

# Cement-Pozzolan Reactions

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Mixtures of calcium hydroxide, pozzolan, and water were reacted at 100F for 1 to 6 months, and the reaction products were examined by X-ray diffraction and thermal analysis. The compounds identified included a poorly crystallized calcium silicate hydrate, tricalcium aluminate hexahydrate (or hydrogarnet), tetracalcium aluminate hydrate containing  $\text{CO}_2$ , and Stratling's quaternary compound,  $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$ . Mixtures of portland cement, pozzolan, and water under similar conditions yielded poorly crystallized calcium silicate hydrate, complex calcium aluminate hydrates containing  $\text{SO}_3$  and/or  $\text{CO}_2$ , calcium hydroxide, and Stratling's compound. The reaction products obtained depended on the type of pozzolan and/or on the composition of the portland cement, and, to a lesser degree, on other factors.

● THE INCREASINGLY common use of pozzolans for the purpose of modifying the properties of concrete is creating a need for a better understanding of the physical-chemical processes by which the pozzolans exert their influence during the hydration period.

Pozzolan is defined (1) 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, react chemically with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties." When used in concrete mixtures, pozzolans react with the calcium hydroxide which forms as a product of the hydration of the calcium silicates in the cement. The resulting products of this reaction between the calcium hydroxide and the pozzolan tend to modify various properties of the concrete, both by their presence and by the influence they may have exerted on the hydration processes of the cement. However, the nature of these reaction products and the manner in which they form is not well understood. Lacking this knowledge, empirical data or extensive trial-and-error testing must be relied on to select a pozzolan for a particular application.

These studies were undertaken in the hope that the information obtained would lead toward establishment of better criteria for pozzolan selection, mix proportions, and cement type which would give optimum results.

Lea (2) has reviewed the older literature on reactions between pozzolans and lime. At that time, very little direct evidence as to the identity of reaction products in set lime-pozzolan mixtures had been accumulated. Indirect evidence obtained by acid solubility or water extraction of these reaction products together with existing data from studies of the systems  $\text{CaO}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$  and  $\text{CaO}-\text{SiO}_2-\text{H}_2\text{O}$  led to the conclusion that the products of the reaction between pozzolan and lime consist of a mixture of calcium silicate hydrates and calcium aluminate hydrates, including the compounds  $\text{CaO} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$ ,  $3\text{CaO} \cdot 2\text{SiO}_2 \cdot n\text{H}_2\text{O}$ ,  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ , and  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 13\text{H}_2\text{O}$ .

Stratling (3) identified the compounds resulting from the reaction between calcined kaolin and limewater as  $3\text{CaO} \cdot 2\text{SiO}_2 \cdot n\text{H}_2\text{O}$ ,  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ , and a previously unknown quaternary compound  $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$ .

Since 1940, very few investigations of the chemical reactions of pozzolans with lime have been undertaken in this country. The literature on the subject during this period is almost entirely confined to European journals, principally Italian, and translations have not been made generally available. During this time, however, considerable work on the systems  $\text{CaO}-\text{SiO}_2-\text{H}_2\text{O}$ ,  $\text{CaO}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ , and  $\text{CaO}-\text{Al}_2\text{O}_3-\text{CaSO}_4-\text{H}_2\text{O}$  has been done. In the meantime, much information has accumulated on the identification of hydrates in these systems by X-ray diffraction and thermal analysis which, with the improved instrumentation now in use, should make possible definite advances in knowledge of the pozzolanic reactions.

## EXPERIMENTAL PROCEDURES

These studies are divided into two parts: one concerning the reactions between pozzolans and calcium hydroxide, and the other concerning the reactions of pozzolans with hydrating portland cements.

Eight pozzolans were chosen so as to include most of the known activity types described by Mielenz, Witte, and Glantz (4). These were ground to at least 95 percent passing the No. 325 screen, and those containing clay were calcined at 1,400F for 2 hr. Approximate mineralogical compositions are given in Table 1.

Two of these materials, gibbsite ( $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ) and quartz ( $\text{SiO}_2$ ), are not pozzolans by definition, gibbsite not being a siliceous material and quartz being insufficiently reactive with calcium hydroxide. The gibbsite is included to provide data on calcium aluminate hydrates and the quartz to provide a control for comparison purposes. The calcium hydroxide used was of analytical reagent grade, but was found during the investigations to contain 5.6 percent calcite. The two cements were a Type V low alkali cement and a Type III high alkali cement.

