# Reactivity of Four Types of Flyash with Lime

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The variables of flyash that affect the pozzolanic reaction between lime and flyash were studied by means of unconfined compressive strength. The samples used in this study were molded from various mixtures of lime, four types of flyash, and water. All specimens were moist cured for a specific period prior to testing.

The pozzolanic activity of flyash was found to be dependent upon its carbon content and its degree of fineness. The rate of the pozzolanic reaction was considerably influenced by the conditions of temperature and humidity under which the samples were cured. The study also revealed that the unconfined compressive strength increases with increased lime contents.

● A POZZOLAN is defined in ASTM Standard Definitions of Terms Relating to Hydraulic Cement as a siliceous or siliceous and aluminous material, which in itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties (1). Although the principle products of the reaction between a pozzolan and calcium hydroxide are considered to be calcium silicates and aluminates, there is some evidence that more complex compounds are formed.

The use of a pozzolan with lime to produce cementation has been known since the time of the early Roman Empire. The Romans utilized the pozzolanic action of volcanic ash with calcined limestone in the construction of such historic landmarks as the Appian Way, the Colosseum and the Pantheon. Since then various other natural substances and some artificially produced materials have been found to possess various degrees of pozzolanic activity (5).

Flyash is an artificial pozzolan which results from burning pulverized coal. The coal, of which about 80 percent passes a No. 200 sieve, is blown into a furnace with primary air, and the combustion of the organic material in the suspended particles occurs almost instantly. The unburned inorganic materials form minute molten globules at a temperature of approximately 2,800 F. These globules congeal into spherical particles about 75 microns in diameter as they leave the zone of high temperature (5, 6). Some partially burned organic particles result and are of a more irregular shape and are somewhat larger. These particles are considered to be mostly carbon. After passing through the super heater, economizer and preheater, the ash (containing both incompletely burned and unburned particles) is separated from the exhaust gas stream by various methods. Collection of flyash in stack gas is usually accomplished through the use of electrical precipitators or mechanical collectors (8).

The design of power plant boilers generally falls into three basic categories: dry bottom, wet bottom and cyclone. The total ash produced in the operation of dry bottom boilers is approximately 90 percent flyash; the remaining 10 percent consists of larger particles (bottom ash) which fall out by gravity. Wet bottom boilers produce about 50 percent of total ash as flyash, whereas cyclone equipment produces only about 15 percent as flyash (8).

Electrical precipitators are more efficient than mechanical collectors and usually remove a higher percentage of the flyash from the flu gases. Flyash collected by electrical precipitators contains a high percentage of fine particles and therefore has a high specific surface which is considered conducive to high pozzolanic activity (3, 4, 9).

Each power plant produces flyash of a relatively different character, that is, it varies in particle size and chemical composition. These variations are due to the type of

TABLE 1

SOURCE AND COLLECTION DATA OF FOUR FLYASHES (14)

| Flyash | Type Boiler | Coal | Collecting Equipment | Collection Efficiency, percent |
|---|---|---|---|---|
| No. 10 | Dry bottom | Western Kentucky | Electrical | 98[a] |
| No. 11 | Wet bottom | 50 percent eastern Kansas and 50 percent petroleum coke | Electrical | Less than 90[b] |
| No. 12 | Dry bottom | Western Kentucky and southern Illinois | Mechanical | Less than 70[c] |
| No. 15 | Dry bottom | Southern Illinois | Electrical | 95[d] |

[a] Electric precipitators were used and since this station is located close to the heart of a city the combustion chamber and coal pulverizing equipment were designed for extremely efficient burning. The precipitators are oversize in order to obtain the high collection efficiency.

[b] This unit has electric precipitators but for the last year has burned a 50-50 blend of coal and petroleum coke. The coke does not fully burn in the short time that it is in the combustion chamber, therefore increasing the loss due to ignition (carbon content).

