Pozzolanic Reactivity Study of Flyash

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In recent years much interest has been shown in soil stabilization methods utilizing the pozzolanic reaction. Limeflyash stabilization is probably the best known and most thoroughly investigated of these methods. Unfortunately, little is known of the nature of the reaction or reactions involved, or of the reaction products that are formed. This information is needed for evaluating the reactants and improving the reaction.

This paper describes a program of basic research on the nature of the pozzolanic reaction between lime and flyash. Six flyashes of various physical and chemical properties were investigated. The reaction between the flyashes and calcium hydroxide was followed by means of an electroconductivity procedure. The reaction was studied at several temperatures and for several concentrations. The reaction products were investigated by means of x-ray diffraction and differential thermal analysis techniques.

Calcium hydroxide absorption tests, using electroconductivity procedures, on flyashes gave essentially the same evaluation results as those obtained from compressive strength results. The influence of temperature on the reaction was most significant in the 20 to 60 deg C range. A crystalline reaction product was detected, but this may be a secondary product.

An explanation is offered for the mechanism of the pozzolanic reaction. The rate limiting step of the reaction is explained on the basis of diffusion.

●DUE TO increased interest in pozzolans for soil stabilization and other purposes, there have been many investigations of certain materials possessing pozzolanic activity. (The term pozzolanic activity is used to describe the ease with which lime reacts at ordinary temperature with any natural or artificial siliceous or aluminous material in the presence of water to form stable, insoluble compounds possessing cementing properties.) For largely economic reasons flyash has received much attention and study as a pozzolan. However, the majority of the investigations have dealt only with the strength contributing properties of the flyashes and not with the fundamental chemical aspects of the pozzolanic reaction.

Basic studies of the pozzolanic activity of flyashes and other pozzolanic materials are necessary for both practical and theoretical reasons. Explanations for the behavior of a given flyash under given field conditions, such as density and temperature, are of practical importance. Theoretically, if the mechanism and the nature of the reaction products were better known, it might be possible to improve the reaction.

A few basic studies have been made of pozzolans (9, 10, 13). Among these studies, Lea (9, 10) and Moran and Gilliland (14) are noteworthy. Many of the basic concepts of pozzolanic activity postulated by Lea over twenty years ago have not been improved upon. Lea theorized that the reaction was a surface reaction between the dissolved lime and the solid resultant product. He also stated that equilibrium would not be reached except after long periods of time.

Many of the factors that influence the pozzolanic reaction have been recognized, but have not been investigated thoroughly. Recognized factors of the pozzolanic reaction are: temperature, nature of the pozzolan, surface area, carbon content, alkali and

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sulfate content, carbon dioxide, hydrogen ion concentration, lime variables, including the calcium to magnesium ratio moisture and time.

The identification of the reaction products of the pozzolanic reaction has been a difficult problem and it has not been completely solved. The problem is analogous to the identification of the hydration products of portland cement. Because of the minute size of particles, the difficulty in isolating them, and the scarcity of necessary identification equipment, very few of the reaction products have been determined. Complex hydrated solid solutions of CaO, SiO_2 and Al_2O_3 are believed to be the major constituents.

PROPERTIES OF THE MATERIALS USED

Six samples of flyash were selected for this study. These samples did not represent all of the property variations found with this material, but it was felt that the major factors were represented. Physical and chemical properties of the flyash used are given in Tables 1 and 2.

It will be noted that the mean diameter values are based on hydrometer and sieve analyses. The difficulty in determining the particle size distribution of flyashes has been discussed by Holton and Reynolds [7]; on the basis of their conclusions, the order of magnitude of the mean diameters is probably close enough for the comparisons made in this study. Ignited samples were used because the combustible portion of flyash has a specific gravity of one or less.

In addition to the physical and chemical analysis, a sodium hydroxide solubility test similar to that used by the Bureau of Reclamation was performed on the flyashes. The results of these tests are shown in Table 3.

Because of the impurities present in commercial limes, reagent grade calcium hydroxide was used to make up all of the lime solutions used in this study.

TABLE 1
PHYSICAL PROPERTIES OF FLYASHES

Flyash No.	Total[1] Specific Gravity	Ignited[2] Specific Gravity	Passing[1] 325 Sieve (%)	Mean[3] Diam. (mm)	Specific[4] Surface, (cm²/gm)
10	2.56	2.65	93.1	0.0305	3479
11	2.25	2 53	48.2	0.0380	N.D.
12	2 42	2.55	81.0	0.0310	3370
13	2.93	3.21	65.1	0.0320	N.D.
14	2.67	2.96	94.3	0.0265	3470
15	2.43	2.54	82.3	0.0333	3649

[1] Total sample as received was used.
[2] Total sample ignited in a muffel at 600 deg C was used.
[3] Based on hydrometer and sieve analysis of ignited samples.
[4] Supplied by Robert W. Hunt Co., Chicago, Ill. Based on a gas adsorption method, total sample used.

TEST PROCEDURE

Absorption methods were explored to determine the rate of reaction between the lime and the flyashes. An electroconductivity method was used to determine the rate of calcium absorption. This method enabled the reaction rate of a single sample to be traced without altering the solution or the material being tested. At certain periods the absorption of calcium was checked by titration procedures.

The test procedure was to place a known amount of material along with 90 ml of lime solution of known concentration in a 10 by 1 in. glass test tube. Each test tube was sealed with a two-holed rubber

TABLE 2
CHEMICAL PROPERTIES OF FLYASHES USED

Chemical Analysis[1] Reported As	FLYASH NO.					
	10	11	12	13	14	15
C	3.20	27.67	10.18	2.90	2.10	15.59
SO₃	3.04	0.41	1.47	2.93	2.00	1.86
CaO	7.30	2.52	5.34	11 22	8.36	6.89
MgO	0.43	1.16	0.77	2.65	0.52	0.85
Fe₂O₃	19.30	13.41	21.23	10.75	21.20	19.63
Al₂O₃	20.10	13.23	18.39	29.25	22.92	18 19
SiO₂	43.40	39.18	41.16	39.20	38.90	35.94
H₂O	0.30	N.D.	N.D.	N.D.	0.17	N.D.
pH[2]	11.50	12.30	12.10	11.80	11.60	11.90

[1] Reported as percent by weight.
[2] Based on 10 gm of total sample in 25 ml of water.

stopper equipped with two glass tubes. One tube reached about 7 in. into the test tube so that the lime solution could be withdrawn, tested, and returned to the test tube. The other tube was rather short and acted as a vent while the lime solution was being withdrawn and returned to the test tube. Both tubes extended about ½ in. above the top of the stopper. A piece of rubber tubing connecting the upper ends of the glass tubes served to keep the test tubes air tight during the reaction period. During testing periods the rubber tube served as a connector between the test tube and the conductivity pipettes. The vent tube was connected to a calcium chloride tube containing barium hydroxide to prevent the formation of calcium carbonate in the solution. Figure 1 shows a test tube in position for testing.

