

Application of Differential Thermogravimetry to the Study of the Hydration of Cements

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In the present report it is shown that differential thermogravimetry is an excellent tool to follow the hydration of cement. We compared DTG curves of several industrial and synthetic portland cements hydrated at room temperature with the curves of pure hydrates and mixtures of pure hydrates. In our experimental conditions (W/C ratio = 0.27), only hydrated calcium silicate, ettringite, AC_4H_{13} , β and calcium hydroxide were observed; AC_3H_6 does not appear.

The paste hydration of cement generally yields hydrates which are poorly crystallized or occur as a gel, and this renders unreliable microscopic observations and radiocrystallographic analyses.

•THE DIFFERENTIAL thermobalance was developed in 1953 by DeKeyser (1) and has since been frequently used in the study of the hydration of portland cement and of its constituents.

The principle of the apparatus is simple: two identical quantities of substance, suspended from the pans of a suitably damped balance, are progressively heated, the temperature of one of the samples being lower than that of the other by a constant amount of several degrees. The deflection of the balance needle is recorded photographically as a function of time, and in this way a differential curve of the loss of weight as a function of time (proportional to temperature) is obtained if the temperature rise of the ovens is a linear function of time (Fig. 1).

Differential thermogravimetry characterizes the different hydrated compounds by their temperature of dehydration in the same way as would be achieved by differential thermal analysis; because the latter method records thermal phenomena which need not be due only to losses of weight, its interpretation is thus more complicated.

Ours is a sensitive method: a 1-mg difference in weight produces a 20-mm deflection of the spot of light and it also enables one to separate two closely related dehydration phenomena (1, 8).

Differential thermogravimetry enables one to work with a wide range of heating velocities, and with a wide range in weight of samples; one can thus characterize substances present at a very low concentration and the decomposition temperatures obtained may be much closer to those of equilibrium. Further information may be found in Wendlandt's book (9).

In the case of sufficiently well-crystallized products, by integration of the differential thermogravimetric curves, one can estimate quantitatively the amount of water liberated in the decomposition of the various hydrates. As far as cement hydrates are concerned, which are generally very poorly crystallized, it is preferable to use the differential curves for a precise quantitative analysis and to determine at the same time the usual thermogravimetric curve to obtain qualitative data.

To this end, we have equipped the differential thermobalance with two sensitivities; the higher for differential analysis, the lower for ordinary analysis. In the latter case, the sample is contained in one of the crucibles with the two crucibles being continually heated at the same temperature. In this way troublesome effects of thermal currents

