

Increasing Cementitious Products of a Class C Fly Ash

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ABSTRACT

The results of using minute quantities of secondary chemical additives with an Iowa Class C cementitious fly ash are presented in this paper. Soil stabilization with fly ash conventionally requires the addition of water and lime to initiate pozzolanic reactions with subsequent formation of cementitious products. The glossy (amorphous) phase of Iowa fly ashes accounts for about 75 percent of their composition. They are known to contain significant amounts of calcium, aluminum, and silicon, the building blocks of cementitious compounds. If these elements could be economically liberated, the need to use lime would be reduced or eliminated. Lime is a costly ingredient available only at a few locations in Iowa. Potential additives were selected on the basis of economical considerations and expected reactions, as agents that either initiate chemical attack and dissolution of the glassy phase and seed crystalline compounds. Ammonium phosphate appeared the most promising of the seven additives studied. At 3.0 percent by weight of fly ash, the average 28-day strength for ammonium phosphate-treated samples was 2.5 times that of untreated. Scanning electron microscopy indicated the glassy phase of treated fly ash was being attacked. X-ray diffraction showed formation of cementitious reaction products not present in untreated samples. A rapid means of evaluating early strength gain and setting time properties of fly ash paste is also presented.

Much existing knowledge of fly ash for soil stabilization was developed in the 1950s, when most fly ash contained small amounts of calcium. In the presence of lime and water, fly ash supports pozzolanic reactions and forms cementitious reaction products. Lime can either be introduced directly, as a compound itself, or indirectly, through secondary reactions with portland cement. However, both lime and portland cement are costly and available at only a few locations in Iowa. Thus, use of fly ash as a stabilizing material for highway bases and sub-bases is often limited by cost.

New coal sources and power plant designs have dramatically changed the composition and character of fly ashes. Recent studies (1) indicate that some Iowa Class C fly ashes are cementitious because calcium is combined as tricalcium aluminate and calcium aluminum sulphate. Other Class C ashes have high calcium contents but no cementitious materials are present. Both types of material have significant amounts of calcium present in the glassy (amorphous) phase. This leads to many new possibilities for more economical and effective use of such fly ashes in soil stabilization.

Recent quantitative X-ray diffraction and fluorescence studies on a Class C cementitious fly ash

from Lansing, Iowa, showed this high calcium fly ash as having about 30 percent elemental calcium as an oxide but only 2.1 percent of this calcium existed as free calcium oxide (1). Combining calcium in several calcium-bearing crystalline compounds accounted for about one-sixth of the measured elemental composition with the remaining calcium residing in the glassy phase. It was determined that crystalline compounds comprised more than 26 percent of the fly ash composition (the remainder being amorphous). Tricalcium aluminate was present at 5.2 percent by weight; this is believed to account for rapid setting behavior.

Further quantitative studies (2) on multiple samples of 7 Iowa fly ashes from Wyoming coal revealed that all the ashes were comprised of about 75 percent amorphous materials. Neal No. 4, Lansing and Council Bluffs Class C fly ashes were shown to contain combined totals of tricalcium aluminate and tetracalcium aluminate sulphate ranging from 6 to 7.5 percent; this is believed responsible for fast setting and high early strength gain. Significantly in these three ashes, elemental calcium as an oxide was about 30 percent by weight whereas free calcium oxide ranged from 1 to 2 percent by weight. Other calcium containing crystalline components accounted for about 5 to 10 percent, indicating that 20 to 25 percent of the calcium is contained in the glassy phase.

Presented in this paper are the results of initial attempts at finding economical and practical means of liberating calcium and other elements necessary to form cementitious compounds from the glassy phase of Iowa Class C fly ashes without the use of lime or portland cement. Such efforts are expected to result in cementitious reaction products for use in soil stabilization. The secondary objective of the study was to determine practical materials and methods to control the rapid setting of Class C fly ashes containing tricalcium aluminate.

EXPERIMENTAL PROGRAM

Materials

Table 1 gives the chemical and physical properties of a cementitious Class C fly ash selected from the Neal No. 4 power plant located near Sioux City, Iowa. The Neal No. 4 ash is derived from lignite/sub-bituminous coal from the Rawhide Ranch Mine in Wyoming. It is classified under ASTM C 618-80 as a Class C fly ash, and it is representative of fly ashes available from several sources in Iowa by class, elemental composition (not crystalline compound composition), and quantity of material contained in the glassy phase.