[c] Low efficiency here is due to the use of mechanical precipitators. The loss on ignition runs on the order of 8 to 12 percent. Most of this loss was evident in the material retained on the No. 200 sieve while the relatively finer material retained on the No. 325 sieve was very low in loss on ignition.

[d] Although electric precipitators are used in this unit the loss on ignition is fairly high. This is due to general overloading of the boilers (approximately 110 percent of rated capacity) resulting in incomplete combustion of the coal

coal, treatment prior to combustion, method of combustion, amount of recirculation and method of collection. Studies of the use of flyash in portland cement mortar and concrete have indicated that fineness and carbon content are possible criteria for differentiating flyashes. Analyses of flyashes include the term "loss on ignition" which is expressed as a percentage of the total flyash and approximately represents the carbon content. The loss on ignition is determined by oxidation, at high temperatures, of the organic material in the flyash. There are several methods of determining fineness, one of the more common is sieving the flyash through a No. 325 sieve to determine the percent passing.

Weinheimer (9), in 1944, conducted an extensive investigation of the chemical properties of flyashes. Chemical analyses of different size fractions of flyash indicated that the non-combustible $SiO_2$, $Al_2O_3$ and $Fe_2O_3$ tend to be concentrated in the finer fractions. The residual carbon, as determined by loss on ignition tests, predominates in the coarser particles. Photomicrographs showed that the carbon in flyash exists as irregular, porous, coke-like particles. The non-combustible particles generally have a characteristic spherical shape, although a small portion of these particles are thin walled polyhedrons called cenospheres.

There has been little information published about the effects of flyash properties on its reactivity with lime. In this study, four flyashes having different properties were used to investigate these effects. The unconfined compressive strengths of lime-flyash mortars were used to evaluate reactivity, the assumption being that strength is a positive function of reactivity.

## MATERIALS

### Flyashes

The sources and properties of each flyash are tabulated and explained in Tables 1 and 2. The flyashes have been assigned the arbitrary numbers shown in the tables and will be referred to by these numbers.

Photomicrographs of flyashes No. 10, 11, 12 and 15 are shown in Figures 1 through 4. These X 100 photomicrographs tend to corroborate Weinheimer's findings. Comparison of the photomicrographs of No. 10 and No. 11 flyashes is particularly interesting as these flyashes contain the least and the most carbon respectively. Notice the greater degree of fineness and the relative absence of carbon in flyash No. 10, whereas the particles in flyash No. 11 appear to be somewhat aggregated and coated by the more abundant carbon.

TABLE 2

PROPERTIES OF FLYASHES

| | | Flyash | | | |
|---|---|---|---|---|---|
| | | No. 10 | No. 11 | No. 12 | No. 15 |
| Specific Gravity | | 2.56 | unknown | 2.30 | 2.24 |
| Fineness | Residue passing a No. 325 sieve, percent by weight | 93.1[a] | 60 3[b] | 81.0[a] | 82.3[a] |
| Chemical Analysis, percent by weight | Silicon dioxide ($SiO_2$) | 43.40 | 39 19 | 41.16 | 35.94 |
| | Aluminum oxide ($Al_2O_3$) | 20.10 | 13.23 | 18.39 | 18.19 |
| | Ferric oxide ($Fe_2O_3$) | 19 00 | 13.41 | 21.23 | 19.63 |
| | Calcium oxide (CaO) | 7 30 | 2 52 | 5.54 | 6.89 |
| | Magnesium oxide (MgO) | 0.43 | 1.16 | 0.77 | 0.85 |
| | Sulphur trioxide ($SO_3$) | 3.04 | 0.41 | 1 47 | 1.86 |
| | Loss on ignition | 3 20 | 27.67 | 10.18 | 15.59 |

[a] Method of test ASTM Designation C204-46T.

[b] Method of test: Material was screened until the percent passing the No. 325 sieve was less than 0.5 percent after five minutes in a mechanical sieve shaker.

