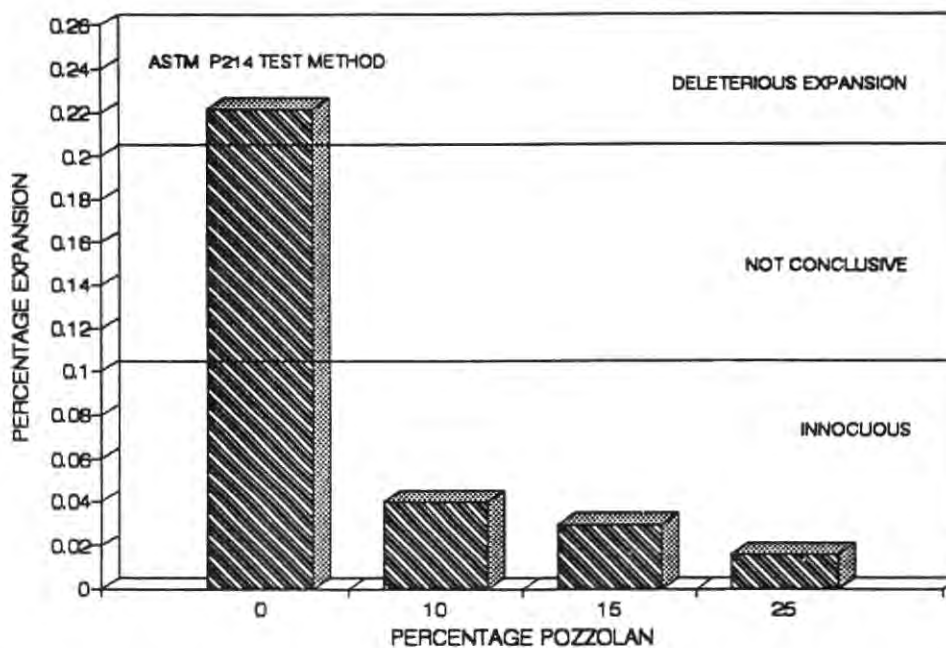




SD Department of Transportation
Office of Research



Development of a Type I (PM) Cement

Study SD91-11
Final Report

Prepared by
South Dakota School of Mines and Technology
Department of Civil Engineering
Rapid City, SD 57701-3995

June, 1994

DISCLAIMER

The contents of this report reflect the views of the authors who are responsible for the facts and accuracy of the data presented herein. The contents do not necessarily reflect the official views or policies of the South Dakota Department of Transportation, the State Transportation Commission, or the Federal Highway Administration. This report does not constitute a standard, specification, or regulation.

This work was performed under the supervision of the SD91-11 Technical Panel:

Sarah Chadima SD Geological Survey
Dan Johnston Office of Research
Court Patterson SD Cement Plant

Howard Schill Materials and Surfacing
David Wang Materials and Surfacing

TECHNICAL REPORT STANDARD TITLE PAGE

1. Report No. SD91-11-F		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle Development of a Type I (PM) Cement			5. Report Date March 31, 1993		
			6. Performing Organization Code		
7. Author(s) V. Ramakrishnan			8. Performing Organization Report No.		
9. Performing Organization Name and Address South Dakota School of Mines & Technology Department of Civil Engineering Rapid City, SD 57701-3995			10. Work Unit No.		
			11. Contract or Grant No. 310066		
12. Sponsoring Agency Name and Address South Dakota Department of Transportation Office of Research 700 East Broadway Avenue Pierre, SD 57501-2586			13. Type of Report and Period Covered Final; May 1992 to June 1994		
			14. Sponsoring Agency Code		
15. Supplementary Notes Project Monitor: Mr. Dan Johnston					
<p>16. Abstract Alkali-silica reactivity (ASR) produces a major problem in concrete structures. This report presents an experimental investigation to identify a natural pozzolan and to determine the optimum quantity that can be blended with cement to produce a Type IP cement for inhibiting the ASR. For comparative evaluation a Class F fly ash has also been investigated along with the pozzolans. Two methods, ASTM P214 and C227 were adopted for assessing the effectiveness of the pozzolans in controlling the ASR. Three percentages of 10%, 20% and 30% replacements of cement with fly ash were investigated.</p> <p>A total of 30 natural pozzolans were collected from the selected sites. Their chemical and mineralogical compositions and some physical properties such as fineness, and density were determined. The strength activity test (ASTM C311) was used in eliminating the pozzolans that would adversely affect the strength of concrete. Based on this test, ten pozzolans were selected for detailed study. The ASR expansions measured using the ASTM P214 test method had shown that two pozzolans were more effective than the Class F fly ash in inhibiting the ASR expansion.</p> <p>This report also presents an extensive experimental investigation to evaluate the performance characteristics and physical properties of the selected natural pozzolan blended cements, cement mortars and cement concretes. There was no significant difference in the physical properties of pozzolan blended cements, cement mortars and cement concretes when compared with those of corresponding unblended cements, mortars and concretes.</p> <p>It is economically feasible to mine the selected pozzolans from the volcanic ash beds within the Lakota Formation. The most favorable deposit is located about 10 miles of the cement plant at Rapid City.</p>					
17. Keyword Natural pozzolans, fly ash, alkali-silica reactivity Accelerated tests, Mining feasibility			18. Distribution Statement No restrictions. This document is available to the public from the sponsoring agency.		
19. Security Classification (of this report) Unclassified		Security Classification (of this page) Unclassified		21. No. of Pages	
				22. Price	

TABLE OF CONTENTS

Contents	Page #
Cover Page	i
Disclaimer	ii
Abstract	iii
Table of Contents	iv
List of Tables	vi
List of Figures	vii
 Executive Summary	 1
Background	4
Objectives	4
Selection of Pozzolans	4
Materials and Test Specimens	5
Test Procedures	6
ASTM P214 Test Method	6
ASTM C227 Test Method	6
Strength Activity Index with Cement	7
Density	7
Fineness by No.325 Sieve	7
Blaine Fineness	7
Test Results & Discussion	7
Density	7
Fineness	8
Strength Activity Index with Cement	8
Effect of Calcining on the Strength Activity Index	8
Effect of Pozzolans on Expansions using ASTM P214 Test Method	9
Effect of Pozzolans on Expansions using ASTM C227 Test Method	10
Comparison of Expansions measured in ASTM C227 & ASTM P214 Test Methods	 10
Mechanism by which the pozzolans effectively control the expansions due to Alkali-Silica Reactions	 11
Evaluation of Pozzolan Blended Cements & Concretes	11
Cement Mortar Properties	12
Cube Compressive Strength	12
Air Content	13

Cement Paste Properties	13
Normal Consistency	13
Early Stiffening	13
Time of Setting by Vicat Apparatus	14
Time of Setting by Gillmore Needles	14
Cement Properties	15
Density	15
Fineness by Sieve No. 325	15
Fineness by Blaine Air Permeability Apparatus	16
Physical & Elastic Properties of Pozzolan Blended Cement Concretes	16
Mixture Proportions	16
Fresh & Hardened Concrete Properties	17
Fresh Concrete Properties	17
Workability	17
Air Content	18
Fresh Concrete Unit Weight	18
Finishability	18
Hardened Concrete Properties	18
Compressive Strength	18
Static Modulus	19
Flexural Strength	19
Load Deflection Curve Behavior	20
Toughness Indices (ASTM)	20
Impact Strength	20
Feasibility of Mining	21
Mineability	21
Land Availability	22
Conclusions	22
Recommendations	24
Supplementary Information	24
Acknowledgments	25
References	25
Tables	
Figures	

LIST OF TABLES

Table #		Page #
1	Chemical & Physical Properties of Cement & Fly Ash	27
1A	Sieve Analysis - Coarse Aggregate	28
1B	Sieve Analysis - Fine Aggregate	28
2	Designation, Deposit & Description of Pozzolans	29
3	Chemical Compositions, Sodium Oxide & Potassium Oxide Concentrations (%) of Pozzolan Samples using ICP	31
4	Chemical Compositions, Sodium Oxide & Potassium Oxide Concentrations (%) of Pozzolan Samples using SEM	32
5	Compressive Strength & Strength Activity Index of Natural Pozzolans with Portland Cement	33
6	Compressive Strength & Strength Activity Index with cement for Calcined & Uncalcined Pozzolans	34
7	Density & Fineness of Pozzolans & Fly Ash	34
8	Blaine Fineness of Selected Pozzolans	35
9A	List of Selected Natural Pozzolans	35
9B	Mixture Designations & Proportions for Test Pozzolans	35
10	Basic Mix Proportions for Control & Pozzolan Blended Cement Concretes	36
11	Mix Designation	36

LIST OF FIGURES

Figure #		Page #
1	Comparison of Mortar Bar Expansion for LK2	37
2	Comparison of Mortar Bar Expansion for PS1E	37
3	Comparison of Mortar Bar Expansion for VA2	38
4	Comparison of Mortar Bar Expansion for Fly Ash	38
5	Comparison of Expansions for Pozzolan Sample LK2	39
6	Comparison of Expansions for Pozzolan Sample PS1E	39
7	Comparison of Expansions for Pozzolan Sample VA2	40
8	Comparison of Expansions for Pozzolan Sample Fly Ash	40
9	Comparison of Expansions for Pozzolan Sample LK2	41
10	Comparison of Mortar Bar Expansion for LK2	41
11	Comparison of Expansions from ASTM C227 & ASTM P214 Test Methods	42
12	Comparison of Compressive Strength of Cement Mortar Blended with LK2	42
13	Comparison of Air Content of Cement Mortar Blended with LK2	43
14	Comparison of Normal Consistency of Cement Blended with LK2	43
15	Comparison of early stiffening of cement paste blended with LK2 by Paste Method	44
16	Comparison of time of setting of cement blended with LK2 by Vicat Needle	44
17	Compariosn of time of setting of cement blended with LK2 by Gillmore Needles	45
18	Comparison of density of cement blended with LK2	45
19	Comparison of fineness of cement blended with LK2 by Sieve No. 325	46
20	Comparison of Blaine Fineness of cement blended with LK2	46
21	Comparison of Slump for concretes with 10% Pozzolan blended cements	47
22	Comparison of Vebe Time for concretes with 15% Pozzolan blended cements	47
23	Comparison of Air Content for concretes with 10% Pozzolan blended cements	48

24	Comparison of Compressive Strength for concretes with 10% Pozzolan blended cements	48
25	Comparison of Static Modulus for concretes with 10% Pozzolan blended cements	49
26	Comparison of Flexural Strength for concretes with 10% Pozzolan blended cements	49
27	Comparison of Impact Strength for concretes with 10% Pozzolan blended cements	50
28	Comparison of Slump for concretes with LK2 Pozzolan blended cements	50
29	Comparison of Vebe Time for concretes with LK2 Pozzolan blended cements	51
30	Comparison of Air Content for concretes with LK2 Pozzolan blended cements	51
31	Comparison of Compressive Strength for concretes with LK2 Pozzolan blended cements	52
32	Comparison of Static Modulus for concretes with LK2 Pozzolan blended cements	52
33	Comparison of Flexural Strength for concretes with LK2 Pozzolan blended cements	53
34	Comparison of Impact Strength for concretes with LK2 Pozzolan blended cements	53

EXECUTIVE SUMMARY

Background

Cement contains many ingredients of which the alkalies are minor components. Alkali reactive sands or coarse aggregates when used in concrete structures cause severe problems due to cracks that form by the expansive reaction between the alkalies in the cement and reactive forms of silica in the aggregates. The use of natural pozzolans as a cement replacement material is effective in inhibiting expansive alkali-silica reactivity. Alkali-silica reactivity (ASR) produces major problems in concrete pavements, bridge decks, bridges and other transportation structures. Some existing concrete pavements in South Dakota show severe deterioration because they have been constructed with alkali-reactive sands.

Objectives

- To find a natural pozzolan which is more efficient, effective and economical than fly ash in reducing deleterious expansion due to ASR.
- To find the optimum quantity of a natural pozzolan close to Dacotah Cement that can be blended with cement to produce a Type I (PM) Cement for minimizing ASR.
- To ensure that the selected natural pozzolan for blending does not in any way adversely affect the fresh and hardened properties of cement, mortar, and concrete.

Identification of Effective Pozzolans

A reconnaissance survey of potential sources of pozzolans within 100 miles of Rapid City resulted in the selection of 26 sites. A total of 30 natural pozzolans were collected from the 26 selected sites. Their chemical and mineralogical compositions and some physical properties such as fineness and density were determined. The strength activity test (ASTM C311) was used in eliminating the pozzolans that would adversely affect the strength of concrete. Based on this test, ten pozzolans were selected for detailed study. A detailed geologic description indicates that the most favorable units are volcanic ash beds typically mixed with fine-grained terrestrial sediments. Chemical analysis on 9 samples by ICP spectroscopy and the scanning electron microscope indicate that the silica content is high, ranging from 56 to 80%, and sodium and potassium concentrations are low. A mineralogical study by x-ray diffraction showed that the predominant minerals present in 8 of the 9 samples are quartz and clay. The ninth sample, Rockyford Ash contained 50% of the zeolite mineral clinoptilolite. Expansion test results and pozzolanic activity index data show that the Rockyford Ash, Lakota fire clay, and Pierre Shale have the most promising pozzolanic qualities.

Evaluation of Blended Cements and Class F Fly Ash for ASR Inhibition

For comparative evaluation a Class F fly ash has also been investigated along with the pozzolans. Two methods, ASTM P214 and ASTM C227 were adopted for assessing the effectiveness of the pozzolans in controlling the ASR. Three percentages of 10%, 20% and 30% replacement of cement with fly ash were investigated.

The ASR expansions measured using the ASTM P214 test method had shown that two pozzolans were more effective than the Class F fly ash in inhibiting the ASR expansion.

Evaluation of Pozzolan Blended Cements and Mortars

The effectiveness of pozzolan in controlling the ASR expansion depended on the type, moisture content, quality, and quantity of pozzolan blended with cement. Calcining the pozzolans has improved the strength activity index.

This investigation also presents the experimental results from evaluating the physical properties of six natural pozzolan-blended Type-IP cements with 10, 15, and 25 percentages of pozzolans. The tests carried out include:

1. Physical properties of cement mortar such as compressive strength (ASTM C109) and air content (ASTM C185).
2. Physical properties of cement paste such as normal consistency (ASTM C187), time of setting (ASTM C191 and ASTM C266), and early stiffening of cement paste (ASTM C451).
3. Physical properties of cement such as fineness (ASTM C430 and ASTM C204), and density (ASTM C188).

From the test results it can be stated that there is no significant difference in the physical properties of cement mortar, cement paste, and cement, blended with 10 percent of LK2 natural pozzolan, when compared to respective properties of plain portland cement mortar, cement paste, and cement. When this pozzolan was blended at 15%, there was a slight reduction in the strength properties and at 25% blending, there was a significant reduction (about 25%) in the flexural strength.

The natural pozzolan sample LK2 was collected from the Fuson Shale Member of the Lakota Formation. It is a fine-grained sandstone exhibiting a conchoidal fracture symbolic of refractory materials.

Evaluation of Blended Cement Concretes

This report also presents the results of an experimental investigation to evaluate the characteristics of pozzolan-blended cement concretes. After careful consideration of the primary costs and the total available quantities, five natural pozzolans were eliminated from further study. Therefore the remaining five natural pozzolans and the fly ash were used for this final comparative study. A comparison of concrete properties with those of unblended cements is also given. The Type I/II cement was blended with three different amounts of 10%, 15%, 25% by weight of cement with the selected five different types of natural pozzolans. The tests carried out include: (1) Fresh concrete properties such as slump, unit weight, vebe time, air content, and concrete temperature and (2) Hardened concrete properties such as compressive strength, static modulus of elasticity, flexural and impact strengths.

All tests were done according to ASTM recommendations and procedures. Good workability of concrete was achieved even though the water content was kept uniformly the

same for all mixes, without adding any water-reducing agent or superplasticizer. The test results indicated that there were no significant difference in the physical properties of pozzolan-blended cement concretes in comparison with control concrete during mixing and placing. An increase in the pozzolan content slightly decreased the compressive strength and modulus of rupture. The static modulus results indicated that the values were almost the same for all the concretes.

From the results of the static flexure test, load deflection curves were plotted from which the toughness indexes were calculated according to the ASTM standard method. The toughness indexes (ASTM) decreased slightly with an increase in the amount of pozzolan.

Mining Potential

A detailed assessment of the mineability of ten potential locations of pozzolans was made. The deposits are all volcanic ash beds within the Lakota Formation, a Cretaceous sedimentary rock which crops out as a hogback, encircling the Black Hills. The most favorable deposit is located about 10 miles from the Cement Plant at Rapid City. There is very little overburden at this location. The deposit is over 30 ft. thick, and could theoretically produce 1 million tons from an area less than 10 acres in size.

Recommendations

There is a great need for a pozzolan-blended cement to minimize or to inhibit the potential for deleterious expansions in concrete due to alkali-silica reactions. This laboratory investigation has shown that a natural pozzolan (sample LK2) available within 10 miles of the Dacotah Cement, is a suitable pozzolan for blending with cement. Laboratory results have indicated that it is not only suitable but it is also superior to the currently available best fly ash to inhibit alkali-silica reaction. It has shown that no adverse affects would be observed in the performance of the cement, cement paste, mortar, and concrete due to the blending of this pozzolan, 10% by weight of cement. In addition to the reduction in expansions due to alkali-silica reaction, test results indicate that the blended cement will also reduce the permeability of concrete and increase its durability. Therefore it is strongly recommended that the Dacotah Cement should consider evaluating the cost-effectiveness and feasibility of producing pozzolan-blended cements.

The concrete industry urgently needs a product to counteract the enormous durability problems caused by the alkali-aggregate reaction. To the author's knowledge, the best and most economical product available so far is this small-scale, laboratory-tested pozzolan-blended I (PM) Cement. It would be a valuable service to the concrete industry, if this product could be made available.

BACKGROUND

Cracks were observed on the pavements in South Dakota due to the use of sands which are prone to alkali-aggregate reaction. Testing of some of the sands done by the South Dakota Department of Transportation (SDDOT) using the ASTM C289 method has indicated the possibility of deleterious nature of the sands used for the construction of the pavements. Even though fly ashes and natural pozzolans like pumice, volcanic ash, diatomaceous earth, and siliceous shales have been used to control alkali-silica reaction (ASR) (1 to 12), there are problems associated with homogeneity, variability in composition and uniformity, anomalous expansion and difficulties in maintaining quality control. The production of a suitable pozzolan under controlled conditions and blending it with the cement in the plant under controlled conditions will eliminate many of the problems mentioned above. Therefore, the use of natural pozzolan-blended Type IP cement is a viable solution. There are adequate supplies of natural pozzolans near Rapid City, South Dakota and the State-owned South Dakota Cement Plant located in Rapid City could manufacture the Type IP Cement. Therefore, the feasibility of obtaining such a natural pozzolan was investigated. There was a need to study the possibility of controlling ASR expansions in pavements by replacing part of the cement with pozzolan. It was also necessary to determine the amount of pozzolan to be blended to obtain the optimum effectiveness in controlling ASR.

