

THE EFFECT OF POZZOLANAS ON THE TRICALCIUM
ALUMINATE HYDRATION

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ABSTRACT

The effect of pozzolanas on the C_3A hydration with and without lime and gypsum was examined. The addition of pozzolana lowers the heat evolution caused by C_3A hydration. Lime combination with C_3A and its hydration product is favoured by the addition of pozzolana, with a different mechanism of reaction depending on the presence of gypsum. Volcanic pozzolana in the presence of lime accelerates the transformation from hexagonal hydroaluminate to cubic C_3AH_6 .

E' stata esaminata l'influenza della pozzolana sull'idratazione del C_3A in presenza ed in assenza di calce e gesso. L'aggiunta di pozzolana abbassa il calore sviluppato dall'idratazione del C_3A . L'aggiunta di pozzolana favorisce la combinazione della calce con il C_3A ed i suoi prodotti di idratazione, ma il meccanismo di reazione dipende dalla presenza di gesso. La pozzolana di origine vulcanica in presenza di calce accelera la trasformazione degli alluminati idrati esagonali nell'idrato cubico C_3AH_6 .

INTRODUCTION

The substitution of pozzolana for clinker Portland cement causes a reduction in the strength at the earlier ages, whilst the ultimate strength at later curing may be increased. This behaviour can be explained by the lime-pozzolana reaction producing a C-S-H gel similar to that arising from Portland cement.

Pozzolanic cements are largely used in Italy because of the advantages deriving on their lower hydration heat and higher durability. The latter aspect too seems to be related to the combination of pozzolana with the calcium hydroxide liberated during the hydration of C_3S and C_2S . The calcium hydroxide, which is readily subject to chemical attack, is thus removed and in its place a lime-pozzolana compound is formed.

Due to these facts the lime-pozzolana reaction was widely studied by many researchers (1-4) also to explain the durability performed by lime-pozzolana mortars, as it is shown by the experience of 2000 years in many Roman monuments and maritime works.

However, particularly for the resistance of the pozzolanic cements to the sulphate attack, it would be very interesting to examine the influence of the pozzolanas on the hydration and the sulphate expansion of the aluminate and ferrite phases. In the present paper the influence of two typical Italian pozzolanas on the C_3A hydration is examined by substituting pozzolana for quartz in the system C_3A lime-gypsum-quartz studied in a previous work (5).

EXPERIMENTAL

Twelve mixes were prepared with the composition shown in Table I. The first group of four samples contains quartz (Q), while in the second and third group quartz is substituted by the pozzolana of Segni (Se) and Sacrofano (Sa) respectively.

Se and Sa materials are natural Roman pozzolanas used for the industrial production of pozzolanic cements. Se is a volcanic pozzolana while Sa is a silica rich (85%) diatomaceous earth, and a detailed description of their properties is reported by Lea (1) and Turriziani (2). A recent chemical analysis and surface properties of both the pozzolanas is reported in reference (6).

C_3A with a Blaine fineness of about 3000 cm^2/g was prepared according the method described in a previous paper (5). Reagent grade C_3S and CH were dry mixed with C_3A and finely ground (40 μm -60 μm) quartz or pozzolana.

Hydration at $20 \pm 0.5^\circ C$ of pastes with a water/solid (w/s) ratio of 0.8 was examined. This is larger than the w/s ratio of 0.4 used in the previous work (5), but the change was necessary since too stiff pastes were obtained when a w/s ratio of 0.4 was used, particularly in the samples containing 40-50% of Sa pozzolana, due to its very large specific surface area of about 60 m^2/g (5).

Table I - Percentage compositions of samples.

Sample	C A	CH	CSH	Q	Se	Sa
A-Q	50	-	-	50	-	-
B-Q	50	-	10	40	-	-
C-Q	50	10	-	40	-	-
D-Q	50	10	10	30	-	-
A-Se	50	-	-	-	50	-
B-Se	50	-	10	-	40	-
C-Se	50	10	-	-	40	-
D-Se	50	10	10	-	30	-
A-Sa	50	-	-	-	-	50
B-Sa	50	-	10	-	-	40
C-Sa	50	10	-	-	-	40
D-Sa	50	10	10	-	-	30

Heat evolution as a function of time was determined according the method previously described (5).

