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EFFECTIVENESS OF MINERAL ADMIXTURES IN PREVENTING EXCESSIVE EX--ETC(U)
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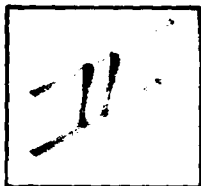
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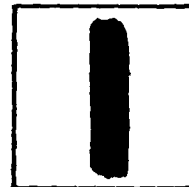
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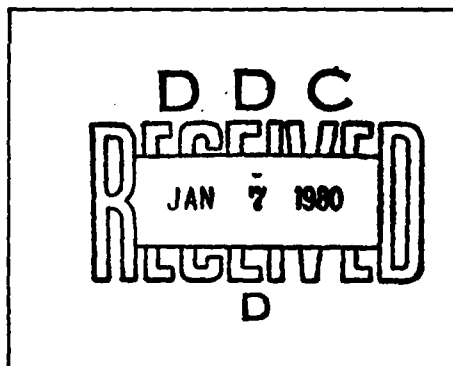
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**EFFECTIVENESS OF MINERAL ADMIXTURES
IN PREVENTING EXCESSIVE EXPANSION
OF CONCRETE DUE TO
ALKALI-AGGREGATE REACTION**



TECHNICAL REPORT NO. 6-481

July 1958

**U. S. Army Engineer Waterways Experiment Station
CORPS OF ENGINEERS
Vicksburg, Mississippi**

PREFACE

The investigation reported herein was authorized by the Chief of Engineers by letter dated 30 January 1950, subject, "Civil Works Investigation, Authorization of Item CW 603, 'Alkali-Aggregate Reaction' for Fiscal Year 1950." The program was outlined in correspondence dated 11 July 1950, subject, "Transmittal of Tentative Program Outline of Investigation of Pozzolans as Inhibitors," and indorsements thereto, and was approved by third indorsement dated 17 April 1951 from the Office, Chief of Engineers.

The work was conducted by the Concrete Division of the U. S. Army Engineer Waterways Experiment Station under the direction of Mr. Thomas B. Kennedy and under the supervision of Messrs. Bryant Mather, J. M. Polatty, C. H. Willetts, R. V. Tye, R. L. Curry, Leonard Pepper, and Mrs. Katharine Mather. The report was prepared by Messrs. Alan D. Buck, B. J. Houston, and Leonard Pepper. Valuable comments were provided by Professor Raymond E. Davis, Director Emeritus, Engineering Materials Laboratory, University of California, Berkeley, California; Dr. Roy W. Carlson, consulting engineer, Berkeley, California; and Mr. R. L. Blaine, Chief, Concreting Materials Section, National Bureau of Standards, Washington, D. C.

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SUMMARY

Twenty materials, representing eight different classes of mineral admixtures, were evaluated, using both chemical and mortar-bar test methods, for their effectiveness in preventing excessive expansion of concrete due to alkali-aggregate reaction. The criteria of the chemical tests were examined, and the test results were compared with the mortar-bar test results. All results were compared with those obtained by two other laboratories. It was found that the chemical tests cannot be used with reliance to evaluate effectiveness, and that the mortar-bar test procedure needs improvement to increase its precision. Each of the replacement materials evaluated will prevent excessive expansion if a sufficient quantity is used. Correlations were found between effectiveness and: fineness, dissolved silica, and percentage of alkali retained by reaction product.

Five of the materials tested (a fly ash, a tuff, a calcined shale, a calcined diatomite, and an uncalcined diatomite) showed a reduction in alkalinity of 40% or more when tested by the quick chemical test and thus complied with the specification used by the U. S. Bureau of Reclamation for Davis Dam. All of these except the fly ash met the requirement later proposed for the relationship between reduction in alkalinity and silica solubility as determined by this method.

Six of the materials tested, two slags, a fly ash, a pumicite, and two calcined shales, reduced mortar-bar expansion at least 75% with high-alkali cement and Pyrex glass aggregates when used as 50, 45, 35, and 30% replacements of the cement.

Calculations were made that suggest that the minimum quantity of each material required for effective prevention of excessive expansion ranged from 10% for the synthetic silica glass to 45% for one of the slags. By groups these calculated minimum percentages were: calcined shales, 19 to 29; uncalcined diatomite, 22; volcanic glasses, 32 to 36; slags, 39 to 45; fly ashes, 40 to 44.

EFFECTIVENESS OF MINERAL ADMIXTURES IN PREVENTING EXCESSIVE
EXPANSION OF CONCRETE DUE TO ALKALI-AGGREGATE REACTION

PART I: INTRODUCTION

1. The investigation of mineral admixtures as cement-replacement materials was initiated by the Office of the Chief of Engineers in the latter part of 1950. The purpose of the investigation was to ascertain the degree to which portland cement may be advantageously replaced by other materials, considering cost and the quality of the resulting concrete.

2. Mineral admixtures may have many desirable effects when incorporated in a concrete mixture. They may prevent excessive expansion caused by alkali-aggregate reaction, contribute to the strength of the concrete, increase its resistance to sulfate attack and leaching, and tend to reduce the heat released by the hydration of the cement. This investigation is concerned with the ability of these materials to prevent excessive expansion of concrete due to alkali-aggregate reaction.

3. Many tests to determine pozzolanic activity have been described in the literature.^{2, 6, 7*} In some, only the admixture is involved; in others, the admixture is mixed with either lime or portland cement. Correlation between tests is inherently difficult; however, some relationships have been established for various desired qualities. The criteria established by these correlations indicate whether or not the admixture under test will satisfactorily contribute the desired quality to concrete; however, very little has been done to rate admixtures with respect to the magnitude of their contribution. The more important tests involved:

- a. Determination of chemical composition and chemical ratios.
- b. Determination of the constituents that will be dissolved as a result of treatment of the admixture with acid, or alkali, or both, and the amount of insoluble residue remaining after such treatment.
- c. Rate of lime absorption.

* Superior numbers refer to items in the list of references at end of text.

- d. Rate of alkali release.
- e. Compressive and tensile strength.
- f. Rate of heat reduction.
- g. The mortar-bar test for reduction of expansion.

4. Several tests to evaluate the effectiveness of mineral admixtures in preventing excessive expansion due to the alkali-aggregate reaction have been proposed in the literature. These tests, as well as those for determination of alkali release and fineness, were selected to evaluate the materials in this investigation. The tests used were evaluated for reliability, and the minimum percentage of the replacement material that would effectively reduce the expansion was determined.

PART II: MATERIALS

Portland Cements

5. Three portland cements were used in this investigation: two type I cements, one of high alkali content (1.07% alkalies calculated as soda) and one of low alkali content (0.37%); and one medium alkali content, type II cement (0.68%). The results of tests of these cements are given in table 1.

Replacement Materials

6. The 20 replacement materials studied represented eight classes. The classes, the specific materials tested, and the abbreviations for the materials used herein, are as follows.

<u>Class</u>	<u>Material</u>	<u>Specific Material</u>	<u>Abbreviation</u>
1	Granulated blast-furnace slags	Slag I Slag II	Slag I Slag II
2	Natural cements	Natural I Natural II	Nat I Nat II
3	Fly ashes	Fly Ash I Fly Ash II Fly Ash III Fly Ash IV	FA I FA II FA III FA IV
4	Natural volcanic glasses	Pumicite, Friant Pumicite, Lassen Tuff Obsidian	Pum F Pum L Tuff Obs
5	Calcined opaline shales	Calcined shale (Monterey) Calcined shale (Napa) Calcined diatomaceous earth	C Sh M C Sh N Cal D
6	Uncalcined diatomite	Uncalcined diatoma- ceous earth	Unc D
7	Uncalcined quartz	SiO ₂ Flour Air ² Float Ad-Mix	Silica Flour Air Float Ad-Mix
8	Synthetic, pure silica glass	Synthetic, pure silica glass	SS glass

Sixteen materials representing the first six classes were also used in an investigation of cement-replacement materials being conducted by the Waterways Experiment Station. The methods of processing these materials, their sources, and their optimum percentages in concrete are given in report 1 of that investigation.¹¹ Classes 7 and 8 consist of four materials, all of which may be regarded as essentially pure silica. The three in class 7 are quartz and the one in class 8 is an amorphous silica. The results of tests of all 20 materials are given in table 2.

Hydrated Lime

7. Some of the tests required the admixtures to be reacted with hydrated lime. The lime selected conformed to ASTM Specifications C 6-46T for Normal Finishing Hydrated Lime and in addition it was required that it contain not less than 75% CaO nor more than 5% MgO based on the nonvolatile portion, and that not more than 5% be retained on the No. 325 sieve. The properties of the lime are given in table 2.

Aggregates

8. Three aggregate combinations were used in making 1- by 1- by 11-in. bars for expansion tests. These three aggregates were Pyrex glass, Sioux quartzite, and a Sioux-Klufa quartzite combination; they have been previously described in Waterways Experiment Station reports.^{10, 12} Both the reactive aggregate, Pyrex glass, and the innocuous aggregate, Sioux quartzite, were graded as required by CRD-C 123.⁹ The combination of 90% Sioux quartzite and 10% Klufa opaline quartzite has been found¹² to be more reactive than any other combination of these materials. This combination was graded as follows:

Sieve	% Retained	
	Sioux	Klufa
3/8-in. to No. 4	2.5	---
No. 4 to No. 8	7.5	---
No. 8 to No. 16	10.0	---
No. 16 to No. 30	32.0	3.0
No. 30 to No. 50	25.6	4.9
No. 50 to No. 100	9.0	2.0
Passing No. 100	3.5	---
Total	90.1	9.9

PART III: TESTS AND RESULTS

Test for Reactivity with Sodium Hydroxide (NaOH)Test method

9. To evaluate admixtures with regard to their effectiveness in preventing excessive expansion of concrete, an adaptation of the quick chemical tests for reactivity of aggregate with sodium hydroxide (CRD-C 128)⁹ has been used. Since some materials will harden when 25 g of the admixture is reacted with 25 ml of 1N NaOH, it was necessary to reduce the weight of admixture used to 12.5 g. In all other respects the test is the same as described in CRD-C 128.

Tests of individual materials

10. Each of the 19 admixtures in classes 1 through 7 and the two type I portland cements were tested alone. The twentieth admixture, synthetic pure silica glass, was not tested because its great absorptive capacity precluded testing without further modification of the test method. Each material was tested in either duplicate or triplicate.

11. The average results of the tests of each of the admixtures and the portland cements are given in table 3. The two type I cements gave values for dissolved silica (S_c) of zero, and for reduction in alkalinity (R_c) of 187 and 137. The 19 admixtures gave results for S_c ranging from 0 to 883 and for R_c ranging from 65 to 545.

Tests of blends

12. The utility of the quick chemical test as described above would be greatly enhanced if either or both of the determined functions (S_c , R_c) were additive. However, it was not known whether the S_c or the R_c value that might result from a blend of a cement and an admixture could be calculated from the proportions of the materials in the blend and their known individual S_c and R_c values. Therefore tests were made on blends of the 16 materials in all classes except uncalcined quartz and synthetic silica glass with both type I cements at the assumed optimum percentage replacement by volume, and with the type I high-alkali cement at a lower and higher percentage replacement. The blends were tested in accordance with the plan on the following page:

Class	Replacement Material	% Cement Replacement Solid Volume	
		Type I	Type I
		High-alkali	Low-alkali
1	Slag I	30, 50, 70	50
	Slag II	50	50
2	Natural I	20, 35, 50	35
	Natural II	35	35
3	Fly Ash I	30, 45, 60	45
	Fly Ash II	45	45
	Fly Ash III	45	45
	Fly Ash IV	45	45
4	Pumicite, Friant	25, 35, 45	35
	Pumicite, Lassen	35	35
	Tuff	35	35
	Obsidian	35	35
5	Calcined shale (Monterey)	20, 30, 40	30
	Calcined shale (Napa)	30	30
	Calcined diatomaceous earth	30	30
6	Uncalcined diatomaceous earth	8, 12, 16	12

13. The results obtained from these tests are also shown in table 3. The data definitely indicate that neither function is additive and therefore that the performance of a given blend cannot be predicted.

