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BY A NEW TEST METHOD

by

P. K. Mehta

To be presented at the American Ceramic Society
77th Annual Meeting
May 3-8, 1975, Washington, D. C.

This research was sponsored by the Office of Naval Research
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I. INTRODUCTION

Portland cement concrete is the most commonly used material for the construction of dams, foundations, pavements, bridge piers, beams and columns, etc. Considerations of cost and public safety require that concrete structures perform satisfactorily over long periods of time. Generally, in mild environments concrete structures do perform well when proper materials and construction practices are employed. However, in aggressive environments premature structural failures have frequently occurred, especially when concrete of questionable quality was used.

Chemical attack by aggressive waters is frequently responsible for concrete distress. The presence of sulfate ions in water is one of the major causes of concrete failure because certain constituents of cement paste can enter into deleterious chemical reactions with sulfates. Sea water, ground water from soils containing alkali sulfates, sewage water, and many industrial effluents contain enough sulfates to be potentially damaging to portland cement concrete.

With regard to the chemical reactions which can take place between portland cement paste and a sulfate solution, one reaction involves C_3A^* or alumina-containing hydrates occurring in ordinary portland cement pastes. In the presence of calcium hydroxide, which is one of the main products of hydration of the calcium silicates of portland cement, this reaction leads to the formation of ettringite ($C_3A \cdot 3\overline{CS} \cdot 32H$), which under appropriate conditions causes considerable expansions and cracking.

*Cement chemistry notations are used: C = CaO; S = SiO₂; A = Al₂O₃; F = Fe₂O₃; \overline{S} = SO₃; H = H₂O.

Ordinary portland cements generally contain 7 to 13% C_3A . In order to reduce the susceptibility of a cement paste to expansion-cracking type of attack associated with ettringite formation, many researchers including Thorvaldson et al (1), and Miller and Manson (2,3), have shown that portland cements of low C_3A content should be used whenever concrete is subject to sulfate exposure. The ASTM C 150 specification for portland cements (4) limits the maximum C_3A to 5% in Type V portland cements which are recommended for sulfate resisting applications.

A review of several case histories of concrete failures due to sulfate attack shows that the expansion-cracking associated with ettringite formation is not the only way in which concretes have failed in sulfate waters. Frequently, a surface softening-spalling type of acidic sulfate attack, which is associated with the conversion of calcium hydroxide to gypsum, has also been reported.

The present laboratory test methods for evaluating the sulfate resisting cements usually ignore the acidic type of sulfate attack. In a recent publication, Mehta and Gjorv (5) discussed the inadequacies in the presently used methods for testing sulfate resistance of cements, and proposed a new test method which takes into account both types of sulfate attack. Results of an investigation on relative sulfate resistance of 5 commercially available sulfate resisting portland cements, and 4 blended portland cements, which were tested in accordance with the new test method, are presented in this report.

II. MATERIALS AND PROCEDURE

The C_3A content of the 5 ASTM Type V portland cements used in this investigation varied from 0 to 4%. The chemical analyses and the computed compound contents are shown in Table 1. Three of the 5 cements are from the United States, one from United Kingdom, and one from West Germany. The tabulated data also includes Al_2O_3/Fe_2O_3 ratios. When the Al_2O_3/Fe_2O_3 ratio is less than 0.64, a calcium alumino-ferrite solid solution, expressed as $ss(C_4AF + C_2F)$, is formed. Content of this solid solution is calculated in accordance with the formula given in ASTM C 150. For Cement Nos. 4 and 5, the calculations for compounds assume that the solid solution is of C_4AF composition.

Cement Nos. 6 and 7 are portland blast-furnace slag cements produced in Germany in accordance with DIN 1164 (German Standard Specifications for Portland Cement). Cement No. 6 contains 80% granulated blast-furnace slag, and is of type HOZ 350-Low Heat. Cement No. 7 contains 30% granulated blast-furnace slag, and is of type EPZ 350 F. The chemical analyses of these cements are reported in the paper by Mehta and Gjorv (5).

Cement Nos. 8 and 9 are portland-pozzolan cements. Cement No. 8 contains 75% of a Type I portland clinker (10% C_3A content), 20% of a fly ash (Type F Class Pozzolan), and 5% gypsum. Cement No. 9 is of German origin, and contains 26% trass.

The 35-day test involved immersion of 7-day old cement paste specimens for 28 days in a 4% sodium sulfate solution (6.2 pH). The immersion solution is maintained at a constant pH with the help of a pH-stat. The relative sulfate resistance of cements is evaluated by measuring the change in compressive strength caused by the 28-day sulfate immersion. Details of the procedure are given below:

Casting of Specimens--In order to accelerate the sulfate attack, it is essential to produce high-porosity cement pastes for immersion. For this purpose, a relatively high water-cement ratio, viz 0.5 is considered necessary. Normally, neat cement pastes of such a water content would exhibit excessive bleeding. This problem was resolved by mixing cement and water in a high-speed kitchen blender for 5 minutes. It seems that uniform dispersion of the colloidal products of hydration which tend to form at the periphery of anhydrous cement grains can stop the bleeding tendency in a high water-cement ratio paste. However, due to vigorous agitation in the blender, the cement pastes made in this manner entrap some air.

