MISCELLANEOUS PAPER C-76-5

DETECTION OF CALCIUM SULFATES AND MAGNESIUM OXIDE IN FLY ASH BY X-RAY DIFFRACTION

by

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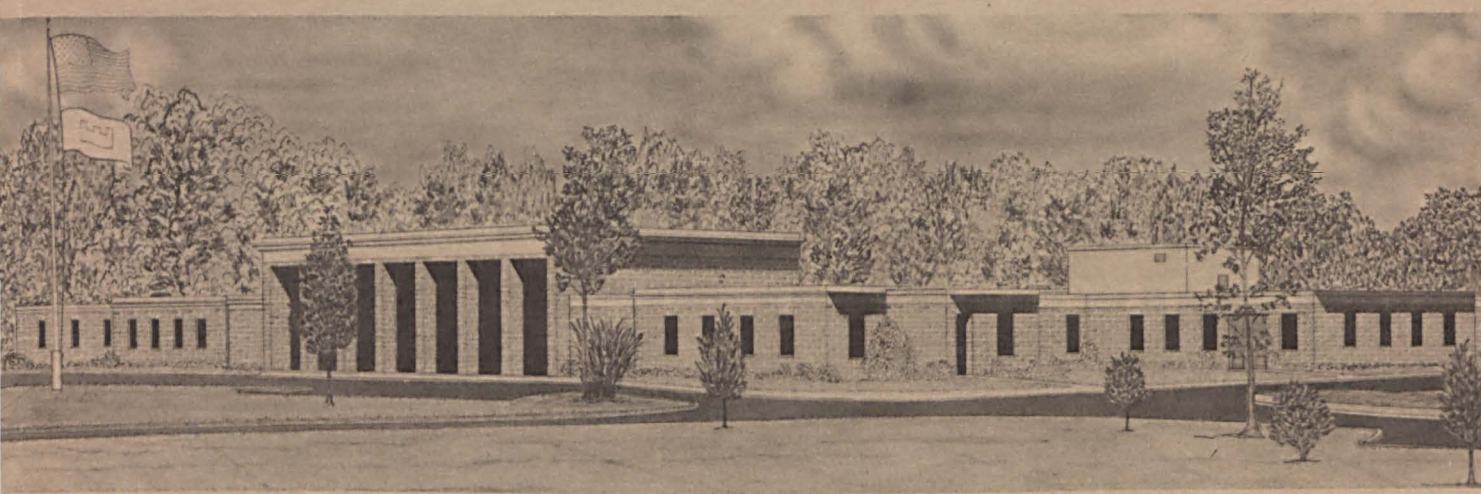
June 1976
Final Report



Prepared for Assistant Secretary of the Army (R&D), Department of the Army
Washington, D. C. 20314

Under Project 4A061101A91D

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: Miscellaneous Paper C-76-5
2. GOVT ACCESSION NO.:
3. RECIPIENT'S CATALOG NUMBER:

4. TITLE (and Subtitle): DETECTION OF CALCIUM SULFATES AND MAGNESIUM OXIDE IN FLY ASH BY X-RAY DIFFRACTION

5. TYPE OF REPORT & PERIOD COVERED: Final report

6. PERFORMING ORG. REPORT NUMBER:

7. AUTHOR(s): Ging S. Wong
Alan D. Buck

8. CONTRACT OR GRANT NUMBER(s):

9. PERFORMING ORGANIZATION NAME AND ADDRESS
U. S. Army Engineer Waterways Experiment Station
Concrete Laboratory
P. O. Box 631, Vicksburg, Miss. 39180

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS:

11. CONTROLLING OFFICE NAME AND ADDRESS
Assistant Secretary of the Army (R&D),
Department of the Army,
Washington, D. C. 20314

12. REPORT DATE: June 1976

13. NUMBER OF PAGES: 15

14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office):

15. SECURITY CLASS. (of this report): Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE:

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Calcium sulfates
Fly ash
Magnesium oxides
X-ray diffraction

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

It was suspected that processes used to reduce the sulfur content of flue gases at coal burning power plants might introduce undesirable amounts of calcium sulfates or other constituents into the fly ash collected for use as an ingredient of concrete.

