

*In celebration of the 60<sup>th</sup> birthday of Dr. Andrew K. Galwey*

## **THE INFLUENCE OF TEMPERATURE AND DIFFERENT STORAGE CONDITIONS ON THE STABILITY OF SUPERSULPHATED CEMENT**

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### **Abstract**

The stability of supersulphated cement(SSC) is investigated. The hydration products of cement pastes prepared at a water cement ratio of 0.27 were determined by thermogravimetry (TG) and X-ray diffraction (XRD). Ettringite, one of the initial hydration products, is shown to be stable under conditions of storage at 25, 50 and 75°C and when subject to relative humidities of 100, 53 and 11% of water vapour in each case. The effect of drying on ettringite stability at the higher temperatures is discussed in relation to the relative humidity.

**Keywords:** cement, stability of supersulphated cement, TG, X-ray

### **Introduction**

Despite the fact that it consists largely of industrial waste products and should be economically viable in terms of its low energy cost of production, supersulphated cement (SSC) has been relatively under-used and is no longer produced in Western Europe. On reviewing the technical literature, the main problem appears to be due to uncertainties over some of its properties.

Concern has been expressed about the hydrated cement's long term stability and durability, centred around one of its principal hydration products, calcium tri-sulphoaluminate hydrate or 'ettringite'. This compound is known to be unstable in Portland cement and has been found to be expansive in certain environments, for example, during sulphate attack of Portland cements. This

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concern has been heightened since the problems with unstable hydration products in High Alumina Cement were experienced.

Supersulphated cement contains a substantial amount of blastfurnace slag. Changes in the composition and amount of slag produced by the Steel Industry have had an effect on a whole range of similar cements. However supersulphated cement may have suffered from the naturally cautious approach to specialised, non-Portland based cements.

The present paper attempts to investigate an area of concern associated with supersulphated cement, namely its stability under storage conditions at different temperatures.

### *Composition and hydration of blastfurnace slag*

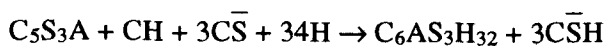
Blastfurnace slag is a by-product of the industrial separation of iron ore at high temperatures. Limestone and magnesia, used in the process, collect together alumina, silica and other impurities, notably sulphur, into slag which floats on the surface of the molten iron in the blastfurnace. The final slag contains oxides, similar to those in Portland cement, which, with the appropriate treatment, gives it cementitious properties. To give the slag these properties it must be cooled rapidly to form a 'glassy' material. After cooling, the granulated slag is ground for subsequent blending into the cement. The range of composition of slags is given below:

| Oxide | CaO   | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | MgO  | Fe <sub>2</sub> O <sub>3</sub> | MnO | S     |
|-------|-------|------------------|--------------------------------|------|--------------------------------|-----|-------|
| wt%   | 30-50 | 28-38            | 8-24                           | 1-18 | 1-3                            | 1-3 | 1-2.5 |

In order to allow progressive hydration, slag needs to be activated to remove the protective layer of aluminat silicate hydrates, and this usually involves the use of sodium or calcium hydroxide, of which the calcium salt is more common. With sodium hydroxide, the hydration products are CSH, C<sub>4</sub>AH<sub>13</sub> and C<sub>2</sub>ASH<sub>8</sub>. Activating with calcium hydroxide produces CSH and C<sub>4</sub>AH<sub>13</sub>.

### *The hydration of supersulphated cement*

SSC usually contains a minimum of 75% slag and a maximum of 5% Portland cement with calcium sulphate as the remaining fraction. The small proportion of Portland cement hydrates initially, to provide calcium hydroxide for the activation of the slag in combination with the calcium sulphate. The total reactions are complex but the main products, ettringite and calcium silicate hydrates are formed as demonstrated in this simplified equation:



The initial product is ettringite which starts to form almost immediately and is thought to stop after 7 days. CSH is detected after 2–3 days and progressively increases as hydration proceeds. The CSH, which forms the major hydration product, has a C/S ratio of approximately 1 and resembles the mineral tobermorite  $C_5S_6H_x$ .

