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Cementitious Properties of Some Iowa Fly Ashes Without Lime Additives[1]

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Abstract. Seven Iowa fly ashes were evaluated as a construction material for embankments. Test specimens were molded at optimum moisture content for standard AASHO density and moist cured at 71°F for 28 and 120 days. Six of the fly ashes gave unconfined compressive strengths between 42 and 665 psi after 28 days curing plus one day immersion in water.

Test specimens were also steam cured in an autoclave to find a possible quick way to evaluate the strength producing characteristics of a fly ash. The strengths obtained after curing for one day in the autoclave give an indication of the strengths that may be obtained at ordinary curing temperature for longer periods.

X-ray diffraction patterns of the fly ashes are included. The peaks show that the reactivity of the fly ashes without lime is related to the amount of free lime present in the fly ash.

The fly ashes tested could be used in the construction of embankments. Some of them developed enough strength to warrant their use in the construction of subbases and subgrades for roads. The low strengths obtained with some fly ashes may be improved, if needed, by the addition of lime.

INTRODUCTION

Fly ash is a by-product of power plants burning powdered coal. As defined in ASTM Designation C 379-56T (1), fly ash is

> ". . . the finely divided residue that results from the combustion of ground or powdered coal and is transported from the boiler by the flue gases."

The annual production of fly ash in the United States is over 10 million tons and that of Iowa is about 200,000 tons. Only a fraction of the material produced is utilized as a pozzolan in mass concrete, as an ingredient in the manufacture of bricks, as an admixture with lime in soil stabilization, etc. Since the electric power industry faces the problem of disposing of the millions of tons of fly ash that are not utilized, there is keen interest in finding new uses or outlets for this product.

During the last seven years, the Soil Research Laboratory of the Iowa Engineering Experiment Station has conducted an investigation to evaluate lime and fly ash stabilization of coarse and fine-grained soils for use in the construction of roads (2).

[1] Work done under Project HR-82, Iowa Highway Research Board of the Iowa State Highway Commission.

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As a result of this investigation, the stabilization of soils with lime and fly ash can now be made on a sound technical basis.

Fly ash is considered an artificial pozzolan. Pozzolan is defined in ASTM Designation C 379-56T (1) as

> ". . . a siliceous or alumino-siliceous material which in itself possesses little or no cementitious value but which in finely divided form and in the presence of moisture will chemically react with alkali and alkaline earth hydroxides at ordinary temperatures to form or to assist in forming compounds possessing cementitious properties."

Other materials known to have pozzolanic properties are: volcanic tuffs, pumicites, diatomaceous earths, burnt clays and shales, etc.

As indicated in the definition, a pozzolan must react with lime and water to form cementing compounds. Since fly ashes may contain a certain amount of lime in their composition, as seen in Table I, it has been suggested that fly ash may develop cementitious properties without the addition of lime (3). In England the use of fly ash, without added lime, for embankment material has been reported recently (4).

This paper presents the results of an investigation to evaluate the inherent pozzolanic characteristics of seven Iowa fly ashes.

MATERIALS

Fly Ashes

The seven fly ash samples were obtained from different power plants in Iowa. The chemical and physical analyses are given in Tables I and II. Information on the coal used and methods of collection can be found in reference (5).

Table I. Chemical composition of fly ashes

Fly ash No.	Percent by weight of						
	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	SO_3	Loss on ignition*
V- 7	36.20	16.68	15.80	8.30	0.92	1.47	18.55
V- 8	36.68	24.33	21.29	3.45	0.98	2.02	7.20
V- 9	43.72	18.37	16.87	6.04	1.32	1.09	8.75
V-10	11.26	68.40	0.90	12.27	0.25	3.19	0.70
V-11	40.08	36.55	13.13	5.80	0.30	2.36	0.15
V-12	38.50	16.20	18.08	3.25	0.17	1.05	13.89
V-13	28.26	22.16	9.88	8.35	0.66	1.09	28.06

* Approximately equal to carbon content.

Table II. Physical properties of fly ashes

Fly Ash No.	Source	Percent Passing # 200 Sieve	Percent Passing # 325 Sieve	Specific Gravity	Specific Surface sq. cm./g.
V- 7	Cedar Rapids	80.9	54.9	2.37	4550
V- 8	Cedar Rapids	86.8	49.8	2.39	2663
V- 9	Cedar Rapids	85.7	51.3	2.04	3112
V-10	Davenport	64.3	22.6	3.43	576
V-11	Des Moines	91.6	31.8	2.82	1460
V-12	Waterloo	72.5	54.9	2.34	4240
V-13	Eddyville	24.7	14.0	2.15	1903

Limes

Two commercial grade limes were used, one a calcitic hydrate, $Ca(OH)_2$, and the other a dolomitic monohydrate, $Ca(OH)_2 + MgO$. The properties of the limes are given in reference (5).