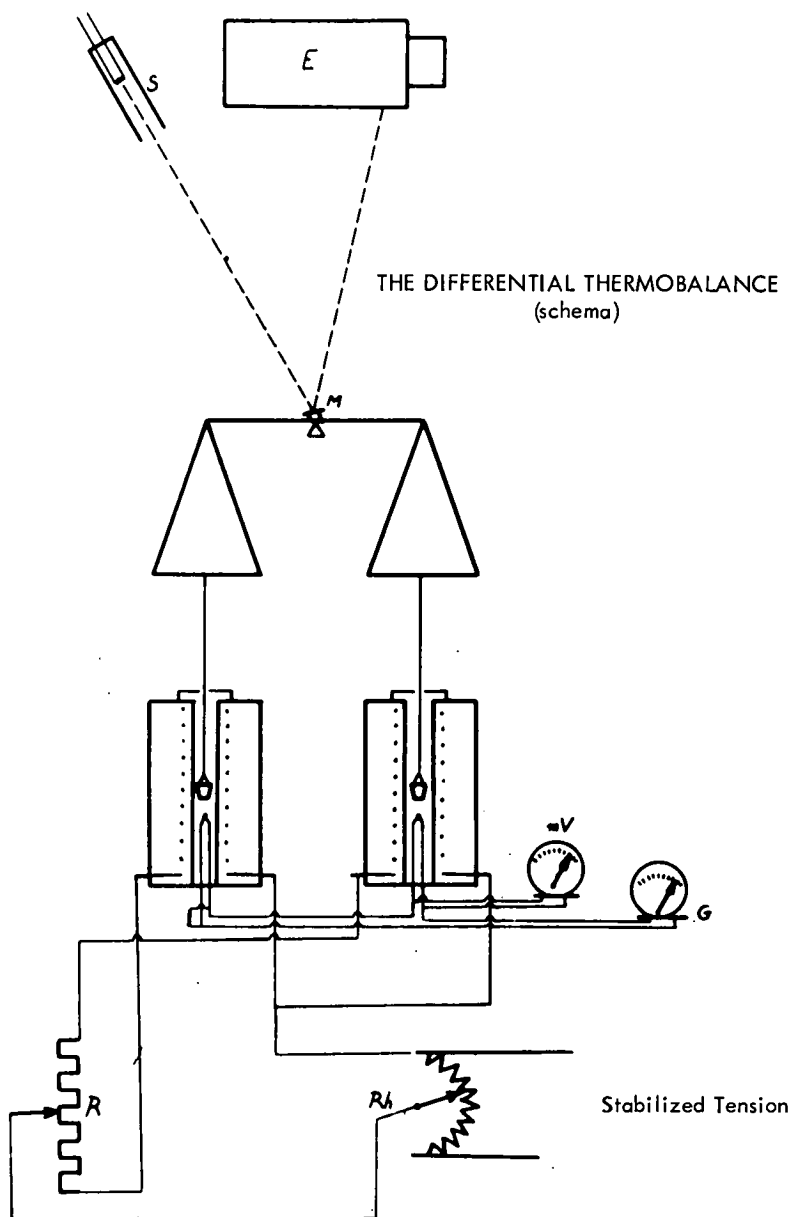


Figure 1. Schematic drawing of apparatus.

are eliminated. The quantity of sample taken is such that the loss of weight can be entirely recorded on the photographic paper.

DIFFERENTIAL THERMOGRAVIMETRIC ANALYSES OF PURE HYDRATES

To interpret the differential thermogravimetric curves of the hydrated cement pastes, the corresponding curves of the pure hydrates must be available. The phases and method of synthesis are as follows: Tricalcium aluminate hexahydrate (C_3AH_6) was prepared by precipitation at 100 deg from a solution of potassium aluminate by a solution of calcium phenate (2). Tetracalcium aluminate hydrate (C_4AH_{13}) was prepared

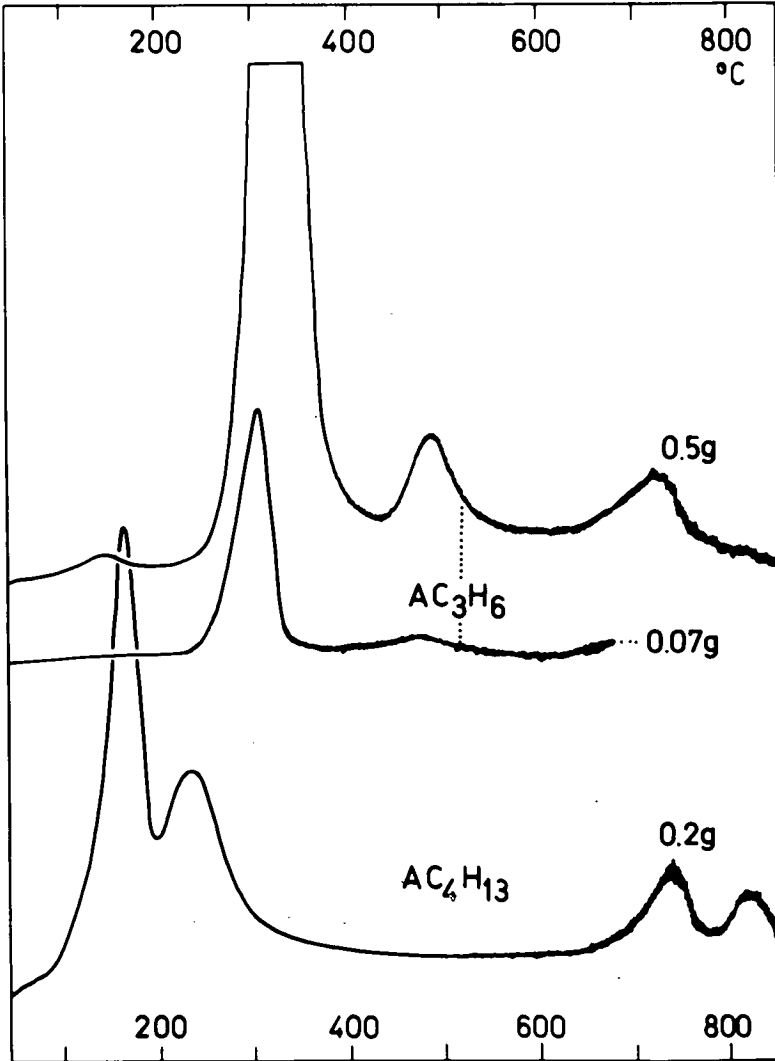


Figure 2. DTG curves of tri- and tetracalcium aluminate hydrates.

in the pure state by precipitation at room temperature from a solution of potassium aluminate and a lime solution (3). After drying at room temperature with alcohol and ether we got $AC_4H_{13} \beta$.

