NBSIR 81-2273

Factors Affecting the Soundness of Blended Cements

June 1981

Prepared for:

Department of Energy
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U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, *Secretary*
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, *Director*

ABSTRACT

Blended cements containing fly ash and blastfurnace slag along with admixed periclase were examined using autoclave curing as specified by ASTM C151 and long-term immersion curing to assess their expansions as a function of the curing conditions. In some instances, measurements of linear expansion were combined with compressive strength measurements. The partial replacement of portland cement by fly ash while maintaining a fixed periclase content was found to significantly reduce expansion as measured by ASTM C151. Partial replacement by fly ash was also found to reduce the expansions which occurred as a result of long-term immersion curing. However, significantly larger expansions were observed in the latter case.

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FACTORS AFFECTING THE SOUNDNESS OF BLENDED CEMENTS

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1. Introduction

Dimensional stability is one of the most important characteristics desired in concrete. Concrete will not be free of cracks or more severe forms of disruption unless a high degree of dimensional stability is exhibited. Among the causes of dimensional instability is the hydration of periclase. Cements exhibiting excessive dimensional instability resulting from the hydration of periclase or free lime are commonly referred to as being unsound. This paper describes research as carried out to determine whether the ASTM autoclave expansion test for soundness of cements (ASTM C151) [1], which was originally developed for portland cements, is suitable for blended cements.

Periclase originating in the manufacture of portland cement clinker normally hydrates at a very slow rate. If present in sufficient quantity, periclase may cause disruptive expansion and cracking of concrete when the internal stresses generated by its hydration exceed the tensile strength of the hardened cement paste matrix. Since this may occur over a period of many years, a variety of accelerated expansion tests have been devised to assess this effect. These include:

1. the ASTM C151 autoclave expansion test (3 hours at 295 psi steam pressure), [1]
2. the Le Chatelier test (1 hour in boiling water),

3. the boiling water test (2 hours in boiling water), and

4. the cold water test (28 days in water at room temperature).[1] It is current practice in the U.S. to rely on the ASTM C151 test to assess the soundness of most types of cement. According to ASTM C151 unsoundness is indicated when autoclave curing causes a length change exceeding:

0.8% for all types of portland cement [3]

0.5% for Type IP portland-pozzolan cement [4]

0.2% for Type IS portland-blast-furnace slag cement [4]

The autoclave expansion test, ASTM C151, has been used since 1940 to assess the soundness of portland cements. Similarly, since the adoption of the ASTM C595 [4] Standard Specification for Blended Hydraulic Cements, this test has been used to detect potential unsoundness of blended cements. However, the technical basis for the test does not seem to be well established in this instance.[2] Additions of granulated blast-furnace slag or pozzolans, such as fly ash, to unsound portland cements have been reported to produce blended cements with acceptable autoclave expansions [6-14]. It has, however, also been reported that blended cements containing bituminous fly ash which have exhibited acceptable autoclave expansions have shown unsoundness when cured for long periods at ambient temperatures [15-17]. This suggests that the autoclave test may underestimate the long-term expansions of such cements.

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[1] Gonnerman, et al. [2] have summarized a number of the soundness tests previously used.

[2] The applicability of the autoclave test to portland cements has recently come under criticism as well [5].

2. Reported Effects of Pozzolan Additions on Soundness

Rosa [7-9] reported that the addition of fly ash has a stabilizing effect on the expansions of high magnesium oxide (MgO) portland cements. Stabilization of portland cements by fly ash containing up to 15% MgO was reported to occur under the autoclave conditions of ASTM C151 and for storage at room temperature for a period of 10 years. Rosa attributes this stabilizing effect to two factors:

1) formation of magnesium silicate hydrates which may inhibit further periclase hydration; and, more importantly,

2) diminished hydration of the portland cement clinker present due to the formation of low permeability C-S-H gel. This gel results in part from the reaction of the lime liberated by the hydrating cement with reactive silica present in the fly ash.

Therefore, it follows that because a smaller amount of clinker is hydrated a smaller amount of periclase trapped within the clinker is available to hydrate and cause expansion. In spite of this, strength is not diminished because additional C-S-H gel forms from the lime-fly ash reaction. There is also a dilution factor which will aid in the diminution of expansion, because the effective periclase content of portland cement-fly ash mixture is reduced commensurately with the fraction of fly ash present.

Dolezsai and Szatura [15] also observed diminished expansions in high MgO (11 to 14%) portland cements containing fly ash when cured at room temperature and under autoclave conditions. However, the expansions which occurred at room temperature were still large enough to cause unsoundness. Based on these findings they concluded that the autoclave results were unduly optimistic and that the expansions observed under these conditions could not be used as a basis for the prediction of expansion in field conditions.

