

EVALUATION OF THE DEGREE OF HYDRATION OF SYNTHETIC ALITES BY QUANTITATIVE DIFFERENTIAL THERMAL ANALYSIS*

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ABSTRACT

The degree of hydration of synthetic alites has been determined by quantitative differential thermal analysis, using strong signals related to the polymorphic transformations of alites. The conditions suitable for noting the various reference signals, obtained with maximum apparatus sensibility, have been described and the data derived from differential thermal tests with those obtained by analysis of the liquid phase in contact with the hydrating solid are correlated.

INTRODUCTION

In a recent paper¹, the possibility of determining the degree of hydration of tricalcium silicate (Ca_3SiO_5) by quantitative differential thermal analysis from literature values has been considered². The method involves measuring the strongest peak area relative to the T_{II} - T_{III} polymorphic transformation of Ca_3SiO_5 ³, an area which diminishes as the hydration reaction proceeds.

In connection with research upon the influence of foreign ions which may enter the Ca_3Si lattice, for which measurement of hydration degree has also been employed, it was deemed useful to widen the investigation, with the same technique, on the solid solutions of MgO -, Al_2O_3 - or Fe_2O_3 -containing Ca_3SiO_5 (alites).

The experiments and relative conclusions are considered in this paper.

EXPERIMENTAL

The preparation and characteristics of the samples examined are reported in a previous paper⁴.

Measurement of the degree of hydration was made by hydrating a fraction of each sample, under the following conditions: water/solid ratio of 0.5; temperature 25°C , as reported in a previous paper¹. A second fraction was hydrated at the same temperature with a water/solid ratio of 2. This enabled the liquid phase in contact

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with the solid to be analyzed at times ranging from 20 min to 7 days, by measuring the OH^- and Ca^{2+} concentrations, by alkalimetry and EDTA, respectively.

The method used for determining the peak areas, the apparatus employed, the operating conditions, and the weight of each sample in every experiment are given in the previous paper¹, which discusses pure tricalcium silicate.

Here below are considered the results derived from extending these investigations to the assessment of the degree of hydration of solid solutions of Ca_3SiO_5 with MgO , Al_2O_3 or Fe_2O_3 , first outlining the criteria used in choosing the reference peaks, on the basis of thermodifferential diagrams obtained.

CHOICE OF REFERENCE PEAKS

Figure 1 gives the thermodifferential diagrams related to anhydrous products, while those in Fig. 2 refer to corresponding hydrated samples at seven days. In these latter diagrams, both the β -wollastonite recrystallization peaks and the reference peak areas after 7 days' hydration are traced.

Sample 1 (pure tricalcium silicate) in Fig. 1 shows two clearly separate endothermic effects, reversible in respect to the $T_{\text{II}}-T_{\text{III}}$ polymorphic transformation at a lower temperature, and $T_{\text{III}}-M_1$ at a higher temperature. That relative to the $T_{\text{II}}-T_{\text{III}}$ transformation in the reheating cycle (curve r') has been chosen for reference, since the corresponding hydrated sample (Fig. 2), in the first heating cycle, shows effects due to decarbonation, dehydration of calcium silicate hydrate and recrystallization of β -wollastonite (maximum exothermic effect at 879°C). These effects disappear after the heating cycle r' in which the $T_{\text{II}}-T_{\text{III}}$ transformation can quite easily be measured.

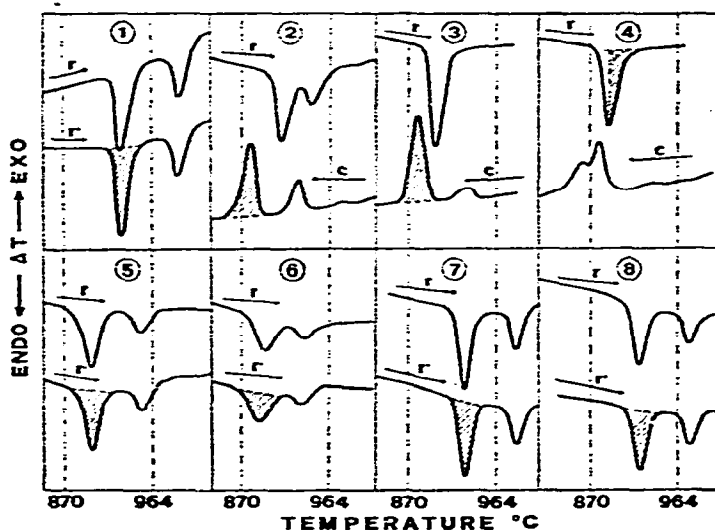


Fig. 1. DTA on anhydrous synthetic alites. The respective reference peaks have been traced (r = first heating curve; c = cooling curve; r = reheating curve).

