AD-A132 041 STUDIES OF THE CONSTITUTION OF FLY ASH USING SELECTIVE DISSOLUTION(U) ARMY ENGINEER WATERWAYS EXPERIMENT STATION VICKSBURG MS STRUC.. A D BUCK ET AL. MAY 83 1/1

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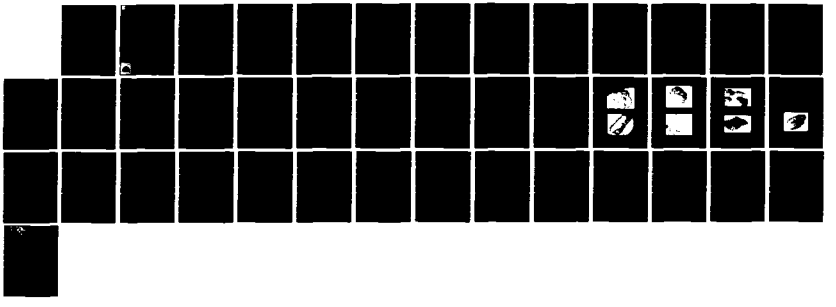

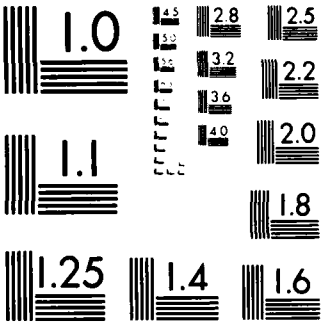

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STUDIES OF THE CONST[illegible] FLY ASH USING SELECTIVE D[illegible]

by

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US Army Corps of Engineers

US ARMY ENGINEER WATERWAYS EXPERIMENT STATION

May 1983

Final Report

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Prepared for Office of Nuclear Wa[illegible]
Battelle Memorial Inst[illegible]
Columbus, Ohio [illegible]

Under Contract DE-A[illegible]

STRUCTURES LABORATORY

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Miscellaneous Paper SL-83-5	2. GOVT ACCESSION NO. AD-A132641	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) STUDIES OF THE CONSTITUTION OF FLY ASH USING SELECTIVE DISSOLUTION		5. TYPE OF REPORT & PERIOD COVERED Final Report 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Alan D. Buck Tony B. Husbands J. Pete Burkes		8. CONTRACT OR GRANT NUMBER(s) Contract DE-A197-81ET46633 Modification M003
9. PERFORMING ORGANIZATION NAME AND ADDRESS U. S. Army Engineer Waterways Experiment Station Structures Laboratory P. O. Box 631, Vicksburg, Miss. 39180		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Nuclear Waste Isolation Battelle Memorial Institute Columbus, Ohio 43201		12. REPORT DATE May 1983 13. NUMBER OF PAGES 35
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

This is CTIAC Report No. 63. Available from National Technical Information Service, 5285 Port Royal Road, Springfield, Va. 22151.

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

Chemical dissolution	Nuclear waste
Concrete	Pozzolan
Fly ash	X-ray diffraction
Grout	

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

Selective removal of the glassy phase from a fly ash permits determination of its amount and removes it as a diluent from the fly ash residue which if not removed, interferes with identification of crystalline phases by X-ray diffraction (XRD) or other methods. We tried and evaluated several types of selective chemical dissolution to determine glass content. We used changes in [illegible] measures of amount of glass and we identified the crystalline phases in the residues by XRD or optical microscopy.

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

20. ABSTRACT (Continued).

All chemical treatments that we tried had the disadvantage that none made an absolutely clean separation between glassy and crystalline phases. The two best methods were a treatment with fluosilicic acid and one with sodium hydroxide. We present details of each method.

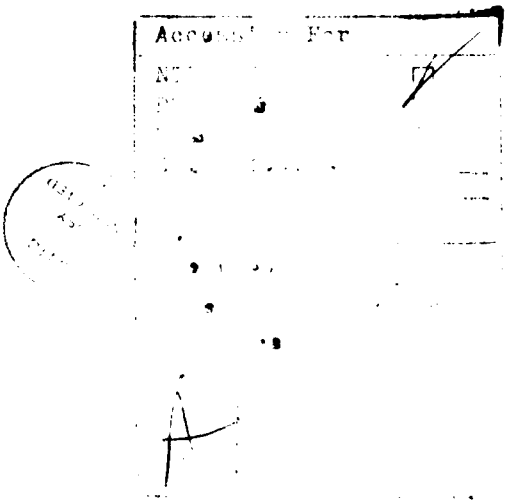
We concluded that chemical dissolution was a useful tool to estimate glass content and to assist in identification of crystalline phases. We judged the fluosilicic acid method to be the preferred procedure to estimate glass content of a fly ash. We give data for four lignite ashes, one subbituminous ash, and one bituminous ash. Glass contents ranged from 57 to 75 percent. Chemical analyses showed the presence of barium, titanium, strontium, and manganese in addition to other elements usually reported. We identified several phases similar to minerals containing these elements. It may not always be possible to determine whether a minor crystalline phase in the residue after chemical dissolution is an original mineral constituent of the coal, an original phase in the ash, or a product of the chemical treatment of the ash.

PREFACE

This work was done for the U. S. Department of Energy under Contract DE-AI97-81ET46633, Modification M003. Mr. Lynn Myers, Office of Nuclear Waste Isolation, Battelle Memorial Institute, Columbus, Ohio, 43201, was Project Manager at that time. Mr. Don Moak is now Project Manager. Funds for the publication of this report were provided from those made available for operation of the Concrete Technology Information Analysis Center (CTIAC). This is CTIAC Report No. 63.

The work was done in the Structures Laboratory (SL) of the U. S. Army Engineer Waterways Experiment Station (WES) under the direction of Mrs. Katharine Mather, Project Leader. Chief of the Structures Laboratory was Mr. Bryant Mather, and Mr. John M. Scanlon, Jr., was Chief of the Concrete Technology Division, SL. The work was done principally by Mr. Alan D. Buck, Mr. Tony B. Husbands, and Mr. J. Pete Burkes, all of whom contributed to the preparation of this report.

During the conduct of this work, Colonel Tilford C. Creel, CE, was Commander and Director of WES, and Mr. F. R. Brown was Technical Director.



CONTENTS

CONVERSION FACTORS, NON-SI TO SI (METRIC)
UNITS OF MEASUREMENT

Values in non-SI units of measurement may be converted to SI (metric) values as follows:

Non-SI Unit Multiply	By	SI Unit To Obtain
angstrom	0.1	nanometre

STUDIES OF THE CONSTITUTION OF FLY ASH USING SELECTIVE DISSOLUTION

Introduction

1. Fly ash is one of the partly glassy incombustible residue by-products of burning powdered coal in thermal generating electric plants. Fly ash including any residual unburned carbon is carried in the gas current from the boiler and trapped in electrostatic precipitators or by other means. Fly ash particles are usually spherical, small (< 45 μm), and wholly or partially glassy. The glass is the pozzolanic constituent of fly ash. X-ray diffraction (XRD) is the technique best suited for the characterization of the nonglassy (i.e., crystalline) constituents of fly ash. The use of XRD is made difficult by the presence of the glass which acts as a diluent and tends to mask the diffraction peaks by an increase of background intensity. In such cases, it is often necessary to attempt identifications of a crystalline phase based on its single strongest XRD peak. Fly ash collected at plants where anthracite or bituminous coal is burned tends to contain small amounts of quartz, mullite, magnetite, and hematite as crystalline phases. Ashes obtained by the burning of subbituminous coal or lignite often also contain calcium oxide, magnesium oxide (periclase), and calcium sulfate (anhydrite). Calcium aluminoferrite, tetracalcium trialuminate sulfate ($C_4A_3\bar{S}$),* alite (substituted C_3S), and tricalcium aluminate (C_3A) are other phases that have been at least tentatively identified in some such ashes. Quantitative data, especially for the glass content, would materially assist in predicting the behavior of an ash when used as a pozzolan.

