

Characterization of Fly Ash by X-Ray Analysis Methods

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Techniques have been developed for quantitative determination of elemental and crystalline composition of fly ash by X-ray fluorescence and diffraction. In addition to being fast, the methods are accurate and the knowledge provided from quantitative crystalline composition explains many of the behavioral characteristics of fly ash. From the study on one Class C, cementitious fly ash it was found that 23 percent of its composition is crystalline and that significant amounts of aluminous cements (tricalcium aluminate and calcium aluminum sulfate) are present. The cements explain this fly ash's capability for high strengths after hydration. A study involving continuous X-ray diffraction monitoring of hydration products showed that both Ettringite and monosulfoaluminate were formed; but when sufficient quantities of gypsum were introduced, Ettringite formation became dominant. Free calcium oxide was also found in this fly ash, and its behavior with water suggests a hard burned form, which is a feature of particular importance to use of fly ash in Portland cement concrete.

The increasing use of fly ash as a construction material has created a need for a better understanding of fly ash reaction mechanisms. Much research has been conducted on the pozzolanic reaction that occurs between fly ash and calcium hydroxide. However, the more recent advent of what is often termed high-lime fly ashes which can result from burning subbituminous coal presents a material that possesses the potentially valuable property of being cementitious. By current ASTM standards (1) self-cementing fly ashes usually fall into Class C, but such categorization based on elemental composition may not adequately define the reason for a cementitious nature. Although the elemental oxide compositional constraints specified in the ASTM standard may under certain burning conditions result in the formation of cementitious compounds, existing standards cannot at present provide an indication of the identity and quantity of these compounds. Thus, a more meaningful approach to classifying and understanding the behavioral characteristics of fly ash may be through identification and quantification of constituent compounds.

X-ray diffraction analysis is the most powerful and probably the only tool for direct identification and determination of constituent minerals and has been extensively used in research (2-8). Recent advances in technology and methodology may make the X-ray technique a reasonable alternative for setting standards and specifications (9).

A methodology for quantitative evaluation of elemental and crystalline composition of fly ashes with X-ray techniques is presented in this paper. The objective of this paper is to provide a basis for correlating cementitious and pozzolanic properties to compound composition. A companion paper by J.M. Pitt, et al. in this Record uses the technique presented here to evaluate fly ashes from seven power plants fueled with western subbituminous coals.

EXPERIMENTAL STUDY AND RESULTS

Materials

A self-cementing fly ash from a power plant located near Lansing, Iowa, was arbitrarily selected for detailed analysis of elemental and crystalline composition. Two-inch cubes of this fly ash displayed 1,325 psi compressive strengths when molded at a 0.26 water/fly ash ratio and cured for 30 min. Three-day strengths on three specimens averaged 2,490 psi. The Lansing fly ash was produced from a Wyoming subbituminous coal (10), and results for

chemical and physical tests as defined in ASTM C 311-77 are shown in Table 1. By the ASTM C 618 classification scheme, the Lansing fly ash is Class C.

The water used for hydration studies was deionized distilled water. The compounds used as reference standards in quantitative X-ray analysis were obtained from three different sources and consisted of tricalcium aluminate (C_3A), calcium aluminum sulfate ($C_4A_3\bar{S}$), quartz (SiO_2), mullite ($Al_6Si_2O_{13}$), magnetite (Fe_3O_4), Hematite (Fe_2O_3), anhydrite ($CaSO_4$), calcium oxide (CaO), periclase (MgO), and sodium chloride ($NaCl$). The first two of these compounds were purchased from the Portland Cement Association; purified quartz, mullite, and magnetite were obtained from the Department of Earth Sciences at Iowa State University; the rest of the compounds were commercially available reagent grade chemicals.

Elemental Analysis

X-ray fluorescence techniques were adapted for rapid determination of the elemental composition of fly ash. The analysis was performed using a Siemens SR-200 sequential X-ray spectrometer controlled by a PDP-11-03 microcomputer. The spectrometer was equipped with a ten-sample specimen chamber and four interchangeable analyzing crystals. Unfiltered excitation radiation was generated using a chromium tube at 50 KV and 48 ma. Programs for the spectrometer were developed by the Siemens Corporation (11).