### Lime-Pozzolan Reactions

The general plan of these investigations was to react mixtures of pozzolan, calcium hydroxide, and water at three levels of alkali hydroxide concentration, and to identify by X-ray and thermal analysis the products of the reaction at intervals of time. The proportions of pozzolan and calcium hydroxide were chosen by estimating the amount of each that would be available in the paste of a typical concrete in which 20 percent by weight of the cement was replaced by pozzolan. The proportions arrived at were 10g of calcium hydroxide, 10g of pozzolan, and 16ml water. The materials were dry-mixed in a covered seamless tinplate container, the water was added and the mass was stirred about 30 sec and covered. The individual containers were then stacked in a large vessel with enough water to maintain a humid atmosphere. The large vessel was then tightly sealed and stored at a constant temperature of  $100 \pm 1\text{F}$ . A second series of mixtures was prepared in which sodium hydroxide was added to the mixing water in the amount that would be available if the hypothetical cement were high alkali and all the alkali were sodium; that is, approximately 1 percent  $\text{Na}_2\text{O}$ . Similarly, a third series included half this amount representing conditions in a medium alkali cement. Analyses were made at 1 week, 1 mon, 3 mon, and 6 mon.

### Cement-Pozzolan Reactions

Studies of the cement-pozzolan reactions were made in similar fashion using six of the same pozzolans, each of which was mixed with cement in the proportion of 20 percent by weight of pozzolan and 80 percent cement. Pulverized quartz, known to have very little pozzolanic activity, was used instead of pozzolan in one series of mixtures to serve as a control. Water was added to give a water-cement ratio of 0.75, the mixture was stirred for 30 sec, and covered. The tins were sealed in a humidified container which was stored at  $100 \pm 1\text{F}$ . Analyses of these samples were made by X-ray diffraction and differential thermal analysis (DTA) at ages of 1 mon, 3 mon, and 11 mon.

X-ray diffraction work on the mixtures made of calcium hydroxide and pozzolan was done by the Debye-Scherrer technique using 10-cm-diameter cameras and filtered copper radiation. The powdered

TABLE 1

Pozzolan	Approximate Composition	Treatment
Pumicite	Acidic volcanic glass with 5% quartz and feldspar	Ground, 90%—325 Calcined 1, 400F
Diatomite	60% opaline silica, 30% quartz and feldspar, 5% montmorillonite-type clay, 5% illite and miscellaneous	Ground, 90%—325 Calcined 1, 400F
Kaolinite	Nearly pure kaolinite	Ground, 90%—325 Calcined 1, 400F
Wyoming bentonite	75% sodium montmorillonite, 25% feldspars, quartz, and miscellaneous	Ground, 90%—325 Calcined 1, 400F
Illite	75% illite clay, 20% quartz and feldspars, 5% miscellaneous	Ground, 90%—325 Calcined 1, 400F
Gibbsite	Reagent grade powder $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$	Used as received
Quartz	Practically pure quartz	Ground, 90%—325
Flyash	65% glass, 25% magnetite, 10% quartz, carbon and miscellaneous	Used as received

samples were mixed with Duco cement to a plastic, nonsticky consistency and rolled into spindles 0.013 in. in diameter between microscope slides held in a jig. The spindles were mounted on the cameras, accurately aligned with the rotation axis by means of the goniometer head, and exposed 3 hr using 30 kv, 25 ma, 0.020-in. pin-holes, and 0.00035-in. -thick nickel foil filter. The beam stops were modified to allow registration of diffraction lines to above 40 Å. No-screen, double-emulsion film was used throughout. The processed films were scanned on a laboratory-built densitometer in order to make comparison easier and to simplify reproduction.

For the X-ray diffraction work on the mixtures made from cement and pozzolan, an X-ray diffractometer was available. The X-ray charts reproduced herein for these materials were obtained using filtered copper radiation at 40 kv, 20 ma, a scanning speed of  $\frac{1}{4}^{\circ}$  2 theta per minute, with  $1^{\circ}$  X-ray beam divergence slit and 0.003-in. receiving slit.

Differential thermal analyses were made using laboratory-built equipment. The furnace is the vertical type with an inconel block containing 10 sample wells  $\frac{1}{4}$  in. in diameter by  $\frac{7}{16}$  in. deep, 2 of which are for control and measurement purposes. The 4 pairs of sample-reference wells contain axial thermocouples of No. 28 B & S chromel-alumel which are connected as differential pairs; each pair drives a separate galvanometer, and the galvanometer traces are recorded photographically. The heating rate is approximately 12C per min. Calcined aluminum oxide is the reference material. The sample and reference material are firmly packed into the wells and access of air is limited (but not eliminated) by a cover. The sensitivity of the individual galvanometers varies somewhat, and the deflections range between 1.2 and 1.8 cm for the quartz alpha-beta inversion at 573C using pure quartz.

The thermal balance is a commercial instrument of the Chevenard type, photographically recording the deflection of the beam, which is suspended by very fine tungsten wires. The heating rate is mechanically controlled reasonably close to 5C per min in these investigations. The instrument has a sensitivity of about 2 mg/mm on the photographic record and a range of 400 mg total weight change. Original and final sample weights were determined on an analytical balance as a check.

## RESULTS

### Pozzolan-Calcium Hydroxide Mixtures

The reaction products of the pozzolan-calcium hydroxide mixtures consist of hydrous calcium silicate, calcium aluminate hydrates, and calcium aluminum silicate hydrates.