Majumdar and Rehsi [18] investigated the important factors which lead to the stabilization of high MgO portland cements under autoclave conditions when fly ash is added. They attribute stabilization associated with the addition of fly ash to several factors:

1) $Mg(OH)_2$ crystals formed are smaller in size than with portland cement; thus, expansion due to anisotropic growth of large $Mg(OH)_2$ crystals is minimized.

2) Formation of a magnesium silicate hydrate similar to Dewylite, in addition to $Mg(OH)_2$ formation. However, because the volume of $Mg(OH)_2$ which forms is large compared to the volume of this magnesium silicate hydrate, the significance of its formation with regard to diminished expansion is uncertain.

3) Development of a higher strength matrix which can better resist expansive forces due to the formation of 11 Å C-S-H.

Rehsi and Garg [19] examined the room temperature expansion along with compressive and tensile strengths of high MgO cements containing 30% fly ash. The portland cement used in this investigation contained 10% MgO and 2.45% free lime. Samples were stored under water for periods of up to 3 years. The cements containing fly ash exhibited diminished expansions as compared to the portland cement. It was also observed that after a curing period of about 100 days, the compressive and tensile strengths of the portland cement specimens began to decrease and that this behavior was accompanied by the onset of large expansion. In contrast, the tensile and compressive strengths of the cements containing fly ash continued to increase throughout the curing period. However, the effect of the high free lime content on the expansion of the portland cement used cannot be ignored.

3. Laboratory Investigations

Five cements and one fly ash were used in the present study: One Type I portand cement, 2 commercially available Type IS cements and 2 commercially available Type IP cements. Table 1 presents the analysis of these materials. Hard burned periclase was used as an admixture to the portland cements and was prepared by grinding, air classifying, and proportioning to simulate the fineness of portland cement. Admixing periclase represents a more severe condition than that resulting from the production of a cement containing an equivalent periclase content since up to about 2% MgO can be incorporated as solid solutions in the anhydrous portland cement phases. In addition, unless the cement hydrates completely, not all the periclase present may be available for hydration. The periclase addition levels were, 0.5, 1.0, 3.0 and 7.0% by weight of total solids. The cements were cured under three different conditions in this study. These were: autoclave curing for 3 hours at 295 psi, and immersion curing at 50, and 95°C. All specimens were initially cured for 24 hours in the molds at room temperature. Distilled water initially saturated with lime was used in the immersion study.

4. Results

4.1 Expansions under Autoclave Conditions

In an experiment to confirm the existence of a stabilizing effect associated with the addition of fly ash, a series of cement pastes containing 0, 15

TABLE I

Chemical and Physical Analysis of Cements and Fly Ashes

	Control Type I	Cement Fraction IP-3	Cement Fraction IP-4	Type IP-5	Type IS-2	Type IS-6
SiO_2	20.66	20.95	20.57	33.75	25.20	22.32
Al_2O_3	5.63	5.69	5.33	5.62	8.38	6.64
Fe_2O_3	2.49	2.24	2.78	2.18	0.60	2.12
CaO	63.09	65.05	64.00	54.03	54.09	60.20
MgO	3.76	1.32	2.70	1.48	4.80	3.97
SO_3	2.71	2.99	2.90	2.45	2.43	2.80
Blaine Fineness	3410	3830	3510	-	5219	4200

	Ash used with Control Type I	Ash Fraction IP-3	Ash Fraction IP-4
SiO_2	43.6	58.60	50.0
Al_2O_3	22.7	30.57	22.0
Fe_2O_3	18.6	6.31	15.0
CaO	6.4	0.87	5.2
MgO	1.1	1.0	1.1
Insol.	-	87.2	86.0
L.O.I	4.5	2.73	4.5
Blaine Fineness	2857	-	-

Physical Data on Types IP

	IP-3	IP-4	IP-5
Blaine Fineness	4796	3900	4015
% Type I	79	75	77
		6	
% Gypsum	3	5	5
% Ash	18	20	18
% Air	4.7	-	6.0

30, or 40 wt% admixed fly ash and 1.0 wt% of admixed periclase were cast as 1 x 1 x 10 inch (2.5 x 2.5, x 25.4 cm) prisms at a water to solids ratio of 0.35 and autoclave cured at 295 psi for 3 hours. The pastes made with the cements containing 0, 15, and 30% fly ash and 1.0% periclase showed extensive cracking and warpage and all fractured during the autoclave curing. The cement containing 40% fly ash and 1% periclase showed slight warpage, no cracking, and an average expansion of 1.8%.

A second series of cements containing 0.5% admixed periclase and a third series containing no admixed periclase were cast and autoclave cured at 295 psi for 3 hours. The expansion data are shown in Figure 1. These data, which are the average of triplicate determinations, indicate that the expansion is reduced by the addition of fly ash. The initial 15% flyash addition had the greatest absolute effect while added increments provided only small additional improvements in dimensional stability. This figure also indicates the samples containing fly ash, when autoclave cured, showed a high degree of dimensional stability in relation to the base portland cement in the absence of admixed periclase.