A procedure was developed to detect rapidly by quantitative X-ray diffraction the presence and amount of magnesium oxide (periclase) or calcium

(Continued)

20. ABSTRACT (Continued).

sulfate (anhydrite) in fly ash. This procedure was found to be capable of detecting these constituents in amounts as low as 0.25 percent by weight.

Samples of material collected at six power plants using each of three flue gas desulfurization processes were examined. They all were found to contain calcium sulfate and all but one contained calcium sulfite. The constituents could be undesirable in material being added to portland-cement concrete if present in significant amounts.

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PREFACE

This project was funded by Department of the Army Project 4A061101A91D, "In-House Laboratory Independent Research Program," sponsored by the Assistant Secretary of the Army (R&D).

This study was conducted at the U. S. Army Engineer Waterways Experiment Station (WES) Concrete Laboratory (CL) during the period September 1974 through June 1976 under the supervision of Messrs. Bryant Mather and Leonard Pepper and Mrs. Katharine Mather. This report was prepared by Mr. G. S. Wong with the assistance of Mr. A. D. Buck.

The Director of WES during the investigation and the preparation and publication of this report was COL G. H. Hilt, CE. The Technical Director was Mr. F. R. Brown.

CONTENTS

DETECTION OF CALCIUM SULFATES AND MAGNESIUM OXIDE IN FLY ASH BY X-RAY DIFFRACTION

PART I: INTRODUCTION

1. The need to reduce emissions of gases containing sulfur from power plants into the atmosphere led to the development of methods of desulfurization of flue gases. Most of these methods have tended to retain the sulfur as a solid and disposing of it in or with the fly ash that is collected following the burning of coal to generate electricity. Since fly ash has been used as an ingredient of portland-cement concrete and probably will be more widely used as a result of energy restrictions, consideration of the possibility that the levels of calcium sulfates or magnesium oxide or both would increase in fly ash was indicated, because their presence can lead to deleterious effects in concrete.

2. The earlier systems to reduce the sulfur content of flue gas were dry processes using powdered limestone.[1] The dry limestone injection process was found to be less efficient than wet processes hence it was abandoned. Some of the newer systems that use limestone and a wet process were described by Princiotto and Ponder.[2] No one system has yet been shown to be the best so sludges from six sources were obtained, representing three processes. Characterization was done by X-ray diffraction to determine if the sludges contained calcium sulfates or magnesium oxide or both in amounts that would be detrimental to concrete if these sludges were combined with the fly ash collected. The combination seems unlikely since at present the sludges are ponded to dewater them and are considered a separate disposal problem from the fly ash.

PART II: MATERIALS AND PROCEDURES

Materials

3. Materials to be used as standards in the X-ray work were obtained and examined. The following materials were used in making synthetic mixtures for X-ray analysis:

a. Fly ash. The fly ash was required to be low in magnesium oxide (MgO) and sulfate (SO_3) by chemical analysis (Table 1). Neither MgO nor calcium sulfate occurred as crystalline phases in detectable amounts as determined by X-ray diffraction. The fly ash is identified as WES-236 F-74. A second fly ash (WES-201 F-74) was also studied.

b. Magnesium oxide (MgO). The magnesium oxide (periclase) used was AD-498 from W. J. Foley, General Refractories Co., Baltimore Research Center. X-ray diffraction (XRD) analysis revealed the presence of no other phases.

c. Calcium sulfate. The calcium sulfate was CD-ANH-1; it was essentially all anhydrite by X-ray diffraction.

d. Iron oxide (Fe_2O_3). The sample was hematite that was in stock; it was not found to contain other phases when examined by XRD.

e. Gypsum. The sample was in stock and was not found to contain other phases when examined by XRD.