All chemical additives used were commercially available reagent grade chemicals. The kiln dust used was bypass dust from kiln number 8 at the Lehigh plant, Mason City, Iowa. Additives and addition rates were selected on the basis of economical considerations and their expected reactions either as catalysts initiating chemical attack and dissolution or breakdown of the glassy phase and seeding crystalline cementitious compounds. Water used for all sample preparation was deionized and distilled.

TABLE 1 Chemical and Physical Properties of Neal No. 4 Fly Ash

	Neal #4
Chemical Composition (%)	
Silicon Oxide (SiO_2)	34.75
Aluminum Oxide (Al_2O_3)	15.47
Iron Oxide (Fe_2O_3)	6.31
Total ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$)	56.53
Physical Test Results	
Fineness (retained on #325 sieve, %)	5.80
Pozzolanic Activity Index with portland Cement (ratio to control at 28 days, %)	110
Pozzolanic Activity Index with Lime at 7 days, psi	1400
Water Requirement (ratio to control, %)	88
Soundness (autoclave expansion, %)	0.07
Specific Gravity	2.66
Sulphur Trioxide (SO_3)	3.55
Calcium Oxide (CaO)	25.76
Magnesium Oxide (MgO)	5.82
Moisture Content	0.02
Loss on Ignition	0.16
Available Alkalies as Na_2O	1.57

Procedures

As a preliminary screening measure, unconfined compressive strength testing was selected as a means to evaluate additive effectiveness. If an additive attacked the glassy phase and liberated calcium, aluminum, and silicon into a usable form, then "neopozzolanic" cementitious reaction products could result. Thus, strength would be expected to be enhanced.

All test samples in this study were prepared at a water/fly ash ratio of 0.24. Fly ash paste mixes were prepared and mixed in compliance with ASTM test method C 109. All chemicals with the exception of

kiln dust were dissolved or completely dispersed in the mix water before incorporation of the fly ash. The kiln dust samples were prepared by hand-mixing the dry materials followed by machine-mixing, before the addition of water. Chemical concentration percentages are based on dry weight of fly ash.

Cylindrical unconfined compression test samples (1.5 in. in diameter by 3 in. high) were cast in split mold assemblies, rodded, overfilled slightly, and clamped between lucite plates. Six cylinders were cast for each test age. On completion of molding operations, cylinders were placed in a room with 100 percent relative humidity at $70^\circ\text{F} \pm 1^\circ$. Cylinders were stripped within 24 hr of molding, and remained in the cure room until testing. Testing in unconfined compression was conducted at a controlled strain rate of 0.05 in./min.

To provide a rapid determination of setting properties and early strength gain in fly ash paste mortars, a Soiltest Model CL-700 pocket penetrometer was used. This instrument could later be adapted in soil stabilization field trials. The procedure consisted of casting a fly ash paste sample into a 4-in. diameter by 0.75-in. deep metal pan and using the penetrometer to obtain periodic readings. When inserted into a material to a specified depth, this device gives an indirect measure of unconfined compressive strength in tons per square foot. Samples were left uncovered at room temperature and measurements were made until a reading of 4.5 tons/ft² was obtained. Figure 1 shows the results of one test. Typically, there is an initial period of slow strength gain with time after which the rate of strength gain increased relatively rapidly. The data generally tended to plot as a straight line for both the initial slow-set period and for the accelerated-set period. The point of intersection of these lines has been defined as the time of initial set. The point at which the penetrometer limit of 4.5 tons/ft² was reached was arbitrarily defined as final set. Reaction time was measured from the time water was added.

Vial samples of the paste mixes were collected, sealed, and stored at room temperature at the time of molding. One vial sample was made for each group of 6 samples at each test age.