The quantity of calcium hydroxide which enters into combination with the pozzolan was measured with some accuracy by thermogravimetric analysis of the pozzolan-calcium hydroxide mixtures of 6-mon age. A comparison of the pozzolans, on the basis of reactivity with calcium hydroxide, is made from these results and shown in Figure 1 where calcined kaolinite displays the greatest activity, having consumed 80 percent of the calcium hydroxide. Next in order is the diatomite, followed by the fly-ash, pumicite, bentonite, illite, and quartz. Gibbsite also used up nearly all the calcium hydroxide in the mixture, but accurate quantitative estimation from thermogravimetric analysis was not possible because of overlapping of the dehydration ranges of the calcium hydroxide and one of the calcium aluminate hydrates.

The chief product in the case of siliceous pozzolans appears to be hydrous cal-

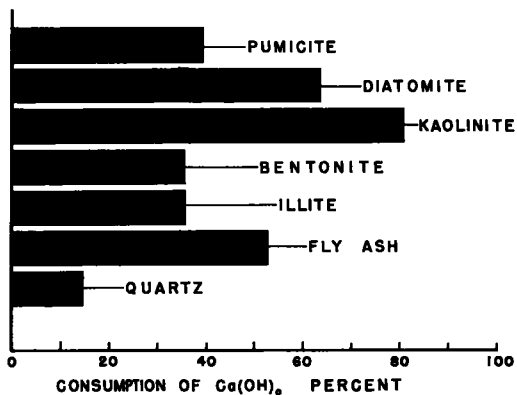


Figure 1. Comparison of the reactivity of various types of pozzolan with calcium hydroxide: Mixtures containing 10g pozzolan, 10g calcium hydroxide, and 16ml water were reacted at 100F for 6 mon.

cium silicate, very poorly crystallized and identifiable only by a broad X-ray diffraction band at about 3.05 Å. This product appears in the mixtures containing pumicite, diatomite, bentonite and, in smaller amounts, in those made with kaolinite, illite, and flyash. It is probably also present in the mixtures containing ground quartz as a pozzolan, but in small amount. Obviously, an identification made on the basis of only one diffraction line is questionable. However, this is the only evidence to be found of the presence of a calcium silicate hydrate which, in the case of the diatomite-calcium-hydroxide mixtures, is about the only possible type of major reaction product. The X-ray diffraction patterns are shown in Figure 2. Taylor (5) has found a very strong line at 3.03 Å in the diffraction patterns of the calcium silicate hydrates he prepared at room temperatures having molar CaO to SiO<sub>2</sub> ratios between 1:1 and 3:2.

Tricalcium aluminate hexahydrate appeared as the chief product in the mixtures containing gibbsite, Al<sub>2</sub>O<sub>3</sub>·3H<sub>2</sub>O, in place of pozzolan, and a hydrogarnet modification of this compound was present in the mixtures made with kaolinite. It was identified both by DTA and X-ray.

All the mixtures containing an aluminous pozzolan (gibbsite, pumicite, flyash, or the calcined clays) yielded a reaction product which appeared to be identical with a sample of tetracalcium aluminate hydrate previously prepared in this laboratory by hydrating C<sub>3</sub>A with added calcium hydroxide. The X-ray pattern of this tetracalcium aluminate hydrate did not completely agree with the published data on this compound; the general sequence of the strongest spacings was similar, but slightly smaller values for the basal spacings (7.6 and 3.8 Å instead of the accepted values, 8.2 and 4.1 Å) were observed on this product. DTA showed a small calcite decomposition endotherm at 700-830 C, but the X-ray pattern showed no detectable amount of calcite. Subsequent analyses revealed that the calcium hydroxide, which had been added to the C<sub>3</sub>A in preparing this compound, contained about 5.6 percent calcite.

These facts led to the conclusion that CO<sub>2</sub> in some form other than calcite was combined in the tetracalcium aluminate hydrate preparation, but had separated as calcite when heated during the DTA analysis and produced the usual calcite endotherm above 700 C. This suggests that the material is a complex salt of the type 3CaO·Al<sub>2</sub>O<sub>3</sub>·Ca(X<sub>2</sub>, Y)·12H<sub>2</sub>O described by Jones (6) in which X is OH and Y is CO<sub>3</sub>. There was not sufficient carbonate present in the ingredients to form the pure carboaluminate, 3CaO·Al<sub>2</sub>O<sub>3</sub>·CaCO<sub>3</sub>·12H<sub>2</sub>O, and precautions against entry of atmospheric CO<sub>2</sub> into the system had been taken. The strongest X-ray diffraction lines appeared at 7.6 and 3.8 Å which do match lines reported by Turriziani and Schippa (7) for the pure carboaluminate. Carlson (8) found no evidence of a solid solution between the carboaluminate and tetracalcium aluminate hydrate. His preparations of the latter compound contained two phases, the most abundant one having a prominent diffraction line at 8.2 Å and the other showing a line at 7.7 Å which he concluded to be the carboaluminate.