2. Selective chemical dissolution of the glass phase along with measurement of changes in mass would serve to both measure the amount of glass and improve the XRD pattern of remaining phases.

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* $C = CaO$, $A = Al_2O_3$, $\bar{S} = SO_3$.

3. The work described in this report was done to develop a procedure by which a satisfactory measure of glass content of fly ash by selective dissolution could be made and to develop a means of obtaining glass-free ash residues for improved XRD characterization of the crystalline residues of fly ashes.

Materials

4. Two fly ashes obtained from power plants where lignite is burned were used for most of the studies. They were:

a. AD-506 from the Big Brown Plant at Fairfield, Texas.

b. AD-592(4) from the Harrington Plant at Amarillo, Texas.

5. Several other ashes were also used in the final stages of this work. They were:

a. AD-505 was an ash from the Hawthorne Plant in Kansas City, Missouri, where subbituminous coal is burned.

b. AD-510 was an ash from the Hoot Lake Plant in Fergus Falls, Minnesota, where lignite is burned.

c. AD-511 was an ash from Carterville, Georgia, where bituminous coal is burned.

d. AD-513 was an ash from the Comanche Plant in Pueblo, Colorado, where lignite is burned.

Procedure

6. The work was done in four phases as follows:

a. Phase I consisted of many different kinds of chemical treatments on different samples of ash AD-506.

b. Phase II consisted of the treatment with hydrofluoric acid (HF) that was described by Hulett et al;[1] it was done using fly ash AD-592(4).

c. Phase III was a modification of Hulett et al[1] using different acid strengths, treatment times, and cleanup procedures using fly ash AD-592(4).

d. Phase IV was a new treatment using fluosilicic acid. Treatment with sodium hydroxide solution on fly ash AD-592(4) and several other ashes (AD-505, AD-506, 510, 511, 513) was also tried.

7. In Phase I about 100 g of ash AD-506 was separated into 1.18-mm (No. 16), 600-μm (No. 30), 300-μm (No. 50), 150-μm (No. 100), 75-μm (No. 200), 45-μm (No. 325), and 38-μm (No. 400) sizes and the separated fractions were weighed. Each size fraction was then separated into magnetic and nonmagnetic fractions. The nonmagnetic fractions were used for the chemical treatments.

a. One gram of each nonmagnetic fraction smaller than the 1.18-mm (No. 16) size was treated with 100 mL of deionized water and stirred for 1 hr; the samples were then allowed to stand overnight.

b. Two-gram samples from most of the same fractions were treated with 3 M NaOH solution for 3 days at 80° C. The 300-μm (No. 50) size was not treated. The 150-μm (No. 100) size was 1 g instead of 2 g. In addition, a 2-g sample of the whole ash was treated the same way.

c. A pair of 2-g samples of the whole ash was treated with 20 percent maleic acid; one sample was stirred for 2 hr at room temperature; the other was stirred 2 hr at 52° C.

d. A pair of 1-g samples of the whole ash was treated with 25 mL of HF acid. One was treated with 5 percent HF for 24 hr at 60° C; the other was as above using 10 percent HF.

e. A 1-g sample of the whole ash was treated with 25 mL of 5 percent HF at 51° C for 1 hr with stirring.

f. A 1-g sample of the whole ash was stirred for 1 hr in dilute hydrochloric acid (HCl) (two parts acid to one part water) at 0 to 3° C.

g. The 45-μm (No. 325) size that had been treated with sodium hydroxide solution was stirred for 30 min in 500 mL of dilute HCl (one part acid to four parts water).

8. The change from size fractions to samples of the whole ash was made because the individual size fractions were too small to provide adequate residues for XRD after treatment. The samples were dried and weighed after all treatments and wered then examined by XRD. Some of the treated material was examined as grain immersion mounts with a polarizing microscope.

9. In Phase II, the nonmagnetic portions of the material larger and smaller than 45 μm of fly ash AD-592(4) were used. The method of Hulett et al[1] calls for treatment of 100 mg of nonmagnetic material in

the 100- to 200-μm size in 10 mL of 1 percent HF for 16 hr. This method was followed except for the sieve sizes as stated and that 200 mg of sample in 20 mL of acid or 400 mg in 40 mL of acid were used to provide more residue for XRD. This procedure calls for elaborate cleanup using five chemical treatments consisting of two acids, two EDTA solutions, and ammonium hydroxide. The residue is also washed seven times with distilled water between the different chemical treatments.

10. In Phase III the nonmagnetic portion of the material finer than 45 μm (No. 325) from fly ash AD-592(4) was used. The method of Hulett et al[1] was followed with variation of acid strength, or treatment time, or cleanup procedure, or combinations of these.

11. The Phase IV details of the method of treatment of fly ash with fluosilicic acid and with sodium hydroxide are given in Appendices A and B. A supplementary treatment to verify and measure the carbon in ash AD-511 residue after the sodium hydroxide treatment consisted of heating at 850° C for 2 hr. In other cases, loss-on-ignition results from standard testing were used as a measure of carbon content.

12. All XRD patterns were made with a diffractometer using nickel-filtered copper radiation. When the amount of sample was adequate, the powder was placed in the cavity of a standard sample holder, pressed, and XRD patterns were made. When the amount of sample was not adequate for this procedure, it was slurried with alcohol, spread on aluminum slides to dry, or sprinkled on adhesive tape and XRD patterns were made of the resulting sample films. In one case the sample was spread on a quartz crystal surface before XRD examination.

Results

13. In general, the Phase I treatments of portions of fly ash AD-506 were not satisfactory because significant amounts of new phases were formed. This meant that changes in mass could not be used to determine glass content and that XRD patterns of treated residues were often more complex rather than simplified. The only treatment that showed

promise was use of dilute HCl to clean up the residue after the treatment of ash with sodium hydroxide solution. This will be discussed later.

14. Use of the method of Hulett et al[1] on the nonmagnetic portions of fly ash AD-592(4) in Phase II showed more promise in that the treated residues did not contain new phases so changes in mass could be useful. However, since the method essentially removed all crystalline phases except quartz, mullite, hematite, and sphene from the ash but did not remove all of the glass, it was not judged to be fully satisfactory for the intended purpose. This method actually removed more material from an ash than any of the other methods that were tried, hence it resulted in the smallest amount of insoluble residue after treatment.

