attack, a few basic observations concerning the field concrete can be made. Certainly, the type of distress exhibited by the pavement was due to an instability within the material rather than to structural weakness. Whatever mechanism caused the cracks initially, it appears safe to assume that the presence of brucite and gypsum indicates some reaction between the original concrete constituents, predominantly Ca(OH)_2 , and Mg^{++} and SO_4^{--} ions that occur in the ground water. Furthermore, the resulting volume increase accompanying formation of these reaction products and ettringite probably helped to widen existing cracks and contributed to the general distress.

The primary evidence suggesting that sulfate attack has not occurred is that the sulfate content of the concrete is not excessive and that the sulfate content of the base material is low. This situation, however, coincides with the experiences cited by Mr. Lossing where there is other strong evidence that sulfate attack has occurred. The inability to establish the presence of excess sulfate might result from a number of causes; for example, difficulties in obtaining a representative sample for analysis, removal of the sulfate from badly deteriorated concrete by percolating waters or by a mechanism involving resolution of the sulfate from the ettringite such as that described by Moum and Rosenqvist (5), or some other as yet unsuspected factors.

Thus, one is led to question seriously the necessity of clearly demonstrating an increase in sulfate content beyond that supplied with the cement in deteriorated concrete suspected of sulfate attack.

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Identification and Occurrence of Thaumasite in Concrete

A Discussion for the 1965 HRB Symposium on Aggressive Fluids

BERNARD ERLIN and DAVID C. STARK

Respectively, Research Petrographer and Assistant Research Petrographer, Field Research Section, Research and Development Laboratories, Portland Cement Association, Skokie, Illinois

•THE REACTIONS between components of concrete and aggressive solutions result in the formation of secondary compounds. Examples of the occurrences of such compounds are well documented in the literature and have also been commented on in this Symposium.

The purpose of this discussion is to bring to the attention of research personnel concerned with the chemistry of portland cement pastes the occurrence of a sulfate-bearing mineral known as thaumasite. Four interesting cases involving the alteration of portland cement concrete and a portland cement grout are investigated, and the means used to distinguish thaumasite from ettringite are described. A review of the literature has failed to disclose any comment on the occurrence of thaumasite in concrete or portland cement pastes, and we feel that it is of value to report our findings at this time.

The precise circumstances leading to the formation of thaumasite in the cases described herein have not been resolved. This may be attributed to the absence of the background information pertinent to the four specific cases investigated. In two of the cases presented, however, field and laboratory data indicate that sulfate was contributed to the concrete from an external source. The concrete environment in one of the two cases contained solutions sufficiently high in sulfate to merit classification as a moderate sulfate exposure. The occurrence of thaumasite, therefore, appears to represent situations involving attack by sulfate solutions.

The mineral thaumasite has the approximate composition $\text{CaSiO}_3 \cdot \text{CaSO}_4 \cdot \text{CaCO}_3 \cdot 14.5 \text{H}_2\text{O}$ and is usually found in metamorphosed rocks that have undergone hydrothermal alteration. Associated minerals in these zones commonly include ettringite ($3 \text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3 \text{CaSO}_4 \cdot 31 \text{H}_2\text{O}$), aragonite and calcite (CaCO_3), portlandite (Ca(OH)_2), spurrite ($2 \text{Ca}_2\text{SiO}_4 \cdot \text{CaCO}_3$) and members of the tobermorite family (calcium silicate hydrates). Usually these minerals occur side by side in thin veinlets, but at Crestmore, Calif., Carpenter (1) found thaumasite as oriented overgrowths on ettringite and, in a few instances, as overgrowths inclosed by a second generation of ettringite. On the basis of analyses of crystallographic data and similarities in physical properties, McConnell and Murdoch (2) concluded that "the structures of ettringite and thaumasite must be closely related in several aspects." Later, McConnell and Verhoek (3) proposed that thaumasite is an intermediate isomorphic variant of a family containing ettringite and "calcium carboaluminate" as end members. Carpenter has suggested there may be a limited solid solution series between thaumasite and ettringite and points toward anomalies in refractive indices of the associated growths as evidence.