4. The following samples were obtained from various power plants in different geographical locations in order to get a range in sample compositions from power plants that used coals with different sulfur content. In addition, the plants also used different sulfur removal systems as indicated below:

Concrete Laboratory Serial No.	Location	Flue Gas Desulfurization System	Sulfur in Coal, %*
AD-526	Alabama	Limestone wet-scrubbing	Unknown
AD-527	Illinois	Limestone wet-scrubbing	3.5
AD-528	Ohio	Double alkali	2.5
AD-529	Arizona	Limestone wet-scrubbing	0.6
AD-530	Florida, No. 1	Chiyoda	Unknown
AD-531	Florida, No. 2	Double alkali	Unknown

* Provided by power plants.

Test Procedures

5. A GE-700 X-ray diffractometer was used with nickel-filtered copper radiation. A differential thermal analyzer (DTA) was used.

6. The first part of the work was to determine the minimum concentrations of calcium sulfate and magnesium oxide that would be detectable in typical fly ash by X-ray diffraction. This was done by adding known amounts of these materials to fly ash WES-236 F-74, blending the mixtures, obtaining X-ray intensities, and making claibration curves of X-ray intensity versus amount of MgO and calcium sulfates.

7. These mixtures were prepared and examined as described by Buck.[3] The components of the mixtures were ground to pass a 45 micrometre sieve (No. 325), put into acetone, blended in a Patterson-Kelly blender for 24 hours and dried under a heat lamp until they were free-flowing. The mixture proportions are given in Table 2. The X-ray diffractometer was standardized daily before operation by the use of an external standard (novaculite), to insure uniformity in the diffractometer output. The mixtures were back-packed into 3-in. aluminum holders to minimize preferred orientation and then X-rayed. Each mixture was packed three times and the average peak intensities were used in the quantitative analysis.

The X-ray diffraction peaks used in the quantitative analysis are listed below:

Mineral Names	Approximate Peak Position, Angstroms (A)*
Periclase	2.11
Anhydrite	3.50
Gypsum	7.56

* Approximate peak positions are given because back-packed specimens are less reliable in spacings but more reliable in intensities, which were the more important measurements.

PART III: DISCUSSION OF TEST

8. The different amounts of fly ash in the synthetic mixtures caused the backgrounds on the diffraction patterns to differ. This difference in background intensities caused the calcium sulfate and magnesium oxide X-ray peak intensities also to differ so that the peak intensities could not be used for quantitative X-ray analysis. The pattern background was adjusted to close similarity by the addition of iron oxide to the mixtures. The results of the bracketing mixtures are shown in Figures 1 and 2.

9. The second part of the work was to examine several samples from field installations by X-ray diffraction to determine if they contained detectable amounts of calcium sulfates or magnesium oxide.

10. The six field samples from the power plants were moist when received. Each sample was air dried, ground to pass a 45 micrometre sieve (No. 325), back-packed in a 3-in. sample holder, and then examined by X-ray diffraction.

11. The samples from power plants using limestone scrubbing contained some unreacted limestone. The amount of this unreacted limestone was determined only for the Alabama sample; it was ground to pass a No. 200 sieve and the amount of limestone was determined using differential thermal analysis with suitable calibration data.

PART IV: RESULTS

12. It was found that calcium sulfate as anhydrite and magnesium oxide as periclase could be detected in the synthetic mixtures by X-ray diffraction at levels as low as 0.25 percent by weight using the calibration curves (Figures 1, 2). Figure 1 can be used to determine the amount of calcium sulfate as anhydrite in fly ash. Figure 2 can be used to determine the amount of periclase in fly ash. The limits of detection are raised as the background is increased but the limits of detection remain well within the range required for screening the materials for periclase and calcium sulfate. The calibration curves apply to fly ash that is collected by electrostatic precipitators.

