

Characterization and Techniques for Rapid Evaluation of Iowa Fly Ashes

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An evaluation of seven fly ashes produced from Wyoming coal and available to the construction industry in Iowa is presented. X-ray spectrometry and diffraction were used to determine quantitative elemental and crystalline composition of the seven fly ashes, and long-term, multiple samples were taken at three sources to define variability in elemental composition. It was found that existing ASTM fly ash classification is not necessarily consistent with the coal type, that elemental variability within a single source can be equivalent to that of Type I portland cement, and that quantitative crystalline composition provides information useful for rational categorization. Of the seven fly ashes evaluated, three contained significant amounts of cementitious aluminum bearing phases; and all the fly ashes were comprised of about 25 percent crystalline compounds. Knowledge of cement led to development of a heat evolution test which may be useful in predicting cement content, and an evaluation of crystalline calcium and magnesium oxides suggests that soundness of fly ash-portland cement mortar is not influenced by magnesium oxide but is influenced by the crystalline calcium oxide present in the fly ashes evaluated.

Many Iowa fly ashes are produced from western subbituminous coals or lignites and, if their content is consistent with fly ashes observed by other investigators, should cover a broader spectrum of chemical composition than the Class F fly ashes normally associated with bituminous coals (1). The extensive variation observed within the Class C family of fly ashes has created the need for a more definitive classification scheme that should be supported with a fundamental understanding of fly ash composition (2). The potential for high variability in samples from the same source means that rapid diagnostic tests suitable for field use should be made available. In a companion paper in this Record Mings et al. (3) presents methods for determining quantitative elemental and crystalline composition of fly ashes by using X-ray analyses. This paper applies these X-ray techniques to characterization of seven

fly ashes that are available to the construction industry in Iowa.

EXPERIMENTATION AND RESULTS

Materials

Seven fly ashes, representative of those typically available in Iowa, were provided by the Iowa Department of Transportation for the research. Table 1 gives a list of the power plants along with the associated coal source. To allow for classification of the fly ashes, elemental oxide composition was determined by X-ray spectrometry according to the technique described by Mings et al. in this Record and the results are given in Table 2. With the exception of that from the Clinton power plant, all of the fly ashes used in this study were derived from Wyoming lignite/subbituminous coals. The ASTM C 618-80 classifications, which are also given in Table 1, suggest that the coal type is not necessarily consistent with the existing classification scheme.

Variability in Elemental Composition

The rapid measurement capability of the X-ray spectrometer made it possible to monitor the elemental composition of the fly ash samples over a period of several weeks. Approximately 30 samples were collected at weekly intervals from each of three power plants (three of the seven included in this study). The elemental oxide composition was determined; and for each plant a mean and standard deviation were

Table 1. Coal sources and fly ash classification.

Fly Ash Source	Coal Source ^a	ASTM Classification C 618-80 ^b
Power Plant		
Neal #3	Hanna South, Rosebud, and Medicine Bow Mine, Wyoming	F
Neal #4	Rawhide Ranch Mine, Wyoming	C
Lansing	Belle Ayr and Eagle Butte Mines, Wyoming	C
Council Bluffs	Belle Ayr and Eagle Butte Mines, Wyoming	C
Nebraska City	Caballo Mine, Wyoming	C
North Omaha	Rosebud Mine, Wyoming	F
Clinton	Illinois-Montana Blend	F

^aInformation from Isenberger (3).

^bASTM, 1980 (4).

Table 2. Elemental composition of fly ash by weight (%).

Fly Ash Source and Classification ^a	MgO	Na ₂ O	Fe ₂ O ₃	TiO ₂	SiO ₂	CaO	Al ₂ O ₃	K ₂ O	SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃
Clinton, Class F	1.3	0.6	18.1	0.8	55.8	4.3	19.2	2.14	93.1
North Omaha, Class F	1.4	0.5	14.6	0.6	50.0	1.5	27.7	0.2	92.3
Neal #3, Class F	3.1	0.5	7.9	0.7	50.5	13.6	18.1	1.2	76.5
Nebraska City, Class C	5.8	1.8	5.5	1.4	34.1	30.3	21.1	0.3	60.7
Neal #4, Class C	7.7	2.2	5.8	1.2	32.1	29.5	19.7	0.3	57.6
Council Bluffs, Class C	5.8	1.8	5.1	1.4	29.7	31.5	20.3	0.3	55.1
Lansing, Class C	6.2	1.8	5.9	1.3	30.0	31.1	19.7	0.4	55.6