Because of the decrease in solubility of $Ca(OH)_2$ with increased temperature and alkalinity, the concentration of $Ca(OH)_2$ solutions used were well below the maximum solubility values. This was done to insure against the precipitation of $Ca(OH)_2$ in the test tube during the reaction period. Concentrations of about 1.1, 1.0, 0.9 and 0.8 gm per liter were used for reaction temperatures of 20, 40, 60 and 80 deg C respectively. At first deionized water was used to make up the solutions, but later it was found that more satisfactory solutions could be made by double filtering $Ca(OH)_2$ solutions made with distilled water. Filtering was necessary to remove small amounts of $CaCO_3$ which was formed by calcium combining with small amounts of CO_2 in the distilled water.

TABLE 3

PERCENT REDUCTION IN ALKALINITY OF THE FLYASHES

Flyash No.	Percent Reduction in Alkalinity, R_a
10	62.80
11	39.36
12	50.60
13	61 34
14	59.79
15	56.17

After filtering, the concentrations of the $Ca(OH)_2$ solutions were checked by titration methods.

Test tubes were exposed to concentrated $Ca(OH)_2$ solutions at the specified temperature before being used. A check of the reactions by electroconductivity methods showed very little reaction between the pretreated glass and $Ca(OH)_2$.

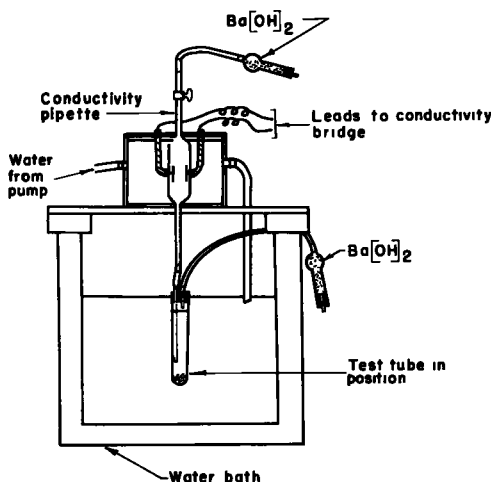The samples were placed in constant temperature baths and ovens. Constant temperature baths were used to maintain reaction temperatures of 20 ± 1 deg C and 40 ± 1 deg C. Ovens were used to maintain the higher temperatures of 60 ± 1 deg C and 80 ± 1 deg C.

Cementation of particles of the reactive material had to be prevented so that the complete sample would remain exposed. In order to prevent cementation the samples were rodded and shaken frequently during the testing period.

Conductivity readings were taken at specified intervals by means of a pipette type conducticity cell (Cenco 700-72). The cell was partially encased in a small water tight plastic box (Fig. 1). Water from the constant temperature bath was pumped through the box to insure a constant temperature during the conductivity reading operation. Samples in the constant temperature baths were tested at their respective temperatures, whereas samples from the ovens were placed in the 40 +1 deg C bath and tested at this temperature.

The set-up for testing a sample is shown in Figure 1. Conductivity readings were taken using a null point conductivity bridge (Industrial Instruments Type RC 16 B). Readings were taken at 1,000 cycles per sec in order to prevent reactions at the electrodes. All air coming in contact with the solution passed through

Figure 1. Calcium absorption test apparatus in position for testing.

calcium chloride tubes containing barium hydroxide to prevent the formation of calcium carbonate during the testing period. Immediately after testing, the 60 and 80 deg C samples were placed in their respective ovens. About two hours was required for the oven samples to reach the bath temperature and be tested and returned to the oven.

Cell constants of the conductivity pipettes were determined using KCl solutions of known specific conductance. Curves giving the relationship between measured resistances and $Ca(OH)_2$ concentrations were prepared for each testing temperature. Specific conductivity data given by Lea (10) for $Ca(OH)_2$ solutions were utilized for these curves.

For a given reaction temperature, three test tubes of each material were prepared. These samples were used to obtain a set of average readings for the initial reaction period and to provide samples for testing the solutions at given time intervals, usually 15, 30 and 45 days after being exposed to the solid material. At the end of the given time intervals, a sample was removed and judiciously filtered to separate the solution from the solid material. The lime concentration of each filtered solution was determined by means of Versenate titrations. The solid material was oven dried at 60 deg C in contact with barium hydroxide to prevent the formation of calcium carbonate.

DISCUSSION OF RESULTS

Three gram samples of each flyash were allowed to react with Ca(OH)$_2$ solutions at 20 deg C for a period of one year. The absorption of lime was followed by electroconductivity methods and checked by Versenate titrations at 90, 180 and 365 days. The values obtained by these two methods checked to within 5 percent. The results of these absorption tests are shown in Figures 2 and 3.

Flyash 10 absorbed the most lime over the 365 day test period and also had the highest rate of lime absorption. The differences between the flyashes were less apparent at the end of the test period than in the initial stages because of the original concentration factor. The absorption by flyash 11, the high carbon flyash, was particularly slow during the initial period, but at the end of 365 days it had absorbed approximately the same amount of lime as samples 12, 13, 14 and 15. The amounts absorbed were limited by the amount of calcium put into solution. Thus, the major differences between the flyashes at this temperature were shown most readily during the initial lime absorption testing period of about 45 days.

Figure 2. Absorption of calcium by flyash samples 10, 11 and 12 at 20 deg C over a one year period.

It will be noted that negative values of lime absorption were observed. These negative values can be explained by the solubility of compounds in the flyash and perhaps by cation exchange. Sodium, magnesium and calcium compounds reported in flyashes are soluble in partially saturated Ca(OH)$_2$ solutions. According to Lerch (12), alkali solutions cannot exist in equilibrium with saturated lime solutions. Referring to Table 2, it is seen that flyash 13 has the largest amount of calcium and
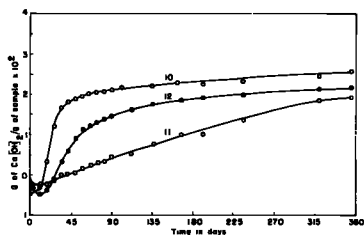
magnesium compounds, 13.87 percent (reported as oxides); the greatest amount of negative absorption is observed with sample 13. Sample 11 has the smallest amount of calcium and magnesium oxides, 3.68 percent, and only a slight amount of negative absorption was observed for sample 11. Samples 10, 12, 14 and 15 had approximately the same amounts of calcium and magnesium compounds, 7.73, 6.11, 8.88 and 7.45 percent respectively, and these have intermediate negative absorption values.

