

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 at 95°C when subjected to relative humidities of 100, 53 and 11% of water vapour. Previously [1] investigations at 25, 50, 75°C under the same conditions of humidity reported the stability of ettringite, one of the initial hydration products. At 95°C, decomposition of ettringite, is found at all humidities and is rapid at 100% relative humidity. The hydration products of cement pastes at a water cement ratio of 0.27 were determined by thermogravimetry (TG) and X-ray diffraction (XRD).

The formation of the hydragarnet, plazolite is recorded during the decomposition/dehydration process enhanced by possible carbonation. Rehydration studies on the products after storage for up to 9 months were carried out using distilled water and the samples tested for ettringite content. It is concluded that ettringite in SSC is inherently unstable at 95°C.

Keywords: cement, TG, XRD

Introduction

In the previous paper [1] the authors reported on the stability of supersulphated cement (SSC) stored at 25, 50 and 75°C and when subjected to relative humidities of 100, 53 and 11% of water vapour in each case. This second paper reports on the stability of SSC stored at 95°C when subjected to the same range of relative humidities.

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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% CaSO₄ 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 days period in water was appropriate and thus 28 days was chosen. The choice of a range of temperatures used in the study were made on the basis of a previous study of synthetic ettringite [2]. The temperature reported here was 95°C. The storage arrangements for such conditions are described elsewhere [3]. For ease of reporting the following code system has been used: SSCX-Y storage at X°C at Y% relative humidity.

Results and discussion

Storage at 95°C

Consistent with results obtained from a study of synthetic ettringite [4], the decomposition of ettringite in SSC was found at all humidities at 95°C. Figures 1 and 2 show clearly a quite dramatic reduction in ettringite after approximately 14–21 days for the SSC95-100 sample. Decomposition by drying could be discounted, since the large free-water peak on the DTG curve remained