OBJECTIVES

- To find a natural pozzolan which is more efficient, effective and economical than fly ash in reducing deleterious expansion due to ASR.
- To find the optimum quantity of a natural pozzolan close to Dacotah Cement that can be blended with cement to produce a Type I (PM) Cement for minimizing the ASR.
- To ensure that the selected natural pozzolan for blending does not in any way adversely affect the fresh and hardened properties of cement, mortar, and concrete.

SELECTION OF POZZOLANS

The search for natural pozzolans began by examining the results of previous geologic investigations of highly siliceous material. Pozzolan materials include natural geologic rocks such as pumice, volcanic ash, diatomaceous earth, and siliceous shales. Previous investigations reveal potential sources near Rapid City, including bentonite, fire clays, zeolites, "fullers earth", and siliceous shales.

Because distance of transportation may be the most costly consideration for delivering pozzolan to the State Cement Plant, the search for minable pozzolan deposits was limited to within 100 miles of Rapid City.

Reconnaissance field work consisted of locating and collecting representative samples, preparing cross-sectional sketches and describing the observed lithology at each sample location. Samples were collected from 26 sites during a reconnaissance survey of western South Dakota and eastern Wyoming. Table 2 provides the sample number, general location, geologic formation name, and a brief description of the 26 potential pozzolans collected during the initial survey.

MATERIALS, AND TEST SPECIMENS

Cement: The cement used was ASTM Type I/II, conforming to ASTM C150 specifications. It was manufactured locally by the South Dakota Cement Plant. The chemical analysis and physical properties are given in Table 1.

Fly Ash: The fly ash used was a low-calcium, ASTM Class F and it was obtained from a source in North Dakota. The fly ash was supplied by the South Dakota Department of Transportation. Its chemical analysis and other properties are given in Table 1.

Pozzolans: Different types of natural pozzolans collected by Ron Holm of the Geology Department, South Dakota School of Mines and Technology, were used in this investigation. The designation, deposit, and description of the pozzolans are given in Table 2. Table 3 contains the chemical compositions determined using an Inductively Coupled Plasma (ICP) Spectrometer. In the ICP method, the samples are subjected to a high temperature which causes the sample to dissociate into individual atoms and ions. These atoms and ions emit light at wavelengths characteristic of the elements present. The spectrometer sorts the various wavelengths and measures the intensity of the specific spectral lines. These intensities are directly proportional to elemental concentrations in the sample. Table 4 gives the chemical compositions obtained by using a Scanning Electron Microscope (SEM).

Aggregates: A highly reactive fine aggregate provided by the South Dakota Department of Transportation was used for alkali aggregate reactive tests (ASTM P214 and ASTM C227). Graded standard sand meeting the requirements of ASTM C778 was used for finding the compressive strength. Standard sand (20-30 sand) meeting the requirements of ASTM C778 was used for finding the air content of cement mortar.

Coarse and Fine Aggregates for Concrete: The coarse aggregate used was crushed lime stone, obtained from a local source in Rapid City. The maximum size of the coarse aggregate was $\frac{3}{4}$ " (20 mm) with absorption coefficient of 0.45% and fineness modulus of 6.57. A sample sieve analysis of the aggregate is given in Table 1A. The fine aggregate used was natural sand with a water absorption coefficient of 1.60% and a fineness modulus of 2.56. The sieve analysis is shown in Table 1B.

Both the coarse and fine aggregates satisfied the grading requirements of ASTM C33.

Water: The water used was tap water from the Rapid City Municipal supply system.

Test Specimen: Four mortar bar specimens were prepared from each mixture for the ASTM P214 test method. For strength activity index, three cubes of size 50 mm (2 inches) were cast for each mixture.

TEST PROCEDURES

ASTM P214 Test Method

ASTM P214 Test Method can determine for detecting within 16 days the potential for deleterious expansion of mortar bars due to alkali-silica reaction. The mixture proportions were selected according to ASTM P214 as 1 part of cement and 2.25 parts of graded aggregate. The cement was replaced by the pozzolan with 10%, 15% and 25% by weight of cement. For the fly ash, two additional percentages of 30% and 40% were also included. The water cementitious ratio used was 0.44 for all mixtures. The aggregate was washed, cleaned and graded, and appropriate size quantities were weighed and mixed to obtain a uniform gradation as specified in ASTM P214.

The specimens (mortar bars) used in this method were made as per ASTM C227. The molds were stripped at one day and the bars were placed in water which was heated up to 80°C. On the second day, the initial measurements were taken and the bars stored in 1N NaOH solution at 80°C. The bar expansions were measured when they were hot, within 15 seconds of removal from the container. Expansions were monitored for 14 days.

ASTM C227 Test Method

This test method covers the determination of the susceptibility of cement-aggregate reaction combinations to expansive reactions involving hydroxyl ions associated with alkalies (sodium and potassium) by measurement of the increase in length of mortar bars. The mixing was done according to ASTM C305. Molds conforming to ASTM C490 specification were used. The specimens were removed from the molds after 24 hours and the zero day or the initial day reading was recorded using a length comparator with an accuracy of 0.00005 inches. The specimens were then stored in a plastic container lined with a wick. One inch of water was added and the specimens were kept over wooden pieces. Care was taken to ensure that the specimens were never in direct contact with the water. The container was sealed airtight such that 100% relative humidity was maintained. The container was stored in a room maintained at 38°C (100° F) for 14 days and removed for the first reading. After the first reading, the container was returned to the temperature controlled room and similarly subsequent readings were monitored every 30 days for a period of 360 days. The expansions were calculated with respect to the initial reading and expressed as percentage expansion.

Strength Activity Index with Cement

Cubes of size 50 mm (2 inches) were cast from a control mixture and from each of the test mixtures in accordance with test method ASTM C109. The mixture proportions were selected according to ASTM C311. For the control mixture, 250 grams of cement, 687.5 grams of sand and a water to cement ratio of 0.484 were used for molding three specimens. For test mixtures, 20% of the cement used in the control mixture was replaced by the pozzolans. For the test mix, the water added was such that adequate workability was achieved. The water/(cement+pozzolan) ratio's are given in Table 5.

The molded specimens were covered with polythene sheets and were stored for 24 hours at 23°C (73°F) and the cubes were removed from the molds and cured in lime saturated water for 28 days. The compressive strength was determined for both the control and test mixtures according to ASTM C109. For studying the effect of calcining, the pozzolans were calcined at different temperatures as shown in Table 6 and the strength activity index was determined at an age of 7 days for the calcined pozzolans.

Density

The density was determined according to the test procedure specified in ASTM C188.

Fineness by No. 325 Sieve

The raw pozzolan materials were crushed, using different sizes of crushing machines and ground in a ball mill to a fine powder form. The fineness of each of the pozzolans was determined by calculating the amount of pozzolan retained when wet sieved on a No. 325 sieve in accordance with test method ASTM C430.

Blaine Fineness

The fineness by the air permeability apparatus (ASTM C204) was adopted for the determination of the Blaine fineness of the pozzolans and fly ash. Since the materials were not cement, the constant "b", necessary in the equation for the determination of the Blaine fineness was obtained. The procedure for calculating the constant "b" was according to the appendix given in the ASTM C204 test procedure.

TEST RESULTS AND DISCUSSION

Density: The densities of all pozzolans, portland cement and class F fly ash are given in Table 7. The densities of all pozzolans were less than that of the cement and they varied between 2.13 gm/cm³ and 2.84 gm/cm³.

Fineness: The fineness obtained by wet sieving through No. 325 sieve for all pozzolans was above 90% passing (Table 7). The objective of obtaining a pozzolan finer than 90% passing was therefore achieved. The fly ash was used as received without further grinding. The Blaine fineness for the pozzolans are given in Table 8.

Strength Activity Index With Portland Cement

The strength activity index results are given in Table 5. The strength activity index was used as a pre-screening method for selecting the pozzolans for further testing. The pozzolans had a wide range of strength activity index. The values ranged between 19.78% and 91.72%. Based on the strength activity index test results, 10 pozzolans were selected for blending with cement and they were tested for their effectiveness in controlling the expansions due to ASR. The pozzolans selected for further testing had a strength activity index of at least 60% except for MW1. Some of the pozzolans were from similar geological formations (for example, VA1, VA2, and LK1, LK2). In such cases one from each geological formation was selected for testing. Pozzolan ERC1, having a strength activity index of 67% was eliminated from further testing due to unsuitable mining conditions. The fly ash used in this investigation had a strength activity index of 75%.

EFFECT OF CALCINING ON THE STRENGTH ACTIVITY INDEX

The strength activity index for some of the pozzolans was low. Therefore the effect of calcining the pozzolans on the strength activity index was studied. For this investigation, MW1, PS1E (expanded shale) and CT1 were selected. The strength activity index for MW1 was 45.3% without calcining. The pozzolan was calcined at three temperatures of 350°C, 700°C, and 1050°C. The effect of calcining was very evident for this pozzolan. The results are given in Table 6. The strength had increased depending on the temperature at which it was calcined. For the pozzolan CT1, the strength activity index increased from 62% to 88.8% when the pozzolan was heated at 1050°C.

The strength activity index for PS1E (given in Table 5), was the percentage obtained when the pozzolan was calcined at about 1050°C. Therefore, for PS1, the strength activity index was determined when the pozzolan was treated at lower temperatures of 115°C, 350°C, and 700°C. The results showed that there was a decrease in the strength activity index when treated at 115°C and 350°C. However there was no significant difference in the strength activity index when treated at 700°C compared to the pozzolan calcined at 1050°C (Table 6).

Hence, from the results obtained, it can be concluded that the calcination of the pozzolans influences the strength activity index. This may be due to the removal of moisture from the pozzolans by the calcining process.

EFFECT OF POZZOLANS ON EXPANSIONS USING ASTM P214 TEST METHOD

According to ASTM P214 (13), when the mean expansions of the test specimens exceed 0.20% at 16 days after casting, it is indicative of potentially deleterious expansion. When the expansion is between 0.10% and 0.20%, the results are not conclusive, and when the mean expansion of the test specimens is less than 0.10%, it is indicative of innocuous behavior.

The comparison of expansions of mortar bars made with a reactive sand and cements with and without 10%, 15% and 25% by weight replacements with pozzolans LK2, PS1E, and VA2, are shown in Figures 1 to 3 respectively. Bar charts showing the comparison of the total expansions at 16 days for the mortar bars made with and without blended cements are given in Figures 5 to 7 respectively for pozzolans LK2, PS1E, and VA2. The most effective pozzolans LK2 and PS1E and the adversely ineffective pozzolan VA2 are selected for discussion and comparison. The other pozzolans' effectiveness was in between these extreme cases. For comparative evaluation, the influence of a Class F fly ash on the ASR expansions in the mortar bars made with the same reactive sand and fly ash blended cements is also shown in Figures 4 and 8.

The test results indicated that 10% replacement of cement with LK2 and PS1E pozzolans decreased the expansions below 0.1%. All other pozzolans except VA2 and PRC1, when blended with cement at 10% replacement level decreased the expansions. However the total expansions at 16 days after casting were between 0.1% and 0.2% expansion. When the cement was replaced with pozzolans at 15% by weight, all the pozzolans except VA2 and PRC1 decreased the ASR expansions to an innocuous level (below 0.1%). When the cements were blended with pozzolan at 25% replacement, all the pozzolans except VA2 decreased the total expansions below 0.1%. Therefore all pozzolans except VA2 are suitable for blending with cement to effectively inhibit the ASR expansions in concrete. In the case of pozzolan VA2, it was observed that its influence on the ASR expansions was entirely different from that of the other pozzolans. When pozzolan VA2 was blended with cement at 10%, 15%, and 25% replacement levels, the mortar bar expansions actually increased compared to the expansions in mortar bars made with unblended cements. This is described as the pessimum phenomenon. A pessimum limit has been observed by other researchers (5, 7) when certain types of fly ash are added to cement. This limit represents a percent replacement of cement below which the addition of fly ash or pozzolan causes equal or greater expansions in the mortar bars than that of the mortar bars without fly ash or pozzolan. When cement is blended with fly ash at a percentage above the pessimum limit, then the expansions are reduced. The 10% replacement of cement with PRC1 pozzolan gave higher expansions than the mortar bars without pozzolan. However at higher percentages of cement replacement with PRC1 pozzolan, the ASR expansions were reduced. The comparisons of ASR expansions in mortar bars with different types of pozzolans, showed that the total expansions at

16 days after casting were below 0.1% in the case of mortar bars made with all pozzolan (except VA2 and PRC1) blended cements.

When a class F fly ash was blended with cement at 10% to 40% by weight replacement levels, it was effective in reducing the ASR expansion. However when the quantity of fly ash blended was less than 20% by weight, the total expansion at 16 days was still higher than the innocuous level (0.1%). The expansions were reduced below the innocuous level only when the fly ash blended was higher than 25% by weight.

EFFECT OF POZZOLANS ON EXPANSIONS USING ASTM C227 TEST METHOD

Typical behavior showing a comparison of the ASTM C227 expansions of the mortar bars for the pozzolan LK2 is shown in Figure 9. A bar chart showing the comparison of the total expansions at 360 days for the mortar bar made with and without blended cements is given in Figure 10.

The effectiveness of the pozzolans varied with the type and quantity of pozzolan added. The test results indicated that three pozzolans LK2, PS1E, and US1 significantly reduced the percentage expansions for the three percentages (10%, 15% and 25%). When pozzolans CT1, SM2, F3, CB1, and MW1 were blended with cement, there was only a slight decrease in the percentage expansions. In case of pozzolan PRC1, when 10% of the pozzolan was blended with cement, the percentage expansions were higher than the expansions of the mortar bars made with unblended cement. At 15% and 25% replacement levels, the expansions were less than the mortar bars made without pozzolan. Therefore the pessimum limit for pozzolan PRC1 is near 15%. When pozzolan VA2 was blended with cement, no significant decrease in the expansions was observed.

COMPARISON OF EXPANSIONS MEASURED IN ASTM C227 & ASTM P214 TEST METHODS

A typical comparison of the percentage expansions of the mortar bars at 16 days obtained from ASTM P214 and the percentage expansions at 360 days from the ASTM C227 is shown in Figure 11. The comparison is shown for unblended cement and the cement blended with pozzolan LK2 in different percentages.

The comparison shows that the trend of the percentage expansions obtained from ASTM P214 and ASTM C227 test methods is similar. However, since the percentage expansions of the mortar bars made without any pozzolan replacement was higher in the ASTM P214 results compared to ASTM C227 results, a higher percentage of reduction in the percentage expansions was observed for the ASTM P214 test method.

MECHANISM BY WHICH THE POZZOLANS EFFECTIVELY CONTROL THE EXPANSIONS DUE TO ALKALI-SILICA REACTIONS

Although the mechanism by which the pozzolans reduce the alkali-aggregate expansions are not clearly understood, it is positive that both the physical and chemical properties of the pozzolan affect its effectiveness in reducing ASR expansion in concrete. Since it is known that the presence of moisture increases ASR, it is possible that the pozzolans are able to reduce the permeability and therefore reduce ASR expansions.

In a study made by Larbi and Bijen (12) on the effect of mineral admixtures on the cement paste-aggregate interface, it was stated that by the use of fly ash or other similar mineral admixture, migration of the hydroxyl ions is reduced due to the densification and the thinning of the interfacial region preventing or reducing the penetration of ions into the reactive zone, and leading to a reduction in the alkali-silica reaction in concrete.

As for chemical properties, it has been suggested that the pozzolans reduce or eliminate the ASR expansion by pozzolanic reaction and by producing lower C/S mole ratio calcium silicate hydrates by reacting with the higher C/S mole ratio hydrates. These new hydrates can absorb large amounts of alkali into their structure, retaining them and therefore reducing their availability for reaction with the silica in the aggregate.

EVALUATION OF POZZOLAN BLENDED CEMENTS & CONCRETES

A Type-I (PM) cement is a blended hydraulic cement meeting the requirements of ASTM C595-89 "Standard specifications for Blended Hydraulic Cements" and is manufactured by inter grinding a pozzolan with Portland cement clinker or by the intimate blending of the pozzolan with a finished cement. The greatest benefit in the reduction of potential ASR expansion has been gained using a Type-I (PM) cement made by intergrinding. There is also a need to establish the suitability of the pozzolan for blending or intergrinding with cement so that maximum benefit in terms of reducing alkali-silica reaction potential can be achieved without adversely affecting or altering other properties of the cement. In this study five natural pozzolans and a class F Fly Ash were selected and cement, cement mortar and cement paste were made with newly developed blended cements to test for desirable physical properties.

The primary objective of this part of the investigation was to determine the physical properties of the pozzolan-blended cement, cement mortar and cement paste specimens and analyze to compare them with Portland cement specimens to evaluate the effect of the pozzolans. This was achieved by carrying out tests to determine:

1. The physical properties of cement such as density, fineness by No.325 sieve, and Blaine fineness.
2. The physical properties of cement mortar such as compressive strength and air content.

3. The physical properties of cement paste such as normal consistency, time of setting, and early stiffening.

The list of selected pozzolans and pozzolan-blended cement mixture designations used for determining the cube compressive strength, air content, normal consistency, early stiffening, Vicat and Gillmore setting times, density, and fineness with various percentage replacements of selected pozzolans are given in the Tables 9A & 9B.

CEMENT MORTAR PROPERTIES

Cube Compressive Strength

The following variations in the mean compressive strength for 10% pozzolan blended cement mortar mixes were observed in comparison with control test mixture specimens: [1] At three days, a minimum decrease of 10.8% for CT1 and a maximum decrease of 23.1% for class F Fly Ash were observed. [2] At seven days, the compressive strength with LK2 pozzolan was increased by 4.4% and PS1E yielded the maximum decrease in compressive strength at 31.8% [3] At 28 days, a minimum decrease in compressive strength of 5.4% was observed for LK2 pozzolan and a maximum decrease in compressive strength of 23.5% was observed for class F Fly Ash.