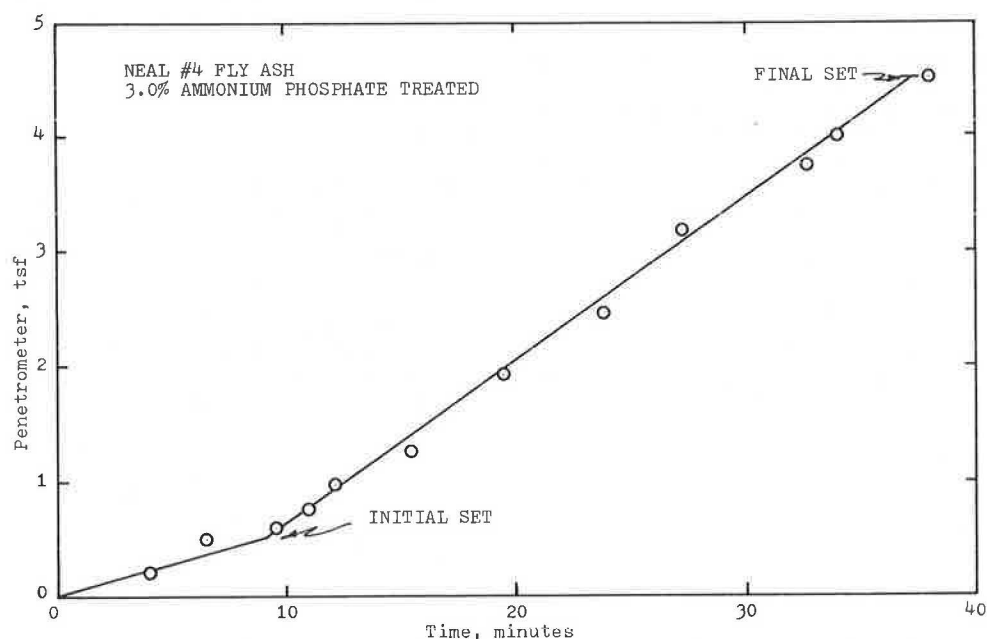


FIGURE 1 Setting times of ammonium phosphate-treated Neal No. 4 fly ash.

RESULTS

Setting Times

The Neal No. 4 fly ash contains approximately 5 percent tricalcium aluminate (2). This compound causes flash set in portland cement, and is believed to be the major cause of flash setting in cementitious fly ashes.

The mechanisms that control retardation of tricalcium aluminate hydration are not clearly understood. One theory (3) suggests calcium hydroxide reacts to form a compound that coats tricalcium aluminate particles and delays further reaction. If this theory is correct, the release of calcium from the glassy phase dissolution and resultant formation of calcium hydroxide could serve to retard tricalcium aluminate hydration. An alternate concept (4) suggests that formation of cementitious precipitates is dependent on pH, with highly alkaline conditions promoting reactions. If this theory is correct, a buffer or additive that can temporarily reduce pH to a lower level or counteract hydration of tricalcium aluminate should also act as a retarder.

The data in Table 2 indicate results of setting time determinations. Neal No. 4 control mixes containing only deionized distilled water exhibited a final setting time of less than 5 min. Generally, most additives affected final set time to a minor degree extending it by only 15 to 25 min at higher concentrations. Ammonium phosphate was the exception. At the 0.1 percent concentration, setting was retarded slightly; at the 1.0 percent level, initial

set was extended to 70 min, and final set was extended to 160 min. At the 3.0 percent level, a reversal occurred with initial set at 10 min and final set slightly retarded at 35 min. Thus, set retardation appears to be sensitive to ammonium phosphate concentration.

Unconfined Compressive Strength

Table 3 presents unconfined compressive strength results. Although some additives appeared to improve strength somewhat at varying concentrations, the most pronounced improvement was again found with ammonium phosphate. At an additive rate of 3.0 percent, average 28-day compressive strength was 4,475 lb/in.², 2.5 times greater than the average 28-day untreated control strength (1,805 lb/in.²). One-day compressive strength results for the 1.0 and 3.0 ammonium phosphate-treated samples were considerably lower than those of control samples indicating retardation of early strength development.