The elements present in the Lansing fly ash were determined qualitatively by measuring the wavelengths of characteristic fluorescent radiation by using continuous $\theta/2\theta$ scans and the appropriate analyzing crystals. Quantitative determination of the elements in each fly ash was then measured by using the Siemens software. The software consists of interactive programs for the automatic operation of the spectrometer data collection and analysis. Programs for calibration and measurement of unknown concentrations are based on a multiple regression (either quadratic or linear) of the characteristic radiation intensity on concentration. The program

Table 1. Chemical and physical properties of Lansing fly ash determined by ASTM C-311 tests.

	Percent
Elemental Oxide	
SiO ₂	32.12
Al ₂ O ₃	18.06
Fe ₂ O ₃	5.34
Na ₂ O ₃	1.77
K ₂ O	0.36
SO ₃	3.69
Physical Tests	
Specific gravity	2.77
Pozzolanic activity	99
Percent passing No. 325 sieve	87.5
Autoclave	0.10
Loss on ignition	0.21
Moisture	0.00

Note: Tests were conducted by the Iowa Department of Transportation.

methodology also takes into account absorption, enhancement, and line overlaps as multiple variants and requires the use of calibration standards (12, 13). For dependable results the range of elemental composition of the standards should cover the expected concentrations of elements in unknown samples.

Twenty standards prepared by blending six fly ashes of known elemental composition served as a basis for the calibration. The calibration was checked against a National Bureau of Standards (NBS) fly ash standard and comparative results are given in Table 2. Table 3 gives the results of an elemental analysis by X-ray fluorescence for the Lansing fly ash which was treated as an unknown; comparison with the conventional analysis in Table 1 shows a reasonable correspondence between the two methods.

Quantitative Component Analysis

A Siemens D-500 computer-controlled X-ray diffractometer was used in developing quantitative techniques for determining crystalline components (minerals) present in fly ash. The diffractometer was equipped with a graphite monochromator and a pulse-height analyzer for efficient monochromatization, and monochromatic copper K α radiation was used for all analyses. The diffractometer was controlled with either a PDP-11-03 microcomputer or, when simultaneous operation of the diffractometer and the spectrometer was needed, a PET microcomputer. Control with the PET was achieved by interfacing it to the diffractometer's logic controller and communicating via data net with a centrally located PDP-11-34 computer (12). The operating software for the diffractometer was developed by the Siemens Corporation (14,15).

The first step in developing a methodology for quantitative assessment of crystalline compounds (minerals) present in fly ash was to define qualitatively the expected mineral compositions. This task was accomplished by performing conventional X-ray diffraction analyses on fly ashes from seven sources and comparing d-spacings with those listed in the Joint Committee on Powder Diffraction Standards (JCPDS) files. The first eight compounds listed in the legend to Figure 1 are the crystalline

Table 2. Comparison of elemental analysis of fly ash by X-ray with the NBS fly ash standard.

Element	Measured (%)	NBS (%)
Mg	0.46	0.46 \pm 0.01
Na	0.18	0.17 \pm 0.01
Fe	9.38	9.40 \pm 0.10
Ti	0.77	0.80
Si	21.73	22.80 \pm 0.80
Ca	0.98	1.11 \pm 0.01
Al	14.06	14
K	1.87	1.88 \pm 0.06

Table 3. Elemental composition of Lansing fly ash determined X-ray fluorescence.

Elemental Oxide	Percent
SiO ₂	30.0
Al ₂ O ₃	19.7
Fe ₂ O ₃	5.9
Na ₂ O	1.8
K ₂ O	0.4
CaO	31.1
MgO	6.2
TiO ₂	1.3

components found in all of the fly ashes, and the top chart of Figure 1 is typical of the qualitative X-ray analysis.