The de-airing operation in the test method reported by Mehta and Gjorv (5) was performed in a dessicator connected with a vacuum pump. An easier de-airing technique was subsequently developed for this investigation. It was found that the de-airing operation becomes unnecessary if a small quantity, 0.4% by weight of cement, of an antifoaming agent such as octyl alcohol is introduced into the paste halfway through the mixing cycle.

Brass gang molds capable of making 1/2-inch (12.5 mm) cubes of cement paste were used for casting the specimens. Photograph of both an assembled as well as an unassembled mold is shown in Fig. 1. For better compaction, the molds were filled in two layers, each layer being rodded 25 times with a 1/16-in. diameter brass rod. The specimens were further compacted by tapping the molds full of paste a few times against the workbench.

The small size of specimen used is advantageous for ease of handling, and for quicker sulfate permeation into the interior. On the other hand, in small size specimens even minor flaws can lead to wide inter-specimen strength variations. In order to get around this problem, a relatively large number of specimens, namely 10, was made for each testing age.

Curing--In order to accelerate the test, the specimens were cured at 50°C for 7 days instead of normal curing. This produced considerable hydration and strength development in the cement pastes before they were immersed in the sulfate solution, while causing no significant differences between the normally-cured and the 50°C cured cement pastes from standpoint of overall microstructure, including the nature of hydration products formed.

Following casting, the specimens in molds were covered with glass plates, and kept at room temperature in a fog room for 4 hours. Thereafter, they were wrapped with a moist towel and placed in a covered container which was then stored in a 50°C chamber. At age 24 hours, the specimens were demolded, and the above procedure of warm-humid curing of demolded specimens was continued until age 7 days.

Sulfate Immersion--Separate, 6-liter capacity, polyethylene immersion tanks were used for immersion in sulfate solution of specimens of each of the 9 cements. Each tank contained 4% Na_2SO_4 solution (6.2 pH). In the beginning there was 10 cc of solution per cm^2 of specimen surface. In accordance with the recommendation of Mehta and Gjorv (5) pH-stats were utilized to maintain the sulfate solution within narrow limits of pH by automatic titration of the lime (leached from the cement pastes) against a 0.1 N H_2SO_4 solution. This arrangement permitted pH control in the range of 5.0 to 7.0 during the first two hours of immersion, and 5.7 to 6.7 thereafter.

Continued sulfate attack on the cement pastes was further ensured by a standardized stirring action in the immersion tanks. This was achieved by using an assembly of polyethylene stirrers driven by a 1/20 HP, 1725 rpm motor. Two 1.75 in.-diameter stirring paddles per storage tank were provided. The stirring and the pH controlling arrangements are shown by photographs in Figs. 2 and 3.

Testing of Specimens--A hydraulic 60-kip capacity, Baldwin Universal Testing Machine was used for determining compressive strength of the cubes. The load was applied at a uniform rate of 1000 lbs/min. For each cement, a group of 10 specimens were tested at age 7 days (i.e. just before the sulfate immersion), and another group of 10 specimens were tested at 35 days (i.e. after 28-day sulfate immersion). In order to determine the effect of continued sulfate exposure, specimens from some cements were also tested at age 63 days (i.e. after 56-day sulfate immersion).

Photographs of the surface after sulfate immersion were taken. X-ray diffraction analyses of selected specimens were also obtained.

III. RESULTS AND DISCUSSION

Results of compressive strength changes in the ASTM Type V portland cements exposed for 28 days to 4% Na_2SO_4 solution maintained constantly at 6.2 ± 0.5 pH are summarized in Table 2. Similar results for the blended portland cements are summarized in Table 3. The data is plotted in Figs. 4 and 5 respectively. The curves also include additional data obtained as a result of further sulfate exposure of the specimens for a total period of 56 days. Corresponding photographs representing typical condition of the surface of the specimens after the sulfate exposure are shown in Figs. 6 and 7.

In some instances, 1 or 2 specimens from a group of 10 were found to yield strengths which were totally inconsistent with the other 8 or 9 specimens. This was due to presence of flaws in casting of such small specimens. These abnormal values were not considered while averaging the results. Therefore, each compressive strength value reported is the average result for 8 to 10 of 1/2-in. cube specimens. In general, for each group of specimens the variation in individual experimental values was within $\pm 10\%$ of the average for the group.

The results show that there are significant differences in the relative sulfate resistance of ASTM Type V portland cements when tested by the above-described method. For instance, assuming 25% as an arbitrary number for maximum permissible strength loss in the 28-day sulfate immersion period, Cement Nos. 3 and 5 would fail to qualify as sulfate resisting. The strength loss was considerably below 25% in case of Cement Nos. 1 and 2. It is interesting to observe that Cement No. 4, rather than losing strength, actually gained strength during the sulfate immersion period. The reasons for such anomalous behavior are not apparent at the moment.

Heavy scaling on the surfaces of the specimens of Cement Nos. 3 and 5 was observed (Fig. 6). Also the edges and the corners of the specimens were severely corroded during the 28-day immersion period. On the other hand, only a thin scaling was observed on the surfaces of specimens from Cement Nos. 1, 2 and 4, and whose edges and corners were only slightly corroded. Except for Cement No. 3, which continued to lose more strength, the strength changes were not significant during the 28 to 56-day sulfate immersion period for Cement Nos. 1, 2, 4 and 5.

