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Sulfate-Attack Resistance and Gamma-Irradiation Resistance of Some Portland Cement Based Mortars

Prepared by P. Soo, L.W. Milian

Brookhaven National Laboratory

Prepared for
U.S. Nuclear Regulatory Commission

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Prepared by
P. Soo, L.W. Milian

Brookhaven National Laboratory
Upton, NY 11973

Prepared for
Division of Engineering
Office of Nuclear Regulatory Research
U.S. Nuclear Regulatory Commission
Washington, DC 20555
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ABSTRACT

Sulfate-attack and gamma-irradiation tests were carried out on three Portland cement mortars. For the sulfate attack work an accelerated test was used involving alternate immersion in Na_2SO_4 solution and oven drying of the samples. Attack was monitored through length-change measurements. Cement mortar containing silica fume gave unexpectedly poor resistance to attack. Reasons for this behavior are unclear. Gamma irradiation was found to cause losses in compressive strength at low doses in the 10^7 rad range. The irradiation time is a major factor in the strength-loss mechanism, whereas the dose rate is of secondary importance for the testing conditions studied.

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1. INTRODUCTION

Current low-level waste in the United States is buried in shallow-land trenches. Because of the potential for water infiltration into the trench and the leaching of radionuclides from the wastes, there is significant interest in alternate disposal technologies (Bennet, et al, 1985; Shaw, et al, 1986). These usually involve disposal within engineered concrete structures which are expected to last for periods of hundreds of years without failure.

In order to demonstrate that such a structure can meet design lifetime goals, it is first necessary to identify the potential failure/degradation modes of concrete and then to carry out additional work to determine the time period for failure for each mechanism under anticipated conditions.

A recent study by MacKenzie, et al, (1986), showed that cement-based materials are susceptible to attack by sulfate, which is often present in soil. Under certain conditions, swelling of the material occurs leading to serious losses in strength. A less likely, but little-studied degradation mechanism, is concerned with gamma irradiation of the concrete. Such radiation is emitted by many types of low-level waste. Until recently, it appeared that the levels of radiation to cause concrete degradation were extremely high ($\sim 10^{10}$ rad); (Hilsdorf, 1978; Kaplan, 1983). However, there do not appear to be any detailed studies on dose rate effects. It is possible that, for a given cumulative dose, the amount of damage is larger for the low dose rates expected in radioactive waste. Thus, it is necessary to systematically check dose rate effects on the damage rate to concrete before it can be confirmed that gamma-type irradiation, at levels appropriate to engineered barriers, is not an important degradation source.

In the sections following are given descriptions of research carried out to scope sulfate-attack and gamma-irradiation degradation processes for three Portland cement based materials. These are Portland I, Portland V, and Portland V/silica fume cement mortars. Since the samples tested were small, it was not advisable to use a regular size aggregate to mix with the cement. Instead, a standard Ottawa sand was employed in the preparation of the test materials.

2. EXPERIMENTAL PROCEDURES

Two sizes of cement mortar specimen were used in this program. For the sulfate-attack tests a 25.4 cm (10") long bar with a 2.54 x 2.54 cm (1" x 1") cross section was used. Sulfate attack was monitored through measurement of changes in length caused by immersion in sulfate solution. In the case of the gamma irradiation tests a smaller 2.54 cm (1") cube specimen was used for compression testing. A larger specimen would be more desirable but it was necessary to use miniature specimens in order to place the samples being irradiated into a region of uniform gamma flux.

2.1 Cement Mortar Compositions

Lea (1971) defines Portland cement as, "A product obtained by intimately mixing together calcareous and argillaceous, or other silica, alumina, and iron oxide-bearing materials, burning them at a clinkering temperature, and grinding the resulting clinker." Typical composition limits for Portland cements are (Lea, 1971):

	Percent
CaO	60-67
SiO_2	17-25
Al_2O_3	3-8
Fe_2O_3	0.5-0.6
MgO	0.1-5.5
$Na_2O + K_2O$	0.5-1.3
SO_3	1-3

Different compositions within these ranges are utilized to tailor the properties of the hydrated cement to particular service conditions. For example, ordinary Portland cement (Type I) was found to be susceptible to degradation through a chemical reaction between sulfate in the service environment and tricalcium aluminate ($3CaO.Al_2O_3$) in the cement. The resulting product had a larger volume, and caused internal stresses in the cement which often led to cracking. Portland V cement has a composition that contains only about 3 percent of $3CaO.Al_2O_3$ compared to 11 percent for Portland I. Its use is considered wherever sulfate attack is a potential failure mode.

An additional procedure to minimize chemical attack on cement-based materials is through the addition of constituents such as silica fume which tends to lower the porosity and, thereby, retard the rate of water ingress into the cement.

In this work three types of cement mortar were evaluated: Portlands I and V and Portland V/silica fume (PV/SF). As mentioned above, normal-size aggregates were not used because of the need to prepare small test specimens. A standard Ottawa sand was used instead.

The proportions of materials used to prepare mortar bars and cubes for both Portland I and V cements are described in ASTM Method C109. The method recommends a cement mortar with a water-to-cement ratio of 0.485 by weight and a graded Ottawa (Specification C778) sand-to-cement ratio of 2.75 by weight.

The PV/SF formulation consists of a water-to-binder ratio of 0.40 by weight which is a very dry mix; but the addition of a 3% Melment superplasticizer by weight of cementing materials yields a very workable mix. An ASTM Type V cement with a 15% by weight silica fume replacement was used. Finally, a one part binder (cement and silica fume) to 2.75 parts of graded Ottawa standard sand by weight completes the mortar composition. The formulation chosen was based on preliminary information from Ontario Hydro and scoping tests at BNL to gain familiarity with cement mortar mixes of this type. These tests involved the determination of optimum procedures for casting the specimens and then removing them from methyl methracrylate molds without damage. Tables 2.1 and 2.2 give the cement mortar compositions.

2.2 Component Mixing Procedure

The procedure for mixing mortars, that is, the sequence in which the different materials are to be added to the bowl and mixed, closely followed ASTM Standard C305. All batches were prepared using "an electrically driven mechanical mixer of the epicyclic type which imparts both a planetary and revolving motion to the mixer paddle." The method recommends the introduction of the materials into the mixing bowl in the following order: water, cement, and sand. The solids are added slowly as mixing is carried out at a slow speed. A similar procedure was incorporated for the mixing of the PV/SF except the Melment admixture was added following the water addition (then mixed thoroughly) and the silica fume was introduced prior to the sand addition (also mixed completely before sand addition).

2.3 Cube and Bar Mold Construction and Interior Surface Preparation

Mortar bar molds for the 25.4 cm long sulfate-attack test specimens were purchased from Soil Test, Inc., which were constructed in accordance with the specifications given in ASTM C490. Information dealing with bar mold dimensions, etc., are given in ASTM C490. Molds for the 2.54 cm cube specimens were fabricated at BNL from clear, rigid methyl methacrylate (acrylic sheet).

ASTM C490 recommends the use of microcrystalline wax to seal all joints and contact lines between the pieces of the mold; however, in this experiment, Dow Corning RTV (room temperature vulcanizing) silicone rubber adhesive/sealant (Type 732) was used. In addition, the method recommends applying a thin layer of mineral oil on all the interior portions of the molds to facilitate removal of mortar bars. However, removal of the samples was quite difficult and mineral oil was deemed unsatisfactory. The substitute release agent used was WD-40, a multi-purpose penetrant/lubricant. The choice was based on a conversation with the co-author of ASTM Standard C490. Both the cubic (acrylic construction) and the bar (metal construction) mold interior surfaces were coated with WD-40. After two hours of ambient air drying, any lubricant that had not evaporated was removed with a tissue. Following the removal of excess WD-40 the molds were allowed to dry for a minimum of one hour before any new casting of cement mortar was initiated.

Table 2.1 Composition of Portland cement mortar bars and cubes.

Component	Weight per Batch (g)
Cement[a]	1180.64
Sand[b]	3246.75
Water[c]	572.61
TOTAL	5000.00

[a] Refers to either Portland I or V cements.
[b] Ottawa standard sand sieved specifically for ASTM C109.
[c] Deionized water.

Table 2.2 Composition of Portland V/silica fume bars and cubes.

Component	Weight per Batch (g)
Cement[a]	921.69
Silica fume[b]	162.65
Sand[c]	2981.93
Water[d]	433.73
Melment superplasticizer[e]	32.53
TOTAL	4532.53

[a] Used the sulfate resisting ASTM Type V cement.
[b] Manufacturer is SKW, Becancover, Quebec. A 15% partial replacement by weight of cement was used, i.e., 15% of 1084.34 g.
[c] Ottawa standard sand sieved specifically for ASTM C109.
[d] Deionized water.
[e] A 3% by weight of cementing materials was used.

2.4 Molding and Curing of Cube and Bar Test Specimens

The procedure for molding cube and bar test specimens was identical for the three cement matrices used. ASTM C157, Section 8.1 and ASTM C109, Section 8.4, describe the procedure that was basically followed in casting the samples.

After the cement mortar was added to the molds it was tamped and compacted, and finally leveled with the surface of the mold. A bead of silicon rubber sealant was applied around the perimeter of each mold taking care not to allow the adhesive to contact the cement mortar mix. Next, a rigid acrylic cover was placed gently onto the top of the silicone rubber bead. This technique was used because preliminary testing showed that if the cover was pressed too tightly on the silicon bead then a very irregular surface was formed on the mortar bars following 28 days of curing. This result, in part, is due to the reabsorption of surface liquid (characteristic bleeding of cement mortars) generated during the cement curing process and which was in contact with the underside of the acrylic cover. This simple technique eliminated most of the upper surface irregularity associated with the tight seal technique.

The majority of cube and bar specimens was cured for 27-34 days at 21°C. One Portland I cement bar and one PV/SF bar, however, were cured for only 22 and 23 days, respectively, so that they could be included in batches of specimens being tested under sulfate-attack conditions.

Density measurements were made on the cement mortar bars. Table 2.3 shows the results of replicate determinations. Within the accuracy of the measurements, the densities are identical.

2.5 BNL Sulfate-Attack Test Procedure

The basic procedures for estimating sulfate attack effects in cementitious materials are documented in ASTM Standards. These include:

a. Standard C109, "Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or 50-mm Cube Specimens)."

   This procedure describes the preparation, curing, and mechanical testing of specimens.

b. Standard C1012, "Length Change of Hydraulic-Cement Mortars Exposed to a Mixed Sodium and Magnesium Sulfate Solution."

   This procedure gives a description of the immersion tests and the associated length-change measurements to quantify sulfate attack.

c. Standard C490, "Apparatus for Use in Measurement of Length Change of Hardened Cement Paste, Mortar, and Concrete."

   A description is given in this Standard of the comparator for measuring length changes in mortar bars as a result of sulfate attack. Techniques for measurement and calibration are specified.

Table 2.3 Densities of cement mortar bars used in sulfate-attack tests.

Cement-Mortar Type	Density (g/cc)
Portland I	2.15
	2.16
	2.13
	2.15
	2.17
	2.16
	Average 2.15
Portland V	2.15
	2.16
	2.16
	2.16
	2.16
	Average 2.16
PV/SF	2.17
	2.14
	2.14
	2.13
	2.17
	Average 2.15

The procedures adopted in the BNL research program closely follow those in the ASTM Standards except for some changes which are thought to offer improvement. One important deviation from the ASTM C1012 procedure is the use of an accelerated test developed by Kalousek and others (1976). Rather than use the continuous-immersion technique for sulfate absorption, they used a cyclic procedure involving immersion in a 2.1% Na_2SO_4 solution followed by forced-air drying at 54°C. Drying causes evaporation of excess pore water so that, upon reimmersion, fresh sulfate solution can rapidly enter the pore structure. Kalousek and others found that their cyclic procedure for sulfate attack gave the same length increase as continuously-immersed cement bars in about one-eighth of the time.