The following variations in the mean compressive strength for 15% pozzolan blended cement mortar mixes were observed in comparison with control test mixture specimens: [1] At three days, a minimum decrease of 12.1% for LK2 and a maximum decrease of 40.7% for class F Fly Ash were observed. [2] At seven days, a maximum decrease of 40% in compressive strength for PS1E and MW1 pozzolans was observed and a minimum decrease in compressive strength by 4.7% with LK2 pozzolan was observed. [3] At 28 days, a minimum decrease in compressive strength by 20.8% was observed for CT1 pozzolan and a maximum decrease in compressive strength by 50.2% was observed with MW1 pozzolan.

The following variations in the mean compressive strength for 25% pozzolan blended cement mortar mixes were observed in comparison with control test mixture specimens. [1] At three days, a minimum decrease of 13.8% for LK2 and a maximum decrease of 45.4% for class F Fly Ash were observed. [2] At seven days, a maximum decrease of 43.1% in compressive strength for MW1 pozzolan was observed and a minimum decrease in compressive strength of 5.33% with LK2 pozzolan was observed. [3] At 28 days, a minimum decrease in compressive strength by 25.7% was observed for LK2 pozzolan and a maximum decrease in compressive strength by 54.6% was observed with MW1 pozzolan.

Of all the natural pozzolans, the adverse effect of LK2 pozzolan was the least on the physical properties of cement and at a 10% replacement level, the decrease in compressive strength is insignificant (Figure 12).

Air Content

The air content of the pozzolan blended cement mortars decreased with an increase in the percentage replacement of cement by pozzolan. The air content increased with an increase in percentage replacement of cement by class F Fly Ash.

The following variations in the air content for pozzolan-blended cement mortar were observed in comparison with control test mortar: [1] At 10% addition, a maximum air content of 5.3% was observed for the PS1E pozzolan and a minimum air content of 3.9% was observed for the CT1 pozzolan. [2] At 15% addition, a maximum air content of 5.1% was observed for the SM2 pozzolan and a minimum air content of 3.3% was observed for the CT1 pozzolan. [3] At 25% addition, a maximum air content of 5.0% was observed for the class F Fly Ash and a minimum air content of 2.7% was observed for the CT1 pozzolan. Figure 13 shows a comparison of the air contents for cement mortars blended with pozzolan LK2.

CEMENT PASTE PROPERTIES

Normal Consistency

There was an increase in the water demand with an increase in the percentage of pozzolan content in the pozzolan blended cement mixes. But the normal consistency decreased with increase in the percentage replacement of cement in case of class F Fly Ash.

The following variations in the normal consistency values for pozzolan-blended cements was observed in comparison with control test cement: [1] At 10% addition, a maximum normal consistency of 28.9% was observed for SM2 pozzolan and a minimum normal consistency of 23.9% was observed for class F Fly Ash. [2] At 15% addition, a maximum normal consistency of 31% was observed for SM2 pozzolan and a minimum normal consistency of 23.5% was observed for class F Fly Ash. [3] At 25% addition, a maximum normal consistency of 34.7% was observed for MW1 pozzolan and a minimum normal consistency of 22.6% was observed for class F Fly Ash. A comparison of the normal consistency values for cements blended with the pozzolan LK2 is shown in Figure 14.

Early Stiffening

The early stiffening of the pozzolan blended cement pastes decreased with increase in the percentage replacement of cement by all the pozzolans and class F Fly Ash. But the air content increased with increase in percentage replacement of cement by class F Fly Ash.

The following variations in the early stiffening for pozzolan-blended cements were observed in comparison with control test cement: [1] At 10% addition, a maximum of 64.5% was observed with CT1 pozzolan and a minimum of 35.7% was observed with PS1E pozzolan. [2] At 15% addition, a maximum of 61.8% was observed with CT1 pozzolan and a minimum of 33.9% was

observed with PS1E pozzolan. [3] At 25% addition, a maximum of 60.6% was observed with class F Fly Ash pozzolan and a minimum of 29.8% was observed with SM2 pozzolan. Figure 15 shows the comparison of early stiffening values for cements blended with the pozzolan LK2.

Time of Setting by Vicat Apparatus

The Vicat initial and final setting time of the pozzolan blended cement pastes increased with increase in the percentage replacement of cement by pozzolans and class F Fly Ash.

The following variations in initial and final setting times for pozzolan-blended cements were observed in comparison with control test cement. [1] At 10% addition a maximum initial setting time of 235 minutes for MW1 pozzolan and a minimum initial setting time of 150 minutes for SM2 pozzolan were observed. A maximum final setting time of 367 minutes for MW1 and a minimum final setting time of 345 minutes for SM2 pozzolan were observed. [2] At 15% addition a maximum initial setting time of 250 minutes for MW1 pozzolan and a minimum initial setting time of 170 minutes for SM2 pozzolan were observed. A maximum final setting time of 360 minutes for MW1 and a minimum final setting time of 305 minutes for SM2 pozzolan were observed. [3] At 25% addition a maximum initial setting time of 265 minutes for MW1 pozzolan and a minimum initial setting time of 182 minutes for PS1E pozzolan were observed. A maximum final setting time of 460 minutes for MW1 and a minimum final setting time of 318 minutes for LK2 pozzolan were observed (Figure 16).

Time of Setting by Gillmore Needles

The Gillmore initial and final setting time of the pozzolan blended cement pastes increased with increase in the percentage replacement of cement by pozzolans and class F Fly Ash.

The following variations in initial and final setting times for pozzolan-blended cements were observed in comparison with control cement: [1] At 10% addition a maximum initial setting time of 285 minutes for MW1 pozzolan and a minimum initial setting time of 185 minutes for PS1E pozzolan were observed. A maximum final setting time of 420 minutes for MW1 and a minimum final setting time of 335 minutes for PS1E pozzolan were observed. [2] At 15% addition a maximum initial setting time of 297 minutes for MW1 pozzolan and a minimum initial setting time of 190 minutes for PS1E pozzolan were observed. A maximum final setting time of 480 minutes for MW1 and a minimum final setting time of 350 minutes for PS1E pozzolan were observed. [3] At 25% addition a maximum initial setting time of 345 minutes for MW1 pozzolan and a minimum initial setting time of 198 minutes for PS1E pozzolan were observed. A maximum final setting time of 520 minutes for MW1 and a minimum final setting time of 385 minutes for LK2 pozzolan were observed (Figure 17).

Load Deflection Curve Behavior

Load deflection curves are a standardized method of showing the energy absorbed by beams during their load induced flexural deflections. The area under the load deflection curve gives the energy absorbed by the beam.

From the load deflection curves it was observed that there was not much difference in elasto-plastic behavior of control and blended pozzolan concretes. All beams failed immediately after the formation of first crack.

Toughness Indices (ASTM)

The results indicate that there was no significant change in toughness with an increase in the percentage of pozzolan. The toughness indices had decreased a little, signifying that with an increase of percentage of pozzolan, a lower energy absorption capacity is achieved.

The following increases in the toughness index I_5 for 10 percent pozzolan blended mixes were observed in comparison with control mix: 6 percent for fly ash, 3 percent for LK2 pozzolan, 4 percent for PS1E pozzolan, 31 percent for SM2 pozzolan were observed, where as 2 percent reduction for CT1 pozzolan and 8 percent reduction for MW1 pozzolan were observed.

The following increases in the toughness index I_5 for 15 percent of pozzolan blended concrete mixes were observed in comparison with control mix: 6 percent for LK2 pozzolan, 4 percent for PS1E pozzolan were observed, where as 20 percent reduction for fly ash, 12 percent reduction for CT1 pozzolan, 28 percent reduction for SM2 pozzolan and 1 percent reduction for MW1 pozzolan were observed.

The following reductions in the toughness index I_5 for 25 percent of pozzolan blended concrete mixes were observed in comparison with control mix: 23 percent for fly ash, 24 percent for LK2 pozzolan, 10 percent for CT1 pozzolan, 5 percent reduction for SM2 pozzolan, and 22 percent reduction for MW1 pozzolan were observed where as no reduction was observed for PS1E pozzolan.

Impact Strength

The drop weight test (ACI Committee 544) was used in this investigation. The comparison of impact strengths (shown in Figure 27) indicates that the number of blows for first crack and the number of blows to failure had decreased with an increase in the percentage of pozzolan. The comparison of impact strength for the pozzolan LK2 with increase of percentage of pozzolan is shown in Figure 34.

- strength of LK2 blended cement mortar cubes was the lowest at 15% and 25% replacement levels when compared to other pozzolans and class F Fly Ash.
7. The air content of pozzolan blended cement mortar decreased with an increase in the percentage of pozzolan for all the test pozzolans and class F Fly Ash. Normal consistency increased with an increase in the percentage of all the pozzolans except class F Fly Ash. The decrease in the percentage final penetration in the early stiffening by paste method with increase in the percentage of LK2 pozzolan was insignificant. A false set was observed in case of SM2 and PS1E pozzolans.
 8. Initial and final setting times by Vicat apparatus and Gillmore needles were within the allowable limits for all the test pozzolans and class F Fly Ash.
 9. The density of pozzolan-blended cements decreased with increase in the percentage of pozzolan and the decrease was insignificant in case of all the pozzolans and class F Fly Ash. The fineness of pozzolan-blended cements increased with the increase in the percentage of pozzolan.
 10. The compressive strengths of natural pozzolan and fly ash-blended cement concretes, for 10 and 15% pozzolans by weight of cement, were not adversely affected due to the addition of pozzolans. When compared to control concretes, compressive strengths of pozzolan-blended cement concretes were not significantly different at 3, 7, and 28 days, because the water to cementitious ratio was the same for all the concretes. However, there was some loss of workability due to the addition of pozzolans. When the pozzolans were blended at 25% by weight of cement, the compressive strengths of pozzolan blended cement concretes decreased slightly at 3, 7, and 28 days. The maximum decrease occurred in the case of pozzolan MW1 and fly ash. The workability of natural pozzolan-blended cement concrete decreased appreciably whereas the workability increased in the case of fly ash blended cement concrete.
 11. The influence of blended cements on the static modulus of elasticity of concrete was similar to that of their effect on the compressive strength. For all concretes, there was a direct relationship between the elastic modulus and the compressive strength.
 12. The toughness indexes (ASTM) decreased with an increase in the pozzolan content. The flexural toughnesses and flexural strengths decreased with an increase in the pozzolan content.
 13. The impact strengths decreased with an increase in the pozzolan content.
 14. All the pozzolan-blended cement concretes performed reasonably well, with no problems with regard to workability, segregation, bleeding and placing. Good finishability was achieved in all concretes and no significant difference in performance characteristics was

observed with an increase in the pozzolan content. However, the air content of concretes decreased slightly with an increase in the pozzolan content.

15. The most favorable deposit of the most effective natural pozzolan (LK2) is located within 10 miles of the Cement Plant in Rapid City. There is very little overburden and the deposit is estimated to average 30 feet in thickness and might produce one million tons from an area less than 10 acres in size.

RECOMMENDATIONS

There is a great need for a pozzolan-blended cement to minimize or to inhibit the potential for deleterious expansions in concrete due to alkali-silica reactions. This laboratory investigation has shown that a natural pozzolan (sample LK2) available within 10 miles of the Dacotah Cement, is a suitable pozzolan for blending with cement. Laboratory results have indicated that it is not only suitable but it is also superior to the currently available best fly ash to inhibit alkali-silica reaction. It has shown that no adverse affects would be observed in the performance of the cement, cement paste, mortar, and concrete due to the blending of this pozzolan, 10% by weight of cement. In addition to the reduction in expansions due to alkali-silica reaction, test results indicate that the blended cement will also reduce the permeability of concrete and increase its durability. Therefore it is strongly recommended that the Dacotah Cement should consider evaluating the cost-effectiveness and feasibility of producing pozzolan-blended cements.

The concrete industry urgently needs a product to counteract the enormous durability problems caused by the alkali-aggregate reaction. To the author's knowledge, the best and most economical product available so far is this small-scale, laboratory-tested pozzolan-blended I (PM) Cement. It would be a valuable service to the concrete industry, if this product could be made available.

SUPPLEMENTARY INFORMATION

The final report contains only the salient information, a few important figures and tables, conclusions and recommendations. The following five supplementary reports contain all experimental data, test procedures, results, detailed analysis, discussions, more figures, detailed tables, complete references, bibliography, and conclusions. These reports are available at the South Dakota Department of Transportation Research Office.

1. "Investigation of Locally Available Natural Pozzolans", by Perry Rahn and Ronald A. Holm, (48 + IV pages).
2. "A Comparative Study of the Physical Properties of Six Natural Pozzolan Blended Type IP Cements", By V. Ramakrishnan and Sainath Anne, (103 + X pages).

3. "Effects of Natural Pozzolans and Fly Ash on Alkali-Silica Reactivity", by V. Ramakrishnan and Nunna Prasad, (297 + XIV pages).
4. "Physical and Elastic Properties of Natural Pozzolan Blended (Type IP) Cement Concretes", by V. Ramakrishnan and V. R. Sure, (147 + V pages).
5. "Feasibility of Mining of Selected Pozzolans", by Perry Rahn, (30 + III pages).

ACKNOWLEDGMENTS

The author gratefully acknowledge the funding of the research by the South Dakota Department of Transportation. The author also express his gratitude to Mr. David Huft, Research Engineer, SDDOT, for the support and encouragement given for conducting this research. The views expressed in this paper are those of the author and they do not necessarily reflect official views of the South Dakota Department of Transportation.

REFERENCES

1. Blight, G. E., Alexander, M. G., Ralph, T. K., and Lewis, B. A., "Effect of Alkali-Aggregate Reaction on the Performance of Reinforced Concrete Structure over a Six-year Period", American Concrete Institute Journal, Vol. 41, No. 147, June 1989, pp. 69-78.
2. Stark, D., and DePuy, G., "Alkali-Silica Reaction in Five Dams in Southwestern United States", Concrete Durability, Katharine and Bryant Mather, International Conference, ACI, SP-100, Vol. 2, 1987, pp. 1759-1786.
3. Alasali, M. M., Malhotra, V. M., and Soles, J. A., "Performance of Various Test Methods for Assessing the Potential Alkali Reactivity of Some Canadian Aggregates", International Workshop on Alkali-Aggregate Reactions in Concrete; Occurance, Testing and Control", Halifax, Canada, May 1990.
4. Ramachandran, S., Ramakrishnan, V., and Johnston, D., "The Role of High Volume Fly Ash in Controlling Alkali-Aggregate Reactivity", Proceedings, Fourth CANMET/ACI International Conference on Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete, Editor V. M. Malhotra, American Concrete Institute SP-132, Vol. 1, Istanbul, Turkey, May 1992, pp. 591-613.
5. Farbiarz, J., and Carrasquillo, R., "Alkali-Aggregate Reaction in Concrete Containing Fly Ash", Concrete Durability, Katharine and Bryant Mather, International Conference, ACI, SP-100, Vol. 2, 1987, pp. 1787-1808.
6. Gaze, M. E., and Nixon, P. J., "The Effect of PFA upon Alkali-Aggregate Reaction", American Concrete Institute Journal, Vol. 35, No. 123, June 1983, pp. 107-110.

7. Carrasquillo, R. L., and Snow, P. G., "Effect of Fly Ash on Alkali-Aggregate Reaction in Concrete", American Concrete Institute Materials Journal, Vol. 84, No. 4, July-August 1987, pp. 299-305.
8. Diamond, S., and Mukherjee, P. K., "Influence of Fly Ash in Alkali-Aggregate Reaction", Concrete Alkali-Aggregate Reactions, Proceedings of the 7th International Conference, Ottawa, Canada, Edited by Patrick E. Grattan-Bellew, 1986, pp. 44-48.
9. Soles, J. A., Malhotra, V. M., and Suderman, R. W., "The Role of Supplementary Cementing Materials in Reducing the Effects of Alkali-Aggregate Reactivity; CANMET Investigations", Concrete Alkali-Aggregate Reactions, Proceedings of the 7th International Conference, Ottawa, Canada, Edited by Patrick E. Grattan-Bellew, 1986, pp. 79-82.
10. Samuel, S., and Tyson P. E., "Control of Alkali-Silica Reactivity in Recycled Concrete Using Fly Ash", Proceedings, Fourth CANMET/ACI International Conference on Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete, Supplementary Papers, Istanbul, Turkey, May 1992, pp. 15-20.
11. Grattan-Bellew, P., and Gillott, J., "Three Decades of Studying the Alkali Reactivity of Canadian Aggregates", Concrete Durability, Katharine and Bryant Mather, International Conference, ACI, SP-100, Vol. 2, 1987, pp. 1365-1384.
12. Larbi, J. A., and Bijen, J. M., "Effect of Mineral Admixtures on the Cement Paste Aggregate Interface", Proceedings, Fourth CANMET/ACI International Conference on Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete, Editor V. M. Malhotra, American Concrete Institute SP-132, Vol. 1, Istanbul, Turkey, May 1992, pp. 655-669.
13. "Annual Book of ASTM Standards", Section 4, Vol. 04.02, Concrete and Aggregates, 1991.