Regarding the portland blast-furnace slag cements, the strength loss for the HOZ cement was found to be insignificant, hence it is considered to possess excellent resistance to sulfate attack. On the other hand, the EPZ cement lost about 35% strength in the 28-day immersion test, and subsequently continued to lose more strength so that 63% strength loss was obtained at the end of the 56-day immersion period. Although the 28-day immersion specimens had only some surface cracking, the 56-day immersion specimens were distinctly cracked (Fig. 7).

Both the portland-pozzolan cements used in this test were found unsatisfactory in their sulfate resisting behavior. The portland-fly ash cement lost about 34% strength in the 28-day immersion. Visual inspection of the specimens gave evidence of expansion, however, cracking was not observed. The portland-trass cement exhibited considerable expansion and severe cracking (Fig. 7).

Comparison of 28-day immersion data with the 56-day immersion data shows that for all practical purpose a 28-day sulfate immersion period would be adequate for relative evaluation of sulfate resistant character of both ASTM Type V portland cements and of blended portland cements.

An attempt was made to explain the differences in the sulfate resisting behavior of cements on the basis of chemical changes occurring within the cement pastes as determined by X-ray diffraction analyses (XRD).

XRD of anhydrous cements did not reveal any significant information except that the composition of Fss was not identical in Type V cements. This conclusion was reached when their residues were carefully examined by XRD after removal of the silicate phases by salicylic acid extraction. In Cement Nos. 1, 3 and 4, the Fss composition corresponded exactly to the published d-spacings for the compound C_4AF . In Cement No. 2, the d-spacings corresponded with a composition which is between C_4AF and C_6AF_2 . In Cement No. 5, the d-spacings indicated a composition which is between C_4AF and C_6A_2F . Although the computed proportion of Fss in Cement Nos. 2 and 3 is identical, the intensity of the X-ray diffraction peaks due to Fss in Cement No. 3 was significantly lower, thus raising the possibility that part of the Fss in this cement may be in a poorly crystalline or more reactive state.

Relative intensity of characteristic XRD peaks from specimens exposed for 28 days to sulfate solution is shown in Table 4. Although XRD examination in this investigation was of preliminary nature in the sense that several anomalies in the strength data remain unexplained, the following tentative conclusions may be drawn from the analysis of the XRD data:

- (a) In the Type V cements, it appears that poor resistance to sulfate attack by Cements Nos. 3 and 5 is associated with considerable gypsum formation.
- (b) The Fss phase present in Cement Nos. 3 and 5 appeared to be more reactive than the Fss phase present in Cements Nos. 1, 2 and 4 since no anhydrous Fss was detected in the 35-day old specimens of Cements No. 3 and 5.

(c) Formation of ettringite alone is not sufficient to cause structural distress in cement paste. For instance, Cement No. 3 had a smaller quantity of ettringite than Cement Nos. 1 and 4, after 28 days of sulfate immersion, yet the former showed relatively high strength loss. Also, the XRD peaks due to ettringite were sharp and strong in the HOZ cement (Cement No. 6), yet this cement did not show significant strength loss even up to 56 days of sulfate immersion. It may be noted that no Ca(OH)_2 and gypsum were detected in this cement.

The other blended cements, namely Cement Nos. 7, 8 and 9 showed considerable strength loss when in addition to ettringite, gypsum and Ca(OH)_2 were also present in considerable quantities. This observation is consistent with the hypothesis proposed by Mehta (6) that ettringite formed in presence of excess of lime and sulfate is micro-crystalline, and that it is this type of ettringite which is associated with large expansions.

The strength gains on sulfate immersion for Cement No. 2 during the 28 to 56-day immersion period, and for Cement No. 4 during the 0 to 56-day immersion period is not considered due to normal experimental error. It is suggested that under the restraining conditions provided by the cement strength, a small quantity of ettringite formed may be serving as a reinforcing rather than a deleterious agent for the system. This explains why the Type V cement having 2% C_3A was found superior in sulfate resisting characteristic than the Zero- C_3A Type V cements.

The procedural details involving casting, curing, sulfate immersion and testing of specimens are standard enough to yield reproducible results as determined by a duplicate round of tests performed on one of the cements, namely Cement No. 6. In the first round of tests, the average 7-day

compressive strength (before sulfate immersion) was 7130 psi, and the strength reductions after the 28-day and the 56-day immersion periods were 5.0% and 8.0% respectively. In the second round of tests, the average 7-day compressive strength was 7350 psi, and the strength reductions after the 28-day and the 56-day sulfate immersion periods were 5.6% and 8.3% respectively.

Although, no attempt is made to correlate the laboratory behavior of the 9 cements used in this investigation with the actual field performance against sulfate attack, the laboratory results appear to be consistent with the state of the art. For instance, in the technology, of portland blast-furnace cements, Locher's (7) finding is well accepted in that portland blast-furnace slag cements containing less than 70% slag are not safe with regard to sulfate attack. The reason appears to lie in the fact that free Ca(OH)_2 from the hydrated portland cement constituents of a blended cement must be reduced to negligible amounts if formation of gypsum and expansive ettringite on sulfate exposure is to be reduced. For the same reason, those portland-pozzolan cements which do not have the capacity to eliminate from the hydrated cement system most of the Ca(OH)_2 , are bound to promote formation of gypsum and expansive ettringite on sulfate exposure. Ettringite formation in the blended cements is further helped by the presence of appreciable quantities of alumina in the slags or pozzolans.