### Lime

The lime used was laboratory reagent powdered calcium hydroxide. The manu-

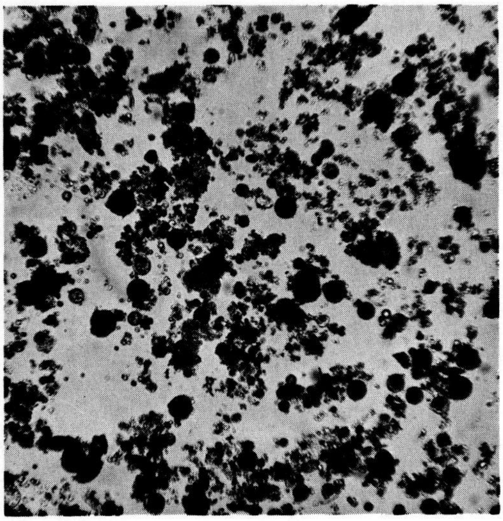

Figure 1. Photomicrograph of No. 10 flyash: X 100.

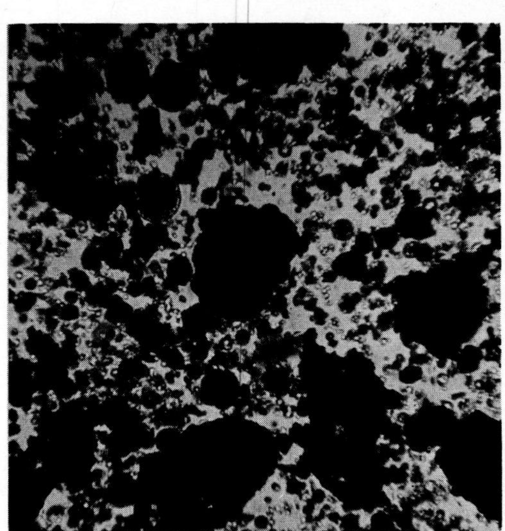

Figure 2. Photomicrograph of No. 11 flyash: X 100.

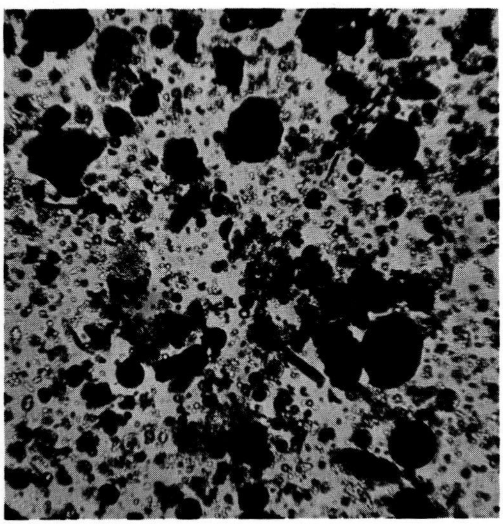

Figure 3. Photomicrograph of No. 12 flyash: X 100.

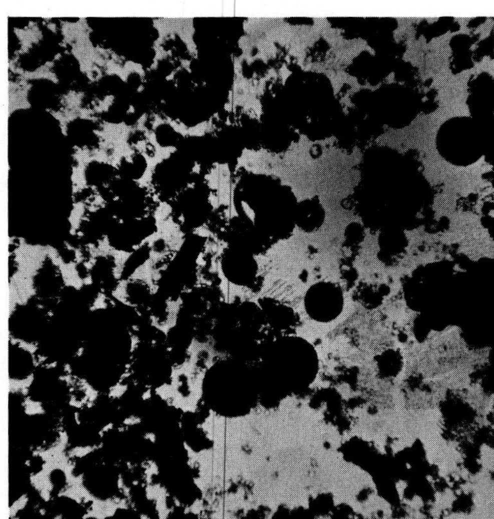

Figure 4. Photomicrograph of No. 15 flyash: X 100.