15. Modification of the method of Hulett et al[1] in Phase III showed promise but still seemed not quite what was wanted at that time. It was concluded that treatment for 3 instead of 16 hr was adequate, that if lumps formed during the treatment, they should be disaggregated, and that a simplified cleanup treatment consisting of 30 min in 2 percent boric acid, followed by 30 min in dilute HCl, washing, and centrifuging was adequate. This method gave about the same amount of insoluble residue as the Phase IV treatment with fluosilicic acid.

16. One of the problems was that all of the treatments that attacked glass also attacked water-soluble phases as calcium oxide, $C_4A_3\bar{S}$, and anhydrite so that mass change data included both glass and water-soluble crystalline phases. Thus, no direct measure of glass content was available. It was apparent that if a separate measure of the amount of water-soluble crystalline phases was made by treatment with water, then these data could be used to modify the other mass change data to obtain a measure of glass content. The difficulty with this is that since some of the water-soluble phases are encased in glass, multiple treatments with grinding between treatments to expose these phases to water are needed.

17. One of the positive findings was that good removal of magnetic material was possible by use of a magnetic stirrer in a beaker

containing the ash sample in acetone. This procedure is quick and coupled with measurements of mass gives good results. The actual procedure is as follows:

a. Place 50 to 60 g of the ash in a 1-L beaker with 500 mL of acetone.

b. The beaker is placed on a magnetic stirrer with a magnetic stirring bar in the beaker; commence stirring.

c. While the sample is being stirred, a hand-held activated magnet is slowly moved through the liquid.

d. About every 30 sec, the magnet is removed from the acetone, allowed to dry for a few seconds, and then deactivated so the magnetic material is dropped into a petri dish. This is repeated until there is no longer any appreciable amount of magnetic material caught by the activated magnet.

e. The magnetic stirring bar is then removed from the beaker and allowed to dry by evaporation. The magnetic material clinging to it is removed and placed into the petri dish. The accumulated mass of the magnetic material is determined and these results provide a good estimate of the amount of magnetic material in the ash. XRD showed the magnetic material in the ashes studied is almost wholly magnetite.

Description of fly ashes

18. General. Several items of interest were apparent as the result of the work that was done; these included:

a. It was found that some of these fly ashes contained appreciable amounts of titanium, barium, strontium, and manganese. These specific elements are not usually included in a routine analysis. The amounts of these four elements are included along with the general chemical analyses for these ashes in Table 1.

b. Fly ashes collected at plants where lignite and subbituminous coal is burned tend to contain more and different crystalline phases than the quartz, mullite, hematite, and magnetite common to almost all ashes. Calcium oxide, anhydrite, periclase, and tetracalcium trialuminate sulfate (C_4A_3S) are probably the most striking differences. In addition, crystalline phases that were identified for the first time included the titanium minerals rutile, perovskite, and titanite (sphene), barium sulfate (barite), and zircon. The basis for much of these tentative identifications was correlation of the presence of maximum

amounts of the elements titanium or barium or strontium or combinations of these in an ash with one or more weak peaks in an XRD pattern of that ash plus any optical properties that could be determined with a polarizing microscope. Zircon was identified solely by microscope on the basis of appearance and high index of refraction. Barite in ash AD-510 with the highest barium content of the six ashes was identified on the basis of a weak XRD peak at about 3.42 A in the water-insoluble residue; this is similar to the strongest peak for barite. The other ashes with less barium did not show this peak in the untreated ash; the fact that the 3.42 A peak was a little short was considered as probably indicative of substitution, perhaps of some strontium for barium in the barite. The fact that acid treatment destroyed this peak while hydroxide treatment strengthened it was considered proper for barite. It was not possible to be positive of such identifications or that these always represented original phases rather than phases due to chemical treatment, but they were considered reasonable identifications of probable original phases. Calculated compositions and listings of crystalline phases identified in whole ashes, acid residues, and sodium hydroxide residues are given in Tables 2 through 7. Tables 2 through 5 are for the four ashes (AD-506, 510, 513, 592(4)) produced at plants burning lignite; Table 6 is for the ash (AD-505) from the plant burning subbituminous coal; Table 7 is for the ash (AD-511) from the plant burning bituminous coal.

c. XRD of the magnetic and nonmagnetic portions of a fly ash after the separation described earlier showed that while the separation was good, it was not perfect. This is to be expected since some of the magnetite and other phases are fused together and thus impossible to separate mechanically.

d. The residues from two treatments, the modified Hulett et al[1] with hydrofluoric acid and using fluosilicic acid, were similar. Both the XRD examination and the examination of grain mounts with an optical microscope gave almost identical results; the main difference being that some fluoride hydrates were formed by the fluosilicic acid treatment and were not removed by the cleanup procedure. The fluoride hydrates were identified by a broad line at approximately 4.9 A on the XRD patterns. The full Hulett et al[1] treatment with HF acid removed more material from an ash than the fluosilicic acid treatment. Comparison indicated the additional material that was removed was largely crystalline phases. The fluosilicic acid method is simpler to use because of the simpler cleanup procedure but has the drawback of creating small amounts

of new fluorine-bearing phases. Examination of residues obtained by the two kinds of acid treatments (modified Hulett et al,[1] fluosilicic) are described together because of the similarity of results.

e. Treatments with sodium hydroxide always left more glass in the residue than the acid treatments. The XRD examinations of the residue after sodium hydroxide treatment gave a complex pattern. Several phases were identified in the residues that were either made by the treatment or were present in the as-received ash and were destroyed by the fluosilicic and hydrofluoric acid treatments. This residue always had more colored particles with birefringence from the residue from acid treatments, indicating more crystalline phases present. Quartz, mullite, and hematite appeared similar to the appearance of these same phases after the acid residues. The glassy particles remaining in the residue after sodium hydroxide treatment were usually those with a higher index of refraction.

f. It was noted that there were more colored particles in the lignite and subbituminous ashes than in the bituminous ash; these colored particles tended to be crystalline.

g. Spherical particles that included both crystalline and glassy material comprised the major portion of all of the as-recieved ashes. Some of the spherical particles were hollow. Carbon particles that were blocky and vesicular or lathlike were present in each ash. Blocky and lathlike quartz particles dominated the crystalline material in each ash.

h. The bituminous ash (AD-511) contained the most quartz, hematite, and magnetite. It and the subbituminous ash (AD-505) contained the most carbon (Tables 2 through 7).

19. Lignite fly ash AD-592(4).

a. The phases believed to be present in this fly ash and the amounts of glass with index of refraction data, water-soluble and water-insoluble crystalline phases, and carbon are shown in Table 5. Specific comments follow:

(1) As-received ash. Earlier comments about all ashes apply here. Colors of individual glassy spheres ranged from clear to shades of light green, light yellow, orange, and brown. The glass had a range in index of refraction from 1.500 to 1.740. Many of the quartz grains in the sample were covered with a thin glassy shell; this shell or rim was known to be present by the fact that grains that were recognizably quartz in immersion mounts had a refractive index of about 1.500 in all possible orientations;

this index is too low for quartz. A particle that is believed to be quartz with a glassy rim and smaller glass spheres fused to its surface is shown in Fig. 1. While this quartz particle is actually from ash AD-513, it is typical of those found only in ashes AD-513 and AD-592(4) of this group of six ashes. The presence of rutile was suggested by an XRD peak; perovskite and titanite were tentatively identified in immersion mounts. These titanium minerals are discussed in more detail in later paragraphs.