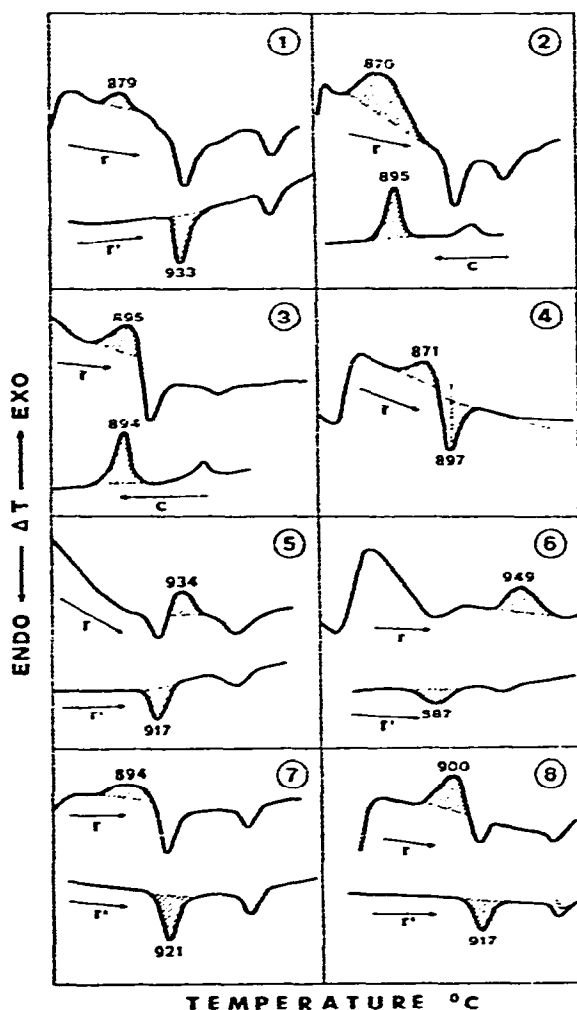


Fig. 2. DTA of samples in Fig. 1 after 7 days' hydration. The reference peak areas and β -wollastonite recrystallization are traced.

Sample 2 (Fig. 1), stabilized in the T_I polymorphic form due to MgO (0.45%) content, agrees with literature in showing a premature $T_{III}-M_I$ transformation at lower temperature⁵ in respect to the signal recorded for pure Ca_3SiO_5 , such as to interfere with the $T_{II}-T_{III}$ transformation (curve r of sample 2 in Fig. 1). Upon cooling (curve c), however, the two signals are clearly separate owing to a hysteresis phenomenon. Thus the peak $T_{III}-T_{II}$ present in the cooling curve (c in Fig. 1) has been chosen. For the corresponding hydrate sample (2, r in Fig. 2) the signals relating to the polymorphic transformations are preceded by the exothermic effect of β -wollastonite recrystallization whose maximum is at 870°C. The signal relating to $T_{III}-T_{II}$ transformation during cooling can be easily read (c in Fig. 2).

Sample 3, stabilized in the T_{II} polymorphic form with MgO (1.00%) content, shows only one peak (r, Fig. 1) upon heating, with signals $T_{II}-T_{III}$ and $T_{II}-M_I$

superimposed. Upon cooling the corresponding reversible signals are clearly separate (curve c). Thus, the reference peak chosen refers to the $T_{III}-T_{II}$ transformation during cooling.

Thermal analyses effected on this sample, hydrated at various intervals, were all carefully made at a prefixed maximum temperature. This precaution was necessary as the thermal history of this sample affects the separation of MgO ⁶ and thus the position and relative areas of the signals. Figure 2 shows the thermodifferential curves for sample 3 during heating and cooling. The area traced for the exothermic peak with a maximum at 895°C, refers to the β -wollastonite recrystallization.

Alite 4, stabilized in the M_I form, with a content of MgO (2.01%), shows a wide exothermic peak between 600–700°C, not reported in the corresponding curve r of Fig. 1 and due to the M_I-T_{II} transformation⁷. The subsequent reported peak, instead, contains the $T_{II}-T_{III}$ and $T_{III}-M_I$ signals. Upon cooling (c, 4 in Fig. 2) the choice of a reference peak for determining the degree of hydration proves difficult, as during heating the sample is subject to various concomitant phenomena such as: separation of MgO from the alite itself, and slowness of the reversible M_I-T_{III} and $T_{III}-T_{II}$ transformation⁸. In this case the reference peak, or rather the reference area, was chosen by considering the area traced in Fig. 1 in the first heating cycle (curve r). This type of choice was necessitated because β -wollastonite recrystallization is also an interference factor, as may be seen from curve r in Fig. 2 of the corresponding hydrate sample.