4.2 Expansion Under Long-term Immersion Curing Conditions

To determine the effects of long-term immersion curing, a series of cements containing 0, 15, and 40 wt% admixed fly ash and 0.5 wt% periclase were cast, cured for 24 hours at room temperature and then immersion cured at 50 or 95°C. Periodically, the specimens were slowly cooled in water (3 to 4 hours) to ambient temperature, removed, and their expansions measured. They were then immediately reimmersed and slowly reheated (3 to 4 hours) to the appropriate temperature. Figure 2 shows the expansions measured during 26 weeks of testing. Control samples containing 0, 15, and 40% fly ash but no admixed periclase

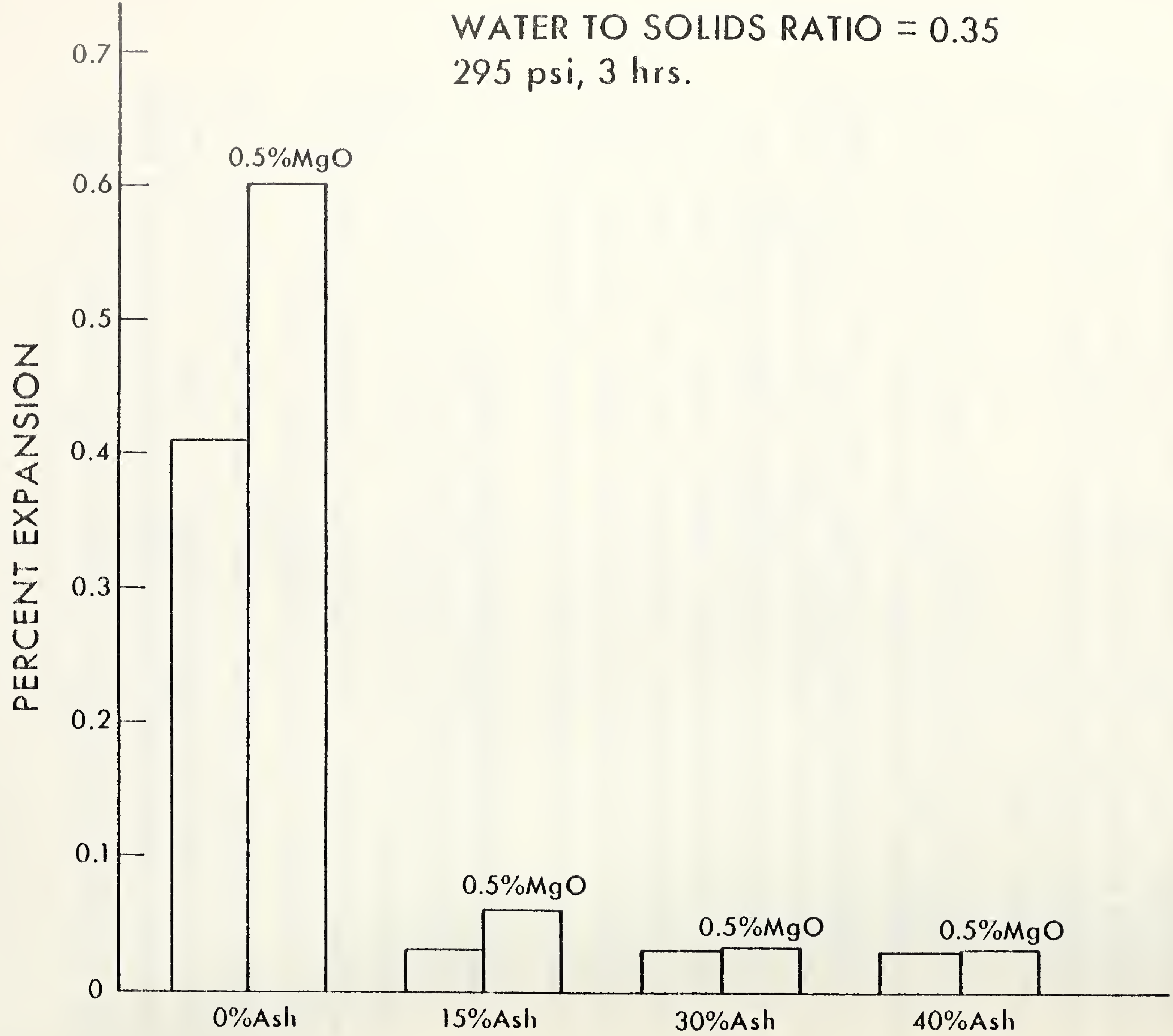

Figure 1. Autoclave expansions of type I portland cement – fly ash mixtures showing the relative stabilizing effects of fly ash additions on blends containing 0.5% admixed MgO.