TABLE 1 - CHEMICAL AND PHYSICAL PROPERTIES OF
CEMENT AND FLY ASH

	PORTLAND CEMENT	FLY ASH
<u>CHEMICAL ANALYSIS(%)</u>		
SiO ₂	22.74	52.66
Al ₂ O ₃	4.75	18.69
Fe ₂ O ₃	3.40	4.65
CaO	63.91	3.12
MgO	1.20	2.79
SO ₃	2.10	-
TiO ₂	-	5.29
Na ₂ O	0.15	0.40
K ₂ O	0.59	2.52
MnO	-	0.28
Moisture Content		0.02
Loss on Ignition	1.50	0.02
<u>Physical Test Results</u>		
Fineness Blaine(m ² /kg)	387	-
Fineness	-	16.72
Retained on #325 sieve		
Soundness		
Autoclave Expansion(%)	-0.01	0.09
<u>Bogue Potential</u>		
<u>Compounds</u>		
C ₃ S	44.57	
C ₂ S	31.58	
C ₃ A	6.83	
C ₄ AF	10.35	

TABLE 1A SIEVE ANALYSIS - COARSE AGGREGATE
(3/4" maximum size)

Sieve size		Percent Retained by weight
Passing through	Retained on	
1.5 in	1.0 in	0.00
1.0 in	3/4 in	3.10
3/4 in	1/2 in	36.00
1/2 in	3/8 in	22.96
3/8 in	1/4 in	23.98
1/4 in	# 4	8.88
# 4	# 8	3.12
# 8	Pan	1.936

$$\text{Fineness Modulus} = 657.03/100 = 6.57$$

TABLE 1B SIEVE ANALYSIS FOR FINE AGGREGATE

Sieve size		Percent Retained by weight
Passing through	Retained on	
1/4 in	# 4	.36
# 4	# 8	3.70
# 8	# 16	22.00
# 16	# 30	28.90
# 30	# 50	21.90
# 50	# 100	17.00
#100	# 200	5.40
#200	Pan	.54

$$\text{Fineness Modulus} = 256.16/100 = 2.56$$

1 INCH= 2.54 CMS

TABLE 2. DESIGNATION, DEPOSIT AND DESCRIPTION OF POZZOLANS

SAMPLE DESIGNATION	DEPOSIT	DESCRIPTION
PR1	Rockyford ash	Light gray tuff (Zeolite)
F1	Fuson shale of Dakota FM	Gray clay weathered to nodules
F2	Fuson shale of Dakota FM	Reddish (burnt color) shale yellowish coat on weathered surface
W1	Sharps FM just above Rockyford ash member	White to light gray, hard, resistant to weathering
W2	Rockyford ash member of Sharps FM	Very white Zeolitic tuff
MW1	Mowry shale	Shale, dark gray weathers medium gray
MW2	Mowry shale	Weathered sample
SM1	Upper part of Rockyford ash	Weathered, light gray volcanic tuff
SM2	Lower part of Rockyford ash	Very white, hard volcanic tuff
CB1	Rockyford ash	White ash (tuff)
CT1	Sharps FM 10-15 ft above Rockyford ash	Light gray, more like a siltstone
US1	Upper unit of Sharps FM	White to gray siltstone
ERC1	Rockyford ash	Highly weathered more like a pumice
PRC1	Probably middle of Sharps FM	Whitish gray, very hard, F.grained contained many 1 inch or smaller vugs w/chalk vugs
FE1	White river group(basal Chadron FM)	Brownish gray clay, sample is fairly weathered
FE2	Brule FM of White river group	Light brown weathered clay
FE3	Brule FM	Brown clay
VA1	Brule FM	White pure ash
BG1	Pierre shale	Yellowish, highly weathered Bentonite
AC1	Belle Fourche shale	Gray Bentonite
TH1	Tomahawk volcanic area	Yellow to light brown Rhyolitic Lithic tuff containing several Xenoliths
F3	Fuson shale	Light gray, nodular clay
F4	Fuson shale	Reddish fissile shale
MO1	Morrison FM	Greenish shale
VA2	Appears to be in Morrison FM	White volcanic ash

TABLE 2. DESIGNATION, DEPOSIT AND DESCRIPTION OF POZZOLANS

SAMPLE DESIGNATION	DEPOSIT	DESCRIPTION
WW1 MOU	Clinker from coal mine Late Jurassic Morrison FM	Light red in color Volcanic tuff
PS1E	Upper Cretaceous	Brown shale, expanded Pierre shale by kiln heating
LK1	Early Cretaceous Lakota FM	Silicified volcanic tuff
LK2	Early Cretaceous Lakota FM	Silicified volcanic tuff

TABLE 3 CHEMICAL COMPOSITIONS, SODIUM OXIDE AND POTASSIUM OXIDE
CONCENTRATIONS (%) OF POZZOLAN SAMPLES USING ICP⁺

SAMPLE	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	SO ₃	MnO	BaO	NiO	H ₂ O	L I*	TOTAL
SM2	61.29	9.88	1.62	4.23	0.61	0.52	5.19	0.23	0.30	0.40	0.60	BDL	5.25	7.56	96.68
CB1	65.47	10.13	1.46	3.48	0.66	0.38	5.13	0.20	0.17	0.03	0.05	BDL	4.22	8.42	99.80
CT1	58.82	10.43	2.39	5.84	1.16	0.30	3.37	0.38	0.03	0.05	0.09	BDL	5.96	7.53	96.45
MW1	57.23	14.51	4.12	0.96	1.58	0.05	2.61	0.62	0.27	0.04	0.01	BDL	5.50	6.52	94.02
PRC1	63.76	10.96	2.89	3.98	1.19	0.34	5.16	0.45	0.20	0.04	0.05	BDL	3.75	4.45	97.22
PS1E	58.98	16.59	6.29	1.57	2.11	0.02	4.53	0.70	1.01	0.05	0.05	BDL	0.15	1.10	93.15
US1	65.24	12.09	3.12	3.24	1.61	0.39	3.52	0.50	0.09	0.04	0.04	BDL	4.90	4.21	98.99
F3	75.00	7.44	1.73	0.95	0.65	0.04	0.92	0.68	0.16	BDL	BDL	BDL	6.00	4.28	97.85
LK2	79.94	7.58	1.11	0.25	0.15	0.01	1.53	0.35	0.13	BDL	BDL	BDL	0.81	4.37	96.23
F1	-	-	-	-	-	0.01	4.12	-	-	-	-	-	-	-	-
F2	-	-	-	-	-	0.03	2.84	-	-	-	-	-	-	-	-
LK1	-	-	-	-	-	0.01	1.71	-	-	-	-	-	-	-	-
MO1	-	-	-	-	-	0.04	6.54	-	-	-	-	-	-	-	-
MOU	-	-	-	-	-	BDL	1.88	-	-	-	-	-	-	-	-
PR1	-	-	-	-	-	0.62	6.19	-	-	-	-	-	-	-	-
W1	-	-	-	-	-	0.40	4.07	-	-	-	-	-	-	-	-
W2	-	-	-	-	-	0.34	4.22	-	-	-	-	-	-	-	-
SM1	-	-	-	-	-	0.32	5.58	-	-	-	-	-	-	-	-
ERC1	-	-	-	-	-	0.58	3.93	-	-	-	-	-	-	-	-
AC1	-	-	-	-	-	0.54	1.28	-	-	-	-	-	-	-	-
BG1	-	-	-	-	-	0.34	1.01	-	-	-	-	-	-	-	-
FE2	-	-	-	-	-	0.19	2.36	-	-	-	-	-	-	-	-
VA1	-	-	-	-	-	0.34	5.98	-	-	-	-	-	-	-	-
VA2	-	-	-	-	-	BDL	2.08	-	-	-	-	-	-	-	-
WW1	-	-	-	-	-	0.27	3.58	-	-	-	-	-	-	-	-
TH1	-	-	-	-	-	0.51	3.55	-	-	-	-	-	-	-	-

L I* - Loss on Ignition

ICP+ - Inductively Coupled Plasma

BDL - Below detection level

SiO₂ and SO₃ were determined using wet chemistry technique.

**TABLE 4 CHEMICAL COMPOSITIONS, SODIUM OXIDE AND POTASSIUM OXIDE
CONCENTRATIONS (%) OF POZZOLAN SAMPLES USING SEM⁺**

SAMPLE	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	SO ₃	MnO	Cl	P ₂ O ₅	H ₂ O	L I [*]	TOTAL
SM2	64.28	11.84	2.06	3.85	0.78	2.03	4.04	0.25	0.10	0.00	BDL	BDL	4.05	6.72	100.0
CB1	63.95	11.46	1.54	3.08	0.99	1.44	4.53	0.29	0.08	0.00	BDL	BDL	4.22	8.42	100.0
CT1	55.52	12.75	4.36	9.70	1.84	1.05	3.20	0.82	0.17	0.29	0.07	0.39	2.31	7.53	100.0
MW1	56.21	19.29	6.26	1.47	1.68	0.48	2.80	1.15	0.86	0.00	0.00	0.35	2.93	6.52	100.0
PRC1	61.99	11.97	4.58	5.17	1.13	1.12	5.10	0.75	0.11	0.27	0.00	0.43	2.75	4.45	100.0
PS1E	56.21	19.48	9.52	2.74	2.31	0.91	3.85	1.04	1.86	0.08	0.07	0.68	0.15	1.10	100.0
US1	60.22	14.58	4.80	5.08	2.53	1.12	3.11	0.60	0.10	0.25	0.13	0.46	2.81	4.21	100.0
LK2	82.77	8.67	0.97	0.38	0.67	0.35	0.47	0.38	0.16	0.00	BDL	BDL	0.81	4.37	100.0
F3	73.62	11.60	3.44	1.38	1.03	0.19	0.22	1.02	0.17	0.00	BDL	BDL	2.88	4.28	100.0

NiO and BaO were below detection level

SEM⁺ - Scanning Electron Microscope

BDL - Below detection level

**TABLE 5 COMPRESSIVE STRENGTH AND STRENGTH ACTIVITY INDEX
OF NATURAL POZZOLANS WITH PORTLAND CEMENT**

Sample	Water*	Compressive Strength, MPa at age 28 days	Strength activity index with cement in %
	Cement + Pozzolan		
CEMENT	0.48	47.0	-
F1	0.47	22.8	48.64
F2	0.45	20.8	44.40
W1	0.50	23.5	50.00
W2	0.50	24.9	53.11
MW1	0.50	21.3	45.27
SM1	0.50	32.2	68.50
SM2	0.50	32.7	69.60
CB1	0.50	37.6	80.15
CT1	0.45	29.1	62.00
US1	0.45	29.9	63.60
ERC1	0.50	32.4	69.01
FE2	0.45	9.3	19.78
TH1	0.47	16.2	34.43
PR1	0.48	24.9	53.11
BG1	0.55	26.8	57.14
MO1	0.48	20.8	44.32
WW1	0.48	22.9	48.71
PRC1	0.46	33.5	71.43
VA1	0.46	34.1	72.67
VA2	0.44	40.2	85.56
AC1	0.44	25.9	55.10
F3	0.46	37.0	78.75
PS1E	0.46	43.1	91.72
LK1	0.47	40.0	85.12
LK2	0.46	39.0	82.93
MOU	0.46	25.9	55.23
Fly Ash	0.44	35.3	75.06

Note:* - Water cement ratios used for strength activity index of natural pozzolans and fly ash with portland cement

**TABLE 6 COMPRESSIVE STRENGTH AND STRENGTH ACTIVITY INDEX
WITH CEMENT FOR CALCINED AND UNCALCINED POZZOLANS**

Sample Designation	Compressive strength, MPa age 7 days	Strength activity index with cement in percent	Calcining temperature °C
Cement	32.8	-	-
MW1A	23.5	71.48	350
MW1B	27.2	82.81	700
MW1C	30.3	92.24	1050
PS1A	27.7	84.38	115
PS1B	28.5	86.79	350
PS1C	31.2	95.17	700
CT1A	29.2	88.78	950

1 psi = 0.00689 MPa

TABLE 7 DENSITY AND FINENESS OF POZZOLANS AND FLY ASH

SAMPLE	DENSITY gm/cm ³	FINENESS (%) PASSING # 325 SIEVE	SAMPLE	DENSITY gm/cm ³	FINENESS (%) PASSING # 325 SIEVE
	ASTM C188	ASTM C430		ASTM C188	ASTM C430
CEMENT	3.13	95.26	PR1	2.27	90.71
F1	2.62	92.25	BG1	2.54	95.36
F2	2.84	91.79	MO1	2.42	96.60
W1	2.73	95.51	WW1	2.39	96.60
W2	2.32	94.89	PRC1	2.38	93.80
MW1	2.41	92.41	VA1	2.53	95.05
SM1	2.50	94.43	VA2	2.48	97.99
SM2	2.22	93.19	AC1	2.59	93.96
CB1	2.13	93.96	F3	2.34	91.79
CT1	2.30	97.05	PS1E	2.34	98.77
US1	2.36	96.90	LK1	2.30	93.65
ERC1	2.42	93.80	LK2	2.27	98.30
FE2	2.33	92.26	MOU	2.25	92.25
TH1	2.59	91.50	FLY ASH	2.67	83.80

Table 8 Blaine Fineness of Selected Pozzolans

Sample	Bulk Volume cm ³	Density gm/cm ²	Constant "b"	Fineness cm ² /gm
Cement	1.816	3.15	0.90	3990
Fly Ash	1.777	2.67	0.92	3530
LK2	2.130	2.27	1.26	3270
PS1E	1.935	2.34	1.07	4910
SM2	2.680	2.22	1.86	4420
MW1	2.000	2.41	1.34	3500
CT1	2.016	2.30	1.14	3570

Table 9A List of Selected Natural Pozzolans

POZZOLAN TYPE	ABBREVIATION
NATURAL POZZOLAN	LK2
NATURAL POZZOLAN	PS1E
NATURAL POZZOLAN	SM2
NATURAL POZZOLAN	MW1
NATURAL POZZOLAN	CT1
CLASS F FLYASH	F

Table 9B Mixture Designations & Proportions for Test Pozzolans

DESIGNATION	TEST POZZOLAN	% POZZOLAN BY WT.
C	CONTROL	NIL
LK21	LK2	10
LK22	LK2	15
LK23	LK2	25
PS1E1	PS1E	10
PS1E2	PS1E	15
PS1E3	PS1E	25
SM21	SM2	10
SM22	SM2	15
SM23	SM2	25
MW11	MW1	10
MW12	MW1	15
MW13	MW1	25
CT11	CT1	10
CT12	CT1	15
CT13	CT1	25
F1	CLASS F FLY ASH	10
F2	CLASS F FLYASH	15
F3	CLASS F FLYASH	25

TABLE 10 BASIC MIX PROPORTIONS FOR CONTROL AND POZZOLAN BLENDED CEMENT CONCRETES

MATERIAL	CONTROL MIX	10% MIX	15% MIX	25% MIX	UNITS
Coarse Aggregate	1753	1753	1753	1753	lb/cu yd
Fine Aggregate	1257	1257	1257	1257	lb/cu yd
Cement	600	540	510	450	lb/cu yd
Water	254	254	254	254	lb/cu yd
Pozzolan	NIL	60	90	150	lb/cu yd
Superplasticizer	NIL	NIL	NIL	NIL	
Air entraining agent	55	55	55	55	CC

1 LB= 0.4536 KGS

1 YARD= 0.9144 METER

TABLE 11 MIX DESIGNATION

MIX NUMBER	TYPE OF POZZOLAN	PERCENTAGE OF POZZOLAN
C	CONTROL	NIL
F-1	FLY ASH	10
F-2	FLY ASH	15
F-3	FLY ASH	25
LK2-1	LK2	10
LK2-2	LK2	15
LK2-3	LK2	25
PS1E-1	PS1E	10
PS1E-2	PS1E	15
PS1E-3	PS1E	25
CT1-1	CT1	10
CT1-2	CT1	15
CT1-3	CT1	25
SM2-1	SM2	10
SM2-2	SM2	15
SM2-3	SM2	25
MW1-1	MW1	10
MW1-2	MW1	15
MW1-3	MW1	25