(2) Residue after treatment with fluosilicic acid or hydrofluoric acid (modified Hulett et al[1] method).

(a) Quartz and mullite were the major phases in the residue. Quartz was usually blocky or irregular, often the grains were pitted and had grooves or canals in the surface (Fig. 2). This was probably caused by partial melting of the quartz during combustion of the coal. In some instances the glassy shell had not been completely removed by the chemical treatment. Mullite had radiating or acicular morphology. Vesicular spheres of acicular mullite were often seen with the polarizing microscope or scanning electron microscope (SEM). Fig. 3 and 4 are scanning electron micrographs of such a vesicular, spherical particle with acicular mullite; it is typical of all the fly ash residues tested.

(b) Hematite was the next most abundant phase found in the residue. Most of the hematite was present as spherical or blocky particles.

(c) Titanium minerals. This ash was higher in titanium than any of the others examined. Rutile was tentatively identified by a 2.48-A XRD peak which is third strongest for this mineral but was not interferred with by other peaks in this XRD pattern. Perovskite was tentatively identified by an orange color and high index of refraction of grains in immersion mounts. Titanite (sphene) was tentatively identified in all chemically treated residues. Most of it was tiny spherical particles with a high index of refraction. Occasionally, a grain showed the diagnostic wedge-shaped or diamond-shaped feature of titanite (Fig. 5, 6). The spherical particles were nearly always about 1 μm to 7 μm in diameter. They had

birefringence up to first order blue. The special effort that was made to identify the small amount of these tiny crystals that were present is described here since it typifies the problem that is common to identification of a small amount of a crystalline phase in an ash. The following three methods were used:

(1) X-ray diffraction (XRD).

(2) Morphology, using a scanning electron microscope (SEM).

(3) Index of refraction of particles thought to be titanite using a polarizing microscope to examine immersion mounts.

A small amount of fluosilicic acid residue from ash AD-513 was placed into a small glass beaker with acetone and stirred. Since the titanite particles in this sample were so small, they were among the last particles to settle. A capillary tube was used to gather these particles. Some were placed on a SEM sample stub, coated, and examined. Another small amount of these fine particles was placed on a quartz crystal that was cut and polished so that the 003 plane was so oriented that only the weak 1.801-A peak at 50.62° 2θ would show in an XRD pattern. An XRD pattern was made of these particles. A small amount of sample was placed in oil with an index of refraction of 1.890 and examined with a polarizing microscope. The SEM examination showed mainly acicular, blocky or irregular, and spherical particles. The spherical particles were probably titanite, however, since they did not show identifable morphology, no micrographs were made. Several wedge-shaped particles were found. Fig. 5 and 6 are micrographs of two of these particles. The XRD pattern showed quartz, mullite, and a line with a spacing at 3.24 A that did not go with either quartz or mullite. No additional lines of titanite were found; however, since titanite has its strongest XRD peak at 3.24 A, this suggested that the material was titanite. The examinations of particles that were thought to be titanite in oil with an index of refraction of 1.89 showed the grains to have an index higher than the oil. Thus, while the evidence is not a positive identification, it is believed that the material is titanite.

(d) Opaque particles of carbon were present. Most of the particles were blocky or vesicular. Fig. 7 shows a micrograph of vesicular carbon. The carbon is probably crystalline to X-rays since the XRD patterns have a 2.03-A peak that may be graphite.

(e) One or two short crystals of prismatic habit were found in this residue. They had parallel extinction, high birefringency, and were length-slow. The crystals had a very high index of refraction and were identified as zircon. Zircon was so rare in the sample that its presence was not mentioned in the tables.

(f) Glass was always present in the residue treated with HF. It was always present in trace amounts. Partial spheres of residual glass were the form of glass most commonly seen in immersion mounts of acid residues. Individual descriptions of the other five ashes are not included because much of what would be said would be repetition and the more pertinent data are in the tables.

Discussion

20. Consideration of the treatments used and the results obtained suggest that the fluosilicic acid treatment or the modified HF treatment gave similar results and were the best of those that were tried to determine glass content. They gave reasonable results without requiring extensive cleanup procedures. More emphasis is placed on the fluosilicic acid procedure since it was used on several ashes while the HF method was only used on one ash (AD-592(4)). The treatment with sodium hydroxide was considered the next best method; it is a method that is probably best used to supplement the fluosilicic acid method or the modified HF method.

21. Neither of these methods (acid or hydroxide) will remove all of the glass from a fly ash. This is not surprising because the glass in an ash is not uniform in composition and thus is not all equally susceptible to dissolution; this has long been known from the fact that glass in a particular ash has a range in refractive index which is due to a range in composition. In addition to differences in glass

composition within an ash, differences between ashes from different sources are important. This was shown particularly well by the use of both fluosilicic acid and sodium hydroxide treatment on all of these ashes. The residue after hydroxide treatment for the four lignite ashes (AD-506, 510, 513, 592(4)) was significantly larger than the residue after the acid treatment whereas the residues from the two kinds of treatments were similar for the subbituminous ash (AD-505) and the bituminous ash (AD-511) (Table 8). This comparison showed that the type of treatment is significant for lignite ashes but not as important for other types of ashes.

22. It should be recognized that neither of these procedures (acid, hydroxide) is necessarily the final answer, but they are the best now available to obtain the desired results.

23. The procedure now recommended for selective dissolution of an ash is as follows:

a. Use the method described in this report to remove the magnetic material from a whole ash; use change in mass to determine this amount.

b. Treat the nonmagnetic ash fraction with fluosilicic acid and clean up as described; determine changes in mass (Appendix A). An alternative is to use the modified HF method as described earlier.

c. Use XRD to determine composition of the whole ash and the nonmagnetic ash fraction before and after acid treatment. Use a polarizing microscope as needed.

d. If water-soluble phases are present, then remove them from a sample of whole ash with water. Since some of the water-soluble material will be encased in glass, it will probably be necessary to do the water treatment several times using grinding between treatments to expose new surfaces. Monitor removal of these soluble phases by XRD. Determine the amount of material removed.

e. At this point by proper combination of mass change data, it should be possible to make a reasonable estimate of glass content and amount of other phases in an ash. The values in Table 8 were adjusted to indicate amounts in the whole ashes and were then used with other data for the values given in Tables 2 through 7. In those tables, the amounts of crystalline phases are shown as water-soluble phases, acid-insoluble phases, magnetite, and

carbon; these four values were added and the total was subtracted from 100 to calculate the glass contents shown.

Conclusions

24. Selective chemical dissolution of fly ash is a useful technique to estimate glass content. However, this will always be an estimate since none of the available treatments will make an absolutely clear separation of glass and crystalline phases. There will always be a little glass remaining and one or more crystalline phases will probably be attacked. Selective dissolution may also lead to improved identification of crystalline phases.

25. Treatment of a fly ash with fluosilicic acid or HF (modified procedure) is considered the preferred method of determining glass content of a fly ash with reasonable effort. Treatment of an ash with a sodium hydroxide solution may also provide useful information, especially as a supplement to the above treatment.