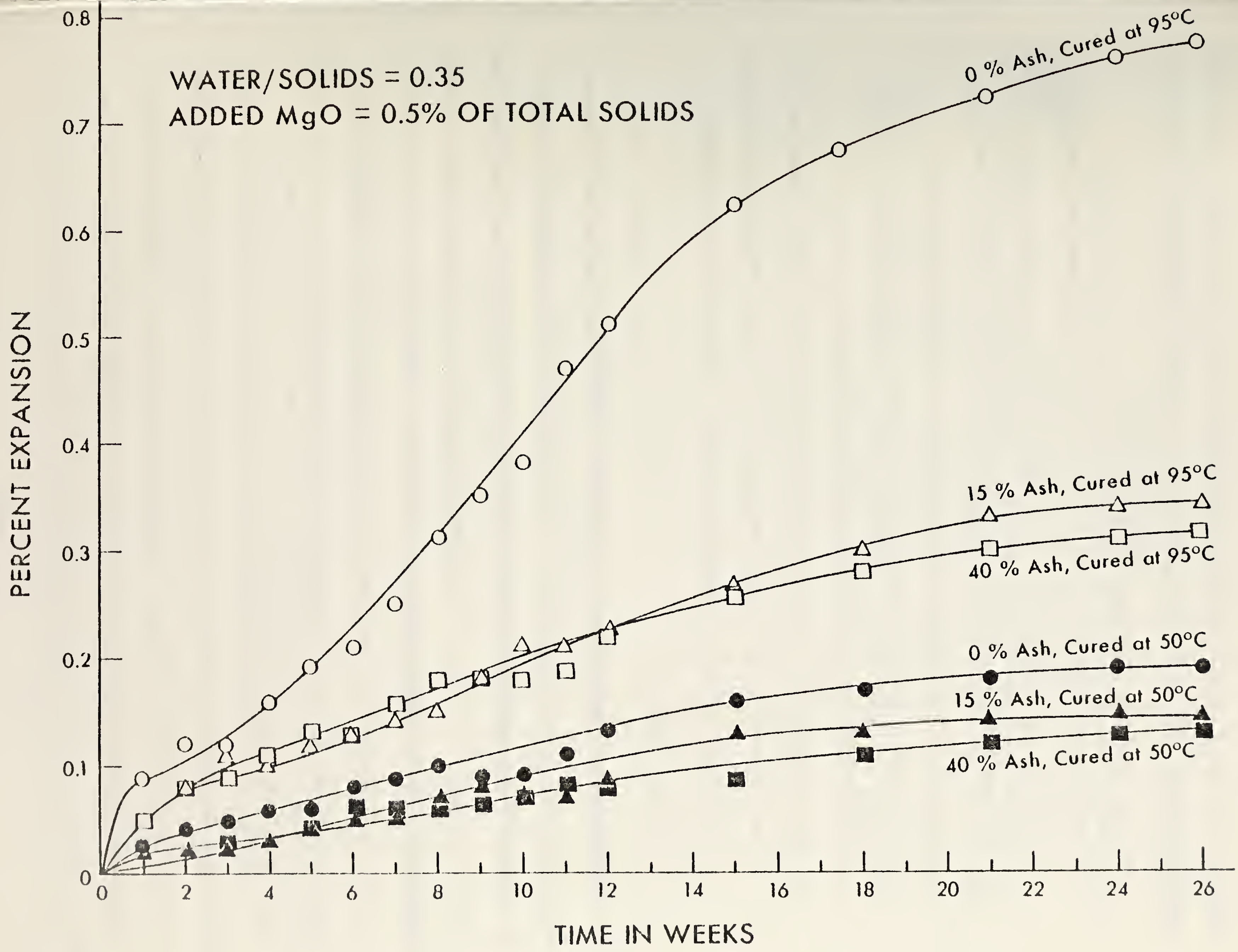

Figure 2. Effect of fly ash addition level and curing temperature on the expansions of type I portland cement. Admixed MgO content, 0.5% of total solids.

expanded by no more than 0.02% when cured at 50°C and no more than 0.04% when cured at 95°C.

Analysis of these data indicate that:

1. partial replacement by 15% fly ash reduced the expansion observed at both curing temperatures, the effect being particularly large at 95°C.
2. the expansions of those specimens containing 15 or 40% fly ash did not differ significantly when cured at the same temperature,
3. the expansions which resulted from curing at 95°C always exceeded those which resulted from curing at 50°C, and
4. with exception of the portland cement paste (0% flyash) cured at 50°C, the expansions which had resulted after 26 weeks of immersion curing at 50°C or at 95°C exceeded those which resulted from autoclave curing (Figure 1).

