

A1  
134m  
6.C-74-1  
p.3

Key

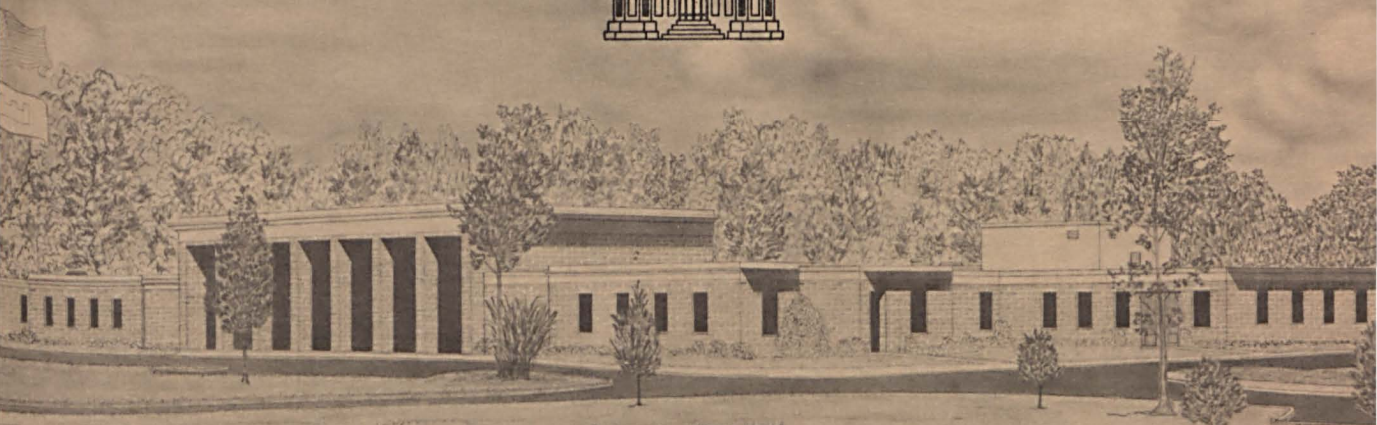
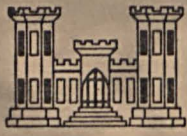


MISCELLANEOUS PAPER C-74-1

# INVESTIGATION OF ACCELERATED METHODS FOR THE DETERMINATION OF AVAILABLE ALKALI IN POZZOLANS

by

W. G. Miller



LIBRARY BRANCH  
TECHNICAL INFORMATION CENTER  
US ARMY ENGINEER WATERWAYS EXPERIMENT STATION  
VICKSBURG, MISSISSIPPI  
February 1974

Sponsored by **Office, Chief of Engineers, U. S. Army**

Conducted by **U. S. Army Engineer Waterways Experiment Station**  
**Concrete Laboratory**  
**Vicksburg, Mississippi**

Miscellaneous Paper C-74-1

INVESTIGATION OF ACCELERATED METHODS FOR THE DETERMINATION  
OF AVAILABLE ALKALI IN POZZOLANS

KEY

<u>Manufacturer</u>	<u>Product</u>	<u>Symbol</u>
Oregon Portland Cement Co. Lime, Oregon	Volcanic Cinders	Vol C
Empire Building Mat. Co. Portland, Oregon	Calcined Keasey Shale	CK Sh
Riverside Cement Co. Crestmore, Calif.	Calcined Diatomaceous Shale	CD Sh
Calif. Portland Cement Co. Mojave, Calif.	Calcined Tuff	CT
Southern Fly Ash Co. Wilsonville, Ala.	Fly Ash	FA I
Chicago Fly Ash Co. Chicago, Ill.	Fly Ash	FA II



MISCELLANEOUS PAPER C-74-1

# INVESTIGATION OF ACCELERATED METHODS FOR THE DETERMINATION OF AVAILABLE ALKALI IN POZZOLANS

by

W. G. Miller



February 1974

Sponsored by **Office, Chief of Engineers, U. S. Army**

Conducted by **U. S. Army Engineer Waterways Experiment Station**  
**Concrete Laboratory**  
**Vicksburg, Mississippi**

W 37-100  
100-10-10-1  
Conf.

