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THE POZZOLANIC ACTIVITY OF DIFFERENT MATERIALS, ITS INFLUENCE ON THE HYDRATION HEAT IN MORTARS

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ABSTRACT

This work presents the relationship that exists between pozzolanic activity in certain materials (opaline rocks, fly ash and silica fume) and hydration heat, measured using the Langavant calorimeter method. Pozzolanic activity is evaluated using an accelerated method that establishes the reaction speed of the different materials considered.

While replacement of part of the cement in a mortar or concrete typically reduces the overall heat of hydration, it is shown that, compared to a control cement, silica fume and opaline rock mixes with cement give increased heat output during early hydration. This is due to their rapid and strong lime-pozzolanic reaction. The much less reactive fly ash decreased early heat output, compared to the control cement. a good correlation of between pozzolanic activity and hydration heat found.

REFEREED PAPERS

Introduction

In previous works the authors have studied the effect of different pozzolanic materials on hydration heat developed by cements mixed with them, in comparison with a control cement. These results have shown that pozzolanic materials do not cause a reduction in heat equivalent to the amount of cement substituted (1).

Thus when silica fume reacts with calcium hydroxide originating from the hydration of portland cement, there is an increase in the hydration heat of the cement made from it, compared with the control cement, particularly in the early stages (2). This increase in hydration heat is not seen in the case of fly ash.

In the present work a relation has been sought between pozzolanic activity in the materials studied and the heat given off during hydration of mixed cements. To do this materials of different sorts and with different pozzolanic activities, were selected: a natural material (opaline rock), and two industrial byproducts (fly ash and silica fume).

Pozzolanic activity was studied using an accelerated test that allowed this property to be evaluated over time, so that a comparative reaction speed could be established between the different materials.