The nature of the improved dimensional stability associated with fly ash replacement was further examined by the measurement of compressive strengths. Two inch (5.1 cm) mortar cubes with sand to (cement plus fly ash plus periclase) to water ratios of 2.75 to 1.0 to 0.5 were cast and cured for 24 hours at room temperature. These cubes were then immersed for 26 weeks at 23, 50 or 95°C. Fly ash replacements of 0, 15, 30, or 40 wt% were used and the admixed periclase content was 0.5% of the weight of the portland cement plus fly ash. The strength data are presented in Table 2.

TABLE 2

Compressive Strengths of Mortar Cubes after 26 weeks of Curing, MPa (psi)

CURING TEMP.	PERCENT FLY ASH 0	15	30	40
23°C #	43.9 (6370)	54.7 (7930)	50.8 (7365)	50.3 (7300)
50°C #	46.5 (6745)	52.2 (7565)	46.2 (6700)	43.7 (6335)
95°C *	57.4 (8330)	74.7 (10840)	56.1 (8130)	52.1 (7555)

average of 3 cubes

* average of 6 cubes

These strength data indicate that:

(1) The highest compressive strengths at each composition resulted from immersion wring at 95°C,

(2) partial replacement of 15% fly ash gave the highest compressive strength at each curing temperature,

(3) those samples which contained fly ash exhibited strength minima when cured at 50°C as compared with those cured at 23 or 95°C.

A comparison of the strength data from Table 2 with the expansion data from Figure 2 indicates that diminution in the expansions observed at 50 and 95°C resulting from presence of 15% fly ash may be attributed to higher compressive strengths. However, the improved dimensional stability resulting from the presence of 40% fly ash cannot be explained on the basis of strength alone; nor can the relative expansions of the portland cement observed at 50 and 95°C.

This does not necessarily imply that the relative rates of strength gain and periclase hydration do not have a significant effect and this was investigated further by examining the effects of higher periclase addition levels. Three or 7% periclase was added to the Type IP and Type IS cements and the control portland cement. Specimens of these compositions were then immersion cured at 50 or 95°C. Those samples containing 7% periclase which were cured at 95°C disintegrated before a definitive assessment of their relative volume changes could be made. The behavior of the cements containing 3% periclase which were cured at 95°C is shown in Figure 3. The two Type IS cements expanded more rapidly than the Type I and Type IP cements; however, by 8 weeks all had expanded beyond 3%. Although all the specimens showed warpage to some degree, only one, Type IS-2, fractured. Immersion curing at 50°C also resulted in large expansions when the periclase content was 7%, Figure 4. In this case the Type I portland cement showed the lowest overall rate of expansion, although ultimately all the cements exhibited expansions exceeding 3%. When the periclase content was reduced to 3% and curing carried out at 50°C, both the rate of expansion and extent of expansion of each cement was reduced, Figure 5. In this case, however, the expansion of the Type I portland cement exceeded those of the Type IS and Type IP cements, while the latter types showed a relatively high degree of dimensional stability.

The data in Figure 3, 4, and 5 indicate that the relative expansions shown by these cement types is not only a function of periclase content but to a large extent, depends on the curing conditions. At a high periclase content or under severe exposure condition, the Type I cement showed the