CONCLUSIONS

- (1) Differences exist in the sulfate resisting behavior of ASTM Type V portland cements, and blended portland cements. A new laboratory test, which is reliable, quick, and reproducible, has been investigated and found useful in evaluating the sulfate resisting characteristic of cements.
- (2) Regarding ASTM Type V portland cements, it is concluded from the laboratory data that zero- C_3A cements are not necessarily superior in their performance against sulfate attack to portland cements which contain some C_3A . In the accelerated test, a portland cement with 2% C_3A did not show any strength loss on exposure up to 56 days to a 4% Na_2SO_4 solution, whereas the three zero- C_3A cements, and a 4% C_3A cement showed some loss in compressive strength.
- (3) On the basis of X-ray diffraction analyses, it is concluded that strength loss on sulfate exposure is not a function of ettringite formation alone. Cement pastes in which considerable gypsum was detected besides ettringite usually exhibited greater strength loss. This conclusion is consistent with field experience.
- (4) It appears that physical character of the ferrite phase present in anhydrous portland cement, and the ettringite phase present in cement paste (as a result of sulfate reaction) have considerable influence on the performance of a cement exposed to sulfate attack. Poorly crystalline ferrite phase may hydrate quickly and thus provide alumina for ettringite formation. Poorly

crystalline ettringite formed in presence of excess of lime and sulfate, is assumed to be responsible for expansion and cracking.

- (5) Blended portland cements containing granulated blast-furnace slag, or pozzolans may not necessarily be sulfate resistant. A portland blast-furnace slag cement containing 30% granulated slag, a portland pozzolan cement containing 20% of a fly ash, and a German trass cement did not possess adequate resistance to sulfate attack when tested in this investigation. On the basis of X-ray diffraction studies it seems that the sulfate resisting behavior of blended cements depends on the total reactive alumina and Ca(OH)_2 present in the hydrated cement paste at the time of sulfate exposure.

ACKNOWLEDGEMENT

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Table 1. Chemical Analysis of ASTM Type V Portland Cements, Percent

Composition	No. 1	No. 2	No. 3	No. 4	No. 5
SiO ₂	20.52	21.54	21.00	21.77	23.00
Al ₂ O ₃	3.52	2.61	2.86	3.77	3.52
Fe ₂ O ₃	5.83	4.92	4.76	5.39	2.75
CaO	65.31	66.32	66.23	63.89	65.34
MgO	0.80	0.72	1.08	1.00	1.23
SO ₃	2.91	2.52	2.85	1.66	2.15
Na ₂ O	0.08	0.10	0.09	0.27	0.31
K ₂ O	0.45	0.40	0.45	0.36	0.28
Ignition Loss	1.34	0.67	0.75	1.24	1.10
A/F Ratio	0.60	0.53	0.60	0.70	1.29
C ₃ S	69	73	75	56	56
C ₂ S	7	6	4	20	24
C ₃ A	0	0	0	2	4
Fss	17	14	14	16	8

Table 2. Compressive Strength Changes in Type V Portland Cements After 28 Days of Immersion in Sulfate Solution.

Cement No.	Compressive Strength Before Sulfate Immersion, psi	Compressive Strength After Sulfate Immersion, psi	Change in Compressive Strength, Percent
1	7680	6670	-13
2	7790	6530	-16
3	7510	5390	-28
4	7660	8410	+10
5	6780	4830	-29

Table 3. Compressive Strength Changes in Blended Portland Cements After 28 Days of Immersion in Sulfate Solution.

Cement No.	Compressive Strength Before Sulfate Immersion, psi	Compressive Strength After Sulfate Immersion, psi	Change in Compressive Strength, Percent
6	7130	6770	-5.0
7	8130	5270	-35.2
8	6640	4410	-33.6
9	7160	2940	-59.0

Table 4. Relative Intensity of Characteristic XRD Peaks from Specimens After 28-Day Sulfate Immersion

Cement No.	Ettringite 9.71 Å	Monosulfate Hydrate, $18 \text{ H}_2\text{O}$ 9.50 Å	Gypsum 7.56 Å	Ca(OH) ₂ 4.91 Å	Fss 7.25 Å
1	Medium	N.D.	Low	High	High
2	Low (broad)	N.D.	Low	High	High
3	Low (broad)	N.D.	High	High	N.D.
4	Medium	N.D.	Low	Medium	High
5	Medium	Present	High	High	N.D.
6	High	Present	N.D.	N.D.	-
7	High	Present	Medium	Medium	-
8	High	Present	High	Medium	-
9	Very High	Present	Very High	N.D.	-

V.D. = not detected.