Differential thermal analysis (DTA) thermogravimetric analysis (TG), and differential thermogravimetric analysis (DTG) were simultaneously

carried out after stopping reaction by grinding samples in methyl alcohol.

DTA curves instead of DTG curves are shown in the present paper, although the latter were found to be better than the former for the resolution of peaks (5). However some difficulties arisen for the presence of pozzolanas which shown a DTA or DTG peak at 150-200°C due to the expulsion of water, and then this would have masked the peaks of C_3S (150-160°C), ettringite (120-140°C), and hexagonal hydroaluminate (about 120, 200 and 280°C). Preliminary heating of pozzolanas at 200°C does not allow to overcome this drawback, as water is immediately reabsorbed on pozzolanas during mixing of samples with water for the preparation of pastes.

For this reason, a mixture of alumina-pozzolana instead of only alumina was used for the reference sample of the thermoanalyser. The same percentage of pozzolana was used in the reference sample as that of the paste sample, so that the heat evolution due to the expulsion of water from pozzolana was approximately the same, and the masking DTA peak was practically removed. Of course the masking DTG peak was doubled due to the presence of pozzolana both in the reference and in the paste sample, and for this reason DTA was preferred to DTG for the present work.

In some cases Scanning Electron Micrographs of the hardened pastes at the age of 3 days were also taken.

RESULTS AND DISCUSSION

In Fig. 1 heat evolution rate as a function of time

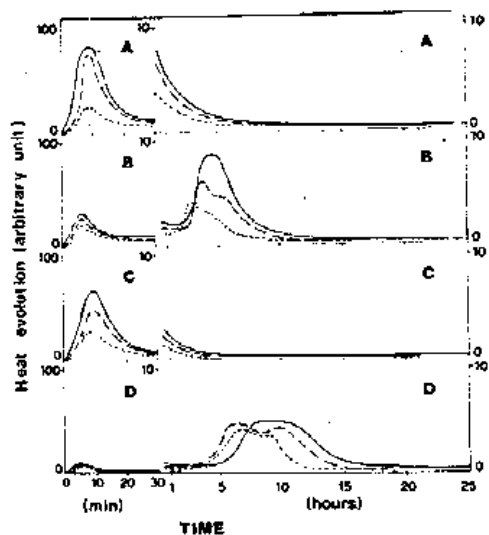


Fig. 1. Heat evolution curves for mixes without CH and CSH_2 (A), with CSH_2 (B), with CH (C), with CH and CSH_2 (D)

————— Q
 - - - - - Se
 - - - - - Sa

is shown. The curves concerning the C_3A hydration without pozzolanas substantially confirm those recorded in the previous work, although less reproducible results were obtained in the present work, possibly due to the higher w/s ratio which causes some bleeding (5,7).

In the samples without gypsum only one peak is observed during the first half an hour of hydration, while two peaks are recorded in the presence of CSH_2 : the second peak is remarkably lower than the first one, and it is shifted towards longer hydration time when CSH_2 is accompanied by CH.

Gypsum retards more than calcium hydroxide, and the two compounds together retard even more strongly C_3A hydration. Moreover, in the present paper the second peak is approximately a single one (Fig. 1, B and D), while in the previous paper

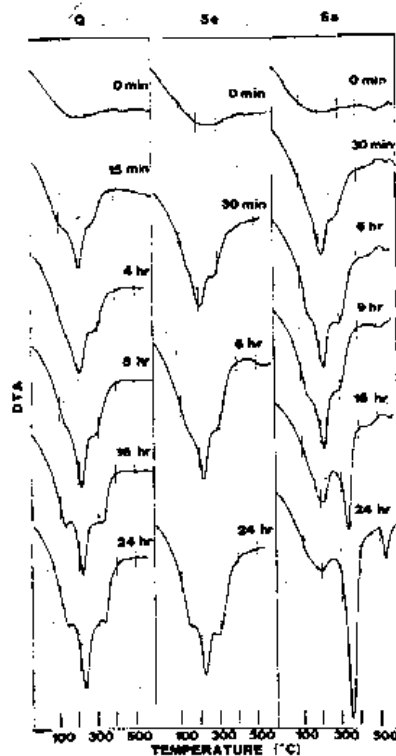


Fig. 2 DTA curves for mixes without CH and CSH_2

(Fig. 1 in ref. 5) it was a double peak. The discrepancy between these results could be ascribed (5,7) to the differences in the difficulty of homogeneously mixing samples with different w/s ratio (0.8 and 0.4).