The BNL immersion/drying cycle is:

Step 1: Immersion of specimens in 2.1% Na_2SO_4 solution (or deionized water) at room temperature for 16 h.

Step 2: Forced-air drying of the specimens for 7 h 40 min at 54 ± 1°C.

Step 3: 20 min cooling of the specimens in still air.

Step 4: Repeat Step 1.

All testing begins with an immersion cycle with specimens placed in plastic containers of Na_2SO_4 solution (or deionized water). Glass rods are placed on the bottoms of the containers to assure solution contact on all sides of the test bars. During weekends the samples are left in the immersion cycle and they accumulate 64 h of soaking during this period.

Four replicate test bars are placed in each container using 4 ± 0.5 volumes of Na_2SO_4 solution (or DIW) to one volume of mortar bar, as recommended in ASTM C1012. Solutions are covered with a rigid acrylic sheet at all times to minimize evaporation and contamination. During the drying cycle, mortar bars are stacked in stainless steel cradles which allow separation and efficient air circulation. Each cradle can accommodate eight bars. Immersion solutions are renewed every two weeks with a pH reading being taken immediately prior to renewal. Containers are cleaned of any deposited debris before fresh solutions are added. Samples are handled with rubber gloves at all times.

Figure 2.1 shows a typical arrangement for samples undergoing immersion. Shown in Figure 2.2 are eight mortar bars that have been placed on a stainless steel cradle prior to being transferred to an oven for the drying portion of the sulfate-attack test. The mortar bars do not contact the metal cradle directly, but are supported on quartz rods for efficient air circulation.

2.6 Gamma Irradiation of Cement Mortar Cubes

Following approximately 28 days of curing, mortar cube dimensions and weight were recorded. The cubes were then separated into four different batches, each batch containing specimens from the three cement mortar formulations. One batch was irradiated in air at about 10°C at a Co-60 gamma dose rate of 3.1×10^3 rad/h, and a second at 3.8×10^5 rad/h. Two unirradiated control batches were tested, also, to measure the extent of any irradiation-induced change in strength. One control batch was maintained at room temperature (~20°C) and the other at 10°C, the average temperature in the irradiation facility. Measurements taken with a thermocouple placed inside a drilled hole in a test cube undergoing irradiation at the higher dose rate confirmed that negligible gamma heating occurred, and that the temperature of the specimen was very close to 10°C. Little difference was expected between the strengths of cement mortar samples cured at 10 and 20°C, but it was decided that this should be confirmed.

Irradiated cubes were periodically removed for compressive strength testing together with specimens from the control batches.

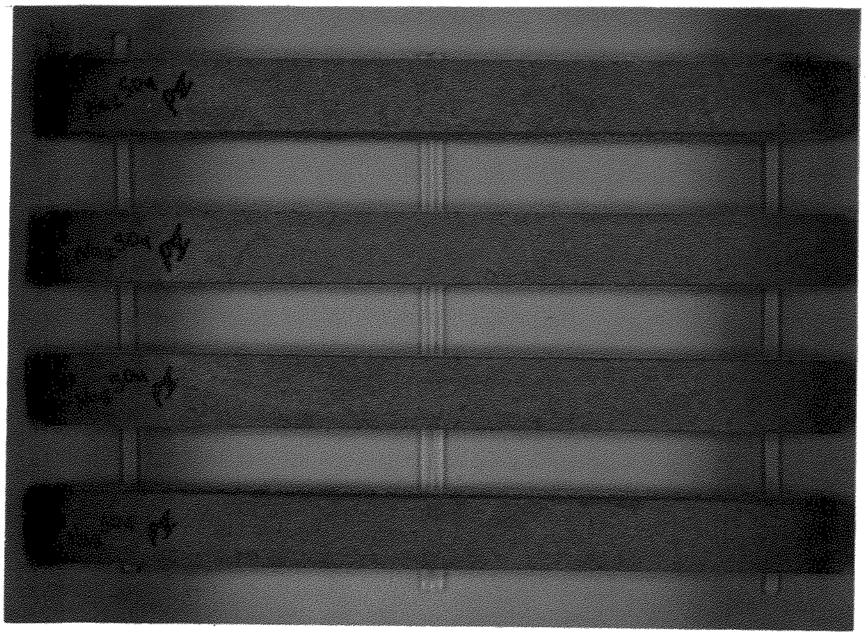

Figure 2.1 Typical arrangement for 10 in (25.4 cm) long cement mortar bars immersed in solution for sulfate-attack tests. In this case, Portland V bars are immersed in 2.1% Na_2SO_4 solution.

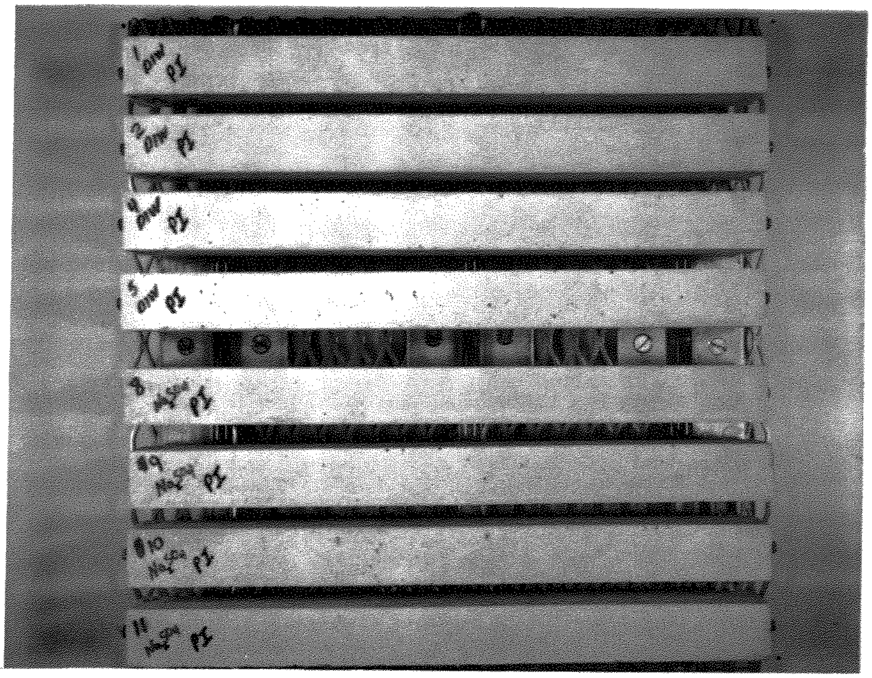

Figure 2.2 Portland I cement mortar bars after an 8 h oven-drying cycle.

3. SULFATE-ATTACK RESULTS AND DISCUSSION

3.1 Length-Change Measurements

The procedure for the accelerated sulfate-attack tests is given in detail in Section 2.5. Damage may be measured by visual inspection, weight loss, strength loss, decrease in the dynamic modules of elasticity, and expansion. From Kalousek's (1976) work failure of the cement/concrete is considered to occur when a 0.5 percent elongation is reached. Table 3.1 gives details of the expansions of the specimens during wet-dry cycling in 2.1% Na_2SO_4 solution. For these measurements a commercially purchased length comparator was used. Its design and use are given in ASTM Standard C490 (Apparatus for Use in Measurement of Length Change of Hardened Cement Paste, Mortar, and Concrete). Parallel wet/dry cycling experiments were conducted in deionized water to serve as controls for the sulfate immersion tests.

Portland I cement mortar shows little expansion in deionized water (DIW) after accumulating 115 cycles in a period of 182 d. When this material is exposed to Na_2SO_4 solution, however, the specimens show large amounts of expansion from the sulfate-attack process. The rate of expansion is initially small (about 0.23 percent after 48 cycles), but it rapidly increases to approximately 2.0 percent (after 115 cycles) as specimen cracking occurs, allowing faster ingress of sulfate into the cement.

Portland V cement is designed to be more resistant to sulfate attack and little change in length is noticed for DIW immersion, as would be expected. In the sulfate-solution tests there is significant expansion but is is only about 20 percent of that for Portland I material.

The PV/SF bars showed surprisingly poor sulfate-attack resistance. After 159 cycles the expansion is about 2.5 percent. Two test bars were so badly cracked that they fractured into two pieces during transfer to the drying oven. Even deionized water caused them to swell at a rate much higher than those for Portlands I and V mortar bars. That PV/SF can swell from exposure to pure water indicates that swelling is not totally attributable to sulfate attack.

Figures 3.1 through 3.6 show photographs of the different types of mortar bar after accumulating the 100-115 test cycles described in Table 3.1. For Portland I samples the length increase for the sulfate-immersed sample is clearly seen in comparison to the DIW control bar (Figures 3.1 and 3.2). Little porosity is seen from the "top surfaces" of the bars (Figure 3.1) which were the uppermost surfaces during casting of the specimens into their molds. More porosity is observed from a "side view" shown in Figure 3.2. Note the fine cracking in areas close to the edges of the specimens.

Portland V specimens show behavior similar to that for Portland I, but the expansion caused by sulfate attack is far less obvious (Figures 3.3 and 3.4). Edge cracking is also less than that for Portland I.

The photographs for the PV/SF (Figures 3.5 and 3.6) show the large amount of expansion from sulfate attack. Edge cracking is seen together with major cracking normal to the major axis of the bar. Compared to the Portland I and V specimens there is a larger amount of porosity, which may contribute to the

Table 3.1 Length increase measurements on cement mortar bars exposed to alternate wet-dry cycling in 2.1% Na_2SO_4 solution or deionized water.

Specimen	Test Solution	Test Time(d)	Number of Cycles	Initial Dial Gage Reading (in)	Final Dial Gage Reading (in)	Length Change(in)	% Change(1)
Portland I							
1	DIW	71	48	0.1810	0.1820	0.0010	0.01
2	DIW	71	48	0.1785	0.1790	0.0005	0.01
4	DIW	71	48	0.1770	0.1775	0.0005	0.01
5	DIW	71	48	0.1740	0.1745	0.0005	0.01
1	DIW	180	115	0.1810	0.1820	0.0010	0.01
2	DIW	180	115	0.1785	0.1795	0.0010	0.01
4	DIW	180	115	0.1770	0.1780	0.0010	0.01
5	DIW	180	115	0.1740	0.1745	0.0005	0.01
8	Na_2SO_4	71	48	0.0470	0.0715	0.0245	0.25
9	Na_2SO_4	71	48	0.0335	0.0580	0.0245	0.25
10	Na_2SO_4	71	48	0.1780	0.2000	0.0220	0.22
11	Na_2SO_4	71	48	0.1800	0.2010	0.0210	0.21
8	Na_2SO_4	180	115	0.0470	0.2480	0.2010	2.01
9	Na_2SO_4	180	115	0.0335	0.2320	0.1985	1.99
10	Na_2SO_4	180	115	0.1780	0.3730	0.1950	1.95
11	Na_2SO_4	180	115	0.1800	0.3710	0.1910	1.91
Portland V							
1	DIW	69	45	0.1605	0.1595	-0.0010	-0.01
2	DIW	69	45	0.1625	0.1615	-0.0010	-0.01
3	DIW	69	45	0.0470	0.0460	-0.0010	-0.01
4	DIW	69	45	0.0340	0.0330	-0.0010	0.01
1	DIW	166	105	0.1605	0.1610	0.0005	0.01
2	DIW	166	105	0.1625	0.1630	0.0005	0.01
3	DIW	166	105	0.0470	0.0475	0.0005	0.01
4	DIW	166	105	0.0340	0.0340	0	0
5	Na_2SO_4	69	45	0.1845	0.1895	0.0050	0.05
6	Na_2SO_4	69	45	0.1790	0.1835	0.0045	0.05
7	Na_2SO_4	69	45	0.0270	0.0335	0.0065	0.07
8	Na_2SO_4	69	45	0.0550	0.0605	0.0055	0.06
5	Na_2SO_4	166	105	0.1845	0.2180	0.0335	0.34
6	Na_2SO_4	166	105	0.1790	0.2125	0.0335	0.34
7	Na_2SO_4	166	105	0.0270	0.0745	0.0475	0.48
8	Na_2SO_4	166	105	0.0550	0.0990	0.0440	0.44
Portland V/Silica Fume							
2	DIW	74	44	0.1710	0.1770	0.0060	0.06
4	DIW	74	44	0.0445	0.0515	0.0070	0.07
5	DIW	74	44	0.1600	0.1665	0.0065	0.07
6	DIW	74	44	0.1525	0.1580	0.0055	0.06
2	DIW	159	100	0.1710	0.1815	0.0105	0.11
4	DIW	159	100	0.0445	0.0565	0.0120	0.12
5	DIW	159	100	0.1600	0.1720	0.0120	0.12
6	DIW	159	100	0.1525	0.1630	0.0105	0.11
7	Na_2SO_4	74	44	0.0250	0.0690	0.0430	0.43
8	Na_2SO_4	74	44	0.0410	0.0875	0.0465	0.47
9	Na_2SO_4	74	44	0.1565	0.1900	0.0335	0.34
11	Na_2SO_4	74	44	0.0300	0.0800	0.0500	0.50
7	Na_2SO_4	159	100	0.0250	0.3030	0.0278	2.78
8	Na_2SO_4	-	-	0.0410	-(2)	-	-
9	Na_2SO_4	159	100	0.1565	0.3915	0.235	2.35
11	Na_2SO_4	-	-	0.0300	-(2)	-	-

Note:

(1) Based on an effective length of 10.00 in.

