**Restoration of Buildings and Monuments**
Bauinstandsetzen und Baudenkmalpflege
Vol. 11, No 2, 111–118 (2005)

# Pozzolanic Components in Lime Mortars: Correlating Behaviour, Composition and Microstructure

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## Abstract

Thermal analysis and scanning electron microscopy were used to evaluate the composition and microstructure of lime mortars containing pozzolanic materials, such as natural pozzolan, fired clays and fly-ash. A correlation between the microstructure and the mechanical performance of these mortars could be drawn. The most uniform growth of calcium silicate hydrates (CSH) was obtained by the addition of metakaolin, in this study obtained by firing natural kaolin to 800 °C for 3.5 hours.

**Keywords:** Lime mortars, pozzolanic materials, pozzolana, fly ash, kaolin, clay dust, metakaolin

## *Puzzolanische Bestandteile in Kalkmörteln: Zusammenhang zwischen den Eigenschaften, der Zusammensetzung und dem Mikrogefüge*

## *Zusammenfassung*

*Um die Zusammensetzung und das Mikrogefüge von Kalkmörteln, die puzzolanische Bestandteile wie etwa natürliche Puzzolane, gebrannten Ton und Flugasche enthielten, zu untersuchen, wurden die Differential-Thermoanalyse und die Rasterelektronenmikroskopie verwendet. Es konnte ein Zusammenhang zwischen dem Mikrogefüge und den mechanischen Eigenschaften dieser Werkstoffe hergestellt werden. Besonders gleichmäßiges Wachstum von Calciumsilikathydraten (CSH) konnte nach Zugabe von Metakaolin beobachtet werden. Für diese Untersuchungen wurde das Metakaolin durch 3,5 stundenlanges Brennen bei 800 °C hergestellt.*

***Stichwörter:*** *Kalkmörtel, Puzzolanische Substanzen, Puzzolane, Flugasche, Kaolin, Tonstaub, Metakaolin*

# 1 Introduction

One of the most frequent and crucial activity required when dealing with the conservation of historic buildings is the replacement of deteriorated mortars. It is fundamental that the formulated replacement mortars be compatible with the existing material in the building in both their mechanical behaviour, i.e. hardness, and their microstructure, i.e., porosity, to ensure that no damage be induced in the historic fabric. Exact replication of the original mortar formulation, even if this could be achieved, would not be appropriate since in most instances the historic fabric, be it stone or brick masonry, no longer has the original characteristics due to its weathering, even if no significant deterioration has affected it [1]. Furthermore, traditional pure lime mortars, given their slow setting time, cannot be used in for in-depth pointing or bedding mortar replacement. For this purpose, hydraulic lime mortars are required. Most of the natural hydraulic limes are very variable and therefore not reliable, while industrially prepared hydraulic limes are usually a mixture of lime and an hydraulic cement. An alternative to this is the development of a hydraulic lime formulation based on the addition of pozzolanic materials.

With the view of developing a range of useful mortar formulations, various local pozzolanic materials were added in different proportion to lime mortars. The pozzolanic materials studied ranged from natural pozzolan from the St. Antão island in Cape Verde, to fly ash and fired clays or kaolin. These last two materials were fired at two different temperatures: 600 °C and 800 °C to enhance their pozzolanic reactivity [2, 3]. The mortars were evaluated for both their mechanical and their salt weathering resistance [4]. The present study complements these tests by correlating the performance of these mortars with the results of the examination of their micromorphology with SEM and thermal analysis to determine the presence of hydraulic components.

# 2 Experimental

## 2.1 Sample Preparation

The samples used in this study all have a 1:1:4 (lime:pozzolanic material:sand) formulation, corresponding to a binder:aggregate ratio of 1:2, as used for the lime:sand control sample. The lime used is a hydrated lime in powder available on the Portuguese market. The sand is a river sand all originating from the same lot. The pozzolanic materials tested were:

- [Poz] natural pozzolan from the St. Antão island (Cabo Verde)
- [Fly] fly-ash from a thermal electricity plant, currently used as an additive in cement production.
- [Cer] ceramic powder obtained from the collectors in a ceramic tile factory. This was fired for 3.5 hours to 600 °C or 800 °C
- [Kao] a natural kaolin from the Santarem region, crushed and sieved to pass the ASTM No. 30 sieve ($\theta < 0.63$ mm). This also was fired to either 600 °C or 800 °C for 3.5 hours.