Very recent work by Buttler, Dent-Glasser, and Taylor (9), however, has given evidence of the existence of two polymorphic forms of tetracalcium aluminate hydrate, one of which has its strongest diffraction line at 7.92 Å and another for which the spacing was calculated to be 8.2 Å. These two phases were considered by the authors to

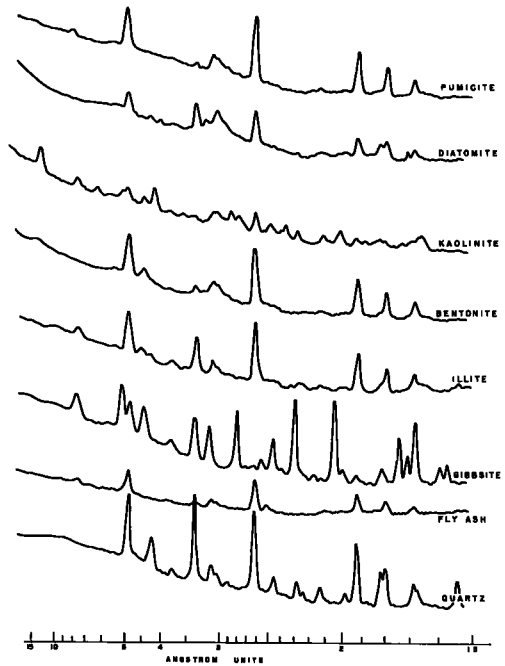


Figure 2. Microdensitometer tracings of X-ray diffraction film patterns of the reaction products of mixtures containing 10g pozzolan, 10g calcium hydroxide, and 16ml water and reacted for 6 mon at 100F.

differ only in the mode of stacking of the structural elements. One cannot help but wonder if the two phases reported by these workers are not the same two that were observed by Carlson (also by Roberts (10) and others). If the chief difference between the 8.2 Å variety and the 7.7 or 7.9 Å variety is in the stacking of the structural elements, is it not possible that small amounts of carbonate ions replacing hydroxyls might be the factor which determines the stacking arrangement?

In any case, the material present in the the pozzolan-calcium hydroxide mixtures which gives the X-ray diffraction lines at 7.6 and 3.8 Å more closely resembles the carbonate-containing preparation just described than it does the pure tetracalcium aluminate hydrate with the diffraction line at 8.2 Å.

The DTA curve of the carbonate-containing tetracalcium aluminate hydrate preparation (not shown) has sharp endothermic reactions beginning at about 90, 170, 280, and 460 C; peaking at 120, 220, 340, and 520 C; followed by a small calcite decomposition endotherm at 700-820 C. The first endotherm is apparently produced by excess water or a higher hydrate of the compound. The endotherms peaking at 340 and 520 C are similar to those of tricalcium aluminate hexahydrate; and it has been concluded from X-ray studies that when the undiluted compound is analyzed by DTA, a partial decomposition to  $C_3A \cdot 6H_2O$  and calcium hydroxide does occur but, when diluted to 10 percent or less for DTA analysis, these  $C_3A \cdot 6H_2O$  endotherms become small or absent. Turriziani and Schippa (7) obtained a DTA curve on the carboaluminate which also shows the  $C_3A \cdot 6H_2O$  endotherms, but much weaker, and a calcite endotherm stronger than was obtained on the undiluted preparation made in this investigation.

The pozzolan-calcium hydroxide mixtures which had X-ray diffraction lines at 7.6 and 3.8 Å all clearly showed the endotherm near 200 C, thereby confirming the presence of a tetracalcium aluminate-carboaluminate hydrate. DTA curves of the pozzolan-calcium hydroxide mixtures of 6-mon age are shown in Figure 4.

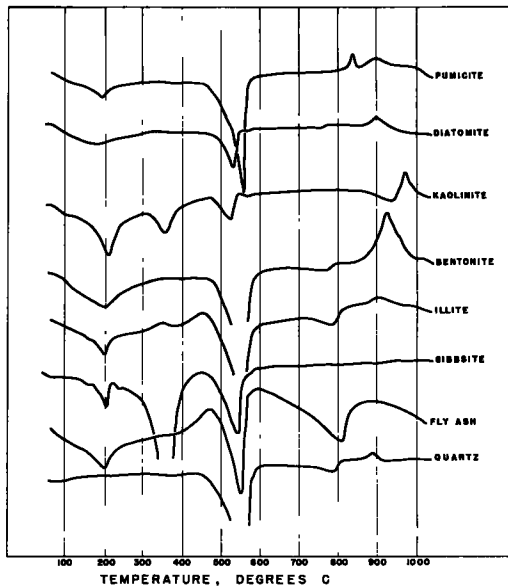


Figure 4. DTA curves of reaction products of mixtures containing 10g pozzolan, 10g calcium hydroxide, and 16ml water reacted 6 mon at 100F.