26. Estimates of glass contents of four lignite ashes, one subbituminous ash, and one bituminous ash were as follows:

	Estimated Glass Content, %
Lignite Ashes	
AD-506	66
AD-510	57
AD-513	75
AD-592(4)	75
Subbituminous Ash	
AD-505	71
Bituminous Ash	
AD-511	64

27. Chemical analysis for specific elements showed that in addition to those already known to be present in most fly ash, these ashes contained barium, titanium, stronium, and manganese.

28. A combination of methods, primarily X-ray diffraction, indicated some of these ashes contained crystalline phases not usually known to be present in ashes. These included titanium oxide or more complex titanium oxide phases. It is believed they were already present and became detectable by the concentration effects of selective chemical dissolution.

29. Determination of whether a crystalline phase found in an insoluble ash residue is a reaction product of the treatment or is the result of concentration of an originally undetectable phase may not always be possible.

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2. Roy, D. M.; Grutzeck, M. W.; Mather, K.; and Buck, A. D., "PSU/WES Interlaboratory Comparative Methodology Study of An Experimental Cementitious Repository Seal Material," USAE Waterways Experiment Station Miscellaneous Paper SL-81-2, Report 2, Final Results, Mar 1982, Vicksburg, Miss.

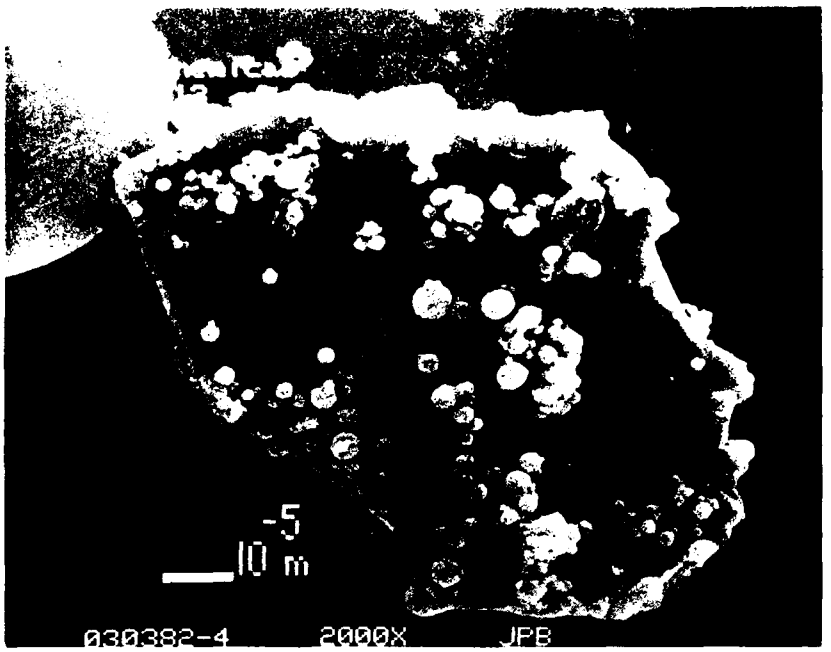

Fig. 1. Scanning electron micrograph of quartz grain with glass shell. Glassy spheres have fused to the surface.

Fig. 2. Scanning electron micrograph of quartz grain after HF acid treatment. The pitted, grooved surface is not as apparent with this grain as it is in many such grains. Fragments of glass still remain on the right side of the grain.

Fig. 3. Scanning electron micrograph 020681-10 of vesicular spherical particle after HF treatment, X370. Believed to be largely or all mullite.

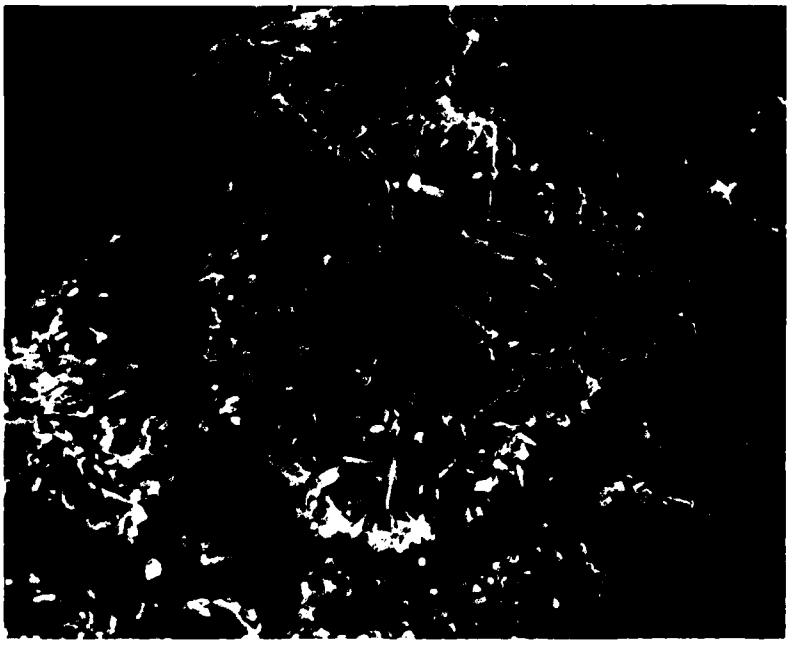

Fig. 4. Enlargement of central portion of above, X4900. No. 020681-10; acicular crystals of mullite.

Fig. 5. Scanning electron micrograph 020582-1 of tiny wedge-shaped crystals believed to be titanite, X9000. Crystals are about 5 μm.

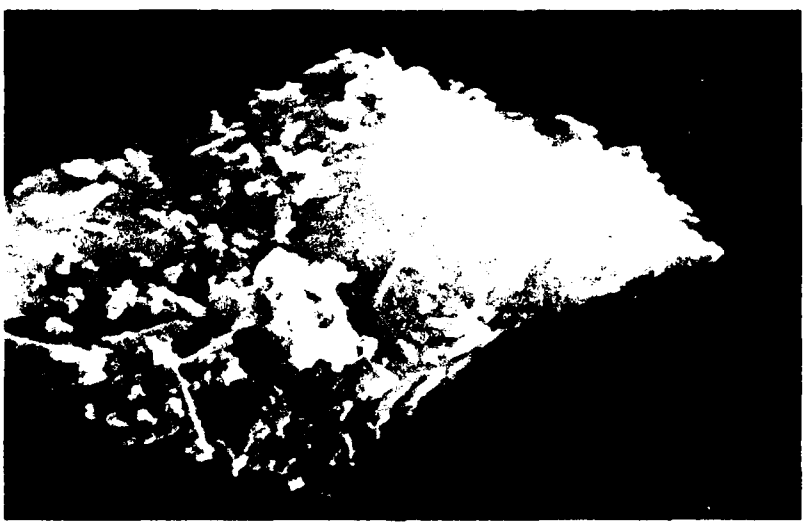

Fig. 6. As above, No. 020582-3. Wedge-shaped crystals of titanite, about 12 μm, with smaller crystals of quartz and mullite on its surface, X9000.