OCCURRENCES OF THAUMASITE IN CONCRETE

During the past 2 yr, four occurrences of thaumasite have been found; two were in sanitary sewer pipes, one was in a grout, and one was at the base of a core taken from a pavement. These occurrences were located in four different states, two in the northeastern portion of the United States and two in the midwest. Initial identification of thaumasite in the grout was made by Stark.

In Pavement

The bottom of one of a series of cores taken from an 11-yr-old highway pavement contained a soft, light gray material that represented cement paste extensively altered to thaumasite, ettringite, aragonite and calcite. Several horizontal fractures located in the bottom 1/4-in. of the core were also filled with thaumasite, aragonite and calcite. Thaumasite and ettringite often occurred as banded intergrowths normal to the long axis (c-axis) of the crystals (Fig. 1) and as overgrowths of thaumasite on ettringite (Fig. 2). Occasionally, intergrowths and overgrowths occurred in a single crystal. In microscopic examinations, the optical extinction positions of the intergrowths and overgrowths were parallel.

In Sewer Pipe

In the first such occurrence, thaumasite was identified as one component of a creamy, white substance filling blisters whose shells were composed of calcite and as a filling in thin veinlets located parallel and adjacent to the inside surface of a 5-yr-old sewer pipe. Associated compounds in both instances were calcite, gypsum and brucite.

The thaumasite occurred as long slender needles and as clusters and bundles of needles similar in morphology to the secondary ettringite often found in concrete.

An analysis of the sewage at the time the materials were submitted for examination indicated a sulfate content of 152.3 ppm and a pH of 8.3. A chemical analysis of material filling a blister, including aggregate, showed about 11.3 percent sulfate.

Interpretation of the petrographic microscopy data for the compound initially suggested that the material was ettringite, although the refractive index of the ordinary ray was considerably higher than normal. This may have resulted from substitution of iron for aluminum. Once positive identification of thaumasite in the grout was made, reinvestigation confirmed that the material was thaumasite.

The second occurrence of this type was in a sewer pipe over 32 years of age at the time of examination. Paste along the inside surface of the pipe was severely deteriorated to depths of about 1/2 in. and converted to gypsum and silica gel. Between the severely deteriorated and sound portions of the pipe were deposits of thaumasite, ettringite, gypsum and traces of calcite. In sound portions of the pipe, tuffs and rosettes of ettringite and thaumasite lined or filled entrapped air voids. In these voids, thaumasite occurred as discrete long slender needles, occasionally as overgrowths incasing ettringite, and as petal overgrowths on bundles of ettringite crystals. In microscopic examinations, the optical extinction positions of the overgrowths were parallel with ettringite.

In Grout

Thaumasite occurred in small clusters and as disseminated crystals in a moist, granulated grout specimen. Associated materials were aragonite, calcite and fine aggregate.

The grout was taken from a pressure pointed abutment in an area adjacent to sodium chloride mines where sulfate-bearing waters could have been.

IDENTIFICATION OF THAUMASITE

The identification of thaumasite and ettringite in the cases discussed was initially and principally by petrographic microscopy. Although this means provided positive identification, failure to find mention of thaumasite in literature pertaining to concrete prompted further investigation by X-ray and electron diffraction, electron microscopy, and chemical analysis. The thaumasite used for these studies was handpicked from the grout and separated from the material filling a blister in the sewer pipe by sedimentation in water.