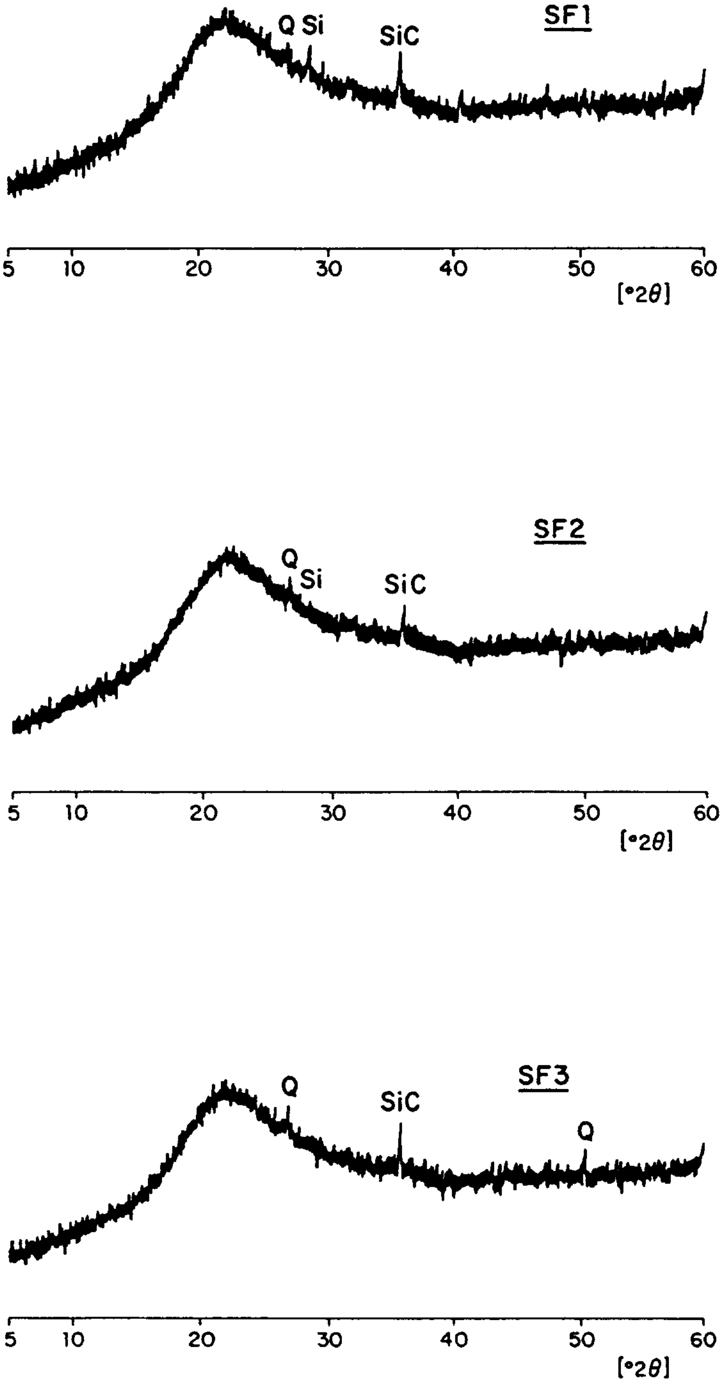

FIG. 1.
X-ray diffraction: silica fumes.

The results of the pozzolanic reaction study are compared with hydration heat developed by mixed cements. The method used to measure hydration heat was the Langavant calorimeter (3). This method is presently covered by Spanish Standards (4).

Experimental

Materials. The materials chosen for this study are: cement, sand and pozzolanic materials, silica fume, opaline rock and fly ash.

- Base Cement: According to the Spanish UNE 80 301 standard (5), the base cement is a Type I/45 A cement with a clinker content equal to or above 95%, that can have up to 5% additional components.
- Sand: The sand used has a silica content of more than 98 % and maximum particle size of less than 2mm.
- Pozzolanic Material: These materials were characterized using chemical and mineralogical analyses and pozzolanic caracteristics.

- Silica Fume (SF1, SF2 and SF3): The three silica fumes used in this study were obtained from differnt countries. The silica fume SF1 has a 93.30% of silica content and 2.94% loss on ignition (LOI); 90.35% SiO_2 and 2.03% LOI for SF2 and 89.85% SiO_2 and 6.30% LOI for SF3. X-ray Diffraction (Figure 1) patterns showed the low crytallinity nature of silica fumes, with low intensity peaks corresponding mainly to quartz (Q), silicon carbide (SiC) and silicon (Si).
- Opaline Rock (OR): This sedimentary material is mostly made up of silica (87.7%) (6). The mineralogical analysis shows that the silica takes different metastable forms. The A-opal is practically amorphous, the position of halo lies at 20-30 (2Θ), and CT-opal contains cristobalite (Cr) as well as quartz (Q), kaolinite (K) and smaller quantities of micas (Mi) (Figure 2). The opaline rock was subjected to a grinding process that gave it a Blaine specific area of 4,500 cm^2/g. Grain fineness strongly influences hydration heat, particularly during the initial moments of the test.
- Fly Ash (FA): This is generated in a power plant that butns bituminous and anthracite coal. The loss on ignition value (0.5%) reflects its low unburned carbon content. The main chemical constituents are silicon oxide (41.5%), aluminium oxide (30.0%) and iron oxide (6.9%), so that it is a fly ash with a low calcium content (2.0%). The main crystalline components are quartz (Q), mullite (Mu) and hematite (He) (Figure 3) (7).

Mixed Cements. The mixed cements were prepared in a high speed powder mixer to ensure homogeneity and maintain their granulometry. Mixtures were made up by weight in the following base cement to addition proportions:

Cement/silica fumes (SF1, SF2 and SF3): 100/0; 90/10.
Cement/silica fume (SF3): 100/0, 95/5, 90/10, 85/15 and 70/30.
Cement/opaline rock (OR): 100/0 and 70/30.
Cement/fly ash (FA): 100/0 and 70/30.

These mixed cements are were used to prepare mortars, whose sand/cement proportion was 3/1 and W/C was 0.5.