Discussion of results

14. Two criteria have been applied to the test to determine the effectiveness of admixtures in reducing expansion due to alkali-aggregate reaction. The Davis Dam Specification¹⁴ required a minimum reduction in alkalinity (R_a)⁷ of 40% for a material to be regarded as effective. Of the materials tested in this investigation, the data in table 3 show that only five meet this requirement. They are: fly ash I, tuff, calcined shale M, calcined diatomite, and uncalcined diatomite, with R_a values of 46, 41, 52, 55, and 44%, respectively. Calcined shale N, with an R_a value of 39%, may be regarded as borderline. The second criterion was proposed by Moran and Gilliland⁷ who plotted the S_c and R_c values for a number of materials and found that those that will reduce mortar expansions 75% or more in two weeks at 20% replacement by weight (25% by volume) will fall above or to the right of a line having the equation $R_c + 2/3 S_c = 630$. The test results in table 3 have been graphed in fig. 1. It is evident

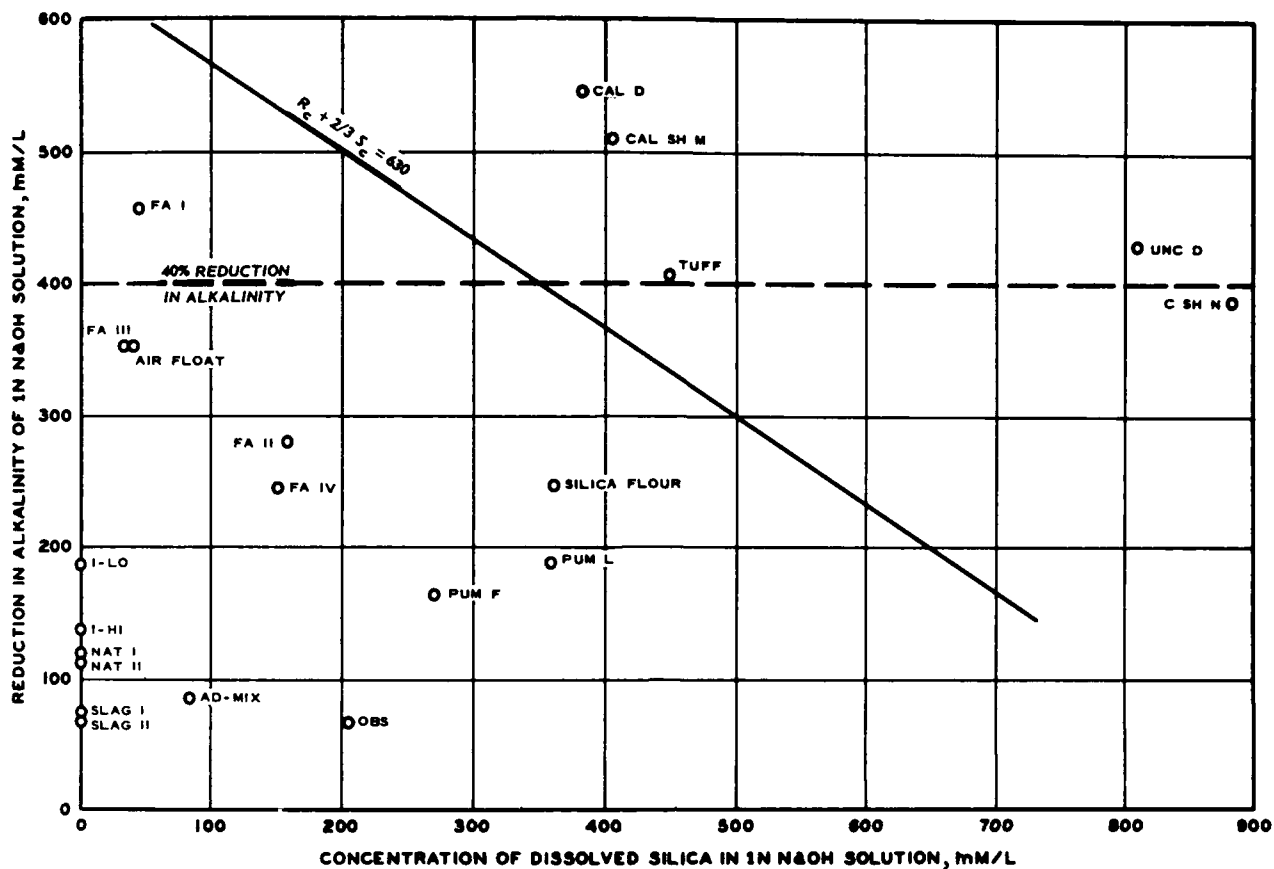


Fig. 1. Reactivity of materials with sodium hydroxide

that calcined diatomite, calcined shale M, tuff, uncalcined diatomite, and calcined shale N meet this requirement. Although fly ash I met the Davis Dam Specifications, it does not conform to this requirement. Table 9 summarizes these data as well as the data obtained by other methods used in this investigation to test the effectiveness of mineral admixtures in preventing expansion due to alkali-aggregate reaction.

Modified Test for Reactivity with NaOH

Test

15. The Bureau of Reclamation used the quick chemical test for some time to assist in the evaluation of admixtures.¹⁴ However, it did not prove to be completely satisfactory, and in 1952,⁶ a description of a modified version of the reactivity test was published. The modified test assumes an admixture-to-cement ratio of 1 to 3 by weight and a tricalcium

silicate (C_3S) content of cement of 40%. Therefore, 25 ml of 0.5N NaOH (instead of 25 ml of 1N NaOH) are reacted with 4.0 g of admixture and 1.5 g of calcium hydroxide ($Ca(OH)_2$). The reaction container, the reaction time, and the temperature are the same as for the original method. The containers are, however, agitated throughout the reaction period by an end-over-end rotation at 30 rpm. In addition to the determination of S_c and R_{OH}^* on the filtrate, the net reduction in concentration of sodium (Na) and potassium (K) was determined and also the concentration of alumina (Al_2O_3).

Criteria

16. The paper by Mielenz, et al⁶ correlated graphically the reduction in alkalies (R_A) and the reduction in alkalinity (R_{OH}) of 63 admixtures representing a wide variety of materials, with the reduction in expansion (R_e) of mortar bars containing Pyrex aggregate, high-alkali cement, and the tested admixture at ages of 14 days, 2 months, and 1 year. The correlations were found to be satisfactory for all three ages, but best at 14 days; therefore, only the 14-day correlations were shown. Admixtures that reduced expansion by 75% in the mortar-bar test were generally regarded as effective. The value of 75% reduction was, therefore, used to determine the criteria for the chemical tests. The values of 180 or greater for reduction in alkalies, and 210 or greater for reduction in alkalinity were apparently selected from the graph as being those that will most efficiently separate admixtures that will reduce mortar-bar expansion by 75% or more from those that will reduce expansion by less than 75%.

Statistical determination of criteria

17. The published data did not include the line of best fit, which may substantiate the criteria. As part of this investigation, the equations of these lines, the correlation coefficients, and the standard errors of estimate were calculated and are as shown on the following page:

* In this report, the reduction in alkalinity as determined in the modified test is designated R_{OH} rather than R_c .

<u>Determination</u>	<u>Test Age</u>	<u>Line of Regression</u> $R_e =$	<u>Correlation Coefficient</u>	<u>Standard Error of Estimate</u>	<u>Value Corresponding to 75% Reduction in Expansion</u>
Net reduction of alkalis	14 days	$0.162R_A + 41.0$	0.84	12.5	209.7
	2 months	$0.161R_A + 41.0$	0.79	15.3	211.3
	1 year	$0.165R_A + 33.2$	0.78	16.6	253.1
Reduction in alkalinity	14 days	$0.154 R_{OH} + 38.2$	0.84	12.4	238.6
	2 months	$0.156 R_{OH} + 37.6$	0.82	14.3	239.7
	1 year	$0.165 R_{OH} + 29.4$	0.82	15.3	276.5

where

R_A = reduction in alkalis, me/L
 R_{OH} = reduction in alkalinity, me/L
 R_e = per cent reduction in mortar expansion

The differences between the equations for the three test ages and between the corresponding correlation coefficients are not significant. The magnitude of the correlation coefficients indicates that the regression lines are not due to random chance. Information concerning the reproducibility of the test was included with the published data. The standard deviation for reduction in alkalis was found to vary between 7.4 and 14.5. The criterion specified for reduction in alkalis is two to three standard deviations less than the values found, using the regression line, to correspond to a 75% reduction in expansion both at 14 days and 2 months. The criterion for reduction in alkalis, and probably for reduction in alkalinity, is too low in that many admixtures that will reduce expansion by only 70% in 14 days will be evaluated as effective along with most if not all admixtures that will reduce expansion by 75% or more. The criterion apparently takes into account the lack of precision of the chemical test without considering the lack of precision of the mortar-bar test.

Additional modification of the test

18. For the purposes of this investigation, further changes were made to the modified method (see paragraph 15). In order to test various blends with both high- and low-alkali cements, the actual admixture-to-cement ratio by solid volume was substituted for the assumed ratio, and the actual C_3S content was used rather than the 40% assumed value. Finally, the SiO_2 and Al_2O_3 determinations were omitted and the double end point titration was used.

Blends tested

19. The reactivity of the following blends was determined by the procedure just described.

<u>Class</u>	<u>Replacement Material</u>	<u>% Replacement, Solid Volume</u>	
		<u>Type I High-alkali</u>	<u>Type I Low-alkali</u>
1	Slag I	30, 50, 70	50
	Slag II	50	--
2	Nat I	20, 35, 50	35
	Nat II	35	--
3	FA I	30, 45, 60	45
	FA II	45	--
	FA III	45	--
	FA IV	45	--
4	Pum F	25, 35, 45	35
	Pum L	35	--
	Tuff	35	--
	Obs	35	--
5	C Sh M	20, 30, 40	30
	C Sh N	30	--
	Cal D	30	--
6	Unc D	8, 12, 16	12

Test results

20. Test results obtained for these blends and for the lime substituting for the two cements are shown in table 4. All the results shown were obtained from duplicate determinations.

21. The following blends, of all those tested, were found to meet both published criteria: 45% pumicite F with high-alkali cement, 35% tuff with high-alkali cement, 30% and 40% calcined shale M with high-alkali cement, 30% calcined shale N and calcined diatomite with high-alkali cement. None of the blends made with uncalcined diatomite were found to meet the requirements; undoubtedly the percentage of uncalcined diatomite used was too low. Some anomalies were also observed: The 35% blend of pumicite L with high-alkali cement gave results greater than 210 for reduction in alkalinity but the results for reduction in alkalies were less than 180; this was also found for the 45% and 60% of fly ash I with high-alkali cement and the 45% blend with low-alkali cement. The 30% blend of fly ash I with high-alkali cement met the 210 criteria only when the double end point titration was used. Only the 45% blend of pumicite F with

high-alkali cement would be affected if the criteria were changed to those devised from the regression line. The other blends (35% tuff, 30 and 40% calcined shale M, 30% calcined shale N, 30% calcined diatomite, all with high-alkali cement) would still be regarded as effective inhibitors. The following general observations were apparent from this test:

- a. The amount of replacement material used must exceed a given minimum before expansion can be effectively reduced and, for the materials tested, the minimum replacement was never lower than 30%.
- b. The values for reduction in alkalies (R_A) and alkalinity (R_{OH}) generally increased with increasing replacement.
- c. Blends made with low-alkali cement will not necessarily give results similar to those obtained with blends made with high-alkali cement.
- d. Changing the numerical values of the criteria does not materially affect the interpretation of the results.

Further possible modifications of the modified test

22. Investigation of modifications. There are certain obvious advantages in using lime in the test rather than a portland cement. To determine whether the advantages are outweighed by some unapparent disadvantage, a limited experiment was performed. The design of this experiment, materials used, and the results obtained are all shown in table 5. All data shown were obtained from single determinations. The data were separated into six groups: three reagents, with each reagent considered in relation to two different tests. The results obtained from the analysis of variance* on each group are shown in table 6.

23. Only tentative conclusions may be drawn from this limited work since the experimental design was such that only ten degrees of freedom are available to evaluate the significance of the experimental factors. Replicate testing would be necessary in order to form more valid conclusions.