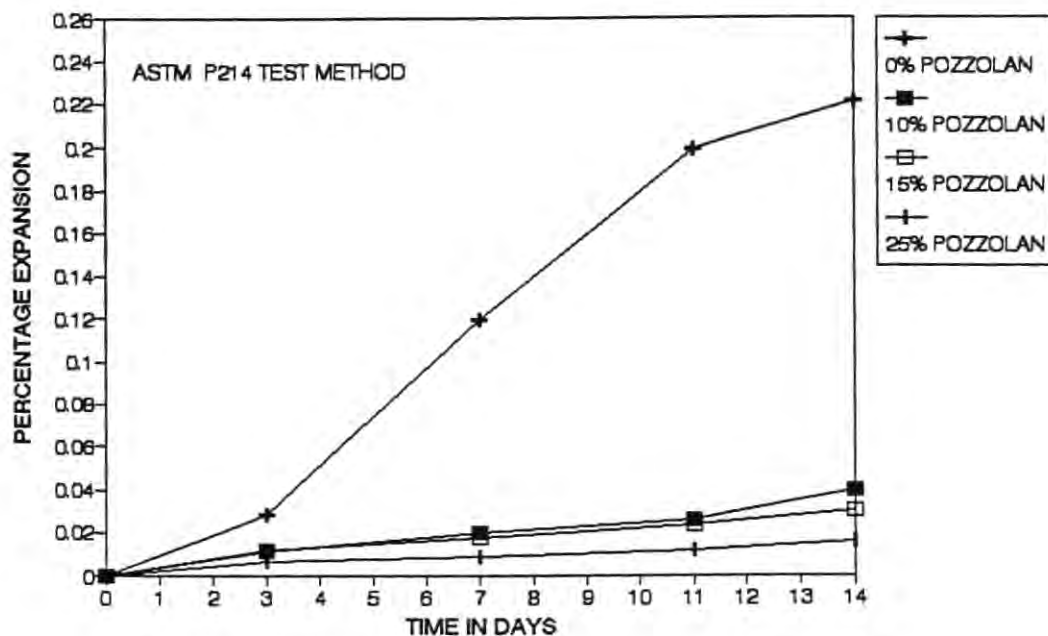


FIGURE 1 COMPARISON OF MORTAR BAR EXPANSION FOR LK2

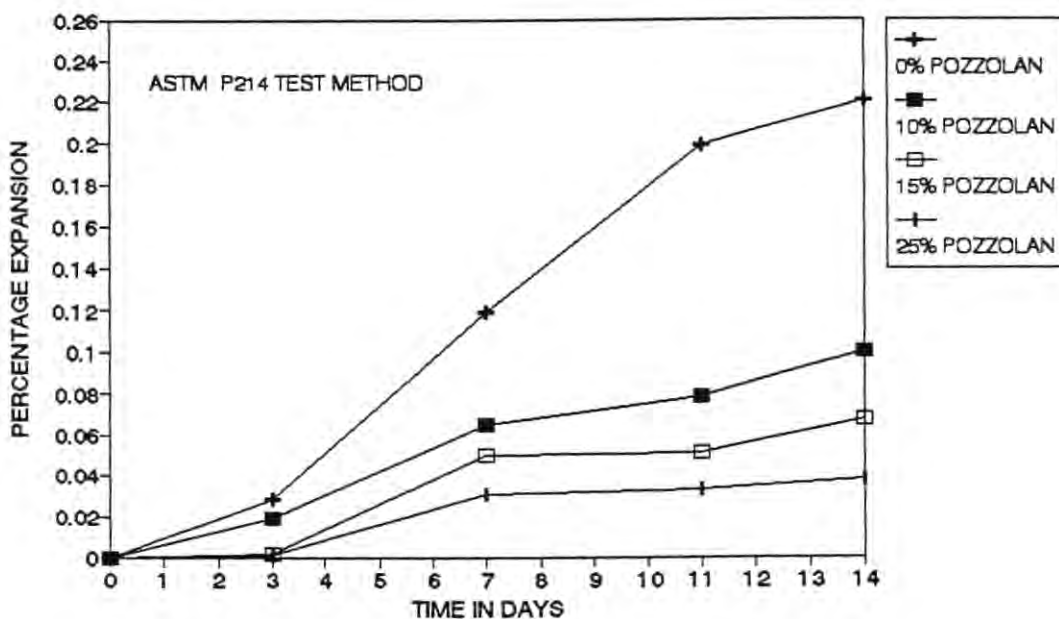


FIGURE 2 COMPARISON OF MORTAR BAR EXPANSION FOR PS1E

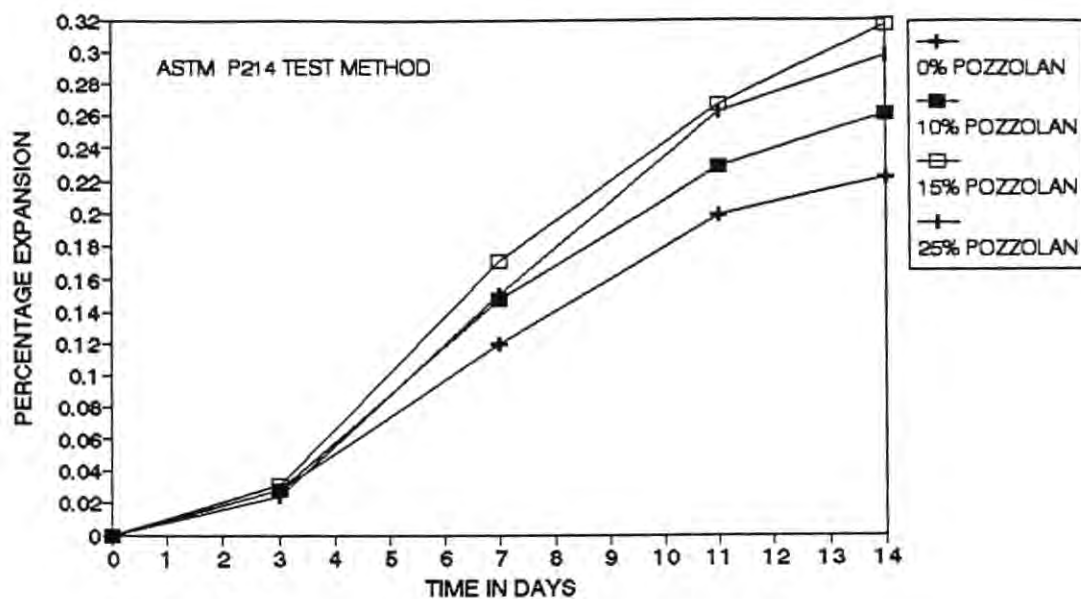


FIGURE 3 COMPARISON OF MORTAR BAR EXPANSION FOR VA2

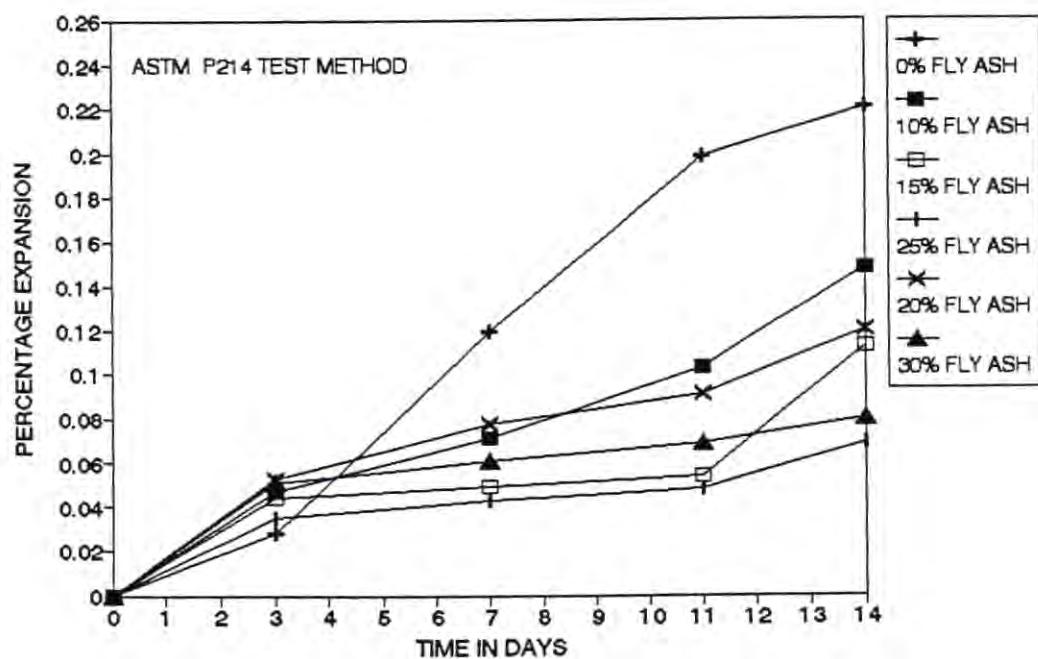


FIGURE 4 COMPARISON OF MORTAR BAR EXPANSION FOR FLY ASH

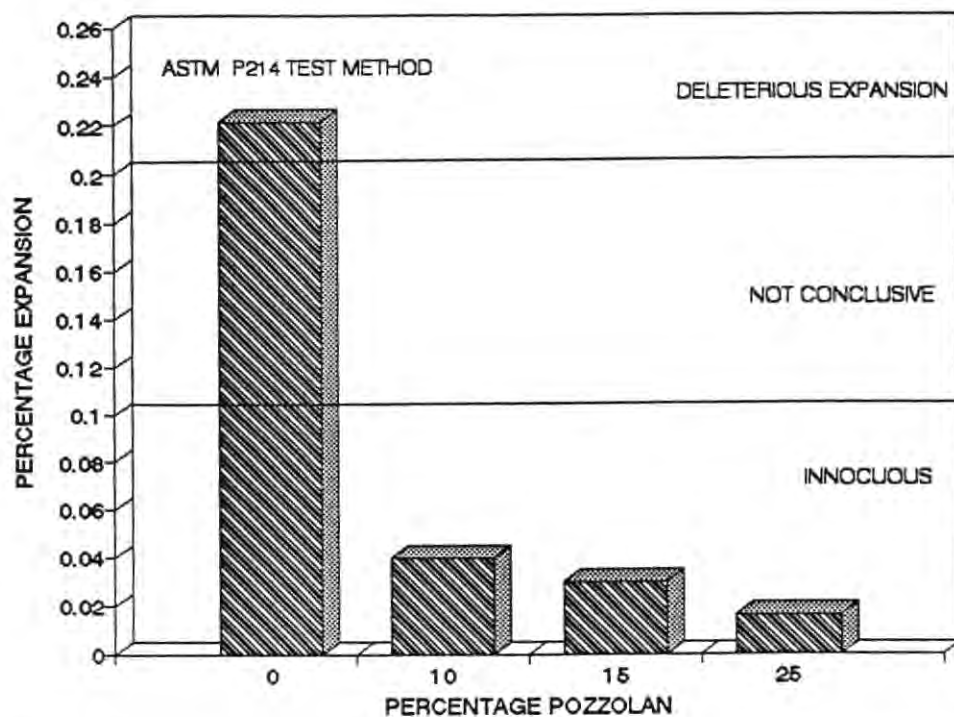


FIGURE 5 COMPARISON OF EXPANSIONS FOR POZZOLAN SAMPLE LK2

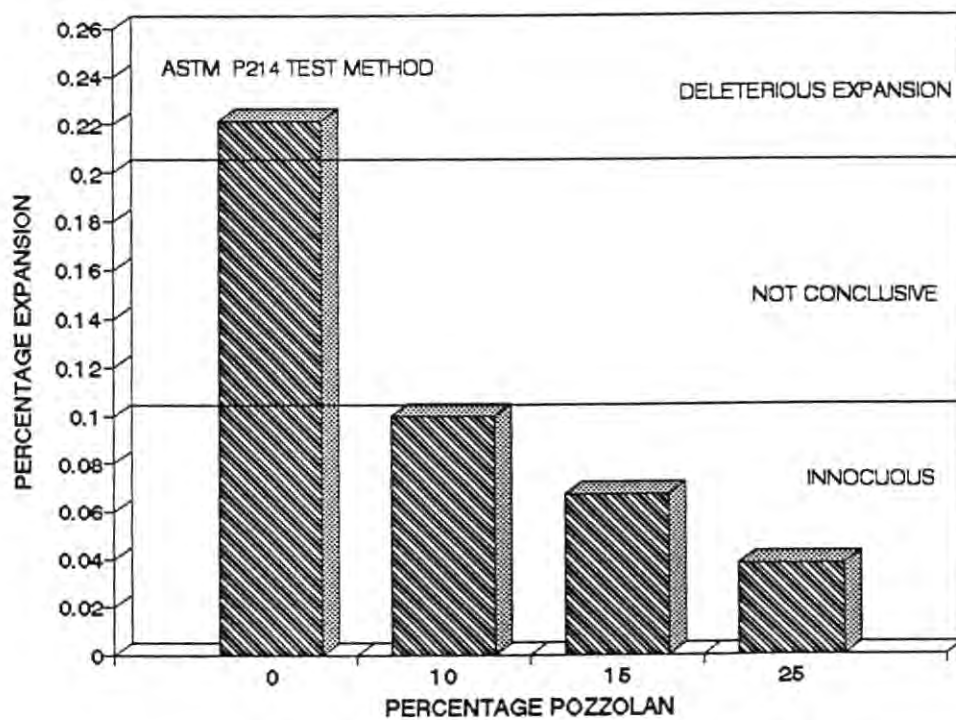


FIGURE 6 COMPARISON OF EXPANSIONS FOR POZZOLAN SAMPLE PS1E

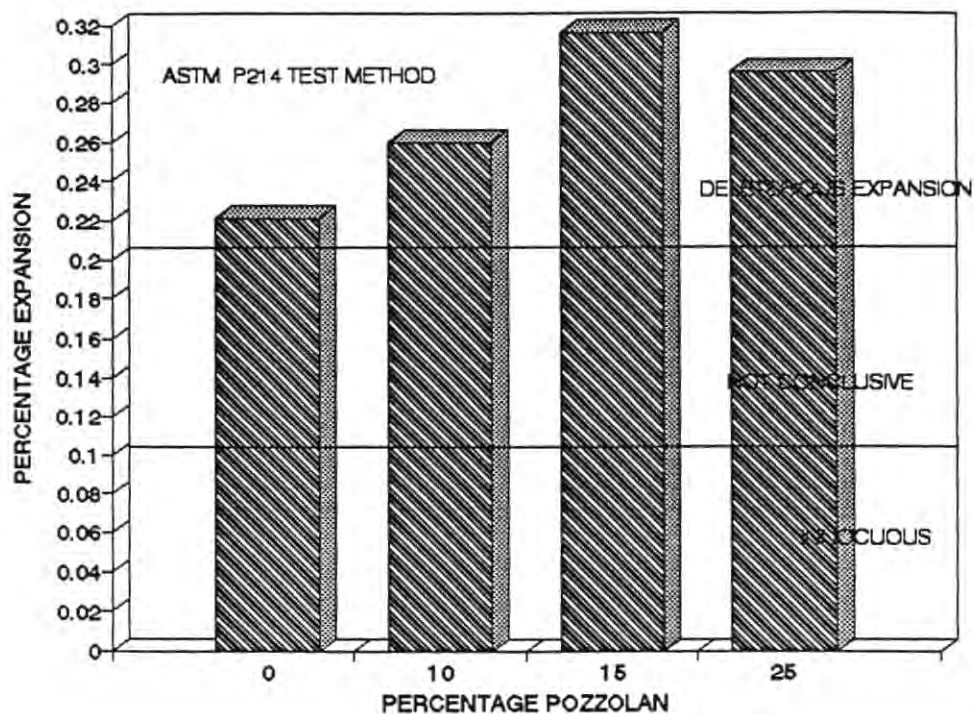


FIGURE 7 COMPARISON OF EXPANSIONS FOR POZZOLAN SAMPLE VA2

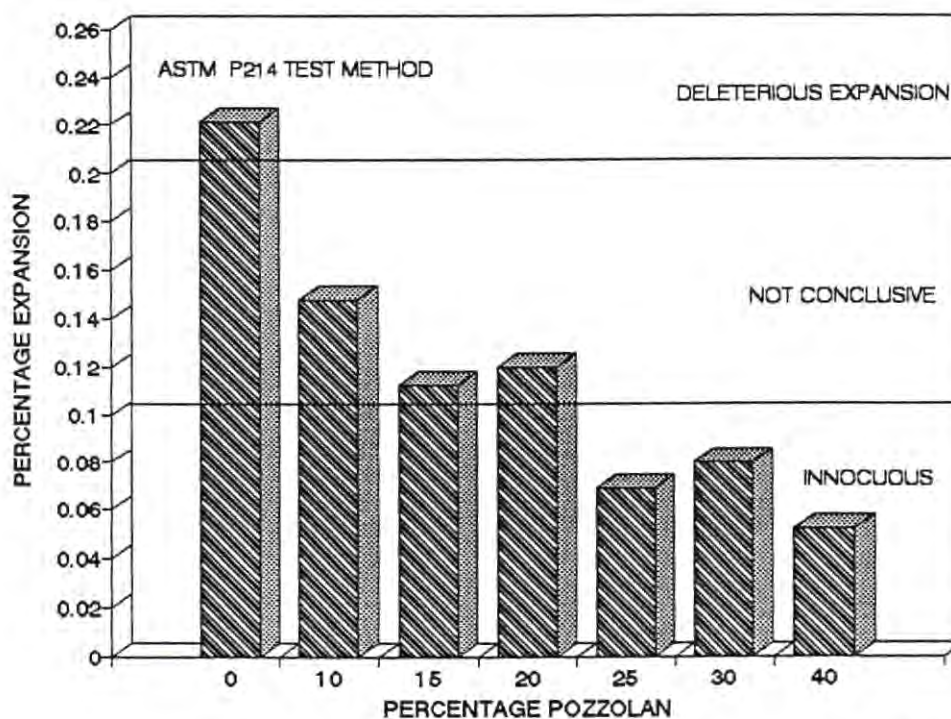


FIGURE 8 COMPARISON OF EXPANSIONS FOR FLY ASH

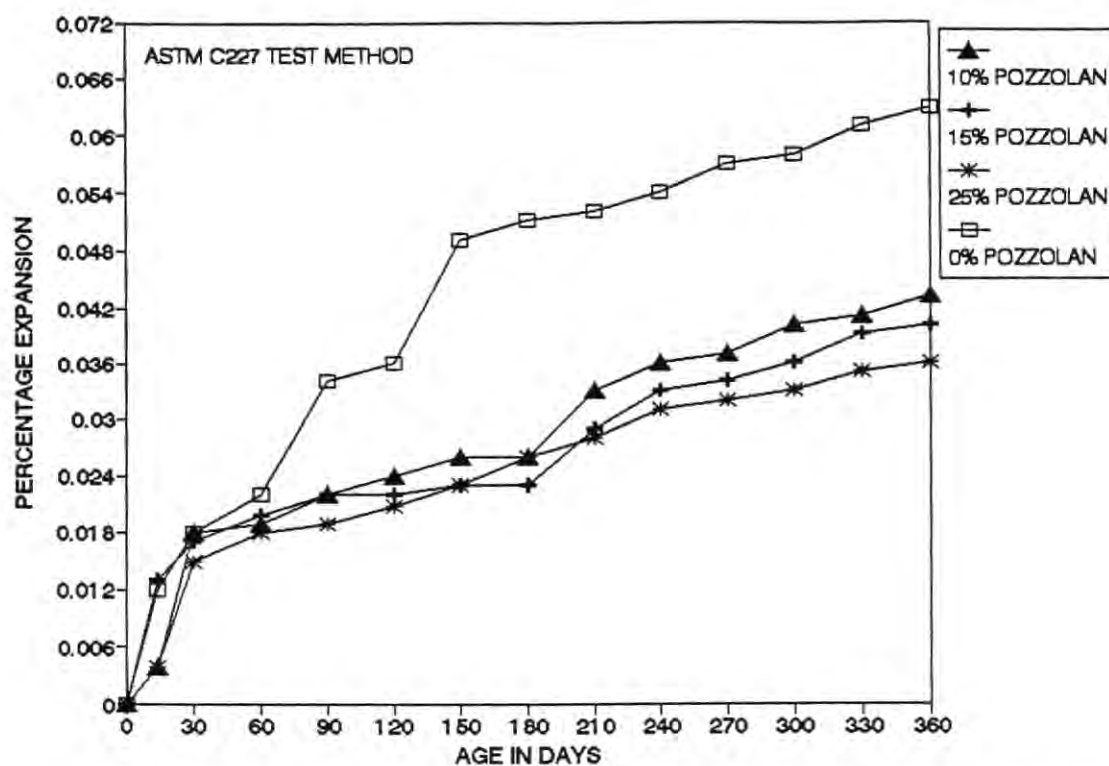


FIGURE 9 COMPARISON OF EXPANSIONS FOR POZZOLAN SAMPLE LK2

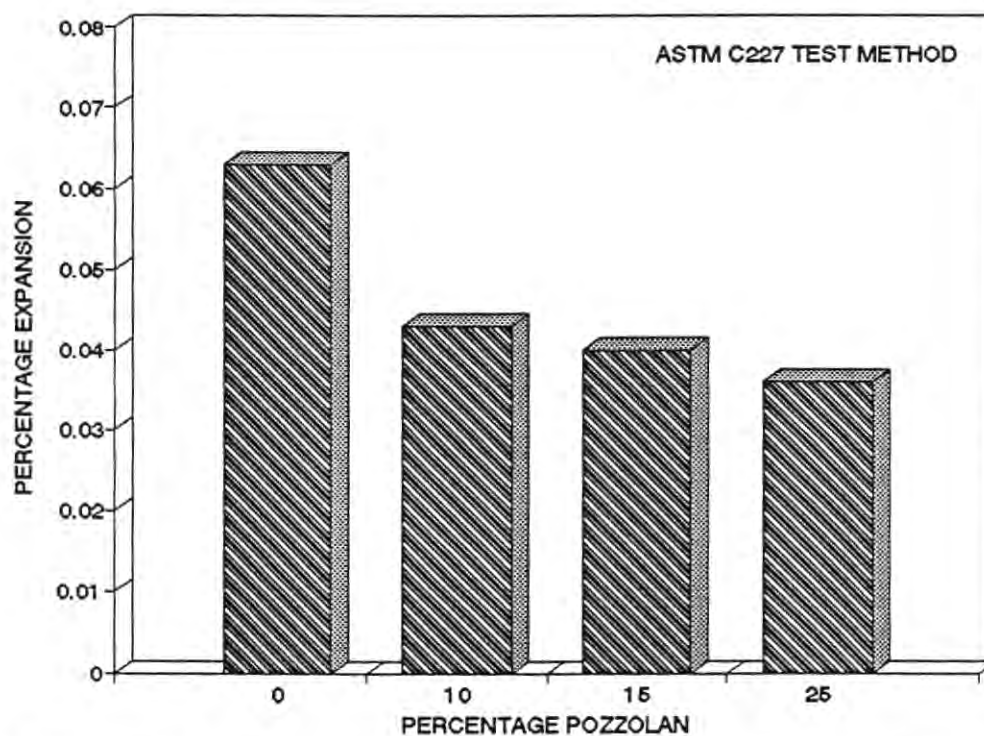