### Foreword

The investigation reported herein was authorized by the Office, Chief of Engineers (OCE), by the first indorsement, dated 30 March 1970, to a letter from OCE to the U. S. Army Engineer Waterways Experiment Station (WES), dated 25 February 1970, subject: "Project Plan for Investigation of Accelerated Methods for the Determination of Available Alkali in Pozzolans."

The work was conducted by the Concrete Laboratory, WES, under the direction of Mr. Bryant Mather and under the supervision of Mr. R. V. Tye, Jr. This report was prepared by Mr. W. G. Miller.

BG E. D. Peixotto, CE, and COL G. H. Hilt, CE, were Directors of WES during the preparation and publication of the report. Mr. F. R. Brown was Technical Director.



## Contents

	<u>Page</u>
Foreword . . . . .	iii
Summary . . . . .	vii
Background . . . . .	1
Purpose and Scope of Investigation . . . . .	1
Materials and Test Methods . . . . .	2
Presentation and Analyses of Test Results . . . . .	3
Conclusions . . . . .	5
Literature Cited . . . . .	6
Tables 1-3	

## Summary

The procedure specified in acceptance testing of pozzolans for the determination of the available alkali released by a pozzolan requires the lime-pozzolan paste to be stored for a period of 28 days prior to test. In order to investigate the possibility of reducing the storage time of the paste prior to test, six pozzolans were tested for available alkali release rate by subjecting the paste to three conditions of storage time and/or temperature. The three conditions were as follows:

- a. Condition 1, Standard Condition, 28 days at 38 C.
- b. Condition 2, seven days at 38 C.
- c. Condition 3, seven days at 65.5 C.

The results of these tests are as follows:

- a. The highest available alkali values for all pozzolans were obtained under Storage Condition 1.
- b. All pozzolans, except calcined tuff, produced higher values for Condition 3 than for Condition 2.
- c. All pozzolans, except calcined tuff, produced available alkali values for Condition 3 that were in excess of two-thirds of the values produced for Condition 1.

Results of this study indicate that if the available alkali value of a pozzolan is 1.0 percent or less when the paste is stored at 65.5 C for seven days, the maximum specification limit of 1.5 percent will not be exceeded when the pozzolan is evaluated by the present Standard Condition, 28 days at 38 C.

In order to reduce the storage time of the lime-pozzolan paste to seven days, storage Condition 3 with a maximum limit of 1.0 percent available alkali is recommended as an optional method for the acceptance testing of pozzolan.

INVESTIGATION OF ACCELERATED METHODS FOR THE DETERMINATION  
OF AVAILABLE ALKALI IN POZZOLANS

Background

1. The Corps of Engineers Standard Guide Specification for Concrete, CE 1401.01,<sup>1</sup> requires the following conditions for release for shipment and approval for use of tested pozzolans: "Release for shipment and approval for use will be based on compliance with seven-day lime-pozzolan strength requirements and other physical and chemical and uniformity requirements for which test can be completed by the time the seven-day lime-pozzolan strength test is completed. Release for shipment and approval for use on the above basis will be contingent on continuing compliance with the other requirements of the specifications." The applicable portion of CRD-C 263, Corps of Engineers Method for Sampling and Testing Pozzolan for Use in Portland Cement Concrete,<sup>2</sup> for the determination of available alkali requires 28 days storage of the lime-pozzolan paste. Under current shipping and construction practices, most tested pozzolan is incorporated in the project construction prior to the completion of the above test.

2. This investigation was conducted as part of the responsibility assigned to the Waterways Experiment Station (WES) for the technical surveillance of cement and pozzolan procurement acceptance testing function of the Corps of Engineers as outlined in ER 1110-1-8100.<sup>3</sup>

Purpose and Scope of Investigation

3. The investigation reported herein was undertaken to determine the alkali release rate of pozzolans and was confined to the effect of

storage time and temperature conditions on the available alkali released by lime-pozzolan paste prepared with pozzolans meeting the requirements of CRD-C 262, Corps of Engineers Specifications for Pozzolan for Use in Portland Cement Concrete.<sup>2</sup>