The methodology for quantitative analysis of crystalline components was adapted from that independently developed by Chung (16) and Demirel (8). This method involves developing a set of standard specimens consisting of compounds present in fly ash along with a reference compound. The reference compound cannot be a constituent of fly ash nor can it react with the host compounds. By mixing known quantities of the reference compound with a fly ash being analyzed and determining integrated X-ray intensities of selected diffraction peaks of the reference compound and the compound of interest, the weight fraction of the compound, W_c , in the fly ash can be computed from

$$W_c = [(I_c/I_r)_{\text{unk.}} / (I_c/I_r)_{\text{std.}}] (W_c'/1 - W_r')_{\text{unk.}} \quad (1)$$

where

$(I_c/I_r)_{\text{unk.}}$ = ratio of integrated intensities of the selected diffraction peaks of the compound of interest and the reference compound measured from fly ash-reference compound mixture.

$(I_c/I_r)_{\text{std.}}$ = ratio of integrated intensities of the selected diffraction peaks of the compound of interest and the reference compound measured from the standard sample of known composition.

W_c = known weight fraction of the compound of interest contained in the standard sample.

W_r = known weight fraction of the reference compound contained in the standard sample.

W_r' = known weight of reference material added to the fly ash being investigated.

In concept, the application of Equation 1 is relatively simple. A calibration matrix for the X-ray intensity ratios of the standard is established by mixing known quantities of individual compounds known to be present in fly ash with a known quantity of a reference material and measuring integrated intensities of selected diffraction peaks. After such a calibration matrix has been established, quantities of compounds can be determined by adding a known amount of reference compound to the fly ash being evaluated and measuring integrated intensities of the selected diffraction peaks established during the calibration.

One task requisite to application of this approach in quantitative evaluation of fly ash is finding pure forms of all the constituent compounds required to develop the calibration. A second requisite is finding a reference compound that preferably has no peak overlaps. Assuming that the principle of superposition is applicable to peak overlaps, Equation 1 can be used for overlap corrections by making use of integrated intensities of other diffraction peaks. However, such adjustments tend to be cumbersome when interferences occur for several compounds. Among several compounds tried, sodium chloride was found to be the most suitable reference compound for fly ash analysis. Samples for diffraction analysis were prepared by combining measured amounts of sodium chloride with fly ash and then thoroughly mixing and grinding them in a shatterbox. Samples were pressed into plexiglas sample rings, and to reduce the influence of crystal orientation measurements were taken three times with the

inaccurate intensity measurement; and it is suspected that this error can be reduced by using the sample spinner which has recently been installed. X-ray diffraction charts of the synthetic standard No. 2 and the obsidian used in preparation are shown in Figure 2.