The mixtures were prepared mechanically and under identical conditions. The samples were also mechanically compacted in their moulds in two layers. The samples were cured for 60 days at either dry (D) conditions, i.e., $23 \pm 3$ °C and $50 \pm 5$ % RH, or humid (H) conditions, i.e., kept in a closed plastic bag for 7 days until demoulding and in a moisture saturated environment for the remainder of the time. Further details on their preparation have been reported previously [4].

## 2.2 Material Characterization

The mineralogical composition of the various pozzolanic materials was obtained by X-ray diffraction and has been reported elsewhere [5]. Apart from the vitreous or amorphous materials, the pozzolan contains mainly phyllosilicates and some illite and feldspars while the fly-ash shows the presence of mullite, some illite and quartz. The ceramic powder is a mixtures of kaolinite with some illite and other phyllosilicates with quartz and traces of a feldspar. Upon heating at 600 °C, the relative amount of kaolinite decreases by decomposition, while heating at 800 °C results in the total decomposition of the illite. The kaolin contains traces of quartz and illite. Upon heating, the same changes observed for the ceramic material are seen.

## 2.3 Mortar Characterization

The pozzolanic materials as well as the mortars prepared with them were examined by scanning electron microscopy (SEM) as well as by thermal analysis (simultaneous thermogravimetry/ differential thermal analysis, TG/DTA). The thermal measurements were carried out in air, at a rate of 10 °C/min, from room temperature to 1200 °C. At the time of the analysis, the mortars were between one and two years old.

Only for some of the mortars, the pair of samples cured under both dry and humid conditions were analyzed. Since the results obtained confirmed previous experience of improved performance for hydraulic mortars cured under humid conditions, and by extension those with pozzolanic materials [4, 6] the study concentrated on those humid cured.

## 3 Results and Discussion

The thermal analysis of the year-old control sample showed that most of the hydrated lime had carbonated though a small amount of it (~1-2 %) remained uncarbonated (Fig. 1 A). Traces of uncarbonated hydrated lime were also detected in the dry-cured fly-ash containing sample (weight loss at around 440 °C). However, the DTG curve also shows a second peak around 475 °C - similar to the one observed in the humid cured sample at 485 °C - that might be attributed to the moisture loss of the hydraulic components formed by the pozzolanic reaction between the clays in the fly ash and the free lime [7] or, as suggested for some pozzolanas, to changes within the vitreous phase [8]. On both these thermograms (Fig. 1, B and C), a shoulder is noticeable at the onset of the DTG peak of the calcium carbonate decomposition, between 575 °C and 625 °C, and corresponding to broad endothermic peak around 500 °C in the DTA curve and attributed to the dehydration of calcium silicate hydrates resulting from the pozzolanic reaction [9].

A similar shoulder appears in the thermograms of the mortar samples containing either ceramic powder or kaolin in humid cure. In the case of the former samples, samples prepared with ceramic powder fired at 600 °C, also show a small weight loss - in conjunction with an exotherm - around 880 °C . This can be attributed to the ceramic powder itself (when heated to 600 °C), since it only appears in this thermogram but neither in the raw ceramic powder nor that fired at 800 °C. It is interpreted as corresponding to the formation of new phases. As mentioned, samples containing kaolin fired at both temperatures and humid cured show the shoulder at the onset of the DTG calcium carbonate decomposition peak, between 575 °C and 625 °C. The sample with kaolin fired at 800 °C also shows an exothermic reaction around 950 °C that might be attributed to the conversion of the calcium silicate hydrates, CSH gel, to wollastonite [10].

Finally, the pozzolan containing sample, also humid cured, shows a weight loss at around 575 °C corresponding to an endothermic reaction (dehydroxylation of illite and other phyllosilicates) superposed to that of the quartz $\alpha$-$\beta$ transition at 577 °C (Fig. 1 D) that masks the reaction that appears as a shoulder in the other samples.

Although the dehydration of the hydraulic components appears in the same temperature range in thermal analysis, their appearance differs when observed by SEM. This can be attributed to the compositional variation of the pozzolanic materials that will result in the crystallization of varying hydraulic compounds, generically called calcium silicate hydrates (CSH).