facturer has listed the maximum limit of impurities as follows:

| | % |
|---|---|
| Insoluble in HCl | 0.03 |
| Chloride | 0.005 |
| Sulfate | 0.10 |
| Heavy metals such as Pb | 0.003 |
| Iron | 0.05 |
| Substances not precipitated by ammonium oxalate | 1.0 |

TABLE 3

OPTIMUM MOISTURE CONTENTS AND CORRESPONDING TRUE MAXIMUM DRY DENSITIES OF THE LIME-FLYASH MORTARS PREPARED WITH THE FOUR FLYASHES

| | Flyash | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | No. 10 | | No. 11 | | No. 12 | | No. 15 | |
| Lime % | Opt. Moist. | Dry Density, lb/ft | Opt. Moist. | Dry Density, lb/ft | Opt. Moist. | Dry Density, lb/ft | Opt. Moist. | Dry Density, lb/ft |
| 2 | 29 | 85.0 | 57 | 51.7 | 36 | 68.5 | 45 | 61.4 |
| 4 | 26 | 83.6 | 57 | 52.7 | 36 | 69.1 | 43 | 60.7 |
| 6 | 28 | 82.2 | 57 | 53.3 | 36 | 69.5 | 43 | 63.1 |
| 8 | 28 | 81.8 | 57 | 53.5 | 36 | 70.6 | 42 | 63.8 |

## SAMPLE PREPARATION AND TESTING

### Preparation of Mixtures

The amounts of lime added to each flyash were 2, 4, 6 and 8 percent based on the dry weight of the flyash. The amount of distilled water in each case was sufficient to produce the maximum dry density for standard Proctor compactive effort. Mixtures contained only lime, flyash and distilled water and are referred to as mortars.

Moisture-density curves for four mortar compositions, using flyash No. 10, are shown in Figure 5. Several definite points of maximum density were found in the lower moisture range, but extension of the moisture-density curve into the upper reaches of moisture content revealed a true maximum density. Similar results were obtained with the other flyashes. The true maximum density occurred in all cases slightly below the moisture content at which the mortar began to act as a viscous liquid. The optimum moisture contents and corresponding true maximum densities are presented in Table 3.

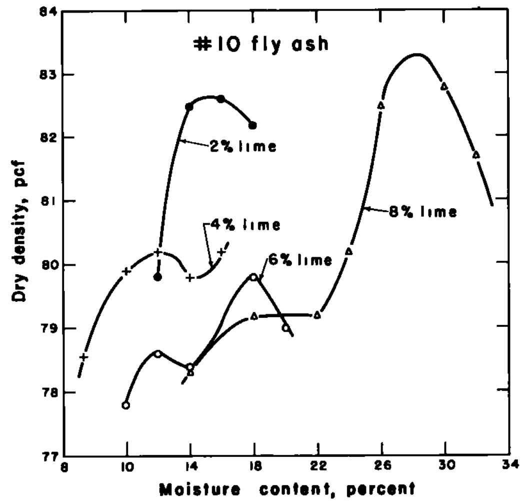


Figure 5. Moisture-density relationship of No. 10 flyash illustrating relative maxima at low moisture contents and the absolute maximum for the 8 percent lime content. These curves are typical for the other three flyashes.

Optimum moisture content tends to decrease with the fineness of the flyash. Davis et al (4) experienced similar results in their investigation of flyash as an additive to portland cement. A correlation of optimum moisture content and loss on ignition is shown in Figure 6. The increase of moisture requirement with increased carbon content is probably due to the porous nature of the carbon. Brink and Halstead (2) found a similar trend in the water requirement of portland cement-flyash mortars.