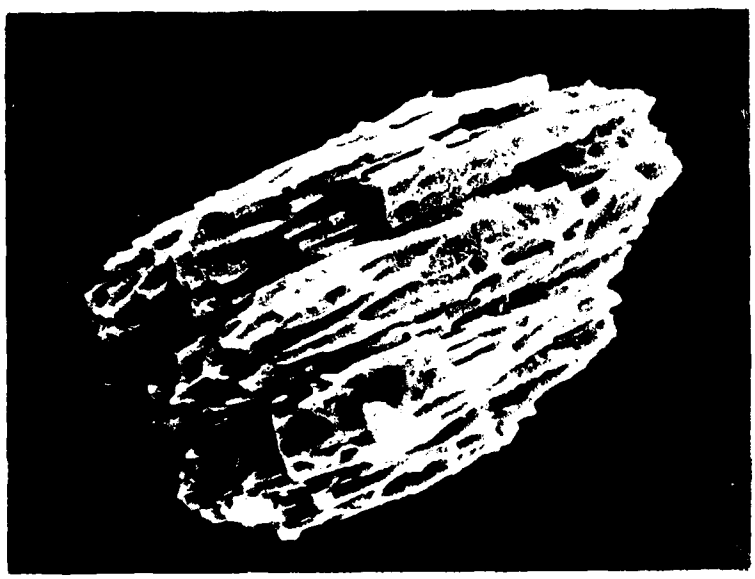

Fig. 7. Scanning electron micrograph 020681-5. An opaque particle of vesicular carbon from ash AD-592(4), X250.

Table 1

Results of Chemical Analyses of Six Fly Ashes*

Chemical Elements as Oxides	Amount in Ashes Shown, Percent				Subbitminous Ash AD-505	Bituminous Ash AD-511
	Lignite Ashes					
	AD-506	AD-510	AD-513	AD-592(4)**		
SiO_2	50.40	23.48	38.12	32.70	45.88	45.40
Al_2O_3	18.41	16.36	25.68	16.70	21.44	24.34
Fe_2O_3	4.61	9.08	4.65	6.40	10.88	15.02
CaO	19.77	29.94	21.01	29.90	11.11	2.69
MgO	3.51	8.43	4.42	5.60	2.50	1.12
SO_3	1.30	5.31	1.55	2.90	1.11	0.73
Na_2O	0.57	3.28	1.30	0.98	0.37	0.38
K_2O	0.53	0.39	0.58	0.36	1.93	2.61
TiO_2	n.d.††	0.53^{Δ}	1.46^{Δ}	$1.58^{\Delta}(1.64)^{\Delta}\dagger(1.63)^{\Delta}\dagger$	0.77^{Δ}	1.17^{Δ}
P_2O_5	n.d.	n.d.	n.d.	$1.04^{\Delta}(1.03)\dagger^{\Delta}$	n.d.	n.d.
Mn_2O_3	n.d.	0.10^{Δ}	0.05^{Δ}	0.04^{Δ}	0.06^{Δ}	0.04^{Δ}
BaO	n.d.	1.13^{Δ}	0.72^{Δ}	0.69^{Δ}	0.23^{Δ}	0.07^{Δ}
SrO	n.d.	0.76^{Δ}	0.43^{Δ}	0.34^{Δ}	0.12^{Δ}	0.06^{Δ}
LOI	0.85	1.14	0.14	0.40	3.81	4.26
Moisture Content	0.17	0.29	0.14	0.10	0.14	0.31

* Done by atomic absorption and Argon plasma emission$^{\Delta}$ methods.
** Reference 2.
† Repeat determinations.
†† Not determined.

Table 2

Compositional and Phase Data for Lignite Fly Ash AD-506

Calculated Composition, %		Index of Refraction, Range
Glass	66	1.495 to 1.740
Crystalline phases	33	
(a) Water-soluble (CaO, $CaSO_4$, and their hydrates)	14	
(b) Acid insoluble	17	
(c) Magnetite	2	
Carbon (loss on ignition)	1	
Total	100	

	Identified in the Material Shown Below		
Crystalline Phases	Whole Ash	Fluosilicic Acid Residue	Sodium Hydroxide Residue
Mullite	X	X	X
Quartz	X	X	X
Hematite	X	X	X
Magnetite	X	Removed before treatment	
Calcium Hydroxide	X	n.d.*	n.d.
Lime	X	n.d.	n.d.
Anhydrite	X	n.d.	n.d.
Periclase	X	n.d.	n.d.
Carbon	X	X	X
Plagioclase	n.d.	n.d.	X(t)**
Calcium Aluminum Silicate	n.d.	n.d.	X(t)
Titanite (Sphene)	n.d.	X	X
Probably Made by the Treatment			
Substituted Fluoride Hydrates	n.d.	X	n.d.

* Not detected.

** Tentative identification.

Table 3

Compositional and Phase Data for Lignite Fly Ash

AD-510

Calculated Composition, %		Index of Refraction, Range
Glass	57	1.496 to 1.700
Crystalline Phases	42	
(a) Water-soluble (CaO, $CaSO_4$, and their hydrates; C_3A; $C_4A_3\bar{S}$)	30	
(b) Acid insoluble	6	
(c) Magnetite	6	
Carbon (loss on ignition)	1	
Total	100	

	Identified in the Material Shown Below		
Crystalline Phases	Whole Ash	Fluosilicic Acid Residue	Sodium Hydroxide Residue
Mullite	X	X	X
Quartz	X	X	X
Hematite	X	X(t)†	X
Magnetite	X	Removed before treatment	
Beta Barium Silicate	n.d.**	X	n.d.
Lime	X	n.d.	n.d.
Anhydrite	X	n.d.	n.d.
C_4A_3S*	X	n.d.	n.d.
Periclase	X	n.d.	n.d.
Calcium Aluminoferrite	X	n.d.	n.d.
Carbon	X	X	X
Melilite	X	n.d.	X
Plagioclase	X(t)	n.d.	n.d.
Barite	n.d.	X	X
Calcium Aluminum Silicate	X(t)	n.d.	X(t)
Perovskite	n.d.	X(t)	X(t)
Titanite (Sphene)	n.d.	X	X
C_3A*	X(t)	n.d.	n.d.
Probably Made by the Treatment			
Barium Hydroxide	n.d.	n.d.	X(t)
Substituted Fluoride Hydrates	n.d.	X	n.d.

* C = CaO, A = Al_2O_3, $\bar{S}$ = SO_3.

** Not detected.

† Tentative identification.

Table 4

Compositional and Phase Data for Lignite Fly Ash AD-513

Calculated Composition, %		Index of Refraction, Range 1.500 to 1.745
Glass	75	
Crystalline Phases	25	
(a) Water-soluble (CaO, $CaSO_4$, and their hydrates; $C_4A_3\bar{S}$)	14	
(b) Acid insoluble	9	
(c) Magnetite	2	
Carbon (loss on ignition)	Trace	
Total	100	

	Identified in the Material Shown Below		
Crystalline Phases	Whole Ash	Fluosilicic Acid Residue	Sodium Hydroxide Residue
Mullite	X	X	X
Quartz	X	X	X
Hematite	X	X	X
Magnetite	X	Removed before treatment	
Lime	X	n.d.**	n.d.
Anhydrite	X	n.d.	n.d.
$C_4A_3\bar{S}$*	X	n.d.	n.d.
Periclase	X	n.d.	n.d.
Carbon	X	X	X
Melilite	X	n.d.	X
Plagioclase	X	n.d.	X
Barite	n.d.	n.d.	X
Calcium Aluminum Silicate	X(t)†	n.d.	X(t)
Perovskite	n.d.	X(t)	X(t)
Titanite (Sphene)	n.d.	X	X
Probably Made by the Treatment			
Barium Hydroxide	n.d.	n.d.	X
Substituted Fluoride Hydrates	n.d.	X	n.d.