FIGURE 10 COMPARISON OF MORTAR BAR EXPANSION FOR LK2

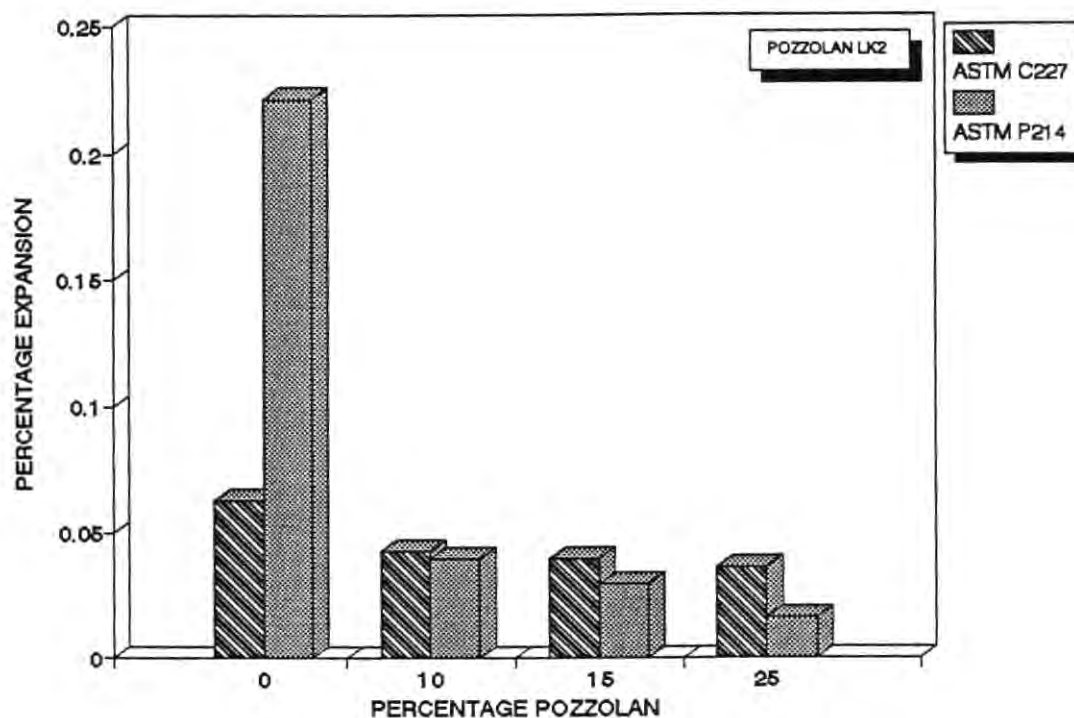


FIGURE 11 COMPARISON OF EXPANSIONS FROM ASTM C227 AND ASTM P214 TEST METHODS

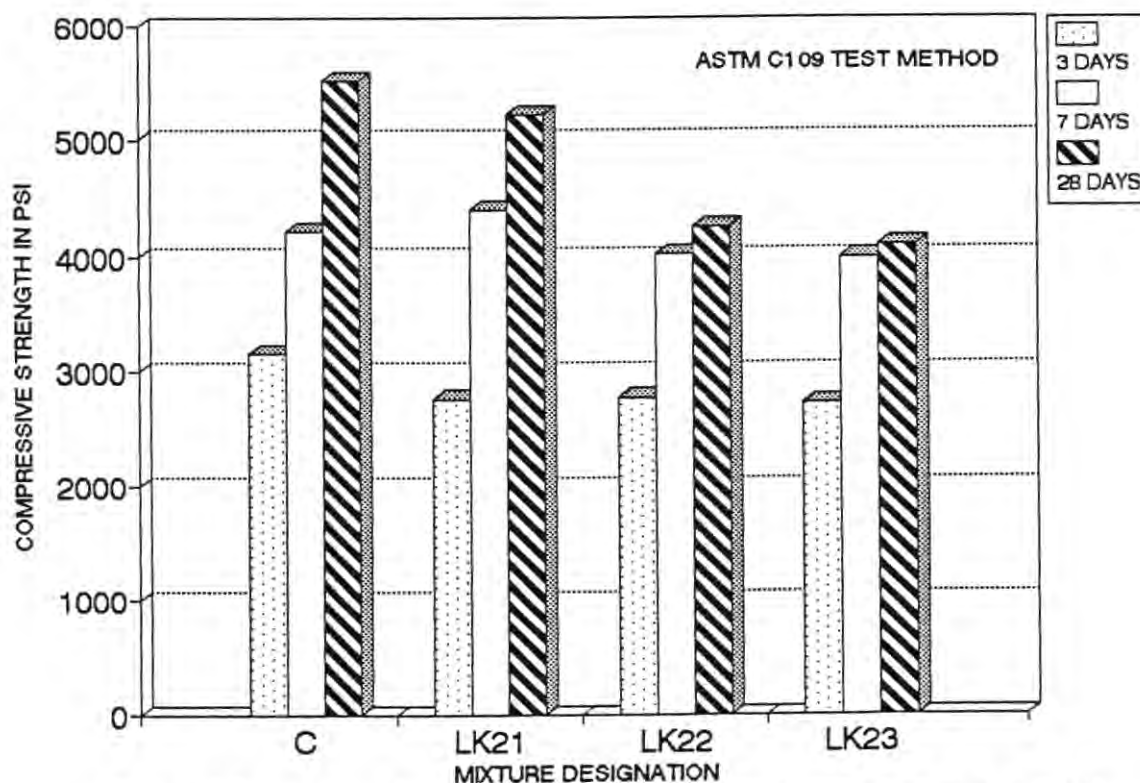


Figure 12 Comparison of compressive strength of cement mortar blended with LK2

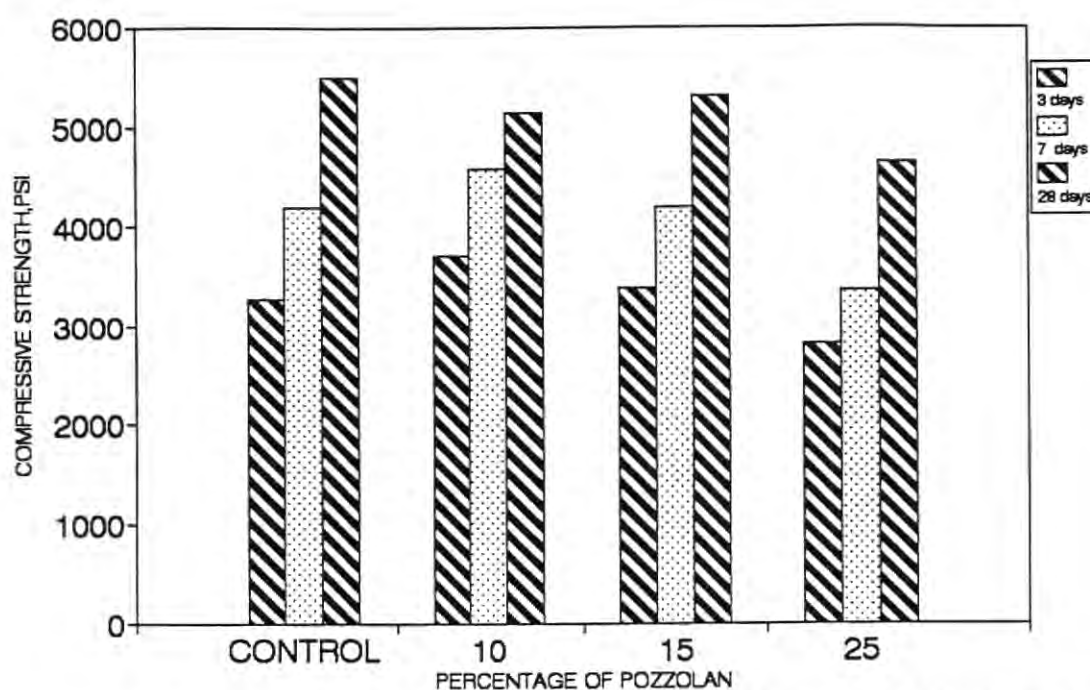


FIG 31 COMPARISON OF COMPRESSIVE STRENGTH FOR CONCRETES WITH LK2 POZZOLAN BLENDED CEMENTS

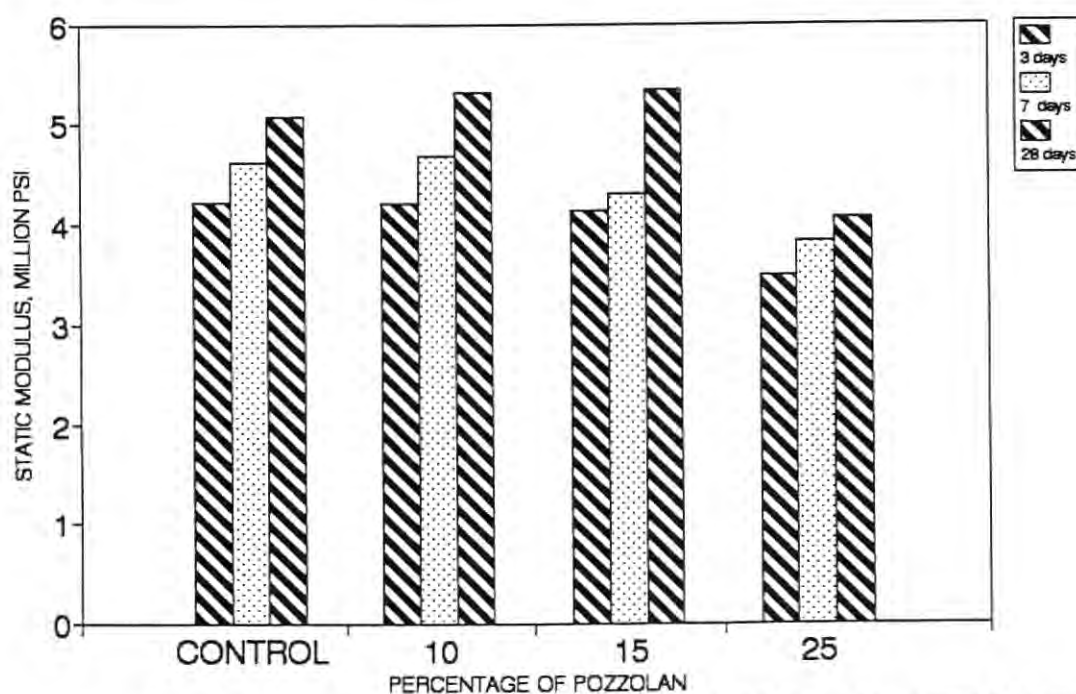


FIG 32 COMPARISON OF STATIC MODULUS FOR CONCRETES WITH LK2 POZZOLAN BLENDED CEMENTS

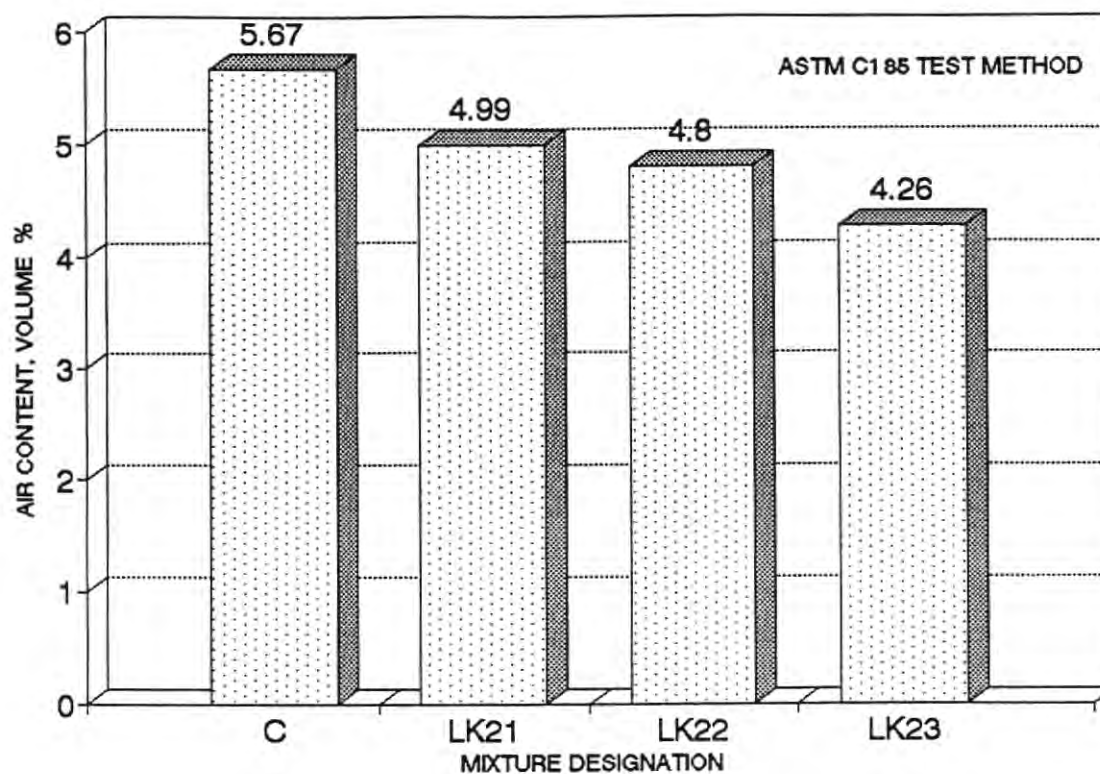


Figure 13 Comparison of air content of cement mortar blended with LK2

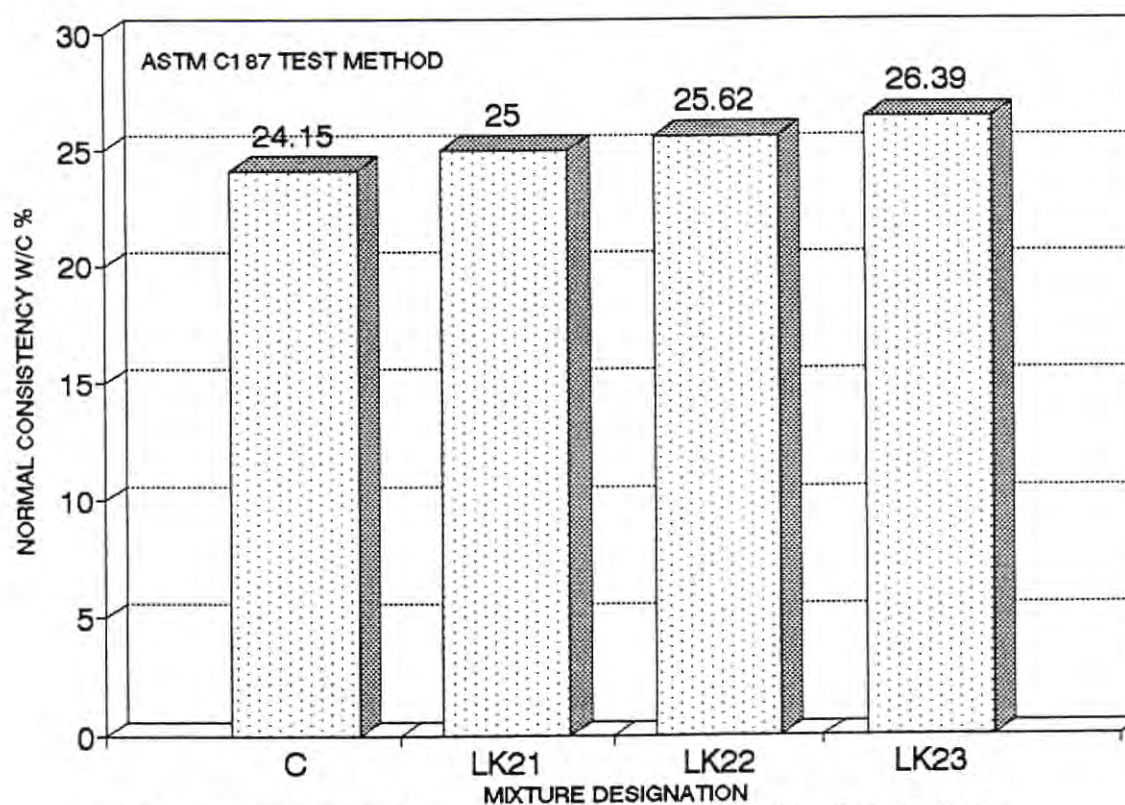


Figure 14 Comparison of normal consistency of cement blended with LK2

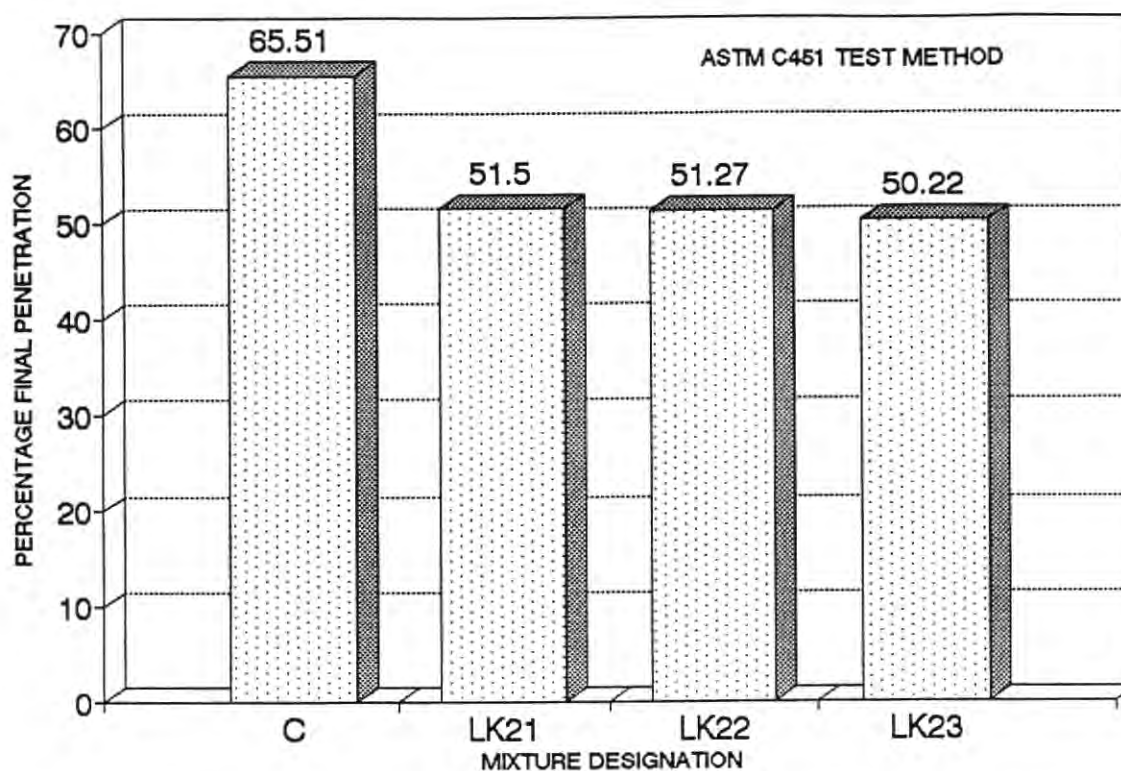


Figure 15 Comparison of early stiffening of cement blended with LK2 by Paste method