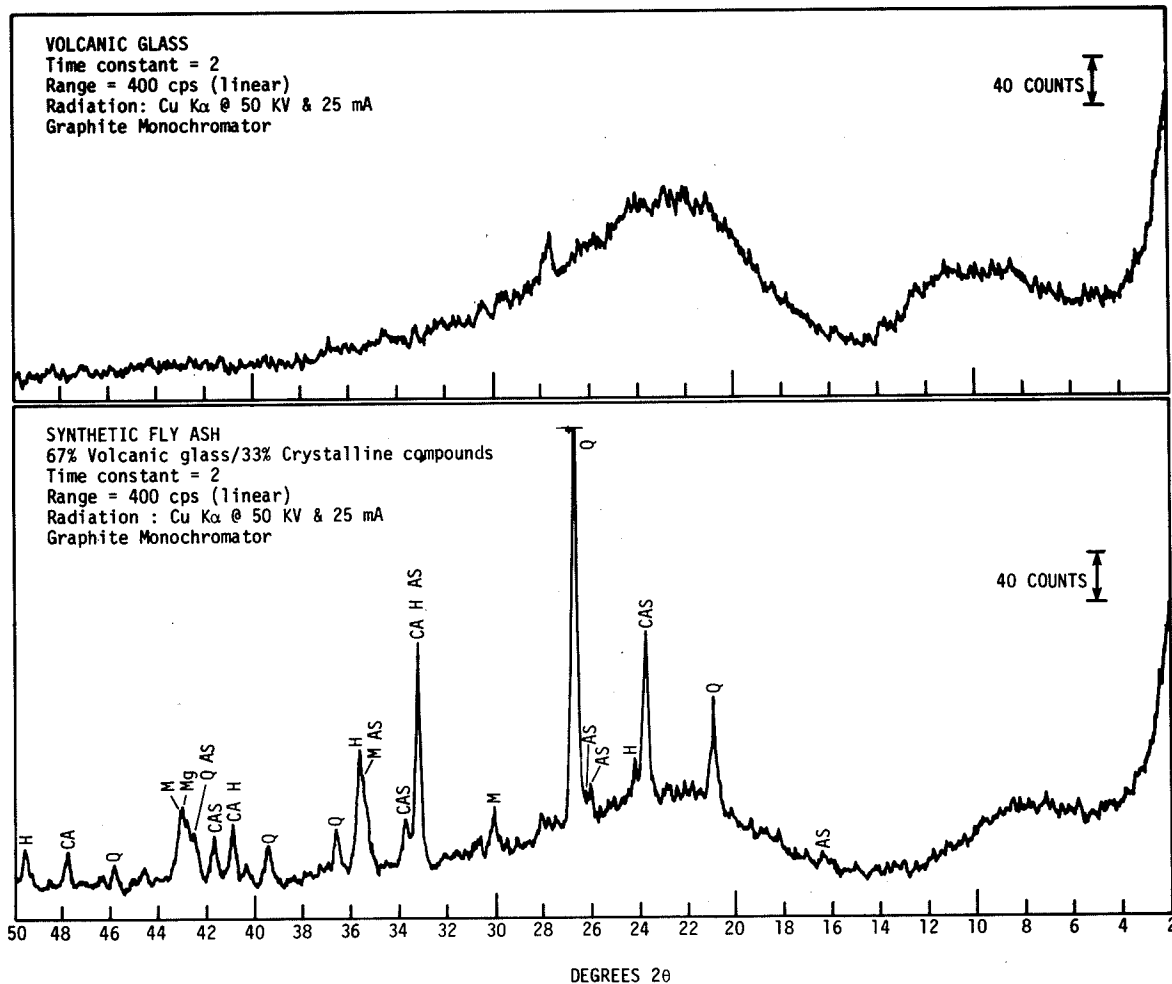
Results of a quantitative compositional analysis of the Lansing fly ash are presented in Table 5. One explanation for the self-cementing properties of this particular fly ash is that it contains a combined 7.5 percent of tricalcium aluminate and calcium aluminum sulfate, both of which are hydraulic

Table 4. Results of quantitative component analysis of synthetic standards.

Component	Known Weight (%)		Weight Measured by X-ray Analysis (%)	
	Std. No. 1	Std. No. 2	Std. No. 1	Std. No. 2
Tricalcium aluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$) (C_3A)	10.0	3.3	10.3	2.8 ± 0.6
Calcium aluminum sulfate ($3\text{CaO}\cdot 3\text{Al}_2\text{O}_3\cdot\text{CaSO}_4$) ($\text{C}_4\text{A}_3\text{S}$)	15.0	5.0	14.8	8.0 ± 0.4
Quartz (SiO_2)	30.0	10.0	39.1	12.2 ± 1.9
Mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$)	10.0	3.3	9.5	2.5 ± 1.2
Magnetite (Fe_3O_4)	10.0	3.3	10.5	4.8 ± 0.93
Magnesium oxide (MgO)	15.0	5.0	15.5	5.0 ± 0.5
Calcium sulfate (CaSO_4)	5.0	0.0	4.90	0.06 ± 0.08
Calcium oxide (CaO)	5.0	0.0	5.07	0.2 ± 0.03
Glass ^a		67.0 ^b		65 ^b

^aObsidian from Mt. St. Helens.
^bEstimated by subtracting sum of crystalline components from the total.