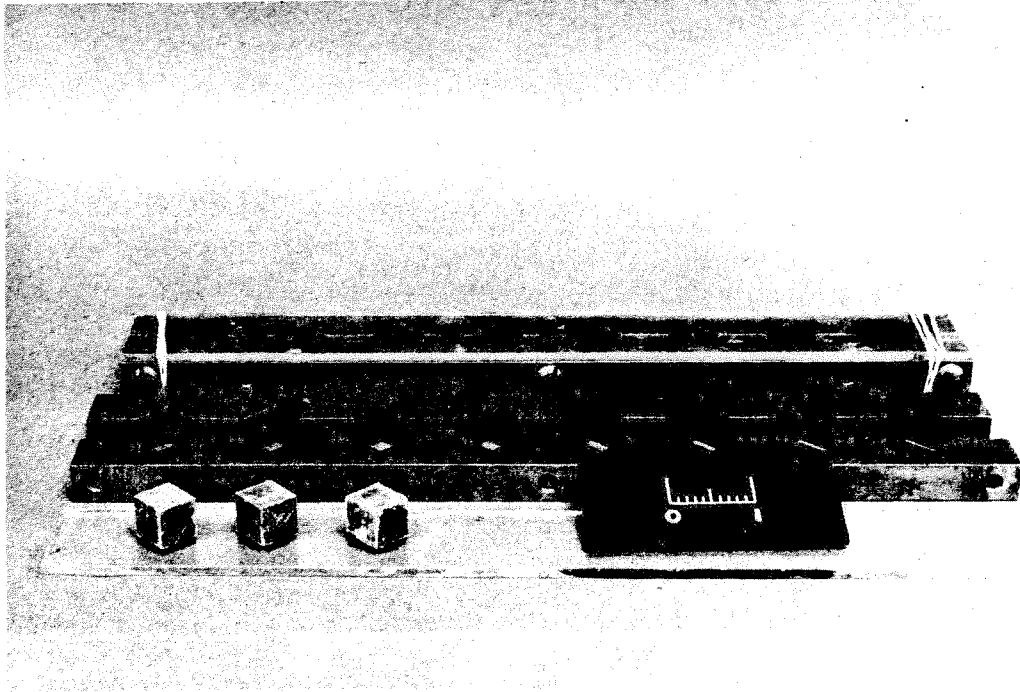


FIG. 1 BRASS GANG MOLDS USED FOR CASTING
1/2 IN. SPECIMENS

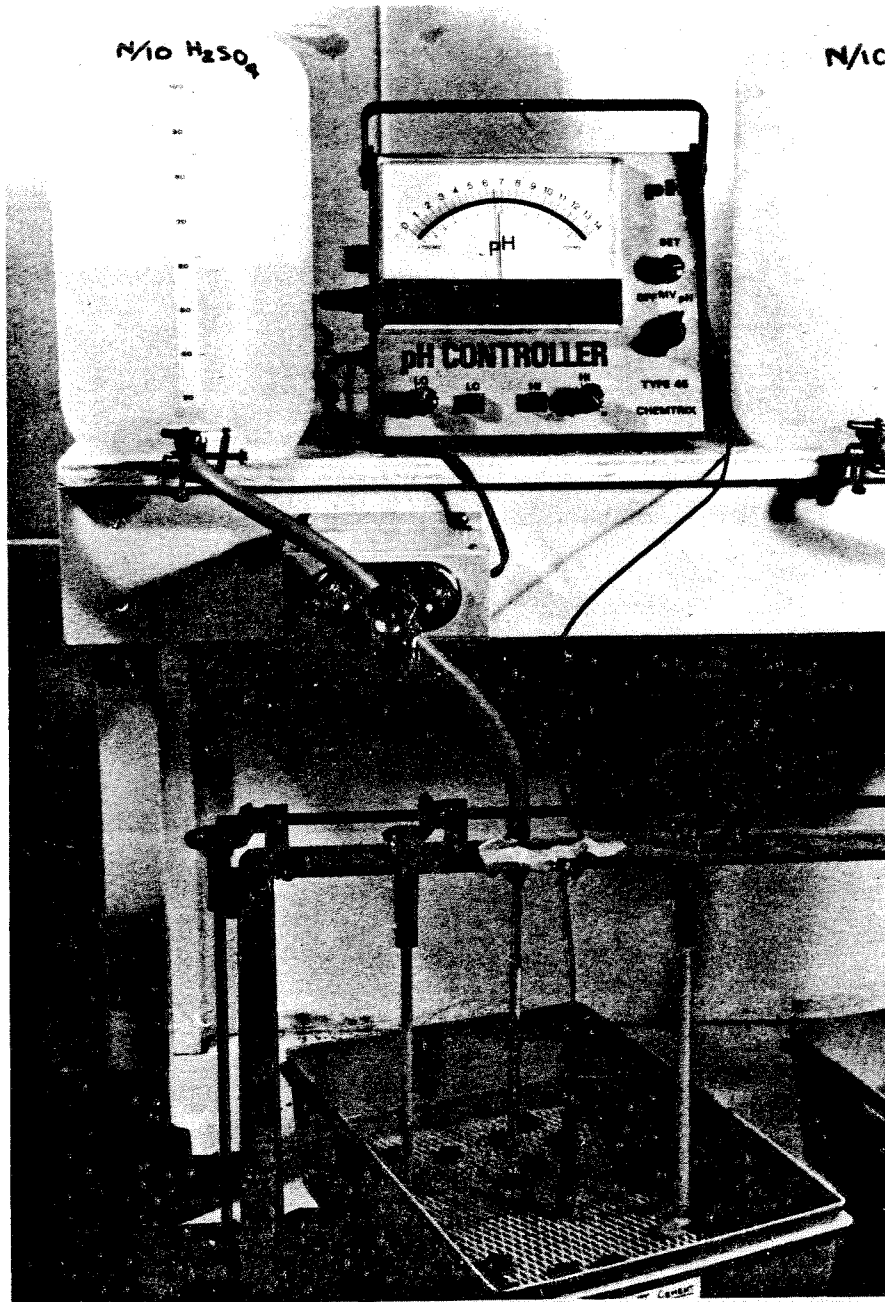


FIG. 2 A TYPICAL IMMERSION TANK WITH STIRRERS AND pH-STAT.