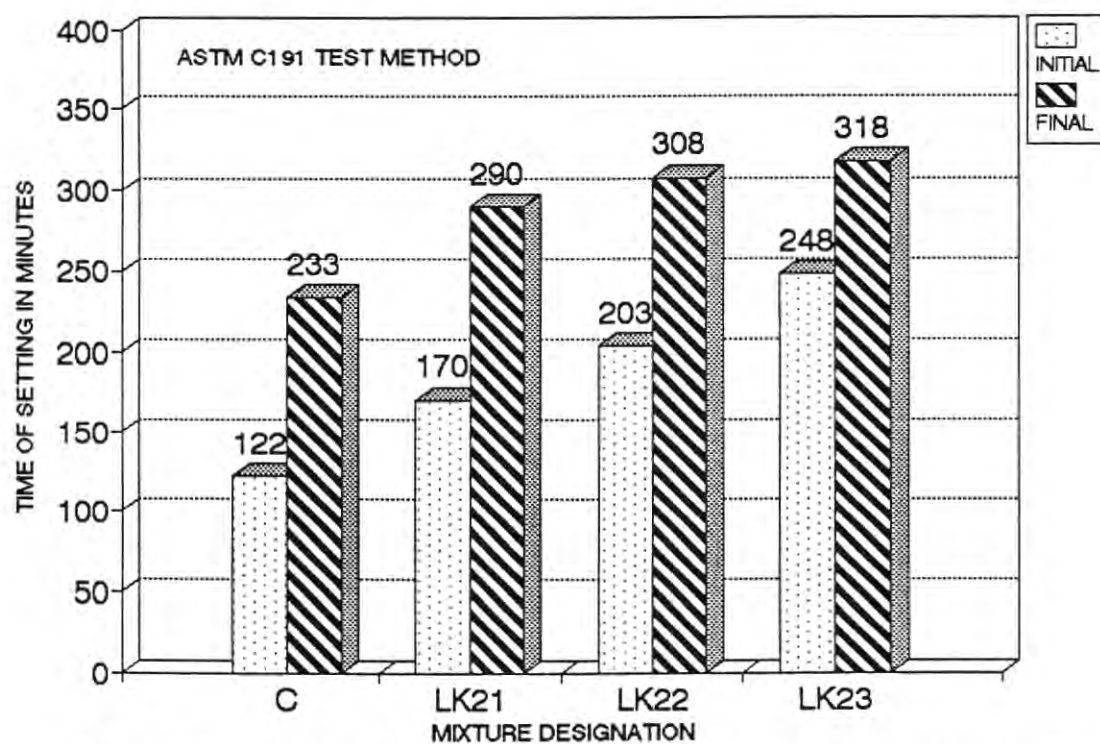


Figure 16 Comparison of time of setting of cement blended with LK2 by Vicat needle

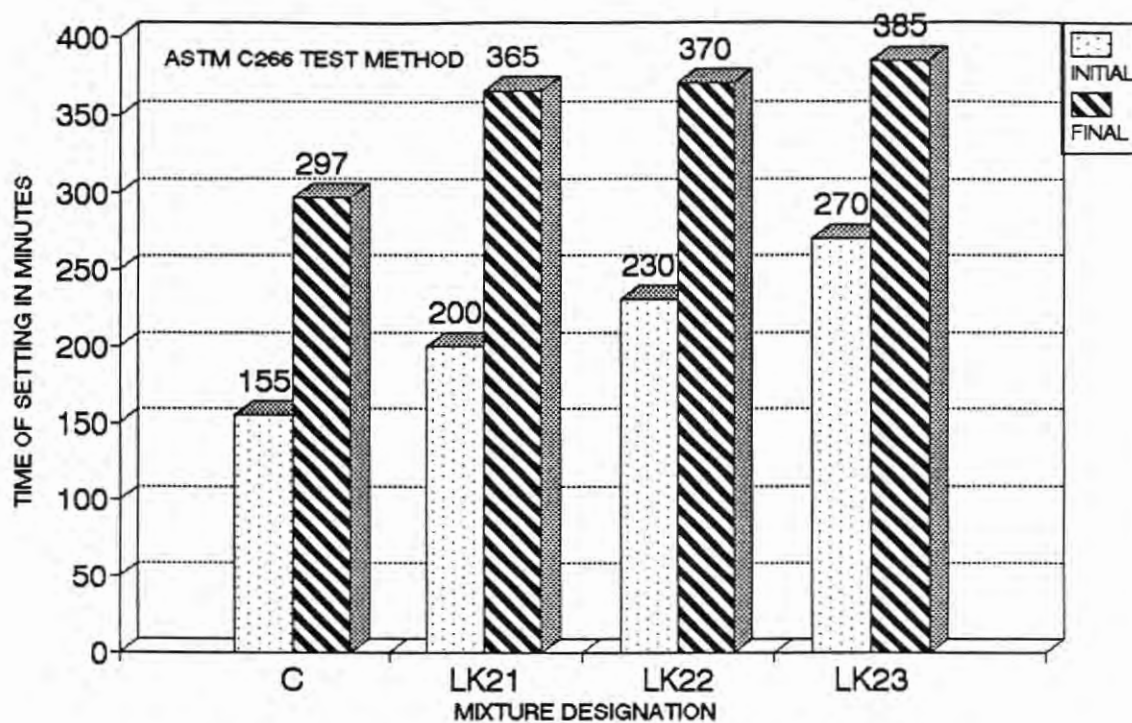


Figure 17 Comparison of time of setting of cement blended with LK2 by Gillmore needles