* $C = CaO$, $A = Al_2O_3$, $\bar{S} = SO_3$.

** Not detected.

† Tentative identification.

Table 5

Compositional and Phase Data for Lignite Fly Ash AD-592(4)

Calculated Composition, %		Index of Refraction, Range
Glass	75	1.500 to 1.748
Crystalline Phases	25	
(a) Water-soluble (CaO, $CaSO_4$, and their hydrates; C_3A; C_4A_3S)	13	
(b) Acid insoluble	9	
(c) Magnetite	3	
Carbon (loss on ignition)	Trace	
Total	100	

	Identified in the Material Shown Below		
Crystalline Phases	Whole Ash	Fluosilicic Acid Residue	Sodium Hydroxide Residue
Mullite	X	X	X
Quartz	X	X	X
Hematite	X	X	X
Magnetite	X	Removed before treatment	
Lime	X	n.d.	n.d.
Anhydrite	X	n.d.	n.d.
C_4A_3S*	X	n.d.	n.d.
Periclase	X	n.d.	n.d.
Calcite	X(t)†	n.d.	n.d.
Calcium Aluminoferrite	X	n.d.	n.d.
Carbon	X	X	X
Melilite	n.d.**	n.d.	X
Plagioclase	n.d.	n.d.	X
Barite	n.d.	n.d.	X
Calcium Aluminum Silicate	X(t)	n.d.	X(t)
Rutile	n.d.	X(t)	n.d.
Perovskite	n.d.	X(t)	X(t)
Titanite (Sphene)	n.d.	X(t)	X(t)
C_3A*	X(t)	n.d.	n.d.
Probably Made by the Treatment			
Barium Hydroxide	n.d.	n.d.	X
Substituted Fluoride Hydrates	n.d.	X	n.d.

* C = CaO, A = Al_2O_3, S = SO_3.
** Not detected.
† Tentative identification.

Table 6

Compositional and Phase Data for Subbituminous Fly Ash AD-505

Calculated Composition, %		Index of Refraction, Range
Glass	71	1.520 to 1.745
Crystalline Phases	25	
(a) Water soluble (CaO, $CaSO_4$, and their hydrates)	8	
(b) Acid insoluble	10	
(c) Magnetite	7	
Carbon (loss on ignition)	4	
Total	100	

	Identified in the Material Shown Below		
Crystalline Phases	Whole Ash	Fluosilicic Acid Residue	Sodium Hydroxide Residue
Mullite	X	X	X
Quartz	X	X	X
Hematite	X	X	X
Magnetite	X	Removed before treatment	
Calcium Hydroxide	X	n.d.*	n.d.
Lime	X	n.d.	n.d.
Anhydrite	X	n.d.	n.d.
Periclase	X	n.d.	n.d.
Carbon	X	X	X
Calcium Aluminum Silicate	n.d.	n.d.	X(t)**
Titanite (Sphene)	n.d.	X	X
Probably Made by the Treatment			
Substituted Fluoride Hydrates	n.d.	X	n.d.

* Not detected.

** Tentative identification.

Table 7

Compositional and Phase Data for Bituminous Fly Ash AD-511

Calculated Composition, %			Index of Refraction, Range
Glass		64	1.500 to 1.675
Crystalline Phases		32	
(a) Water soluble	4		
(b) Acid insoluble	14		
(c) Magnetite	14		
Carbon (loss on ignition)		4	
Total		100	

	Identified in the Material Shown Below		
Crystalline Phases	Whole Ash	Fluosilicic Acid Residue	Sodium Hydroxide Residue
Mullite	X	X	X
Quartz	X	X	X
Hematite	X	X	X
Magnetite	X	Removed before treatment	
Carbon	X	X	X
Perovskite	n.d.*	X(t)**	X(t)
Titanite (Sphene)	n.d.	X	X
Probably Made by the Treatment			
Substituted Fluoride Hydrates	n.d.	X	n.d.

* Not detected.

** Tentative identification.

Table 8

Amounts of Insoluble Residue After

Chemical Treatment of Fly Ashes*

Type of Treatment	Amount of Insoluble Residue in Fly Ashes Shown Below, %					
	Lignite Ash				Subbituminous Ash	Bituminous Ash
	AD-506	AD-510	AD-513	AD-592(4)	AD-505	AD-511
Mulett et al[1] Method, HF Acid	n.d.†	n.d.	n.d.	4	n.d.	n.d.
Modified Mulett et al[1], HF Acid	n.d.	n.d.	n.d.	6-9	n.d.	n.d.
Fluosilicic Acid**	19	8	9	9	14	21
Sodium Hydroxide**	25	14	16	19	16	20

* Based on nonmagnetic portion of each ash.

** Initial treatment was constant; cleanup procedures varied slightly.

† Not determined.

APPENDIX A: FLUOSILICIC ACID METHOD

1. Scope. This method is used for extracting the glass phase from fly ash; it will usually also remove some of the crystalline material.

2. Apparatus.

   a. Magnetic stirrer.

   b. Teflon container. The teflon container has a capacity of 60 mL (2 oz), with an inside diameter of 1-7/8 in. (48 mm) and a height of 1-5/8 in. (41 mm). The container has a teflon screw cap.

   c. Magnetic stirring bar. The bar is teflon coated and is 1-3/8 in. (35 mm) in length.

   d. Centrifuge tubes. Polypropylene with a capacity of 100 mL.

   e. Vortex mixer.

   f. Centifuge.

   g. Analytical balance.

   h. Oven.

3. Reagents.

   a. Fluosilicic acid (hydrofluorosilicic acid). Reagent grade, 30.0 percent.

   b. Boric acid solution (2 percent). Dissolve 20 g of reagent grade boric acid in 980 mL of distilled water.

   c. Hydrochloric acid solution (1 + 9). Mix one part reagent grade hydrochloric acid with nine parts of distilled water by volume.