24. Result of analysis of variance. Ideally the test should clearly differentiate between the effects of the variables without interference of

* For a discussion of procedures for and significance of analysis of variance, see reference 5.

interactions. In addition, the more important variable should produce the greater effect. The variables, in order of decreasing importance, are: mineral admixture, percentage replacement, and cement. The six groups may, therefore, be listed in order of decreasing effectiveness as a test as follows:

- a. Reagent II, reduction in alkalies; variables are clearly separated and interactions do not interfere.
- b. Reagent II, reduction in alkalinity; the effect of cement, the least important variable, is lost and interactions do not interfere.
- c. Reagent III, reduction in alkalies; effect of cement is lost and that of percentage of admixture reduced and one interaction may interfere.
- d. Reagent III, reduction in alkalinity; effect of cement is reduced but one interaction will definitely interfere and another may.
- e. Reagent I, reduction in alkalies; effect of percentage admixture is lost and one interaction will interfere and another may.
- f. Reagent I, reduction in alkalinity; the three interactions will definitely interfere.

25. The tentative conclusions to be drawn from table 6 are that a cement (reagent II) rather than the $\text{Ca}(\text{OH})_2$ equivalent of a cement (reagent III) should be used in testing admixtures by the modified method. The use of cement and water (reagent I) need no longer be considered. It has been observed previously that the amount of replacement material used must exceed a given minimum before mortar expansion can be effectively reduced. In addition, the greater the percentage of replacement, the greater will the values be for reduction in alkalies and alkalinity. Therefore, the use of the single cement-admixture ratio of 3 to 1 will not develop sufficient information about the effectiveness of the admixture. However, additional information should be developed before any recommendations are made for changes in the method of Mielenz, et al.

The Mortar-bar Test

Mortar bars

26. The only direct method available for determining the degree of expansion caused by alkali-aggregate reaction is the mortar-bar test.

Similarly, the only direct method available for determining the effectiveness of an admixture in preventing excessive expansion due to the reaction is to compare the expansion of bars made with the admixture and a reactive aggregate with bars made without the admixture (control bars), all other conditions being the same. For this phase of the investigation, each of the 14 materials in classes 1 and 3 through 6 and the one admixture in class 8 were used both at the assumed optimum and at one-half the assumed optimum percentages by solid volume (the class 8 material was, in addition, used at one-fourth optimum) with the type I, high-alkali portland cement. Three sets of three bars each, each set made on a different date, were made for each blend using Pyrex glass as the aggregate. The bars were fabricated in accordance with Method CRD-C 123⁹ except that:

- a. The water content of the mortar was adjusted for a flow of 110 + 5% using ten 1/2-in. drops in 6 sec.
- b. The quantity of cementing material used per batch did not equal 450 g; however, the volume of cementing material used per batch did equal that of 450 g of portland cement.

27. In addition, three sets of bars were made using the first admixture in each of the above classes at the assumed optimum percentage only (class 8 material was also blended at one-half optimum percentage), blended with the type I high-alkali cement and using the Sioux-Klufa combination as the aggregate. Finally, these same admixtures at the same percentage replacement were blended with the type II medium-alkali cement, and bars were made with Pyrex glass as the aggregate. The following control mixtures were used; each was represented by three sets of three bars.

- a. Type I high-alkali cement, Pyrex glass.
- b. Type I high-alkali cement, Sioux-Klufa combination.
- c. Type I high-alkali cement, Sioux quartzite.
- d. Type II medium-alkali cement, Pyrex glass.
- e. Type II medium-alkali cement, Sioux-Klufa combination.

Tests and results

28. The bars were stored for a period of 1 year, and their length change was determined at 14 days, 6 months, and 1 year by the procedures given in Method CRD-C 123. The percentage reduction in expansion was calculated by means of the formula on the following page:

$$R_e = \frac{E_r - E_t}{E_r} \times 100$$

where

R_e = per cent reduction in mortar expansion
 E_t = average per cent expansion of bars containing the admixture
 E_r = average per cent expansion of the applicable control bars

The average results of all these tests are shown in table 7 both as percentage expansion and percentage reduction in expansion at bar ages of 14 days, 6 months, and 1 year.

Discussion of test results

29. The expansion due to alkali-aggregate reaction was reduced for every combination tested except in three cases: the bars made from mortars containing blends of high-alkali cement and both 2.5 and 5.0% of the synthetic silica glass with Pyrex glass aggregate (1/4 and 1/2 optimum percentages of the admixture), and the blend of 12% uncalcined diatomite with the Sioux-Klufa aggregate. The degree of reduction of the expansion was increased by increasing the percentages of admixture in the mortar. Maximum reduction of expansion for bars made with Pyrex glass aggregate was found for the blend of 30% calcined shale N with high-alkali cement. For mortars made with the Sioux-Klufa combination as the aggregate, the maximum reduction in expansion was found for the blend containing the synthetic silica glass at its optimum percentage. Three of the mortars made with the medium-alkali cement showed shrinkage at the age of one year. They were those containing calcined shale M, slag I, and synthetic silica glass at their optimum percentages.

30. The following materials may be regarded as effective at a test age of 14 days using the criterion of a reduction in expansion of at least 75% when tested in mortars made with high-alkali cement and Pyrex glass: slags I and II, fly ash IV, pumicite L, calcined shale M, calcined shale N, and synthetic silica glass at their optimum percentage replacements. At test ages of 6 months and 1 year, all the admixtures tested (at their optimum percentage replacement) except uncalcined diatomite caused reduction in expansion of 75% or more. When the Sioux-Klufa combination was used as the aggregate, slag I, calcined shale M, and synthetic silica caused reduction in expansion of 75% or more at all three ages, and pumicite F at a

test age of 14 days. All the admixtures tested with the medium-alkali cement (Pyrex glass aggregate) caused a percentage reduction in expansion of 75 or greater at all three ages.

Petrographic examination of bars

31. After expansion measurements were completed, the bars were examined to determine the correlation, if any, between their condition and expansion. One bar from each group of 3 sets of 3 bars was selected to represent the group. The condition of the selected bar was determined by examination of the exterior and interior surfaces, both visually and with a stereoscopic microscope. A petrographic microscope was used as needed. The condition of the bars, unless there was evidence to the contrary, was assumed to be the result of the mechanism of alkali-aggregate reaction. Each bar was rated numerically on a condition scale devised for this purpose. The ratings depended on the presence and amount of: (a) external signs of reaction, such as warping, surface gel, and surface cracking, and (b) internal signs of reaction, such as gel and reacted aggregate. The scale is as follows:

- 0 No signs of reaction, bar as cast
- 1 Slight evidence of reaction
- 2 Slight evidence of reaction, signs are more abundant
- 3 Moderate reaction, some damage
- 4 Intermediate between conditions 3 and 5
- 5 Severe reaction, damage, and deterioration

32. The results of the bar examination are shown in table 8, and are discussed in the following subparagraphs.

a. General.

- (1) There was a definite over-all relationship between the observed condition and the expansion of the bars examined. The actual relationship was that the observable signs of alkali-aggregate reaction increased as the expansion increased.
- (2) Every bar examined showed some evidence of alkali-aggregate reaction.
- (3) Calcium sulfoaluminate was not found in any of the bars.
- (4) All bars containing slag had the typical blue-green color in the interior and across the bottom of the bar as cast. The area covered by the color varied directly

with the slag content. The color faded on exposure to air, but was still quite apparent after two months exposure. In an investigation of portland blast-furnace slag cements conducted by the Waterways Experiment Station,¹³ the blue-green color was found to fade more rapidly than it did in these bars.

b. Specific.

- (1) All the bars made with Pyrex glass as the aggregate were rated as being condition 1 or 2. Of the 14 admixtures in classes 1 and 3 through 6, ten had the same rating at both the optimum and half optimum percentages replacement. The other four were rated as showing more reaction with increasing expansion.
- (2) The bars made with the Sioux-Klufa combination as the aggregate show, in general, higher expansion and higher ratings, varying from 2 to 5, than those made with Pyrex glass aggregate.
- (3) Both the condition scale rating and the expansion indicate that uncalcined diatomite is not effective when used as a 12% replacement of high-alkali cement with the Sioux-Klufa combination aggregate.
- (4) All the bars made with the synthetic silica glass required such large amounts of water in mixing that they were abnormally weak. This made it impossible to use bar strength, which normally diminishes with increased reaction, in arriving at rating conditions.

Rate of Alkali Release

33. In addition to the other chemical tests described previously, the rate of alkali release of the replacement materials in the presence of lime and water was determined by the method described in Appendix B of the paper by Moran and Gilliland.⁷ The concentration of the alkalies in solution was determined at 0, 2, 7, 28, and 90 days for each of the 16 materials in classes 1 to 6 and for the 4 materials in classes 7 and 8 at 28 days only. The alkali content of each material was also determined in accordance with CRD-C 244⁹ as well as the water-soluble alkalies as directed in CRD-C 209.⁹ The results of all these analyses are shown in table 14. The alkali content of the solution at various test ages is reported in terms of total alkali, as Na_2O , as a percentage of the replacement material, and also as a percentage of the alkali content of the material.

The rate of release curves are similar for both sets of data and are shown in fig. 2 based on the alkali content. The rate of alkali release of the

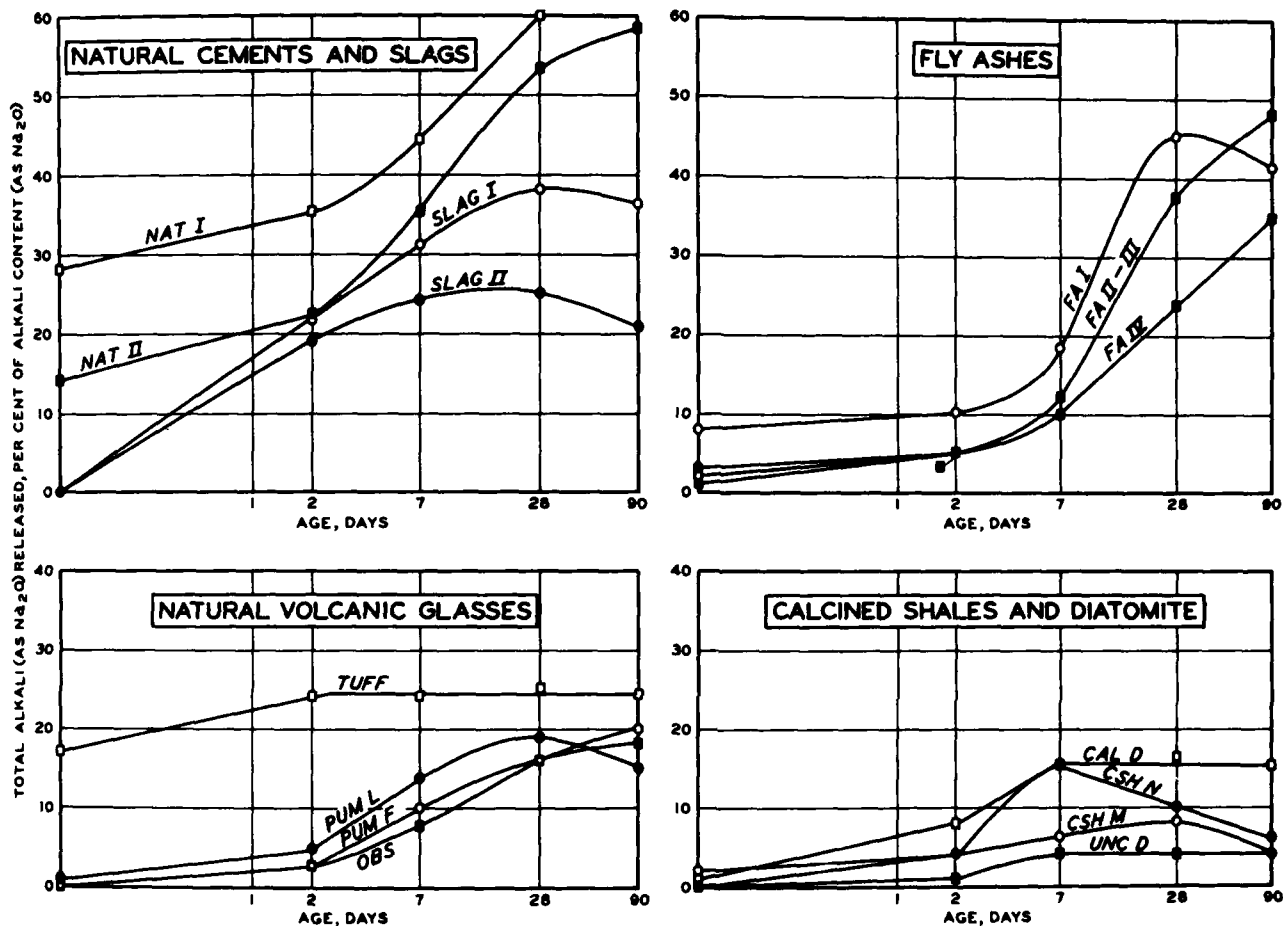


Fig. 2. Rate of alkali release from replacement materials

majority of the admixtures increased after the second day, becoming zero or decreasing after 28 days. The diatomites ceased releasing alkali after 7 days, and calcined shale N absorbed alkali at a uniform rate after 7 days. For slags I, II, and calcined shale M the rate of release was constant up to 28 days and then became negative. Tuff stopped releasing alkali after the second day. The amount of alkali released, as a percentage of alkali content, was greatest for the natural cements, then the fly ashes, followed by the slags and volcanic glasses. The calcined earths released the least alkali. As a percentage of the replacement material, the greatest amount of alkali was released by the volcanic glasses and fly ash I. The least amount was released by the calcined earths and the slags.