Reaction Products

Evaluation of reaction products was conducted by X-ray diffraction analysis of the interior portions of the vial specimens using a Siemens D-500 computer-controlled X-ray diffractometer equipped with a graphite monochromator and pulse height analyzer. Step-scan analyses using monochromatic copper K alpha radiation at a 50 kv, 25 ma setting were

TABLE 2 Initial and Final Setting Times for Neal No. 4 Fly Ash

Additive	Concentration Percent (1)	Initial Set Time Min.	Initial Set Pressure psi	Final Set Time Min. (3)
Control	0	<5	15+	5
Zinc Oxide	0.1	5+	15+	5+
	1.0	5	15	10
	3.0	5	15	10
Aluminum Sulphate	0.1	5+	15	10
	1.0	5+	5	10
	3.0	15	10	30
Sodium Fluoride	0.1	<5	15+	5
	1.0	<5	15+	<5
	3.0	5	10	15
Ammonium Phosphate (Dibasic)	0.1	10	10	15
	1.0	70	5	160
	3.0	10	5	35
Magnesium Oxide	0.1	<5	15+	5+
	1.0	10	5	15
	3.0	10	5	15
Magnesium Oxide + Calcium Oxide (2)	0.1	10	5	15
	1.0	10	5	15
	3.0	10	5	20
Kiln Dust	0.1	<5	15+	5+
	1.0	10	5	15
	3.0	10	5	20

(1) by dry weight of fly ash

(2) ratio of MgO=0.57 CaO by weight

(3) all final set times determined at a pressure of approximately 60 psi (4.5 tsf)

TABLE 3 Unconfined Compressive Strength of Neal No. 4 Fly Ash
(pounds per square inch)

Additive	Concentration Percent (1)	Test Age, Days		
		1	7	28
Control	0	1040	1195	1805
Zinc Oxide	0.1	1340	885	1214
	1.0	450	1345	1235
	3.0	760	1750	2050
Aluminum Sulphate	0.1	1225	1110	1765
	1.0	1510	1330	2200
	3.0	1180	1800	2725
Sodium Fluoride	0.1	1055	1040	800
	1.0	410	760	930
	3.0	40	330	1015
Ammonium Phosphate (Dibasic)	0.1	1145	1030	1670
	1.0	250	480	1025
	3.0	390	2390	4475
Magnesium Oxide	0.1	1400	910	1730
	1.0	825	2170	2610
	3.0	780	2465	2405
Magnesium Oxide + Calcium Oxide (2)	0.1	1080	1210	1400
	1.0	60	1420	2600
	3.0	1015	1090	3055
Kiln Dust	0.1	1280	900	1645
	1.0	960	1670	2740
	3.0	810	1465	1755

(1) by dry weight of fly ash

(2) ratio of MgO=0.57 CaO by weight

performed. Step size was 0.05 degrees; count time was 2 sec. Figure 2 shows results for air dry unhydrated Neal No. 4 fly ash. Figure 3 shows data for hydrated, untreated Neal No. 4 fly ash. Figure 4 shows results for hydrated, 3.0 percent ammonium phosphate treated Neal No. 4 fly ash.

Some differences are apparent when cement chemistry is compared with pozzolan chemistry (4,5). The reaction of portland cement with water is essentially a hydration reaction producing calcium hydroxide and forming cementitious calcium silicate

and aluminate hydrates. The pozzolanic reaction uses lime (CaO) and a pozzolan (fly ash) in the presence of water to form cementitious compounds. When a fly ash contains a significant amount of tricalcium aluminate, a combination of the complex chemistries of cement hydration reactions and pozzolanic reactions is involved, even in the absence of free reactive lime. If a chemical additive is included in the system to attack and dissolve the glassy phase; and to liberate calcium, aluminum, and silicon in a usable form, then additional "neo-pozzolanic" cemen-