(2) No measurement performed because mortar bar fractured during immersion/oven transfer.

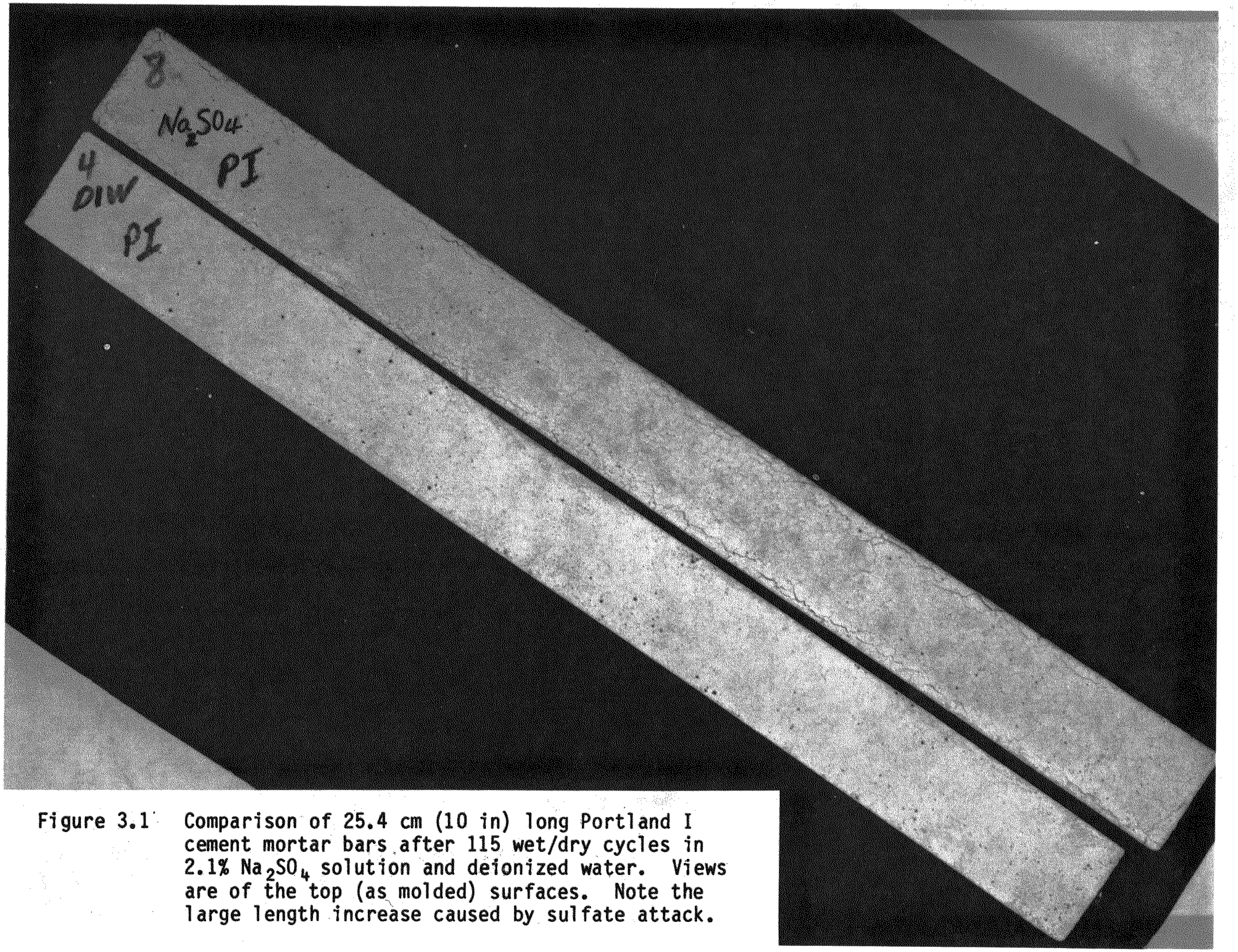

Figure 3.1 Comparison of 25.4 cm (10 in) long Portland I cement mortar bars after 115 wet/dry cycles in 2.1% Na_2SO_4 solution and deionized water. Views are of the top (as molded) surfaces. Note the large length increase caused by sulfate attack.

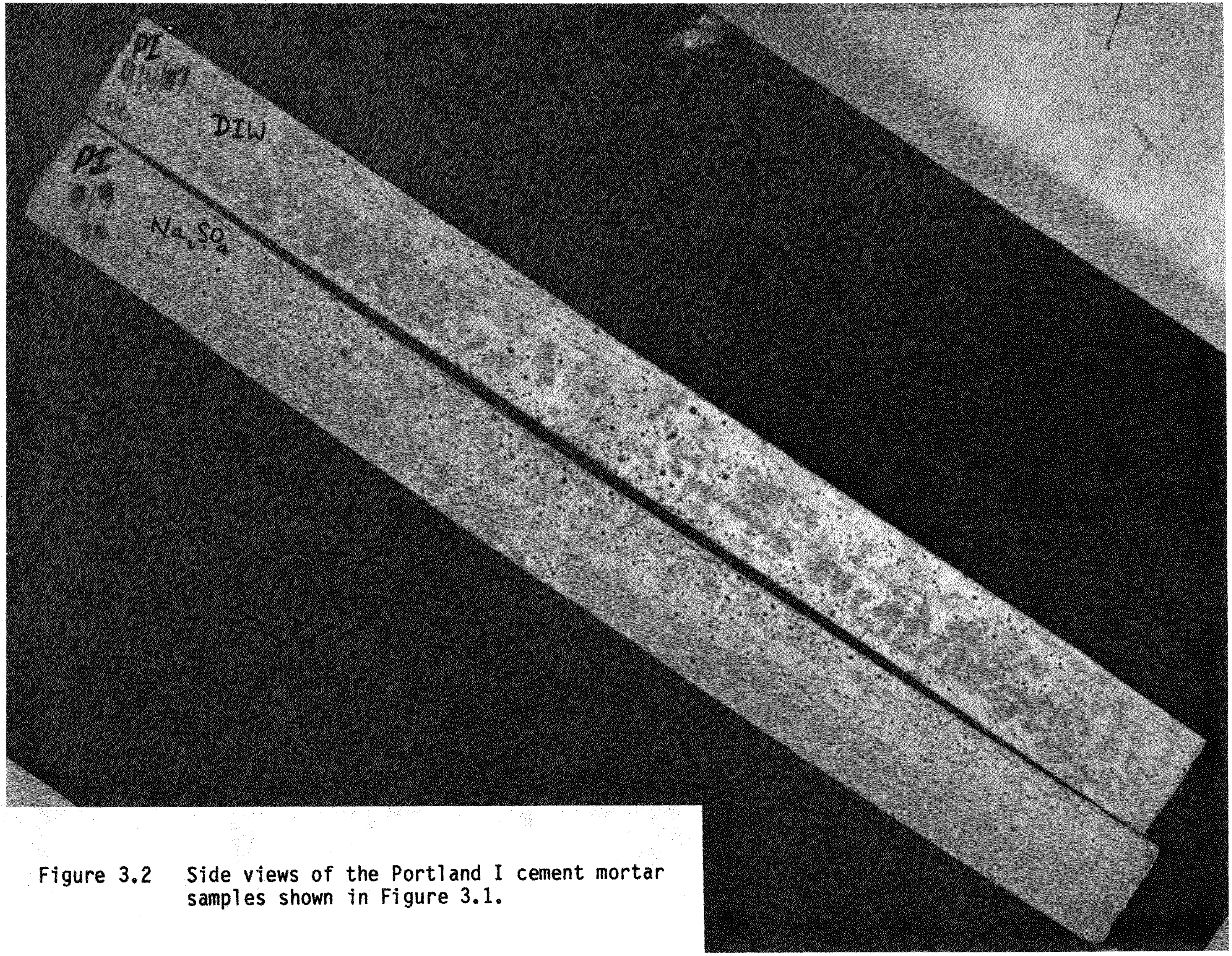

Figure 3.2 Side views of the Portland I cement mortar samples shown in Figure 3.1.

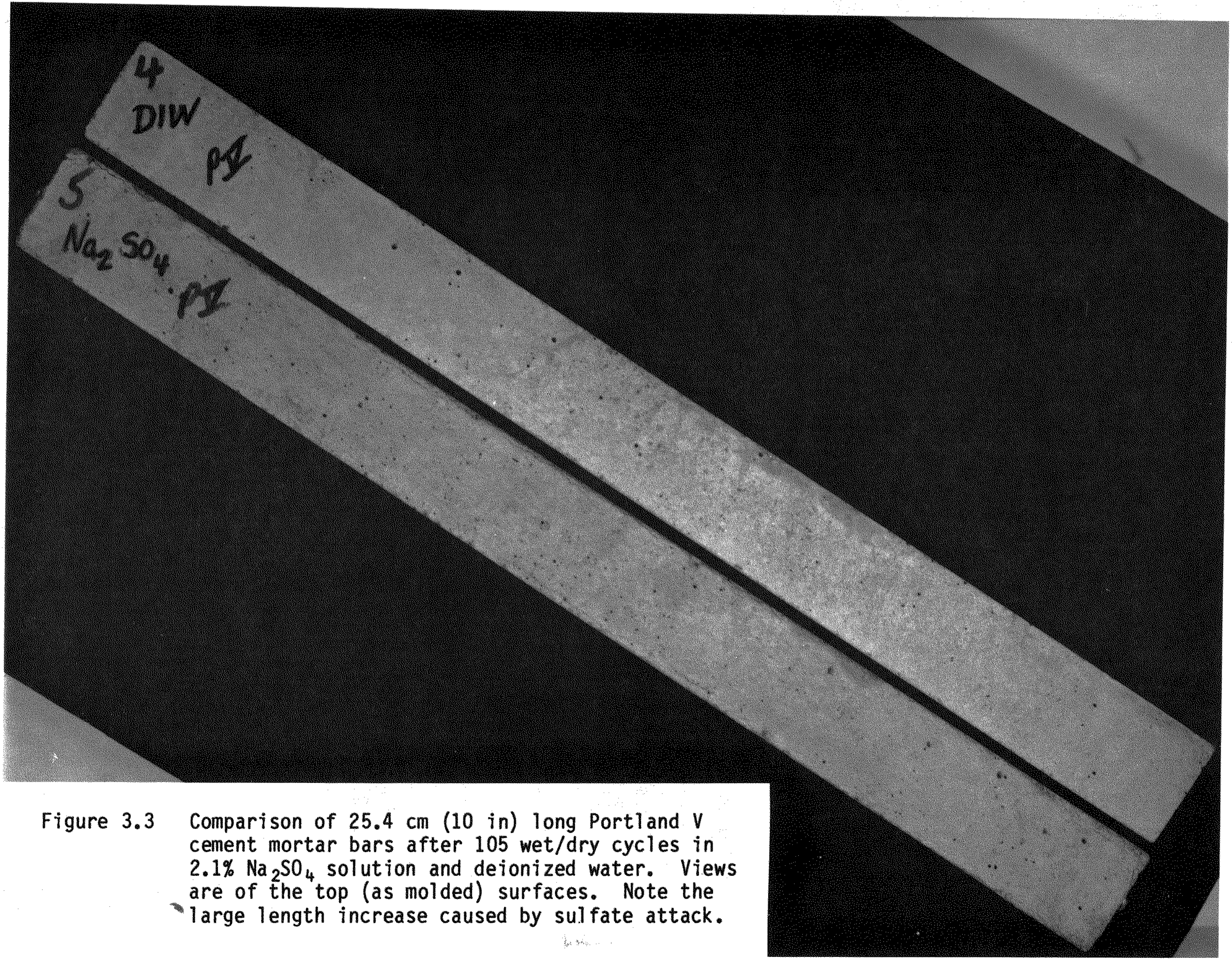

Figure 3.3 Comparison of 25.4 cm (10 in) long Portland V cement mortar bars after 105 wet/dry cycles in 2.1% Na_2SO_4 solution and deionized water. Views are of the top (as molded) surfaces. Note the large length increase caused by sulfate attack.