## Experimental

TG and XRD analysis were used to study the mineralogy both after a 28 day water treatment at 25°C and at frequent times during the humidity tests. A Stanton TG760 thermal balance, suitably damped, was used to obtain TG curves. Derivative thermogravimetric (DTG) curves were derived from the TG curves by using a Linseis N42 derivative unit and a N31 pre-amplifier with the data recorded on a Linseis multipen flatbed recorder.

The SSC used was Frodingham SSC of approximate composition: 85% slag, 10%  $CaSO_4$  and 5% ordinary Portland cement(OPC). Pastes were prepared at a water:cement ratio of 0.27 and made in the form of cubes. All samples were cured in water at 25°C to allow sufficient hydration. Tests indicated that a 14–28 day period of water was appropriate and thus 28 days was chosen. The choice of a range of temperatures used in this study were made on the basis of a previous study of synthetic ettringite [7]. Ettringite undergoes rapid hydration between 40 and 70°C. Therefore it was considered that a range of storage conditions encompassing these temperatures would be appropriate, namely 25, 50 and 75°C. In order to study the susceptibility to drying, three different humidity conditions corresponding to 'wet', 'intermediate' and 'dry' were included for each temperature. The storage arrangements for such conditions are described elsewhere [5]. For ease of reporting the following code system has been used:

SSCX-Y storage at X°C at Y% relative humidity.

## Results and discussion

Figure 1 shows the TG and DTG curve for a sample of SSC immediately after a 28 day water treatment. The first of the two large DTG peaks was considered to be the loss of the more easily evaporable water from within the pores of the hydrated cement paste similar to that described by Sabri & Illston [1]. Bensten & Bye [2], Ogawa and Roy [3], Odler and Abdul-Maula [4] all describe large DTA peaks for ettringite in cement at approximately 100–130°C. XRD analysis showed the presence of substantial amounts of ettringite and comparison with a TG/DTG curve for a synthetic sample of ettringite confirmed that the second DTG peak was largely due to the dehydration of ettringite [5]. However,

each of the above authors recognised a peak due to CSH dehydration in approximately the same temperature range. Decomposition of  $\text{CaCO}_3$  was responsible for the mass loss between 600–700°C.