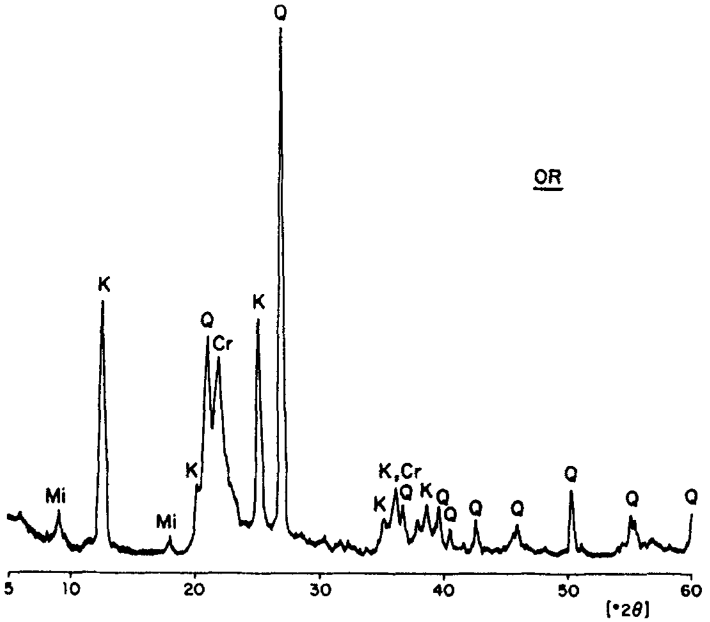

FIG. 2.
X-ray diffraction: opaline rock.

Methods.

1. *Pozzolanic activity test.* In order to study the pozzolanic activity of these materials, an accelerated method was used, follows the material-lime reaction with time. The test consisted of putting the different pozzolanic materials in contact with a saturated lime solution at 40 ± 1 °C for 2 hours, 1 day, 7 days, 28 days and 90 days. At the end of that time, the CaO concentration in the solution was established. The fixed lime (mM/L) was obtained by the difference between the concentration in the saturated lime solution an the CaO found in the solution in contact with the sample, at the end of the given period.

2. *Hydration heat test.* The method given for determining hydration heat in the Spanish standard (4) is based on the Langavant Calorimeter (3). This semi-adiabatic method consists in quantifying the heat generated during cement hydration using a Dewar flask, or, more exactly, a thermally isolated bottle. Since the exterior conditions are very influential, the test is carried out in a climatized room at 20°C ± 2°C.

The measurements were made over five days, as is indicated in the standard (4), since the heat increase is observed to be very low at later times, and also since the relative error of the measurement increases beyond that time.

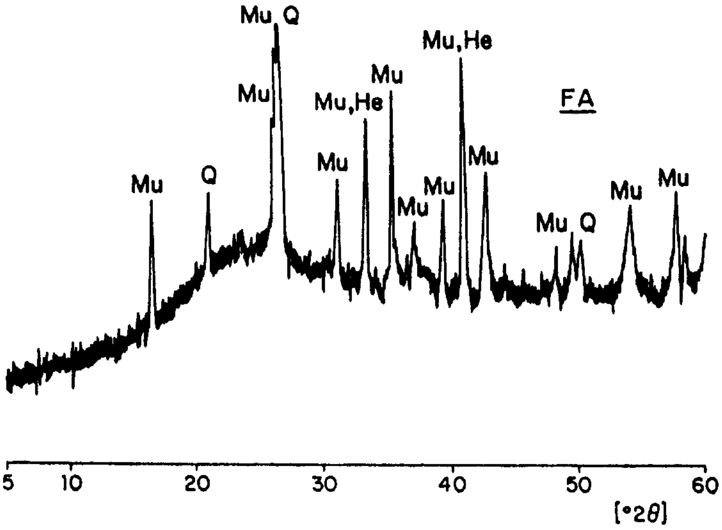

FIG. 3.
X-ray diffraction: fly ash.