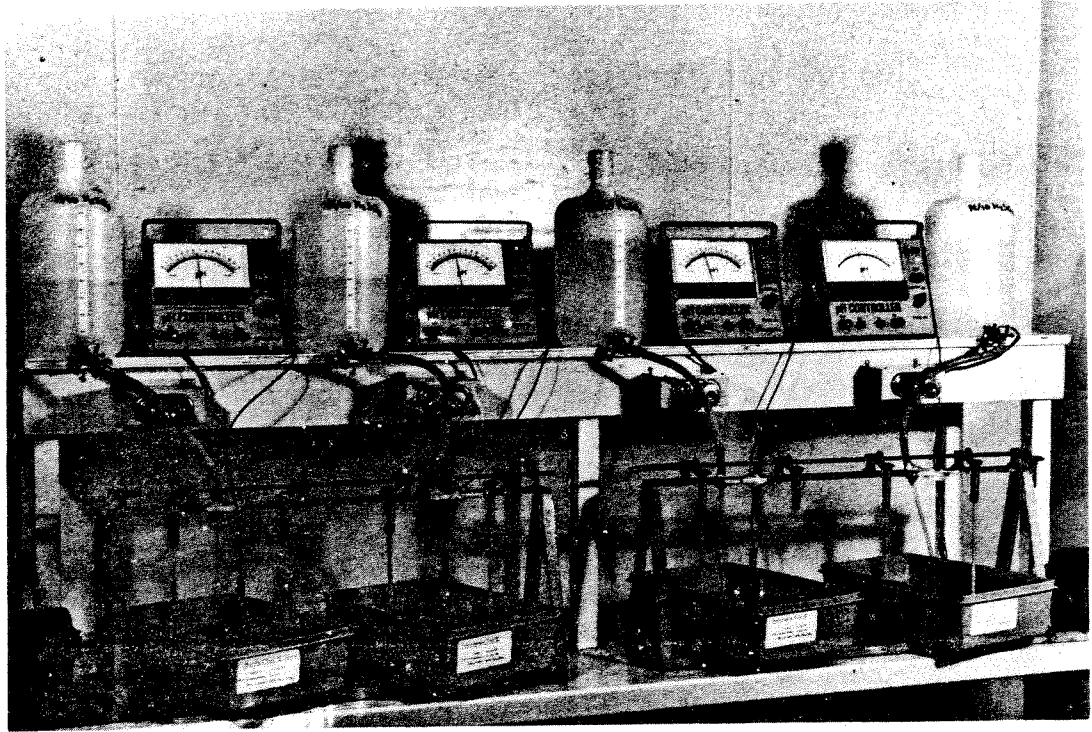


FIG.3 AN ASSEMBLY OF IMMERSION TANKS FOR TESTING SEVERAL CEMENTS SIMULTANEOUSLY

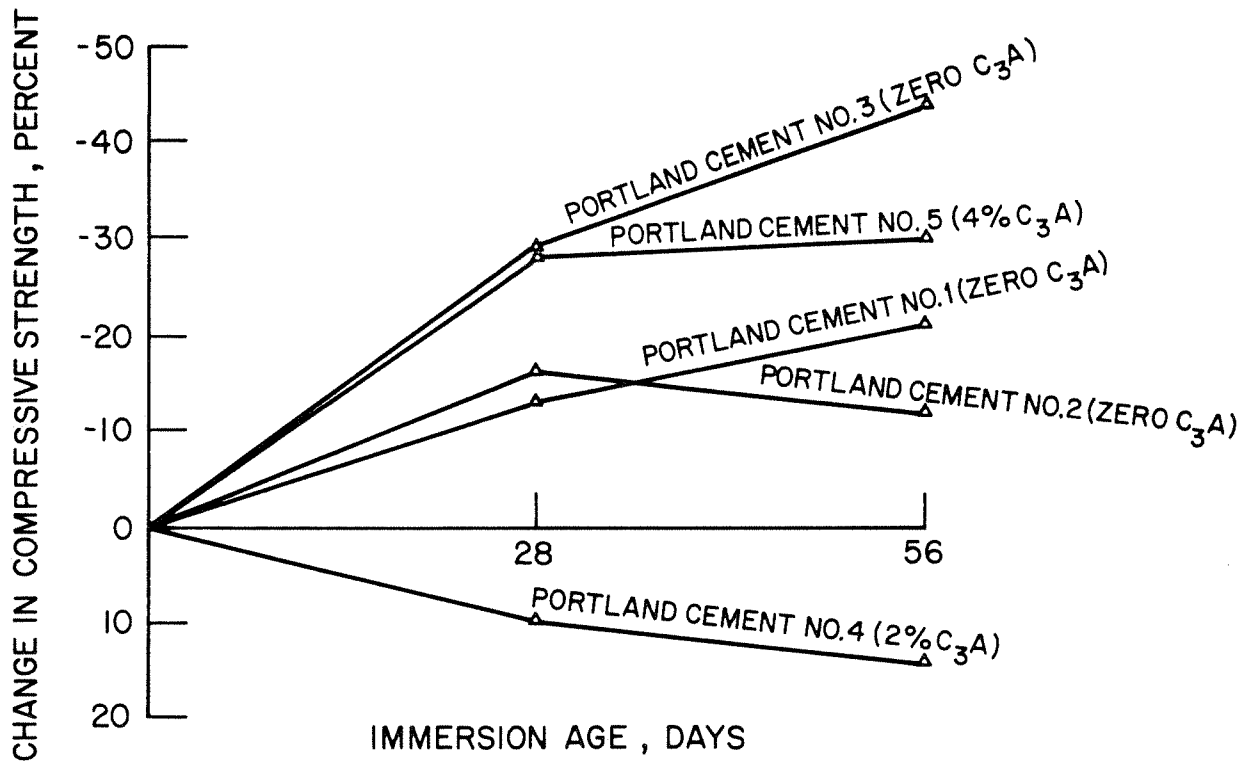


FIG. 4 COMPRESSIVE STRENGTH CHANGES IN TYPE V PORTLAND CEMENTS DURING 56 DAYS OF IMMERSION IN SULFATE SOLUTION