13. Two fly ashes (WES- 236 F-74 with 0.6 percent MgO and 0.8 percent SO_3 and WES-201 F-74 with 1.4 percent MgO and 1.0 percent SO_3) were examined by X-ray diffraction. The MgO and SO_3 were not detected as crystalline components in either of these samples.

14. The qualitative composition of the six field samples is shown in Table 3. None of the samples contained periclase or anhydrite, but all contained some calcite and gypsum. Gypsum is $CaSO_4 \cdot 2H_2O$. Only the sludge from the Chiyoda process did not contain calcium sulfite ($CaSO_3 \cdot 1/2H_2O$) or the unidentified compound with the 5.30 A spacing which may be $CaSO_3$. The sample from Alabama was the only sample to contain dolomite; it was part of the original carbonate rock used in the scrubber. About 20 to 30 percent of this sample was unreacted calcite, estimated by DTA.

PART V: CONCLUSIONS

15. This project was developed with the concept that limestone injection would prove to be a practical method of desulfurizing flue gases in coal-fired electrical generating stations. Limestone injection did not develop as a practical approach and was abandoned. The method of quantitative mineralogical analyses by X-ray diffraction[3] was found to be suitable for determining small amounts of synthetic periclase or anhydrite.

16. The six field samples of sludges from wet processes of flue gas desulfurization all contained gypsum, all but one contained calcium sulfite, and some contained sodium sulfate and calcium sulfate hemihydrate (Table 3). If several of these sludges were dried and combined with fly ash they would introduce an undesirable amount of sulfate, sulfite, and in some cases sodium, which could be undesirable constituents of fly ash for use in concrete. Since the sludges are difficult to dry and have been considered as waste products, they probably will not be recombined with fly ash. The samples came from widely separated power plants and represent three processes for desulfurizing flue gases.

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2. Princiotta, F. T., and Ponder, W. H., Current Status of SO_2 Control Technology, presented at the Lawrence Berkeley Laboratory Seminar entitled "Sulfur, Energy and Environment," U. S. Environmental Protection Agency, Apr 1974.

3. Buck, A. D., "Quantitative Mineralogical Analysis by X-Ray Diffraction," Miscellaneous Paper No. 3-72-2, Feb 1972, U. S. Army Engineer Waterways Experiment Station, CE, Vicksburg, Miss.

Table 1

Partial Chemical Composition of Fly Ash

WES-236 F-74

Chemical Constituent	Percent
$SiO_2 + Al_2O_3 + Fe_2O_3$	89.6
MgO	0.6
SO_3	0.8

Table 2

Mixture Proportions for Synthetic Mixtures*

Mixture	Fly Ash WES-236 F-74	$CaSO_4$ (Anhydrite)	MgO (Periclase)	Fe_2O_3 (Hematite)
1	98.0	1.0	1.0	0.0
2	98.0	0.5	1.5	0.0
3	94.0	3.0	3.0	0.0
4	90.0	5.0	5.0	0.0
5	99.5	0.25	0.25	0.0
6	97.0	0.5	1.5	1.0
7	92.0	3.0	3.0	2.0
8	87.0	5.0	5.0	3.0

* By weight.

Table 3

Composition of Six Field Samples of Fly Ash Sludge by X-Ray Diffraction

Mineral Constituents	Samples					
	Limestone Wet Scrubbing			Double Alkali		Chiyoda
	AD-526	AD-527	AD-529	AD-528	AD-531	AD-530
Gypsum	X	X	X	X	X	X
Calcium sulfite ($CaSO_3 \cdot 0.5H_2O$)	X	X	X	X	X	*
Na_2SO_4	X	*	*	X	*	*
Hemihydrate	*	*	*	X	*	X
$Ca(CH)_2$	*	X	*	X	*	*
Calcite	X	X	X	X	X	X
Dolomite	X	*	*	*	*	*
Quartz	X	X	X	X	*	X
Magnetite	X	*	*	*	*	*
Hematite	X	*	*	*	*	*
Mullite	*	*	*	X	*	*
Unidentified X-Ray Spacings						
5.30 A ($CaSO_3$?)	X	X	X	X	X	*
9.6 A	*	X	*	*	*	*
14 A (clay)	*	*	*	*	*	X

* Not detected.