Results and Discussion

I. Pozzolanic Activity in the Materials. The pozzolanic activity results obtained are shown in Figure 4. There it can be seen that after two hours both the silica fume and the opaline rock show pozzolanic activity, since the samples have fixed significant amants of calcium hydroxide (lime) while the fly ash, due to its lesser activity at the early stages (1), hardly shows any reaction with the lime before the 28th day.

The behaviour of the samples of silica fume is similar and comparable to that of opaline rock; however, in the latter case lower lime fixing is observed in the early stages, but later, at 90 days, it is equal to, or even slightly higher than the lime fixing ability of silica fume.

II. Hydration Heat. Mortars that have pozzolanic material incorporated in them usually increase hydration heat, with respect to the base cement, during the first hours of the test, depending on the pozzolanic activity of the material, because the reactions taking place with the lime also give off heat. However, beginning with the fifth hour, and up to the first 12 hours of the test, reactions due to the portland cement are strongly exothermal, which makes the ascending slope of the curves very steep; after 48 hours the temperature begins to stabilize and the heat given off is of little significance.

Figure 5 shows the hydration heat (J/g) for the three mortars made with each silica fume (SF1, SF2 and SF3), mixed at a ratio of 90% base cement/10% silica fume. The behaviour of these mortars is similar, with an increase in hydration heat being noted at all stages of the test in mixed cements, as compared with the mortar made with base cement. Due to this similarity, the sample SF3 was selected to study the effect of different percentages of silica fume on hydration heat in mixed mortars.

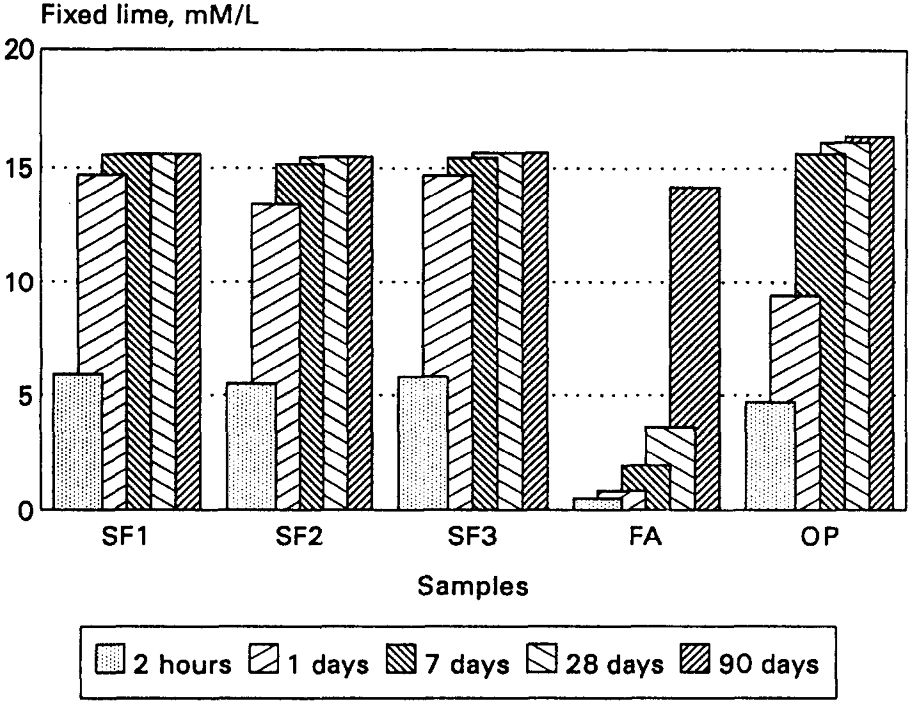

FIG. 4.
Pozzolanic activity: fixed lime over time.