Figure 3. Absorption of calcium by flyash samples 13, 14 and 15 at 20 deg C over a one year period.

If the absorption results are compared with the compressive strength results shown in Figure 4, it will be noted that the initial 45 day absorption results seem to agree with the compressive strength results. In some cases the compressive strength and absorption curves are very similar in shape. The corresponding similarity between the slopes of the compression curves and the absorption curves is particularily striking.
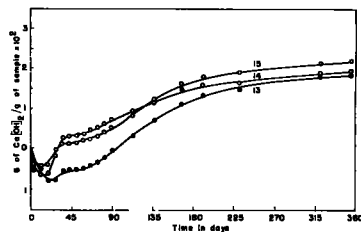
It is evident that flyash 10 is the best pozzolan on the basis of compressive strength and lime absorption. The second best pozzolan appears to be sample 12; this conclusion is reached from both the absorption and the compressive strength results. Sample 15 had a rather flat and constant slope in both absorption and compressive strength curves. Sample 11 did not achieve an apparent equilibrium until after about 300 days. The very shallow constant slope of the absorption curve for sample 11 agrees very well with the slope of the strength curve for this flyash.

From the compressive strength and absorption data it appears that a quantitative or semi-quantitative relationship exists between calcium absorption by flyash and its compressive strength in lime-flyash
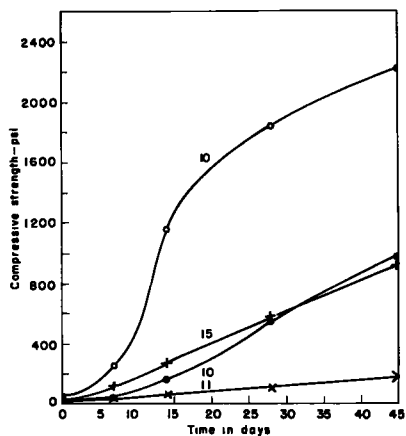
Figure 4. Unconfined compressive strengths of four flyash mortars with 8 percent $Ca(OH)_2$ cured at 20 deg C (5). Strengths are for 2 in. diameter by 2 in. specimens at near standard Proctor density which were moist cured at 20 deg C for indicated times, then immersed in water 24 hours before testing.

Figure 5. Maximum rate of compressive strength development versus maximum rate of $Ca(OH)_2$ absorption based on standardized tests.

mixtures. By comparing the maximum slope of the compressive strength curves to the maximum slope of the absorption curves in the figures previously discussed, the relationship given in Figure 5 was obtained. The relationship given in this figure is significant in that it indicates a correlation between absorption and strength; however this relationship is likely to vary with temperature and concentration factors and other physical factors. If a relationship is to be established it should be on the basis of standardized tests.
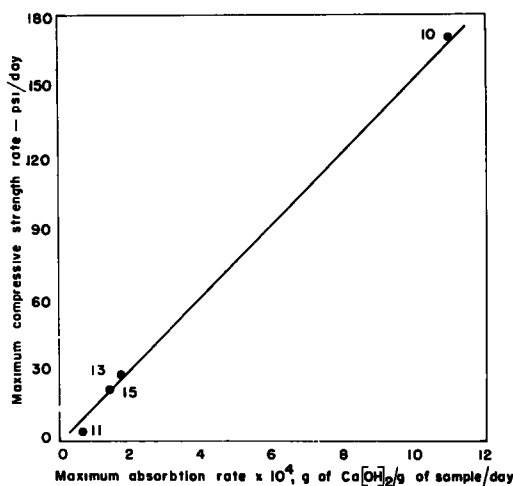

Figure 6. Absorption of calcium at 20 deg C by flyash samples 10, 11 and 12 (3 gm samples).

INFLUENCE OF TEMPERATURE

Each sample of flyash was tested by means of the lime absorption method at 20, 40, 60 and 80 deg C. The results of these tests are shown in Figures 6 through 13.

Although 20 deg C absorption curves for the six flyashes have been discussed previously, the curves presented in Figures 6 and 7 represent another set of test data. One day readings are shown in these curves. It will be noted that there was an apparent initial absorption of calcium before the negative absorption that was evident in Figures 2 and 3. There are two plausible explana-
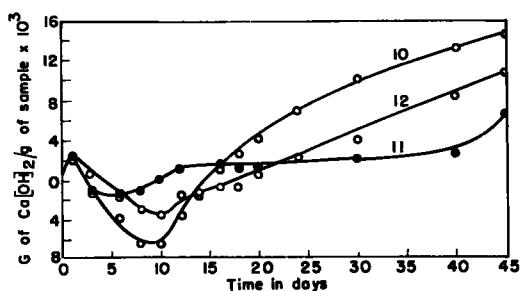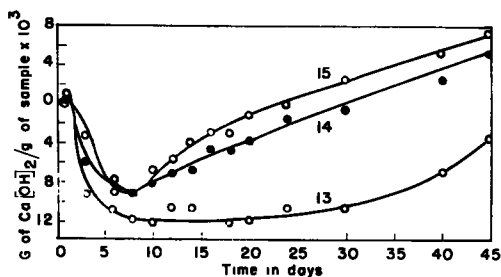
Figure 7. Absorption of calcium at 20 deg C by flyash samples 13, 14 and 15 (3 gm samples).
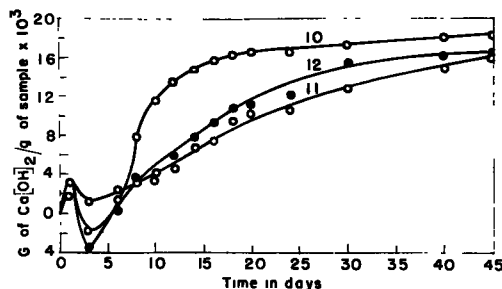

Figure 8. Absorption of calcium at 40 deg C by flyash samples 10, 11 and 12 (3 gm samples).

tions for the initial up-take of calcium. Possibly it is due to an ion exchange reaction, such as calcium ions replacing other ions in the flyash. Another possibility is that it is due to charge deficiencies that exist with the flyash as a consequence of it non-crystalline glassy nature.