Figure 2. Diffraction patterns of synthetic standard No. 2 and the glassy component (see Figure 1 for legend.)



cements. A second explanation is that crystalline compounds comprise more than 26 percent of this fly ash and could have a significant effect on pozzolanic reactions which are frequently considered to be the essence of fly ash reactions when used as a portland cement additive or in lime-fly ash stabilization of soils. An appreciable amount of this fly ash should have neither a positive nor negative effect on reactions because about 12 percent of this fly ash consists of stable compounds such as quartz, mullite, and magnetite. It is interesting to note that this high-lime fly ash, which has an elemental calcium oxide composition of about 30 percent, contains only 2.1 percent calcium oxide. The total calcium combined in crystalline compounds accounts for about one-sixth of that measured for elemental calcium oxide. The remaining portions should be included in the amorphous phase. Depending on their nature, both calcium and magnesium oxides could play a role in soundness of portland cement-fly ash concretes.

Hydration Reactions

To provide additional information about the chemical properties of the constituents in a reactive-type fly ash, the hydration mechanism of the Lansing fly ash was monitored by using the oscillation capability

of the X-ray diffractometer. The oscillation feature monitors crystalline compound growth and consumption by automatic repetitious scanning of the relevant portions of a diffraction pattern over time. This investigation consisted of preparing fly ash pastes at a 0.26 water/fly ash ratio, placing specimens into X-ray diffraction sample holders, and starting the oscillating X-ray diffraction analysis. Extensive analysis was performed on the fly ash pastes during the period from 2 min after the ash was mixed with water until 90 min after mixing. Diffraction peaks selected for the analysis of each compound are presented in Table 6. To provide information about the behavior of the aluminate compounds, 3 percent gypsum was added to some samples. To evaluate the behavior of CaO moist air, moist CO₂ free curing environments were used. The CO₂ free curing condition was achieved in a desiccator containing a 20 percent solution of NaOH.

The lower two diffraction patterns shown in Figure 1 are for Lansing fly ash after 3 days curing in both environments, and typical segments of oscillation diffraction patterns are shown in Figure 3. Table 7 is a summary of the reactions and their status at various times. For each compound, a relative intensity of 100 is assigned to the highest intensity obtained during the period of analysis. A relative intensity of 100 corresponds to the largest amount of the compound present during the period of analysis. All other intensities of that compound are relative to 100 and correspond to its abundances during the hydration process.

Oscillation X-ray diffraction of the Lansing fly ash-water paste showed that calcium oxide was consumed during the period 7 to 38 min to a relative intensity of about 60 percent and then consumption leveled off. (Period refers to the time interval after the addition of water to fly ash.) Diffraction showed no calcium hydroxide formation during the period 2 to 90 min. Calcite formed in the period of 7 to 77 min and then leveled off. These data suggest that part of the calcite was formed from direct conversion of calcium oxide to calcite without an intermediate hydroxide stage. The atmosphere appeared to be a likely source of carbon dioxide for direct carbonation and proved to be so. This was determined when several samples that were cured in a carbon dioxide-free environment showed no calcite formation and approximately 100 percent calcium oxide retention for up to 20 hr. These results also indicate that even after long curing periods a good deal of calcium oxide remains unreacted.

Table 5. Crystalline composition of Lansing fly ash.

Component	Percent
Tricalcium aluminate (C ₃ A)	5.2
Calcium aluminum sulfate (C ₄ A ₃ S)	2.3
Calcium sulfate (CaSO ₄), (anhydrite)	1.7
Calcium oxide (CaO)	2.1
Quartz (SiO ₂)	10.1
Mullite (Al ₆ Si ₂ O ₁₃)	0.9
Magnetite (Fe ₃ O ₄)	1.0
Magnesium oxide (MgO), (periclase)	2.8
Amorphous contribution (glass) ^a	73.9

^aEstimated by subtracting sum of crystalline components from the total.

Table 6. Diffraction peaks selected for oscillating X-ray analysis with Cu-Kα radiation.