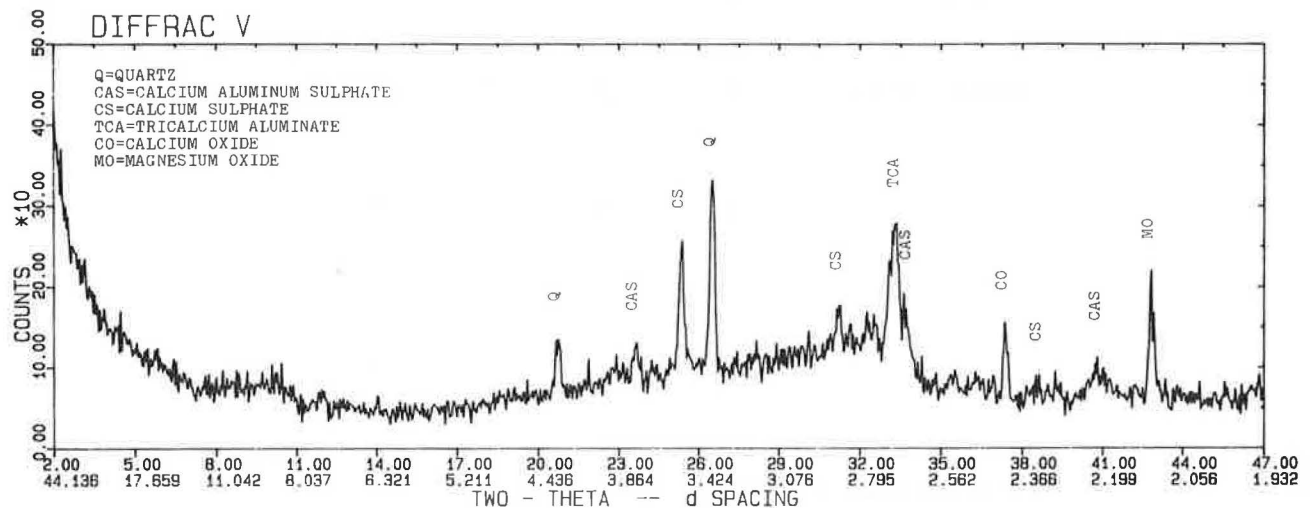


FIGURE 2 X-Ray diffraction trace, Neal No. 4 fly ash, air dry.

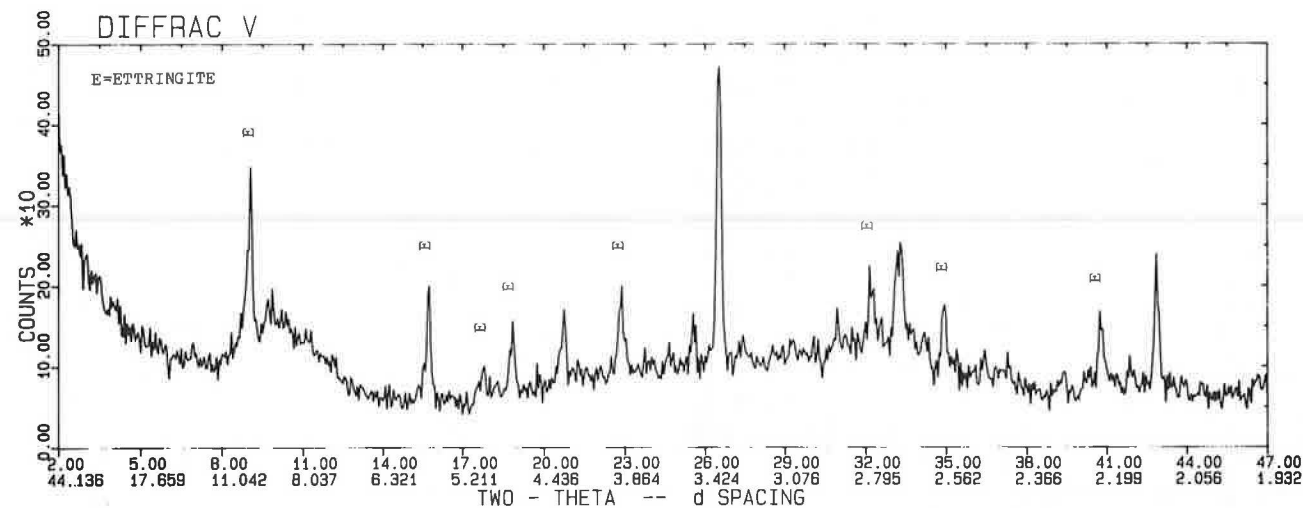


FIGURE 3 X-Ray diffraction trace, Neal No. 4 fly ash, untreated, cured at room temperature, sealed from air, age 36 days.