When the base cement/silica fume ratio is varied (Figure 6) it can be seen that in general all the mortars that include silica fume undergo greater heat liberation than the reference cement during the first stages. However when the proportion of pozzolan is 30%, after 10 hours, the hydration heat from the mixed cement is below that of the base mortar. This is because the percentage of cement substitution counteracts the heat from the pozzolanic reaction, and the substitution effect predominates over the effect of the pozzolanic activity (2).

Figure 7 shows the evolution of hydration heat over time in mortars made with fly ash and opaline rock, with a 70/30 proportion of base cement/pozzolanic material. This figure shows that even though these materials substitute for cement in the same proportion, they show very different behaviour. The fly ash is capable of reducing hydration heat to a greater degree than opaline rock.

Figure 8 represents the behaviour of mortars made with the different pozzolanic materials, with a reference point of zero being the heat developed by the base cement mortar. This plot covers the first 14 hours of the test, when the pozzolanic materials usually give an increase hydration heat in comparison to the base cement, since after 48 hours the temperature begins to stabilize and the heat given off is of little significance.

It can be seen from this figure how, during the first hours, the silica fume and opaline rock show similar behaviour, increasing hydration heat (positive values), while the fly ash decreases hydration heat with respect to the base cement (negative values). This is because the fly ash is

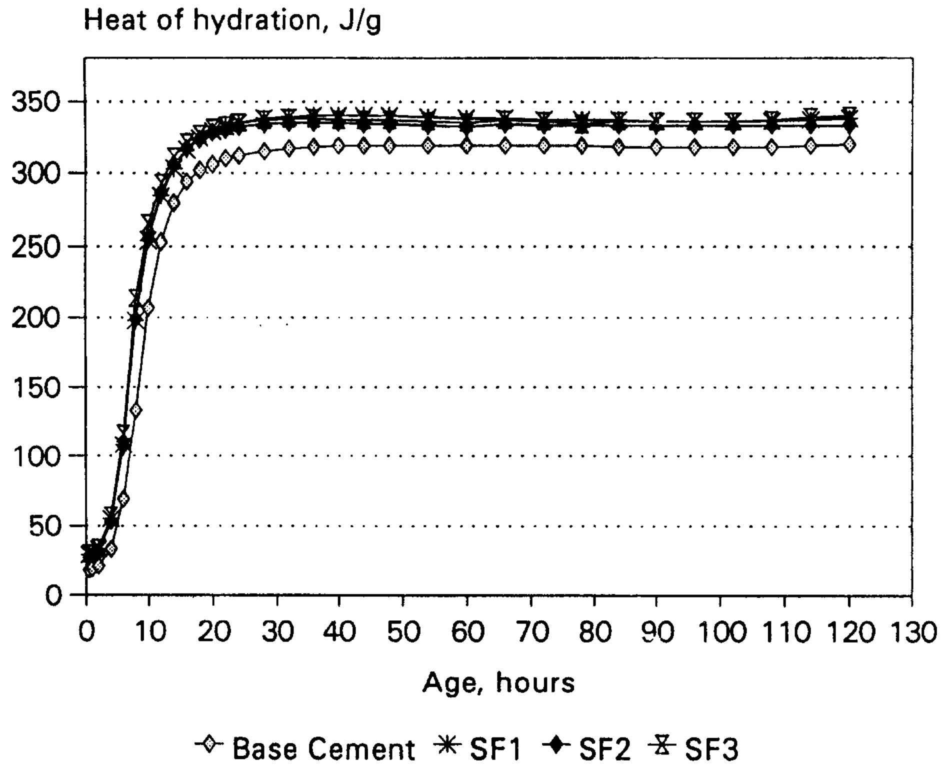

FIG. 5.
Effect of different silica fumes on the heat of hydration.

a slow material with regard to this activity and therefore the heat given off during this reaction cannot compensate for the decrease in heat caused by the cement substitution.

After 5 hours, in mortars made with silica fume (30%) and opaline rock (30%) we begin to detect different behaviour; the mortar with opaline rock shows how the effect of cement substitution predominates over pozzolanic activity, although the percentage of lowered heat is less than that corresponding to the mortar with fly ash. The mortar with silica fume delays this phenomenon up to 10 hours, due to the greater pozzolanic activity of this material, at which stage negative values begin to appear in hydration heat.