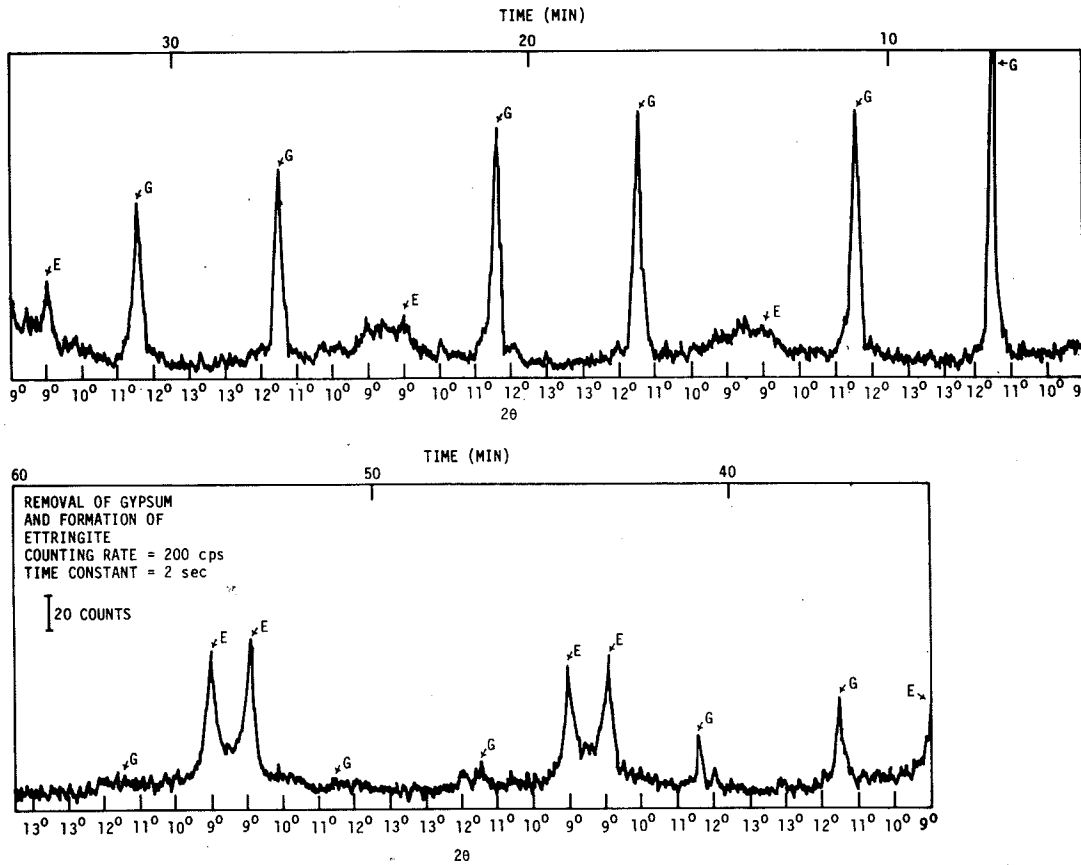
Component	Defraction Peak Selected		Oscillation Range, 2θ (degrees)
	Relative Peak Intensity (%)	d Spacing (Å ^o)	
Gypsum (CaSO ₄ ·2H ₂ O)	100	7.56	8.5 - 13.5
Calcium hydroxide (Ca(OH) ₂)	100	2.63	33 - 35
Calcite (CaCO ₃)	100	3.035	27 - 32
Calcium oxide (CaO)	100	2.405	36.5 - 38.5
Anhydrite (CaSO ₄)	100	3.49	24.5 - 26.5
Calcium aluminum sulfate (3CaO·3Al ₂ O ₃ ·CaSO ₄)	100	3.74	22.5 - 24.5
Ettringite (6CaO·Al ₂ O ₃ ·3SO ₃ ·32H ₂ O)	100	9.67	8.5 - 13.5
Monosulfoaluminate (Ca ₃ Al ₂ O ₆ ·CaSO ₄ ·13H ₂ O)	100	8.92	8.5 - 13.5
Calcium aluminum silicate hydrate (Ca ₂ Al ₂ SiO ₇ ·8H ₂ O)	?	12.5	6.5 - 8.5

Table 7. Summary of oscillating X-ray diffraction analysis of Lansing fly ash.