Tricalcium ferrite hexahydrate (C_3FH_6) was prepared at 100 deg by the reaction of $FeCl_3$ and lime solutions; the product thus obtained is not silica free (4). Tetracalcium ferrite hydrate (C_4FH_{13}) was prepared by the slow addition, in the cold, of a solution of two chlorides, in 1:4 molar proportions, to a normal solution of caustic soda.

The hydrated calcium sulfoaluminate ($C_3A \cdot 3CaSO_4 \cdot 32H_2O$ —ettringite or Candlot's salt) was prepared by the addition of saturated lime water to a solution of aluminium sulfate saturated with $CaSO_4$. The hydrated calcium sulfoaluminate ($C_3A \cdot CaSO_4 \cdot 12H_2O$) was prepared by mixing a saturated solution of monocalcium aluminate and a solution which is a mixture of a saturated solution of $CaSO_4$ and a solution of $Ca(OH)_2$, the total molar proportions being $15 CaO + 1 Al_2O_3 + 1 CaSO_4$ (5).

We then proceeded to the paste hydration, lasting 45 days at 25 C (water/solid ratio = 0.4), of tricalcium silicate which gives us at the same time the characteristic curve of hydrated calcium silicate and that of calcium hydroxide (6).

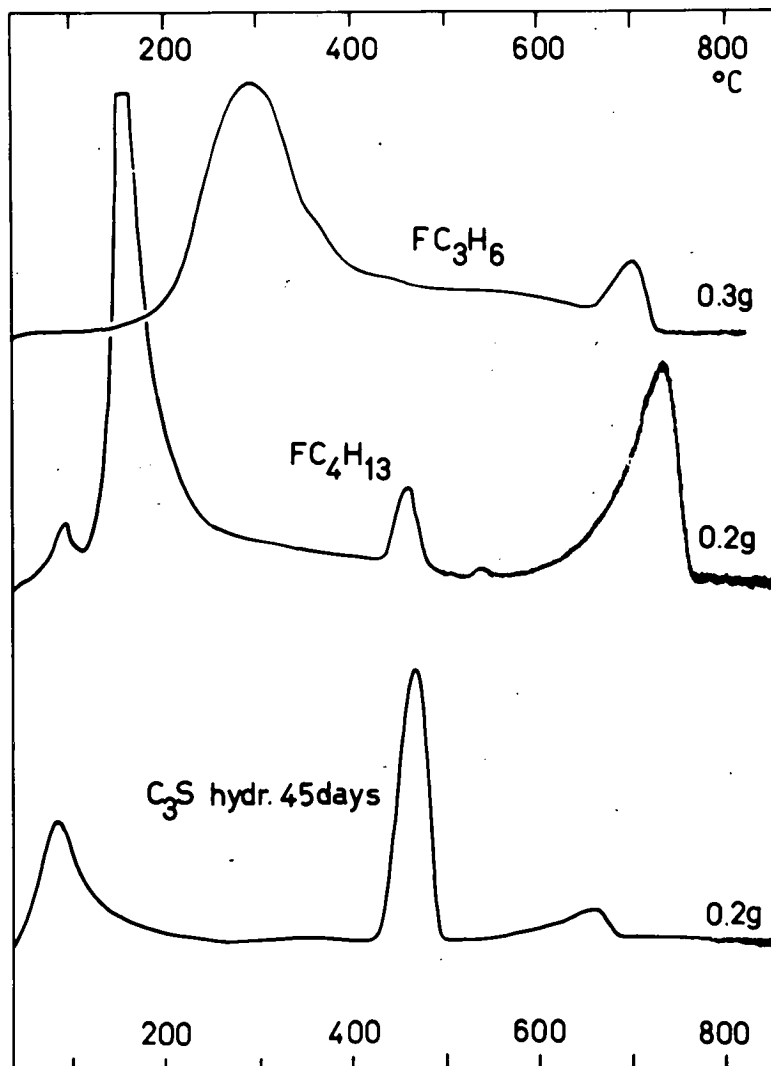


Figure 3. DTG curves of tri- and tetracalcium ferrite hydrates, and of C_3S after 45 days paste hydration.