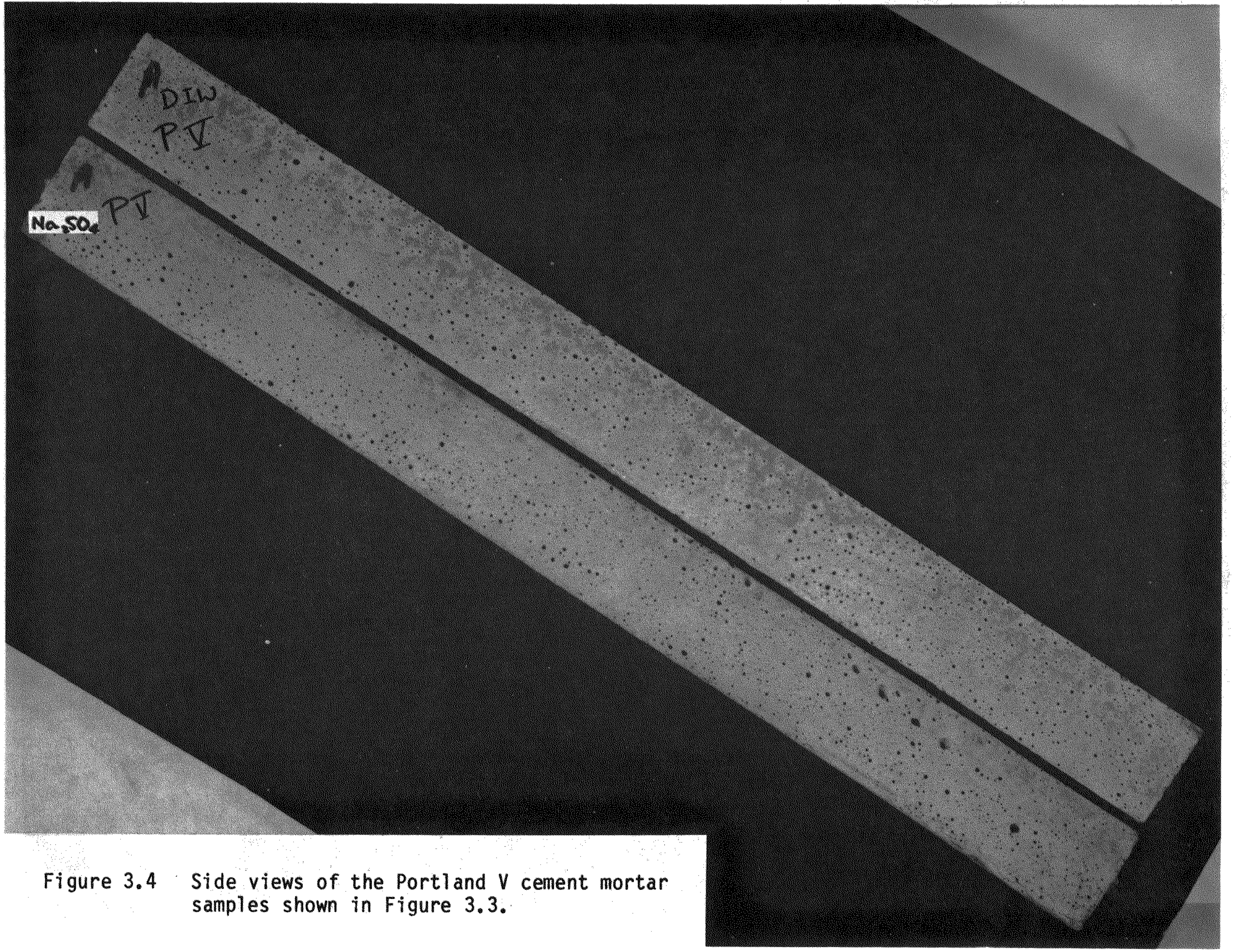

Figure 3.4 Side views of the Portland V cement mortar samples shown in Figure 3.3.

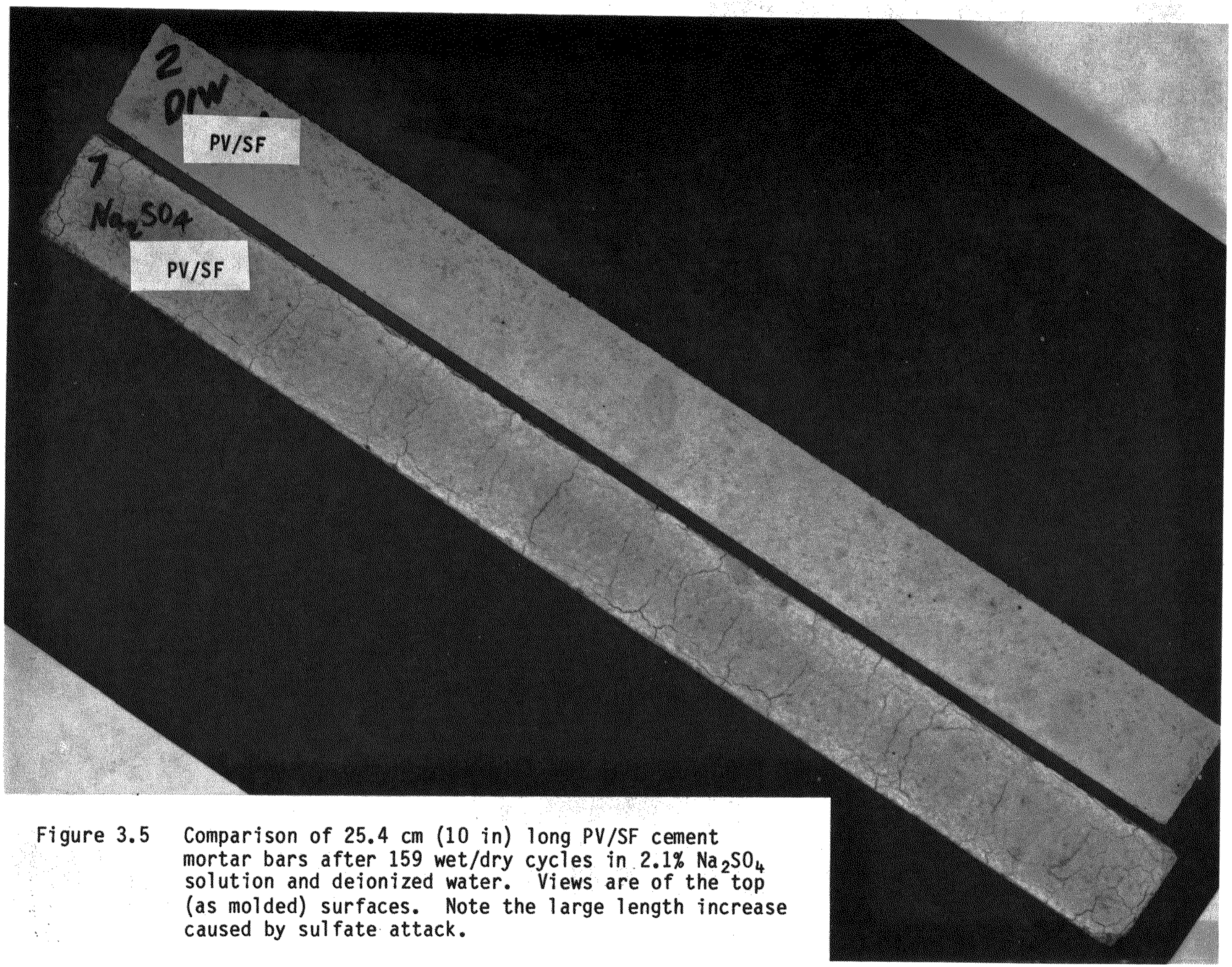

Figure 3.5 Comparison of 25.4 cm (10 in) long PV/SF cement mortar bars after 159 wet/dry cycles in 2.1% Na_2SO_4 solution and deionized water. Views are of the top (as molded) surfaces. Note the large length increase caused by sulfate attack.

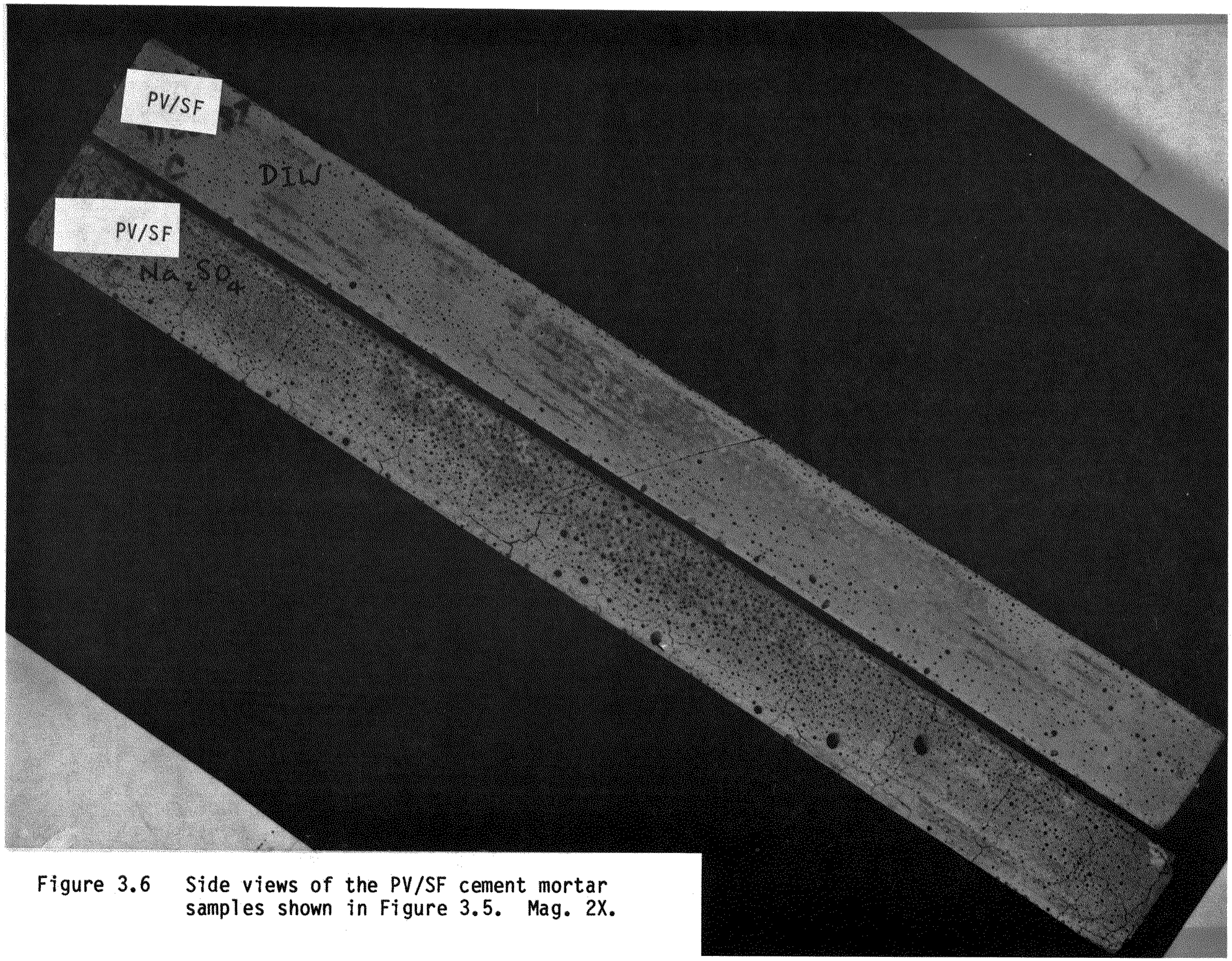

Figure 3.6 Side views of the PV/SF cement mortar samples shown in Figure 3.5. Mag. 2X.

ingress of sulfate solution and expansion. Nevertheless, the large amount of expansion and cracking is still surprising because the cement used in the PV/SF specimens is sulfate-resistant Portland V.