Reaction	Duration of Reaction (min)				Relative Amount (%)			
	Without Added Gypsum		With 3% Gypsum Added		Without Added Gypsum		With 3% Gypsum Added	
	Start	End	Start	End	Start	End	Start	End
Removal of calcium oxide	7	38	11	46	100	60 ^a	100	38
Removal of anhydrite	10	61	14	64	100	12	100	20
Removal of calcium aluminum sulfate	12	88	38	87	100	38	100	19
Formation or removal of gypsum	None	None	7	58	0	0	100	0
Formation of calcite	7	77	16	>90	0	100	0	100
Formation of Ettringite	4	22	13	55	0	100	0	100
Formation of monosulfoaluminate	12	58	None	None	0	100	0	0

^aWith sample in CO₂ free atmosphere, relative amount still 100 percent.

Figure 3. Example of oscillation diffraction pattern.



It appears that calcium oxide might react to form a thin shell of calcite on the outer surface of the diffraction sample in ambient conditions. In order to check this hypothesis several inner portions of hydrated fly ash samples were analyzed. These portions had not been directly exposed to the atmosphere and showed no calcite formation. An explanation derived from these data is that free, crystalline CaO exists in some fly ashes in a hard burned form. The exact reason for hard burned behavior is not thoroughly understood, but it is believed to be caused by glassy coatings formed on CaO particles. If this were so, however, carbona-

tion should also be hindered. Some evidence obtained during this study suggests that a thin carbonate coating on CaO particles may be the cause for the hindered hydration. Such a coating could form in the CO₂ rich atmosphere prevalent in combustion gases. Hard burned lime is known to be a critical component detrimental to the performance of portland cement and may be equally detrimental for some fly ash applications. Under normal conditions the hydration of hard burned lime proceeds at a very slow rate because of a high diffusion energy barrier and may, if present in sufficient quantity, produce expansion detrimental to portland cement concrete.

During the oscillation analysis, it was observed that the magnesium oxide in the Lansing fly ash did not hydrate as is evidenced by the diffraction patterns shown in Figure 1.

Aluminate hydrates appear to be the key reaction products in the Lansing fly ash. Oscillation diffraction analysis showed formation of Ettringite in the period 4 to 22 min, monosulfoaluminate formation in the period of 12 to 58 min, and anhydrite removal in the period of 10 to 61 min. This seems to represent a good example of portland cement chemistry and can be rationalized as follows. Tricalcium aluminate is present in the fly ash (5.2 percent by weight) and is very reactive with water. Also present is an internal source of calcium sulfate in the form of anhydrite. When hydration begins, the free calcium sulfate content of the paste is high and Ettringite begins to form. As the sulfate content decreases because of consumption by Ettringite formation, monosulfoaluminate begins to form and continues to form, at the expense of Ettringite formation, until the anhydrite is nearly exhausted (17). The consumption of tricalcium aluminate is quite important to this mechanism but has not yet been determined because of diffraction peak interference caused by formation of Ettringite. The precise reaction mechanism might also be complicated because the fly ash contained 2.3 percent calcium aluminum sulfate which might hydrate directly to Ettringite.

Oscillation diffraction analysis was also performed during hydration on the fly ash mixed with 3 percent gypsum by weight as given in Table 8. The consumption trends of calcium oxide, anhydrite, and calcium aluminum sulfate were quite similar to those of the fly ash without gypsum. The major difference caused by the addition of gypsum was in the formation of the aluminate hydrates. Ettringite formed in the period 13 to 55 min while no monosulfoaluminate was formed within the 90 min analysis period. The added gypsum was completely consumed in the period 7 to 58 min. Relatively twice as much Ettringite was formed in the gypsum-treated ash compared with the ash without added gypsum. These findings appear to parallel tricalcium aluminate reactions observed in portland cement hydration and can be explained by the fact that gypsum greatly increased the calcium sulfate content of the paste that promoted Ettringite formation.

SUMMARY AND CONCLUSIONS

The techniques described allow for relatively accurate, rapid quantitative evaluation of both elemental and crystalline composition of fly ash. A detailed evaluation of one Class C fly ash shows that a significant fraction of the material is crystalline; and of the crystalline components, tricalcium aluminate and calcium aluminum sulfate can account for its rapid setting behavior. This study also illustrates that at least for the Lansing fly ash, the composition and potential for reaction can be complex. It was also found that free calcium oxide was not present in significant quantities but appeared to be hard burned and could have a detrimental effect on the soundness of concrete.

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