Sample 5, stabilized in the T_I form for Al_2O_3 content⁹ of 0.32%, gives well separated $T_{II}-T_{III}$ and $T_{III}-M_I$ signals during heating. Upon cooling the reversible $T_{III}-T_{II}$ transformation is slow and covers a wide temperature range¹⁰; the peak flattens out and so is difficult to read. Therefore the reference peak has been chosen from the second heating cycle (r' in Fig. 1). A similar choice was made for sample 6 stabilized in T_{II} form with Al_2O_3 content of 0.90%.

The thermodifferential curves for samples 5 and 6, hydrated for 7 days are shown in Fig. 2. The β -wollastonite recrystallization effects in these cases are displaced to much higher temperatures than those previously recorded for the other samples. In fact, these effects are found at 934 and 949°C, respectively. Such high values may be explained by the different degree of crystallinity and composition of calcium silicate hydrate produced during hydration of alites doped with Al_2O_3 .

Sample 7 is stabilized in the T_I form for 0.80% Fe_2O_3 , while sample 8 is stabilized in T_{II} form with a Fe_2O_3 content of 1.08%. Their behaviour under differential thermal analysis is similar to that found for samples 5 and 6 containing Al_2O_3 . In this case too, the choice of reference peak was made on $T_{II}-T_{III}$ transformation during the reheating cycle (curves r' of samples 7 and 8 in Fig. 1).

RESULTS AND DISCUSSION

The values of the degree of hydration for the various samples have been calculated by the relationship between the reference peak areas recorded at various hydra-

tion intervals and the reference peak area of the corresponding anhydrous sample. The overall results are given in Fig. 3, from which it is possible to note the hydration degree progress from 1 to 30 days. At long hydration ages, i.e. from 7 to 30 days, the

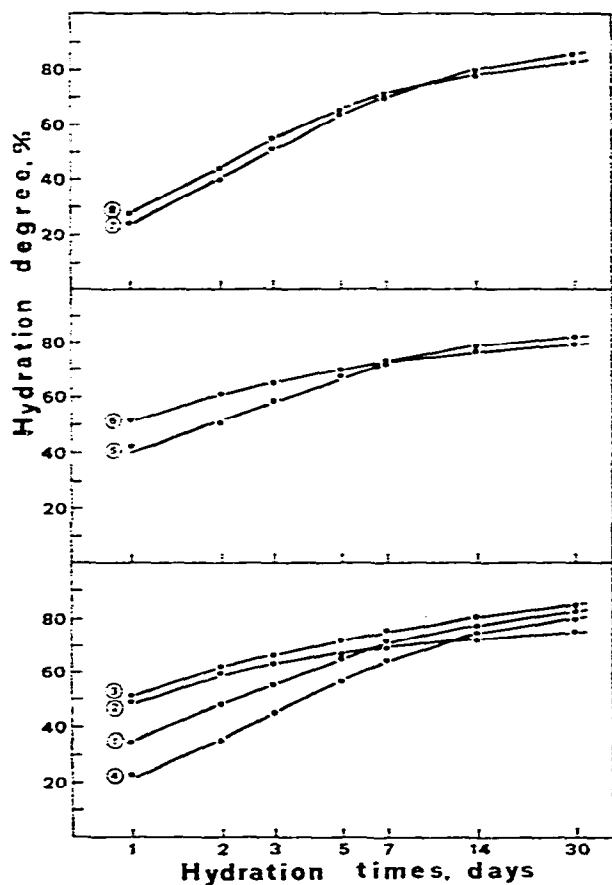


Fig. 3. Variation of hydration degree in function of time for samples in Fig. 1.

various samples show degrees of hydration of about the same value, while conspicuous differences can be noted from 1 to 7 days' hydration. Thus a comparison of hydration degree values for short ages would seem convenient to be done. For Ca_3SiO_5 (sample 1) reference is reported in a previous paper¹. Samples 2 and 3 with MgO added, show a degree of hydration of slightly less than 50% at 1 day, while the average value at 7 days is just below 70%. Sample 4, stabilized with MgO in the M_1 form, shows a degree of hydration slightly above 20% at 1 day, while it exceeds 60% at 7 days. Thus, the change in degree of hydration from 1–7 days, for this sample, is considerable in respect to the corresponding values for samples 2 and 3. Alites with Al_2O_3 added, samples 5 and 6, show comparable progress, but higher hydration values for sample 6, which is richer in Al_2O_3 . This sample at 1 day shows a higher value than all the samples examined: in fact it exceeds 50%.