Methods

Preparation of Specimens

The proportions of lime and fly ash mixtures are based on the dry weight of the total lime plus fly ash. The ratios of lime to fly ash in the mixtures made with these two materials were 1:4 and 1:9. The test specimens were molded at the optimum moisture content for standard density using the Iowa State Compaction Apparatus (2, 5, 6, 7).

Curing

The specimens cured at normal temperature were wrapped in waxed paper, sealed with cellophane tape, and placed in a humidity (90% R.H.) room at 71 ± 4°F. The specimens cured in an autoclave were first wrapped in Saran wrap, sealed with cellophane tape, and placed in an oven at 140°F (60°C) for 2 hours before being transferred to the autoclave operated at 248°F (120°C) and one atmosphere of pressure.

Testing

After curing, specimens were tested for unconfined compressive strength after 24 hours immersion in water, except some that were tested without immersion. In the unconfined compression test, specimens were loaded to failure in the testing machine at the rate of 0.1 inch per minute; the average strengths of 3 specimens are recorded in pounds per square inch (psi).

X-ray Diffraction

The fly ash without any processing was mixed with a very small amount of water in order to hold it in the slide. The mounting slide was of bakelite. The powder method was used and the X-rays were produced in a molybdenum tube; a zirconium filter was used to let pass only the $K\alpha$ radiation.

Presentation and Discussion of Results

Fly Ashes Without Added Lime

As shown in Figure 1, condition A, six of the seven fly ashes tested produced some immersed strength without added lime after curing at normal temperature. The strengths obtained with these six fly ashes ranged between 42 and 665 psi after 28 days curing plus one day immersion, and between 92 and 1736 psi after 120 days curing plus one day immersion. A fly ash capable of developing such strengths should be of value as a compacted material for embankments, land fill or road subbases. Fly ash No. 12, which had 33 psi unimmersed and no strength after immersion (Table III) probably would not be stable on embankment side slopes exposed to weathering.

Table III. Comparison of immersed and unimmersed strengths of specimens cured at 70°F

Fly Ash No.	Strength, psi	
	28 days curing	28 days curing plus I day immersion
V- 7	105	87
V- 8	49	42
V- 9	93	80
V-10	203	192
V-11	621	665
V-12	33	0
V-13	53	46

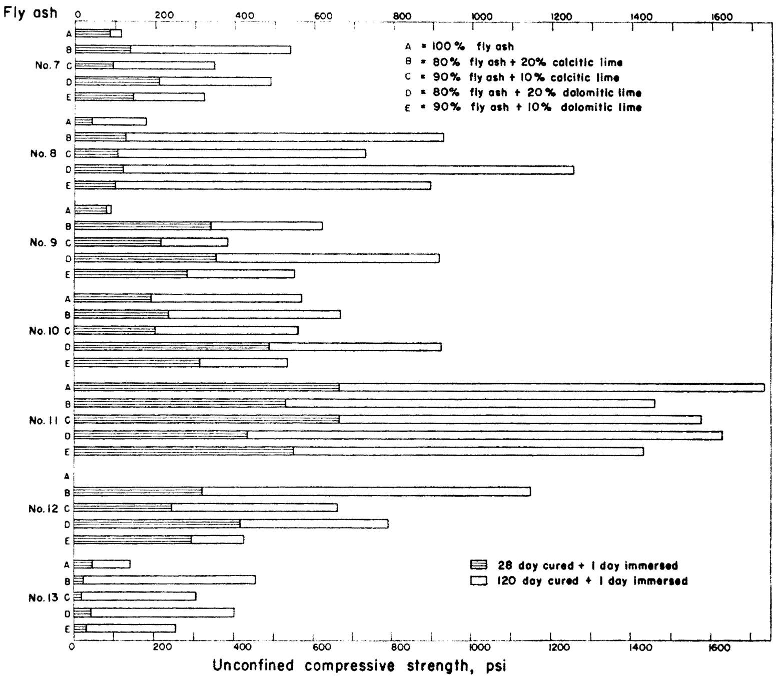

Figure 1. Strength of fly ash and lime-fly mixtures

Fly Ashes Treated with Lime

The addition of lime to fly ashes Nos. 7, 8, 9 and 12 increased strengths (Figure 1). However, fly ash No. 10 without added lime showed almost the same strengths as with added lime; added lime did not improve fly ash No. 11; and fly ash No. 13 without added lime developed higher strengths after 28 days curing, but lower strengths after 120 days curing, than with added lime.