Mean Particle Diameter

34. In addition to the determination of particle size by microscopic methods (table 2), the mean particle diameter for each of the replacement materials was calculated using the data developed in the determination of specific surface by the air-permeability method, CRD-C 218.⁹ The equation used for this calculation was:

$$d = \frac{60,000 (1 - e) \sqrt{n} \sqrt{e_s^3} \sqrt{T_s}}{S_s \rho_s (1 - e_s) \sqrt{n_s} \sqrt{e_s^3} \sqrt{T}}$$

where

- d = mean particle diameter of test sample in microns
 - e = porosity of prepared bed of the test sample (see note)
 - e_s = porosity of prepared bed of standard sample (see note)
 - n = viscosity of air in poises, when test sample is tested (see note)
 - n_s = viscosity of air in poises, where standard sample is tested (see note)
 - T = time, in seconds, of manometer drop for test samples (see note)
 - T_s = time, in seconds, of manometer drop for standard sample (see note)
 - S_s = specific surface, in sq cm per g, of standard sample
 - ρ_s = specific gravity of standard sample
- Note: Values for \sqrt{n} , $\sqrt{n_s}$, $\sqrt{e^3}$, $\sqrt{e_s^3}$, \sqrt{T} , and $\sqrt{T_s}$ may be obtained from tables 2101A, 2101B, and 2101C, respectively, of Method C 218.⁹

The calculated values are shown in tables 2 and 13, and correspond very well to the microscopic results.

Autoclave Expansion

35. Pastes containing the type II cement and the replacement materials in classes 1, and 2 through 8, in the proportion of 4 to 1 were tested for autoclave expansion by Method CRD-C 224.⁹ All ten bars tested were sound; the maximum percentage expansion was 0.13 for pumicite L.

PART IV: COMPARISON OF TEST RESULTS AND CORRELATIONS

Comparison of Chemical and Mortar-bar Test Results

36. Most of the results of the various tests previously described are compared in table 9. Only the results concerning materials in classes 1 and 3 through 6 are shown. For those tests involving blends of an admixture and a cement, or an admixture in a mortar, only the high-alkali cement and the Pyrex glass aggregate results are shown. In addition, the criteria were rigidly interpreted to determine whether a material would be effective; that is, when a test result was found to be one unit less than the criteria, the admixture was judged to be noneffective. As can be seen from the table, complete agreement between the methods was obtained only for calcined shale M, which is effective as a replacement of 25% by volume or greater. If it is assumed that the percentage replacement used for uncalcined diatomite was too low, the methods agree and uncalcined diatomite will not be effective as replacements of 16% or less. It was noted in paragraph 30 and is also evident in table 9 that all the materials tested, except uncalcined diatomite, caused reduction in expansion of 75% or greater at test ages of 6 months and 1 year at their optimum percentage replacement. If the 6-month and 1-year test results are not considered, agreement between the methods was also obtained for fly ash II, fly ash III, obsidian (all noneffective at their optimum percentage replacement or lower), pumicite F (effective at 45% replacement but not at the optimum or lower), and calcined shale N (found effective at optimum percentage replacement, but disagreement found between the two criteria for reactivity with NaOH at 25% replacement). Slag I and II, and fly ash IV were found effective at their optimum percentage replacement by the mortar-bar test but ineffective by any of the chemical tests. Tuff and calcined diatomite were found to be effective by the chemical tests at their optimum percentage replacement but ineffective by the mortar-bar tests at 14-day test age. The lack of agreement in the results for fly ash I and pumicite L is between the chemical methods.

Comparisons of Test Results Obtained at Three Laboratories

Comparison of mortar-bar test results

37. Both the U. S. Bureau of Reclamation¹⁴ (USBR) and the U. S. Naval Civil Engineering Research and Evaluation Laboratory (NAVCEREL)⁸ have investigated the use of mineral admixtures in preventing expansion due to alkali-aggregate reaction and have published mortar-bar data. Six of the admixtures tested in these programs were similar to those tested in this investigation. The methods of test used to obtain these results differed in the following respects:

- a. All three laboratories used a high-alkali cement (alkali content greater than 1%); however, USBR used a type II, and the other laboratories a type I cement.
- b. The grading of the Pyrex aggregates differed as follows:

Sieve Size		% Used	
Passing	Retained	WES	NAVCEREL and USBR
3/8-in.	No. 4	2.5	0
No. 4	No. 8	7.5	20
No. 8	No. 16	10.0	20
No. 16	No. 30	35.0	20
No. 30	No. 50	30.5	20
No. 50	No. 100	11.0	20
No. 100	Pan	3.5	0

- c. The USBR bars were made with a constant water-cement ratio of 0.5. In the NAVCEREL and WES tests, the water content for each admixture blend was adjusted for a flow of 105 to 120% for NAVCEREL and 105 to 115% for WES, as measured on a flow table using ten 1/2-in. drops in six seconds.
- d. Both USBR and NAVCEREL made the admixture-cement blends on a weight basis, WES on an absolute volume basis. (For the purpose of comparison in table 10, all blends are shown as per cent by volume.)
- e. Both USBR and WES fabricated three specimens from each batch. NAVCEREL fabricated two specimens from each batch.
- f. USBR made control bars at the same time as the test mixture, and at least one control bar was stored in the same container with each test mixture. WES, and apparently NAVCEREL, did not store the control bar with the test mixture, nor were all test mixtures fabricated at the time the control bars were fabricated.

- g. Both USBR and NAVCEREL removed the bar from its mold and determined its length 24 + 2 hr after molding. WES allowed the bar to cure in the moist room for 44 + 4 hr after molding before removing the mold and measuring the length.

38. The percentage expansion of both the control and test bars and the percentage reduction in expansion at mortar-bar ages of 14 days, 6 months, and 1 year for the comparable admixtures tested at the three laboratories are shown in table 10.

Differences in mortar-bar test results

39. Examination of table 10 immediately reveals one difference. The expansion of the control bars fabricated by WES, with one exception, was much less than the expansion of control bars made by the other laboratories. The exception was the 14-day expansion of the control bar for fly ash I fabricated by USBR. Since the factors that affected the expansion of the control bars may or may not have affected the test bars to the same extent, the percentage expansion and percentage reduction in expansion of the test bars cannot be directly compared between laboratories. However, it may be noted that WES values for percentage reduction in expansion at 14 days tend to be lower than those of the other laboratories, and at both 6 months and 1 year WES values tend to be higher. Two differences in the test procedure may account in part for the lower expansion of WES control bars: The first is the longer time the bar was allowed to cure; the bar cannot expand while it is in the mold, therefore the WES bars had only 12 days to expand at the 14-day test age, whereas the bars made by the other laboratories had 13 days to expand. The second and more important difference is in the aggregate gradation. Andreasen and Christensen³ have noted that the finer fractions (passing a No. 125 sieve) in the Pyrex aggregate may act as admixtures, and have stressed the importance of removing these finer fractions by washing the aggregate. The WES aggregate gradation specifies 3-1/2% of the aggregate passing the No. 100 sieve without any control of the degree of fineness below the No. 100 sieve. This specification may account for the lower expansion of the control bars and may also introduce another variable by failure to require control of the degree of fineness below the No. 100 sieve. NAVCEREL washed their aggregates. It is not known whether USBR washed the aggregates they used; however, the USBR control bars expanded less than the NAVCEREL control bars.

Comparison of chemical test results

40. Fewer chemical test results were available for comparison since USBR and NAVCEREL did not use the same chemical test. Comparison of results of the modified quick chemical test and the quick chemical test are shown in table 11. In table 11A, the results from the modified quick chemical test, in general, correspond to the percentage replacement, although there are not enough data to form any conclusions. In table 11B, the differences in the results of the quick chemical test are of the magnitude expected for interlaboratory testing. With the exception of uncalcined diatomite, WES results were lower than NAVCEREL for reduction in alkalinity and higher for dissolved silica. In both tables, complete agreement was found between laboratories as to the effectiveness of the tested admixtures, when the data are compared to the appropriate criteria.

Comparison of minimum percentage replacement for effective admixtures

41. U. W. Stoll, in reporting the test performed at NAVCEREL,⁸ compared the expansion of bars made with Pyrex glass aggregates with cements of different alkali contents. The comparison revealed "that a cement with approximately 0.50 per cent alkali is required to be used in order that the resulting expansion at 14 days may be 75 per cent less than that observed for bars containing cement with an alkali content of 1.2 per cent. If an inert material replacement was used with the high-alkali-content cement to reduce the total alkali of the cementitious material to 0.50 per cent; that replacement would amount to about 60 per cent of the amount." Effective admixtures should exhibit some additional beneficial effect in addition to that of dilution. To determine the extent of this additional beneficial effect, the applicable data in tables 4 and 7 were graphed in fig. 3. The curves were interpolated (or extrapolated) to determine the percentage replacement that corresponded to the appropriate criteria for effectiveness. The interpolated values are shown in table 12 along with the corresponding values reported by NAVCEREL. All the admixtures tested do have some additional beneficial effect other than dilution of cement. Such effects are manifested at different levels of replacement ranging from a minimum of 10% for synthetic silica glass at both 14 days and 6 months to 52% for fly ash III at 14 days. The agreement

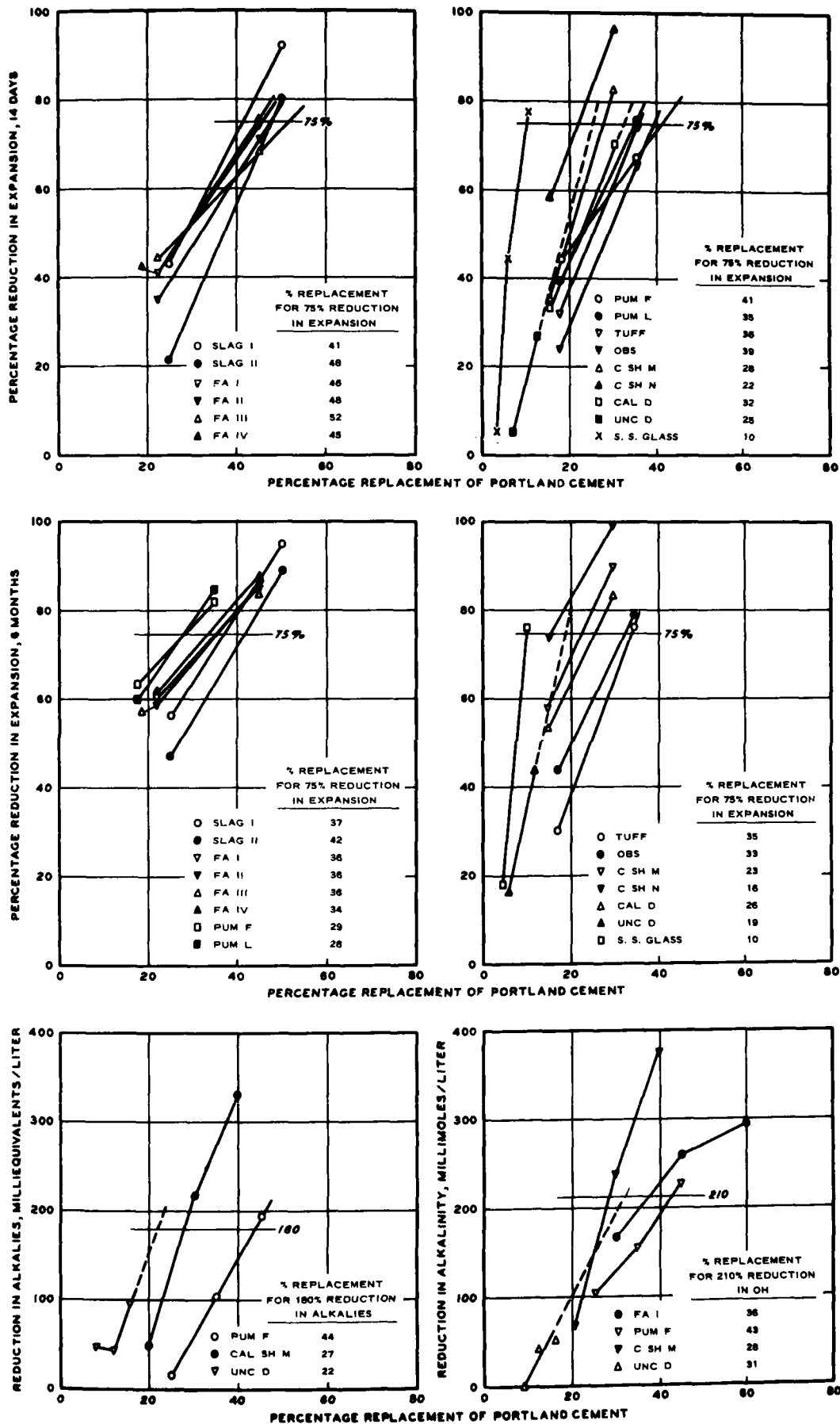


Fig. 3. Determination of minimum percentage replacement of cement to achieve reduction in expansion, alkalis, and alkalinity

between the results obtained by two laboratories and test methods is very good considering that these are interpolated results.