^aASTM classification C 618-80.

computed for each oxide. To facilitate comparison among the different oxides, coefficients of variation (defined as the standard deviation of the oxides in the samples from one plant divided by the mean of the samples) are presented along with the means in Table 3. The variability assessment includes one Class F and two Class C fly ashes.

On the average, the ASTM C 618-80 classifications for the three fly ash sources used in the variability analysis are consistent with the single specimen analysis given in Table 2. When the product of these three plants is viewed in the context of variation for the major constituents by averaging coefficients of variation for SiO₂, Al₂O₃, Fe₂O₃, and CaO; the Council Bluffs fly ash is the least variable, the Neal #3 product is the most variable, and the Neal #4 fly ash is an intermediate. The minor constituents (i.e., MgO, Na₂O, K₂O, and TiO₂), of the Neal #3 and #4 fly ashes displayed about the same variability which was approximately three times that for the Council Bluffs plant, and a similar pattern held when all elements were considered.

An obvious pattern illustrated in Table 3 is that elemental variability for these fly ash sources bears little or no relation to the class of fly ash being produced. The least variable source is a Class C fly ash and the most variable sources are both C and F materials. In addition, Table 3 data show that in all three fly ashes the greatest degree of variability occurs among the minor compounds.

Significance of the magnitude of the variability resulting from this study is difficult to assess because the importance of individual compounds to various applications has not been clearly established. In an attempt to offer a comparison, however, elemental composition resulting from 12 Type I portland cements from different producers is presented in Table 4. The variability for the combined major

constituents for the Council Bluffs fly ash is equivalent to that of the portland cements, whereas the combined minor constituents for the fly ashes in Table 3 display significantly less variability than the portland cements. It should be recognized that data in Table 4 represent a sample of the cement industry as it existed several years ago and that advances in quality control may have reduced this variability. However, the data available thus far suggest that all three power plants operate within limits of overall elemental composition for Type I portland cement production as it did several years ago.

CRYSTALLINE COMPOSITION

Variability analysis of elemental composition in itself cannot adequately address the negative or positive results of using fly ash because such factors as the amount of the elements present and the form they take could easily dominate the behavior of fly ash in its various applications. For example, it has been shown by Mings et al. in this Record that in the Lansing fly ash calcium and aluminum combine to form a cementitious phase, calcium exists in limited quantities as a crystalline oxide, and a portion of the magnesium also exists as periclase. Based on experience with portland cement, all of these compounds could easily be significant. To allow for evaluation of the crystalline composition, the seven fly ashes defined in Table 1 were evaluated by X-ray diffraction and the results are shown in Table 5. The amorphous fractions of the seven fly ashes were computed from the complete crystalline component analysis by subtracting the sum of the crystalline component percentages from 100.

These results appear to represent the first definitive measurement of the quantitative phase

Table 3. Summary of fly ash chemical variability for three sources.

Oxide	Source					
	Neal #3 (26) ^a Class F		Neal #4 (34) ^a Class C		Council Bluffs (28) ^a Class C	
	Mean Weight (%)	CV (%) ^b	Mean Weight (%)	CV (%) ^b	Mean Weight (%)	CV (%) ^b
Major constituents						
SiO ₂	46.9	6.8	34.0	9.0	30.6	5.3
Al ₂ O ₃	17.4	9.4	19.8	1.8	20.8	2.3
Fe ₂ O ₃	9.0	10.3	6.6	7.9	5.3	5.2
CaO	16.0	18.4	26.0	14.6	31.1	4.5
CV, major constituents	-	11.2	-	8.3	-	4.3
Minor constituents						
MgO	3.7	21.0	6.8	18.5	6.0	10.7
Na ₂ O	0.4	37.9	0.9	23.9	1.8	6.5
K ₂ O	1.3	18.0	0.4	58.8	0.4	12.2
TiO ₂	0.7	23.8	1.2	10.1	1.5	7.3
CV, minor constituents	-	25.2	-	27.8	-	9.2
CV, all constituents	-	18.2	-	18.1	-	6.8

^aNumber of samples included in the analysis.