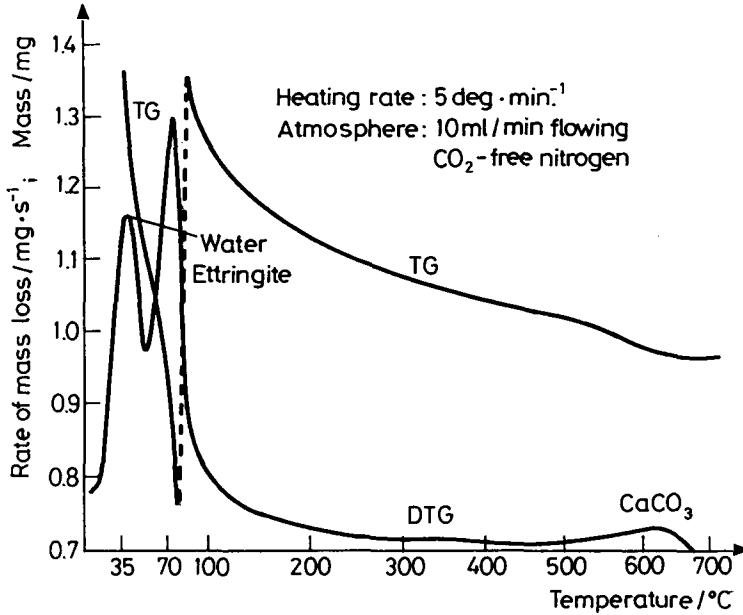


Fig. 1 TG and DTG curves for SSC paste water-cured for 28 days at 25°C

A heating rate of 5 deg·min<sup>-1</sup> was used up to 200°C below which all the dehydration peaks had taken place, after which the heating rate was increased to 25 deg·min<sup>-1</sup> in order to reduce the time taken for each TG experiment. This caused a peak to appear due to the rate increase and exaggerated the  $\text{CaCO}_3$  decomposition but caused no other changes in the analysis. XRD was also used to identify phases present after various treatments. The trace obtained from the 28 day hydrated paste (Fig. 2) clearly shows the formation of crystalline ettringite and the reduction of calcium sulphate. There is also evidence of CSH formation and the peaks for gehlenite remained prominent. This indicates that this material has not hydrated. The method used here assumes that the gehlenite impurity in the slag fraction does not hydrate (see above and Lea [6]) and can be used as a standard in this way. For the quantitative analysis of hydrated cement, it is usual to express the proportion of each phase in terms of the mass of cement paste. The ettringite content would then be expressed as a proportion of the original mass of SSC.

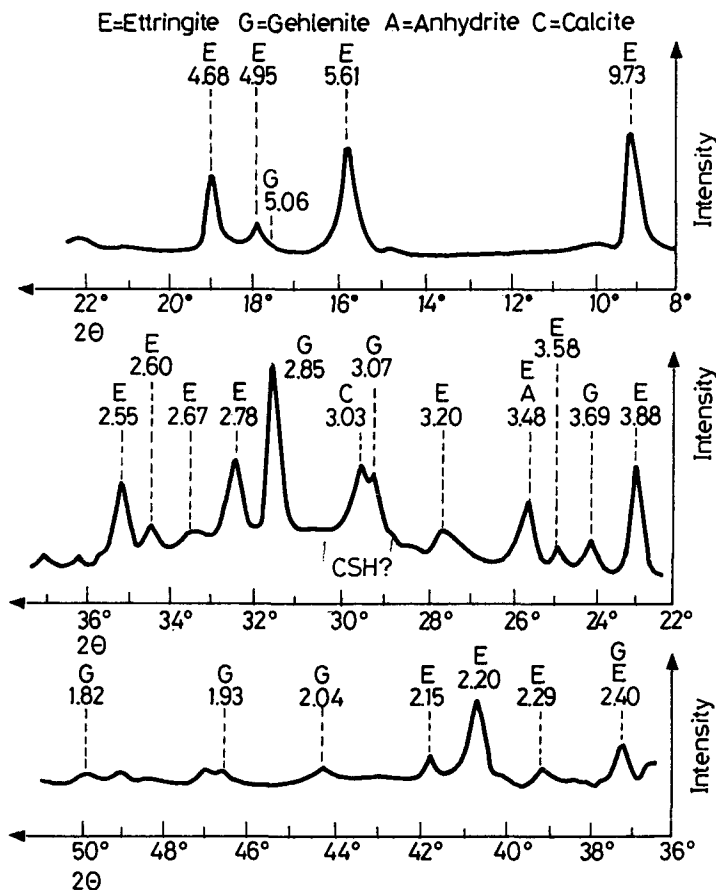


Fig. 2 XRD pattern for SSC paste water-cured for 28 days at 25°C

The hydration of SSC during the 28 days water cure at 25°C is presented to illustrate the relationship between the two main areas of mineralogy and physical properties.

The change in the XRD pattern during this period is shown in Figs 3a and 3b and indicates the development and increase of peaks due to ettringite together with a rapid reduction in those due to anhydrite. From 1 day up to 14 days gypsum is present but gradually reduces, indicating that the anhydrite forms a solution of calcium and sulphate ions which is saturated with respect to gypsum. This causes precipitation of gypsum which is then gradually used in reaction with aluminates from the slag to form ettringite. TG and DTG confirmed this as shown in Fig. 4. The full DTG curve for the sample after a day includes three peaks due to evaporable water, ettringite and gypsum. The large peak at 700°C is attributed to the loss of carbon dioxide from the calcite, being emphasized by

the increase in heating rate from 5 to 25 deg·min<sup>-1</sup> just prior to this peak. The inset of Fig. 4 shows clearly the reducing gypsum and increasing ettringite peaks with time.