Light Microscopy

Optical data for naturally occurring thaumasite and for the compound found in all

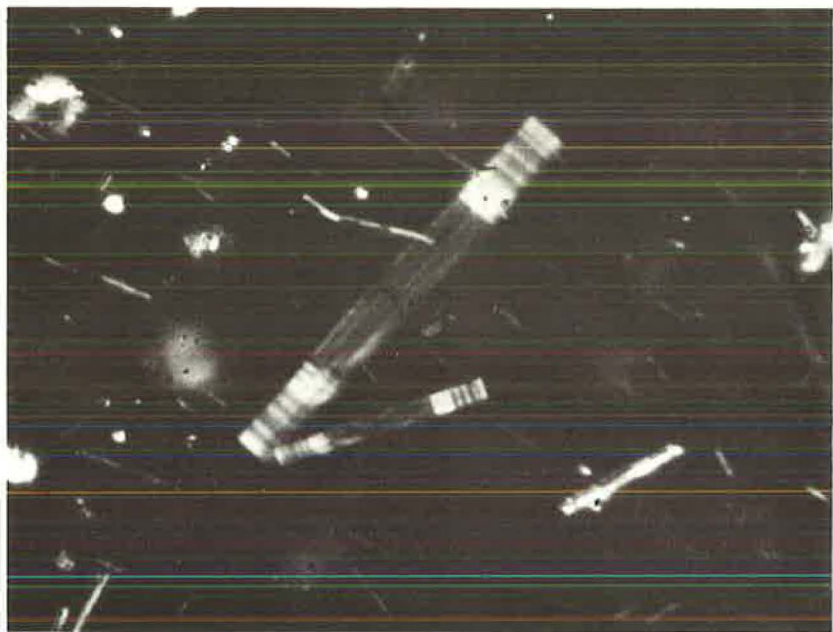


Figure 1. Photomicrograph showing bands of thaumasite and ettringite oriented normal to c-axis of crystal; crossed nicols (magnification 1,360X).

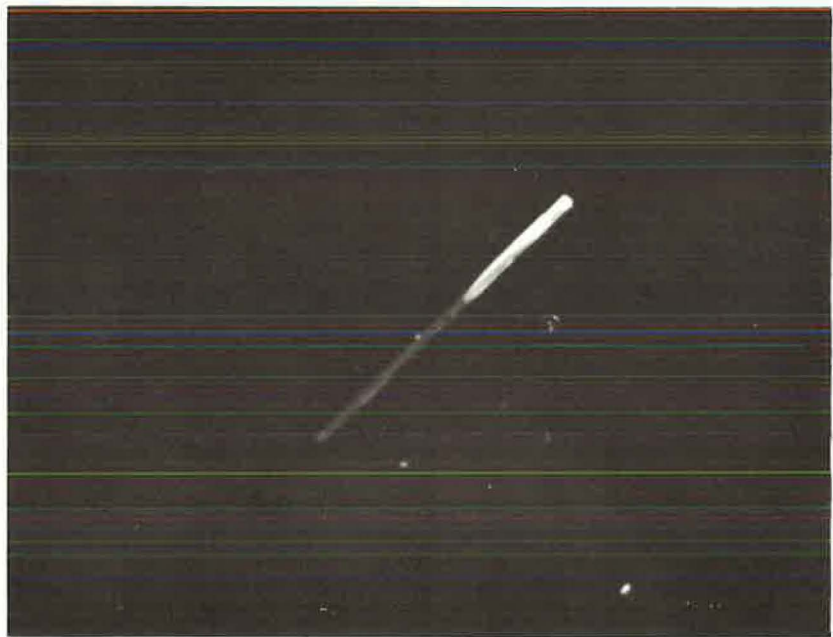


Figure 2. Photomicrograph showing overgrowths of thaumasite on ettringite; crossed nicols (magnification 1,090X).