^bCoefficient of variation.

Table 4. Variability among samples of Type I portland cement from twelve different producers.

Oxide	Mean Weight (%)	CV (%) ^a	Oxide	Mean Weight (%)	CV (%) ^a
Major constituents			Minor constituents		
SiO ₂	21.31	2.6	MgO	2.18	45.5
Al ₂ O ₃	5.39	10.0	Na ₂ O	0.16	54.7
CaO	63.94	1.5	K ₂ O	0.43	72.3
FeO	No data	No data	TiO ₂	0.25	11.7
CV, major constituents	-	4.7	CV, minor constituents	-	46.0
			CV, all constituents	-	28.3

Note: Data from Journal of the American Concrete Institute (5).

^aCoefficient of variation.

Table 5. Crystalline components in fly ashes from seven power plants.

Component	Source and Weight (%)						
	Neal #3 Class F ^a	Neal #4 Class C ^a	Lansing Class C ^a	Council Bluffs Class C ^a	Nebraska City Class C ^a	North Omaha Class F ^a	Clinton Class F ^a
Tricalcium aluminate	0.0	4.9	5.2	6.0	0.5	0.0	0.1
Tetracalcium aluminate sulfate (C ₄ A ₃ S̄)	0.1	1.1	2.3	0.2	0.0	0.0	0.1
Calcium sulfate (CaSO ₄), (anhydrite)	0.3	1.3	1.7	0.9	0.1	0.3	0.2
Calcium oxide (CaO)	2.3	0.8	2.1	1.4	0.1	0.2	0.2
Quartz (SiO ₂)	7.0	8.0	10.1	5.3	7.1	9.9	8.2
Mullite (Al ₆ Si ₂ O ₁₃)	0.0	2.3	0.9	0.0	2.9	3.6	3.0
Magnetite (Fe ₃ O ₄)	0.7	0.0	1.0	0.2	0.0	10.0	7.4
Magnesium oxide (MgO), (periclase)	1.0	3.2	2.8	2.0	0.4	0.0	1.3
Amorphous contribution (glass) ^b	88.6	78.4	73.9	84.0	88.9	76.0	79.6

^aASTM classification C 618-78.^bEstimated by subtracting sum of crystalline components from the total.

composition of fly ashes and also to illustrate the potential for refining the existing ASTM classification scheme which is based largely on elemental composition. Neal #4, Lansing, and Council Bluffs fly ashes contain significant amounts of tricalcium aluminate and tetra-calcium trialuminate sulfate phases and are reactive with water in that they exhibit high heats of reaction and set within a few minutes. By ASTM standards these three fly ashes are categorized as Class C.

On the other hand, the North Omaha and Clinton fly ashes are relatively inert because they contain small amounts of the cementitious compounds and rightfully fall into another category, which in this case is ASTM Class F. The problem is with the Nebraska City ash which also contains negligible amounts of the cement compounds and in terms of reaction with water is relatively inert. The Nebraska City fly ash is marginally designated as Class C, yet its compound composition is more akin to that of the Class F ashes. A more logical scheme to guide future research and possibility for field application would be classification according to reactivity with water which could then be used to make inferences about the presence, type, and amount of cementitious compounds.

The data in Table 5 also serve to illustrate two additional points. The high heat of hydration of some fly ashes was thought to be caused by hydration of lime. At least for the three reactive fly ashes used in this study, CaO is only a minor constituent; therefore, reaction heats should be caused largely by hydration of the cementitious compounds. Also the ability to quantify amorphous contributions which contribute to pozzolanic reactions with lime, either added directly or derived from hydration of portland cement, suggests that for the seven fly ashes tested, the pozzolanic potential based on quantity alone should be about the same. Tests that are currently used to assess pozzolanic activity should result in misleading information for three of the fly ashes investigated because they incorporate the effects of strength due to cement hydration and the pozzolanic reactions. Finally, these fly ashes display a considerable range of inert compounds such as quartz, mullite, and magnetite which should contribute little, either positively or negatively, to performance. The lowest combination of relatively inert materials was 5.5 percent for the Council Bluffs ash and the highest was 23.5 percent for North Omaha. The influence of CaO and MgO, which have the potential for causing poor performance, will be discussed in a subsequent section.