4. Procedure.

   a. Remove the magnetite from the fly ash by the acetone-magnetic stirring bar method. Dry to a constant weight at 105° C.

   b. Weigh out 1.5 g of the fly ash with the magnetite removed into the teflon container. Add 40 mL of the fluosilicic acid, and a magnetic stirring bar to the container. Seal the container and place the container on a magnetic stirrer. Stir for 24 hr.

   c. Remove the container, and transfer the contents to a tared centrifuge tube (dried overnight at 80° C). Any residue remaining in the container is removed by the use of a rubber policeman, and distilled water, and transferred to the centrifuge tube.

d. Centrifuge for 10 min at 3000 rpm. Remove the centrifuge tube from the centrifuge and decant off the fluosilicic acid.

e. Add 40 mL of the boric acid solution to the centrifuge tube and mix for approximately 1 min using the vortex mixer. Wait 5 min then repeat the mixing. Wash down the sides of the centrifuge tube with distilled water and centrifuge for 10 min.

f. Decant off the boric acid solution, and repeat the mixing and washing step above using 40 mL of the hydrochloric acid solution. Centrifuge for 10 min and decant off the hydrochloric acid solution .

g. Wash the residue twice with 40 mL aliquots of distilled water mixing each time with the vortex mixer and centrifuging and decanting after each wash.

h. Place the centrifuge tube in an oven set at 80° C and leave the centrifuge tube in overnight. Remove the centrifuge tube the next day and place in a desiccator. After 1 hr weigh the centrifuge tube on an analytical balance.

5. Calculations. Calculate the percentage of residue, expressed as a percent of the whole ash, as follows:

Weight of sample corrected for magnetite (Sw)

$$Sw = \frac{\text{Weight of sample, g}}{\text{1- fraction percent of magnetite}}$$

$$\text{Residue, \%} = \frac{A - B}{Sw} \times 100$$

A = Weight of centrifuge tube and residue, g, and

B = Weight of centrifuge tube, g.

6. Comment. This insoluble residue will be largely quartz and mullite plus other crystalline phases that may resist the treatment; there will also be an insignificant amount of residual glass. The amount of material removed by the treatment, 100 percent - percent residue, is glass and usually includes some crystalline material. If the amount of this crystalline material can be determined, then a good estimate of total glass content in the fly ash can be made.

APPENDIX B: SODIUM HYDROXIDE METHOD

1. Scope. This method is used for extracting the glass phases from fly ash; some crystalline material will probably also be dissolved.

2. Apparatus.

   a. Hot-plate stirrer. This apparatus stirs magnetically with a teflon-coated bar. The top plate on the apparatus is heated by the use of a thermostat. The apparatus heats and stirs separately or simultaneously.

   b. Teflon container. The teflon container has a capacity of 60 mL (2 oz), with an inside diameter of 1-7/8 in. (48 mm); and a height of 1-5/8 in. (41 mm). The container has a teflon screw cap.

   c. Magnetic stirring bar. Teflon coated, 1-3/8 in. (35 mm) in length.

   d. Centrifuge tubes. Polypropylene centrifuge tubes with 100 mL capacity.

   e. Vortex mixer.

   f. Centrifuge.

   g. Analytical balance.

   h. Oven.

3. Reagents.

   a. Sodium hydroxide solution (3M). Dissolve 120 g of reagent grade sodium hydroxide in 500 mL of distilled water. Cool to room temperature and dilute to 1 L.

   b. Hydrochloric acid solution (1 + 9). Mix one part reagent grade hydrochloric acid with nine parts of distilled water by volume.

   c. Hydrochloric acid solution (1 + 24). Mix 1 part reagent grade hydrochloric acid with 24 parts of distilled water by volume.

4. Calibration of temperature for the hot-plate stirrer. Transfer 40 mL of distilled water to the teflon container and screw on the container cap. Place the container on the hot plate and adjust the thermostat to obtain a temperature of 80 ± 2° C. Leave the container on the hot plate overnight and measure the temperature the next day. The temperature of the water should be within the tolerance above.

5. Procedure.

a. Remove the magnetite from the fly ash by the [illegible] magnetic stirring bar method. Dry to a constant weight at 105° C.

b. Weigh out 1.5 g of the fly ash with the magnetite removed into the teflon container. Add 40 mL of the sodium hydroxide solution and a magnetic stirring bar to the container. Seal the container and place on the hot plate stirrer, and start the stirrer. The stirrer should be adjusted to keep the fly ash in suspension.

c. Remove the container from the hot plate stirrer after 24 hr, and transfer the contents to a tared centrifuge tube (dried overnight at 80° C). Any residue remaining in the container is removed by the use of a rubber policeman and distilled water and transferred to the centrifuge tube.

d. Centrifuge for 10 min at 3000 rpm. Remove the centrifuge tube from the centrifuge, and decant off the sodium hydroxide solution.

e. Add 40 mL of the HCl (1 + 9) to the centrifuge tube and mix for approximately 1 min using the vortex mixer. It may be necessary to loosen the residue with a glass stirring rod before mixing with the vortex mixer. Wait 1 hr, then repeat the mixing. Wash down the sides of the centrifuge tube with distilled water and centrifuge for 10 min.

f. Decant off the HCl (1 + 9), and repeat the mixing and washing step above using HCl (1 + 24). Wash the residue once more with the HCl (1 + 24), centrifuging and decanting after each wash.

g. Wash the residue twice with distilled water. Transfer the centrifuge tube to an oven set at 80° C, and leave the centrifuge tube in overnight. Remove the centrifuge tube from the oven and place in a dissicator. After 1 hr weigh the centrifuge tube on an analytical balance.

6. Calculations. Calculate the percentage of residue, [illegible] as a percent of the whole ash, as follows:

$$\text{Weight of sample corrected for magnetite (g)} = \text{Weight of sample, g} \times \text{fraction percent of magnetite}$$

$$\text{Residue, \%} = \frac{A - B}{W} \times 100$$

A = Weight of centrifuge tube and residue

B = Weight of centifuge tube

7. Comment. This insoluble residue will be mostly quartz and mullite plus other crystalline phases that may not dissolve; there will also be some residual glass. The amount of material that was removed, 100 percent - percent residue, is glass and usually includes some crystalline material. If the amount of this crystalline material can be determined, then an estimate of total glass content can be made. This method is best used to supplement the fluosilicic acid method.

In accordance with letter from DAEN-RDC, DAEN-ASI dated 22 July 1977, Subject: Facsimile Catalog Cards for Laboratory Technical Publications, a facsimile catalog card in Library of Congress MARC format is reproduced below.

Buck, Alan D.
Studies of the constitution of fly ash using selective dissolution / by Alan D. Buck, Tony B. Husbands, and J. Pete Burkes (Structures Laboratory, U.S. Army Engineer Waterways Experiment Station). -- Vicksburg, Miss. : The Station ; Springfield, Va. : available from NTIS, 1983.
35 p. in various pagings : ill. ; 27 cm. -- (Miscellaneous paper ; SL-83-5)
Cover title.
"May 1983."
Final report.
"Prepared for Office of Nuclear Waste Isolation, Battelle Memorial Institute under Contract DE-A197-81ET46633, Modification M003."
Bibliography: p. 18.

1. Concrete. 2. Fly ash. 3. Grouts (Mortar). 4. Radioactive wastes. 5. X-rays--Diffraction. I. Husbands, Tony B. II. Burkes, J. Pete.

Buck, Alan D.
Studies of the constitution of fly ash using : ... 1983.
(Card 2)

I. Battelle Memorial Institute. Office of Nuclear Waste Isolation. II. U.S. Army Engineer Waterways Experiment Station. Structures Laboratory. III. Title IV. Series: Miscellaneous paper (U.S. Army Engineer Waterways Experiment Station) ; SL-83-5.
TA7.W34m no.SL-83-5