TABLE 1
COMPARISON OF REFRACTIVE INDICES
FOR THAUMASITE

Source	E	O
Crestmore, Calif.	1.470 ± 0.002	1.492 ± .002
	1.468 ± 0.002	1.507 ± .002
Great Notch, N. J.	1.468	1.505
Co. Down, N. Ireland	1.470	1.504
Sewer pipe, grout, pavement	1.468 ± 0.002	1.504

TABLE 2
CHEMICAL ANALYSES OF THAUMASITE

Source	Percentage by Weight						
	CaO	SO ₃	R ₂ O ₃	SiO ₂	H ₂ O + CO ₂	Na ₂ O + K ₂ O	MgO
Crestmore, Calif.	27.6	13.0	0.8	9.1	49.5	-	-
Areskuta, Sweden	27.4	13.1	0.2	9.6	49.1	0.3	-
PCA	24.7	10.1	3.6	10.8	43.6	0.01	5.1

a Analysis totals 97.9 percent which probably resulted from presence of undetermined oxides and separate ignition loss determination.

four of the concretes investigated are compared in Table 1. These indices are in sufficient agreement for positive identification of the compound as thaumasite.

X-Ray Diffractometry

X-ray diffraction data for naturally occurring thaumasite and for the compound from the grout and sewer were identical. A few of the minor peaks reported for naturally occurring thaumasite were not present in the diffraction pattern obtained from the compound in the grout.

Electron Microscopy and Diffractometry

Specimens identified under the petrographic microscope as thaumasite were taken from the grout and the sewer and studied by electron microscopy and electron diffraction. Unit cell dimensions calculated from the electron diffraction patterns are in close agreement with those determined from X-ray diffraction data reported by other investigators for naturally occurring thaumasite. Although the precise orientation of the crystals in these studies was not known, their preferred orientation noted under the petrographic microscope was also observed in the electron microscope. In addition, close examination of the diffraction pattern showed that the c-axis of the crystal was, within several degrees, oriented normal to the electron beam (Fig. 3).

Chemical Analysis

A chemical analysis of thaumasite from the sewer pipe is given in Table 2 and com-

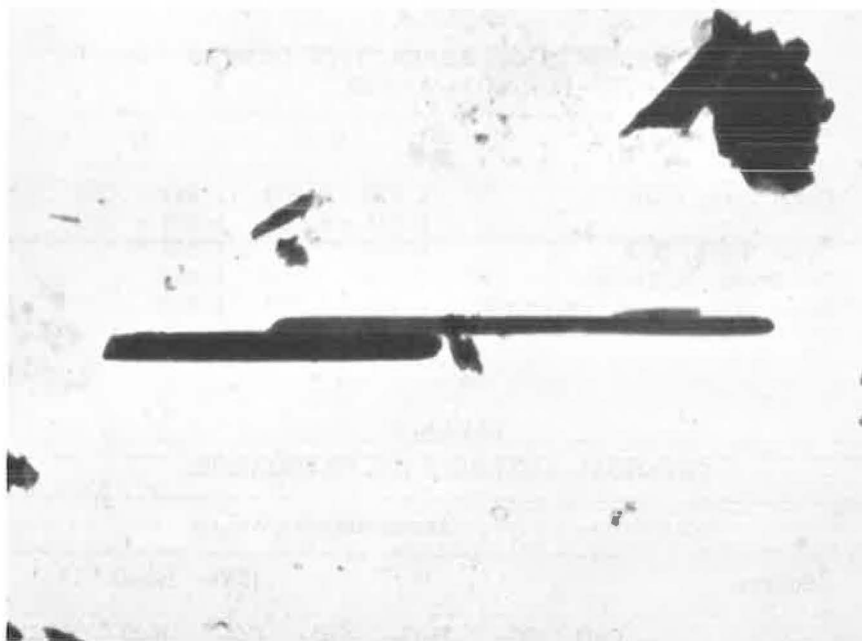


Figure 3. Electron micrograph showing crystals of thaumasite from which electron diffraction patterns were obtained (magnification 13,750X).