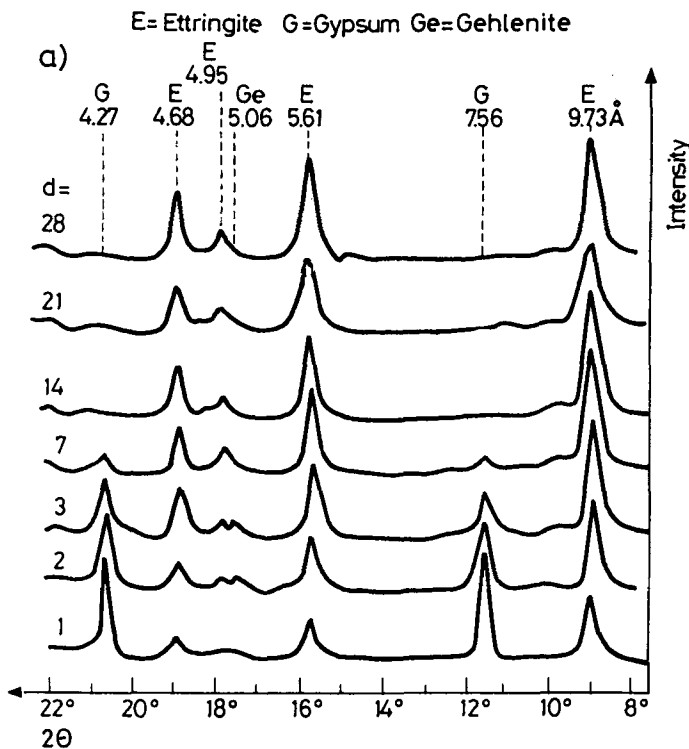


Fig. 3a Changes in composition of SSC paste during initial 28 days water-cure at 25°C

There are differences in the amount of ettringite determined by the DTG and XRD methods. The intention of the study was primarily to monitor changes in the ettringite content of SSC. In order to do this using TG/DTG, calibration of either curve was necessary. This calibration was achieved by using a synthetic sample of ettringite to obtain an area for the main DTG peak. This was used to estimate the mass of ettringite in SSC by comparison of the peak areas [5]. The method proved to be consistent and reliable. The use of the measurement of DTG areas has a disadvantage that it will generally over-estimate the ettringite content by an unknown amount due to CSH dehydration loss. For the present study it was considered that an overestimate was unavoidable but the method was valid since the work was to be comparative. For the XRD determinations the same synthetic ettringite and SSC was used to make up a series of calibration mixtures. Using gehlenite as an internal standard, it was possible to estab-