Discussion

The discussion pertains only to the relative strengths obtained with the fly ashes with and without added lime. The differences in pozzolanic reactivity of the fly ashes have been already discussed in reference (5). The pozzolanic reactivity of a fly ash is related to the fineness, loss of ignition and other factors.

The good performance of fly ashes Nos. 10 and 11, which showed the same strengths with and without lime, should correlate with their composition. The same can be assumed for less reactive fly ashes. The natural lime content of each fly ash should be related to the strengths attained without added lime. The chemical analysis given in Table I show that there are appreciable differences in the amounts of CaO and MgO in the different fly ashes. However, these amounts are not necessarily available and no correlation was found between CaO and MgO contents and the relative strengths of a fly ash without added lime. To check on the free lime content in each fly ash, pH measurements and X-ray diffraction analyses were made.

The pH measurements, Table IV, indicated that fly ashes Nos. 10 and 11, which showed the greatest strengths without added lime, are more alkaline than the other fly ashes. Fly ash No. 12 had the lowest pH; it also had the lowest strengths without added lime.

X-ray diffraction analysis (Figure 2) showed that fly ashes Nos. 10, 11 and 13 have a "hump" at 2.63 Å corresponding to the basal

Table IV. pH of fly ashes without added lime

Fly ash No.	pH*
V- 7	12.33
V- 8	12.33
V- 9	11.76
V-10	12.55
V-11	12.47
V-12	9.92
V-13	12.07

*Measured in a Leeds and Northrup glass electrode pH meter.

space of the $Ca(OH)_2$ lattice. There is no indication of the existence of free lime in the other fly ashes; however, the amount of free lime may not be enough to show in the diffractometer chart. Fly ashes Nos. 7, 8, 9, 12 and 13 showed some content of $CaCO_3$, as reflected in the formation of a small peak at 3.03 Å. The $CaCO_3$ content of fly ashes Nos. 10 and 11 appears to be very small. The relatively low strengths of fly ashes Nos. 7, 8, 9 and 12 may be because the free lime originally present has been converted to calcium carbonate. This is apt to occur as fly ashes are moistened for transportation to waste areas and there exposed to carbon dioxide from the atmosphere. It is possible that fresh samples of all the fly ashes would react similarly to fly ashes Nos. 10 and 11. In a short storage period the amount of lime converted into calcium carbonate should be insignificant.

Composition of Fly Ashes

The X-ray diffraction pattern of the different fly ashes provides information for identification of some of the materials

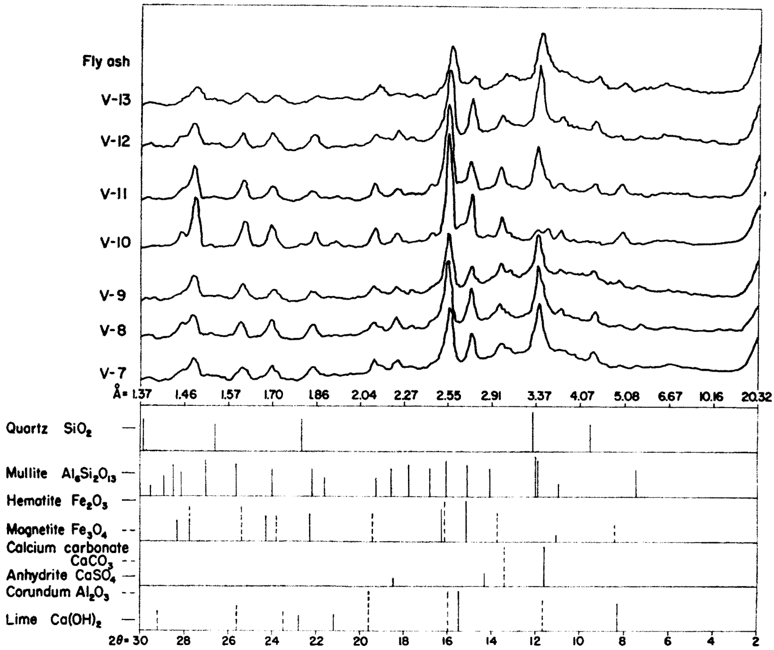

Figure 2. X-ray diffractometer pattern of fly ashes

present. As seen in Figure 2, the peaks correspond to crystalline forms of quartz, mullite, hematite, calcium carbonate, anhydrite, corundum and lime. The wide hump extending between values of 2θ of 8° and 20° is caused by amorphous materials: particles of unburned coal and amorphous compounds of silicon, aluminum and iron.