The differential thermogravimetric curves of the above hydrates, as well as that of gypsum, $CaSO_4 \cdot 2H_2O$, are shown in Figures 2, 3 and 4.

We found that gypsum, when powdered, exhibits only one dehydration peak, but shows two peaks when compressed, as in DTA.

DIFFERENTIAL THERMOGRAVIMETRIC ANALYSIS OF HYDRATED CEMENT PASTES

We have studied the hydration of eight portland cement pastes (water/cement ratio = 0.27): three commercial cements (H_C , L_C , M_C), one (H_C) being a super cement; three semisynthetic cements of the same potential composition as the commercial products, which were synthesized in the laboratory from the industrial raw materials (H_S , L_S , M_S); and two synthetic cements (S and S') prepared from Zettlitz Kaolin, Fe_2O_3 reagent grade, precipitated $CaCO_3$ and amorphous SiO_2 . Their compositions are given in Table 1.

The mixing operation was carried out in a small polythene bag which was immediately sealed after homogenization of the paste. The sealed samples were cured at

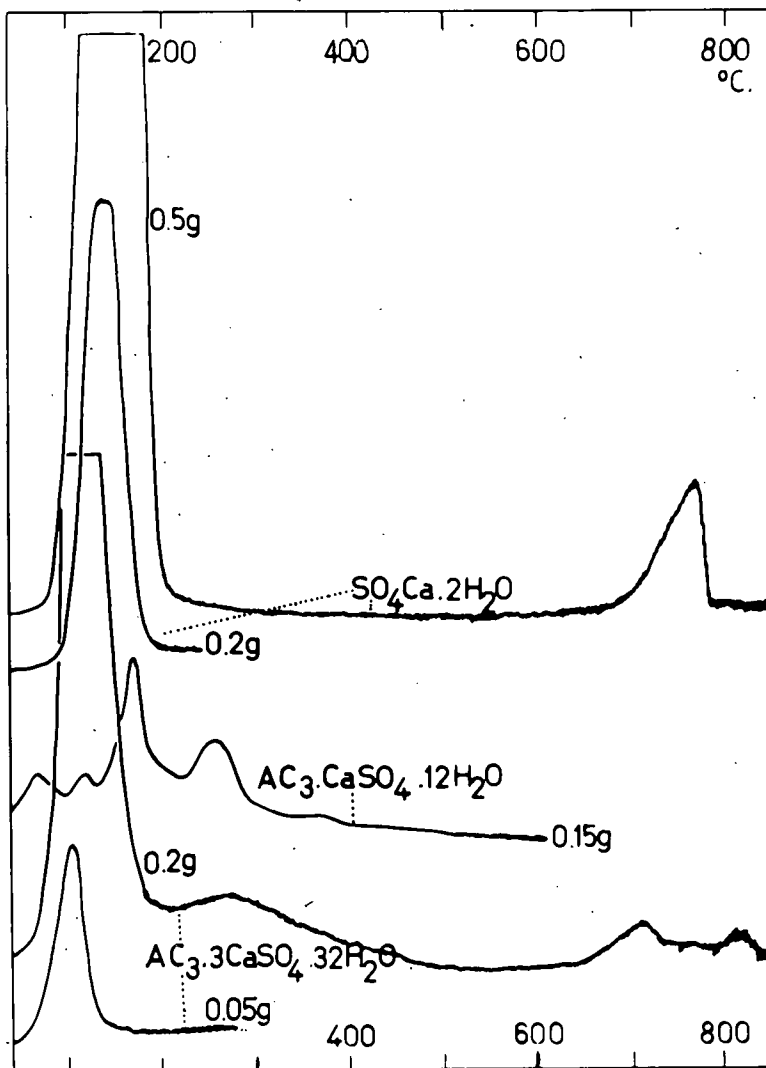


Figure 4. DTG curves of gypsum and the two calcium sulfoaluminate hydrates.

25 C in an atmosphere saturated with CO_2 -free water vapor. After 1, 7, 28, 90 or 700 days the hardened cement was pulverized and dried with acetone and ether.

In Figure 5 is shown the development of the differential thermogravimetric curves for the cement L_c as a function of the time of hydration.

The weight of the sample is always about 500 mg. For all the cements studied the general qualitative appearance of the curves is the same; no notable quantitative difference is observed between the curves of commercial cements, semisynthetic and synthetic cements of the same composition. The following observations can be made:

The anhydrous cement ($L_{c,0}$) presents a loss of weight at 120 deg (dehydration of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), a second loss of weight at 450 deg (dehydration of $\text{Ca}(\text{OH})_2$ formed during storage) and finally a loss of weight at about 680 deg due to the decomposition of CaCO_3 which is formed from atmospheric CO_2 during the heating in the thermobalance. (We have now constructed a differential thermobalance which can be operated with a controlled atmosphere, with the aim of avoiding carbonation of the samples.) The total loss of weight is 2.1 percent.