Heat Evolution Test

Knowledge that some of the fly ashes being investigated contain aluminous compounds leads to the

notion that a practical method for diagnosing the presence and possibly the quantity of these compounds could be to evaluate the heat generated during hydration or more simply correlate their formation to temperature change in an inexpensive calorimeter.

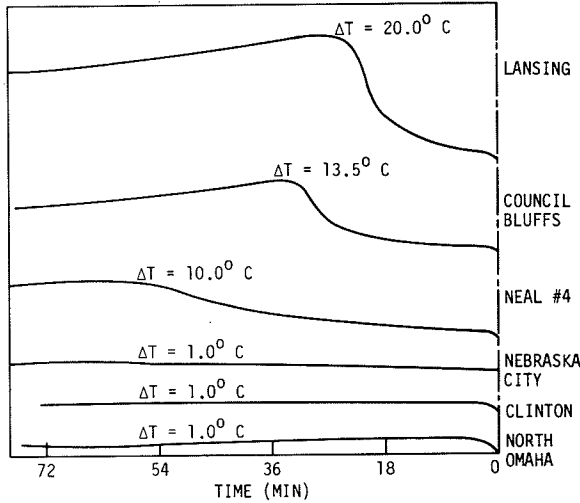
Knowing the quantity of cementitious compounds in fly ashes could have particular significance when these materials are used as soil stabilizers; thus a test using a dewar vacuum flask, a chromel-alumel thermocouple, and an electronic chart recorder was devised. The procedure involves placing 20 ml of tap water in a Styrofoam cup, placing the cup inside the dewar flask, and positioning the thermocouple junction in the water. Thirty grams of fly ash are then sprinkled into the water, and a cork is used to seal the dewar flask. The recorder and thermocouple system produce a curve that shows temperature increase versus reaction time during hydration.

The heat evolution test was performed on all but the Neal #3 fly ash; and to evaluate the potential for retarding C₃A hydration, the Lansing ash was mixed with different percentages of gypsum. It should be noted that a similar test was developed at the Texas Transportation Institute in an attempt to find a quick method of correlating elemental calcium oxide content to the temperature rise that occurs when fly ash reacts with hydrochloric acid (1).

The results obtained from the heat evolution tests are shown in Figures 1 and 2 and are summarized in Table 6. Peak temperature increases for fly ashes containing aluminous compounds were in the range of 10 to 20°C. These fly ashes definitely belong to Class C. Nonreactive ashes showed a temperature increase of 1°C over a period of 30 to 60 min. Two of these fly ashes, Clinton and North Omaha, are definitely Type F ashes. The Nebraska City fly ash, however, behaves similarly to Type F ash in all aspects except for the sesquioxides plus silica content, which place it in the Class C category.

The data obtained from the heat evolution test on Lansing fly ash are of interest because they show the influence of gypsum in delaying the time-to-peak temperature. The test performed on the Lansing ash without gypsum showed a temperature increase over a period of 22.5 min with the peak temperature increase at 22.5 min being 20°C. The analysis of the ash with 3 percent gypsum showed a 19°C temperature increase over an extended period of 66.0 min. When the oscillation diffraction data described by Mings et al. in this Record are compared with these results, an interesting trend can be seen. The periods of Ettringite formation or consumption of tricalcium aluminate from Mings et al. correspond to those of time-to-peak temperature as shown in Figure 3.

Figure 1. Heat evolution results for six fly ashes.



Although the data available thus far are not adequate to support a predictive correlation, the trends indicate that the potential exists for developing a correlation between temperature rise and the amount of aluminous compounds, providing that such phases are present alone in fly ash. Such a test would require nothing more than a Styrofoam container and thermometer.