4. This report describes the materials tested, test methods used, results obtained, and conclusions derived therefrom.

### Materials and Test Methods

#### Materials

5. Pozzolans. From the many pozzolans available for use, six (four natural and two fly ash) were selected and identified as follows:

- a. Volcanic cinders (Vol C)
- b. Calcined Keasey Shale (CK Sh)
- c. Calcined Diatomaceous Shale (CD Sh)
- d. Calcined Tuff (CT)
- e. Fly Ash (FA I)
- f. Fly Ash (FA II)

6. Each pozzolan was blended in a one-quart blender for four hours. Approximately 150 grams of each material was placed in a sealed jar and retained for chemical analysis and preparation of lime-pozzolan paste for determination of available alkali. The remaining portion was placed in a plastic bag, sealed, and retained for use in the preparation of physical test specimens.

7. Lime. The lime conformed with the requirements of ASTM Designation C6-49, "Standard Specifications for Normal Finishing Hydrated Lime."<sup>4</sup>



8. Cement. The cement conformed with the requirements of CRD-C 200, "Federal Specification Cement, Portland."<sup>2</sup>

### Test Methods

9. Tests conducted on each pozzolan were as follows:

- a. Evaluation of each material for compliance with the requirements of CRD-C 262.<sup>2</sup>
- b. Determination of the total acid soluble alkali in accordance with the procedure outlined in CRD-C 209, Method 1401.1 para 4.1.<sup>2</sup>
- c. Determination of water soluble alkali in accordance with the procedure outlined in ASTM C 114, "Chemical Analysis of Hydraulic Cement."<sup>5</sup>
- d. The available alkali of lime-pozzolan paste was determined in accordance with the procedure outlined in CRD-C 263. Three rounds of test were conducted, a round consisting of the determination of the available alkali of each lime-pozzolan paste after exposure to the following storage conditions:

Condition 1, 28 days @ 38 C (Standard Condition)  
Condition 2, 7 days @ 38 C  
Condition 3, 7 days @ 65.5 C

### Presentation and Analyses of Test Results

10. The results of tests for compliance with CRD-C 262, acid soluble alkali,\* and water soluble alkali are shown in table 1.

- a. All the pozzolans, except the CK Sh and CT, met the requirements of CRD-C 262. The CK Sh and CT failed to comply with the minimum 75 percent of control for pozzolanic strength of cement-pozzolan mortar at 28 days.

---

\* The method used was that used for cement. In order to determine the total alkali content of a pozzolan, the material must be rendered soluble by fusion with ammonium chloride and calcium carbonate or some other appropriate material.

- b. The test for acid soluble and water soluble alkali is not required for specification compliance and the results obtained failed to indicate any correlation with the alkali release of the pozzolans.

11. The results of tests for available alkali of lime-pozzolan mixtures stored at three conditions of temperature and/or time are shown in table 2.

- a. All six pozzolans met the specifications requirement of 1.5 percent maximum for available alkali, calculated as  $\text{Na}_2\text{O}$ , after exposure to the three storage conditions.
- b. All pozzolans, except CT, stored at a temperature of 65.5 C for seven days, produced available alkali values in excess of two-thirds of the value obtained under standard conditions of storage.
- c. The available alkali value for CT was lower for the seven-day 65.5 C storage condition than the values obtained for the other two storage conditions.

12. The anomalous results for available alkali obtained for pozzolan CT prompted an examination of that material by X-ray diffraction. This study indicated the CT material to be composed of volcanic glass, a zeolite of the clinoptilolite-heulandite type, potassium feldspar, plagioclase feldspar, and quartz. The behavior of the CT material in the lime-pozzolan paste indicates that at the 38 C storage temperature there is an early reaction in which calcium exchanges potassium and sodium out of the zeolite. This results from the high calcium concentration of the liquid phase in the initial stage. However, it appears that at the 38 C storage temperature the potassium and sodium concentration never becomes high enough in the liquid phase to drive the calcium out of the zeolite, therefore, a fairly high water-soluble alkali content is indicated at seven days. The increase in water-soluble alkali from seven days to 28 days represents either slow

progress of the pozzolanic reaction or the additional exchange of calcium for potassium and sodium. At 65.5 C storage temperature the diffusion rates are more rapid and this is particularly true for the monovalent cations which have larger diffusion rates. Thus if the early calcium for potassium and sodium exchange takes place, the reverse exchange takes place to a more complete extent and less water-soluble alkali is available at seven days.