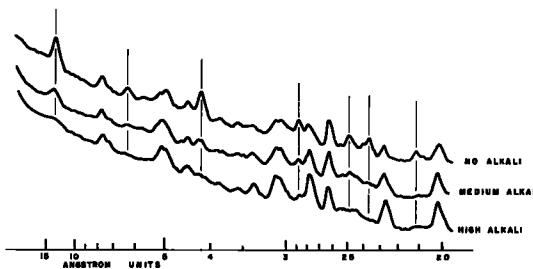


Figure 3. Effect of alkali on formation of Stratling's compound in kaolinite /  $Ca(OH)_2$  mixtures of 6-mon age. Vertical lines mark the peaks of Stratling's compound.

of a tetracalcium aluminate-carboaluminate hydrate. DTA curves of the pozzolan-calcium hydroxide mixtures of 6-mon age are shown in Figure 4.

The compound,  $2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot xH_2O$ , originally described by Stratling (3) in 1940 and known as Stratling's compound, appeared only in the kaolinite mixtures and was identified by its X-ray pattern. It dehydrates in the same range as the tetracalcium aluminate hydrate showing an endothermic peak on the DTA trace near 200 C (Fig. 4). The formation of this compound is considerably suppressed by alkali hydroxide in the system (Fig. 3). The X-ray diffraction pattern of this compound is given in Table 2 along with that obtained by Stratling. Only the lines of moderate-to-strong intensity are observed in the kaolinite series of mixtures because the compound is a minor constituent of this complex system. The lack of close agreement between the spacings listed by Stratling and those obtained in the reaction products in this investigation suggests this compound is variable as to composition or water content. The strong lines at 12.6

TABLE 2  
X-RAY DIFFRACTION PATTERN OF STRATLING'S  
COMPOUND,  $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$

Pattern Obtained by Stratling		Compound Present in Kaolinite-Ca(OH) <sub>2</sub> Hydration Products	
d (A)	Intensity	d (A)	Intensity
		12.6	10
		6.3	6
4.13	MS	4.18	10
2.83	M	2.88	6
2.60	W	—	—
2.45	M	2.49	4
2.35	M	2.37	4
2.10	M	2.12	4
2.00	M	1.89	2
1.59	VW		
1.53	W		
1.43	W		
1.35	VW		
1.08	VW		
1.04	VW		

and 6.3 A were not reported by Stratling. This is probably because most X-ray diffraction cameras at that time were not designed to register lines at such low angles.

The composition of Stratling's compound, reported as  $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$ , is the same (on a water-free basis) as that of the mineral gehlenite and it has been described by Bussem (11) and others as the hydrated gehlenite compound. After heating the kaolinite-calcium hydroxide reaction products to 1,000 C during thermal analysis, gehlenite is, in fact, the principal resulting crystalline phase. However, as Bussem has pointed out, gehlenite does not react directly with water to form a gehlenite hydrate.