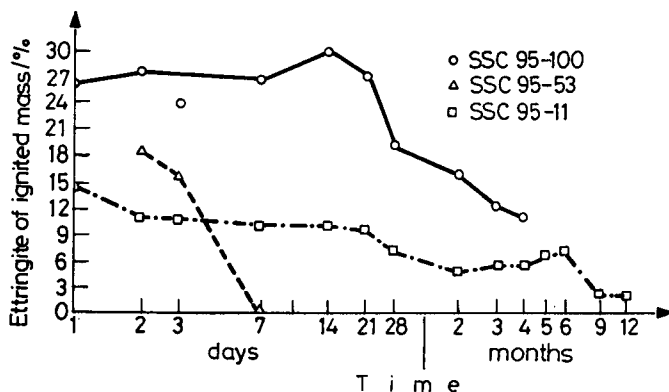


Fig. 1 Variation on ettringite content for samples at 95°C by DTG

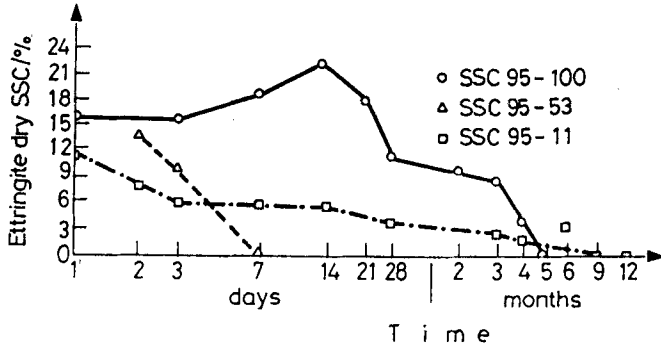


Fig. 2 Variation in ettringite content for samples at 95°C by XRD

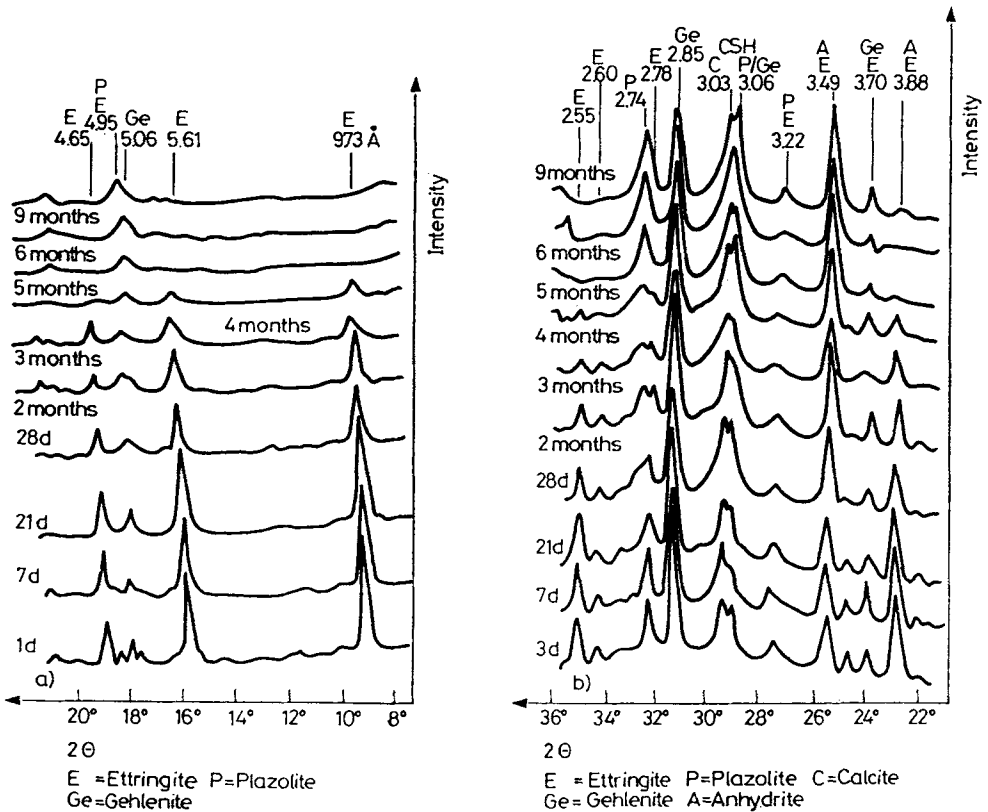
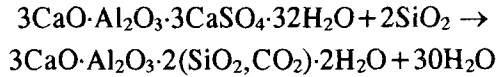


Fig. 3 Changes in composition SSC95-100 by XRD

clear. Figures 3a and 3b shows the overall changes in the XRD pattern over the 9 months storage period. There is a reduction in the peaks due to ettringite after 21 days until none remained after 5 months. The peak due to CaSO_4 at 3.49 Å had substantially increased with the double peak in the 29–30° 2θ region. Most

of the remaining peaks were characteristic of gehlenite, but several others are present which could be attributed to hydrogarnet, plazolite, $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2(\text{SiO}_2, \text{CO}_2)\cdot 2\text{H}_2\text{O}$ (ASTM 3-0801). This mineral was discussed by Yang [5] as being found during autoclaving of some slag cements, along with other hydrogarnet calcium aluminate silicate hydrates. It could also be a possible minor product from the carbonation of ettringite. This would suggest that the following reaction takes place in SSC95-100.



The possibility of some carbonation occurring simultaneously may have caused plazolite formation in preference to any other hydrogarnet. No evidence of monosulphate was found although small amounts of C_3AH_6 were a possibility.