The data in Table 2.3 show that the densities of the three cement mortars are essentially identical. To check the porosity in the interior of the test bars, some of the test specimens were examined after sulfate-immersion testing. Figures 3.7 through 3.9 show low-magnification photographs of the three materials after prolonged cycling in water and sodium sulfate solution. Portland I and V cement mortars show very similar types of porosity, viz., very small pores with a number of much larger pores distributed throughout the section. For the PV/SF the pore structure is similar but the larger pores are slightly more numerous and larger than those for Portlands I and V cement mortars. However, they are not obviously interconnected and do not appear to provide rapid flow pathways for sulfate solution. Thus, excessive porosity in the PV/SF samples does not offer a satisfactory explanation for the poor resistance to sulfate attack. In fact, there is evidence that air entrainment in cement could be beneficial with respect to sulfate attack (Lea, 1971).

Higher-magnification photographs are shown in Figures 3.10 through 3.12 showing cross-sectional areas adjacent to the bar surfaces. The large pores are clearly visible among the smaller regular pores.

At this time, there is no satisfactory explanation for the poor sulfate-attack resistance of the PV/SF cement mortar. Since some workers have shown that this class of material is indeed capable of satisfactory behavior (Hooton, 1986), it is possible that sulfate-resistance is sensitively dependent on composition and the mixing procedure. If this is proved to be the case, then great care must be exercised to determine optimum conditions for the preparation of PV/SF cement-mortars for engineered structures.

3.2 Solution pH Changes

At the end of each immersion cycle the pH values of the solutions were measured and compared to the starting values for fresh solutions, viz., 6.5 for deionized water and 5.6 for 2.1 percent Na_2SO_4. Table 3.2 shows the results obtained. It is well known that water in contact with Portland cement becomes alkaline because of the leaching of alkaline constituents. During the first few immersion cycles the solution becomes very alkaline with pH values greater than about 10. With successive immersions, as the rate of leaching becomes slower, the pH values change less and, eventually, seem to stabilize. For deionized water the stable pH value is close to 8.2 and for the Na_2SO_4 solution it lies between 9 and 10 depending on the material being immersed. This stabilized behavior is very likely to be equivalent to the linear leach rate range which is commonly seen in cementitious waste forms (Hoyle, 1987). Note that for deionized water there is a much smaller pH change compared with the sulfate solution. This seems to confirm the observation that a more pronounced chemical reaction occurs between the cement mortars and the sulfate, leading to larger pH changes. It may be associated with internal cracking of the cement by the formation of higher-volume reaction products during the sulfate-attack process which, in turn, would allow an increase in the effective surface area being leached.

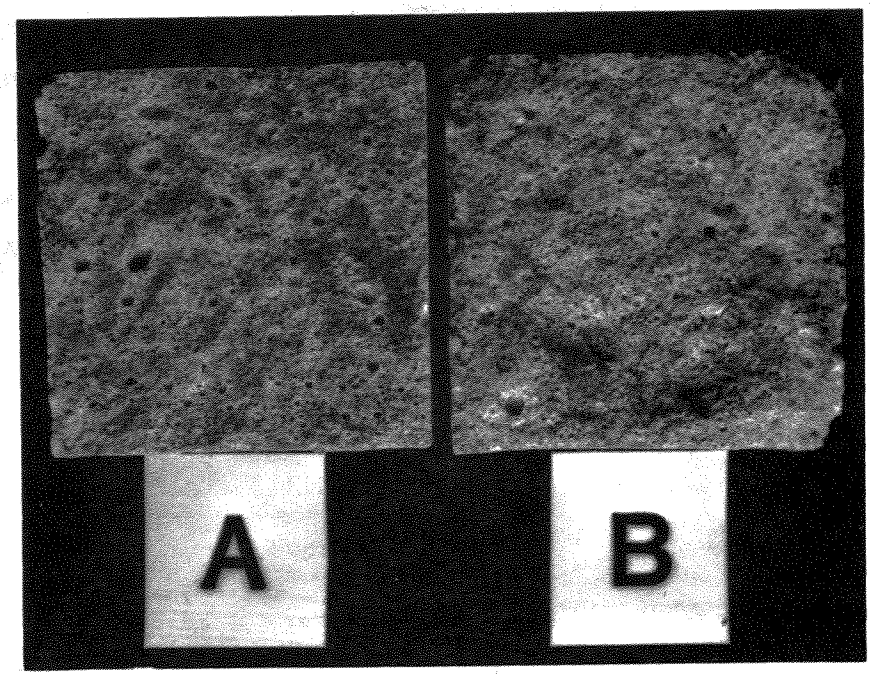

Figure 3.7 Pore structure in Portland I cement mortar bars after 115 wet/dry cycles in deionized water (A) and sulfate solution (B). Mag. 2X.

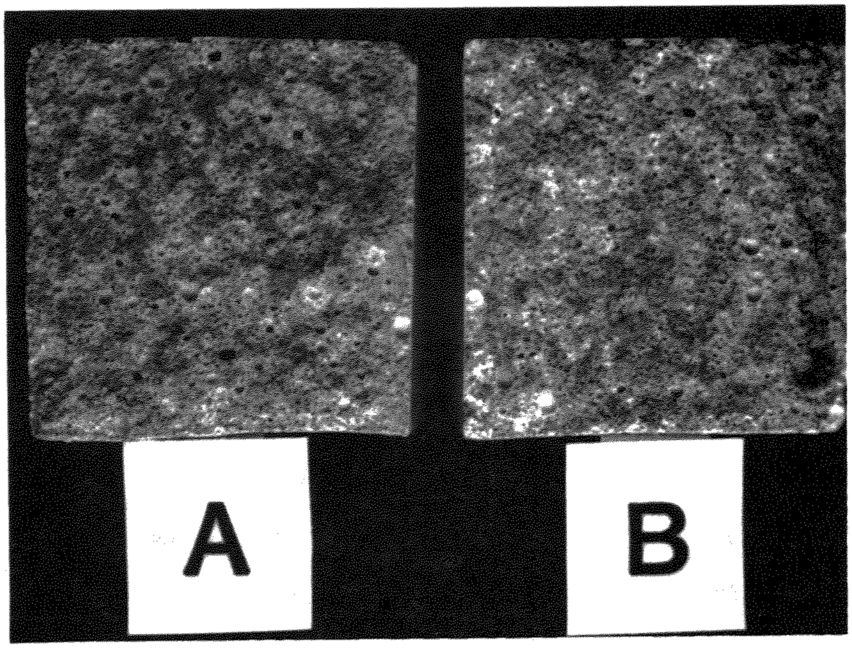

Figure 3.8 Pore structure in Portland V cement mortar bars after 105 wet/dry cycles in deionized water (A) and sulfate solution (B). Mag. 2X.

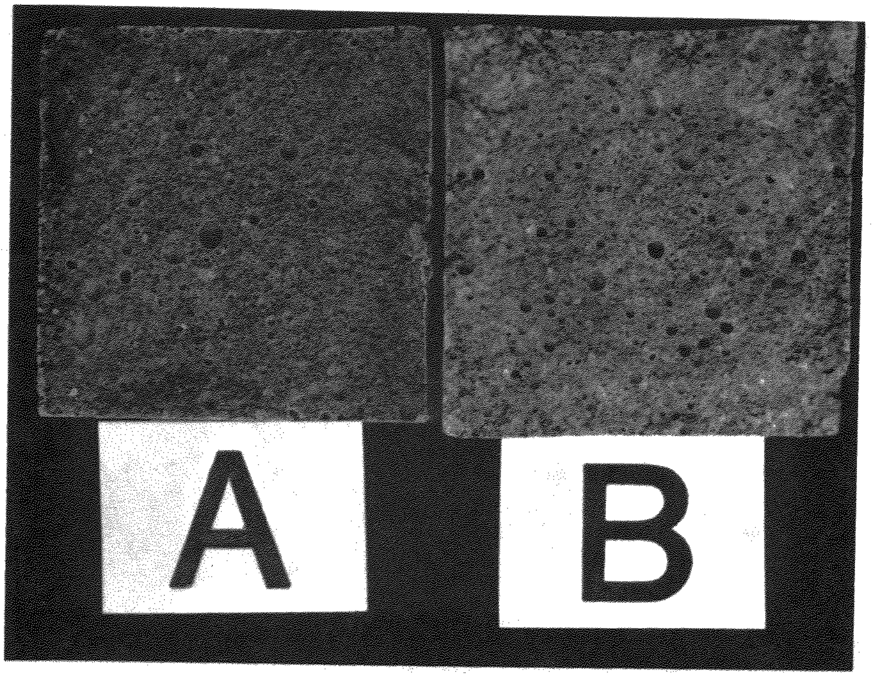

Figure 3.9 Pore structure in PV/SF bars after 100 wet/dry cycles in deionized water (A) and sulfate solution (B). Mag. 2X.

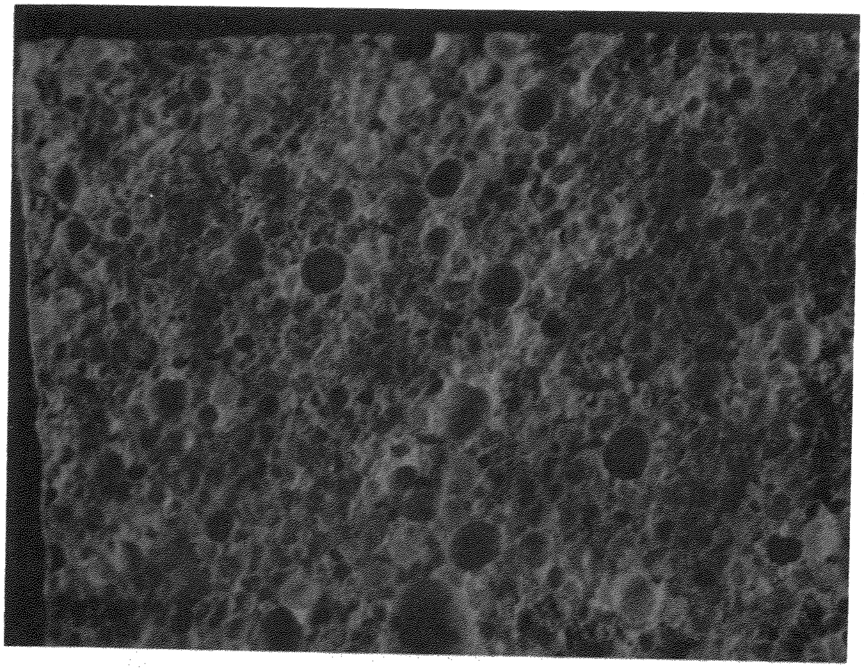

Figure 3.10 Pore structure in Portland I cement mortar bars after 115 wet/dry cycles in deionized water. Mag. 7X.