The influence of temperature on the rate of absorption of $Ca(OH)_2$ by the flyashes was very pronounced with all flyashes. In all cases, after initial reactions, the rate of absorption increased with temperature. After examining these figures, it is obvious that the pozzolanic reaction or reactions observed were endothermic reactions, that is, flyash $Ca(OH)_2$, and H_2O pozzolanic reaction products. Increasing the amount of heat drives the reaction faster to the right. This increase in reaction rate due to an increase in temperature has been termed the Arrhenius effect (6).

It will be noted that the periods of initial and negative absorption decrease as the temperature increases. At 60 deg C very short periods of negative absorption were observed. Neither initial reactions or negative absorptions were evident during the 80 deg C test period. All curves at 80 deg C have the same shape and the maximum ordinates are essentially the same. High temperature results are of little use for the selection of desirable pozzolans because of the rapidity of the reaction.
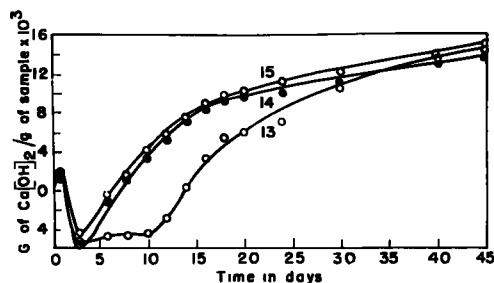

Figure 9. Absorption of calcium at 40 deg C by flyash samples 13, 14 and 15 (3 gm samples).

The curves shown in Figure 14 illustrate the over-all effect of the temperature range used on the six flyashes studied. Because of the initial reactions and solubility effects observed, the times given for one-half of the original $Ca(OH)_2$ concentrations to be depleted are not true half lifes. By means of Figure 14 it is possible to estimate the effect of temperature on the pozzolanic reaction for the flyashes beyond the range of temperature used in this study. Relatively speaking, little was gained by raising the reaction temperature above 50 deg C. However,
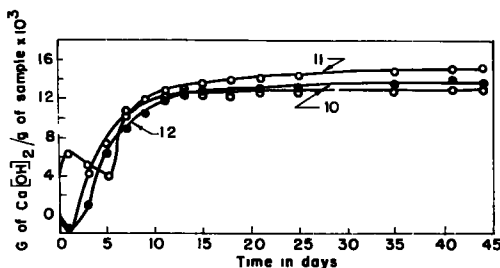

Figure 10. Absorption of calcium at 60 deg C by flyash samples 10, 11 and 12 (3 gm samples).
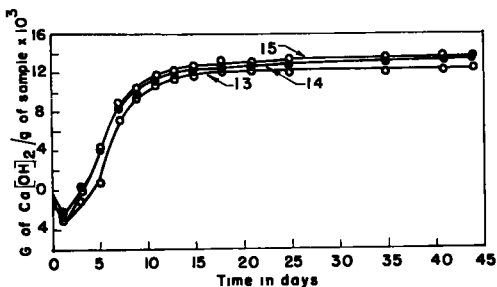
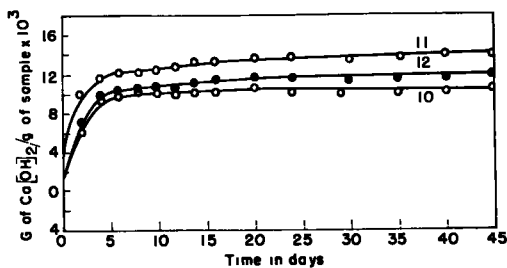Figure 11. Absorption of calcium at 60 deg C by flyash samples 13, 14 and 15 (3 gm samples).

Figure 12. Absorption of calcium at 80 deg C by flyash samples 10, 11 and 12 (3 gm samples).

between 20 and 50 deg C the influence of temperature on the reactions was quite notice-able. Only at temperatures less than 50 deg C was it possible to distinquish between the flyashes from their absorption rates. The curves shown in Figure 14 asymptoti-cally approach time infinity as the temperature decreases below 20 deg C. For practi-cal purposes, at temperatures below 20 deg C most of the flyashes can be assumed to be almost non-reactive.

Compressive strengths of lime-flyash mortars at 60 deg C using four of the six fly-ashes are shown in Figure 15. The strength differences between the flyashes at this temperature are more pronounced than at 20 deg C (Fig. 4). From the figure it is noted that samples 10 and 11 are respec-tively the most satisfactory and the most unsatisfactory pozzolans; this is also the case when the mortars were cured at 20 deg C. Unlike the compressive strengths at the 20 deg C curing temperature, all samples reached about 90 percent of their strengths in about seven days. From Fig-
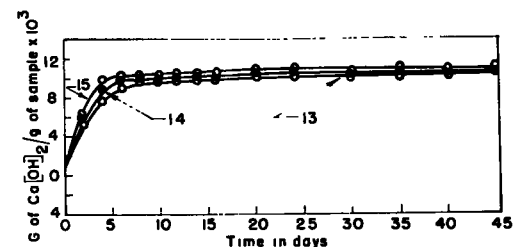

Figure 13. Absorption of calcium at 80 deg C by flyash samples 13, 14 and 15 (3 gm samples).

ures 10 and 11, it can be seen that the major portion of the lime absorption oc-curred within the first ten days. The rates of initial strength gains correspond with the rates of initial calcium absorption for each flyash. However, the maximum ordinates of the absorption curves are nearly the same, due to calcium depletion whereas the maximum ordinates of the compressive strength curves are consider-

Figure 14. Effect of temperature on time required for one-half of $Ca(OH)_2$ to be absorbed.

ably different. Therefore, it is evident that there is a relationship between the ab-sorption of lime and the compressive strength, but the total strength development of lime-pozzolan mortars is dependent on factors in additions to the pozzolanic reaction.