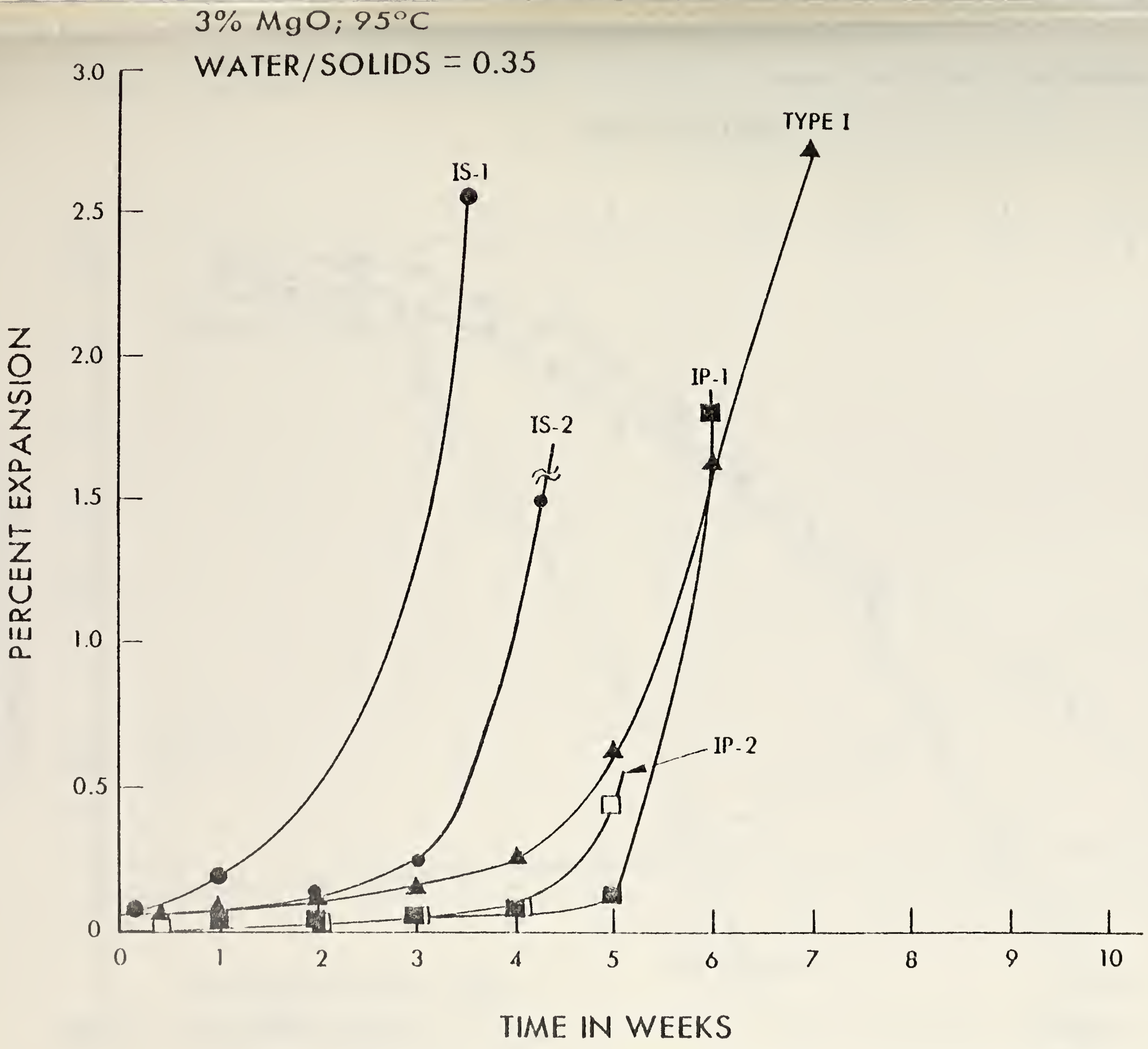

Figure 3. Relative expansions of types I, I-S and I-P cements containing 3.0% admixed MgO when cured at 95°C.