Soundness

Experience with portland cement indicates that the presence of crystalline calcium and magnesium oxides can cause poor performance because of slow hydration and the development of expansive reaction products that form after the cement paste has set (6). Calcium oxide or free lime is thought to be intercrystallized with other compounds such that it is only partially exposed to water during early stages of hydration, and it has been shown that the influence of magnesium oxide on soundness is highly dependent on grain size--smaller grains tend to produce less

Figure 2. Heat evolution results for Lansing fly ash with gypsum.

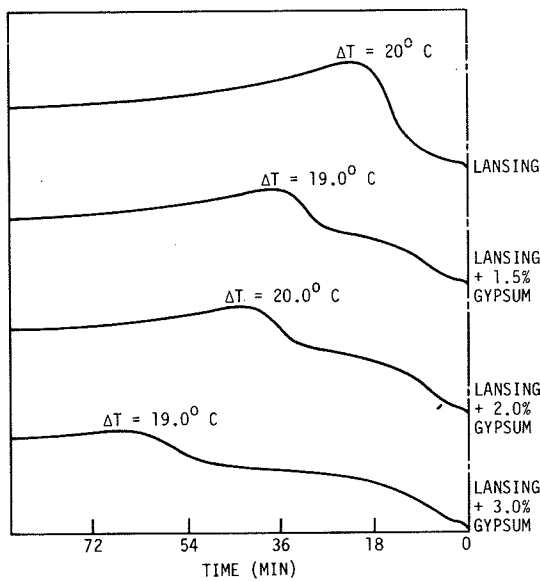


Table 6. Summary of heat evolution tests.

Fly Ash	Maximum Temperature Rise, ΔT (°C)	Elapsed Time for Attainment of Maximum Temperatures (min)
Council Bluffs	13.5	38.3
Neal #4	10.0	70.0
Lansing	20.0	22.5
Lansing + 1% gypsum	18.0	32.5
Lansing + 1.5% gypsum	19.0	36.0
Lansing + 2% gypsum	20.0	43.5
Lansing + 3% gypsum	19.0	66.0
Nebraska City	1.0	60.0
Clinton	1.0	30.0
North Omaha	1.0	30.0

expansion (7). All of the seven fly ashes evaluated in this study contain either or both of the oxides in question and their potential for detrimentally influencing soundness when fly ash is used in portland cement concrete is important.

A series of ASTM C 151 autoclave expansion tests using the Neal #3, Neal #4, and North Omaha fly ashes was performed on samples where 20 to 50 percent of the portland cement was replaced by fly ash. Replacement was based on weight and the results are shown in Figure 4. Of interest is the one noncementitious Class F fly ash (Neal #3) that displayed far more expansion than the other two fly ashes that fall in cementitious and noncementitious categories, particularly at replacements in excess of 30 percent. From Table 5, it can be seen that the Neal #3 fly ash contained 2.3 percent calcium oxide and 1.1 percent magnesium oxide, but the two fly ashes that did not display significant expansion had one feature in common--calcium oxide contents less than 0.8 percent. Also, the fly ashes that did not display detrimental expansion contained extreme differences in magnesium oxide contents. The Neal #4 fly ash had 3.2 percent magnesium oxide while the North Omaha ash had none. These data suggest that the detrimental expansion of the Neal #3 fly ash was due to crystalline calcium oxide contents on the order of 2.3 percent and that magnesium oxide in quantities up to 3.2 percent does not influence soundness.

Figure 3. Effect of gypsum on the rate of hydration of Lansing fly ash.

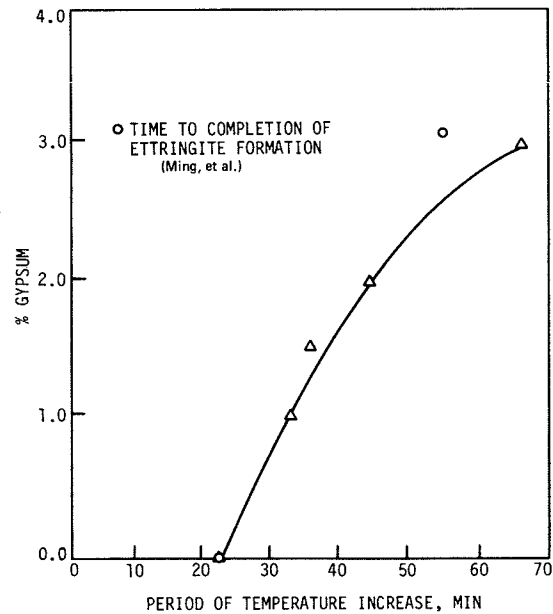


Figure 4. Effect of various replacements of portland cement by fly ash on autoclave expansion.