TABLE 3
COMPARISON OF OPTICAL DATA FOR
ETTRINGITE AND THAUMASITE

Property	Thaumasite	Ettringite
Crystal system	Hexagonal	Hexagonal
Crystal habit	Acicular	Acicular
Elongation and sign	Negative	Negative
O - Ray	1.504	1.464 ± 0.002
E - Ray	1.468 ± 0.002	1.458 ± 0.002
Birefringence	0.036	0.006

pared with data reported for two natural occurrences. The water plus carbon dioxide content reported for the PCA analysis is the weight loss on ignition of another portion of the specimen used for the analysis. Our data are close to those reported but deviate slightly, possibly because other phases of the concrete may have been present in the analyzed material.

Comparison of Optical and X-Ray Properties of Thaumasite and Ettringite

Although thaumasite may be identified by means of X-ray diffractometry and optical microscopy, some difficulties may arise in distinguishing it from ettringite in portland cement concrete. The optical data for the two compounds are similar (Table 3); the only appreciable differences are in the birefringence and refractive index of the ordinary ray. With the exception of the sign of elongation, which is identical for both compounds, the extremely small crystal sizes of thaumasite and ettringite encountered

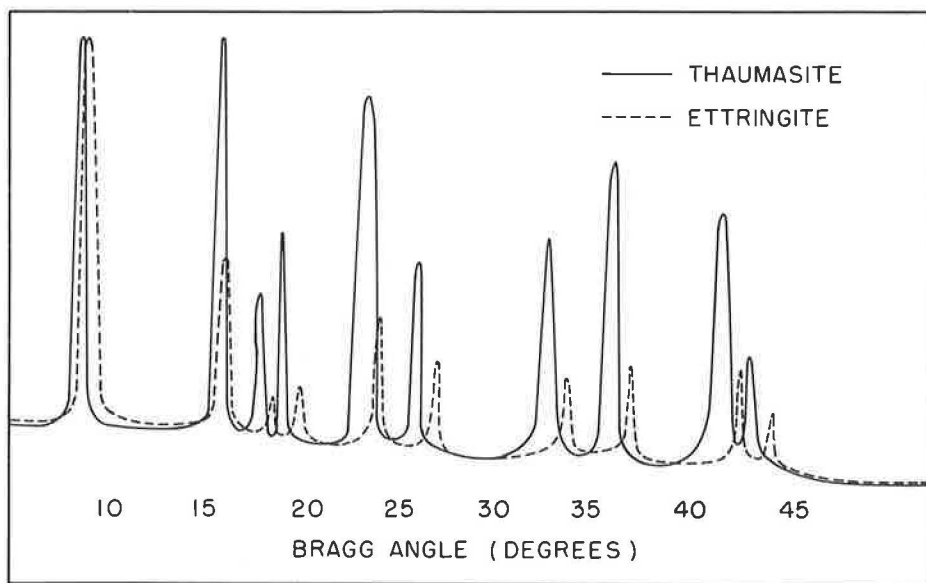


Figure 4. X-ray diffraction patterns for thaumasite and ettringite.

in concrete and the similarity in refractive index of the extraordinary ray require the determination of the ordinary ray to distinguish between the two compounds.

X-ray diffraction patterns for thaumasite and ettringite are likewise similar, as shown in Figure 4. These patterns were obtained on thaumasite removed from the sewer pipe and on ettringite synthesized at our laboratories. The greatest differences occur at the higher Bragg angles where, in impure specimens, the peaks are of relatively low intensity and, in some instances, may be obscured by peaks produced by other compounds.

CONCLUSION

The four occurrences of thaumasite described cannot represent the only cases where the compound has formed in deteriorated concrete. Difficulties may be encountered in identifying the compound by petrographic microscopy and X-ray diffractometry. These difficulties may explain the absence of reports in the published literature describing the presence of secondary thaumasite in portland cement concrete.