When there is a 10% substitution of cement by silica fume, this effect is not seen since the degree of substitution is not sufficient to compensate for the heat given off during the pozzolanic reaction.

Conclusions

These results show the influence of the pozzolanic activity of the materials on hydration heat developed in mixed mortars. Thus a direct correlation has been found between the value of

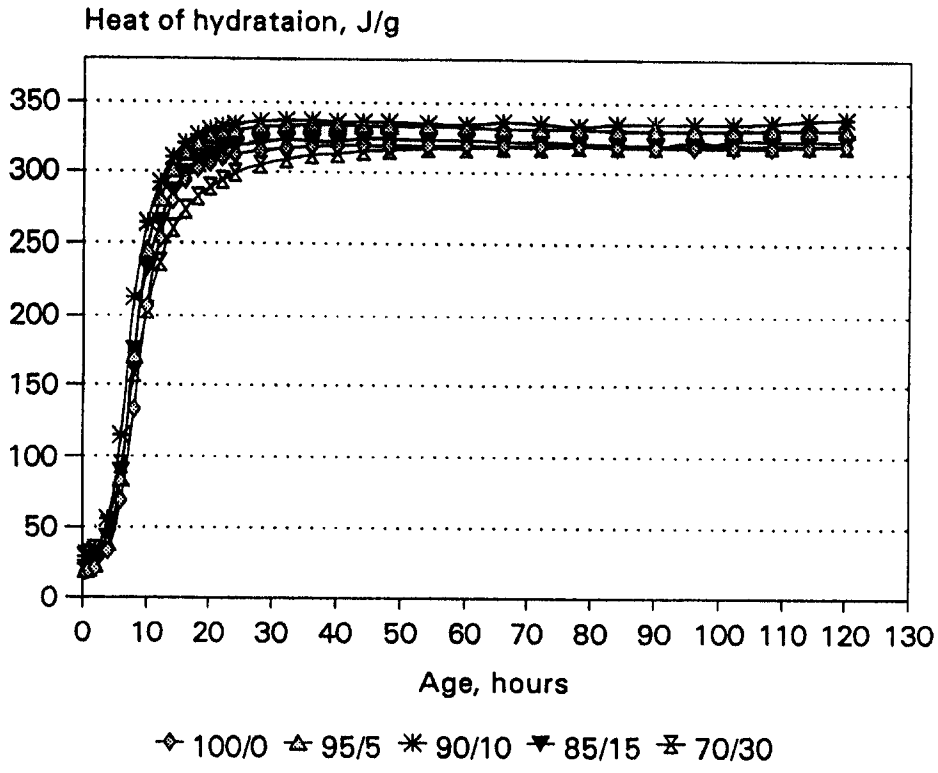

FIG. 6.
Influence of the silica fume percentage.

lime fixed by the pozzolanic material and the positive or negative increase in hydration heat with respect to the base cement, at the 2 and 24 hour stages (Figures 9a and 9b).

Figure 9a shows that with greater pozzolanic activity in the materials there is greater lime fixing, and more positive or less negative values for the increase in hydration heat. Also, after 24 hours (Figure 9b) we observe the same tendency, but heat increments are always negative because at this age the substitution effect usually predominates over the pozzolanic phenomenon, as indicated above.

From all the above it can be seen that the two methods used to evaluate pozzolanic activity in the materials, lime fixing and hydration heat developed by mixed mortars, both offer similar data on the behaviour of the materials considered, since there is a good correlation between both, in spite of their being different methods based on the observation of different properties and effects.