The lime present in the fly ashes appears to be in the hydrated form, that is, as calcium hydroxide. The X-ray diffraction pattern of calcium oxide was compared with the peaks given by the fly ashes. There was no indication of the existence of lime in the oxide form in the mineral composition of the fly ashes. The limestone and/or dolomite particles present in the coal are burned during the combustion process and converted to calcium and/or magnesium oxides. When the fly ash is collected, water usually is applied to reduce blowing during transportation in open trucks to the waste areas. This water may convert the calcium oxide into calcium hydroxide. The magnesium oxide may not be hydrated; it is difficult to detect in the X-ray diffraction of the fly ashes because its peaks coincide with mullite, magnetite and hematite peaks, and also because the possible amount present is very small as deducted from Table I.

Autoclave Curing

Specimens made with fly ash without added lime were subjected to autoclave curing to find a possible relation between the strengths obtained at ordinary curing temperatures and those obtained when curing at high temperatures for a much shorter period. The comparative results are given in Table V.

Table V. Comparison of strengths obtained at ordinary temperatures and in the autoclave

	Moist cured at 70°F		Steam cured at 248°F			
Fly Ash No.	28 days + 1 day immersion	120 days + 1 day immersion	1 day + 1 day immersion	3 days + 1 day immersion	7 days + 1 day immersion	Expansion %
V- 7	87 psi	116 psi	81 psi	87 psi	100 psi	1
V- 8	42 psi	179 psi	81 psi	101 psi	105 psi	1.5
V- 9	80 psi	92 psi	35 psi	43 psi	69 psi	1.0
V-10	192 psi	572 psi	187 psi	221 psi	317 psi	4.0
V-11	665 psi	1736 psi	687 psi	827 psi	884 psi	3.5
V-12	0	0	0	0	0	0.5
V-13	46 psi	141 psi	134 psi	165 psi	191 psi	1.0

For fly ashes Nos. 7, 10, 11 and 12, the 28 day strength at ordinary curing temperature may be perfectly predicted by curing for one day in the autoclave. For fly ashes Nos. 8 and 9, the prediction is within plus or minus 100 percent, and with fly ash No. 13 the strength after one day in the autoclave is about three times the strength after 28 days at ordinary curing temperature. The strengths obtained after 120 days at ordinary curing temperature are, for all the seven fly ashes, within plus or minus 100 percent of those obtained after 7 days curing in the autoclave.

For a quick evaluation of a fly ash without added lime, the strength obtained after curing for one day in the autoclave may be indicative of the strength potential with ordinary curing temperature. Until more information is obtained, a fly ash could be used as a construction material for embankments when the immersed strength after one day in the autoclave (one atmosphere, 248°F) is 50 psi or over.

It was observed that the specimens cured in the autoclave increased in volume during the first few hours of curing. It is interesting to note that fly ashes Nos. 10 and 11, which developed about the same strengths with and without added lime, showed the greatest expansion. This expansion is believed to be caused by a quick hydration of the anhydrite present in the fly ashes. Fly ashes Nos. 10 and 11 had the highest sulphur content, as indicated in Table I; this also is shown by the X-ray analyses where sulphur shows up in the form of anhydrite.

Conclusions

This study shows that Iowa fly ashes, which at present are wasted, can be used as a construction material. Some of them develop, in a moist compacted state, very good strengths without any added lime, and the strength of other fly ashes may be increased, if needed, by the addition of lime.

Some of the fly ashes may be used, without added lime, as a subbase or subgrade material for roads or embankments. All the fly ashes tested may be used in the construction of embankments, although some of them may need added lime when used in exposed surfaces subjected to rain or freezing conditions. When lime is needed to increase the strength of a fly ash, it can be added as lime water during the wetting process of the fly ash in the hopper.

The strength properties of a fly ash without added lime depend on the amount of free lime present, as indicated by X-ray diffraction studies.

The mineral composition of a fly ash includes quartz, mullite, hematite, magnetite, calcium carbonate, anhydrite, corundum, calcium hydroxide, unburned particles of coal, and possibly certain amorphous compounds. The quantitative mineral composition varies with each fly ash.

Acknowledgments

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