TABLE 1
COMPOSITION OF EXPERIMENTAL CEMENTS

| Designation | Composition (%) | | | | |
|--|------------------|------------------|------------------|-------------------|-------------------|
| | C ₃ S | C ₂ S | C ₃ A | C ₄ AF | CaSO ₄ |
| H _S H _C ^a | 49.5 | 22.5 | 6.7 | 14.2 | 4.6 |
| H _S ^b | 52.3-54.3 | 20.8-21.6 | 6.1 | 12.6 | 4.6 |
| L _S , L _C ^a | 53.0 | 24.3 | 9.0 | 8.5 | 3.6 |
| L _S ^b | 53.2-54.0 | 26.0-26.3 | 8.6 | 8.3 | 3.6 |
| M _S , M _C ^a | 52.2 | 23.8 | 8.6 | 9.1 | 4.1 |
| S ^a | 60.0 | 22.2 | 7.4 | 6.8 | 3.8 |
| S ^a | 51.8 | 22.0 | 6.9 | 14.5 | 4.6 |

^a Potential composition calculated by Bogue's method.

^b PCA X-ray diffraction analysis (7).

Cement hydrated for 1 day (L_{C,1}) presents, in addition to the important peaks due to Ca(OH)₂ and CaCO₃, two approaching peaks at 80 deg and at about 105 deg which can be attributed to hydrated calcium silicate and to the sulfoaluminate C₃A · 3 CaSO₄ · 32 H₂O. The total loss of weight is 12.4 percent.

After 7 days (L_{C,7}) there appears a new peak at about 160 deg which we attribute to C₄AH₁₃; which could contain a little C₃A · CaSO₄ · 12 H₂O in solid solution. The loss of weight is 17.8 percent. Experimental conditions exclude the presence of notable quantities of carboaluminate.

The appearance of curves corresponding to samples hydrated for 28 days (loss of weight 19.1 percent) or more (up to 2 years) is similar to the curve of the sample hydrated for 7 days: the first peak of dehydration around 80 deg due to dehydration of the hydrated silicate shows itself less and less clearly.

THERMOGRAVIMETRIC ANALYSIS OF PURE HYDRATE MIXTURES

Thus the only hydrates that are recognized are C₄AH₁₃, C₃A · 3 CaSO₄ · 32 H₂O, Ca(OH)₂ and hydrated calcium silicate. To verify the accuracy of these views, we have tried to reproduce these thermogravimetric curves by starting with a mixture of the pure hydrates. In Figure 6 the curves corresponding to three hydrated mixtures are shown in comparison with the curve of the hydrated cement paste (L_{C,28}).

Curve (1) corresponds to a paste of 9 percent C₄AH₁₃, 19 percent C₃A · 3 CaSO₄ · 32 H₂O and 72 percent C₃S hydrated for 45 days. Curve (2) corresponds to a paste of 9 percent C₄AH₁₃, 4.5 percent C₃AH₆, 18 percent C₃A · 3 CaSO₄ · 32 H₂O and 68.5 percent C₃S hydrated for 45 days. Curve (3) corresponds to a paste of 6 percent C₄AH₁₃, 4.5 percent C₄FH₁₃, 18.5 percent C₃A · 3 CaSO₄ · 32 H₂O and 71 percent C₃S hydrated for 45 days.

One can thus see the perfect agreement in position of the peaks in the curves L_{C,28} and (1). Curves (2) and (3) assure us of the absence of appreciable quantities of C₃AH₆ as well as C₄FH₁₃ in our hydrated pastes.

CONCLUSIONS

These few simple tests show that by differential thermogravimetry one can rapidly give a qualitative description of the composition of the hydrated paste from the temperatures of the different dehydration maxima. In general one could detect the presence of a hydrate if present at a concentration greater than about 1 percent.

If all the possible hydrates are available, including all the forms of the solid solutions, then one can reproduce experimentally the differential thermogravimetric curves of the studied hydrated cements, thus obtaining an immediate semiquantitative interpretation.