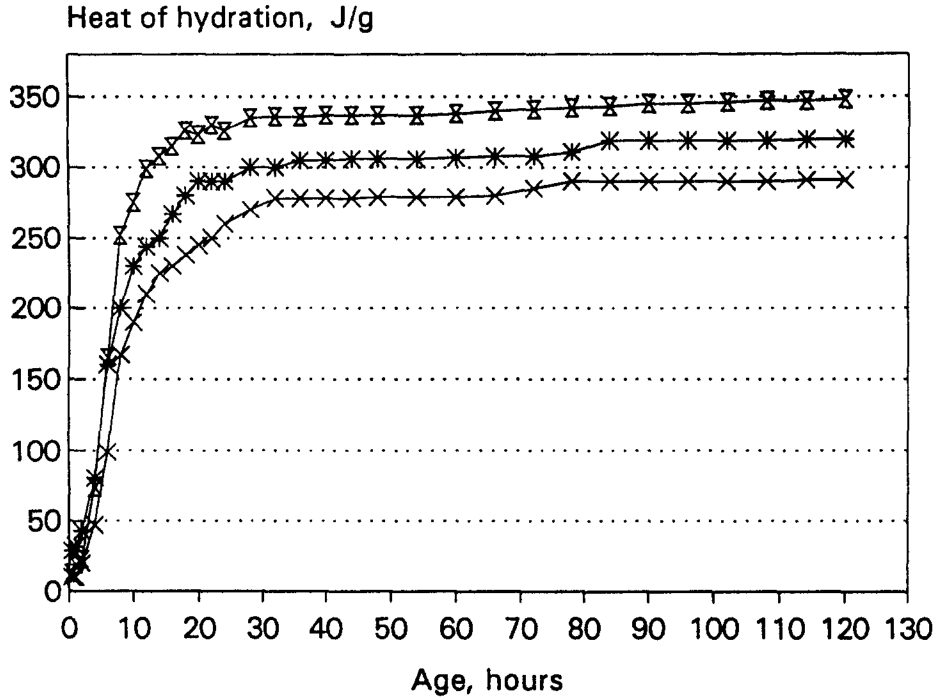

FIG. 7.
Heat of hydration: opaline rock and fly ash.

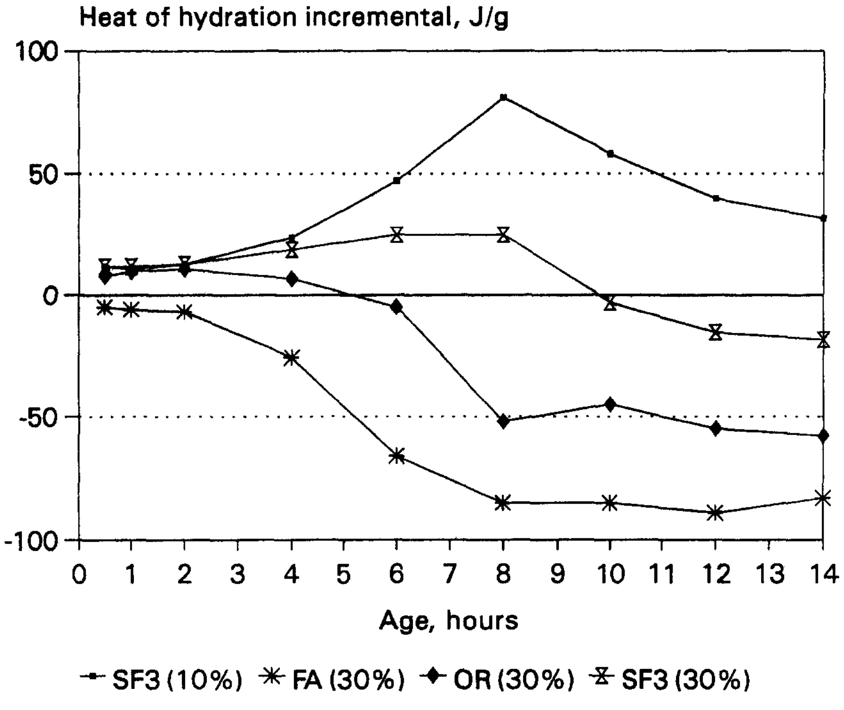

FIG. 8.
Heat of hydration incremental over time.