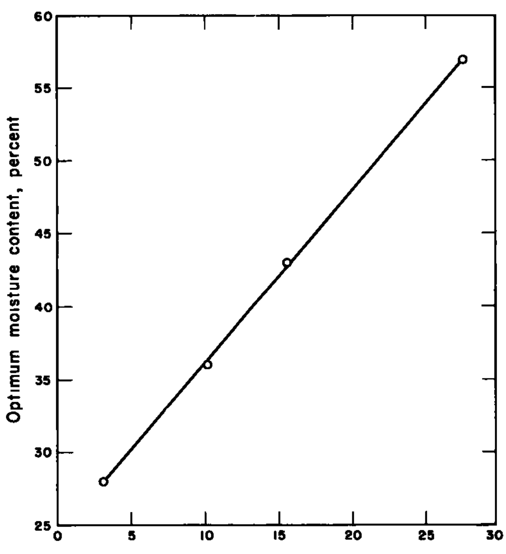


Figure 6. Optimum moisture content for maximum density of the lime-flyash mortars plotted as a function of flyash loss on ignition. The optimum moisture contents are the average values of four lime-flyash mortars.

### Mixing and Molding

Lime-flyash mixtures were proportioned and mixed dry. Optimum water was added and the materials machine mixed for four minutes. Specimens, 2-in. diameter by 2-in. high, for unconfined compressive strength tests were prepared at approximate standard Proctor density with a double plunger drop-hammer molding apparatus.

### Curing

Specimens were cured for various times at two different constant temperatures to study the rate and duration of the pozzolanic reaction. Curing times were 0, 7, 14, 28 and 45 days; curing temperatures were 20 C and 60 C. Each specimen was first wrapped in either Saran Wrap or wax paper, then wrapped with aluminum foil and sealed with Scotch

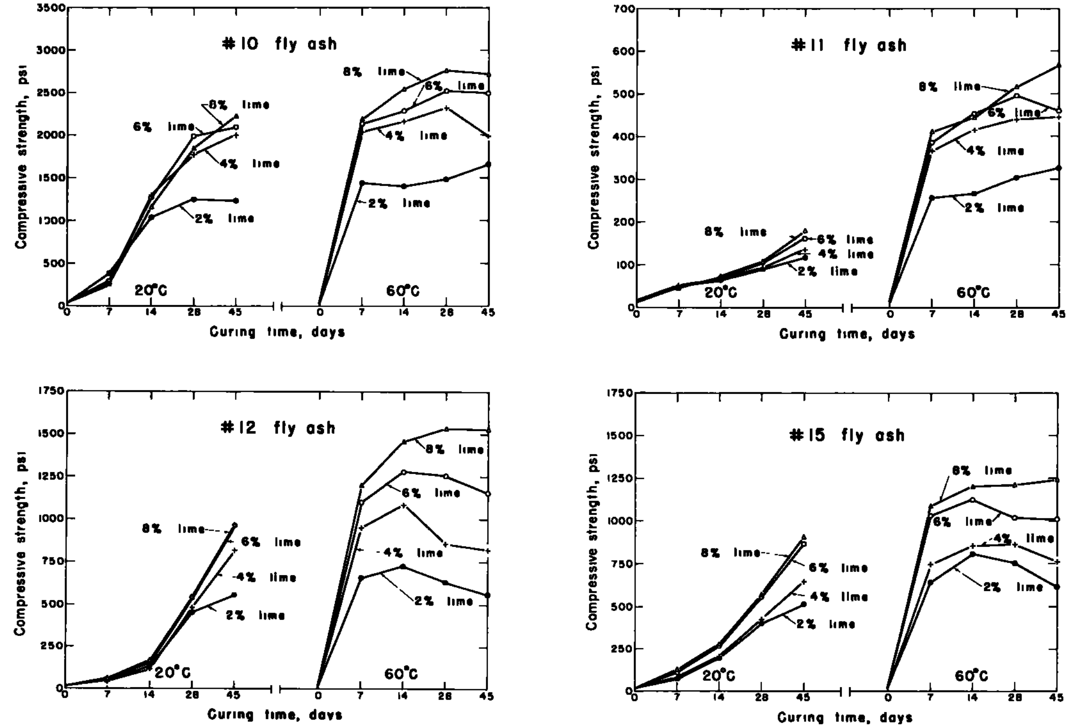


Figure 7. Effect of variation in the amount of lime, curing time and curing temperature on the compressive strength of 2-in. by 2-in. specimens prepared from the four flyashes.