42. The minimum percentage replacement values may also be used to compare admixtures with each other. The lower the minimum replacement value, the more effectively the admixture will prevent expansion due to the alkali-aggregate reaction. This comparison is made in table 13. The admixtures are listed in ascending order of the average minimum replacement values. The average of the 14-day and 6-month values was used, since it was observed in paragraph 39 above that the percentage reduction in expansion tended to be low at 14 days and high at 6 months. The changes in the order would not be significant if either the 14-day or 6-month values were used. The synthetic silica glass heads the list as most effective followed by the calcined shales and uncalcined diatomite, then the natural glasses, and finally the blast-furnace slags and fly ashes.

Correlation of Minimum Replacement Values with Fineness,
Alkali Release, and Dissolved Silica

43. The correlation* between the interpolated minimum replacement value for each admixture and the fineness of the admixture (mean particle diameter), the rate of alkali release at 28 and 90 days, and the amount of silica dissolved in the quick chemical test may be seen in table 13. The minimum replacement value did not correlate with the 0-, 2-, and 7-day alkali-release data. The correlations may be more clearly seen in fig. 4 along with the curve of best fit. The equations of these curves, the correlation indices or coefficient, and the standard errors of estimate are as follows:

<u>Correlation between Minimum Replacement Value and</u>	<u>Regression Curve</u>	<u>Correlation Index, ρ, of Coeffi- cient r</u>	<u>Standard Error of Estimate S_y</u>
Total alkali as Na_2O , 90 days	$R = 9.79 + 8.58 \ln A$	0.890	3.71
% of alkali content, 28 days	$R = 4.20 + 10.34 \ln A$	0.852	4.26
Fineness, mean particle diameter	$R = 18.87 + 12.52 \ln D$	0.908	4.21
Dissolved silica	$R = 42.73 - 0.027 S_c$	0.922	3.12

* The procedures employed in obtaining the data presented in this section are described in reference 4.

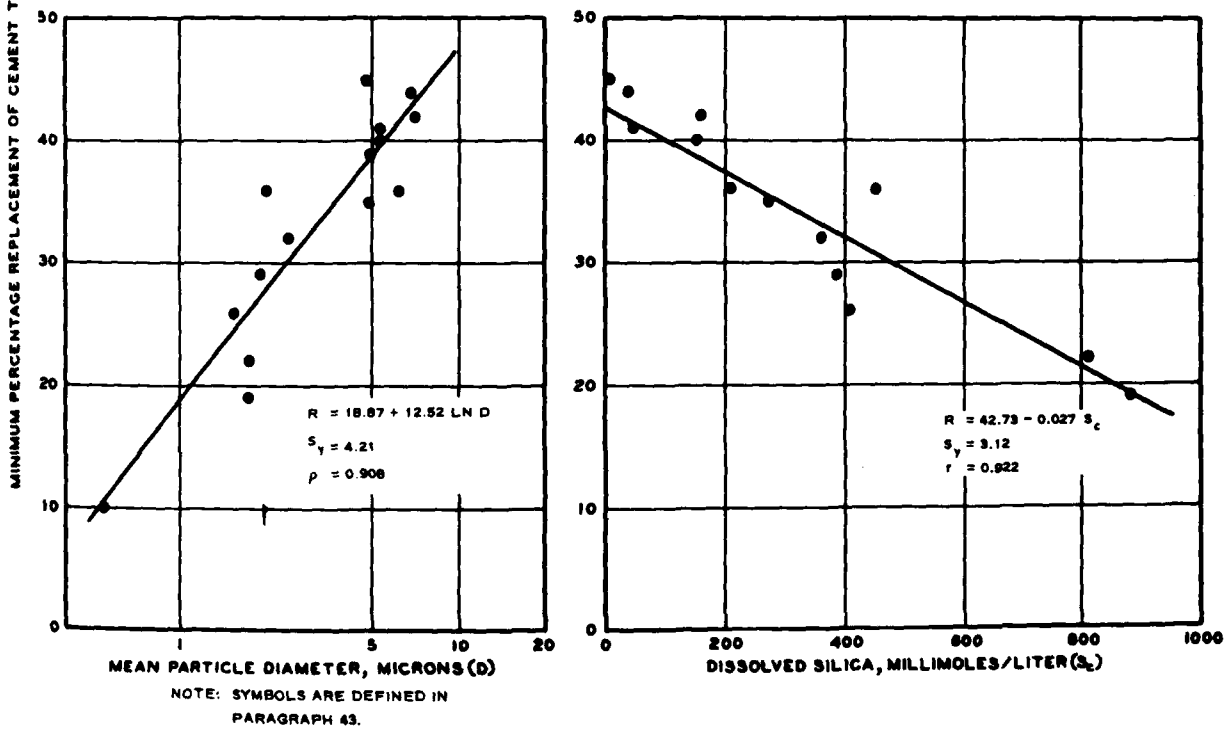
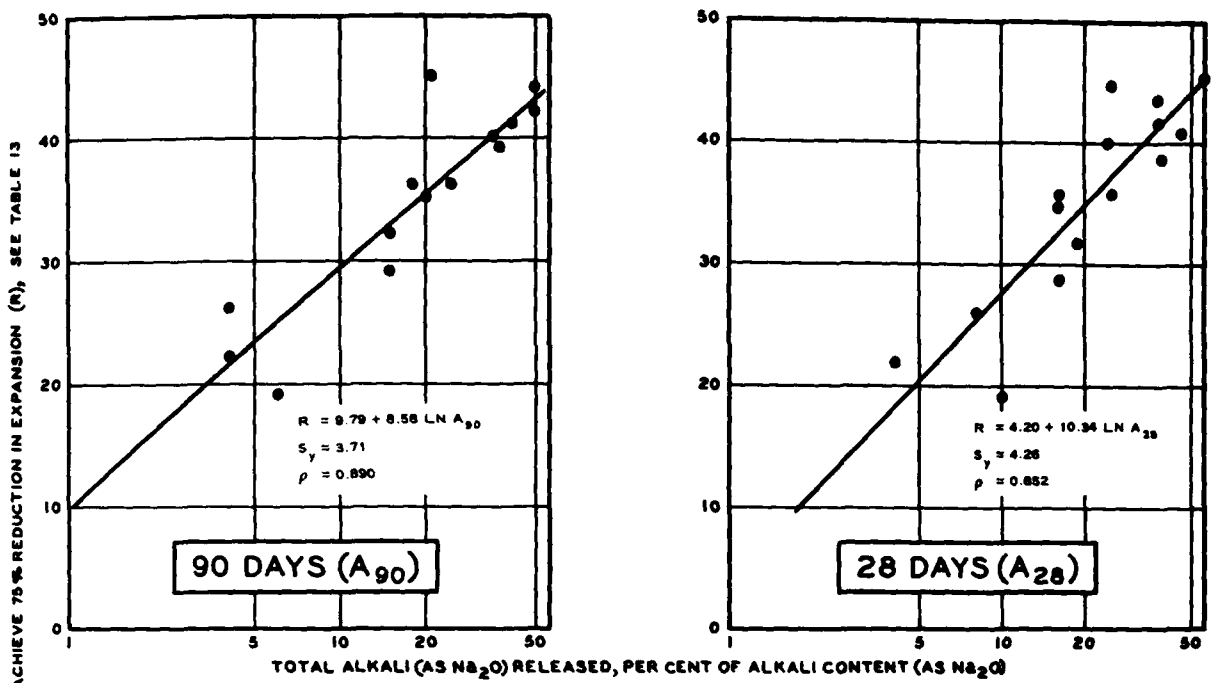


Fig. 4. Correlation of minimum replacement values with alkali release, fineness, and dissolved silica

where

R = minimum replacement value, per cent

S_c = dissolved silica, quick chemical test, mM/L

D = mean particle diameter, microns

A = total alkali as Na_2O , as per cent alkali content

44. The correlations, with due consideration of the small sample, are not due to random chance. Since evidence of correlation between the independent variables was not found, a multiple linear regression curve for the data in table 13 was calculated with the following results:

$$R = 27.3 - 0.0158 S_c + 1.6 \ln D + 3.5 \ln A$$

Multiple correlation coefficient: 0.951

Standard error of estimate: 2.50

Beta coefficients for : $S_c = 0.542$

$A = 0.366$

$D = 0.109$

The sample size is too small for a sound opinion to be formed regarding the multiple correlation, although it appears to be a good correlation. The beta coefficients indicate that the S_c value of an admixture has the greatest effect on the minimum percentage replacement value, and the mean particle diameter, the least. Other correlations were attempted including silica content, alkali content, alkali release as a percentage of the amount of admixture used, all versus the minimum replacement value, without success. The correlations and also the lack of correlations indicate to some extent the factors that are necessary for effective reduction of expansion due to the alkali-aggregate reaction. Further work is necessary to determine the relative effect of lime on the reactions. The multiple correlation does not suggest the mechanism of the reaction but rather serves to evaluate the relative effect of the factors, when considered together, on the reaction.

Reactions Involved in Preventing Excessive Expansion

45. Many hypotheses have been advanced to explain alkali-aggregate reaction and the effectiveness of measures to prevent its causing excessive expansion in concrete, however a great deal of work still remains to be done to provide a basis for an adequate hypothesis. With the thought that

some benefits might be derived from simplification of what appears to be a complex reaction, Mather prepared a summary of an hypothesis concerning the reactions involved, part of which has been published.¹ It proposes a working hypothesis concerning phenomena involved in pozzolanic reaction, alkali-aggregate reaction, and prevention of excessive expansion of concrete due to alkali-aggregate reaction. The hypothesis was based on the assumption that all three phenomena are fundamentally the same: the reaction of calcium, alkalies, and hydroxide ions with soluble silica. The degree of reaction was thought to depend on the silica content, the metastability of the silica, and the fineness of the material. This investigation substantiates part of the working hypothesis. Since precise knowledge of the actual reactions that will cause the phenomena is lacking, the hypothesis will certainly aid in determining the type of chemical test needed to evaluate materials with respect to the phenomenon. A chemical test to evaluate effectiveness of admixtures will have to determine, in the presence of lime, the reactive (glassy or noncrystalline) silica content of the material, and the alkalies that will be removed from solution. The chemical tests used in this investigation do not fulfill these requirements since:

- a. The quick chemical test does not evaluate the reductions in alkalies directly, nor does the reaction take place in the presence of lime.
- b. The modified quick chemical test does not correlate the effects of dissolved silica and reduction of alkalies with effectiveness in preventing excessive expansion. In addition, both tests lack the precision normally desired in chemical tests. The precision of the quick chemical test has been previously examined and reported.¹⁰

PART V: CONCLUSIONS

46. All the materials tested in this study will effectively reduce expansion if sufficient amounts are employed in the mixture. All the materials exhibit a beneficial effect with regard to expansion other than by dilution. The synthetic silica glass was found to be the most active admixture. Only 10% replacement by volume is needed to reduce the percentage expansion by 75% in two weeks; next the calcined shales, requiring 19 to 29% replacement; the uncalcined diatomite, requiring 22%; the volcanic glasses, requiring 32 to 36%; and lastly, the slags and fly ashes, requiring 39 to 45%.