INFLUENCE OF PARTICLE SIZE ON THE REACTION

The influence of particle size on the reaction was studied by using material passing the number 200 sieve (0.074 mm) and the number 325 sieve (0.044 mm) from flyashes
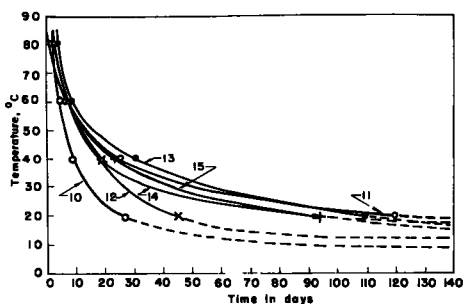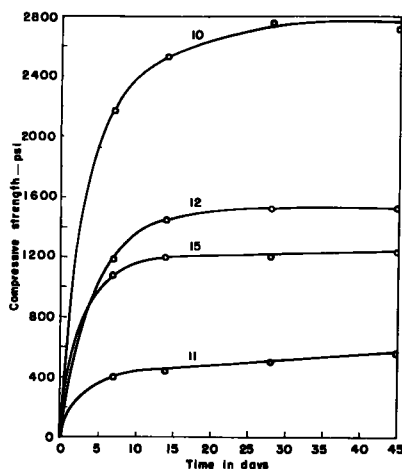
Figure 15. Unconfined compressive strengths of four flyash mortars with 8 percent Ca(OH)$_2$ cured at 60 deg C (5). Strengths are for 2 in. diameter by 2 in. specimens at near standard Proctor density which were moist cured at 60 deg C for indicated times, then immersed in water 24 hours before testing.

The majority of the larger particles in flyashes are composed of unburned coal and coke which is reported as loss-on-ignition in Table 4. From this table the decrease in organic content with grain size is very evident. The larger flyash particles are not very active. Also, the larger particles have low specific gravity, less
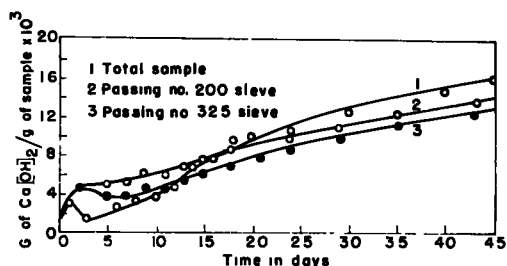
Figure 17. Influence of grain size of flyash sample 11 on calcium absorption at 40 deg C.

10 and 11. Flyash 10 was used because all tests indicated it was the most reactive flyash of the six tested, whereas flyash 11 was used because all tests indicated it was unsuitable as a pozzolan. Ca(OH)$_2$ solutions used at each temperature were of equal concentrations. Three gram samples were used.

Figures 16 and 17 are two sets of curves given to illustrate the influence of particle size on Ca(OH)$_2$ absorption at a given temperature. Practically speaking, there was little difference between the rates of absorption and the maximum amounts of absorption for the different fractions at a given temperature.

An increase in reaction rate with increasing surface area was not evident in these tests; this may be explained on the basis of another property of the flyashes.
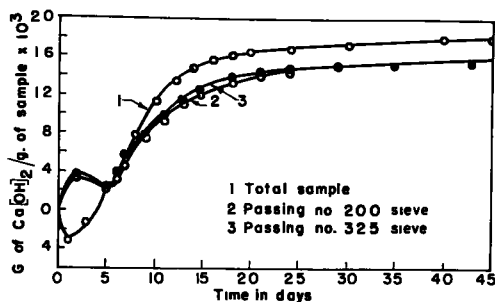

Figure 16. Influence of grain size of flyash sample 10 on calcium absorption at 40 deg C.

than 1.0. Hence, there was little change in the amount of active surface area present when the particle size samples used were compared on the basis of weight. Although the presence of organic material had little effect on the chemical activity of the flyashes, there is reason to believe that it influences the compressive strength results; this will be discussed later.

INFLUENCE OF THE LIME-FLYASH RATIO

The influence of the lime-flyash ratio on the reaction was studied by decreasing sample weights one-half while keeping Ca(OH)$_2$ concentrations constant. The curves obtained had essentially the same characteristics as the 3 gram sample curves. However, at any time interval, the amount of Ca(OH)$_2$ absorbed per gram by the 1½ gram samples was nearly twice that absorbed by the 3 gram samples. The influence of concentration on the reaction will be discussed on the basis of diffusion later in this report.

Percent increases in compressive strengths due to doubling the amount of $Ca(OH)_2$ at two temperatures are shown in Tables 5 and 6. At 20 deg C negative values were obtained for some of the 7 and 14 day test periods. This probably indicates that cementation had not taken place to a significant extent during the test period and that the $Ca(OH)_2$ decr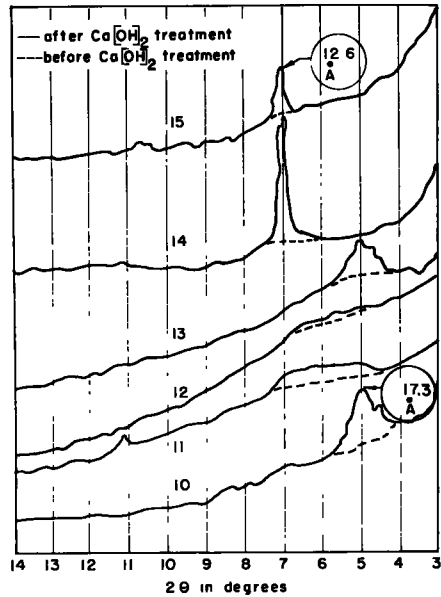eased the shear strength by acting as a lubricant during the initial period. Although all of the 45 day percentage increases in compressive strengths are positive they are erratic and do not correspond to the increases in absorption. The compressive strengths of the lime-flyash mixtures increased with increasing amounts of $Ca(OH)_2$, but the amount of increase was dependent on other factors in addition to absorption factors.

TABLE 4

INFLUENCE OF PARTICLE SIZE ON LOSS-ON-IGNITION

Size Fraction Finer Than	Percent Loss-on-Ignition	
	Flyash 10	Flyash 11
0.420 mm	3.20	27.67
0.074 mm	2.34	19.55
0.044 mm	2.11	10.32

REACTION PRODUCTS

After flyash samples had been tested by means of the absorption test procedure, they were removed from the solutions. The solid material was filtered from the solutions and dried in the presence of barium hydroxide to prevent carbonation. After being dried, the flyash samples were subjected to optical, differential thermal analysis and x-ray diffraction procedures in order to determine the nature of the reaction products formed.

TABLE 5

PERCENT INCREASE IN COMPRESSIVE STRENGTH AT THE END OF VARIOUS TEST PERIODS DUE TO INCREASING $Ca(OH)_2$ CONTENT FROM 2 TO 4 PERCENT AT 20 AND 60 DEG C (5)

Flyash Sample No.	Percent Increase in Compressive Strength							
	20 Deg C				60 Deg C			
	Test Period, Days				Test Period, Days			
	7	14	28	45	7	14	28	45
10	-31.1	24.7	41.6	62.0	41.6	54.4	56.7	19.8
11	0.8	2.7	2.2	15.1	43.3	38.0	45.2	36.4
12	-51.2	0.2	6.2	47.2	44.1	49.1	36.5	46.1
15	4.3	7.5	6.3	25.8	15.7	6.3	23.3	15.5

Figure 18. X-ray spectrometer curves for flyash samples used in the absorption tests.