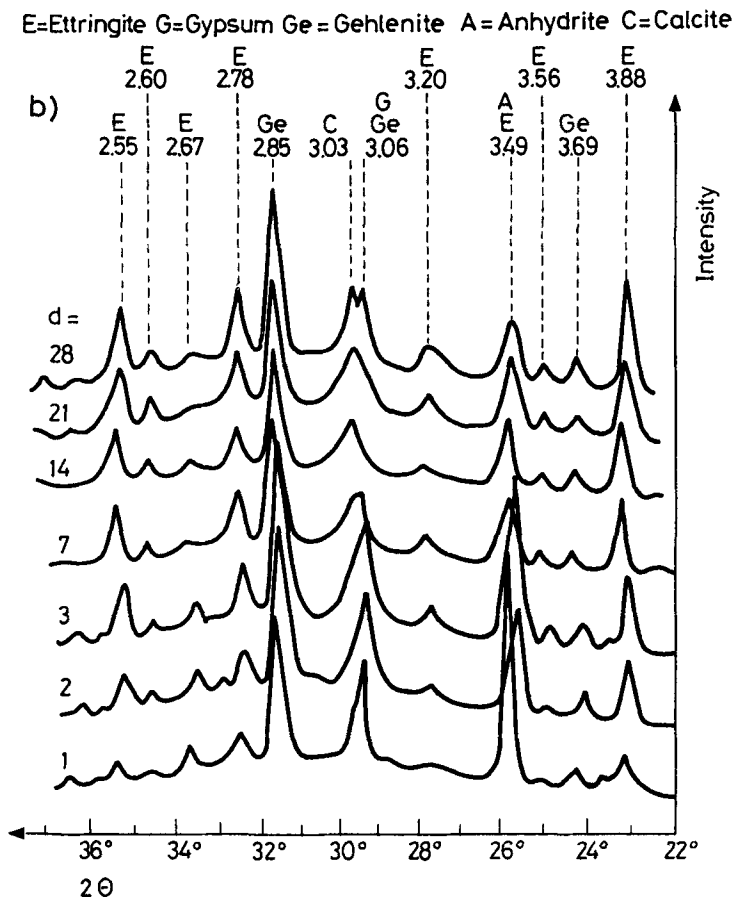


Fig. 3b Changes in composition of SSC paste during initial 28 days water-cure at 25°C (cont.)

lish a linear relationship between the masses of the materials in the mixtures and the intensities of above the background of ettringite (5.61 Å) and gehlenite (2.85 Å). The peaks involved were sufficiently sharp to consider that the peak height was proportional to intensity. The mean values of the two calibration methods for the batches of SSC after 28 days water curing were: ettringite content 29.6% (ignited mass) by DTG; 16.2% (dry SSC) by XRD. Comparison of these values reveal substantial differences which are presented in Figs 5–10. One reason for these differences is that the two methods do not express the value as a proportion of the same mass, although the two should be similar. The over-estimate given by the DTG method caused by the CSH background together with the possibility of reduced crystallinity in SSC compared to that in the calibration samples might also be factors. The comparative nature of the