The influence of curing conditions is illustrated for the case of mortars containing fly ash, where a humid cure shows a higher proliferation of typical fibrous CSH-gel growth as compared to a dry cure where the growth can be seen starting on the surface of the fly-ash particles (Fig. 2, A and B). For the case of the clay containing mortars, only those mortars with clays fired to 800 °C and cured in humid conditions were examined. Although these materials are the most similar, as compared to the other pozzolanic materials tested, the developed microstructure is significantly different. For the case of the mortar with fired ceramic material, the growth of the CSH-gel results in some few larger fibrous crystal clumps with smaller growth beginning on the surface of the clay particles. On the other hand, the mortar with fired kaolin, a more uniform and denser growth covers the surface of the particles (Fig. 2, C and D). Finally, the pozzolan containing sample (humid cured), shows a uniform coating of very fine needles on most all particles (Fig. 2 E). For comparison, the appearance of the control sample, lime:sand 1:2 is also shown (Fig. 2 F).

The improved mechanical performance for humid cured lime mortars when additioned with pozzolanic materials could be correlated with the microstructure observed under SEM and confirmed by thermal analysis as illustrated for the case of fly ash. The data are summarized in Table 1 below.

## 4 Conclusions

Scanning electron microscopy and thermal analysis were used to characterize the presence of the hydraulic components resulting from the pozzolanic reaction between various additives and the hydrated lime in mortars with a 1:1:4 composition.