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Investigation of Resistance of Cement Paste to Sulfate Attack

JØRGEN NIELSEN, Betonforskningslaboratoriet Karlstrup, Pr. Karlslinde, Denmark

•THE PRELIMINARY test described here was carried out to investigate the effect of the "density" of the cement paste on the course of the reaction, partly by means of microscopic examination of thin sections from the test specimens and partly by determining the quantity of sulfate consumed. The effect of the metal ions on the course of the reaction was also investigated by storing test specimens in sodium sulfate, magnesium sulfate, ferrous sulfate, and ferric sulfate. The effect of ferric sulfate will not be discussed in this connection.

The test specimens consisted of cement paste cubes with an edge length of 25 mm. Three different w/c ratios were used: 0.38, 0.34 and 0.30 (corrected for bleeding). After 7 days curing in water, the cubes were stored in 0.07 molar solutions of each of the four salts. The solutions were changed each month to keep the concentrations approximately constant.

After the specimens had been stored for about 2 months, systematic determination of the sulfate consumption was commenced. At the same time, the content of non-evaporable water in the cubes was ascertained and found to be $W_n = 0.255$ g/cc paste, regardless of the original w/c ratio. W_n was determined by the method given by Copeland and Hayes (1). There is, thus, every reason to believe that the gel porosity and specific surface of the cubes were identical at this time, regardless of the original w/c ratio, so that only the permeability varied.

RESULTS OF CHEMICAL ANALYSIS

There is a strong increase in the total sulfate consumption in the series, sodium sulfate, magnesium sulfate and ferrous sulfate, but the obvious differences between the solutions become apparent only after some time. The strong increase in sulfate consumption begins first with ferrous sulfate and last with sodium sulfate; the density of the cubes influences the quantity of sulfate transformed, the sulfate consumption being lowest in cubes cast with a w/c ratio of 0.30.

MICROSCOPIC INVESTIGATIONS

Examination of the thin sections showed gypsum is the predominant sulfate reaction product. Ettringite was found only in specimens that had been stored in sodium sulfate and, rather surprisingly, in a specimen stored for 1 month in ferric sulfate. It was further seen that the increases in sulfate consumption determined by chemical analysis coincided with observation of development of cracks in the thin sections.

The micrographs in Figures 1 through 4 give a general impression of how the deterioration appeared in thin sections. All specimens had been stored for 8 months.

Figure 1 shows a crack parallel to and near the surface of a specimen that had been stored in sodium sulfate. The crack is filled with gypsum. Only very limited deterioration appears to have taken place.

Figure 2 shows a corresponding parallel crack in a test specimen that had been stored in magnesium sulfate. The crack perpendicular to the surface is not filled with gypsum; it is probably a shrinkage crack that has occurred during preparation of the thin section. On the right of the photograph (torn off the surface) a band of gypsum and magnesium hydroxide can be seen. The gypsum is always precipitated on the surface and the magnesium hydroxide on the gypsum.