When C_3A hydrates in the presence of pozzolanas, the heat evolution curves show about the same trend but they are quite lower except samples D containing CH and CSH_2 too. The retarding effect of Sa pozzolana is stronger than that caused by Se pozzolana. This retarding effect would indicate that some absorption of pozzolana on the C_3A surface can occur. The absorption would be much lower when CH and CSH_2 are simultaneously present, probably for the presence of "colloidal" (8) ettringite coating C_3A grains.

The second heat evolution peak recorded in the (B-Se, D-Se, B-Sa, D-Sa) samples containing CSH_2 and pozzolanas is a double peak, and this could be explained by the lower homogeneity caused by the higher stiffness of these samples. Moreover, in the presence of pozzolana the second heat evolution occurs at earlier hydration time in respect to the pastes containing quartz (Fig. 1, B and D).

In Fig. 2-5 DTA curves for mixes hydrated at different times are shown.

Fig. 2 shows the results of the samples without CH and CSH_2 . In all the mixes DTA peaks at about 130, 210 and 290°C, are observed with the peak at about 210°C much stronger than the other ones. Similar results were obtained by DTG with the peaks at temperatures slightly lower (10°C), and the three peaks were assigned to the hexagonal hydroaluminates C_2AH_6 and C_4AH_4 (5). Some cubic hydrate (C_3AH_6) is observed at 24 hours in the paste containing quartz (Fig. 2, Q), while this product, with DTA peaks at about 330 and 510°C, is much abundant in the paste containing Se pozzolana (Fig. 1, Se), and it is practically absent in the sample with Sa pozzolana (Fig. 1, Sa). It seems, then, that Se pozzolana accelerates the transformation of hexagonal hydroaluminates into the cubic hydrate.

In Fig. 3 DTA curves for C_3A pastes containing gypsum are shown. Ettringite with DTA peak at about 140°C is formed immediately in all the samples and this can explain the retardation of C_3A hydration (5,7) and then the lower heat evolution peak during the first half an hour of reaction (Fig. 1, A and B). Then ettringite disappears after some hours and peaks at 120, 210 and 290°C appear which could be assigned to monosulphate and hexagonal hydroaluminates.

The transformation rate of ettringite into monosulphate increases in order for samples containing quartz, Se pozzolana, Sa pozzolana.