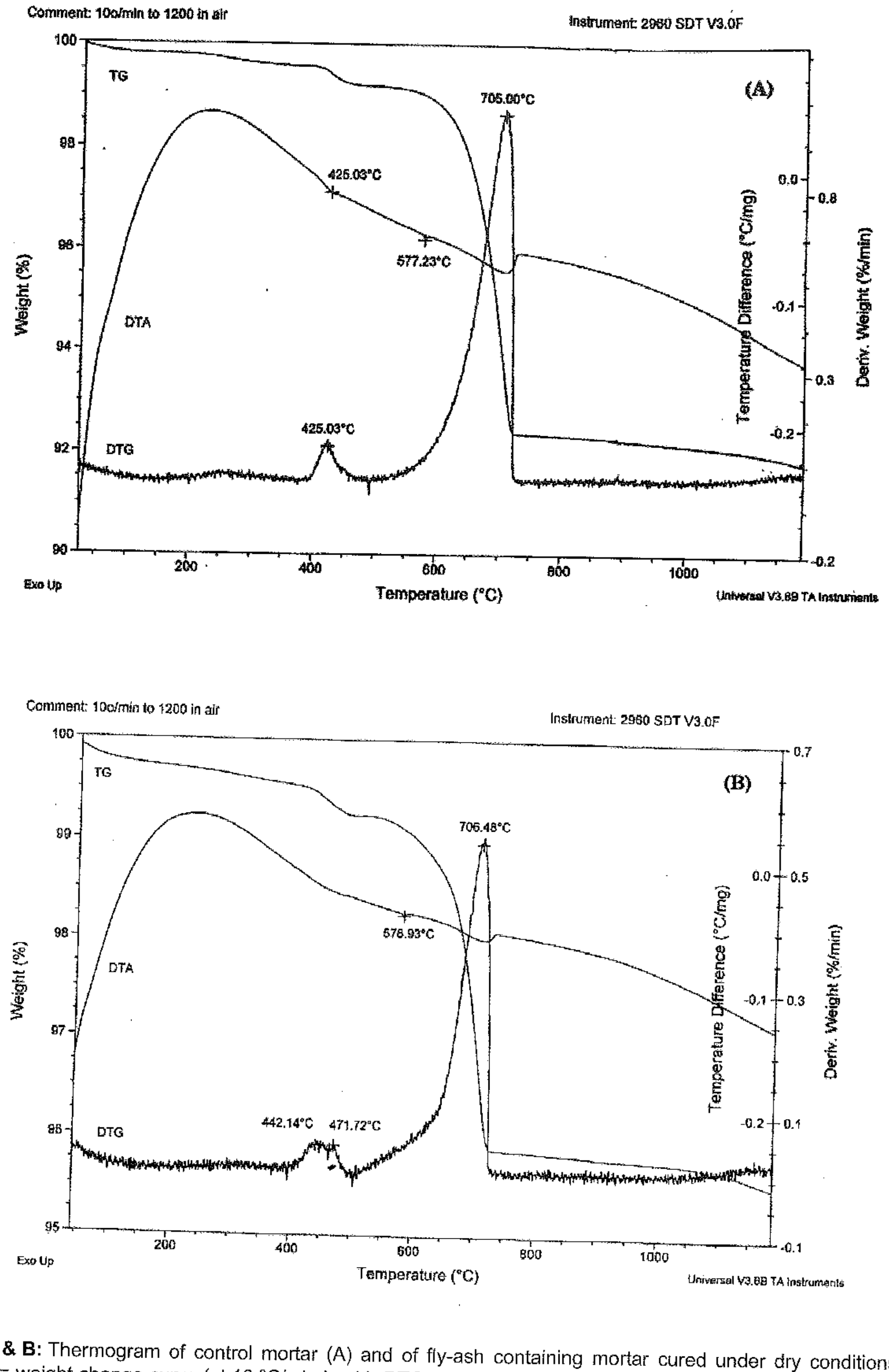
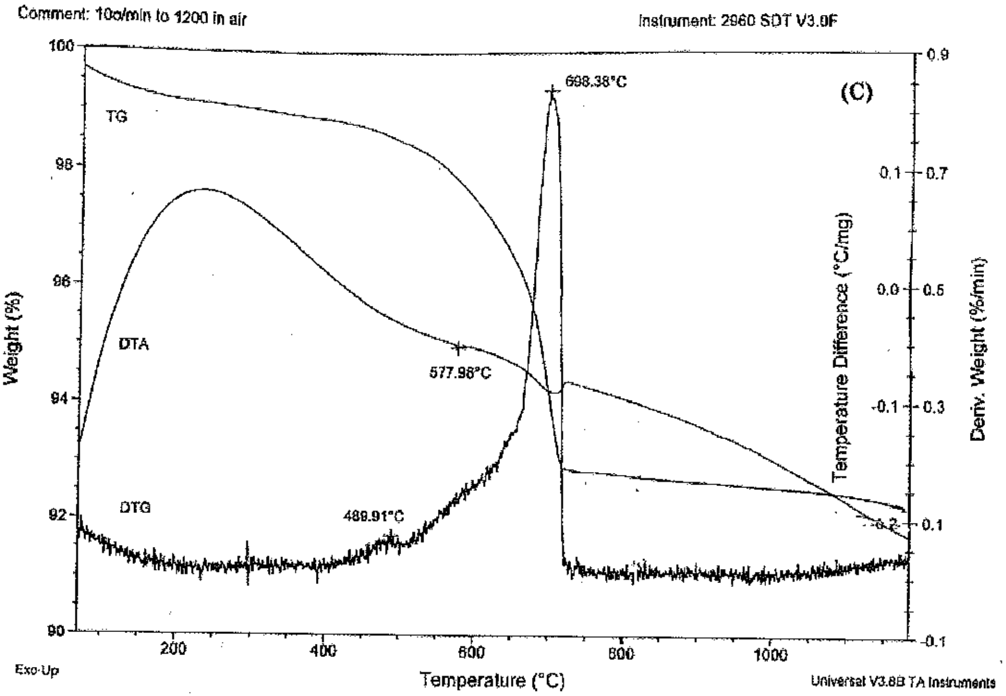



**Figure 1 A & B:** Thermogram of control mortar (A) and of fly-ash containing mortar cured under dry conditions (B), where: TG = weight change curve (at 10 °C/min in air); DTG = derivative of the weight changes; and, DTA = differential thermal analysis curve.