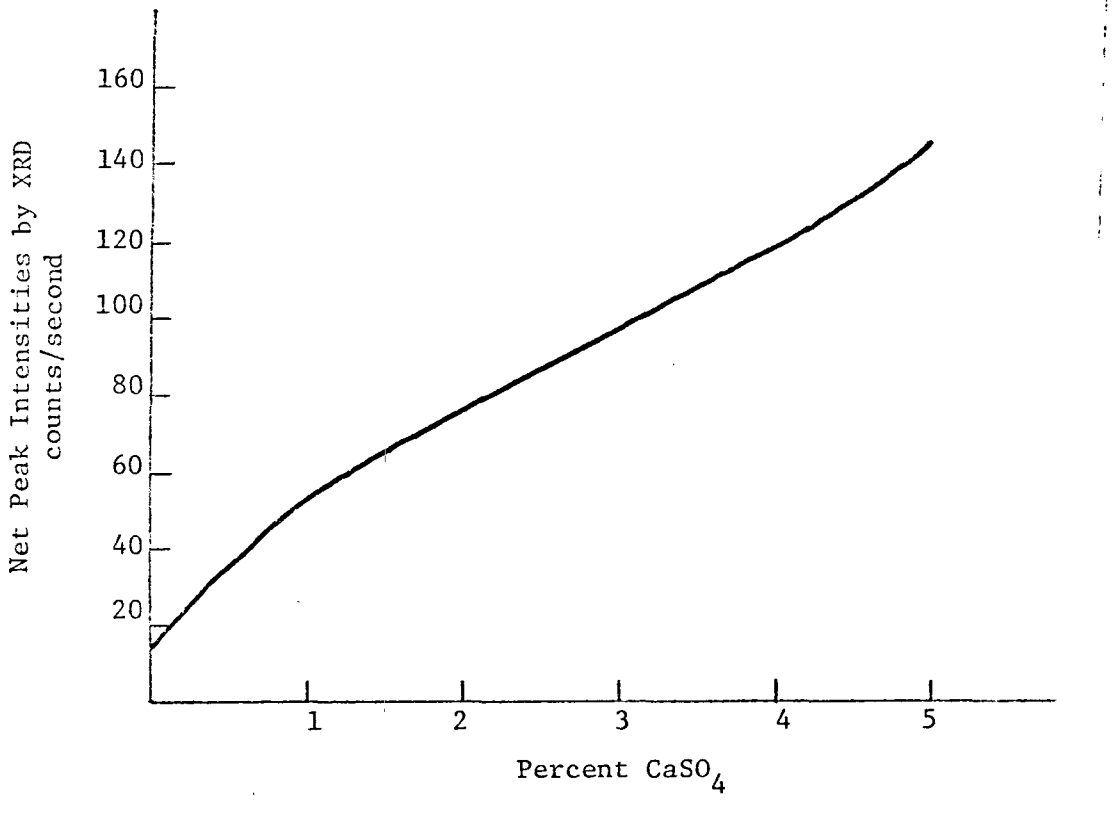

Figure 1. Calibration curve for determination of anhydrite in fly ash by X-ray diffraction.