### Conclusions

13. Most pozzolans that produce an available alkali content of less than 1.0 percent when stored under Condition 3 would be expected to meet the specification requirement of 1.5 percent maximum when stored under Condition 1. Method 3 allows the completion of the test for available alkali in seven days and is recommended as an optional method in the acceptance testing of fly ash pozzolans. Method 3 is also recommended as an optional method for testing natural pozzolans which have been shown not to contain a zeolite.

### Literature Cited

1. Department of the Army, Office, Chief of Engineers, "Standard Guide Specifications for Concrete," CE 1401.01.
2. U. S. Army Engineer Waterways Experiment Station, CE, Handbook for Concrete and Cement, August 1949 (with Quarterly Supplements), Vicksburg, Miss.
3. Department of the Army, Office, Chief of Engineers, ER 1110-1-3100, "Laboratory Investigation and Material Testing for Military and Civil Works Construction Projects."
4. ASTM, "Standard Specification for Normal Finishing Hydrated Lime," Designation C6-49, 1968 Book of ASTM Standards, Part 9, 1968, Philadelphia, Pa.
5. ASTM, "Chemical Analysis of Hydraulic Cement," Designation C 114, 1968 Book of ASTM Standards, Part 9, 1968, Philadelphia, Pa.

TABLE 1

Results of Chemical Tests of Pozzolans, Percent

<u>Sample</u>	<u>Loss on Ignition</u>	<u>Moisture</u>	<u>SO<sub>3</sub></u>	<u>SiO<sub>2</sub></u>	<u>R<sub>2</sub>O<sub>3</sub></u>	<u>SiO<sub>2</sub> + R<sub>2</sub>O<sub>3</sub></u>	<u>CaO</u>	<u>MgO</u>	<u>Acid Sol. Alkali</u>			<u>Water Sol. Alk. Total as Na<sub>2</sub>O</u>
									<u>Total as Na<sub>2</sub>O</u>	<u>Na<sub>2</sub>O</u>	<u>K<sub>2</sub>O</u>	
Vol. C	1.69	0.29	0.38	54.2	22.6	76.8	9.9	3.1	0.52	0.43	0.14	0.016
CK Sh	1.28	0.62	0.17	61.7	26.2	87.9	5.0	2.9	0.42	0.25	0.26	0.019
CD Sh	1.76	0.33	2.88	60.1	22.9	83.0	8.1	2.5	0.32	0.17	0.23	0.009
CT	2.11	1.99	0.04	71.3	16.2	87.5	3.1	0.2	1.89	0.44	2.20	0.032
FA I	3.56	0.13	0.85	51.3	35.6	86.9	2.9	1.3	0.17	0.07	0.15	0.012
FA II	1.38	0.13	2.02	49.3	38.4	87.7	7.3	1.1	0.45	0.28	0.26	0.063

TABLE 2

Results of Physical Tests of Pozzolans

<u>Sample</u>	<u>Specific Gravity</u>	<u>Fineness Sq cm/cc</u>	<u>Water-Req. Increase in Flow %</u>	<u>Lime-Pozz Strength, psi*</u>	<u>Soundness Autoclave Exp., %</u>	<u>Pozz Activity % of Control</u>	<u>Incr. in Drying Shrinkage</u>
Vol C	2.71	20,135	32	1095	-0.01	86	0.004
CK Sh	2.52	24,075	3	1300	-0.02	74**	0.006
CD Sh	2.61	29,825	17	1830	-0.03	87	0.008
CT	2.34	28,190	8	930	0.02	73**	0.018
FA I	2.23	8,240	21	1330	0.01	94	
FA II	2.52	7,935	23	1155	0.01	92	

\*  $\text{psi} \times 0.006894757 = \text{MPa}$

\*\* Failed to meet the minimum requirement of 75 percent.