No differences between treated and untreated samples could be ascertained by the use of the petrographic microscope. Previous research in the field of cement chemistry has also indicated that petrographic techniques are of little value for this type of work because of the small amounts of reaction products and their minute colloidal size.

For the most part, the differential thermal analysis results were not as satisfactory as the x-ray diffraction results. The presence of unreacted flyash in the absorption samples partially masked the peaks of the small amounts of reaction products. Also, the lack of established data about the reaction products as determined by this method tended to limit the applications of the apparatus.

X-ray diffraction patterns of the $Ca(OH)_2$ treated flyash samples were compared with patterns for untreated samples. All samples were treated with ethylene glycol before x-ray examination.

Flyash samples that had been exposed to $Ca(OH)_2$ in solution for 365 days at 20 deg C

TABLE 8

K CONSTANTS FOR FLYASH SAMPLES

Flyash Sample No.	Solution Temperature, deg C	Constant $Kx10^7$ cm²/day/gm/liter	
		3 gm Sample	1½ gm Sample
10	20	5.88	16.52
	40	7.37	21.50
	60	9.80	37.40
	80	14.15	55.40
11	20	1.43	3.25
	40	3.02	9.60
	60	6.10	20.60
	80	8.53	27.60
12	20	3.43	7.64
	40	4.66	16.00
	60	6.40	20.90
	80	9.10	25.60
13	20	0.00	0.00
	40	4.91	19.58
	60	9.98	24.90
	80	12.00	31.00
14	20	3.48	14.45
	40	5.18	18.20
	60	8.05	32.50
	80	11.25	49.80
15	20	3.95	14.10
	40	7.02	18.45
	60	9.98	29.80
	80	14.03	49.10

prevents contacts of the cementitious material that forms on the surface of the pozzolan and may be a gel that later forms a cyrstalline product.

If the desired cementitious product forms on the surface, it follows that in order for any more reaction product to be formed, the necessary calcium must pass through the reacted layer to react with the enclosed pozzolan. Thus, the mechanism of the pozzolanic reaction is one of simultaneous diffusion and chemical reaction of the calcium. The activity of the reacting material is limited by the rate of diffusion of calcium through the reaction product.

The mathematical theory of diffusion in isotropic substances, according to Crank (4) and Barrer (1), is based on the hypothesis that the rate of diffusion through a unit area of section is proportional to the concentration gradient normal to the section, that is, $\frac{dQ}{dt} = -D \frac{c}{x}$ where $\frac{dQ}{dt}$ is the rate of transfer per unit area of section, c is the concentration of the diffusing substance, x is the space coordinate measured normal to the section, and D is called the diffusion coefficient.

It is assumed that the rate-limiting step is diffusion of calcium through the reaction zone. The reacting material is assumed to be in the form of a sphere. It is also assumed that the thickness of the reaction zone is negligible in comparison to the diameter of the reacting material so the surface can be considered a plane, and the following mathematical development can be made.

Let x = thickness of reacting zone
 Q = amount of $Ca(OH)_2$ which has reacted/unit area
 $\overline{V}$ = molar volume of the product
 C = concentration of $Ca(OH)_2$ at any time
 C_0 = initial concentration of $Ca(OH)_2$
 R = total amount of $Ca(OH)_2$ reacting
 S = specific surface of solid

If $x = Q\overline{V}$

then $\frac{dQ}{dt} = \frac{DC}{x} = \frac{DC}{Q\overline{V}}$.

The amount removed by reaction will be $\overline{V}(C_0 - C)$. By reaction stoichiometry

$$\overline{V}(C_0 - C) = \alpha QS$$

where α is a "ratio of small whole numbers." Hence

$$C = C_0 - \frac{\alpha QS}{\overline{V}} = C_0 - \beta Q$$

where $\beta = \alpha \frac{S}{\overline{V}}$

hence $\frac{dQ}{dt} = \frac{D(C_0 - \beta Q)}{Q\overline{V}}$

thus $\frac{Dt}{\overline{V}} = \frac{-Q}{\beta} - \frac{C_0}{\beta^2} \ln \left(1 - \frac{\beta Q}{C_0}\right)$.

Expanding the equation by MacLaurin's power series the equation becomes

$$\frac{Dt}{\overline{V}} = \frac{Q^2}{C_0}\left[0 + \frac{1}{2}\left(\frac{\beta}{C_0}\right)\frac{Q}{3} + \ldots + \left(\frac{\beta}{C_0}\right)^{n-2}\frac{Q^{n-2}}{n} + \ldots\right]$$

If $\frac{\beta Q}{C_0}$ is less than 0.1 then all terms greater than the third term are negligible.

Then

$$\frac{Dt}{\overline{V}} = \frac{Q^2}{2C_0}$$

and

$$Q = \left(\frac{2C_0 D}{\overline{V}}\right)^{1/2}(t)^{1/2}$$

If

$$K = \left(\frac{2C_0 D}{\overline{V}}\right)^{1/2}$$

and $R = QS.$

The following relationship is obtained

$$R = KS\,(t)^{1/2}$$

Assuming that the reacting particles are spherical in shape and heterogeneous, the following equation may be used for the specific surface.

$$S = \frac{4\pi r^2}{\frac{4\pi r^2 \lambda}{3}} = \frac{3}{\lambda r}$$

where γ and r are, respectively, the specific gravity of the material and the mean radius of the reacting matter. Hence, the following relationship can be obtained

$$R = \frac{3K(t)^{1/2}}{\lambda r}$$

This equation is valid only for cases where the concentration is high. The K values given in this report are for the initial portion of the reaction. The relationship for the lower concentrations can be developed using the adjustable parameters β and D instead of K.

Absorption data for the flyashes in $Ca(OH)_2$ solutions satisfied the relationship given previously since linear plots of R versus $\sqrt{t}$ were obtained until the concentration of $Ca(OH)_2$ dropped to about 0.1 gm/liter. From the slopes of these plots, average values of K were calculated. The K values obtained for the flyash samples are given in Table 8.