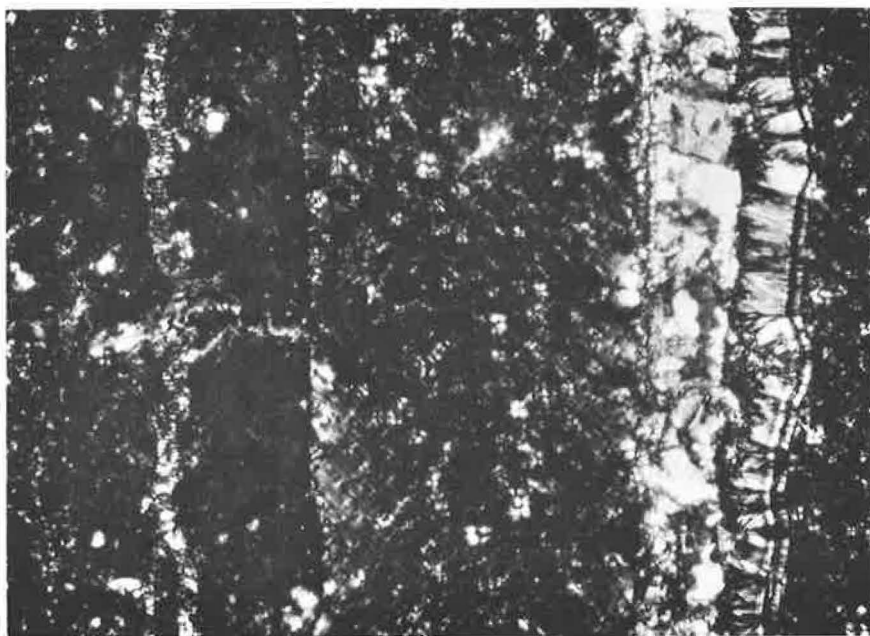


Figure 1. Thin section of cube stored 8 months in sodium sulfate, 120X magnification, parallel nicols.

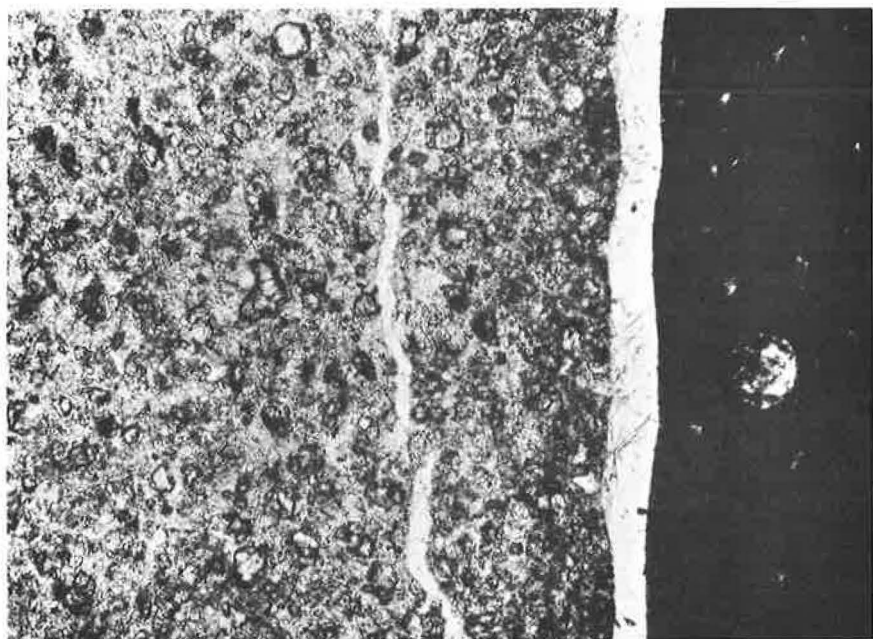


Figure 2. Thin section of cube stored 8 months in magnesium sulfate, 120X magnification, crossed nicols.