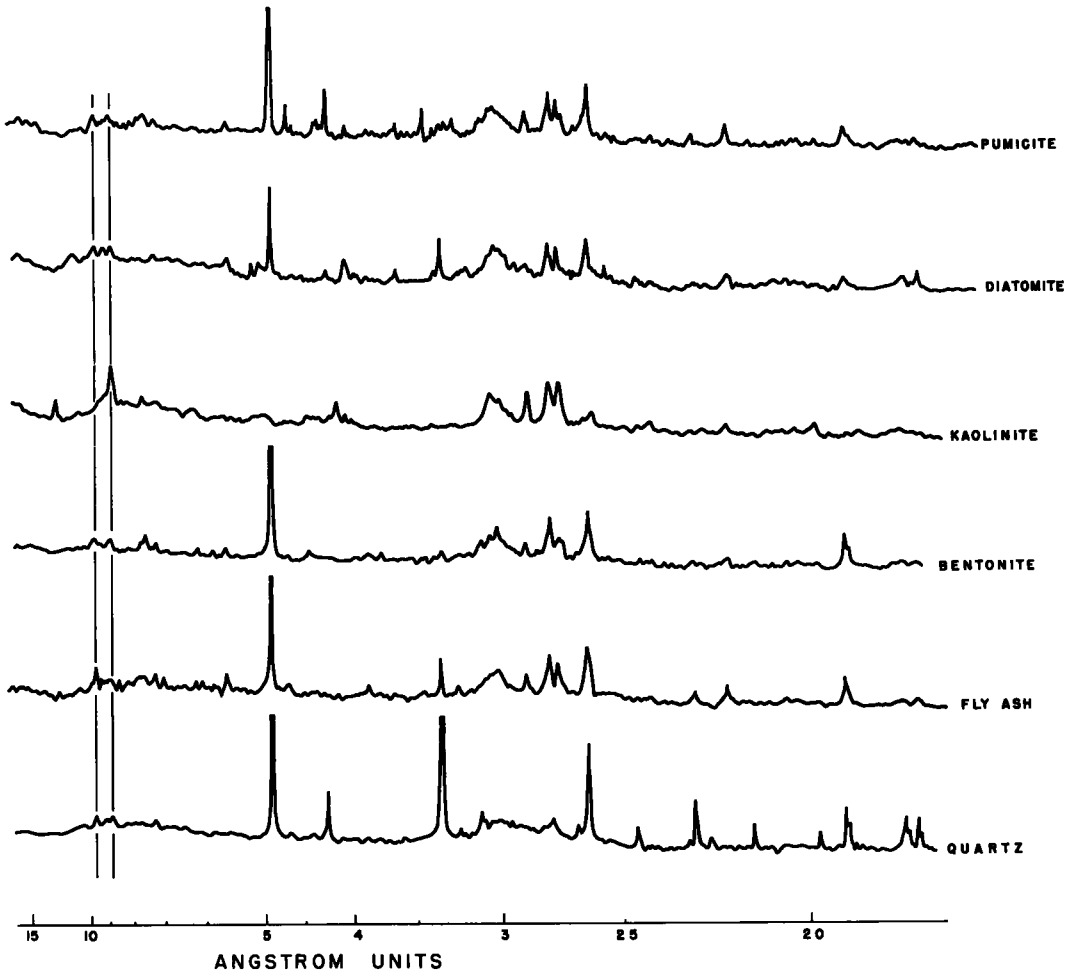


Figure 5. X-ray diffractometer charts of reaction products of mixtures containing 4g pozzolan, 16g low alkali Type V cement, 15ml water and reacted 11 mon at 100F.

### Pozzolan-Cement Mixtures, Type V, Low Alkali Cement

The reaction products of the cement-pozzolan mixtures are considerably more difficult to identify because of the complicating effects of the presence of additional hydrate phases, as well as unhydrated clinker minerals. The poorly crystallized calcium silicate hydrate, showing the broad X-ray diffraction peak at about 3.05 Å, is probably the principal reaction product in the mixtures made with the Type V low alkali cement. X-ray diffraction charts of these mixtures appear in Figure 5.

Stratling's compound is among the reaction products of the cement-kaolinite mixtures; the diffraction peaks at 12.6, 6.3, and 4.18 Å being present on the X-ray chart.

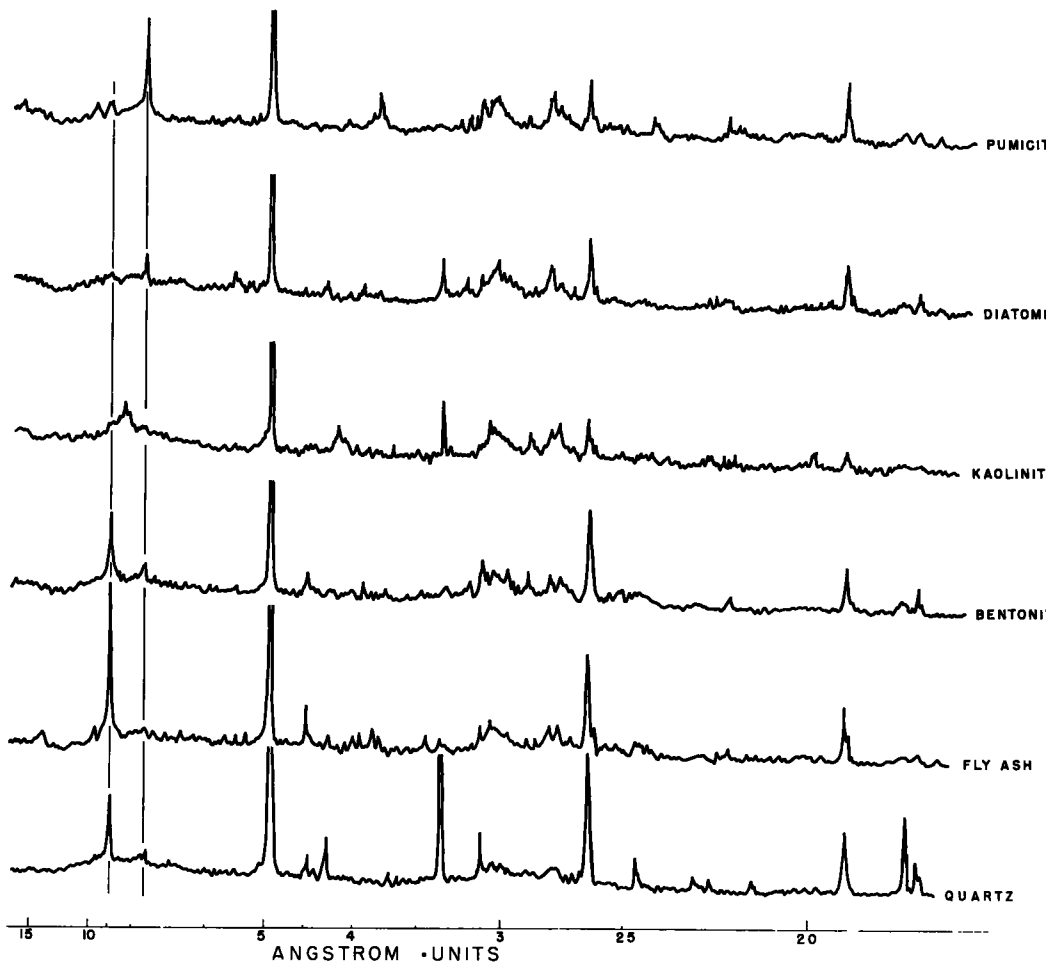


Figure 6. X-ray diffractometer charts of reaction products of mixtures containing 4g pozzolan, 16g high alkali Type III cement, 15ml water and reacted 11 mon at 100F.