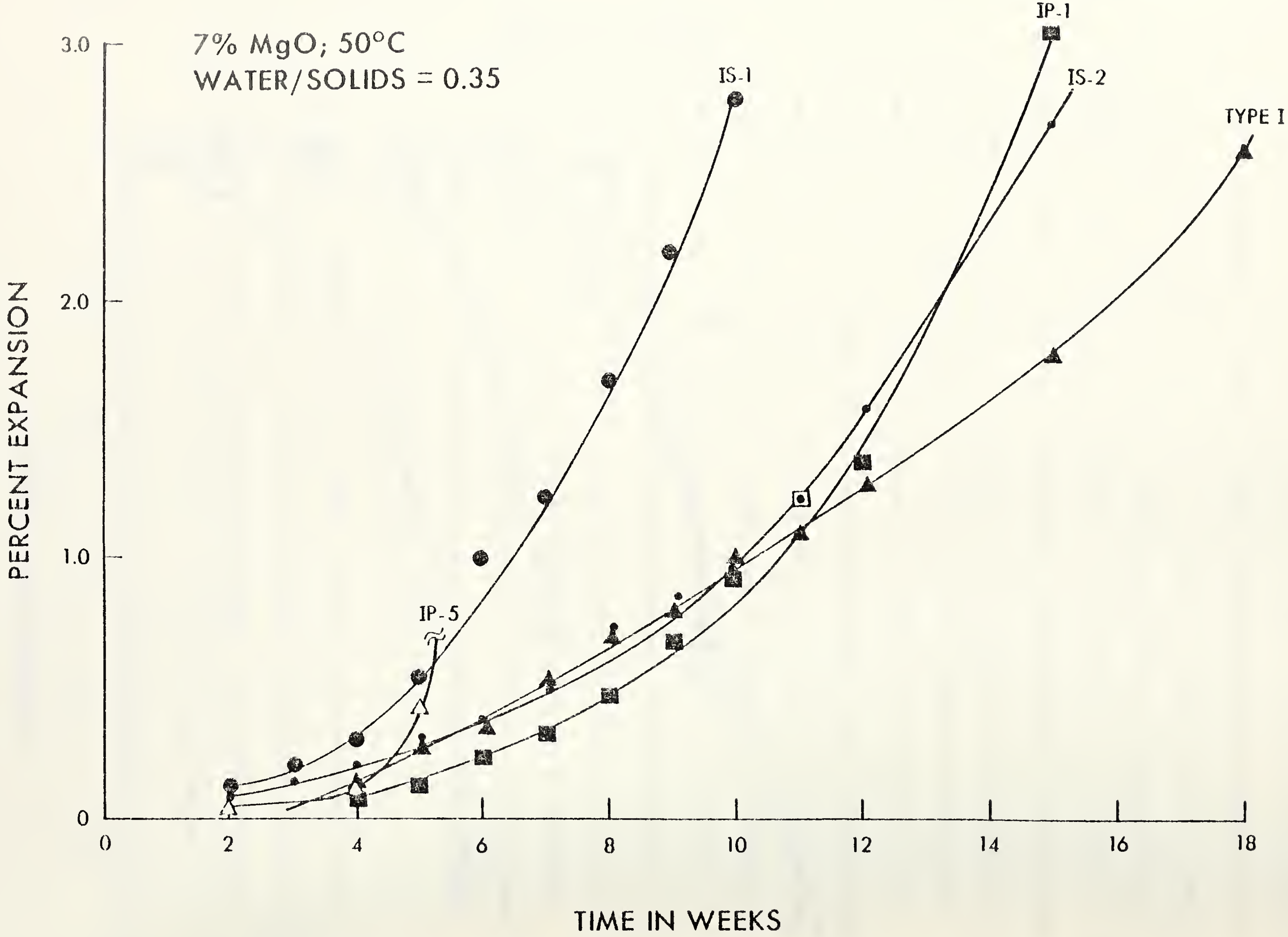

Figure 4. Relative expansions of types I, I-S and I-P cements containing 7.0% admixed MgO when cured at 50°C.