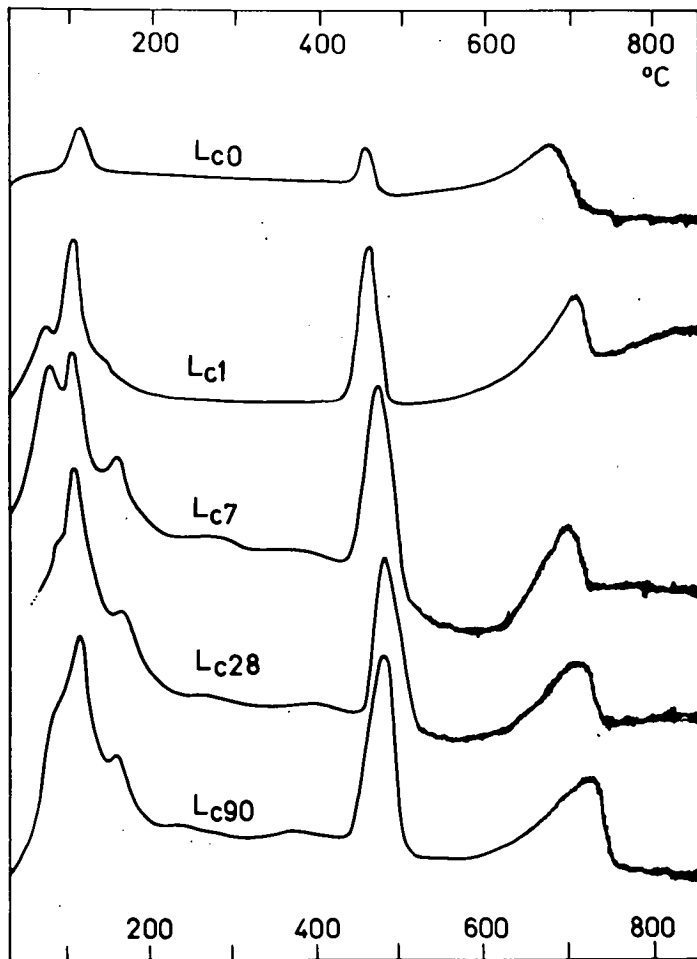


Figure 5. DTG curves of cement L_c : anhydrous (0) and hydrated 1, 7, 28 and 90 days.

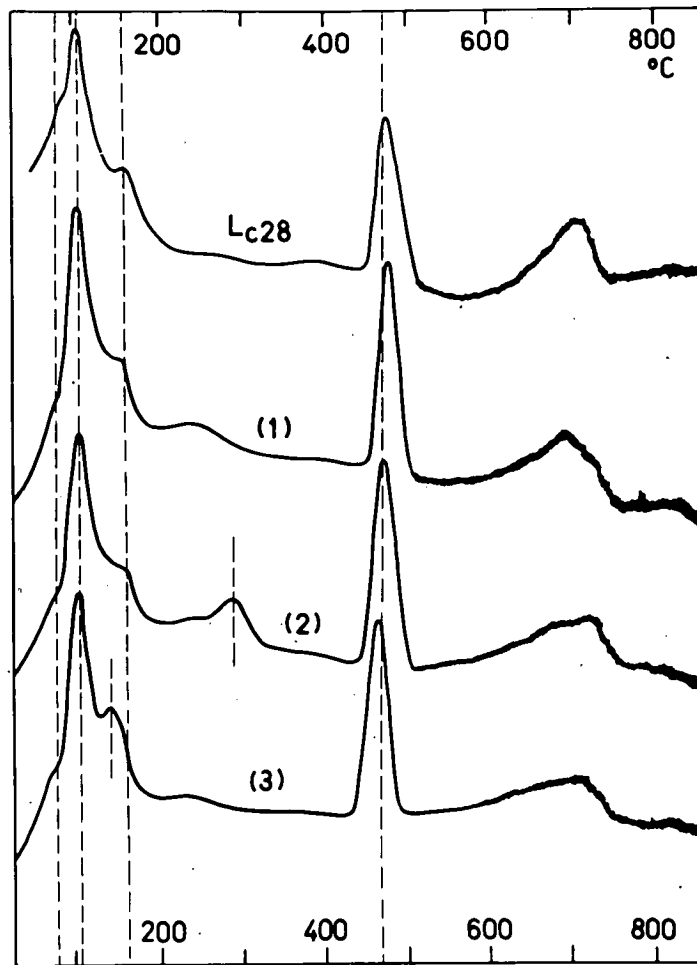


Figure 6. DTG curves of synthetic mixtures of hydrates compared with curve of cement L_c after 28 days hydration.

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