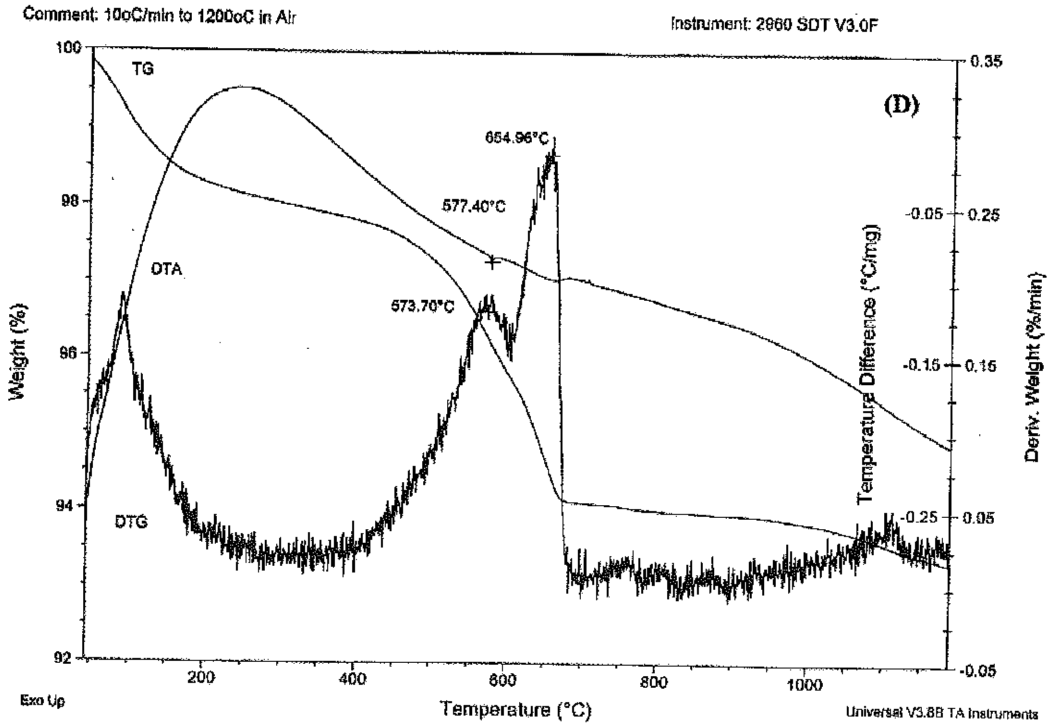




**Figure 1 C & D:** Thermogram of fly-ash containing mortar cured under humid conditions (C) and natural pozzolan containing mortar also humid cured (D), where: TG = weight change curve (at 10 °C/min in air); DTG = derivative of the weight changes; and, DTA = differential thermal analysis curve.

**Table 1:** Mechanical resistance of the mortars and correlation with the observed microstructure. Resistance to chlorides reports % weight change after 50 cycles [4]. **(Bold)** indicates longer crystals.

| | Microstruct. (CSH growth) | Compress. Str. [MPa] | Flexural Str. [MPa] | % Open Porosity | Resist. Chlor. % weight change |
|---|---|---|---|---|---|
| Fly-ash (D) | + | 0.7 | 0.26 | 29 | + 2.5 |
| Fly-ash (H) | **(++)**+ | 2.4 | 0.52 | 31 | + 4.5 |
| Cer 800 (H) | **(+)**++ | 2.2 | 0.22 | 35 | - 1.5 |
| Kao 800 (H) | ++++ | 8 | 1.07 | 33 | + 4.1 |
| Pozz (H) | +++ | 1.3 | 0.17 | 36 | - 28 |