Cubic hydrate C_3AH_6 was not observed in all the samples

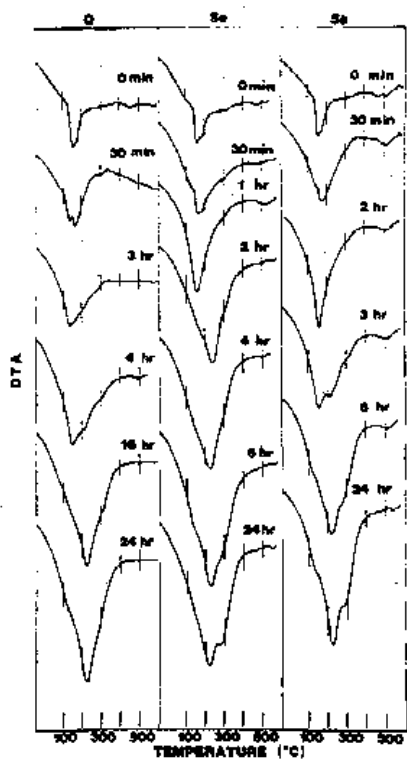


Fig. 3 DTA curves for mixes with CSH_2

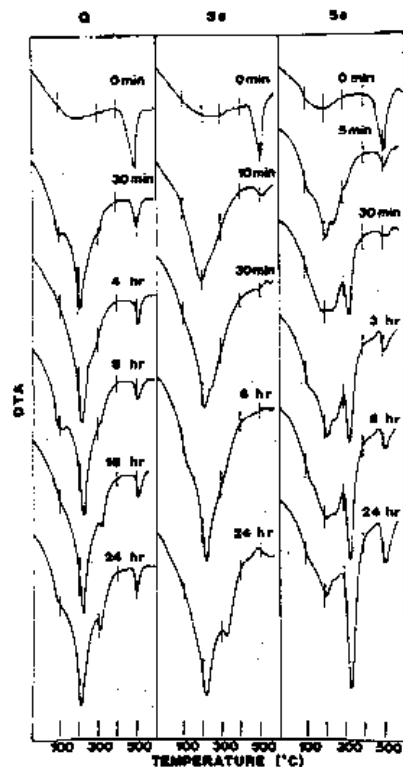


Fig. 4 DTA curves for mixes with CH

containing gypsum independently of the presence of pozzolana.

In Fig.4 DTA curves for pastes containing calcium hydroxide are illustrated. Hexagonal hydroaluminates are firstly formed which subsequently transform into cubic hydrate with the same trend observed in Fig. 2. However CH accelerates in general this transformation in all the samples, and the effect is particularly remarkable for the paste containing Se pozzolana, thus confirming the results obtained in the samples containing Se pozzolana without CH (Fig. 2, Se).

The transformation of hexagonal hydroaluminates into the cubic phase for the samples containing CH and Se pozzolana is so rapid that some C_3AH_6 can be observed after 5 min, while it clearly appears after 30 min of hydration (Fig. 4, Se). Thus, this transformation occurs when the paste is still in the plastic state and a very interesting change in the rheological properties is observed: a stiff paste is changed

in a flowing one after 10-30 min of hydration.

A similar phenomenon was pointed-out by Traetteberg and Grattan-Bellew (9) on pure C_3A paste with higher w/s ratio of 1 and when relatively large samples liberating remarkable heat of hydration were used. These authors believe that when, for some reasons (for instance the temperature is higher than 30°C) the transformation from laminar crystals of hexagonal hydroaluminates into the cubic crystals of C_3AH_6 occurs during the first minutes of reaction and the paste is not yet hardened, the change in the morphological character of the hydrated products causes the above mentioned change in the rheological properties.

In the experimental conditions of the present work, the change from stiff into a flowing paste is not observed in the sample A-Q which is similar to that examined by Traetteberg and Grattan-Bellew. This is probably due to the lower w/s used in the present work, and in particular to the smaller size of sample which causes a lower increase in the temperature. However, in such a conditions the change from stiff to flowing one is observed in the presence of CH and Se pozzolana. Some tests carried out with another type of volcanic pozzolana (Salone) gave results similar to those obtained in the presence of Se pozzolana.

Another interesting aspect of the influence of pozzolanas on the C_3A hydration in the presence of CH concerns the disappearance of this product. After 30 min of reaction the peak at about 500°C assigned to CH is practically disappeared for the samples containing both Se and Sa pozzolana (Fig.4, Sa and Se). Then the peak at about the same temperature appears again but it can be assigned to C_3AH_6 which shows two endothermal effects at about 320 and 510°C .

A decrease in the CH content is also recorded in the sample containing quartz (Fig.4, Q), but it is remarkably lower than that observed in samples containing pozzolanas.

Some tests on CH-pozzolana mixes demonstrated that the combination of calcium hydroxide with Se and Sa pozzolana is a relatively slow reaction, and a complete combination of CH requires weeks or months thus confirming the results obtained in other works (6,10). Then the very rapid disappearance of CH in sample C-Se and C-Sa must be ascribed to some other reaction between hexagonal hydroaluminates and CH promoted by the presence of pozzolana. Possibly C_2AH_3 can be transformed into the more basic " C_2AH_3 " in the presence of CH and pozzolana, but DTA and also XRD could not adequately demonstrate this hypothesis.