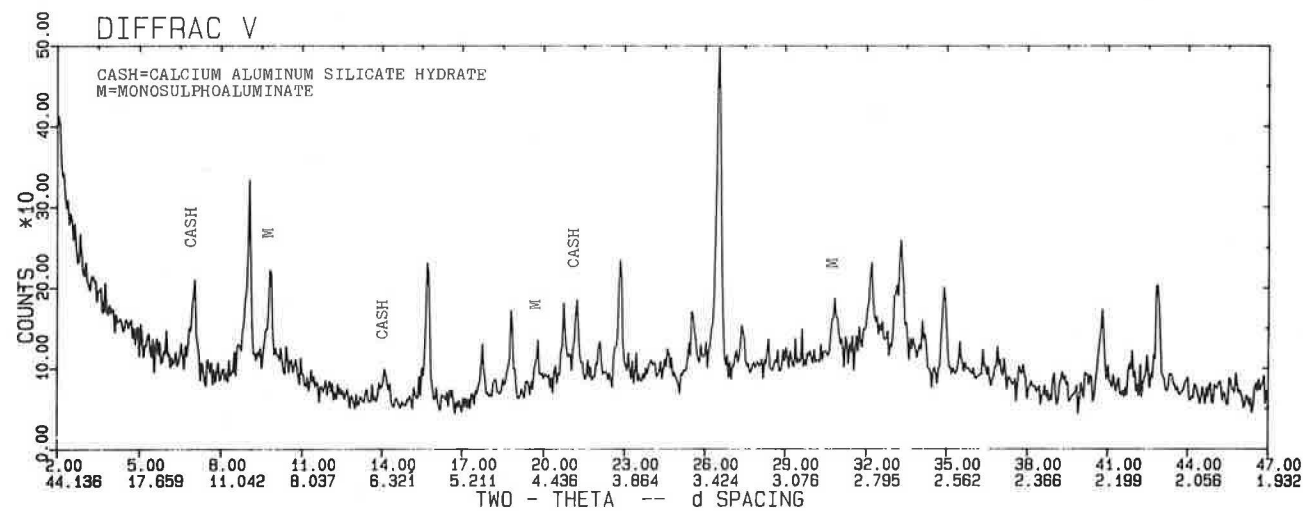


FIGURE 4 X-Ray diffraction trace, Neal No. 4 fly ash, 3.0 percent ammonium phosphate-treated, cured at room temperature, sealed from air, age 35 days.

titious compounds could form; that is, calcium aluminate and silicate hydrates.

The X-ray diffraction patterns shown in Figures 2-4 identify only those peaks not present in the preceding figure. Comparing Figure 2 with Figure 3 indicates that the major reaction product of hydrated, untreated Neal No. 4 fly ash is primarily in the form of calcium aluminum sulphate hydroxide hydrate (ettringite). Comparing the ammonium phosphate treated pattern (Figure 4) with the hydrated untreated pattern (Figure 3) indicates the additional formation of relatively strong calcium aluminum silicate hydrate peaks (stratlingite). Relatively strong calcium aluminum oxide sulphate hydrate peaks are also evident (monosulphoaluminate).

Scanning electron micrographs of the interior portion of the hydrated vial samples are shown in Figures 5-7. Spiky ettringite crystals (4) are evident in Figure 5 (untreated hydrated Neal No. 4). Figures 6 and 7 clearly indicate disintegration and breakdown of the glassy phase (hydrated ammonium phosphate treatment). The formation of relatively massive crystalline reaction products and monosulphoaluminate crystals is also evident. The ammonium phosphate additive was selected because silica and phosphate tetrahedra are similar, suggesting that

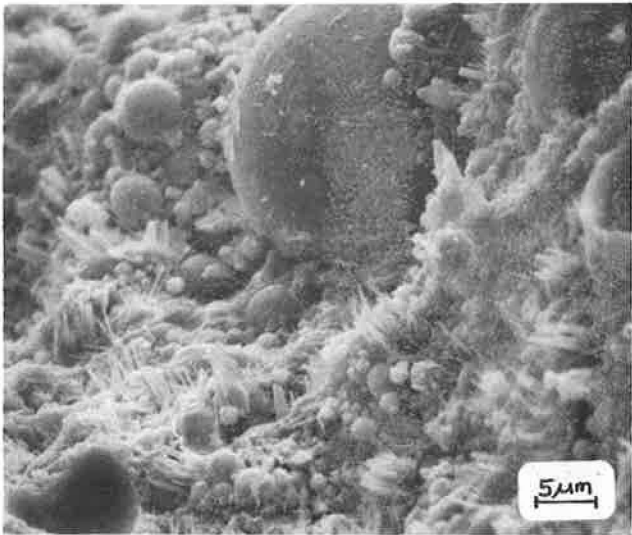


FIGURE 5 Scanning electron micrograph, Neal No. 4 fly ash, untreated, cured at room temperature, sealed from air, age 36 days, 1900X.