The K values indicated are not diffusion coefficients, but they do indicate the trend of the diffusion coefficients. It will be noted, from Table 8, that the rate of diffusion increases with temperature. The relationship

$$\log KC_0^{1/2} = C_1 + \frac{C_2}{T}$$

where T is the absolute temperature, may be used to express the influence of temperature on the rate of diffusion. Secondly, the rate of diffusion was increased by decreasing the amount of reacting sample while keeping the concentration of the $Ca(OH)_2$ constant.

It will be further noted that the better flyashes, as determined by the other tests, also give the higher K values. Probably, this results from the fact that there is normally more reactive material in these samples and they have a higher specific surface area.

CONCLUSIONS

The rate of compressive strength development by lime-flyash mortars is directly related to the rate of lime absorption of the flyash. The greater the rate of lime ab-

sorption, the greater the rate of compressive strength development. The rate of lime absorption is limited by the rate of diffusion of the calcium through the reaction product. The rate of diffusion, which is increased by increasing the temperature and the lime concentration, varies with the type of flyash used. At temperatures less than 20 deg C most flyashes may be considered non-reactive.

The source of the strength of lime-flyash mortars is the reaction products that form as the result of the pozzolanic reaction. From x-ray diffraction studies, it appears that a crystalline product does not form at first, but develops from a non-crystalline reaction product. The initial product is probably a gel. The final crystalline product is believed to be calcium silicate hydrate I, a reaction product that has been found in set portland cement pastes.

Unburned organic material that is found in most flyashes is nonreactive with calcium hydroxide and its presence seems to indicate a flyash of coarse grain size in both the organic and inorganic phases. Since the total mortar strength developed depends on the number of contacts of the cementitious reaction products, the organic material breaks the continuity of this system and thus decreases the total strength.

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Discussion

Z. C. MOH, <u>Massachusetts Institute of Technology</u> — In the past few years considerable increase in the interest in using pozzolanic materials, both natural and synthetic, has led to the recognition of the importance of understanding the nature of the pozzolanic activity and the reaction products. The authors have made an important contribution in this respect. However, some of the conclusions described in the paper seem to be somewhat inconsistent with the data presented. The writer wishes to discuss these inconsistencies.

The authors interpreted the products of the reaction between lime and flyash after one year as calcium silicate hydrate I (CSH-I) based on their x-ray diffraction pattern. However, the evidence, as shown in Figure 18, is not conclusive. The x-ray patterns reveal only the presence of one line, the 12.6 A line, which is only one of the strong lines of CSH-I (Table 9). The two strongest lines of CSH-I, 3.06 A and 2.80 A (15, 16, 19), are not present in the authors' data. Furthermore, the 17.3 A of flyash No. 10 does not correspond with any calcium silicate hydrate pattern reported in the literature. Moreover, CSH-I has a very large exothermic peak at about 830 to 900 deg C on the DTA pattern (17). The authors did not indicate such.

According to Bogue (16), Taylor (19), and others, the calcium silicate hydrates formed in a lime solution of concentration well below saturation are low in lime. If one accepts the authors' interpretation of the end products as CSH-I, this naturally would be the low lime hydrous silicate, that is, $CaO \cdot SiO_2$ aq. The maximum lime absorption after one year at 20 deg C, as reported in the paper, was 2.5 gm $Ca(OH)_2$/gm of flyash x 10^2 (flyash No. 10 in Fig. 2). This value is equivalent to 0.0189 gm CaO/gm of flyash. With CaO-to-SiO_2 ratio of one, this means only 0.0435 gm/gm of the flyash was reacted (flyash No. 10 has 43.4 percent SiO_2); that is, only 4 percent of the pozzolan participated in the reaction in a period of one year. Furthermore, in the authors' experiments the flyash was prevented from cementation. The total surface area exposed to the reaction would undoubtedly be much greater than that in a compacted lime-flyash mortar. In other words, if the experiments described really represent the type of reaction postulated by the authors in a lime-flyash mixture, it is inconceivable that such a small percentage of reactants was able to bind all the fine particles providing fairly high compressive strength. (Although there are no strength data of mixtures with 2 to 4 percent lime presented in the paper, however, it can be deduced from Figure 4 and from Tables 5

TABLE 9
X-RAY DIFFRACTION PATTERNS OF CALCIUM SILICATE I

References	d Spacing in Å	Relative Intensity
Taylor (15)	10.0 - 11.5	Strong
	3.03	Very strong
	2.80	Medium strong
	1.81	Medium strong
Bogue (19)	13.72	100
	3.06	100
	2.80	100
Bernal (16)[1]	10 - 15	7
	3.1	10
	2.8	9

[1] Interpreted from line diagram.

and 6 that the one-year strength of such mixtures would be fairly high.)

Furthermore, the decreases in strength (20 deg C) at 7 and 14 days by increasing the calcium hydroxide contents in the mixture (Tables 5 and 6) contradict the absorption data discussed. The increase in absorption by lime at all curing ages would indicate to the writer an increase in the total amount of reaction product at all curing ages. Hence, higher strength would be expected—as stated by the authors: "The strength of lime-flyash mortars is dependent on the amount and number of contacts of the cementitious materials." Therefore, it seems likely that the absorption test is not adequate to account for the proposed mechanism.

The authors explained the reaction rate on the basis of diffusion. It is clearly stated

by the authors that rate of diffusion is a function of $Ca(OH)_2$ concentration. Therefore, at higher lime content the rate of calcium ion diffusion is faster; the reaction rate between lime and flyash should then be faster. In other words, the strength development should also be faster at high lime content than at low lime content, but the data in Tables 5 and 6 do not agree with this explanation.

The negative absorption and also the initial absorption at temperatures above 20 deg C cannot be satisfactorily explained by exchange reaction or due to soluble components of the flyash as stated by the authors. Otherwise, the conductivity measurement would not represent the lime concentration in solution and definitely would not agree with titration data if titrations were carried out at those ages. The reverse absorption phenomena may be explained by the view of uneven distribution of ions on the flyash particles as described for cements (18).

The majority of large particles in flyashes are composed of unburned coal and coke which generally have little effect on the chemical reactivity of the pozzolans, as stated by the authors. Yet, as shown in Figure 6, Sample No. 10 has a pronounced negative absorption by using the entire sample, while the No. 200 and No. 325 fractions exhibited positive absorption (the sample has 93 percent passing No. 325). It would seem that a more plausible explanation for this difference of 8 gm of $Ca(OH)_2$ absorption per gm of flyash x 10^3 is due to the small percentage of the coarse fraction.

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R.J. LEONARD and D.T. DAVIDSON, Closure — Although Mr. Moh's discussion does not make known any new information about the lime-flyash pozzolanic reaction, it is appreciated for it offers the authors an opportunity to clarify and discuss further some of the major points of their study.