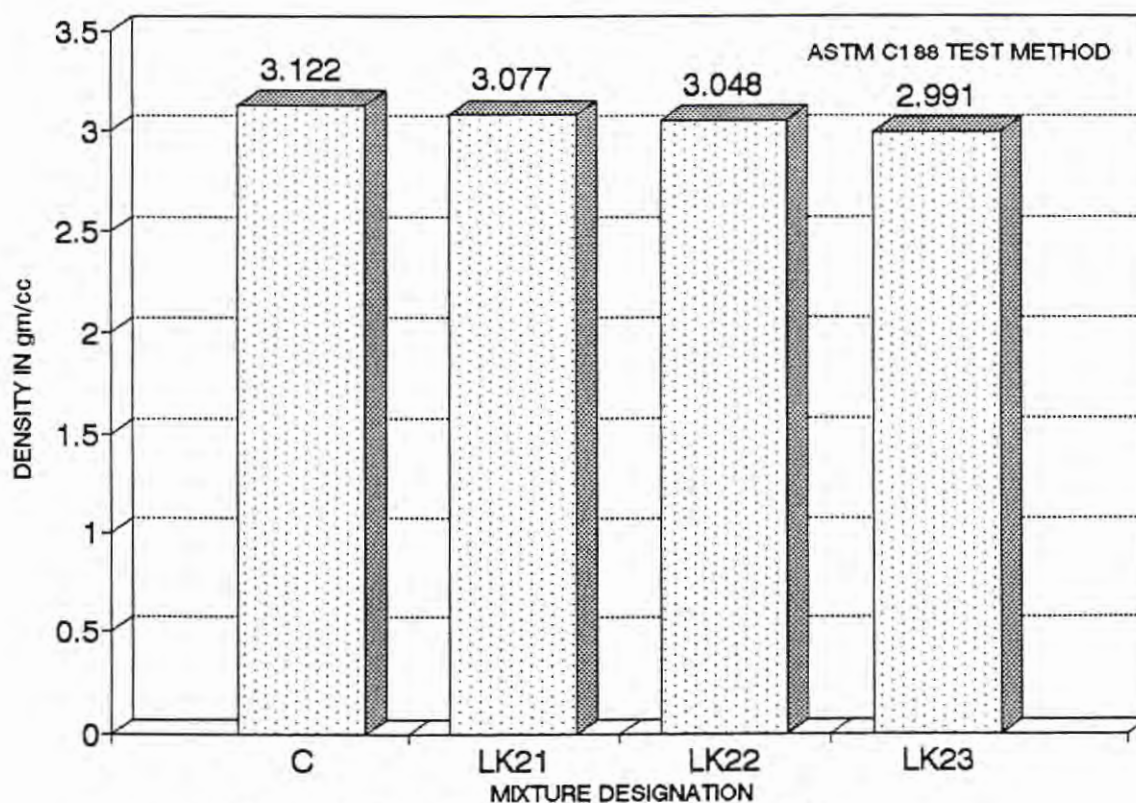


Figure 18 Comparison of density of cement blended with LK2

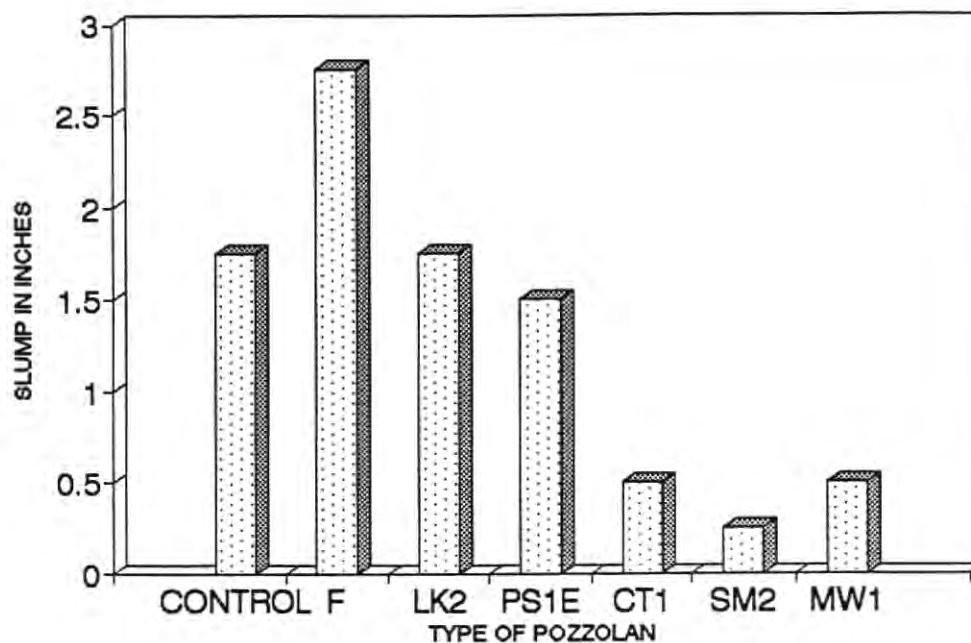


FIG 21 COMPARISON OF SLUMP FOR CONCRETES WITH 10% POZZOLAN BLENDED CEMENTS

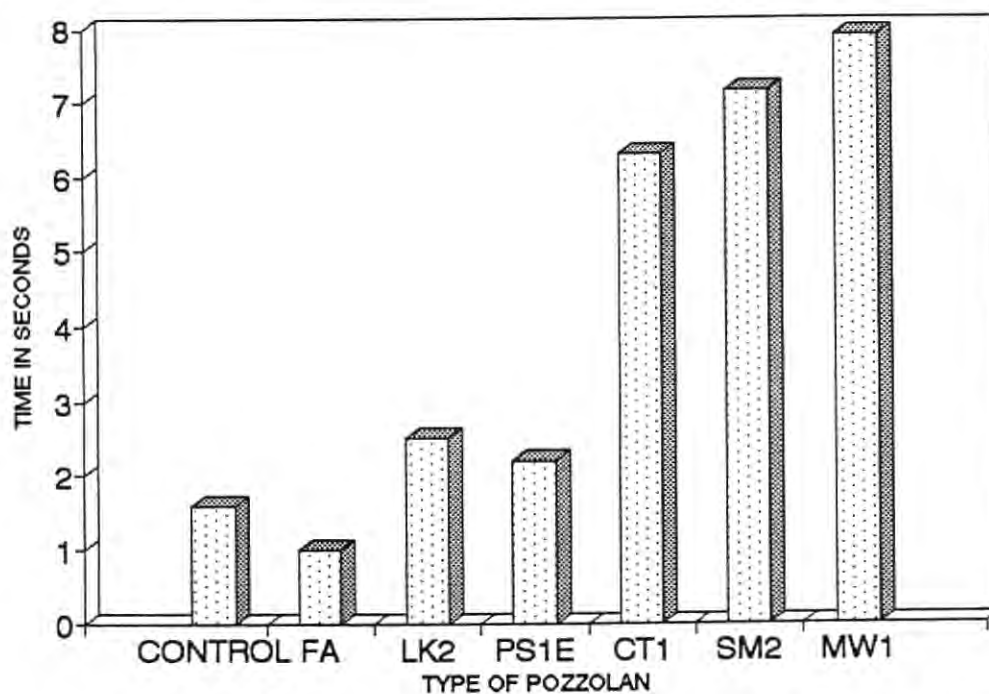


FIG 22 COMPARISON OF VEBE TIME FOR CONCRETES WITH 15% POZZOLAN BLENDED CEMENTS

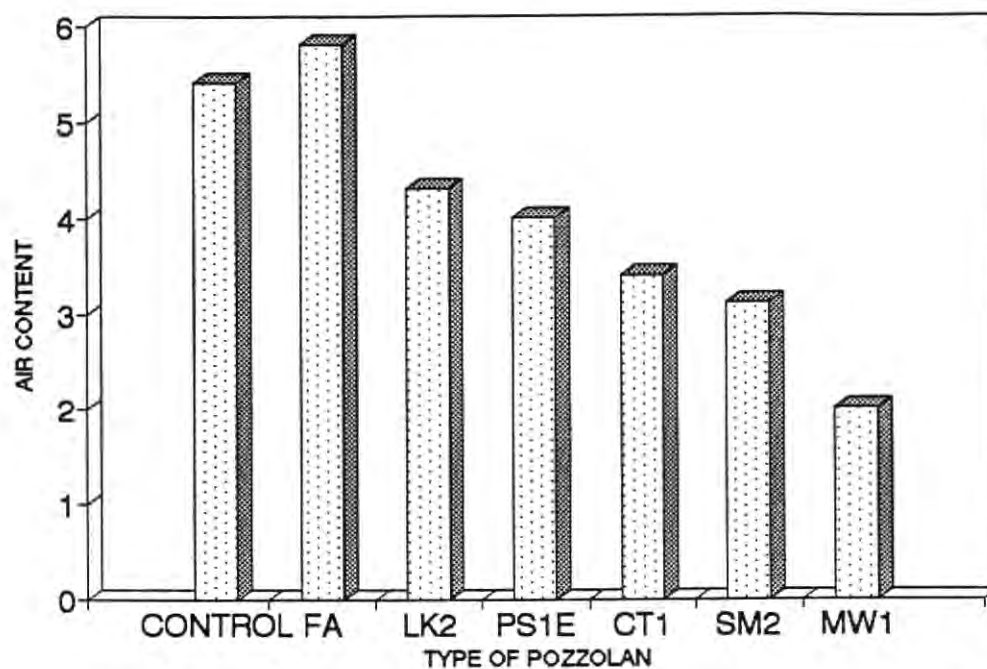


FIG 23 COMPARISON OF AIR CONTENT FOR CONCRETES WITH 10% POZZOLAN BLENDED CEMENTS

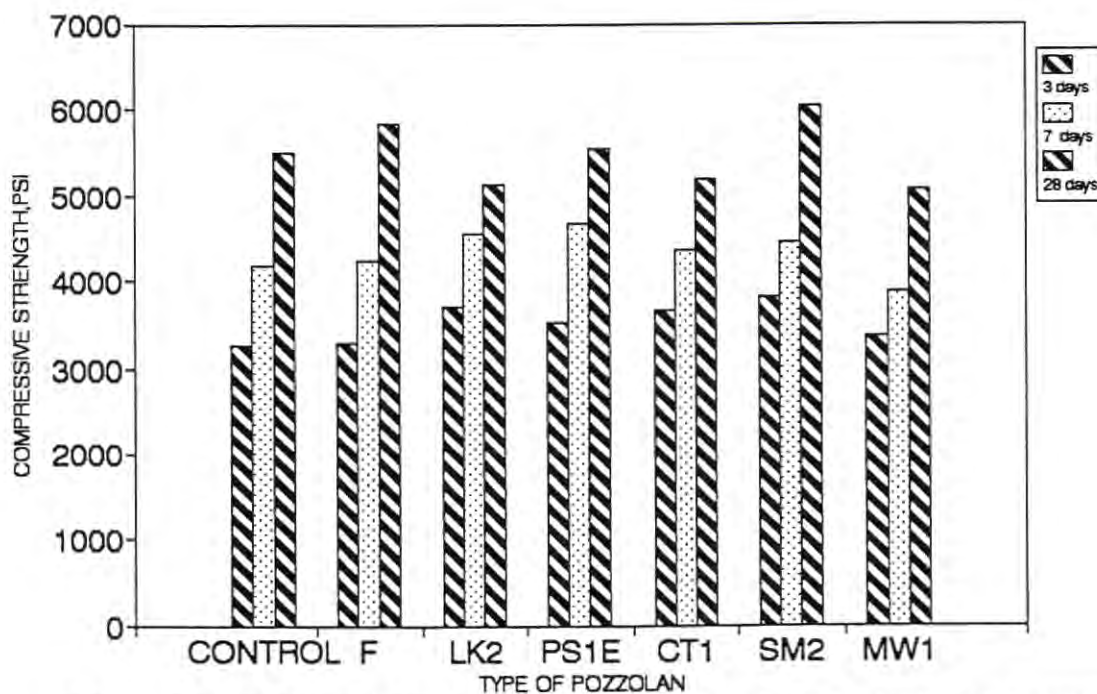


FIG 24 COMPARISON OF COMPRESSIVE STRENGTH FOR CONCRETES WITH 10% POZZOLAN BLENDED CEMENTS

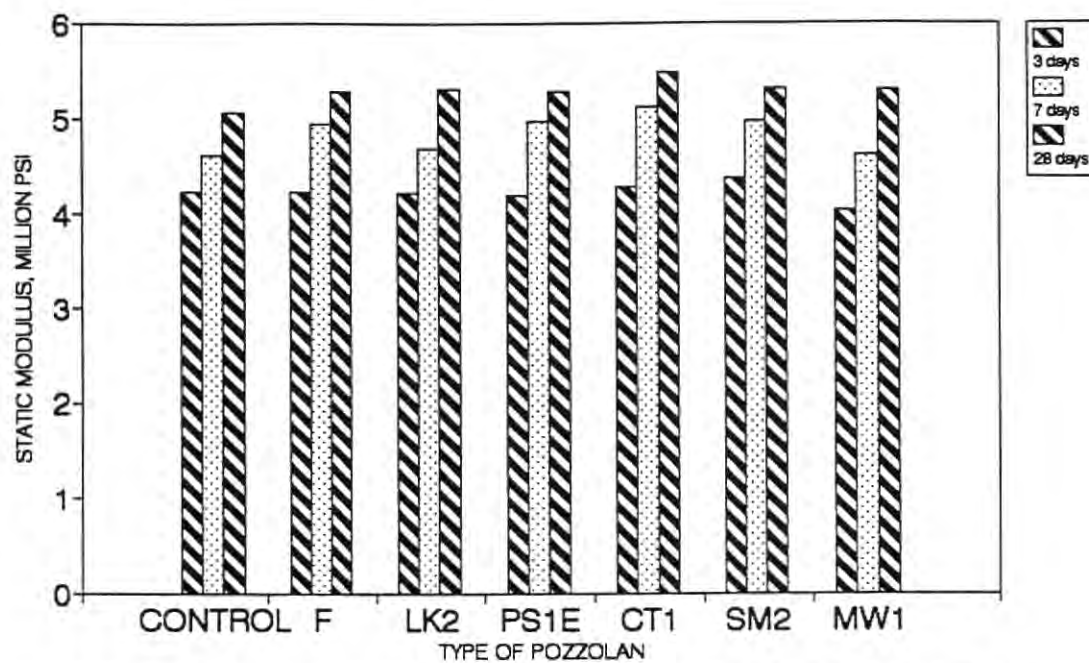


FIG 25 COMPARISON OF STATIC MODULUS FOR CONCRETES WITH 10% POZZOLAN BLENDED CEMENTS

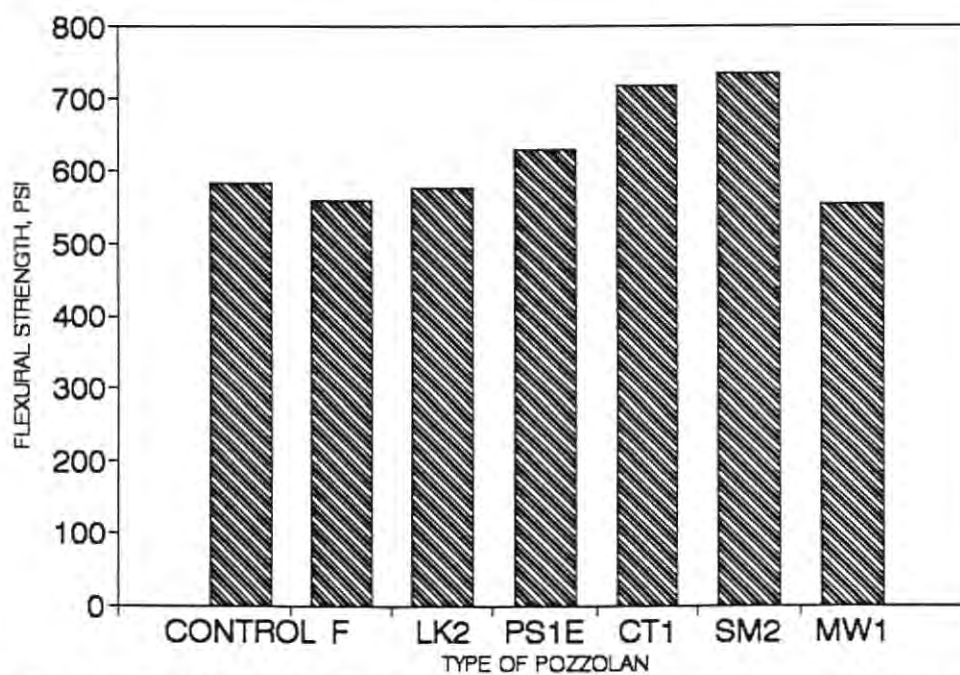


FIG 26 COMPARISON OF FLEXURAL STRENGTH FOR CONCRETES WITH 10% POZZOLAN BLENDED CEMENTS

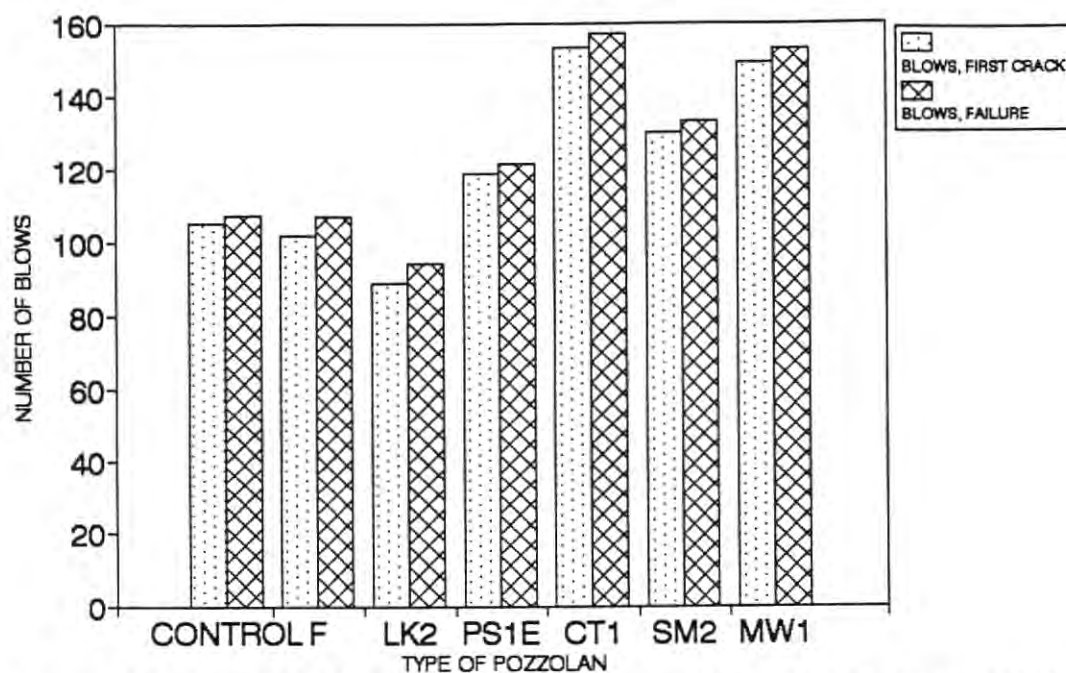


Fig. 27 COMPARISON OF IMPACT STRENGTH FOR CONCRETES WITH 10% POZZOLAN BLENDED CEMENTS

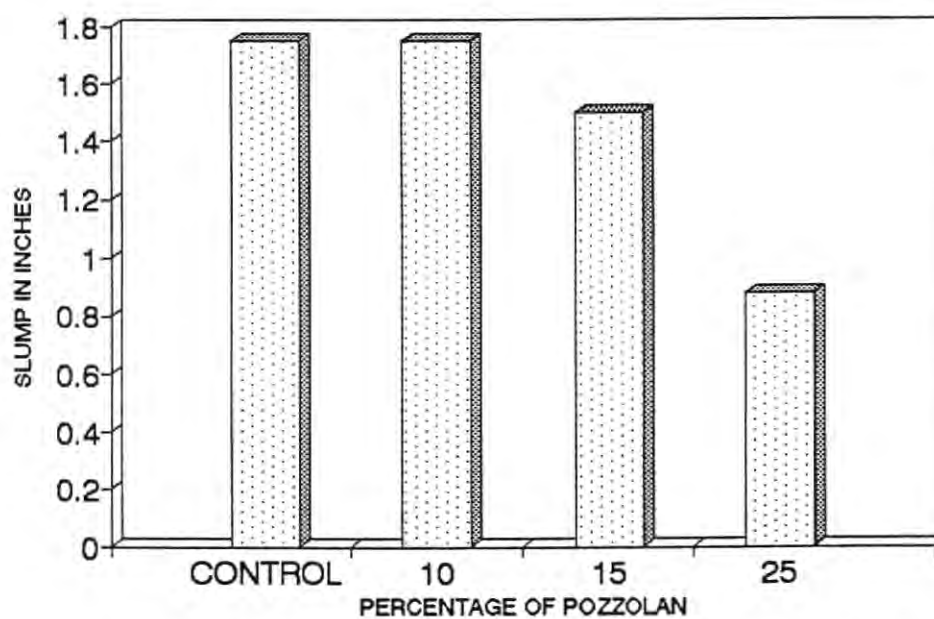


FIG 28 COMPARISON OF SLUMP FOR CONCRETES WITH LK2 POZZOLAN BLENDED CEMENTS

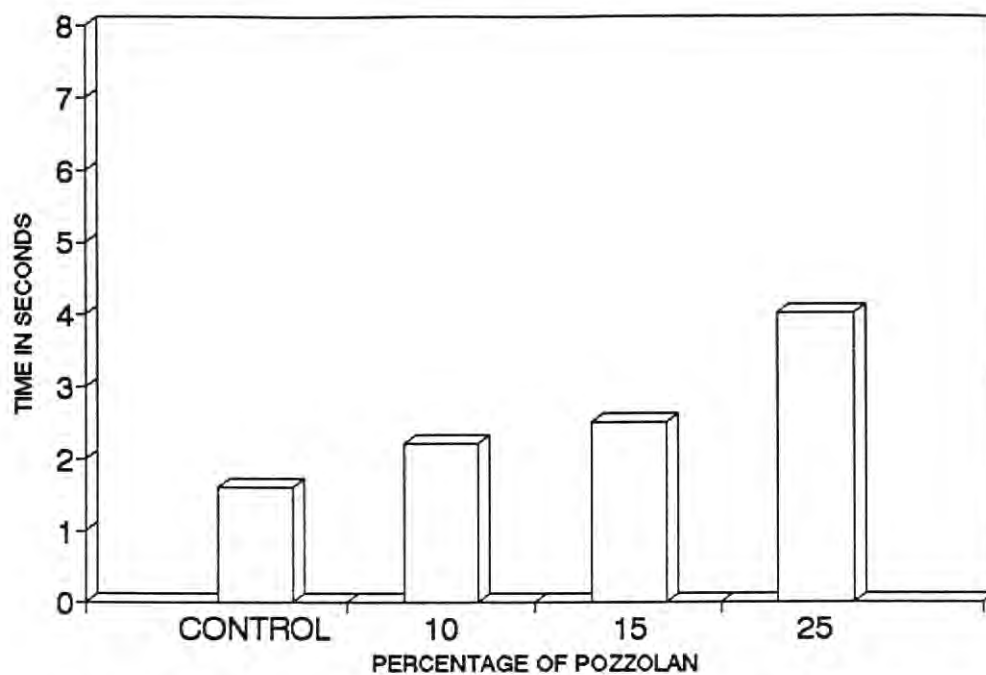


Fig 29 COMPARISON OF VEBE TIME FOR CONCRETES WITH LK2 POZZOLAN BLENDED CEMENTS

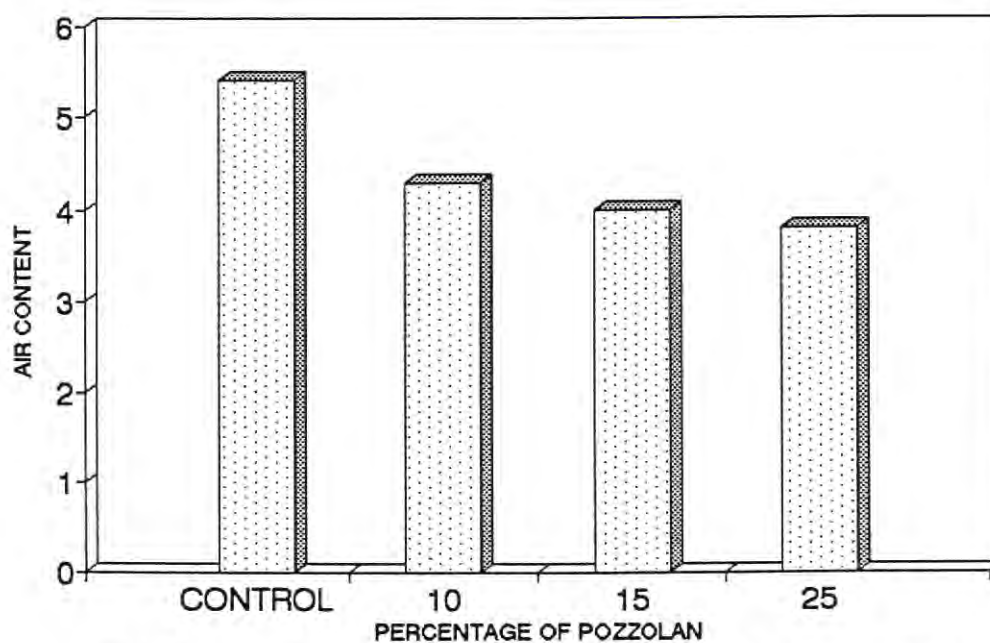


FIG 30 COMPARISON OF AIR CONTENT FOR CONCRETES WITH LK2 POZZOLAN BLENDED CEMENTS

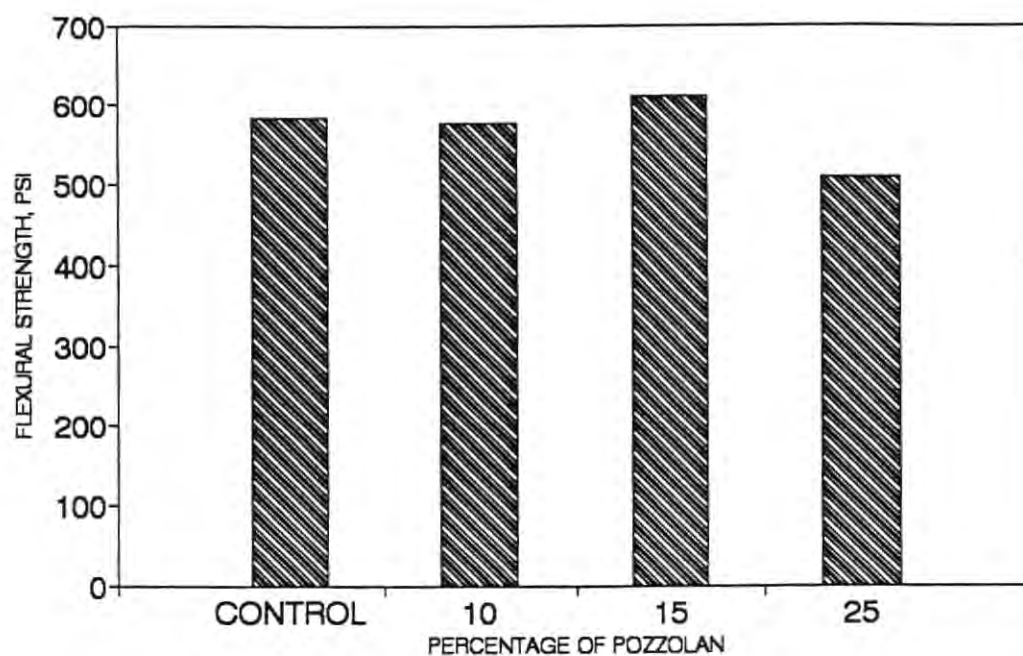


FIG 33 COMPARISON OF FLEXURAL STRENGTH FOR CONCRETESS WITH LK2 POZZOLAN BLENDED CEMENTS

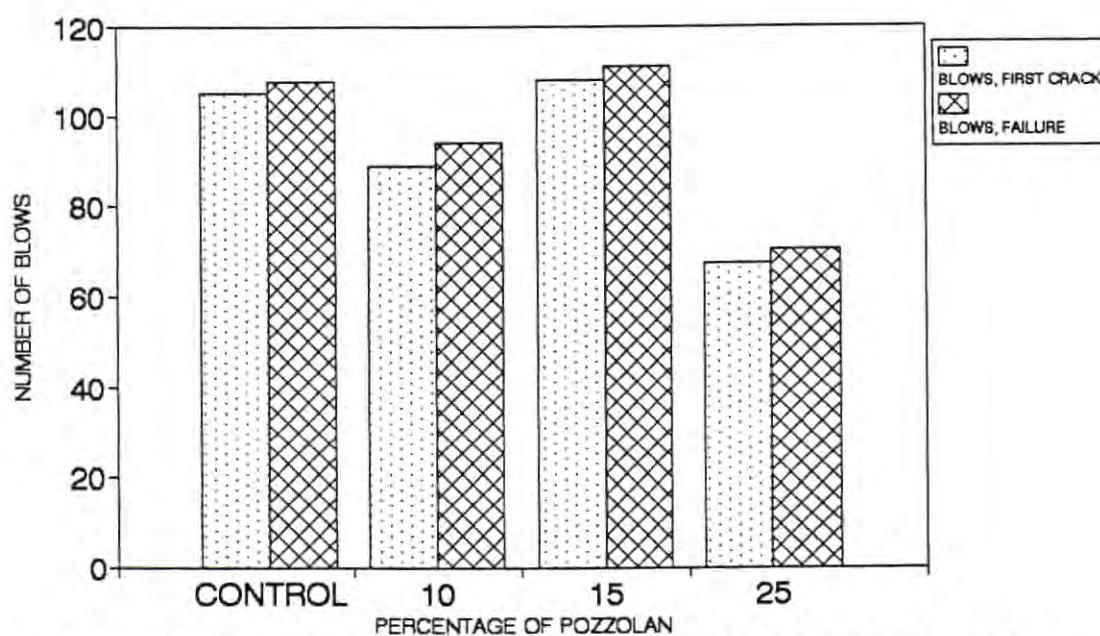


Fig. 34 COMPARISON OF IMPACT STRENGTH FOR CONCRETES WITH LK2 POZZOLAN BLENDED CEMENTS