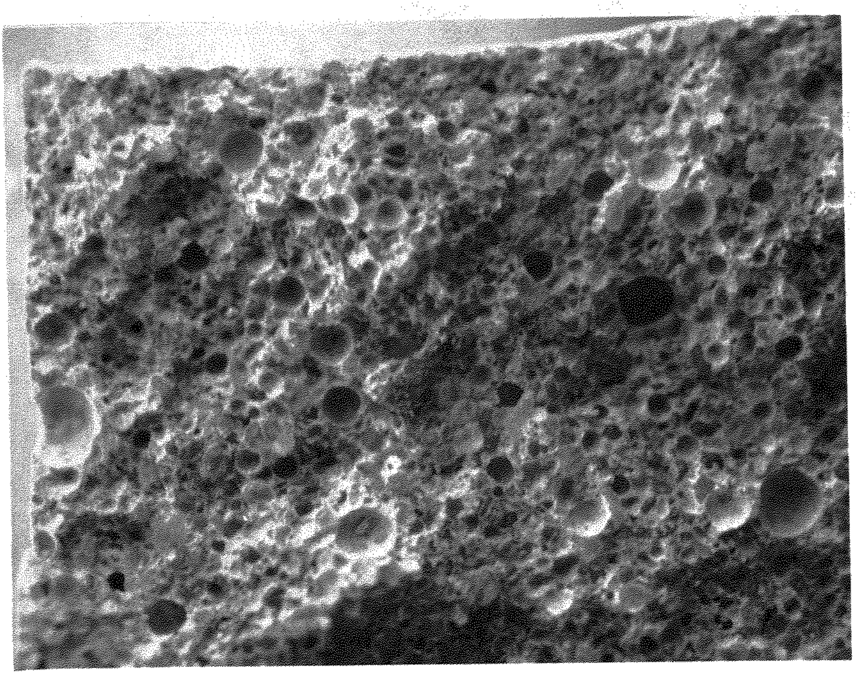

Figure 3.11 Pore structure in Portland V cement mortar bars after 105 wet/dry cycles in deionized water. Mag. 7X.

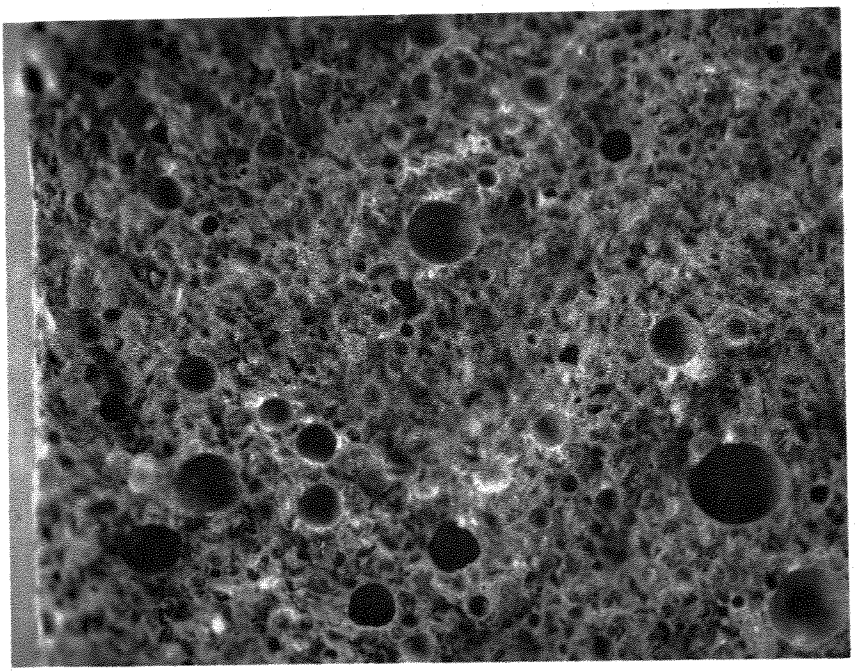

Figure 3.12 Pore structure in PV/SF cement mortar bars after 100 wet/dry cycles in deionized water. Mag. 7X.

Table 3.2 pH of 2.1% Na_2SO_4 solution and deionized water after 2-week immersions of various cement mortars.

Material	Portland I		Portland V		PV/SF	
Cycle	DIW	Na_2SO_4	DIW	Na_2SO_4	DIW	Na_2SO_4
1	(1)	(1)	12.23	12.56	10.68	10.79
2	10.14	11.51	9.73	10.77	9.10	9.81
3	9.42	10.69	8.97	10.20	8.81	9.50
4	8.92	10.19	8.70	10.05	8.59	9.33
5	8.66	10.05	8.68	9.89	8.58	9.47
6	8.59	10.09	8.57	9.88	8.50	9.24
7	8.44	10.16	8.60	9.75	8.45	9.32
8	8.59	10.10	8.51	9.74	8.46	9.46
9	8.24	10.03	8.34	10.02	8.34	9.50
10	8.33	10.55	7.99	9.60	8.29	9.30
11	8.03	9.91	8.18	9.70	8.30	9.11
12	8.27	9.93	8.28	9.64	8.00	9.18
13	8.09	9.76	8.19	9.66	8.29	9.14
14	8.08	9.74	8.17	9.61	8.38	9.21
15	8.04	9.51	8.37	9.68	8.27	(2)
16	8.34	9.75	8.35	9.59	8.39	(2)
17	8.21	9.53				

Notes: 1) pH not measured.
2) Specimens fractured; pH not measured.

4. GAMMA-IRRADIATION EFFECTS AND DISCUSSION

As mentioned in Section 2.6, the test specimens were made in the form of small 2.54 cm cubes in order to ensure that each specimen in a given batch was located in a uniform gamma field during irradiation. Only two duplicates could be tested for irradiated cement mortars but, for the unirradiated controls, up to five replicates were evaluated. All samples were compression tested with the cube aligned so that its top and bottom surfaces, as cast, were normal to the direction of loading. Prior to mechanical testing, these surfaces were "capped" with a special compound to ensure that they were parallel. The compressive strength data are shown in Table 4.1 and plotted in Figures 4.1 through 4.3. Note that since samples being irradiated after simultaneously being cured, the abscissa in the figures is also the irradiation time for the irradiated specimens.

The following conclusions may be drawn from the results:

(a) All materials show an early increase in strength with cure time. However, close-to-maximum compressive strength is attained after 28 days of curing.

(b) Portland I and PV/SF control specimens cured at 21°C appear to have higher compressive strength compared to materials cured at 10°C. The strength difference is in the range of about 10 percent, but it is consistent. No curing temperature effect is observed for Portland V.

(c) Portland V cement-mortar is slightly stronger than Portland I material and both of these are far weaker than PV/SF.

The analysis of irradiation effects on compressive strength are complicated by the use of two different dose rates. Comprehensive data for each dose rate could not be obtained within the scope of this effort, but several interesting facts emerged. For example, the results in Figures 4.1 through 4.3 show that cure time (equivalent to irradiation time for irradiated materials) has the most pronounced effect on strength changes. Both irradiated and unirradiated materials maintain high levels of strength after the initial 28 d transient period. However, there are subtle differences between the strengths of irradiated and unirradiated specimens. This may be studied in terms of a "relative strength value" defined by:

$$\text{Relative compressive strength} = \frac{\text{Strength of Irradiated Sample}}{\text{Strength of Controls Cured at } 10^{\circ}\text{C}}$$

A value close to unity indicates that irradiation effects are small or negligible.

Figure 4.4 shows the results plotted against total accumulated gamma dose. Clearly the low-dose-rate and high-dose-rate results do not correlate well. Irradiation at the lower rate gives a larger decrease in strength. For Portland V cement mortar the decrease is about 28 percent.

Table 4.1 Effect of gamma irradiation on the compressive strength of cement mortars.

Cement Type	Gamma Dose (rad)	Dose Rate (rad/h)	Cure (Irrad.) Time (d)	Cure (Irrad.) Temp. (°C)	Strength	
					(psi)	(MPa)
Portland I	0	0	7	20	4170 ± 552	28.8 ± 3.8
	0	0	28	20	5675 ± 487	39.1 ± 3.4
	0	0	48.5	20	5310 ± 164	36.6 ± 1.1
	0	0	78	20	5540 ± 251	38.2 ± 1.7
	0	0	110.5	20	6810 ± 164	47.0 ± 1.1
	0	0	182	20	6590 ± 738	45.4 ± 5.1
	0	0	245	20	7040 ± 303	48.5 ± 2.1
	0	0	365	20	5300 ± 212	36.5 ± 1.5
	0	0	48.5	10	5045 ± 733	34.8 ± 5.1
	0	0	110.5	10	6383 ± 401	44.0 ± 2.8
	0	0	182	10	5933 ± 176	40.9 ± 1.2
	0	0	245	10	7017 ± 448	48.4 ± 3.1
	0	0	365	10	5868 ± 666	40.5 ± 4.6
	1.4×10^7	3.1×10^3	182	10	5125 ± 35	35.3 ± 0.2
	2.6×10^7	3.1×10^3	365	10	5000 ± 212	34.5 ± 1.5
	4.4×10^8	3.8×10^5	48.5	10	5150 ± 71	35.5 ± 0.5
	1.0×10^9	3.8×10^5	110.5	10	6325 ± 177	43.6 ± 1.2
	2.0×10^9	3.8×10^5	245	10	5925 ± 460	40.9 ± 3.2
Portland V	0	0	7	20	3570 ± 148	24.6 ± 1.0
	0	0	28	20	5850 ± 302	40.3 ± 2.1
	0	0	48.5	20	5380 ± 252	37.1 ± 1.7
	0	0	78	20	5710 ± 282	39.4 ± 1.9
	0	0	110.5	20	6930 ± 115	47.8 ± 0.8
	0	0	182	20	6455 ± 498	44.5 ± 3.4
	0	0	232	20	7150 ± 660	49.3 ± 4.6
	0	0	365	20	6200 ± 529	42.8 ± 3.7
	0	0	48.5	10	5483 ± 76	37.8 ± 0.5
	0	0	110.5	10	6912 ± 544	47.7 ± 3.8
	0	0	182	10	6925 ± 421	47.8 ± 2.9
	0	0	232	10	7100 ± 726	49.0 ± 5.0
	0	0	365	10	6900 ± 346	47.6 ± 2.4
	1.4×10^7	3.1×10^3	182	10	6150 ± 990	42.4 ± 6.8
	2.6×10^7	3.1×10^3	365	10	4950 ± 250	34.1 ± 1.7
	4.4×10^8	3.8×10^5	48.5	10	5925 ± 248	40.9 ± 1.7
	1.0×10^9	3.8×10^5	110.5	10	7100 ± 141	49.0 ± 1.0
	2.0×10^9	3.8×10^5	232	10	6825 ± 35	47.1 ± 0.2
PV/SF	0	0	7	20	5670 ± 601	39.1 ± 4.1
	0	0	28	20	8650 ± 280	59.6 ± 1.9
	0	0	48.5	20	8320 ± 641	57.4 ± 4.4
	0	0	78	20	8680 ± 484	59.9 ± 3.3
	0	0	110.5	20	8210 ± 641	56.6 ± 4.4
	0	0	182	20	9700 ± 705	66.9 ± 4.9
	0	0	225	20	10100 ± 503	69.6 ± 3.5
	0	0	365	20	7290 ± 823	50.3 ± 5.7
	0	0	48.5	10	8283 ± 757	57.1 ± 5.2
	0	0	110.5	10	7467 ± 723	51.5 ± 5.0
	0	0	182	10	8617 ± 425	59.4 ± 2.9
	0	0	225	10	8500 ± 218	58.6 ± 1.5
	0	0	365	10	7667 ± 501	52.9 ± 3.5
	1.4×10^7	3.1×10^3	182	10	8375 ± 530	57.7 ± 3.7
	2.6×10^7	3.1×10^3	365	10	5725 ± 1732	39.5 ±11.9
	4.4×10^8	3.8×10^5	48.5	10	8150 ± 71	56.2 ± 0.5
	1.0×10^9	3.8×10^5	110.5	10	8050 ± 1131	55.5 ± 7.8
	2.0×10^9	3.8×10^5	225	10	8450 ± 424	58.3 ± 2.9

Notes: 1) For unirradiated controls the cure time is the time between cement casting and testing. For irradiated specimens it is the irradiation time.