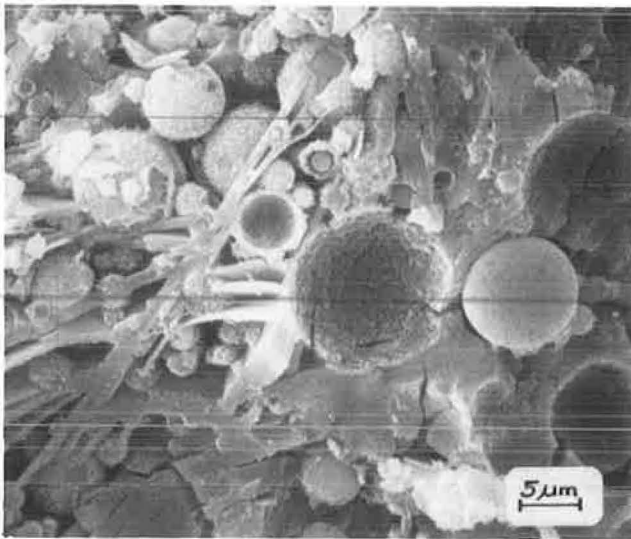


FIGURE 6 Scanning electron micrograph, Neal No. 4 fly ash, 3.0 percent ammonium phosphate-treated, cured at room temperature, sealed from air, age 35 days, 1900X.

the phosphate ion might go into solid solution in the glassy phase and form a seed for the recrystallization of silicates. This would disrupt the unstable glassy phase, producing stable crystalline compounds. Again, the exact mechanism of glassy phase dissolution is not yet known, but the hypothesis appears to be valid.

SUMMARY AND CONCLUSIONS

Ammonium phosphate appears to attack and break down the calcium-rich glassy phase of Neal No. 4 fly ash, making available liberated calcium, aluminum, and silicon to form neo-pozzolan cementitious reaction products. This is evidenced by X-ray diffraction and scanning electron microscope data indicating formation of stratlingite and monosulphoaluminate in the hydrated treated samples not present in the untreated hydrated control samples. Depending on concentration, ammonium phosphate also appears to be acting as a retarding agent by delaying rapid hydration of tricalcium aluminates as evidenced by setting time tests and low one-day compressive strengths compared to the control samples.

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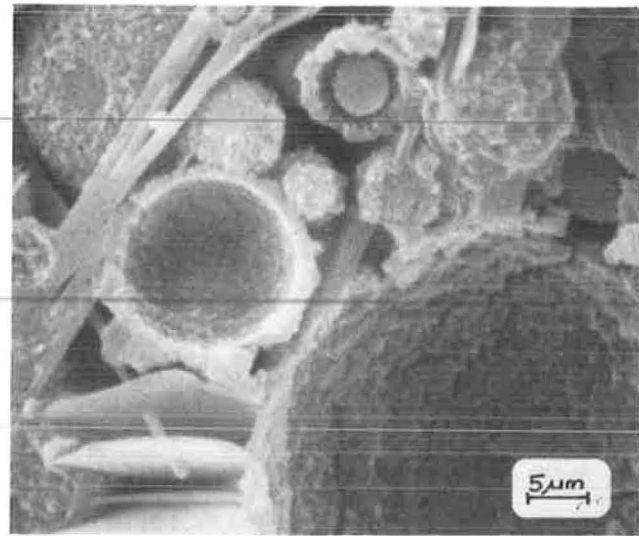


FIGURE 7 Scanning electron micrograph, Neal No. 4 fly ash, 3.0 percent ammonium phosphate-treated, cured at room temperature, sealed from air, age 35 days, 5000X.

Research Board, and the Iowa State University Mining and Mineral Resources Institute but does not necessarily reflect the opinions of those organizations.

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