tape. The difference in the inner wrapping should be noted since this inconsistency accounts for a variation in the test results. Specimens cured at 20 C were stored in an atmosphere with a relative humidity of approximately 90 percent. Specimens cured at 60 C were kept in an oven having a non-humid atmosphere; the sealing of each specimen was assumed to be sufficient to prevent any loss of moisture by evaporation.

## Testing

At the end of the curing periods specimens were unwrapped, weighed to determine moisture loss during curing and then tested in unconfined compression using a load travel rate of 0. 05 in. per minute. The results reported are the average of three test samples and represent the load at failure, uncorrected for height-diameter ratio.

## DISCUSSION OF RESULTS

The position of the strength-time curves of the lime-flyash mortars fluctuated somewhat during the early stages of curing at 20 C as shown in Figure 7. However, the curves appear to have reached their proper positioning in relation to each other after 45 days curing. The 45 day strength values show that increased lime contents are directly responsible for higher strengths.

Time and temperature are two very significant factors responsible for some of the variations apparent in Figure 7. The slopes of the strength-time curves at 20 C are still definitely positive after 45 days curing, indicating that the pozzolanic reaction has not yet reached completion. The lone exception is shown by the curve for No. 10 flyash with 2 percent lime. Here the reaction appears to be nearly complete after 28 days curing. These data support the validity of the assumption that compressive strength is a criterion for studying the progress of the pozzolanic reaction. Apparently strength develops at a rate that parallels the rate of the reaction. As the lime combines with the flyash, and the amount of free lime decreases, the rate of strength increase gradually slows and the curve tends to become horizontal. This is best shown by the mortars containing 2 percent lime.

Samples cured at 60 C showed a decidedly higher rate of strength development during the first few days than those cured at 20 C. The increase in temperature caused an increase in reaction rate during the first 7 days in all cases. Acceleration of the reaction was anticipated because it has long been known that many chemical reactions may double or treble their velocity with a 10 deg rise in the temperature of the reactants. Arrhenius has given a quantitative relation to this phenomenon through a mathematical description relating reaction rate to absolute temperature.

Figure 7 shows that in all but a few cases, curing beyond 7 days at 60 C caused the strength-time curves to flatten out and then to decrease. The loss of strength is apparently due to an excessive loss of moisture caused by improper choice of interior wrapping material (wax paper). Specimens (No. 10 flyash with 2 percent lime and No. 11 flyash with 2, 4 and 8 percent lime) wrapped with Saran Wrap did not show a decrease in strength or a significant loss of moisture during curing. A comparison of the moisture losses after curing showed an extreme loss of moisture at 28 days for all specimens wrapped in wax paper, for example, 13 grams moisture loss in 45 days for a Saran wrapped specimen as opposed to 30 grams moisture loss in 45 days for a wax paper wrapped specimen.

Other investigators have suggested the use of strength after 7 days curing at 60 C for predicting 28 day strengths of room temperature cured specimens. Comparison of these values in Figure 7 shows that there is no simple relationship between them. However, the strength values after 7 days curing at 60 C place the flyashes in their correct order of reactivity. This suggests the possibility of using accelerated curing for rating flyash reactivity when time does not permit the longer periods of curing required at room temperatures.