As in the pozzolan-calcium hydroxide series, this compound is much more abundant in the mixtures made with low alkali cement. Ettringite,  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O}$ , is probably present in small amounts in most of the mixtures showing a very small diffraction peak at 9.6 Å. A prominent peak at 8.9 Å on the X-ray chart of the kaolinite mixture is attributed to the compound  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$ , sometimes called the low sulfate form of calcium sulfoaluminate, and which bears the same relationship to tetracalcium aluminate hydrate as does the carboaluminate previously discussed, except that sulfate instead of carbonate ions replace hydroxyls.

Peaks at 2.78 and 2.73 Å belong to unhydrated dicalcium silicate. It is evident that in all the mixtures containing an active pozzolan these peaks are higher than in the mixture made with inactive powdered quartz. The peak at 2.88 Å partly belongs to unhy-

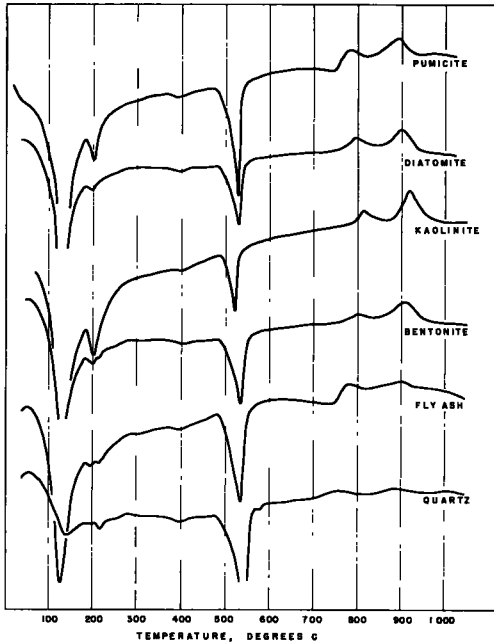


Figure 7. DTA curves of reaction products of mixtures containing 4g pozzolan, 16g high alkali Type III cement, 15ml water and reacted for 11 mon at 100°F.

endotherm near 500 C provides some indication of the activity of the pozzolan, being smaller for the more active ones. In the mixtures made with the Type V cement, the 200 C endotherms (Fig. 8) are generally very small (except for the kaolinite mixture) and demonstrate the virtual absence of the tetracalcium aluminate hydrate phase or related sulfate and carbonate complex salts in good agreement with the X-ray analyses. The calcium hydroxide endotherm scarcely shows on the trace of the kaolinite mixture. The exothermic high temperature reactions, as observed on the DTA traces, have greater amplitude in the mixtures in which an active pozzolan is present. In general, these result from crystallization of the dehydrated reaction products into such minerals as wollastonite, beta dicalcium silicate, and melilite.

## CONCLUSIONS

The calcium silicate hydrate, resulting from cement-pozzolan reaction, slowly increases in amount with time and develops a more orderly structure when an active pozzolan is present. Assuming that this is the same calcium silicate hydrate phase found in ordinary cement paste, the more nearly crystalline character of this material is likely the result of lowering the lime-silica ratio to a value closer to the approximately 1:1 molar ratio of well-crystallized tobermorite which Kalousek (12) has shown to be capable of holding

drated dicalcium silicate, but seems to be reinforced in some of the charts by an unidentified constituent.

## Pozzolan-Cement Mixtures with Type III High Alkali Cement

Diffraction peaks at about 8.9 Å in most of the mixtures made with the Type III cement (Fig. 6) are produced by the low sulfate form of calcium sulfoaluminate. In the pumicite mixture rather strong diffraction peaks at 7.6 and 3.8 Å indicate the presence of the aluminate-carboaluminate hydrate, the same that was found in the lime-pozzolan mixtures; while smaller peaks at 9.0 and 9.6 Å suggest the presence of both forms of calcium sulfoaluminate. The 8.9 Å peak in all these mixtures shifts to about 8.1 Å upon heating for a few minutes at 105 C, or even at much lower temperatures for longer periods. The 7.6 Å peak moves very little upon heating at 105 C.