47. It is evident from this investigation that neither chemical test can be used, with reliance, to evaluate the effectiveness of an admixture in preventing excessive expansion. Further work may develop a reliable chemical test, since a relation was found between minimum percentage replacement value, fineness of the material, reactive silica, and the amount of alkalies retained by the reaction product.

48. The mortar-bar test requires improvement to increase the precision for both intra- and interlaboratory testing. Seven differences were found in the procedures used by three laboratories. The more important differences were: bar age at the time the molds were stripped, aggregate gradation, and removal of fines from the aggregate.

49. Specifications for evaluating admixtures for effectiveness in preventing excessive expansion due to the alkali-aggregate reaction require the material to be tested at one percentage replacement, generally 25% by volume. As indicated in this study, materials may be more effectively evaluated and compared if they are tested at two or three different percentage replacements. The minimum percentage replacement for effectiveness may then be determined by interpolation.

50. Pending additional development work, the criteria and procedures

set forth in CRD-C 262- and 263-57* appear to be the most reasonable means of establishing the effectiveness of a material in preventing excessive expansion due to alkali-aggregate reaction.

* CRD-C 262-57, Corps of Engineers Specifications for Pozzolan as an Admixture for Use in Portland-cement Concrete, CRD-C 263-57, Corps of Engineers Methods for Sampling and Testing Pozzolan as an Admixture for Use in Portland-cement Concrete, provide that when pozzolan is to be used with aggregate which is regarded as potentially deleteriously reactive with the alkalies in cement, the pozzolan shall develop a reduction of mortar expansion at 14 days of at least 75% when tested in mortar bars made with a cement containing at least 1.0% total alkalies calculated as Na_2O and Pyrex glass aggregate and a replacement of the cement by pozzolan in the amount of 25% by absolute volume.

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Table 1
Results of Tests of Portland Cements

Test Result	Type I Cement		Type II Cement
	High-alkali RC-211	Low-alkali RC-210	Medium-alkali RC-330
<u>Chemical Data</u>			
<u>Major components, %</u>			
SiO ₂	20.6	20.1	23.1
Al ₂ O ₃	5.4	6.6	5.0
Fe ₂ O ₃	3.9	3.1	3.9
CaO	61.0	65.5	61.1
MgO	3.9	1.2	2.8
SO ₃	2.1	2.0	2.0
Loss on ignition	1.9	0.97	1.6
<u>Minor components, %</u>			
Na ₂ O	0.62	0.11	0.23
K ₂ O	0.68	0.39	0.69
Total as Na ₂ O	1.07	0.37	0.68
P ₂ O ₅	0.13	0.20	---
Mn ₂ O ₃	0.07	0.12	---
<u>Separate determinations, %</u>			
Insoluble residue	0.54	0.12	0.23
Chloroform solubility	0.002	0.004	---
Moisture content	0.36	0.19	---
<u>Calculated compounds, %</u>			
C ₃ S	44	56	29
C ₂ S	26	16	44
C ₃ A	8	12	7
C ₄ AF	12	9	12
CaSO ₄	4	3	3
<u>Physical Data</u>			
Fineness, passing No. 325 sieve, %	90.1	93.2	94.8
Fineness, Blaine, sq cm/g	3765	3450	3590
Specific gravity	3.11	3.15	3.17

(Continued)

Table 1 (Continued)

Test Result	Type I Cement		Type II Cement
	High-alkali	Low-alkali	Medium-alkali
	RC-211	RC-210	RC-330

Physical Data (Continued)

Time of setting (Gillmore)

Initial, hr:min	2:50	2:45	5:30
Final, hr:min	4:20	5:45	8:00
Autoclave expansion, %	0.28	0.14	0.10
Normal consistency, %	24.0	27.2	24.6
Air in mortar, %	10.2	7.6	8.8
Compressive strength, psi			
3 days	1510	2600	1745
7 days	2065	3900	2665
28 days	3065	5565	5140
Heat of hydration, cal/g (70 F w/c = 0.40)			
3 days	56	66	---
7 days	65	84	71
28 days	71	99	82
6 mo	86	106	---
1 yr	86	111	89
Bleeding (w/c 0.4)			
Rate, ml/cm ² /sec x 10 ⁶	64	59	37
Capacity, ml/cc x 10 ³	18	15	7
Bleeding (w/c 0.45)			
Rate	114	---	37
Capacity	29	---	7

Table 3
Results of Quick Chemical Test

Material	Cements and Replacement Materials Alone			% Admixture in Blend	Blends with					
	S _c *	R _c **	R _a †		High-alkali Cement			Low-alkali Cement		
					RC-211, mM/L			RC-210, mM/L		
	S _c	R _c	R _a	S _c	R _c	R _a	S _c	R _c	R _a	
Type I cement low-alkali	0	187	18	--	--	---	--	--	---	--
Type I cement high-alkali	0	137	14	--	--	---	--	--	---	--
Slag I	0	74	8	30	0	108	11			
				50	0	98	10	0	129	13
				70	0	109	11			
Slag II	0	68	7	50	0	99	10	0	116	12
Nat I	1	119	12	20	0	119	12			
				35	0	123	12	0	172	17
				50	0	131	13			
Nat II	0	113	11	35	0	106	11	0	160	16
FA I	44	456	46	30	1	175	18			
				45	5	228	23	5	236	24
				60	4	341	35			
FA II	158	280	28	45	58	292	29	5	212	21
FA III	33	352	36	45	19	277	28	3	197	20
FA IV	151	246	25	45	59	307	31	10	267	27
Pum F	270	167	17	25	4	185	19			
				35	60	250	25	7	219	22
				45	79	307	31			
Pum L	359	188	19	35	70	267	27	24	327	33
Tuff	450	406	41	35	13	353	36	4	284	29
Obs	204	65	7	35	3	141	14	2	146	15
C Sh M	405	510	52	20	2	206	21			
				30	2	365	37	2	351	35
				40	17	503	50			
C Sh N	883	390	39	30	75	523	52	25	476	48
Cal D	382	545	55	30	32	435	44	12	399	41
Unc D	810	430	44	8	0	155	16			
				12	0	148	15	0	193	19
				16	0	181	18			
SiO ₂ Flour	360	248	28							
Air Float	39	351	38							
Ad-Mix	82	85	11.6							

* Dissolved silica in mM/L.

** Reduction in alkalinity in mM/L.

† Reduction in alkalinity in per cent.

Table 4

Results of Modified Quick Chemical Test

Material	% Replacement	Blends Made with Ca(OH) ₂ Equivalent of Type I High-alkali Cement, me/L*				Blends Made with Ca(OH) ₂ Equivalent of Type I Low-alkali Cement, me/L*				
		Reduction in Na ⁺	K ⁺ Released	Reduction in Alkali (Na ⁺ + K ⁺)	Net Reduction in Alkalinity (OH ⁻)	Reduction in Na ⁺	K ⁺ Released	Reduction in Alkali (Na ⁺ + K ⁺)	Net Reduction in Alkalinity (OH ⁻)	
		End Point	Single End Point	Double End Point	Single End Point	Double End Point	Single End Point	Double End Point	Single End Point	Double End Point
Cement	0	6	0	6	-2	-4	5	0	5	5
Slag I	30	34	10	24	16	32	32	19	5	1
	50	25	6	19	35	59	-4	19	-23	49
	70	10	13	-3	90	142				73
Slag II	50	162	8	154	37	54				
Nat I	20	8	19	-11	-5	-19				
	35	3	24	-21	45	32		28	-44	41
	50	-19	-39	-58	70	73				32
Nat II	35	-12	21	-32	35	31				
FA I	30	69	13	56	167	223		19	41	239
	45	52	22	30	261	327				312
	60	87	13	75	295	376				
FA II	45	134	18	116	170	200				
FA III	45	52	11	41	148	182				
FA IV	45	110	15	95	146	198				
Pum F	25	60	45	15	104	121		49	91	144
	35	152	48	104	154	185				
	45	220	26	194	227	256				
Pum L	35	199	24	175	235	265		6	145	175
Tuff	35	224	16	208	257	293				172
Obs	35	47	33	14	50	73				
C Sh M	20	50	2	48	68	72				
	30	216	0	216	238	243				
	40	325	-6	331	377	381				
C Sh N	30	356	0	356	386	390				
Cal D	30	258	6	252	355	362				
Unc D	8	47	0	47	-2	-6		8	-25	36
	12	43	4	39	44	37				23
	16	95	-2	97	53	72				

* me/L = milliequivalents per liter.

Table 5

Results of Determination of the Effect of Different Reactants
on the Modified Quick Chemical Test

Admixture Type	Vol %	Reduction in Alkalies (Na ⁺ plus K ⁺), me/L						Reduction in Alkalinity (OH ⁻), me/L					
		Reagent I*		Reagent II**		Reagent III		Reagent I		Reagent II		Reagent III	
		High-alkali Cement	Low-alkali Cement	High-alkali Cement	Low-alkali Cement	High-alkali Cement	Low-alkali Cement	High-alkali Cement	Low-alkali Cement	High-alkali Cement	Low-alkali Cement	High-alkali Cement	Low-alkali Cement
Slag I	70	88	-10	63	28	8	6	60	-6	36	-24	96	55
	50	45	-41	51	-1	-21	4	18	-16	-78	-14	33	50
	30	10	-21	37	-40	-18	-12	-22	-28	-27	-68	32	15
Nat I	50	47	-19	-6	-20	-67	-69	57	3	5	9	50	64
	35	18	-25	-13	-12	-57	-48	9	-33	-28	-20	40	16
	20	-1	-6	5	-52	-46	-33	-8	1	-20	11	-13	27
FA I	60	20	-63	73	30	6	10	97	30	251	249	263	291
	45	18	-65	75	16	8	23	71	-2	205	133	258	228
	30	-24	-36	-1	-53	5	18	-2	-25	122	25	192	218
Pum F	45	66	-107	140	61	87	112	153	51	138	103	208	154
	35	12	-63	86	32	198	67	88	5	173	93	258	149
	25	18	-52	16	7	24	27	26	-12	15	-11	174	107
C Sh M	40	97	-24	179	167	275	168	90	10	145	307	314	370
	30	86	17	159	86	137	108	84	28	119	127	249	143
	20	40	3	42	64	68	-7	20	34	127	45	93	75
Unc D	16	43	-1	16	63	18	39	12	-2	-23	52	28	48
	12	27	2	38	40	20	24	-4	1	45	5	53	5
	8	19	3	42	15	-3	16	-18	8	-8	23	-9	19

* Cement and distilled water.

** Cement and 9.5 N NaOH.

† Ca(OH)₂ equivalent of the cement and 0.5 N NaOH.

Table 6

Conclusions from Analysis of Variance on Results of
Determination of the Effects of Different Reactants
on the Modified Quick Chemical Test

	<u>Reagent I*</u>	<u>Reagent II**</u>	<u>Reagent III†</u>	<u>Degrees of Freedom Associated with Each Variable</u>
<u>Test: Reduction in Alkalies (Na⁺ plus K⁺)</u>				
<u>Source of variation</u>				
Cement (C)	VS	VS	NS	1
Admixture (P)	VS	VS	VS	5
Percentage of pozzolan (%)	NS	VS	Sig	2
<u>Interactions</u>				
C x P	Sig	NS	NS	5
C x %	VS	NS	NS	2
P x %	NS	NS	Sig	10
				10 residue

Test: Reduction in Alkalinity (OH⁻)

<u>Source of Variation</u>				
C	VS	NS	Sig	1
P	VS	VS	VS	5
%	VS	VS	VS	2
<u>Interactions</u>				
C x P	VS	NS	NS	5
C x %	VS	NS	Sig	2
P x %	VS	NS	VS	10
				10 residue

Note: VS, very significant.

Sig, significant.

NS, not significant.

* Cement and distilled water.

** Cement and 0.5 N NaOH.

† Ca(OH)₂ equivalent of the cement and 0.5 N NaOH.