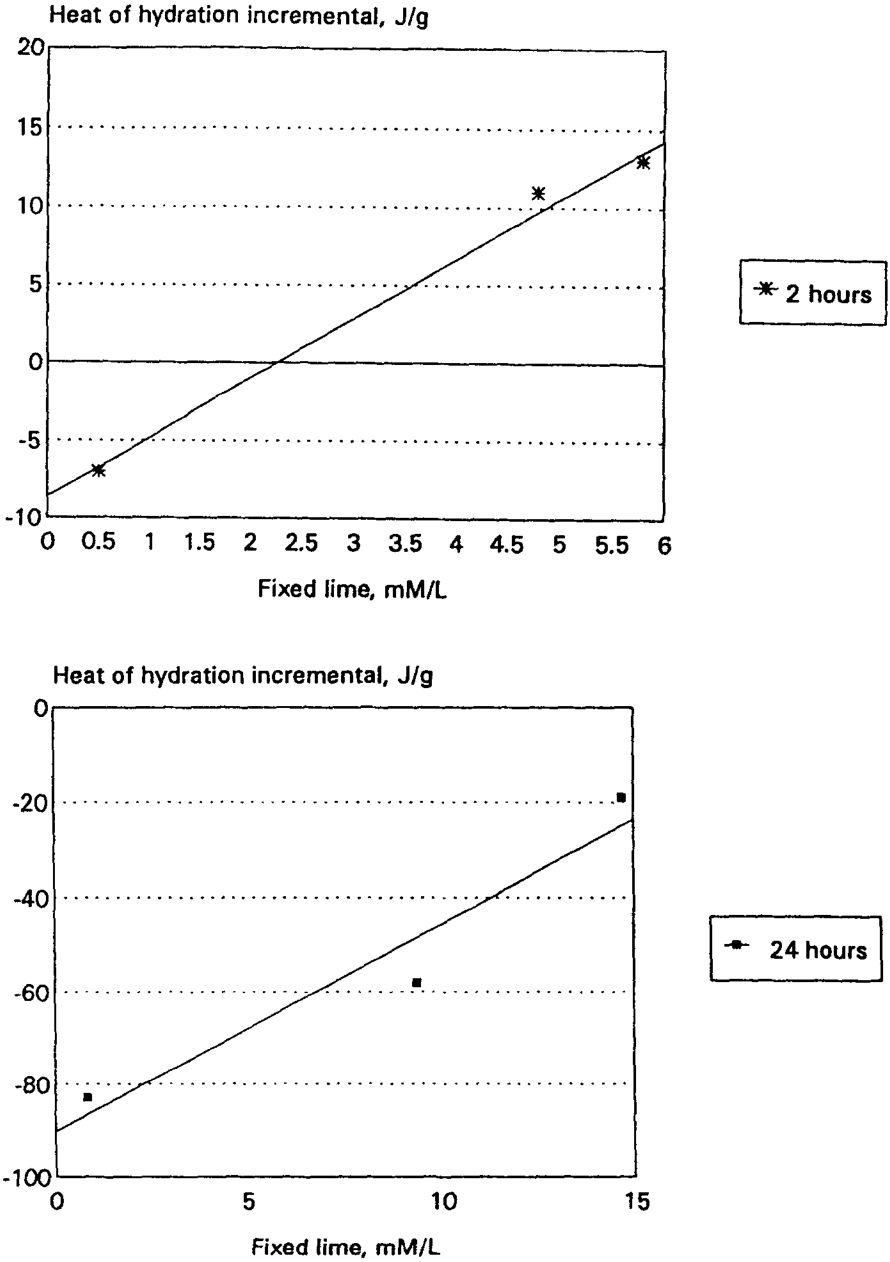

FIG. 9.
Correlation between pozzolanic activity and heat of hydration: a: 2 hours b: 24 hours.

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