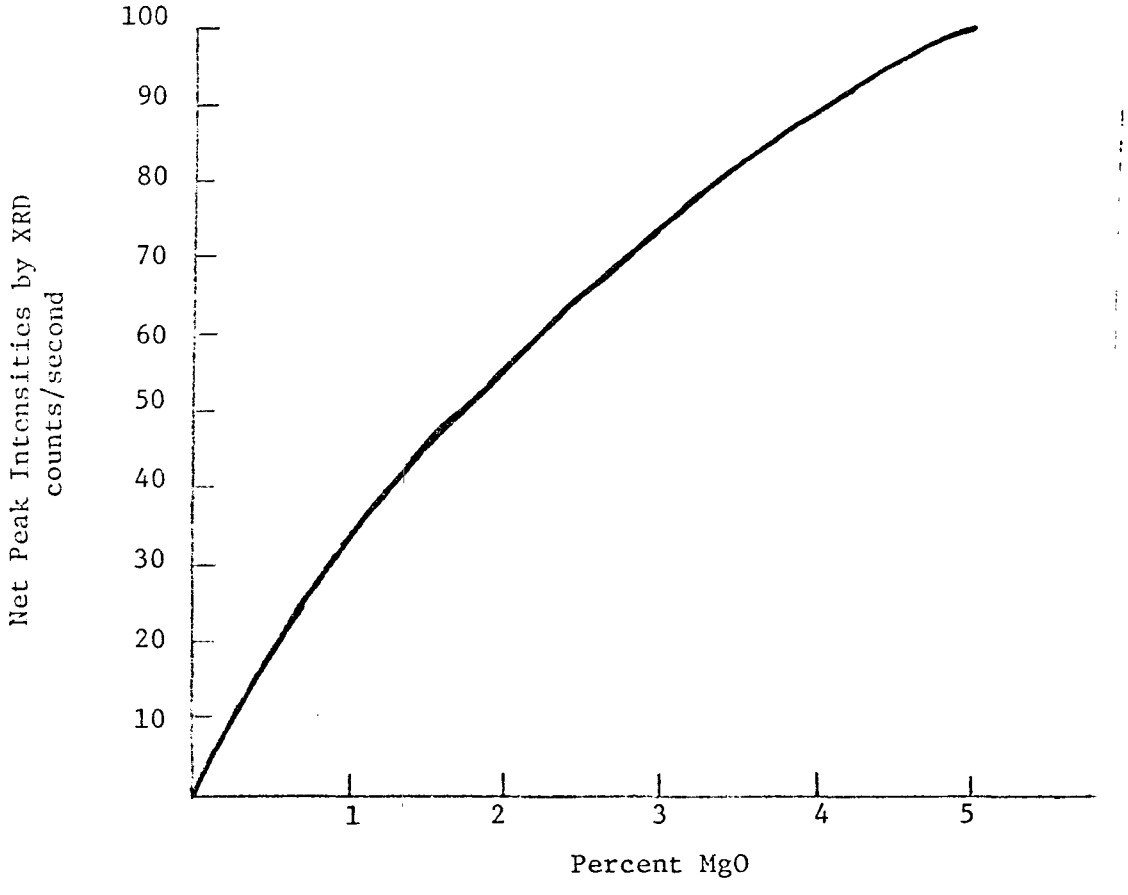

Figure 2. Calibration curve for determination of periclase in fly ash by X-ray diffraction.

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Wong, Ging S
Detection of calcium sulfates and magnesium oxide in fly ash by X-ray diffraction, by Ging S. Wong [and] Alan D. Buck. Vicksburg, U. S. Army Engineer Waterways Experiment Station, 1976.
1 v. (various pagings) illus. 27 cm. (U. S. Waterways Experiment Station. Miscellaneous paper C-76-5)
Prepared for Assistant Secretary of the Army (R&D), Department of the Army, Washington, D. C., under Project 4A061101A91D.
Includes bibliography.

1. Calcium sulfates. 2. Fly ash. 3. Magnesium oxides. 4. X-ray diffraction. I. Buck, Alan D., joint author. II. U. S. Office of the Chief of Research and Development. (Series: U. S. Waterways Experiment Station, Vicksburg, Miss. Miscellaneous paper C-76-5)
TA7.W34m no.C-76-5