Table 7
Results of Mortar-bar Expansion Tests

<u>Replacement Material</u>		<u>% Reduction in Expansion</u>						<u>%</u>
<u>Type</u>	<u>% Vol</u>	<u>% Expansion</u>			<u>Expansion</u>			<u>Warp*</u>
		<u>14 days</u>	<u>6 mo</u>	<u>1 yr</u>	<u>14 days</u>	<u>6 mo</u>	<u>1 yr</u>	<u>1 yr</u>
<u>A. Type I High-alkali Cement</u>								
<u>Pyrex Aggregate</u>								
None	----	0.106	0.221	0.230	--	--	--	0.05
Slag I	50	0.008	0.011	0.014	92	95	94	0.0
	25	0.060	0.098	0.102	43	56	56	0.03
Slag II	50	0.021	0.025	0.028	80	89	88	0.02
	25	0.084	0.117	0.123	21	47	47	0.04
FA I	45	0.028	0.033	0.035	74	85	85	0.0
	22.5	0.063	0.089	0.093	41	60	60	0.0
FA II	45	0.031	0.032	0.037	71	86	84	0.0
	22.5	0.069	0.090	0.095	35	59	59	0.0
FA III	45	0.034	0.035	0.037	68	84	84	0.0
	22.5	0.059	0.086	0.093	44	61	60	0.0
FA IV	45	0.027	0.026	0.028	75	88	88	0.0
	22.5	0.063	0.083	0.091	41	62	60	0.0
Pum F	35	0.035	0.040	0.045	67	82	80	0.0
	17.5	0.059	0.082	0.087	44	63	62	0.0
Pum L	35	0.025	0.034	0.040	76	85	83	0.0
	17.5	0.065	0.088	0.094	39	60	59	0.02
Tuff	35	0.028	0.052	0.060	74	76	74	0.0
	17.5	0.072	0.155	0.170	32	30	26	0.01
Obs	35	0.036	0.046	0.053	66	79	77	0.0
	17.5	0.081	0.127	0.136	24	43	41	0.03
C Sh M	30	0.018	0.021	0.029	83	90	87	0.0
	15	0.069	0.092	0.104	35	58	55	0.0
C Sh N	30	0.004	0.002	0.009	96	99	96	0.0
	15	0.044	0.057	0.067	58	74	71	0.02
Cal D	30	0.032	0.037	0.043	70	83	81	0.0
	15	0.071	0.104	0.110	33	53	52	0.0
Unc D	12	0.077	0.123	0.134	27	44	42	0.03
	6	0.101	0.185	0.198	5	16	14	0.03
Syn silica glass	10	0.024	0.053	0.086	77	76	63	0.03
	5	0.059	0.182	0.236	44	18	-3	0.04
	2.5	0.101	0.260	0.293	5	-18	-27	0.05

(Continued)

* Determined as directed in CRD-C 123.

Table 7 (Continued)

<u>Replacement Material</u>		<u>% Expansion</u>			<u>% Reduction in Expansion</u>			<u>% Warp*</u>
<u>Type</u>	<u>% Vol</u>	<u>14 days</u>	<u>6 mo</u>	<u>1 yr</u>	<u>14 days</u>	<u>6 mo</u>	<u>1 yr</u>	<u>1 yr</u>
<u>A. Type I High-alkali Cement (Cont'd)</u>								
<u>Sioux-Klufa Aggregate</u>								
None	----	0.159	0.681	0.803	--	--	--	0.06
Slag I	50	0.010	0.117	0.180	94	83	78	0.0
FA I	22.5	0.065	0.381	0.464	59	44	42	0.04
Pum F	35	0.018	0.282	0.361	89	59	55	0.04
C Sh M	30	0.018	0.051	0.102	89	93	87	0.02
Unc D	12	0.119	0.792	0.964	25	-16	-20	0.05
Syn silica glass	10	0.021	0.044	0.059	87	94	93	0.01
	5	0.053	0.281	0.317	67	59	61	0.03
<u>Sioux Aggregate</u>								
None	----	0.004	0.027	0.057				0.0
<u>B. Type II Medium-alkali Cement</u>								
<u>Pyrex Aggregate</u>								
None	----	0.046	0.068	0.075	--	--	--	0.0
Slag I	50	-0.003	-0.009	-0.005	107	113	107	0.0
FA I	45	0.008	0.005	0.008	83	93	89	0.0
Pum F	35	-0.002	-0.004	0.003	104	106	96	0.0
C Sh M	30	0.000	-0.005	-0.002	100	107	103	0.0
Unc D	12	0.001	0.002	0.004	98	97	95	0.0
Syn silica glass	10	0.008	-0.019	-0.022	83	128	129	0.0
	5	0.006	0.004	0.016	87	94	79	0.0
<u>Sioux-Klufa Aggregate</u>								
None	----	0.100	0.454	0.537	--	--	--	0.02

* Determined as directed in CRD-C 123.

Table 8

Results of Petrographic Examination of Mortar Bars

Replacement Material	Expansion in 1 year	Petro- graphic Rating of Bar Cond*	Signs of Alkali-aggregate Reaction					
			External			Internal		
			Apparent Warp**	Surface Crack	Gel	Void Gelt	Reacted or Frosted Particlestt	
Type	% Vol							
<u>A. Type I High-alkali Cement</u>								
<u>Pyrex Aggregate</u>								
None	----	0.230	2	N†	N	F††	F	F
Slag I	50	0.014	1	N	N	F	N	F
	25	0.102	2	N	N	F	F	F
Slag II	50	0.028	2	N	N	F	F	F
	25	0.123	2	N	N	F	F	F
FA I	50	0.035	1	N	N	F	F	F
	25	0.093	2	N	N	F	F	F
FA II	50	0.037	1	N	N	F	N	F
	25	0.095	1	N	N	F	N	F
FA III	50	0.037	1	N	N	F	N	F
	25	0.093	1	N	N	F	F	F
FA IV	50	0.028	1	N	N	F	N	F
	25	0.091	1	N	N	F	F	F
Pum F	35	0.045	2	N	N	F	F	F
	17.5	0.087	2	N	N	F	F	F
Pum L	35	0.040	1	N	N	F	F	F
	17.5	0.094	1	N	N	F	F	F
Tuff	35	0.060	1	N	N	F	F	F
	17.5	0.170	2	N	N	F	F	F
Obs	35	0.053	1	N	N	F	F	F
	17.5	0.136	2	N	N	F	F	F
C Sh M	30	0.029	1	N	N	F	F	F
	15	0.104	1	N	N	F	F	F

(Continued)

* Explanation of numerical ratings is given in paragraph 31.

** Warping determined by visual observation.

† Gel found in air voids.

†† A thin, brittle, white, translucent film of secondary material found on aggregate surfaces which gives the particles of Pyrex glass and Sioux quartzite a frosted appearance. The opaline matrix of the Klufa particles softens and may be partially dissolved.

* N refers to no evidence of that condition.

** F refers to evidence of the condition.

Table 8 (Continued)

Replacement Material	§ Expansion in 1 year	Petro- graphic Rating of Bar Cond*	Signs of Alkali-aggregate Reaction					
			External			Internal		
			Apparent Warp**	Surface Crack	Gel	Void Gelt	Reacted or Frosted Particlest†	

A. Type I High-alkali Cement (Continued)

Pyrex Aggregate (Continued)

C Sh N	30	0.009	1	N	N	F	N	F
	15	0.067	1	N	N	F	F	F
Cal D	30	0.043	1	N	N	F	F	F
	15	0.110	1	N	N	F	F	F
Unc D	12	0.134	1	N	N	F	F	F
	6	0.198	1	N	N	F	F	F
Syn	10	0.086	1	F	N	F	F	F
silica	5	0.236	1	F	F	F	F	F
glass	2.5	0.293	2	F	F	F	F	F

Sioux-Klufa Aggregate

None	----	0.803	5	F	F	F	F	F
Slag I	50	0.180	3	F	F	F	F	F
FA I	50	0.464	3	F	F	F	F	F
Pum F	35	0.361	3	F	F	F	F	F
C Sh M	30	0.102	3	F	F	F	F	F
Unc D	12	0.964	5	F	F	F	F	F
Syn	10	0.059	2	N	F	F	N	F
silica	5	0.317	3	F	F	F	F	F
glass								

Sioux Aggregate

None	----	0.057	2	N	N	F	F	N
------	------	-------	---	---	---	---	---	---

(Continued)

* Explanation of numerical ratings is given in paragraph 31.

** Warping determined by visual observation.

† Gel found in air voids.

†† A thin, brittle, white, translucent film of secondary material found on aggregate surfaces which gives the particles of Pyrex glass and Sioux quartzite a frosted appearance. The opaline matrix of the Klufa particles softens and may be partially dissolved.

Table 8 (Continued)

Replacement Material	% Expansion in 1 year	Petro- graphic Rating of Bar Cond*	Signs of Alkali-aggregate Reaction					
			External			Internal		
			Apparent Warp**	Surface Crack	Gel	Void Gelt	Reacted or Frosted Particlest†	

B. Type II Medium-alkali Cements

Pyrex Aggregate

None	----	0.075	2	N	N	F	F	F
Slag I	50	-0.005	1	N	N	F	N	N
FA I	45	0.008	1	N	N	F	F	F
Pum F	35	0.003	1	N	N	F	F	F
C Sh M	30	-0.002	1	N	N	F	N	N
Unc D	12	0.004	1	N	N	F	F	N
Syn	10	0.022	1	N	N	F	N	F
silica	5	0.016	1	F	N	F	N	F
glass								

Sioux-Klufa Aggregate

None	----	0.537	4	N	F	F	F	F
------	------	-------	---	---	---	---	---	---

* Explanation of numerical ratings is given in paragraph 31.

** Warping determined by visual observation.

† Gel found in air voids.

†† A thin, brittle, white, translucent film of secondary material found on aggregate surfaces which gives the particles of Pyrex glass and Sioux quartzite a frosted appearance. The opaline matrix of the Klufa particles softens and may be partially dissolved.

Table 9

Summary of Results of Tests on Effectiveness of Admixtures

Admix- ture	% Vol Repl Matl	Reactivity with		Modified Reactivity with NaOH			Mortar-bar Reduction in Expansion > 75%		
		Na ⁺ (OH ⁻)*		Na ⁺ plus K ⁺ me/L	OH ⁻ me/L		Expansion > 75%		
		Ra ≥ 40%	R + 2/3 S ≥ 630		Single End Point	Double End Point	14 days	6 months	1 year
Slag I	70			n	n	n			
	50			n	n	n	e	e	e
	30			n	n	n			
	25	n	n				n	n	n
Slag II	50			n	n	n	e	e	e
	25	n	n				n	n	n
FA I	60			n	e	e			
	45			n	e	e	n	e	e
	30			n	n	e			
	22.5	e	n				n	n	n
FA II	45			n	n	n	n	e	e
	22.5	n	n				n	n	n
FA III	45			n	n	n	n	e	e
	22.5	n	n				n	n	n
FA IV	45			n	n	n	e	e	e
	22.5	n	n				n	n	n
Pum F	45			e	e	e			
	35			n	n	n	n	e	e
	25	n	n	n	n	n			
	17.5						n	n	n
Pum L	35			n	e	e	e	e	e
	17.5	n	n				n	n	n
Tuff	35			e	e	e	n	e	n
	17.5	e	e				n	n	n
Obs	35			n	n	n	n	e	e
	17.5	n	n				n	n	n
C Sh M	40			e	e	e			
	30	e	e	e	e	e	e	e	e
	20			n	n	n			
	15						n	n	n

(Continued)

Note: n, the admixture was found to be noneffective.

e, the admixture was found to be effective.

* In this test, the admixture is used by itself. The criterion correlates the results with mortar-bar results in which 20% portland cement by weight (25% by volume) is replaced by the admixture.

Table 9 (Continued)

Admix- ture	% Vol Repl Matl	Reactivity with		Modified Reactivity with NaOH			Mortar-bar Reduction in Expansion > 75%		
		Na ⁺ (OH ⁻)*		Na ⁺ plus K ⁺	OH ⁻ me/L		14	6	1
		Ra ≥ 40%	R + 2/3 S ≥ 630	me/L > 180	Single End Point > 210	Double End Point > 210	days	months	year
C Sh N	30	n	e	e	e	e	e	e	e
	15						n	n	n
Cal D	30	e	e	e	e	e	n	e	e
	15						n	n	n
Unc D	16	e	e	n	n	n			
	12			n	n	n	n	n	n
	8			n	n	n			
	6						n	n	n

Note: n, the admixture was found to be noneffective.
e, the admixture was found to be effective.

* In this test, the admixture is used by itself. The criterion correlates the results with mortar-bar results in which 20% portland cement by weight (25% by volume) is replaced by the admixture.