Samples 7 and 8, with Fe_2O_3 added, on the contrary have an average value of slightly more than 20% at 1 day, while at 7 days their value is 70%. Here the change in value between 1 and 7 days is higher than those for the other samples.

The different hydration degree patterns recorded between 1 and 7 days, for the various samples, have been indirectly compared, by analyzing the liquid phase in contact with the hydrating solid. The water/solid ratio used, as already stated, is 2. The adoption of a higher liquid/solid ratio, at least for absolute concentration values^{11,12}, does not invalidate comparison of data relating to the liquid contact phase with those of hydration degree found by using a lower liquid/solid ratio.

Figure 4 shows the oversaturation curves of Ca^{2+} and OH^- concentrations of four samples thus chosen; Ca_3SiO_5 (sample 1), alite with 1.00% MgO (sample 3), alite with 0.90% Al_2O_3 (sample 6) and alite with 1.08% Fe_2O_3 (sample 8).

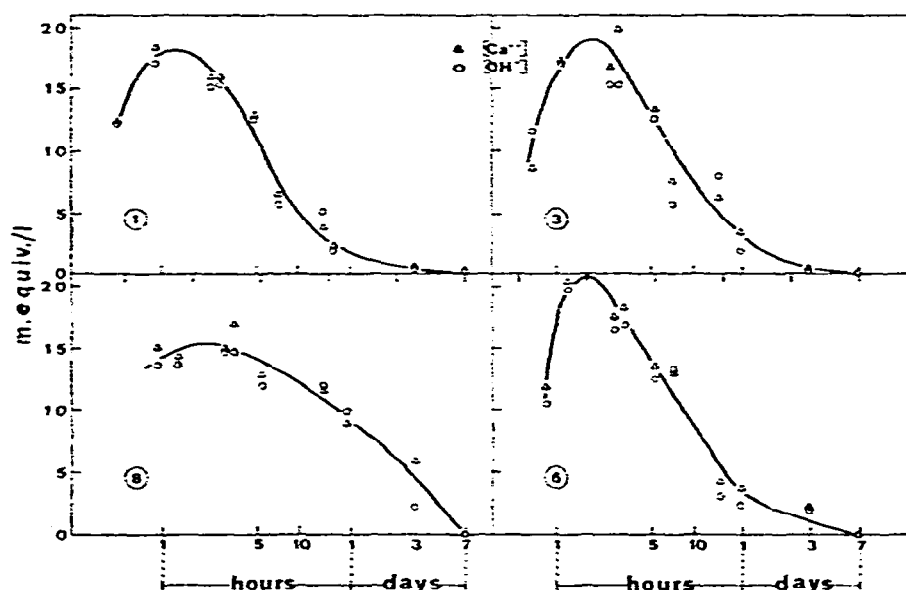


Fig. 4. Variation of oversaturation of Ca^{2+} and OH^- concentrations in the liquid contact phase, for some samples in Fig. 1.

The oversaturation for each sample, has been calculated as difference between the existing values in concentrations, recorded from the 20th minute and the value noted at 7 days' hydration. The oversaturation is at maximum for sample 6 (Fig. 4) which has also its maximum hydration degree at 1 day; while for sample 8 the oversaturation is minimum, as is the hydration degree, at 1 day (Figs. 3 and 4). Samples 1 and 3 show intermediate oversaturation values, as well as intermediate degree of hydration at 1 day (Figs. 3 and 4). Thus the lime oversaturation, in the first hours of hydration, is directly related to the hydration degree at 1 day. Figure 4 shows that sample 8 has lower oversaturation values, which linger for a longer time interval. This peculiarity may be related to the change in the degree of hydration at short ages.

In fact, sample 8 gives a maximum variation (Fig. 3), passing from 25% at 1 day to above 70% on the 7th day. This notable difference means that the oversaturation also lasts for a relatively longer period. The other samples in Fig. 4 do not display this peculiarity, as the variations in the degree of hydration for the corresponding hydration times are less marked.

CONCLUSIONS

Quantitative differential thermal analysis can be advantageously used for the evaluation of the hydration degree of alites which show intense and reversible signals due to polymorphic transformations. The necessary conditions are: a high sensibility and an appropriate choice of an intense reference signal.

The hydration degrees calculated have shown good agreement with data derived from analysis of the aqueous phase in contact with the hydrating solid. Indeed, it has been shown that the oversaturation entity in Ca(OH)_2 in the first hours of hydration is directly related to the degree of hydration at 1 day. Moreover the change in the degree of hydration at short ages may be related to the oversaturation time.

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