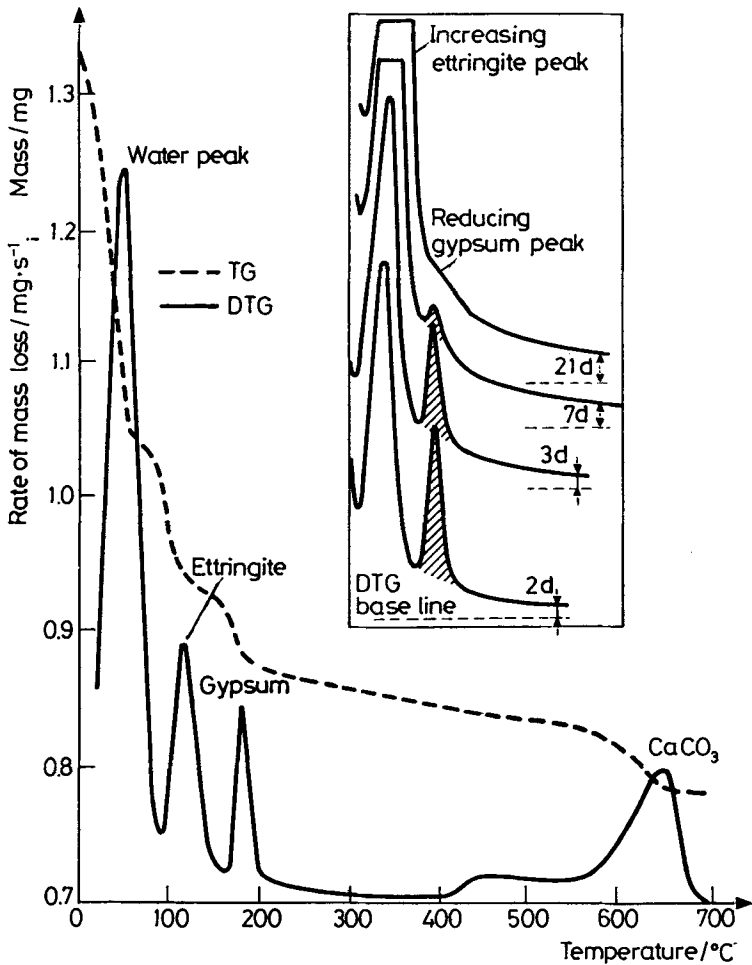


Fig. 4 Change in shape of the DTG curve for early dehydration of SSC

studies and the calibration methods employed is considered to make both methods valid.

### Storage at 25°C

During storage of SSC25-100, no new compound formation over time was observed using XRD to indicate decomposition, indeed there was very little change in the pattern over 12 months. Using the area of the DTG curve and the XRD results for the estimation of ettringite, indicated that it remained stable over the period. The peak at 3.48 Å on the XRD is attributable to both ettringite



and anhydrite. However this peak remained larger than would be expected for the ettringite peak alone, suggesting the continued presence of solid anhydrite.

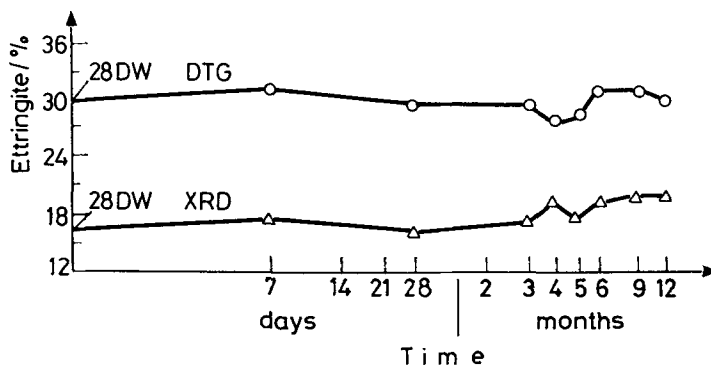


Fig. 5 Variation in ettringite content for SSC25-53

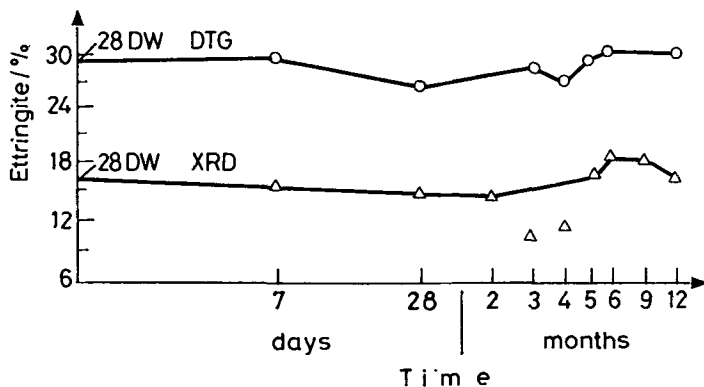


Fig. 6 Variation in ettringite content for SSC25-11

For the SSC25-53 and SSC25-11 samples, the patterns were very similar indicating the general stability of ettringite (Figs 5 and 6). The only difference between the results from those samples stored at the three different humidities at 25°C was a slightly higher value for ettringite at 100% RH both from DTG and XRD data. This could be attributable to ettringite achieving its maximum hydrate water content at 100% RH with improved crystallinity.

*Storage at 50°C*

Figures 7 and 8 show the changes in the ettringite content for samples stored at 50°C under each of the humidity conditions. For sample SSC50-100, the et-

tringite remained stable, confirmed by the lack of decomposition products on the XRD pattern.

However, the two drying regimes of 53 and 11% RH at 50°C showed interesting results with regard to ettringite; both showed a general reduction in the ettringite content, but in neither case did XRD indicate definite decomposition products. This would suggest either decomposition by drying or conversion to amorphous products. However, if decomposition was simply due to the drying of the ettringite hydrate water, then the greater reduction that occurred at 53% RH would be unexpected.