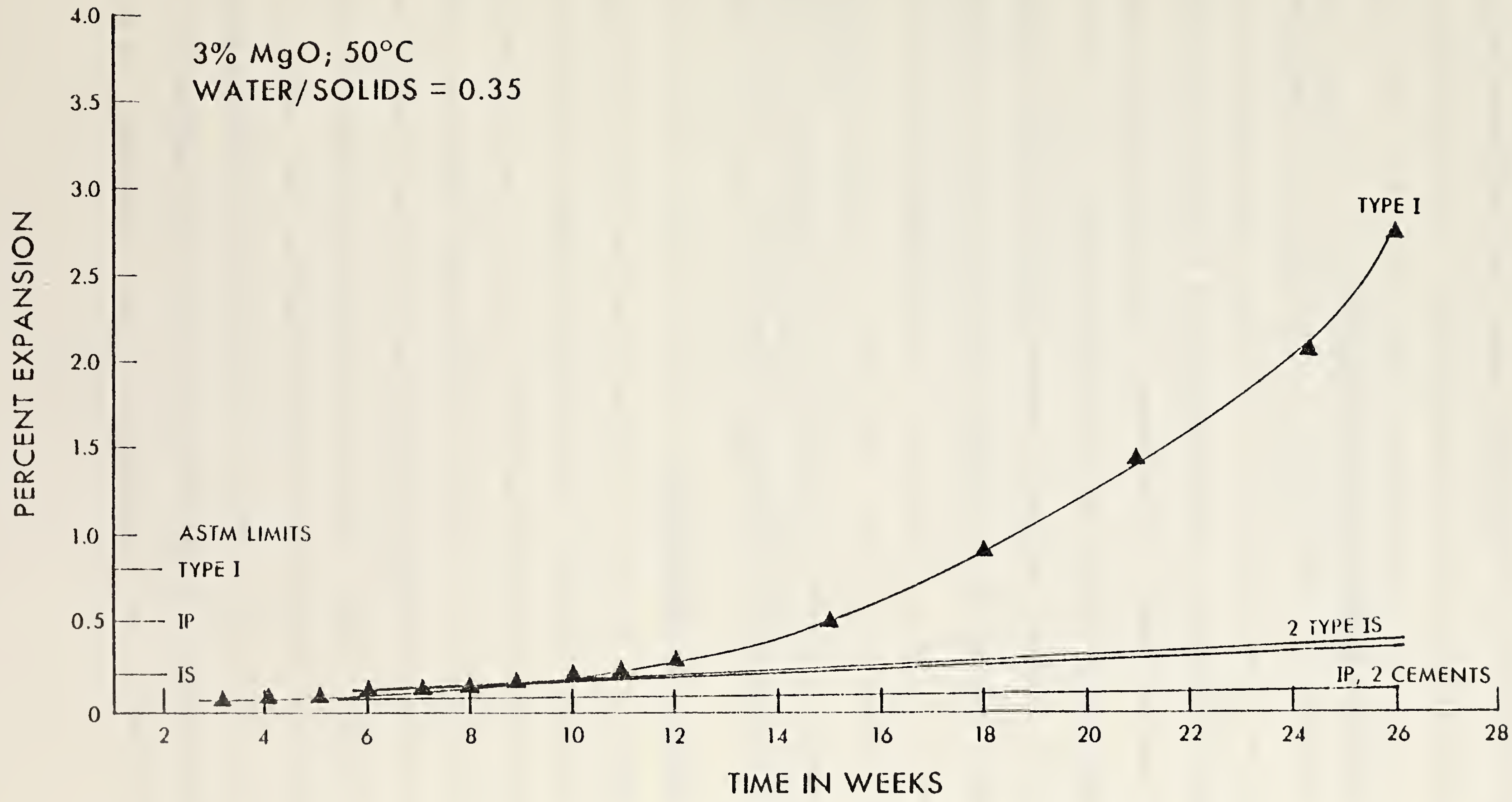

Figure 5. Relative expansions of types I, I-S and I-P cements containing 3.0% admixed MgO when cured at 50°C.

lowest overall rate of expansion whereas under less severe conditions or periclase contents, it showed the greatest.

4.3 Formation of Magnesium Silicate Hydrate

To assess the possible effects of the formation of magnesium silicate hydrate on volume stabilization, an analysis using scanning electron microscopy was performed on fracture surfaces of a Type I portland cement and a Type I portland cement, 30 wt% fly-ash blend containing 15% admixed periclase. The cements were cured at 95°C for 28 days and the formation of a magnesium silicate hydrate was confirmed in both cements by energy dispersive X-ray analysis. However, an X-ray powder diffraction analysis revealed only the presence of $Mg(OH)_2$, in addition to the peaks expected from the hydrating cement, indicating that only a small amount of magnesium silicate hydrate was formed. Therefore, it appears that the of magnesium silicate hydrate does form in quatities sufficient to have an effect on diminishing expansion.

5. Discussion and Conclusions

The results of this study indicate that the partial replacement of portland cement by bituminous fly ash while maintaining a fixed periclase content can improve stability under autoclave curing or under long-term curing at temperatures up to 95°C. A 15% fly ash replacement reduced the autoclave expansions by about 5-fold when the periclase content was maintained at 0.5% of total solids. Similar reductions in expansion were observed in specimens containing 15% fly ash and 0.5% admixed periclase when immersion cured for 26 weeks at 50 or 95°C. However, the autoclave test yielded expansions which were consistently less than those taking place when samples were immersion cured indicating that the autoclave test may underestimate the potential expansions of cements containing fly ash. Alternatively, samples containing 0.5% admixed periclase and cured at 95°C were still continuing to expand after 26 weeks. This indicates that, while the ASTM C151 atuoclave test may underestimate expansion in some instances, immersion curing does not result in full expansion in a reasonable time frame.

The formation of a matrix of higher strength than that of the portland cement appears to be one of the factors responsible for the reduction in expansion associated with replacement by 15% fly ash regardless of curing condition. However, the relationship between strength and expansion is not straightforward in that specimens having higher strengths also showed larger expansions in some instances.

6. Acknowledgements

The authors gratefully acknowledge the U.S. Department of Energy, Office of the Assistant Secretary for Conservation and Solar Applications, Alternative Materials Utilization Brance for supporting this study.

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NBS-114A (REV. 9-78)

U.S. DEPT. OF COMM. BIBLIOGRAPHIC DATA SHEET	1. PUBLICATION OR REPORT NO. NBSIR 81-2273	2. Gov't. Accession No.	3. Recipient's Accession No.

4. TITLE AND SUBTITLE

Factors Affecting the Soundness of Blended Cements

5. Publication Date August 1981

6. Performing Organization Code

7. AUTHOR(S) Paul W. Brown & James R. Clifton

8. Performing Organ. Report No.

9. PERFORMING ORGANIZATION NAME AND ADDRESS

NATIONAL BUREAU OF STANDARDS
DEPARTMENT OF COMMERCE
WASHINGTON, DC 20234

10. Project/Task/Work Unit No.

11. Contract/Grant No.

12. SPONSORING ORGANIZATION NAME AND COMPLETE ADDRESS *(Street, City, State, ZIP)*

Department of Energy
20 Massachusetts Avenue, N.W.
Washington, D.C. 20545

13. Type of Report & Period Covered

14. Sponsoring Agency Code

15. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

16. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

Blended cements containing fly ash and blastfurnace slag were examined to assess their soundness in the presence of admixed MgO. Measurements of linear expansion were combined with compressive strength determinations to evaluate the volume stabilities of samples cured under various conditions. The effects of magnesium silicate formation on volume stability were also examined.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)*

Cement, MgO, Fly ash, Slag, Strength, Expansion, Soundness

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19. SECURITY CLASS (THIS REPORT)	21. NO. OF PRINTED PAGES
UNCLASSIFIED	25
20. SECURITY CLASS (THIS PAGE)	**22. Price**
UNCLASSIFIED	$5.00

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