Regrouping the curves in Figure 7, so that the curves of identically proportioned

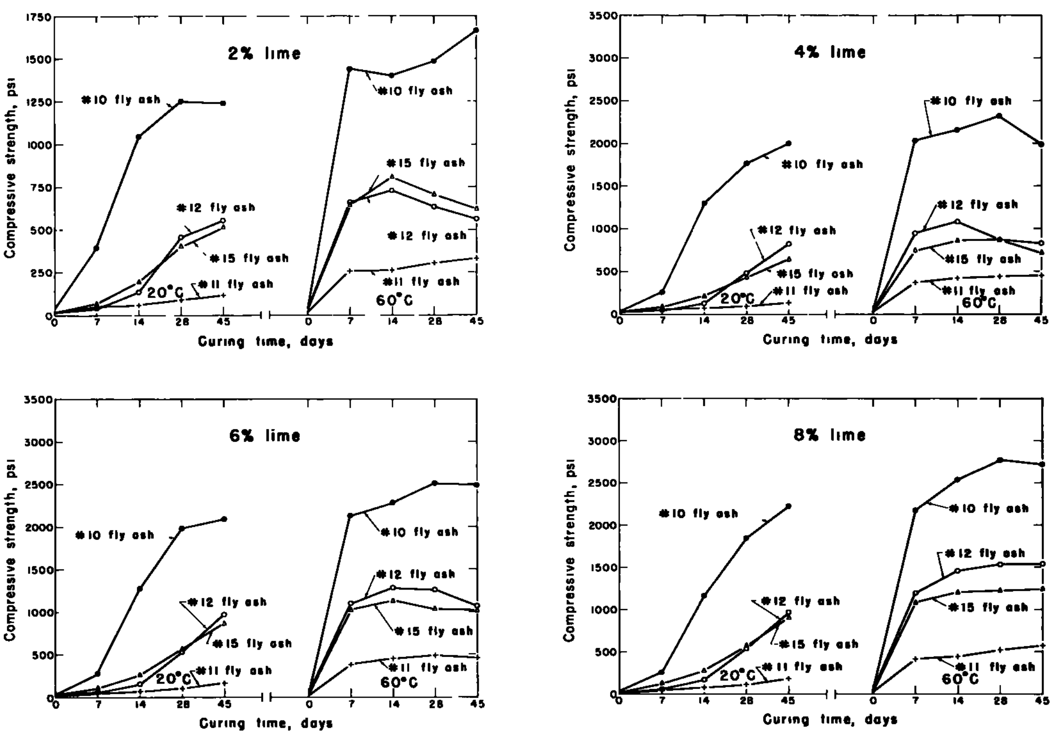


Figure 8. Comparison of compressive strengths of 2-in. by 2-in. specimens prepared from the four flyashes and the indicated percentages of lime.

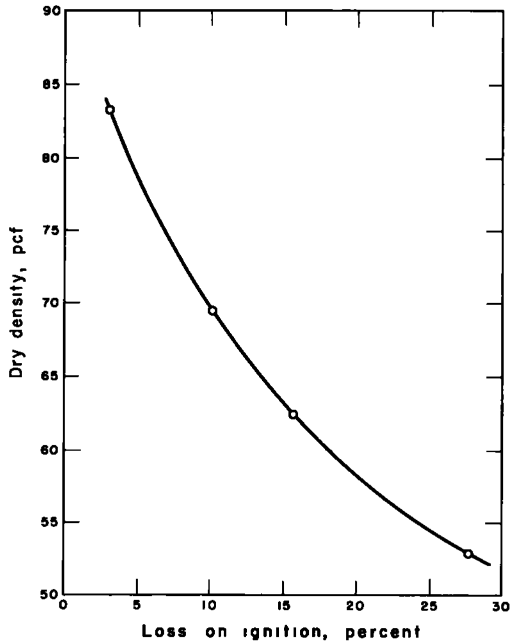


Figure 9. Dry density of lime-flyash mortars plotted as a function of flyash loss on ignition. Each dry density value is an average value for four lime-flyash mortars.