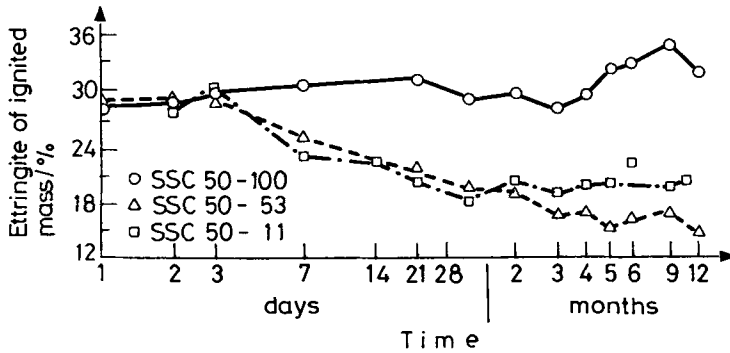


Fig. 7 Variation in ettringite content for samples at 50°C by DTG

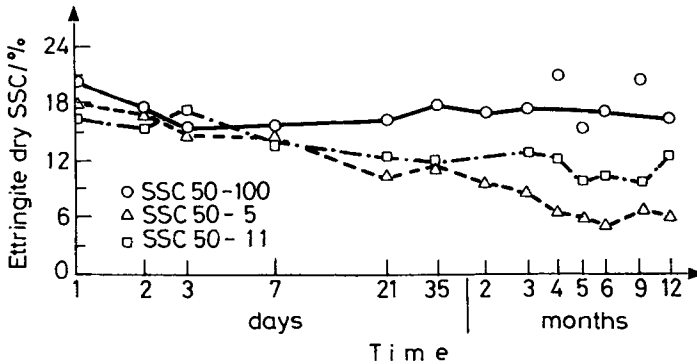


Fig. 8 Variation in ettringite content for samples at 50°C by XRD

A check on the humidity conditions confirmed that the tanks containing the samples designated 11% RH were in fact at a lower humidity than that at 53% RH. Due to the lack of notable decomposition products, it is suggested that the predominant reaction was one of dehydration but that simultaneous decomposition occurred at 53% RH which reduced the ettringite content below

that in the samples held at 11% RH. The only mineralogical evidence for this is the maintenance of the height of the 3.48 Å XRD peak, despite the reduction in the other ettringite peaks. This could indicate the formation of anhydrous CaSO<sub>4</sub>, although no consistent relationship could be found to confirm this fact. When studying synthetic ettringite [7] a link between carbonation and humidity was suggested. Carbonation, therefore could be a factor in this instance.

### Storage at 75°C

The results taken on samples stored at 75°C showed similar patterns to those at 50°C, but with a more exaggerated decomposition in drying atmospheres. Figures 9 and 10 show the changes in the ettringite content with time. The ettringite remained stable in the SSC75-100 sample with a possibility of an increase at later stages in time. This increase would not be expected, unless the increase in temperature caused a change in the solubility characteristics of the residual CaSO<sub>4</sub> and thus promoted reaction. A general increase was observed from the XRD curves. From the DTG curve there was quite a sharp increase in the ettringite content shown in Fig. 9. The free water peak on the DTG trace showed a certain amount of broadening during the storage period, which could indicate a change in the CSH background. XRD showed a slight increase in the intensity of the peaks at approximately 3.0 Å. It is likely that the apparent increase in ettringite shown by DTG is due to an increase in the CSH background, shown by XRD to have an increased crystallinity.