2) For unirradiated specimens, 3-5 specimens were tested. For irradiated specimens 2 specimens were tested. Standard deviations are given for the strength values.

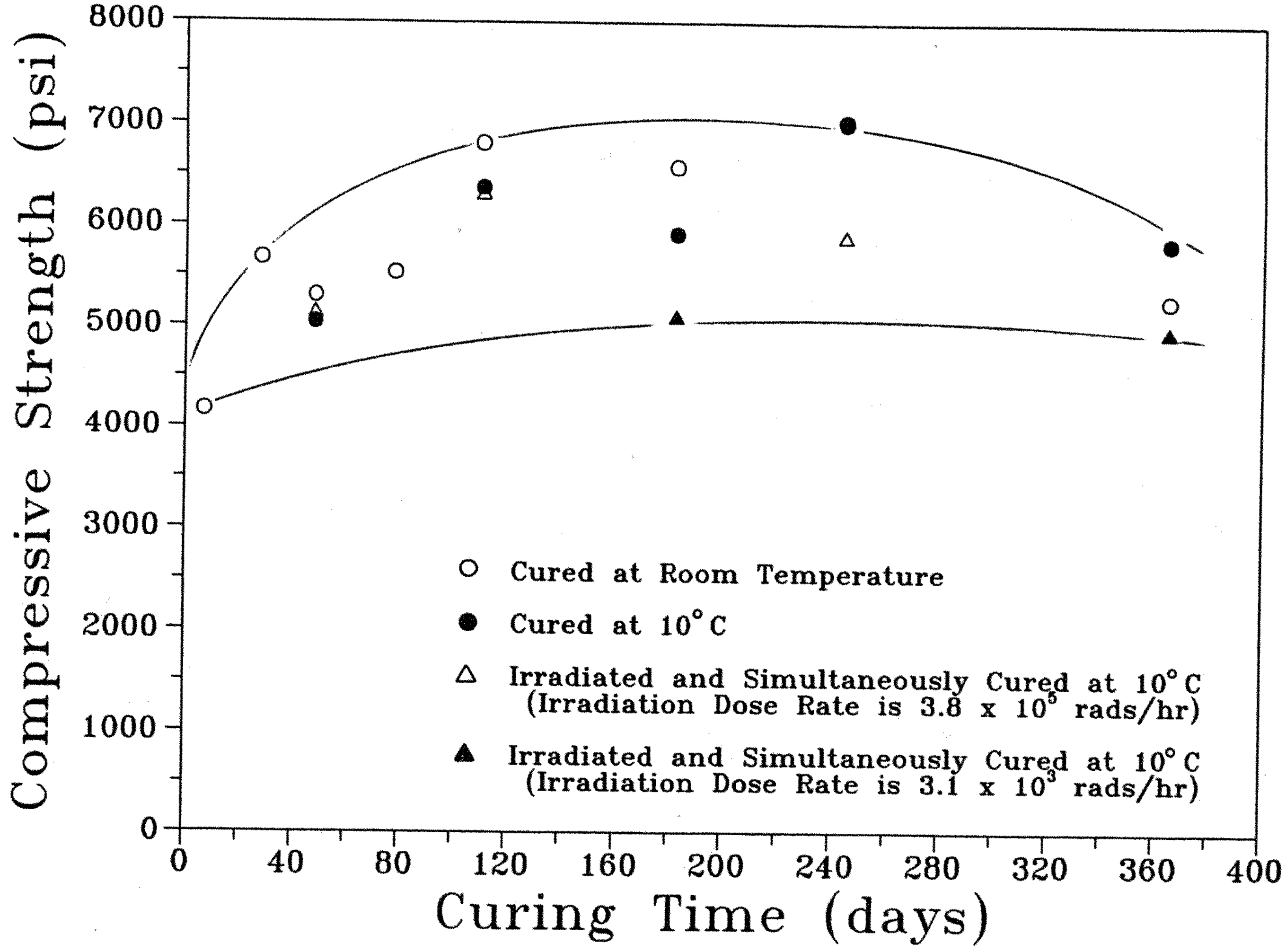

Figure 4.1 Compressive Strength of Portland I cement mortar as a function of cure time and gamma irradiation.

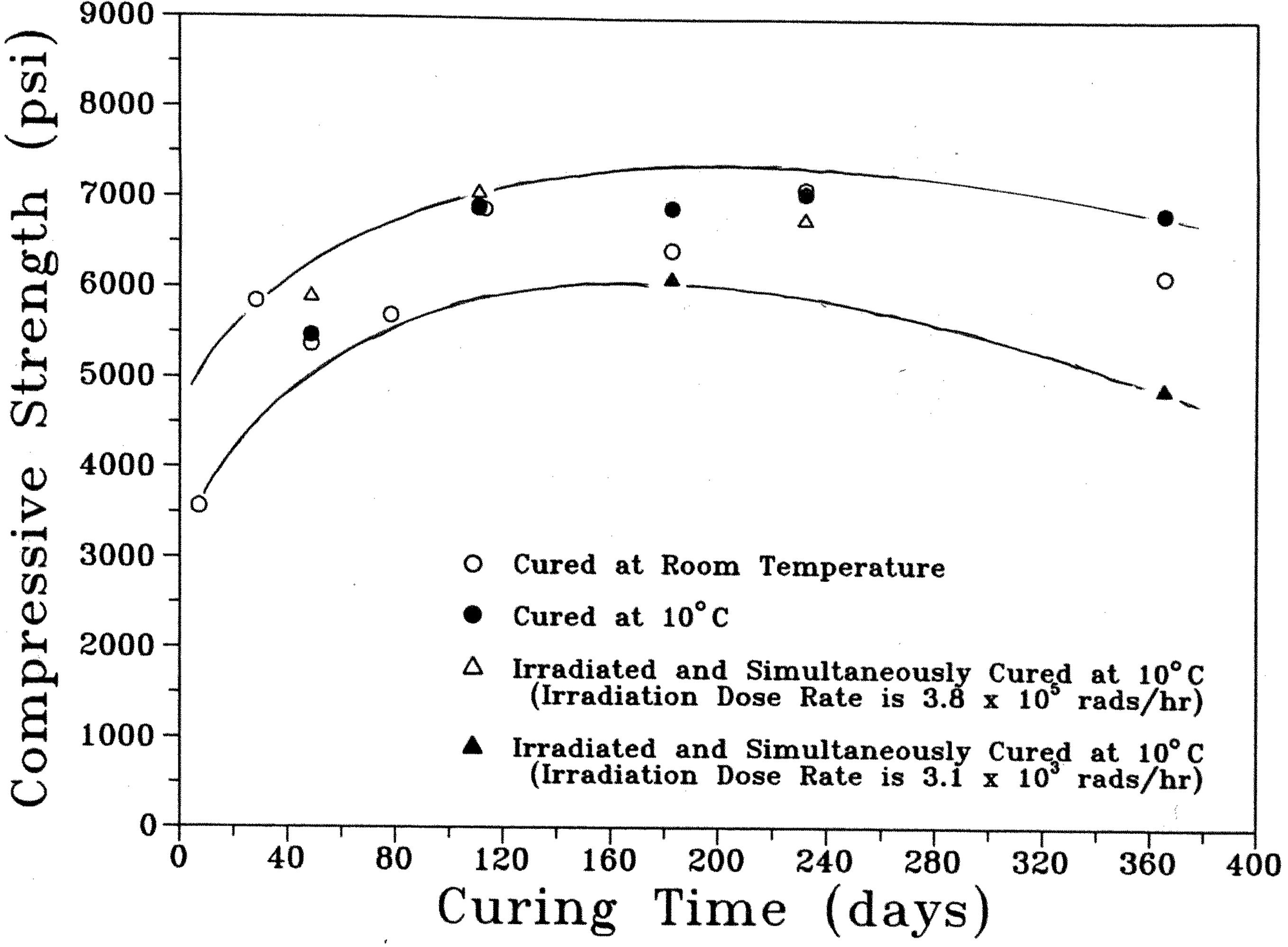

Figure 4.2 Compressive Strength of Portland V cement mortar as a function of cure time and gamma irradiation.

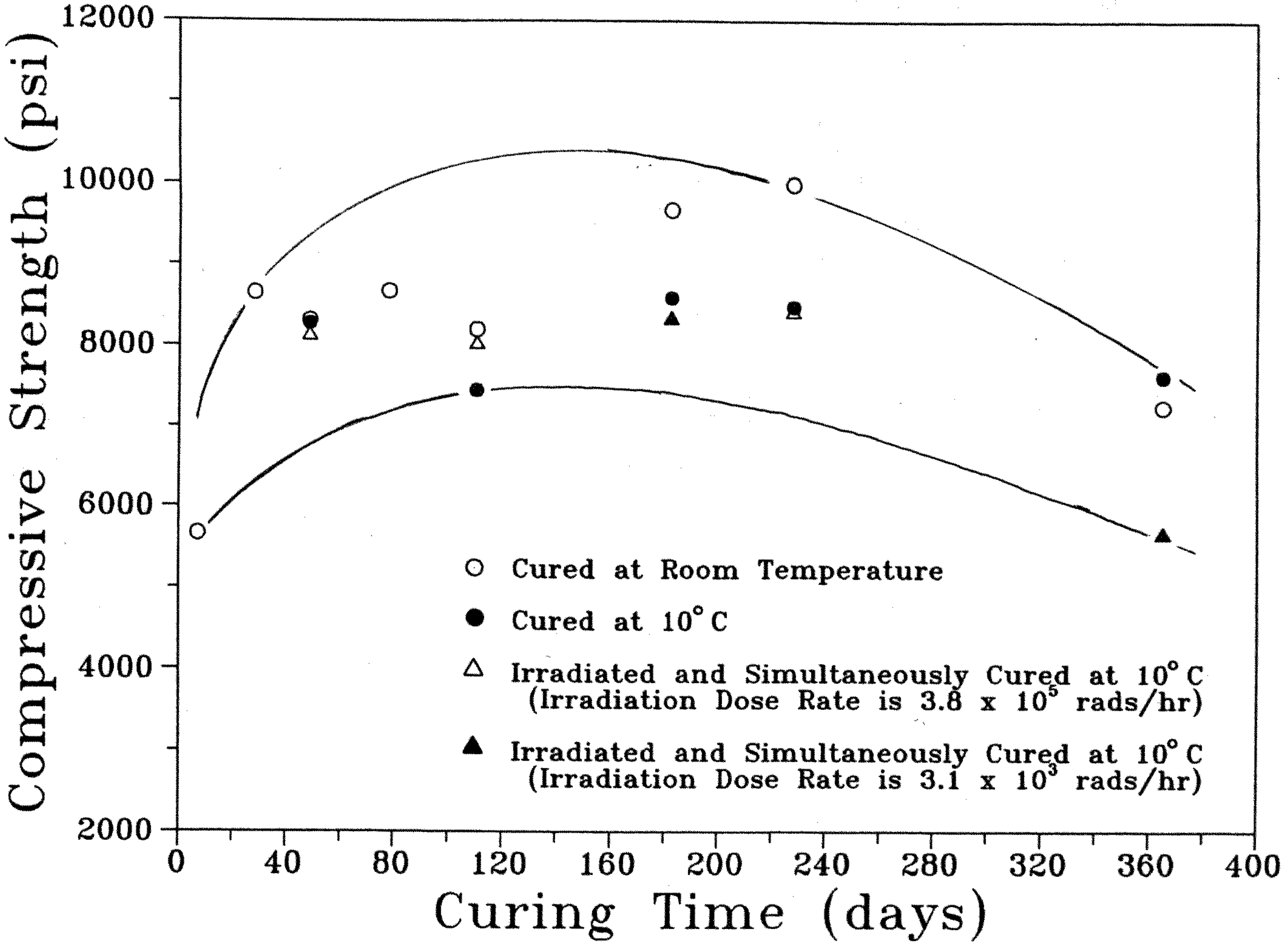

Figure 4.3 Compressive Strength of PV/SF cement mortar as a function of cure time and gamma irradiation.