Table 10

Comparison of Mortar-bar Test Results between Laboratories

Test Age	Repl Matl % by Vol	% Expansion						% Reduction in Expansion		
		Control Bars			Test Bars					
		WES	USBR	NAV CEREL	WES	USBR	NAV CEREL	WES	USBR	NAV CEREL
A. Fly Ash WES, FA I; USBR, Chicago fly ash #9407										
14 days	45	0.106			0.028			74		
	24		0.092			0.034			63	
	22.5	0.106			0.063			41		
1 year	45	0.230			0.035			85		
	24		0.320			0.112			65	
	22.5	0.230			0.093			60		
B. Pumicite WES, Pum F; USBR, Pumicite 1 (A-226), 2 (A-688); NAVCEREL, Madera 1 (-100 + 200 mesh), 2 (-325 mesh)										
14 days	36	1			0.058			83		
	2			0.347		0.013			96	
	35	0.106			0.035			67		
25	1		0.326		0.090	0.061		72	82	
	2		0.193	0.347	0.084	0.035		56	90	
	25*	1/2		0.347		0.070			80	
						0.092			73	
	17.5	0.106			0.059			44		
13	1				0.194				44	
	2			0.347		0.153			56	
	6 months	36	1		0.230				76	
	2			0.942		0.106			89	
	35	0.221			0.040			82		
25	1				0.343				64	
	2			0.942		0.254			73	
	25*	1/2		0.942		0.385			59	
						0.429			55	

(Continued)

Note: All bars made with high-alkali cement and Pyrex glass aggregate.

* Duplicate determination.

Table 10 (Continued)

Test Age	Repl Matl % by Vol	% Expansion						% Reduction in Expansion		
		Control Bars			Test Bars					
		WES	USBR	NAV CEREL	WES	USBR	NAV CEREL	WES	USBR	NAV CEREL
<u>B. Pumicite (Continued)</u>										
6 months (Contd)	17.5	0.221			0.082			63		
	13 ¹ / ₂			0.942			0.538 0.600			43 36
1 year	35	0.230			0.045			80		
	25 ¹ / ₂		0.587 0.542			0.190 0.231			68 57	
	17.5	0.230			0.087			62		
<u>C. Monterey Shale</u> WES, C Sh M; USBR, Opaline Shale 1 (8147), 2 (A-268), 3 (A-548); NAVCEREL, Colton										
14 days	35			0.347			0.019			94
	30	0.106			0.018			83		
	1		0.228			0.050			78	
	24 ² / ₃		0.139	0.347		0.022	0.064		84	82
	3		0.326			0.085			74	
	24*			0.347			0.077			78
6 months	15	0.106			0.069			35		
	12			0.347			0.095			73
	35			0.942			0.057			94
	30	0.221			0.021			90		
	24			0.942			0.278			71
	24*			0.942			0.425			55
6 months	15	0.221			0.092			58		
	12			0.942			0.443			53

(Continued)

Note: All bars made with high-alkali cement and Pyrex glass aggregate.
* Duplicate determination.

Table 10 (Continued)

Test Age	Repl Matl % by Vol	% Expansion						% Reduction in Expansion		
		Control Bars			Test Bars			WES	USBR	NAV CEREL
		WES	USBR	NAV CEREL	WES	USBR	NAV CEREL			
<u>C. Monterey Shale (Continued)</u>										
1 year	30	0.230			0.029			87		
	1		0.442		0.095			79		
	24	2	-----		-----			--		
		3	0.587		0.289			51		
	15	0.230			0.104			55		
<u>D. Napa Shale</u> <u>WES, C Sh N; NAVCEREL, Napa</u>										
14 days	36		0.347		0.004			99		
	30	0.106			0.004			96		
	25		0.347		0.023			93		
	25*		0.347		0.030			91		
	15	0.106			0.044			58		
6 months	13		0.347		0.060			83		
	36		0.942		0.000			100		
	30	0.221			0.002			99		
	25		0.942		0.090			90		
	25*		0.942		0.160			83		
	15	0.221			0.057			74		
	13		0.942		0.379			60		
<u>E. Calcined Diatomite</u> <u>WES, Cal D; USBR, Oil Shale 1 (A-245), 2 (A-974); NAVCEREL, Airox</u>										
14 days	36		0.347		0.007			98		
	30	0.106			0.032			70		
	25	1	0.219	0.347	0.060	0.098		73	72	
		2	0.381		0.074			81		
	25*		0.347		0.106			70		

(Continued)

Note: All bars made with high-alkali cement and Pyrex glass aggregate.

* Duplicate determination.

Table 10 (Continued)

Test Age	Repl Matl % by Vol	% Expansion						% Reduction in Expansion		
		Control Bars			Test Bars			WES	USBR	NAV CEREL
		WES	USBR	NAV CEREL	WES	USBR	NAV CEREL			
<u>E. Calcined Diatomite (Continued)</u>										
14 days (contd)	15	0.106			0.071			33		
	13			0.347			0.219			37
6 months	36			0.942			0.082			91
	30	0.221			0.037			83		
	25			0.942			0.360			62
	25*			0.942			0.430			54
	15	0.221			0.104			53		
	13			0.942			0.547			42
1 year	30	0.230			0.043			81		
	25	1 2		0.468			0.190			59
				0.725			0.220		70	
	15	0.230			0.110			52		
<u>F. Uncalcined Diatomite</u> WES, Unc D; NAVCEREL, Johns-Manville Pozzolan										
14 days	25			0.347			0.018			95
							0.057			84
	18			0.347			0.165			53
	12	0.106			0.077			27		
6 months	10			0.347			0.222			36
	6	0.106			0.101			5		
	25			0.942			0.293			69
							0.459		51	
	18			0.942			0.504			46
	12	0.221			0.123			44		
	10			0.942			0.695			26
	6	0.221			0.185			16		

Note: All bars made with high-alkali cement and Pyrex glass aggregate.
* Duplicate determination.

Table 11

Comparison of Chemical Test Results between Laboratories

A. Modified Quick Chemical Test

Admixture	% Repl by Vol	Reduction in Alkalies (Na ⁺ plus K ⁺), mM/L		Reduction in Alkalinity (OH ⁻), mM/L	
		WES	USBR	WES	USBR
WES, FA I	60	75		295	
USBR, Chicago fly ash # 9407	45	30		261	
	30	56		167	
	24		-9		85
WES, Pum F	45	194		227	
USBR, pumicite					
1. A-226	31	104		154	166
2. A-688	25 ₂	15	144	104	59
			24		
WES, C Sh M	40	331		377	
USBR, opaline shale	30	216		238	
1. 8147	24		187		231
2. A-268	24		268		285
3. A-548	24		228		245
	20	48		68	
WES, Cal D	30	252		355	
USBR, oil shale					
1. A-245	25		166		226
2. A-974	25		328		403

B. Quick Chemical Test

Admixture	Reduction in Alkalinity (mM/L)		Dissolved Silica (mM/L)	
	WES	NAVCEREL	WES	NAVCEREL
Pum F Madera Pum -325 -100 + 200	163	225	270	189
		154		135
C Sh M Colton	510	576	405	152
C Sh N Napa	390	419	883	772
Cal D Airox	545	581	382	270
Unc D Johns-Manville pozzolan	430	385	810	993

Table 12

Minimum Percentage Replacement by Volume for Effectiveness

Replacement Material	Mortar-bar Test			Mod Reactivity with NaOH		
	WES		NAVCEREL 14 days	Reduction in Alkalies	Reduction in Alkalinity	
	14 days	6 mo				Avg
Slag I	41	37	39			
Slag II	48	42	45			
FA I	46	36	41		36	
FA II	48	36	42			
FA III	52	36	44			
FA IV	45	34	40			
Pum F	41	29	35	24	44	43
Pum L	35	28	32			
Tuff	36	35	36			
Obs	39	33	36			
C Sh M	28	23	26	19	27	28
C Sh N	22	16	19	11		
Cal D	32	26	29	28		
Unc D	25	19	22	24	22	31
Syn silica glass	10	10	10			

Table 13

Comparison of Effectiveness of Admixtures; Correlation of Minimum Replacement Values with Physical Properties of the Admixture

Replace- ment Material	Minimum % Replace- ment, Sol Vol, for Effective Inhibition	Particle Size		Total Alkali as Na ₂ O, Released, % of Alkali Content		S _c Dissolved Silica mM/L
		Mean Diameter Calculated microns	Predominant Range Microscope microns	28 days	90 days	
Syn silica glass	10	0.5				
C Sh N	19	1.8	1-7	10	6	883
Unc D	22	1.8	0.5-1	4	4	810
C Sh M	26	1.6	2-6	8	4	405
Cal D	29	2.0	2-10	16	15	382
Pum L	32	2.5	2-14	19	15	359
Pum F	35	4.8	2-20	16	20	270
Tuff	36	2.1	2-8	25	24	450
Obs	36	6.1	6-15	16	18	204
Slag I	39	4.8	2-9	38	36	0
FA IV	40	5.2	3-14	24	35	151
FA I	41	5.3	1-10	45	41	44
FA II	42	7.1	3-13	37	48	158
FA III	44	6.9	4-20	37	48	33
Slag II	45	4.7	2-15	25	21	0

Table 14
Rate of Alkali Release

Replacement Material	Alkali Content*		Water-soluble**		Alkali Content		Total Alkali as Na ₂ O Released†		% of Replacement Material		% of Alkali Content					
	Na ₂ O	K ₂ O	Total	Na ₂ O	K ₂ O	Total	Initial	28 days	90 days	Initial	28 days	90 days				
													% of Repl Matl	% of Repl Matl	% of Alkali Content	
Slag I	0.20	1.17	0.97	0.00	0.01	0.01	0.00	0.21	0.30	0.37	0.35	0	22	31	38	36
Slag II	0.24	0.99	0.89	0.00	0.00	0.00	0.00	0.17	0.21	0.22	0.19	0	19	24	25	21
Net I	0.11	1.06	0.81	0.01	0.31	0.22	0.23	0.28	0.36	0.49	0.54	28	35	44	60	67
Net II	0.26	0.78	0.77	0.02	0.11	0.09	0.11	0.17	0.27	0.41	0.45	14	22	35	53	58
FA I	1.62	1.98	2.92	0.23	0.04	0.26	0.24	0.28	0.52	1.31	1.20	8	10	18	45	41
FA II	0.38	1.75	1.53	0.03	0.02	0.04	0.04	0.08	0.18	0.56	0.68	3	5	12	37	48
FA III	0.63	1.02	1.30	0.02	0.01	0.03	0.03	0.07	0.16	0.48	0.62	2	5	12	37	48
FA IV	0.30	1.72	1.43	0.02	0.01	0.02	0.02	0.07	0.14	0.35	0.50	1	5	10	24	35
Pum F	1.38	4.96	4.64	0.01	0.02	0.02	0.02	0.14	0.46	0.74	0.91	0	3	10	16	20
Pum L	1.82	2.94	3.75	0.02	0.01	0.03	0.05	0.18	0.52	0.71	0.56	1	5	14	19	15
Tuff	2.01	3.82	4.52	0.02	0.03	0.04	0.75	1.09	1.08	1.13	1.11	17	24	24	25	24
Obs	3.52	3.78	6.01	0.01	0.00	0.01	0.01	0.19	0.51	0.97	1.11	0	3	8	16	18
C Sh M	0.88	1.14	1.63	0.02	0.02	0.03	0.04	0.07	0.09	0.13	0.07	2	4	6	8	4
C Sh N	0.40	0.61	0.80	0.00	0.02	0.01	0.00	0.03	0.12	0.08	0.05	0	4	15	10	6
Cal D	1.21	1.56	2.24	0.03	0.01	0.04	0.03	0.18	0.34	0.37	0.33	1	8	15	16	15
Unc D	1.72	1.68	2.83	0.04	0.00	0.04	0.02	0.02	0.12	0.10	0.10	1	1	4	4	4
SiO ₂ Flour	0.00	0.00	0.00							0.00					--	--
Air Float	0.00	0.20	0.13							0.00					--	--
Ad-Mix	0.00	0.02	0.01							0.00					--	--
Syn silica glass	0.00	0.00	0.00							0.00					--	--

* Determined as described in CRD-C 244.
 ** Determined as described in CRD-C 209 (ASTM C 114-53).
 † Total alkali as Na₂O = Na₂O + 0.658 K₂O.