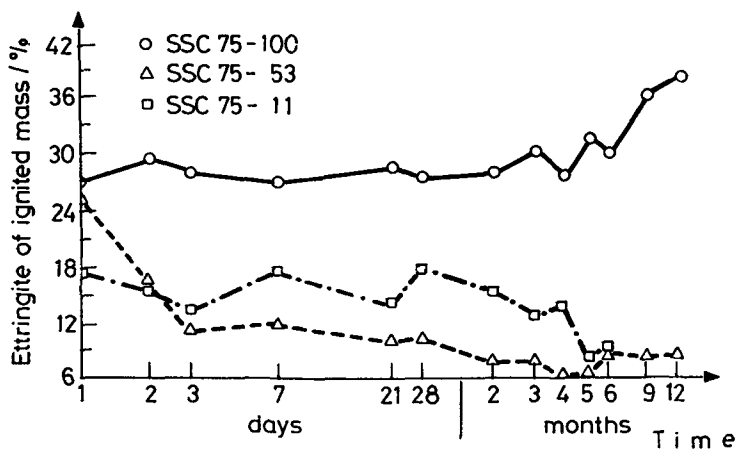


Fig. 9 Variation in ettringite content for samples at 75°C by DTG

For both the SSC75-53 and the SSC75-11 samples there is a reduction in the ettringite content and, as at 50°C, samples stored at 53% RH show a greater

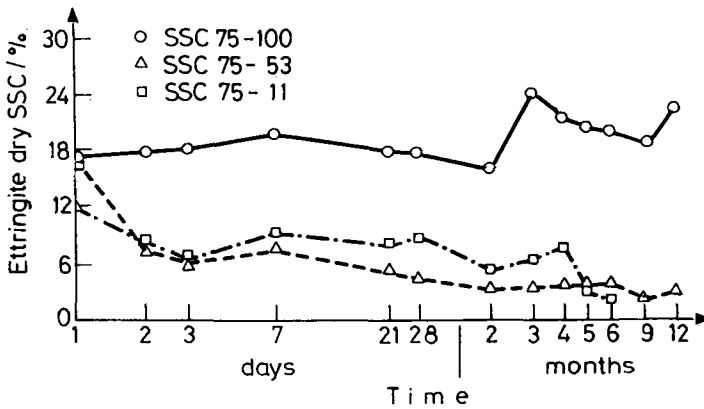


Fig. 10 Variation in ettringite content for samples at 75°C by XRD

reduction that those at 11% RH. In both cases there was no evidence of decomposition products. The situation is very similar to that at 50°C but accelerated by the increase in temperature.

## Conclusions

### *Stability at 25°C*

Ettringite has been shown to be stable at 25°C under all conditions of humidity. Conversion to monosulphate, which happens in Portland cement, did not occur in SSC paste. This is attributed to the presence of solid anhydrite (calcium sulphate) which remains, despite there being more alumina present than would be required to react with all of the anhydrite to form ettringite. The excess alumina was probably bound into the general CSH structure without having definite crystalline phases at this temperature.

### *Stability at 50 and 75°C*

The ettringite in SSC showed greater susceptibility to drying even at 50°C. However, the ettringite content was reduced more at 53% RH than at 11% RH and it is suggested that at 53% RH simultaneous drying and decomposition has occurred. This has been confirmed by rehydration studies, which show complete restoration of ettringite from the 11% RH but not from the 53% RH samples. The absence of distinct decomposition products made explanation difficult, however it was suggested that carbonation could be a significant cause.

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**Zusammenfassung** — Es wurde die Stabilität von übersulfatierem Zement (SSC) untersucht. Mittels TG und Röntgendiffraktion wurden die Hydratationsprodukte von einem mit einem Wasser/Zement-Verhältnis von 0.27 hergestellten Zementleim bestimmt. Für Ettringit, eines der anfänglichen Hydratationsprodukte, wird gezeigt, daß es unter Lagerungsbedingungen bei 25, 50 und 75°C und einer relativen Luftfeuchte von 100, 53 und 11% Wasserdampf in jedem Falle stabil ist. Desweiteren wird der Einfluß des Trocknens auf die Stabilität von Ettringit bei höheren Temperaturen in Beziehung der relativen Feuchtigkeit erörtert.