Although x-ray spectrometer curves were obtained for the absorption test flyashes for a range of 2θ of 2 to 100 deg, only that portion showing the interesting peaks at 12.6 Å and 17.3 Å were shown in Figure 14. The other significant peaks that were observed at 3.08 Å and 2.81 Å were reported in the text of the paper. The data for CSH(I) reported in Table 7 of the paper are more recent than that presented by Mr. Moh and it may be significant to give Dr. Lea's addendum to these data, "This is the data for the poorly crystalline material. The long spacing can vary considerably and may also be undetected." It should be noted that the peaks appear to be transitional; this is particularly evident with sample 11. Sample pretreatment and the small amount of reaction product available in any particular sample probably play major roles in the location of the first peak. On the basis of the evidence of the 12.6 Å to 17.3 Å peak and the presence of the second peaks it seems reasonable to identify one of the reaction products as CSH(I).

The size of the DTA exothermic peak at about 830 to 900 deg C reported by Kalousek (22) for CSH(I) is a function of the mass of this reaction product. Since only a small amount of reaction product was available for each flyash sample this affected the DTA results. Peaks were observed at 830 to 900 deg C, but they were not very significant.

Also, the large amounts of unburned carbonaceous material in some of the flyashes caused some drift despite the fact that a nitrogen atmosphere was used in the furnace. In addition to Kalousek's (22) work, Greenberg (21) and others have done DTA work on CSH(I); however, most researchers prefer the use of x-ray diffraction procedures for the examination of crystalline minerals of this type. None of these reports include information on the reaction of lime with flyash and the resulting products; also most of the reports dealt with pure mixtures of $Ca(OH)_2$ with silica gel or minerals that had been exposed to solutions of high concentrations of $Ca(OH)_2$ for long periods of time.

At the 38th Annual Meeting of the Highway Research Board, Benton (20) of the Bureau of Reclamation, presented some information on the reaction products of pozzolans. Mr. Benton indicated that there were two reaction products of the lime-flyash reaction, one product is CSH(I) and the other is a calcium-alumino-hydrate. The latter product may or may not contribute to the strength of the lime-flyash mixture.

The lime-absorption reported in Figure 2 should not be misconstrued to be the maximum amount of $Ca(OH)_2$ that these flyashes can possibly absorb in that length of time and at that temperature. The curves shown in Figures 2 and 3 represent the amounts absorbed from an original $Ca(OH)_2$ solution of slightly less than saturated concentration. At 20 deg C a saturated $Ca(OH)_2$ solution is 0.165 gm per 100 gm of water (23). The concentrations of the solutions used were kept below the saturated concentration because of the presence of soluble constituents in the flyashes. Any precipitation of calcium in the solution would make the absorption test meaningless.

Since the pozzolanic reaction is between calcium and the reactive constituents that occur on the surface of the flyash particles, total exposure of the flyash surface area is necessary for the absorption test results to be significant. Although No. 10 flyash has 43.4 percent SiO_2 not all of this SiO_2 will be available for immediate reaction. The amount reacted for a particular pozzolan will be dependent on the surface area of the flyash, the rate of diffusion of calcium through the reaction product that forms on the surface of the particles and the availability of calcium in the system. Lea (24), among others, has estimated that under normal conditions a pozzolan will not react in a year with more than about 20 percent of its weight of lime.

Due to concentration restrictions only a small amount of the flyash was reacted in the absorption tests, nevertheless, there was enough calcium present to cause cementation of the particles. The samples were stirred to prevent this cementation from forming aggregates. Some of the flyashes have enough calcium to provide significant compressive strength without the addition of lime.

Mr. Moh has confused the term mechanism; it is not clear whether he means chemical or mechanical mechanism. The authors sought to explain the chemical mechanism of the pozzolanic reaction. By the use of absorption tests and x-ray spectrometer methods the chemical reactions were investigated. If there were no reactions that produced the cementitious material there would be no strength development, hence the importance of the chemical mechanism should be obvious.

There are various physical factors in addition to the chemical factors that affect the development of compressive strength. The strength of lime-flyash mortars is dependent on the amount and number of contacts of the cementitious material; therefore, anything that affects either the amount or number of contacts will affect the strength. Physical effects such as the depletion of lime at certain points in the mortar, or an excess of lime may even prevent the cementitious material from making contact; these factors may arise from inadequate mixing of the mortars. Non-reactive material may prevent contact of the cementitious material. Density is another physical factor that may affect the strength (26); increasing the density of the mortar increases its compressive strength. However, despite the physical effects it seems reasonable there must be a relationship between the chemical reactions and the strength development of the lime-flyash mortars.

The rate of compressive strength development of lime-flyash mortars at ordinary temperatures generally is low initially, then the strength development is rapid and finally the rate decreases significantly, but the strength continues to increase; this was shown in Figure 4 of the paper. The rate of absorption of flyashes in $Ca(OH)_2$ solutions proceeds in the same manner. The rapid increase in strength is due to the cementitious

material produced by the lime-flyash reaction, and the decrease in compressive strength is due to the local depletion of lime and limitation due to the diffusion of calcium through the reaction products. By increasing the concentration of the lime the rate of strength development will be increased after the initial period, but the rate of strength development will not be exactly the same as the rate of absorption. This is due to the physical factors that are not involved in the absorption tests. It was noted in the paper that flyashes having a high rate of calcium absorption also have a high rate of compressive strength development. Therefore, the correlation between the rate of absorption and the rate of strength development must be made on the basis of standardized tests if it is to have interpretation meaning.

The negative absorption can be satisfactorily explained by the presence of soluble components in the flyashes. The presence of calcium compounds in the flyashes will be noted in the chemical analysis of the flyashes given in Table 2 of the paper. Some of the flyashes possess enough soluble calcium to be weakly cementitious without the addition of lime. The solubility of these flyash compounds is of little importance to the pozzolanic chemical mechanism. The inconsequental initial absorption values may be due to charge deficiencies that are associated with glasses, or other phenomena; they do not enter into any of the calculations. Lea (24) chooses to ignore the initial reactions in his studies.

From the physical data given in Table 4 and the discussion given in the paper it should be obvious that the minor differences are due to the coarse fraction; the major role of the coarse fraction, containing the majority of the unburned coal and coke, is not in the chemical reactivity of the pozzolans, but in the physical factor of preventing the contact of cementitious material. The presence of unburned coal and coke also generally indicates a coarser flyash and hence a lower specific surface.

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