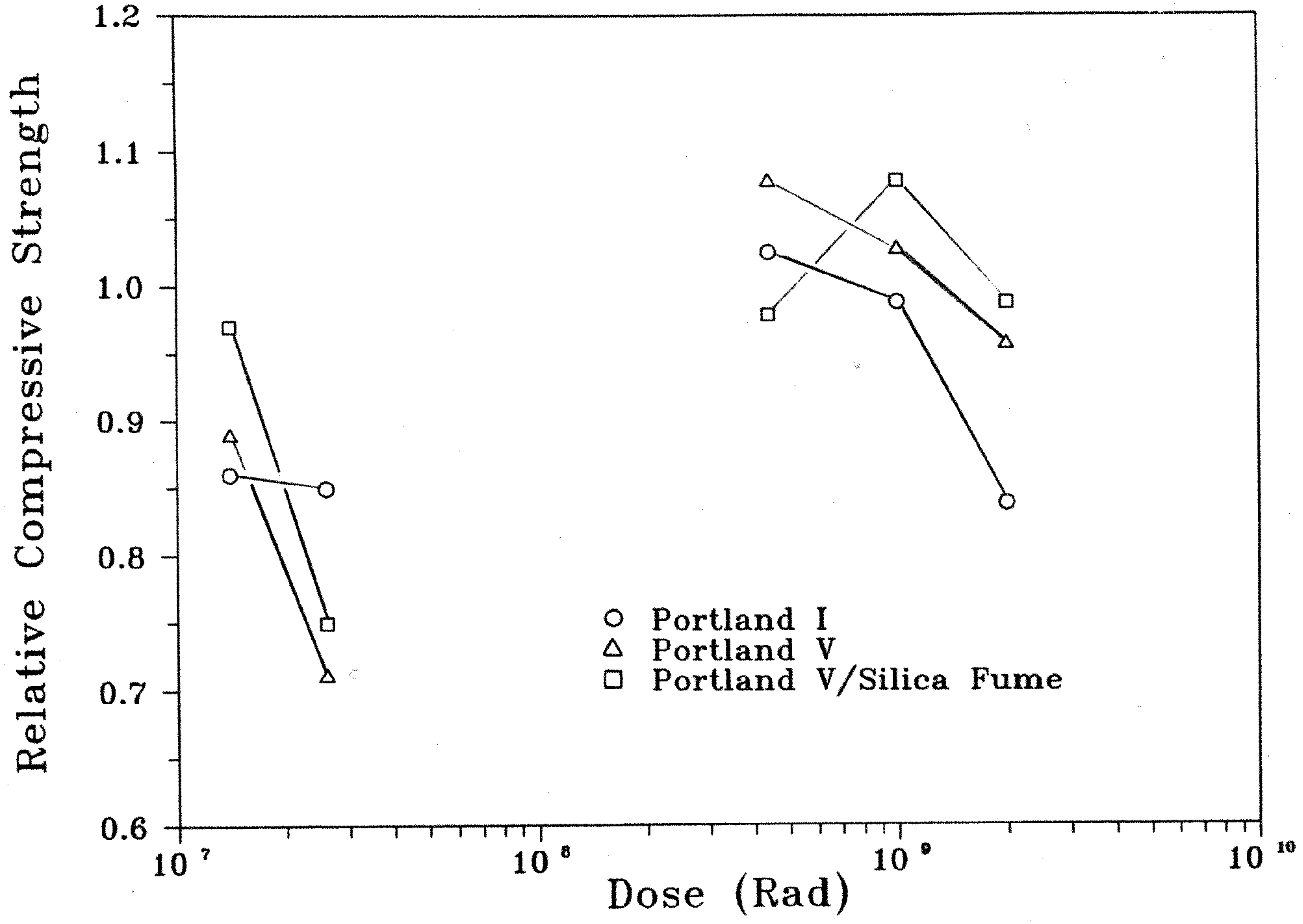

Figure 4.4 Effect of gamma dose in the relative compressive strength of cement mortar cubes.

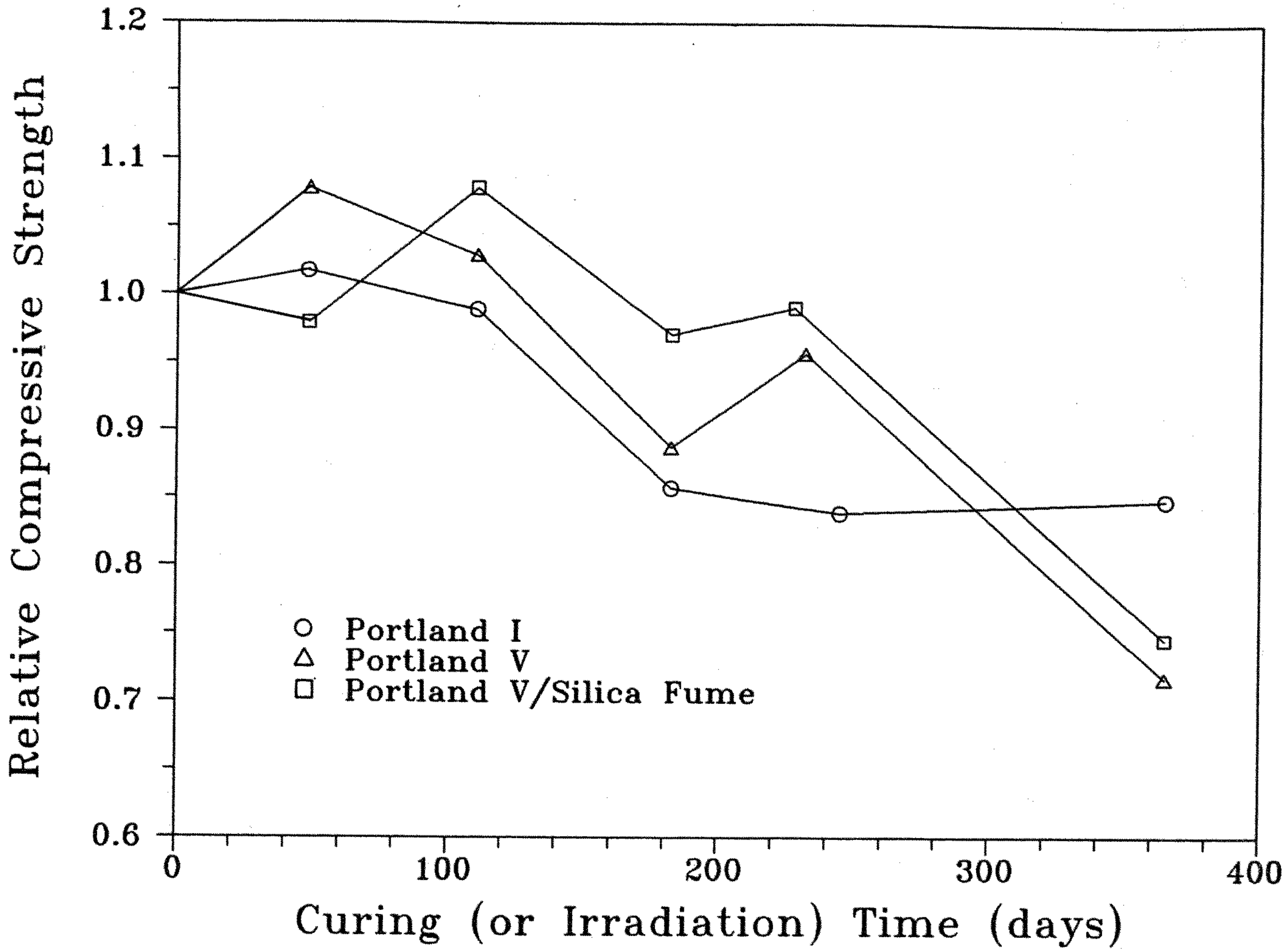

Figure 4.5 Effect of gamma irradiation time on the relative compressive strength of cement mortar cubes.

If the data are plotted against the cure (irradiation) time, a much better correlation is found (Figure 4.5). For the first 110 days the effect of irradiation is small with maximum strength increases of only 8 percent. For longer times consistent and significant strength losses caused by irradiation are observed. The important point to note is that irradiation time is the controlling parameter; changing the dose rate from 3.1 x 10^3 to 3.8 x 10^5 rad/h does not greatly change the degree of strength deterioration for a given irradiation time.

At this time, a satisfactory explanation for the strength losses caused by irradiation is not available. It is not likely to be caused by irradiation damage to the aggregate (Ottawa sand) since the doses are relatively low and the largest effect was for the lower dose. The humidity level during curing and irradiation could possibly be important but all irradiated and all control samples were enclosed in loosely capped containers. Major differences in humidity should not be experienced unless radiolysis of water in the irradiated specimens generated hydrogen and oxygen which escapes from the irradiation vessel. In such a situation, it is conceivable that some loss in strength could occur.

That gamma irradiation can exert measurable effects on cementitious materials is shown in work by McDowall (1971). He gamma irradiated concrete specimens for about 320 d at a dose rate of 1.14 x 10^4 rad/h. This irradiation is within the range used in the current study. It was found that irradiation caused shrinkage in the specimens that was approximately three times greater than for non-irradiated controls. This shrinkage effect could be closely related to the strength loss effect observed in the current program.

5. SUMMARY AND CONCLUSIONS

The preliminary studies carried out in this program on Portland cement mortars indicate that there may be degradation mechanisms associated with long-term exposure to sulfate solutions and to gamma irradiation. These problems should be more fully studied if these types of materials are to be considered for use as barrier materials for low-level radioactive wastes.

With respect to sulfate attack, the Portland V based cement mortar showed a higher resistance to attack compared to Portland I mortar, as expected. However, silica fume additions, rather than enhance the resistance of Portland V cement mortar to sulfate, actually led to increased attack. Even deionized water caused Portland V/silica fume cement mortar to degrade. This indicates that sulfate is not the only factor in the degradation mechanism. It is recommended that caution be exercised in specifying the composition and mixing procedure for this cement mortar. The fact that some workers have produced successful products appears to show that cement mortar quality sensitively depends on these processing variables.

Gamma radiation also degrades the strength of these cement mortars at doses much less than the 10^{10} - 10^{11} rad value specified in at least one prior study on concrete. It was found that curing time during irradiation is an important variable in determining the degree of strength loss. The gamma dose rate, on the other hand, is relatively unimportant. This indicates that although irradiation is a necessary part of the strength degradation mechanism, it does not control it. Some radiation-induced cement dehydration process could be responsible, but the details are not known at this time.

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Sulfate-attack and gamma-irradiation tests were carried out on three Portland cement mortars. For the sulfate attack work an accelerated test was used involving alternate immersion in Na_2SO_4 solution and oven drying of the samples. Attack was monitored through length-change measurements. Cement mortar containing silica fume gave unexpectedly poor resistance to attack. Reasons for this behavior are unclear. Gamma irradiation was found to cause losses in compressive strength at low doses in the 10^7 rad range. The irradiation time is a major factor in the strength-loss mechanism, whereas the dose rate is of secondary importance for the testing conditions studied.

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