DTA curves for the mixtures made with the Type III cement show pronounced endotherms around 200 C, some of them being double (Fig. 7). The calcium hydroxide

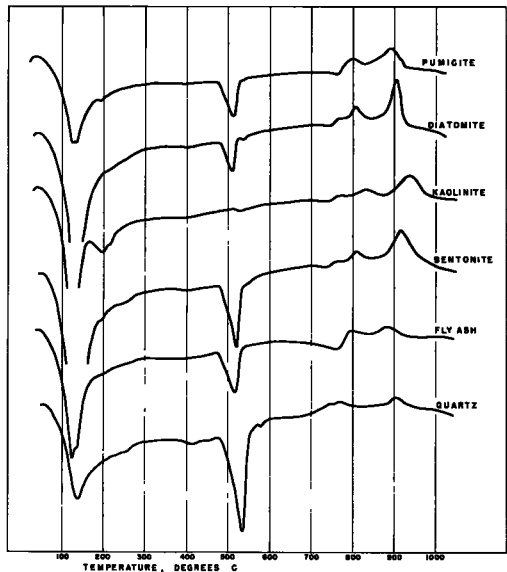


Figure 8. DTA curves of reaction products of mixtures containing 4g pozzolan, 16g low alkali Type V cement, 15ml water and reacted for 11 mon at 100°F.



considerable aluminum in its crystal lattice. It would be surprising if the poorly crystallized material resulting from cement-pozzolan reaction did not have even greater capacity for substitution of aluminum and, perhaps, iron into its structure.

The very weak indications of aluminate hydrates or related complex salts in most of the hydrated mixtures made with the Type V cement which, although very low in crystalline  $C_3A$  content, still contain some 60 percent as much  $Al_2O_3$  as the Type III cement pose a question: Where has the alumina gone? It is unlikely that it could persist in an amorphous state in the presence of saturated calcium hydroxide solution. It appears that the alumina in these mixtures tends to enter the calcium silicate hydrate structure. However, when considerable crystalline  $C_3A$  is present in the cement, the tetracalcium aluminate hydrate crystallizes more quickly than the calcium silicate hydrate and aluminum liberated later from the glassy portions of the clinker or from an aluminous pozzolan crystallizes, in part, as tetracalcium aluminate hydrate and related complex salts on these nuclei. This indicates that a sulfate-resisting cement, low in crystalline  $C_3A$ , will not necessarily produce more tetracalcium aluminate hydrate when used with an aluminous pozzolan and can thus maintain its sulfate resistance unimpaired. On the other hand, a high early strength cement, high in crystalline  $C_3A$ , will produce even more of the calcium aluminate hydrate when combined with an aluminous pozzolan, thereby becoming more susceptible to sulfate attack than when no pozzolan is used. A completely siliceous pozzolan, such as diatomite, will reduce the amount of calcium aluminate hydrate in the paste and bring about an improvement in sulfate resistance.

These conclusions are based on the assumption that the tetracalcium aluminate hydrate and the related carboaluminate and monosulfoaluminate are the only compounds in the cement paste which contribute to deterioration in the presence of sulfate-bearing water. The results have shown, also, that one extremely active and highly aluminous pozzolan, calcined kaolinite, will increase the yield of calcium (carbo-, sulfo-) aluminate hydrate regardless of the  $C_3A$  content of the cement.

Although Kalousek (13) has found that tetracalcium aluminate hydrate forms a complete isomorphous series with the low sulfate calcium sulfoaluminate, it is observed in these studies that two distinct variations of this compound exist in most of the reacting mixtures. The sulfate-rich portion has its strongest diffraction line at about 8.9 Å, while the sulfate-free portion corresponds to the product found in the lime-pozzolan mixes with its chief lines showing at about 7.6 Å and 3.8 Å. DTA curves in Figure 7 show two endotherms, one beginning at 175-180 C, the other beginning just above 200 C. An attempt to correlate one of these endotherms with the sulfate-rich phase and the other with the sulfate-free phase has not been entirely successful. At least there is a tendency in some of the mixtures for the 7.6 Å diffraction peak and the endotherm beginning around 180 C to gain strength as the reaction time goes on relative to the diffraction peak at 8.9 Å and the endotherm beginning just above 200 C. This suggests that the sulfate-rich portion forms first in a sulfate-rich environment and persists at least in part for many months, while the continuing reactions yield the sulfate-free compound when the interstitial solutions become depleted of sulfate ions. In the X-ray charts for the kaolinite mixture made with Type III cement (Fig. 6) there is some evidence that the aluminate compound is of intermediate composition, or a mixed-layer aggregate of the complex aluminate hydrates, the X-ray diffraction peak being broad and occupying an intermediate position.

Stratling's compound, found only in the kaolinite mixtures, is the only hydration product identified in these studies which has not been observed among the normal hydration products of cement. It forms in relatively minor amounts and is of unknown significance in its effect on the properties of concrete which contains it. It was observed previously in experimental concrete not containing kaolinite among the corrosion products around an embedded aluminum pipe and was accompanied by a hydrogarnet phase.

From the amount of unhydrated clinker mineral remaining in the mixtures, it appears that pozzolans generally retard the hydration of at least the dicalcium silicate. This effect undoubtedly is partly responsible for the slower development of strength that has been reported for pozzolanic concrete.

All the compounds identified among the cement-pozzolan reaction products, except for Stratling's compound, are recognized normal hydration products of cement. There are, however, minor X-ray peaks and thermal effects which remain unexplained. It is apparent that the role of pozzolans in modifying the properties of concrete does not necessarily include altering the usual hydration processes or formation of entirely different end products in the cement paste. Rather, it seems to be chiefly one of modifying the composition and relative amounts of existing hydrate phases.

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