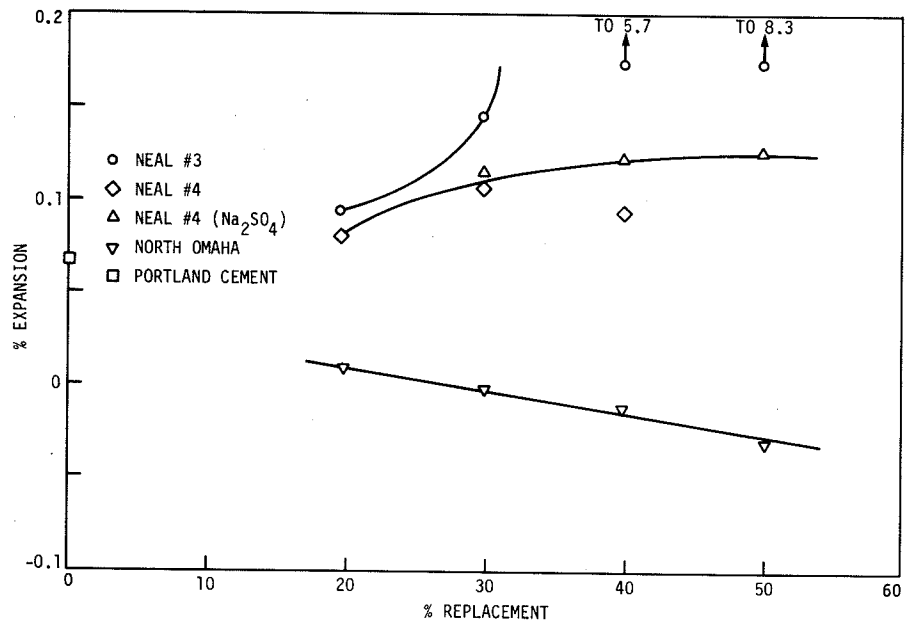
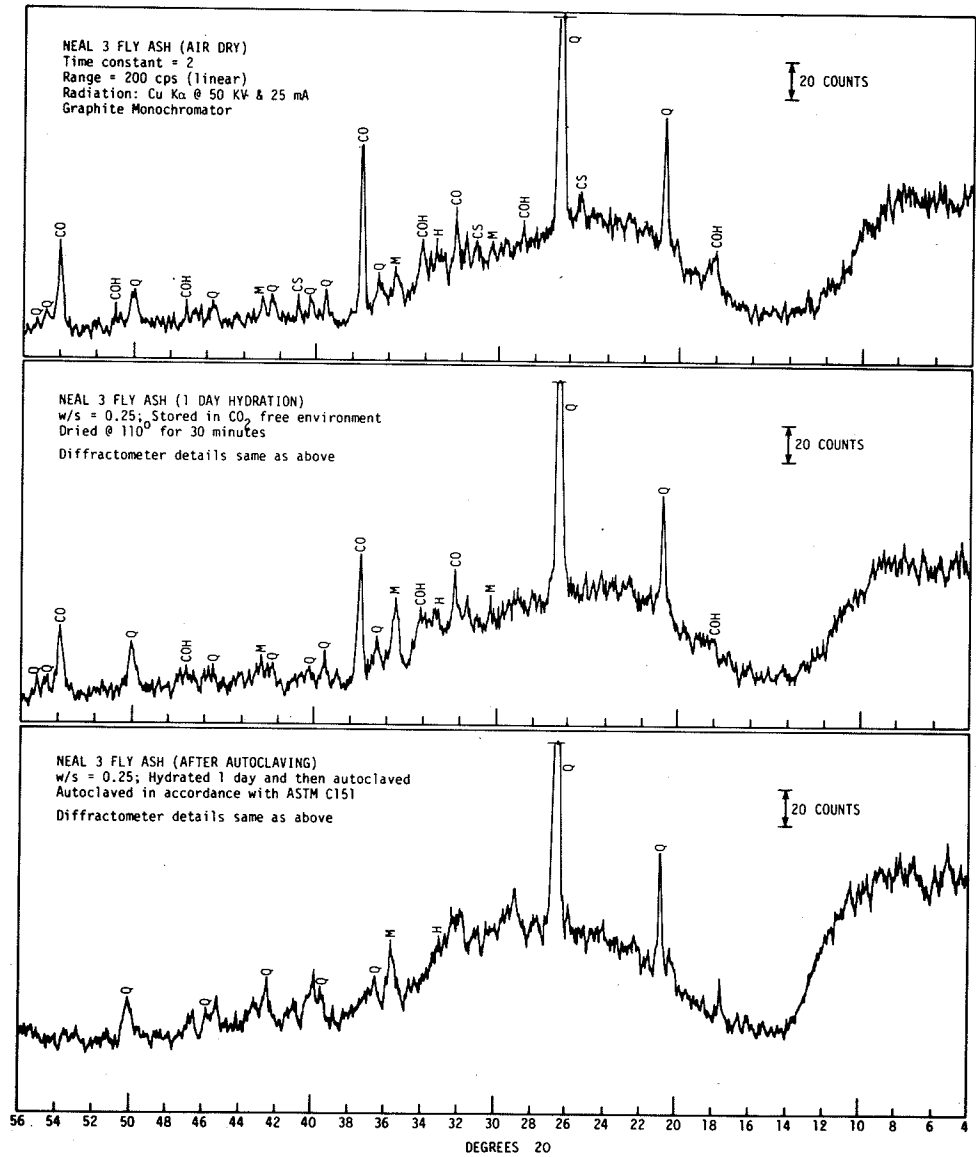