Fig. 5 illustrates DTA curves for pastes containing CH and CSH_2 . Approximately the same trend of Fig.3 (CSH_2 without CH) is observed, except a slower rate of transformation of

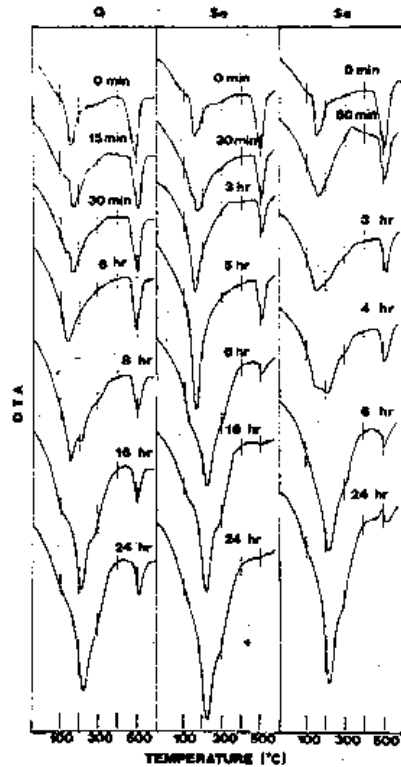


Fig. 5 DTA curves for mixes with CH and CSH₂

ettringite into monosulphate and/or hexagonal. This agrees with the fact that the second heat evolution peak appears later in samples containing CSH₂ and CH (Fig. 1, D) than in those containing C \bar{S} -H₂ only.

In the presence of pozzolana the disappearance of ettringite is accelerated (Fig. 5). Similar results were observed also in the pastes containing C \bar{S} -H₂ without CH (Fig. 2).

The disappearance of CH in the samples containing pozzolanas CH and CSH₂ (Fig. 5, Se and Sa) is observed as well as in the samples with pozzolanas and CH (Fig. 4, Se and Sa). However the rate of disappearance is slower in the presence of C \bar{S} -H₂, and a complete combination of CH requires about 16 hours or 24 hours for Sa or Se respectively (Fig. 5). Moreover the disappearance of CH is very rapid in the period during which ettringite too disappears. This means the mechanism of CH combination in sample D-Se and D-Sa is different from that expected for samples C-Se and C-Sa. In the former case a reaction between CH, C₃A and ettringite to form the hexagonal solid solution (C₃A·CH₂·C \bar{S} _{0.5}·H₁₂) can be

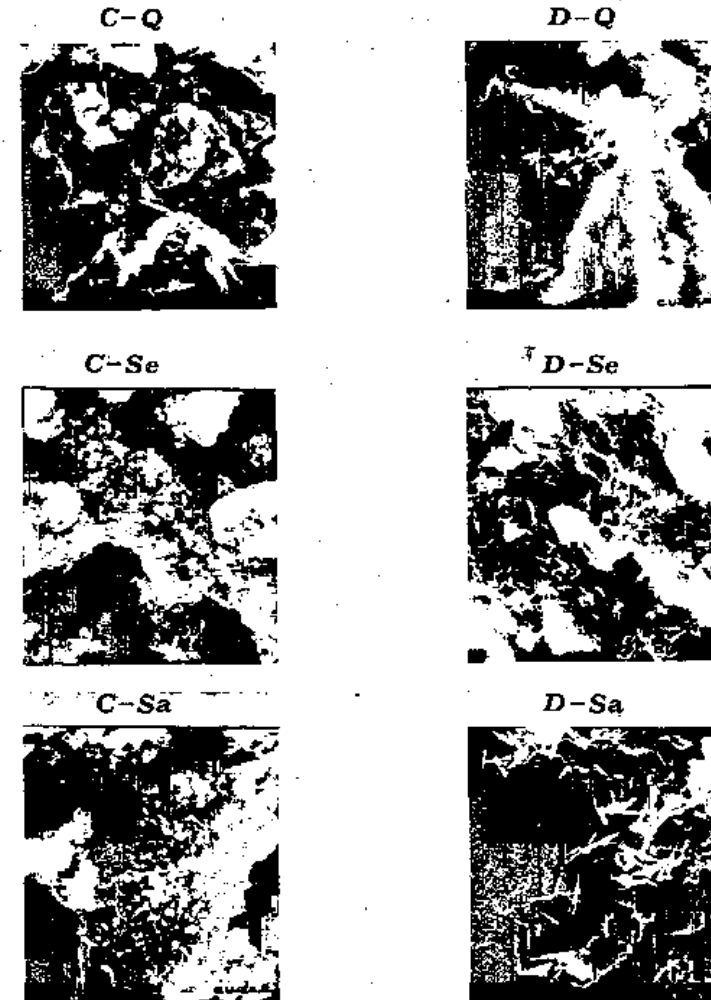
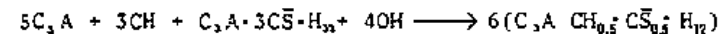