TABLE 3

Results of Tests for Available Alkali of Pozzolans

Sample Symbol	Storage Conditions of Lime-Pozzolan Paste					
	Condition #1		Condition #2		Condition #3	
	28 days at 38 C		7 days at 38 C		7 days at 65.5 C	
	Av. %	Std. Dev.	Av. %	Std. Dev.	Av. %	Std. Dev.
Vol C	1.43	0.065	0.64	0.053	1.01	0.040
CK Sh	0.57	0.035	0.29	0.047	0.48	0.029
CD Sh	0.73	0.035	0.48	0.024	0.67	0.018
CT	0.93	0.024	0.86	0.044	0.48	0.019
FA I	0.81	0.120	0.11	0.012	0.76	0.035
FA II	1.13	0.071	0.27	0.024	0.80	0.012



Unclassified  
Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) U. S. Army Engineer Waterways Experiment Station Vicksburg, Mississippi		2a. REPORT SECURITY CLASSIFICATION Unclassified	
		2b. GROUP	
3. REPORT TITLE INVESTIGATION OF ACCELERATED METHODS FOR THE DETERMINATION OF AVAILABLE ALKALI IN POZZOLANS			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Final report			
5. AUTHOR(S) (First name, middle initial, last name) William G. Miller			
6. REPORT DATE February 1974		7a. TOTAL NO. OF PAGES 13	7b. NO. OF REFS 5
8a. CONTRACT OR GRANT NO.		9a. ORIGINATOR'S REPORT NUMBER(S) Miscellaneous Paper C-74-1	
b. PROJECT NO.		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
c.			
d.			
10. DISTRIBUTION STATEMENT Approved for public release; distribution unlimited.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY	
13. ABSTRACT The procedure specified in acceptance testing of pozzolans for the determination of the available alkali released by a pozzolan requires the lime-pozzolan paste to be stored for a period of 28 days prior to test. In order to investigate the possibility of reducing the storage time of the paste prior to test, six pozzolans were tested for available alkali release rate by subjecting the paste to three conditions of storage time and/or temperature. The three conditions were as follows: a. Condition 1, Standard Condition, 28 days at 38 C; b. Condition 2, seven days at 38 C; c. Condition 3, seven days at 65.5 C. The results of these tests are as follows: a. The highest available alkali values for all pozzolans were obtained under Storage Condition 1. b. All pozzolans, except calcined tuff, produced higher values for Condition 3 than for Condition 2. c. All pozzolans, except calcined tuff, produced available alkali values for Condition 3 that were in excess of two-thirds of the values produced for Condition 1. Results of this study indicate that if the available alkali value of a pozzolan is 1.0 percent or less when the paste is stored at 65.5 C for seven days, the maximum specification limit of 1.5 percent will not be exceeded when the pozzolan is evaluated by the present Standard Condition, 28 days at 38 C. In order to reduce the storage time of the lime-pozzolan paste to seven days, storage Condition 3 with a maximum limit of 1.0 percent available alkali is recommended as an optional method for the acceptance testing of pozzolan.			

DD FORM 1473

1 NOV 66

REPLACES DD FORM 1473, 1 JAN 64, WHICH IS OBSOLETE FOR ARMY USE.

Unclassified  
Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Acceptance tests Alkalies Lime-pozzolan pastes Pozzolans						

In accordance with ER 70-2-3, paragraph 6c(1)(b), dated 15 February 1973, a facsimile catalog card in Library of Congress format is reproduced below.

Miller, William G

Investigation of accelerated methods for the determination of available alkali in pozzolans, by W. G. Miller. Vicksburg, U. S. Army Engineer Waterways Experiment Station, 1974.

1 v. (various pagings) illus. 27 cm. (U. S. Waterways Experiment Station. Miscellaneous paper C-74-1)

Sponsored by Office, Chief of Engineers, U. S. Army.  
Includes bibliography.

1. Acceptance tests. 2. Alkalies. 3. Lime-pozzolan pastes. 4. Pozzolans. I. U. S. Army. Corps of Engineers. (Series: U. S. Waterways Experiment Station, Vicksburg, Miss. Miscellaneous paper C-74-1)  
TA7.W34m no.C-74-1