Figure 5. Diffraction patterns for Neal #3 fly ash.



An explanation for the phenomena displayed in Figure 5 may lie in the fact that the crystalline calcium oxide is hard burned, as was discussed by Mings et al. in a paper in this Record and that the particle size of crystalline magnesium oxide is such that it does not produce detrimental expansion. Further support for the significance of calcium oxide to soundness can be seen in Figure 5 which shows X-ray diffraction patterns of the Neal #3 fly ash before hydration, after 1-day hydration, and after 1-day hydration and autoclaving. A look at the 100 percent calcium oxide peak, identified by CO at $2\theta = 38$ degrees, shows little change in intensity after normal hydration. However, autoclaving causes the calcium oxide peak to vanish. The insignificant effect that magnesium oxide has on hydration may be substantiated by grain size measurements with a Le Mont image analyzer where the mean crystal size was found to be 3 microns (8). It has been shown that grain sizes of 5 microns or less do not produce expansion in portland cement until crystalline magnesium oxide is present in quantities ranging between 4 and 6 percent (7). The presence of small periclase grains in fly ash seems a logical event because of rapid cooling associated with fly ash production.

Physical tests now stipulated in ASTM C 618-80 would have diagnosed the problem with the Neal #3 fly ash; however, the optional limits placed on magnesium oxide may, at least for the fly ashes used in this study, not be appropriate.

SUMMARY AND CONCLUSIONS

If the fly ashes used in this study are representative of the compositional nature of all fly ashes, characterization by crystalline composition and in particular the amount of cementitious compounds could be more definitive than the existing classification based on elemental composition. It was found that fly ashes from seven different sources contained a wide spectrum of crystalline compounds including reactive cementitious aluminous compounds and inert minerals, but all of these fly ashes also contained nearly equal amounts of amorphous materials. A quick heat evolution test was evaluated and found to have potential for evaluating the presence and quantities of cementitious compounds. Crystal-

line magnesium and calcium oxide were detected in most of the fly ashes evaluated, and an autoclave expansion study suggests that calcium oxide and not magnesium oxide in these fly ashes is responsible for detrimental expansion.

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