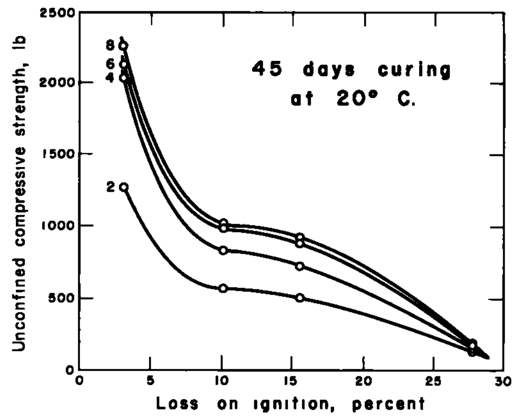


Figure 10. Unconfined compressive strength of lime-flyash mortars plotted as a function of flyash loss on ignition. The lime contents of 2, 4, 6 and 8 percent are shown at the left of each curve.

mortars made from different flyashes are grouped together, reveals the results shown in Figure 8. The highest strength was attained by No. 10 flyash mortars in all cases, which indicates that this flyash is by far the most reactive of those tested.

There are two apparent reasons for the superior performance of No. 10 flyash. Comparison of the photomicrographs of the four flyashes in Figures 1 to 4 shows that No. 10 flyash is much finer and contains less carbon than the other flyashes. Table 2 also verifies this.

Correlations of various mortar properties with the amount of flyash passing the No. 325 sieve were attempted. These correlations were not good but did indicate a rough relationship of density, of optimum moisture, and of strength to flyash fineness. However, by using loss on ignition as the independent variable, better correlations were established. Figure 9 shows the relation between maximum dry density of lime-flyash mortars and loss on ignition. The decrease in density with increase in carbon content cannot be allayed to the difference in specific gravity between carbon and the $Al_2O_3$ and $SiO_2$ replaced by the carbon. A material balance comparison of the highest and lowest densities shows that specific gravity differences account for a density change of only about 2 pcf, whereas the true density difference is about 31 pcf. The difference is thought to be due to aggregating and porosity effects of the carbon.

The unconfined compressive strength after 45 days curing at 20 C has a significant relation to loss on ignition as shown in Figure 10. The curves show that the strength of lime-flyash mortars drops rapidly with increasing carbon content up to about 10 percent carbon, here the curves begin to level off. It is interesting to note that a flyash with a carbon content near 30 percent probably would show little or no pozzolanic activity. Apparently flyashes containing less than about 10 percent carbon are needed to produce lime-flyash mortars having high compressive strength. The advantage of using low carbon content flyashes is evident, but additional work with more flyashes is needed to establish an upper specification limit of carbon content.

Carbon in flyash appears to be deleterious to pozzolanic reactivity and strength of lime-flyash mortars because of its adverse effects on reactive surface area and mortar density. Microscopic examinations of the flyashes showed that the carbon tends to adhere to and partially cover the reactive surfaces, reducing the interfacial area available for pozzolanic reactions with lime. In addition to reducing reactive surface area of individual particles, carbon coatings also act as links between adjacent particles to produce a porous aggregated structure. This structure, in addition to further reducing the available active surface area, reduces the compacted density attainable; the decreased density results in fewer and less intimate contacts between cementitious particles.

## CONCLUSIONS

1. Carbon content as determined by loss on ignition seems to be a reliable indicator of the pozzolanic reactivity of flyashes with lime. The upper limit of carbon content for good pozzolanic cementation appears to be less than 10 percent. Additional work with more flyashes is necessary to establish a specific upper limit.
2. The amount of flyash passing a No. 325 sieve decreases as carbon content increases and is, to a lesser extent, also an indicator of the pozzolanic reactivity of flyash. Evaluation from this criterion was not as reliable as from loss on ignition.
3. The use of lime-flyash mortar strength tests for evaluating flyash reactivity appears to give valid results. The results at both room temperature (20 C) and at 60 C are consistent. Curing at the higher temperature has the advantage of less time requirement for reactivity evaluation.

## ACKNOWLEDGMENT

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