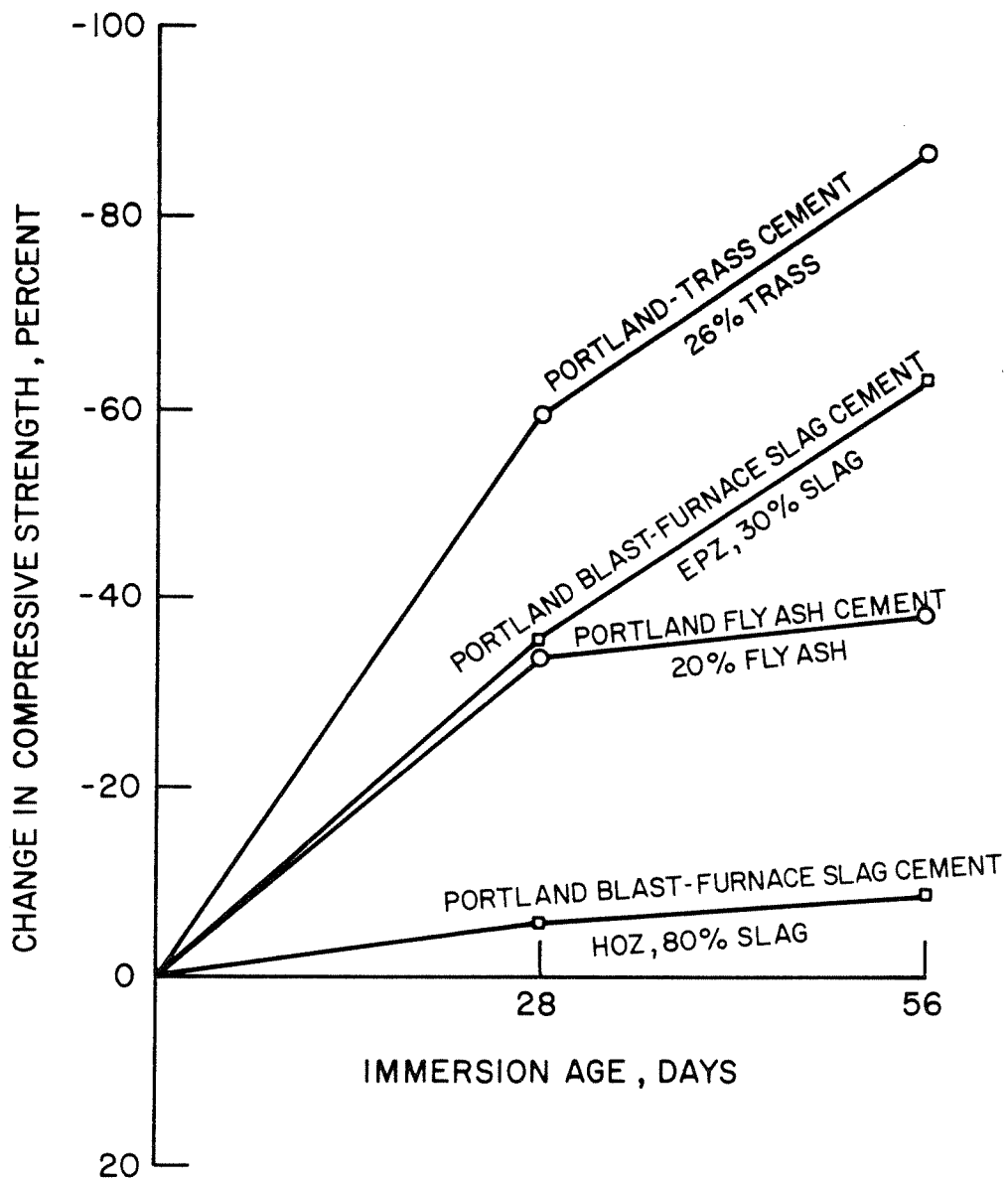


FIG. 5 COMPRESSIVE STRENGTH CHANGES IN BLENDED PORTLAND CEMENTS DURING 56 DAYS OF IMMERSION IN SULFATE SOLUTION

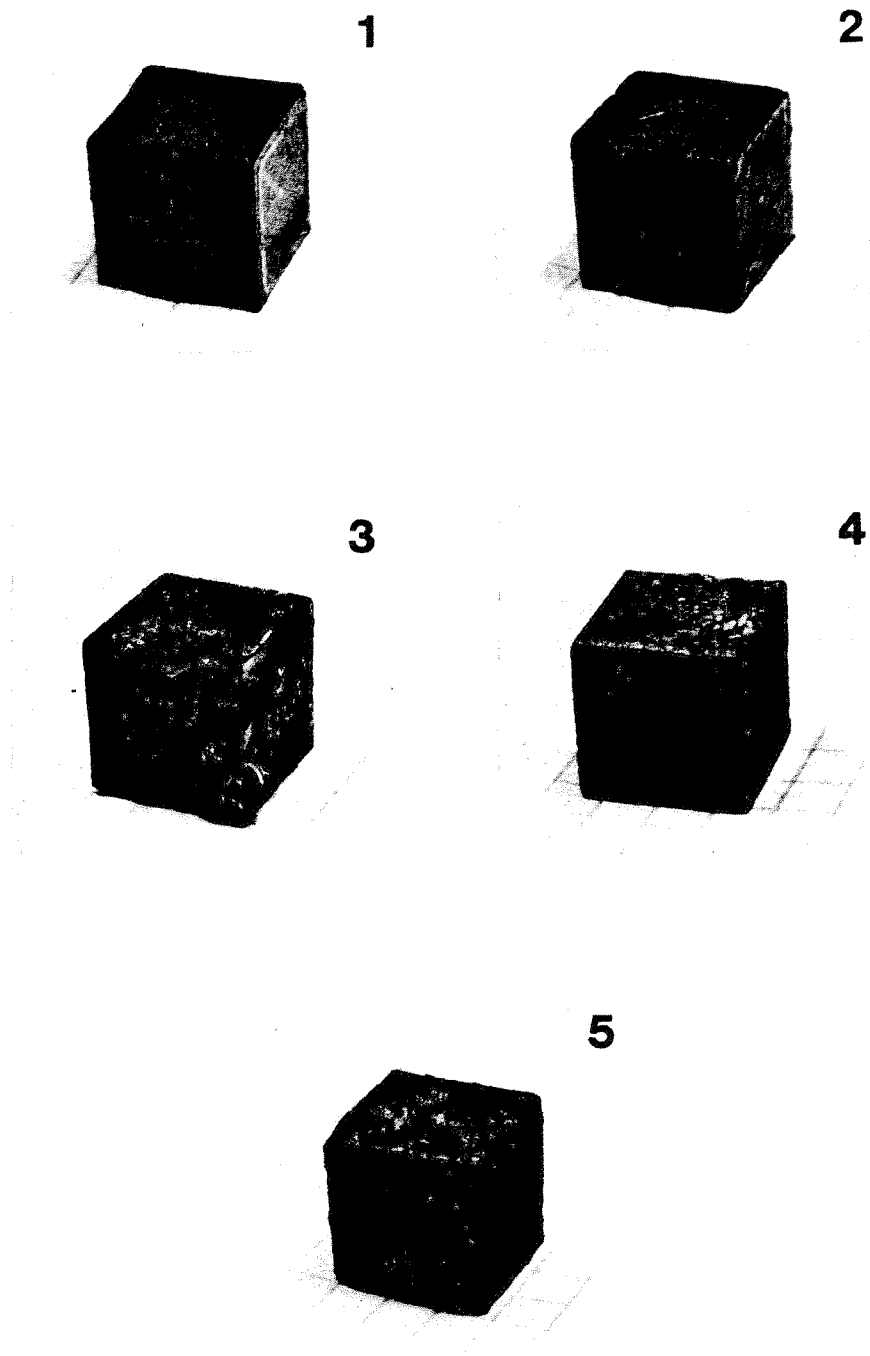
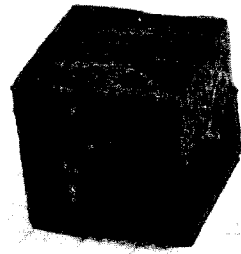
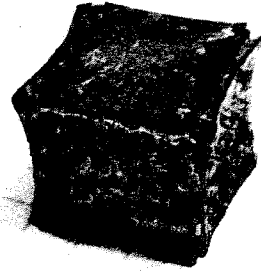


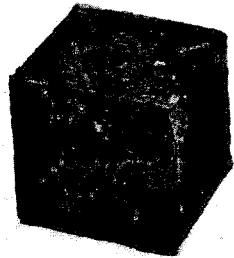
FIG. 6 SPECIMENS OF ASTM TYPE V PORTLAND CEMENTS
AFTER 28 DAYS OF IMMERSION IN SULFATE SOLUTION



6



7



8



9

FIG.7 BLENDED PORTLAND CEMENTS AFTER 56 DAYS OF IMMERSION IN SULFATE SOLUTION