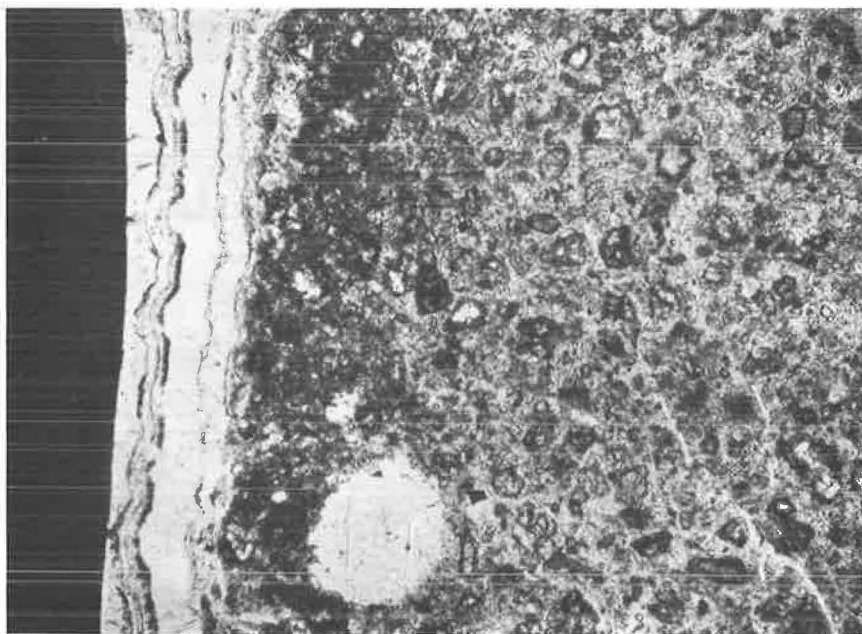


Figure 3. Bubble filled with gypsum in thin section stored 8 months in magnesium sulfate, 120X magnification, parallel nicols.

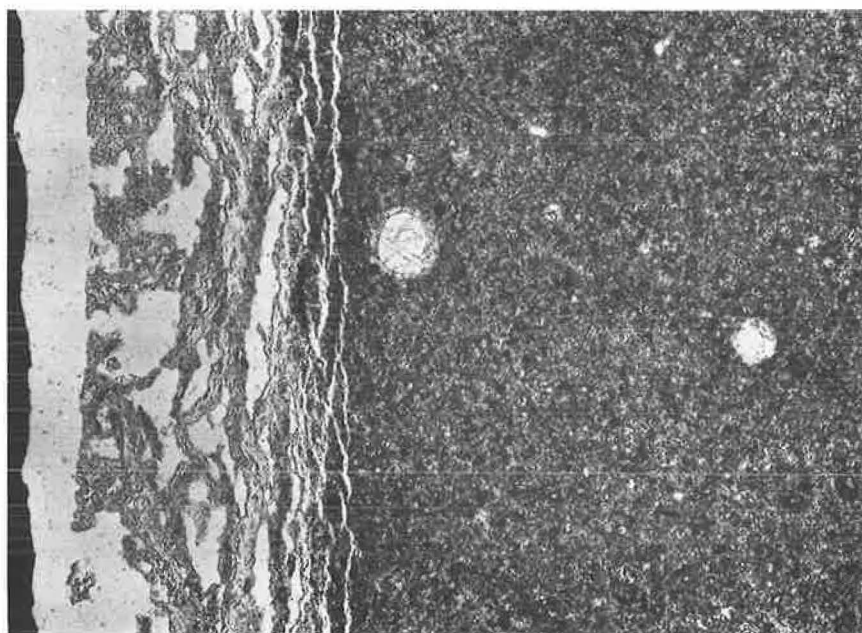


Figure 4. Thin section of cube stored 8 months in ferrous sulfate, 120X magnification, parallel nicols.

Figure 3 shows a bubble, in the same specimen as in Figure 2, that is almost completely filled with gypsum. The thin section gives a reason to believe that almost all magnesium hydroxide is precipitated on the surface; it might, therefore, have been expected that large quantities of ettringite would have formed in such a bubble. However, as can be seen, this is not the case.

Figure 4 shows a test specimen that had been stored in ferrous sulfate. As in other cases, gypsum is the dominant reaction product, together with various unidentified iron hydroxides. The general impression is that the deterioration has been much more comprehensive than in the other solutions.

CONCLUSION

From the rather limited investigations discussed, the following preliminary conclusions can be drawn:

1. All other things being equal, the aggressiveness of the solutions increases from sodium sulfate, over magnesium sulfate, to ferrous sulfate;
2. The resistance of the cement paste can be considerably improved by increasing its "density"; and
3. The thin-section examinations show that ettringite is rarely formed in sufficient quantities to be reasonably considered a cause of the crack formations.

These results seem to warrant more detailed investigation of the importance of the pore structure and the various sulfates to the durability of the concrete. It would be interesting to investigate the effect of ettringite, and to a certain extent the content of C_3A in the cement, on the resistance to sulfate attack. Ettringite crystals found in cracks after storage in sodium sulfate apparently formed after occurrence of the cracks.

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