Fig. 6 SEM for samples (Table I) Hydrated for 3 days, $\bar{\text{—}} = 5 \mu\text{m}$

supposed. For example, if x is 0.5 the following stoichiometry can be suggested for the reaction:



In Fig. 6 SEM of some samples with and without pozzolana

are shown. Cubic and laminar crystals are observed in sample C-Q, while only laminar crystals of hexagonal hydroaluminat are observed in sample D-Q due to the presence of CS_2H_2 that inhibits the C_3AH_6 formation. Similar microstructures are observed in samples containing Sa pozzolana, (C-Sa and D-Sa), while in the presence of Se pozzolana and CH, cubic crystals of C_3AH_6 are much more abundant (C-Se). This agrees with DTA curves (Fig.4, Se) and moreover confirms the above mentioned hypothesis of Traetterberg and Grattan-Bellew (9) to explain the transformation from stiff to flowing paste.

CONCLUSIONS

Some interesting changes in the C_3A hydration were observed due to the addition of pozzolana.

A lower evolution rate was recorded in the presence of pozzolanas particularly when the diatomaceous silica rich pozzolana (Sa) was used. The retarding effect could be explained by the absorption of pozzolana on C_3A grains. However, the effect was much smaller when the hydration rate of C_3A was retarded by gypsum and calcium hydroxide.

Calcium hydroxide decreases much more rapidly in the C_3A pastes containing pozzolana but the reaction cannot be related to the lime-pozzolana reaction which is much slower. Moreover, the mechanism and the rate of the calcium hydroxide combination appears to be quite different whether or not also gypsum is present. Ettringite, lime and C_3A seem react to form hexagonal solid solution when gypsum is present. In samples not containing gypsum the combination of lime is more rapid but the reaction product could not be individuated.

In the C_3A sample containing calcium hydroxide and the volcanic pozzolana (Se) a rheological change from a stiff paste to a flowing one is observed during 10-30 min of hydration, while the laminar crystals of hexagonal hydroaluminat are transformed into the cubic crystals of C_3AH_6 . Similar results were obtained with another type of volcanic pozzolana (Salone).

All these results seem to indicate that, besides the well-known combination between lime and pozzolana (1-4), some other reaction between pozzolana and C_3A or its hydration products can occur in pozzolanic cements.

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REFERENCES

- (1) F. M. Lea "The Chemistry of Cement and Concrete", pg.414, Edward Arnold, London, (1970).
- (2) R. Turriziani, "The Chemistry of Cements", Vol. II, pg. 69, Ed. by H.W.F. Taylor, Academic Press, London (1964).
- (3) G. Malquori, Proceedings of the Fourth International Symposium on the Chemistry of Cements, Vol. II, pg.983, Washington (1960).
- (4) F. Massazza "Chemistry of Pozzolanic Additions and Mixed Cements", Principal Paper of the VI International Congress on the Chemistry of Cement (preliminar paper) Moscow, (1974).
- (5) M. Collepari, M. Corradi, G. Baldini and M. Pauri, Cem.Concr. Res. 8, 571 (1973).
- (6) M. Collepari, A. Marcialis, U. Sanna, Cem. Concr. Res. 6, 497, (1976).
- (7) M. Collepari, M. Corradi, G. Baldini and M. Pauri, J. Am. Cer. Soc., publication planned for January 1979.
- (8) P.K. Mehta, J. Amer. Cer. Soc., 52, 521, (1973).
- (9) A. Traetterberg and P.E. Grattan-Bellew, J. Am. Cer.Soc., 58, 221, (1975).
- (10) A. Celani, M. Collepari, A. Rio, Rev. Matèr. Constr., 614, 1, (1966).