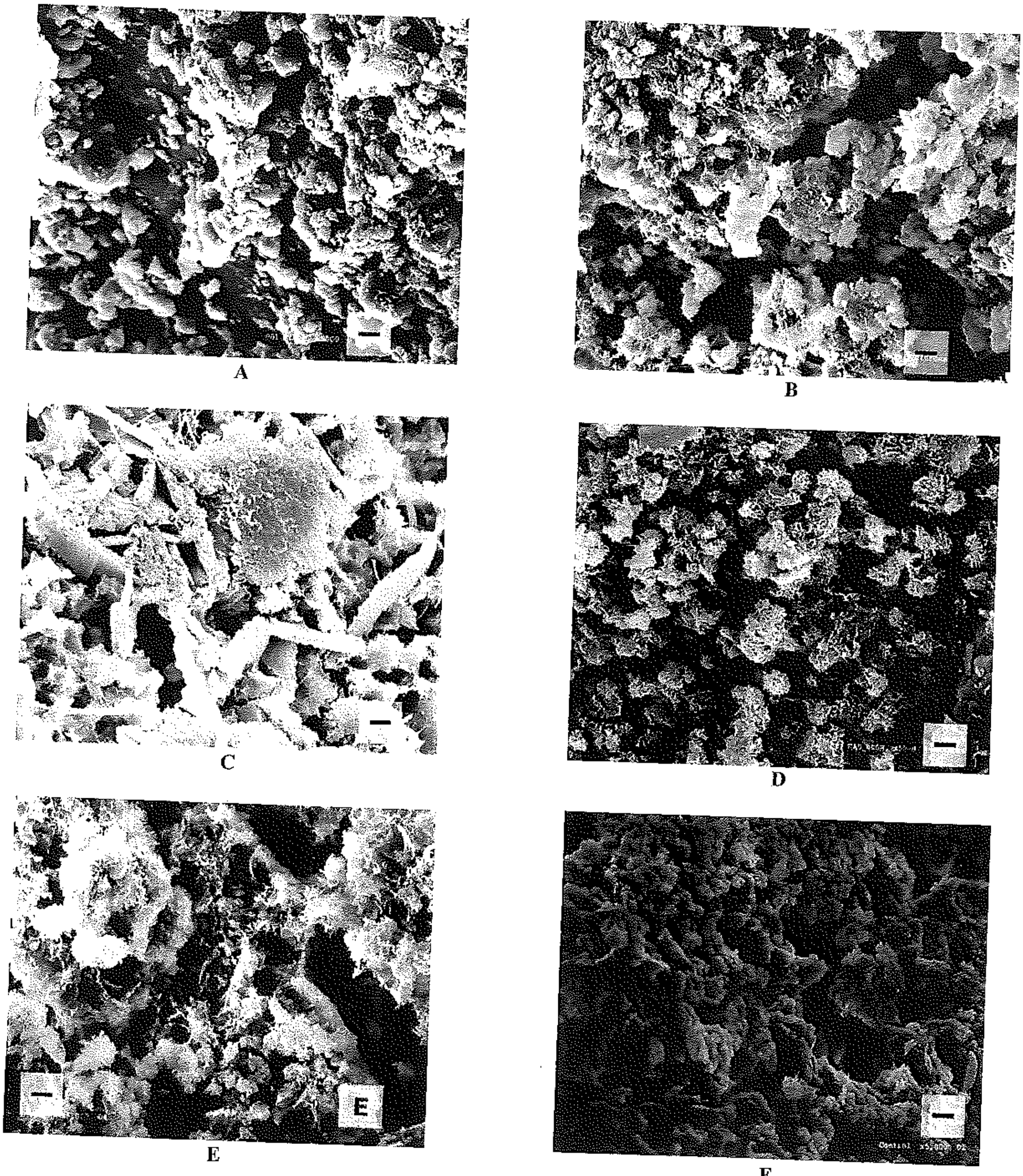



**Figure 2:** SEM photomicrographs of fracture surfaces of mortars additioned with various pozzolanic materials (5000 x —Marker: 1$\mu$m)
**A** and **B** fly-ash dry and humid cured, respectively. **C** and **D** clay materials fired at 800 °C and humid cured, ceramic powder and kaolin, respectively. **E** natural pozzolan humid cured. **F** control sample lime:sand 1:2.

The presence of these hydraulic components was evidenced by the shoulder observed on the DTG curve (corresponding to the dehydration of the calcium silicate hydrates formed) in the 600 °C range and with the broad endotherm around 500 °C.

In spite of the similarity of the thermal curves, SEM examination of these samples showed the presence of different crystal growths depending on the pozzolanic material used. The abundance and size of these newly formed crystals correlated semi-quantitatively with the mechanical performance of these mortars.

## Acknowledgements

The authors gratefully acknowledge the collaboration of James Ferris and Kevin Macke (LRSM, UPenn) for their support in obtaining the SEM images and John Hinchman (Grad. Prog. Hist. Preserv, UPenn) for formatting them for inclusion in this paper.

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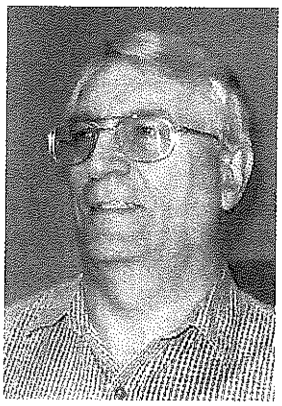

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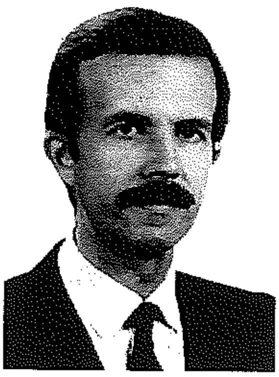

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Received January 6, 2005