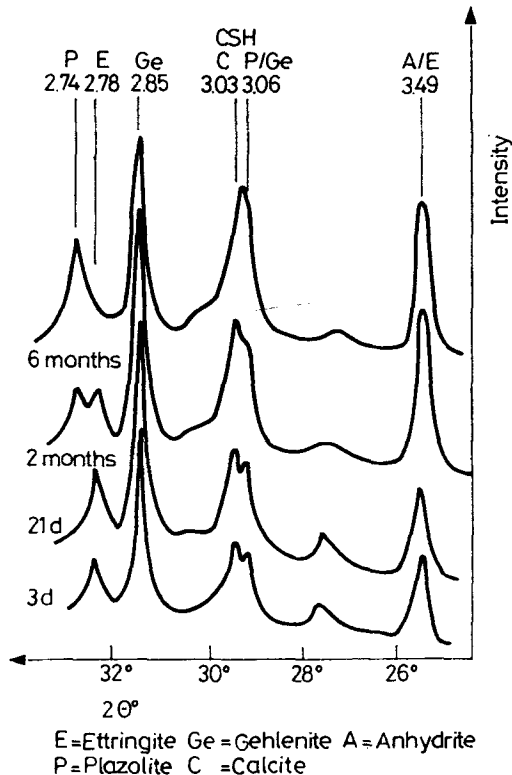


Fig. 4 Detail of section of XRD pattern for SSC95-100 at various ages

With regard to changes in the CSH composition, the area of the XRD trace at 29–30° 2θ could be significant. Figure 4 shows a detail from the XRD pattern between 25 and 30° 2θ. When peaks are compared to the gehlenite peak at 2.85 Å, the increase in intensity at 3.49 Å (CaSO₄) and the area at 3.0 Å can be clearly seen. The reduction in the 2.78 Å ettringite peak and appearance and growth of the 2.72 Å plazolite peak also illustrated. None of the XRD traces so far has shown clear evidence of CSH peaks, indicating a generally poorly crystalline material. Several types of CSH exhibit main peaks in the region of 3.0 Å. Autoclaving has been reported to improve the crystallinity of CSH phases and Hara and Midgley [6] used a 3.08 Å tobermorite peak as a measure of crystallinity. Tobermorite (ASTM 19-1364) and xonotlite (ASTM 23-125) both exhibit main peaks around 3.0 Å and both have a C/S ratio of approximately 1.0. Tobermorite-like CSH has often been reported in SSC(3) and xonotlite was also discussed by Yang [5] as a product of autoclaving slag cement. Plazolite also shows a large peak at 3.03 Å. The overall increase in the intensity of this area of the XRD pattern is likely to be related to the formation of plazolite, although it can also be inferred that improvements in the crystallinity of the CSH have occurred.

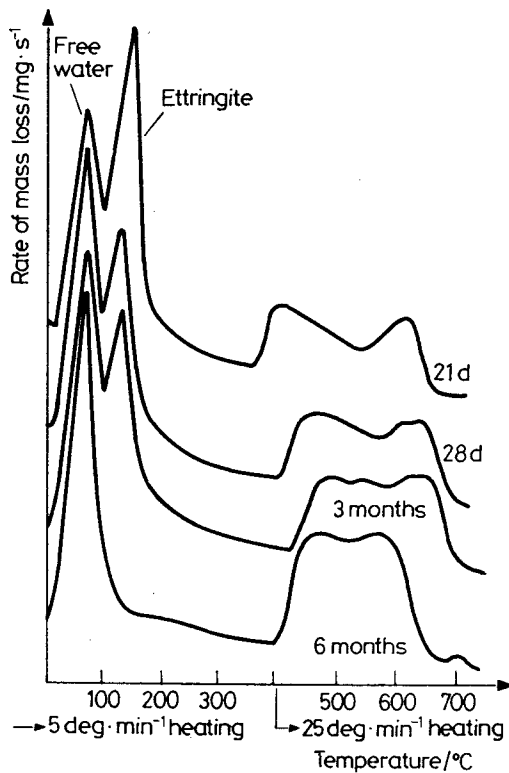


Fig. 5 Change in shape of the DTG curve for SSC95-100 as ettringite decomposed

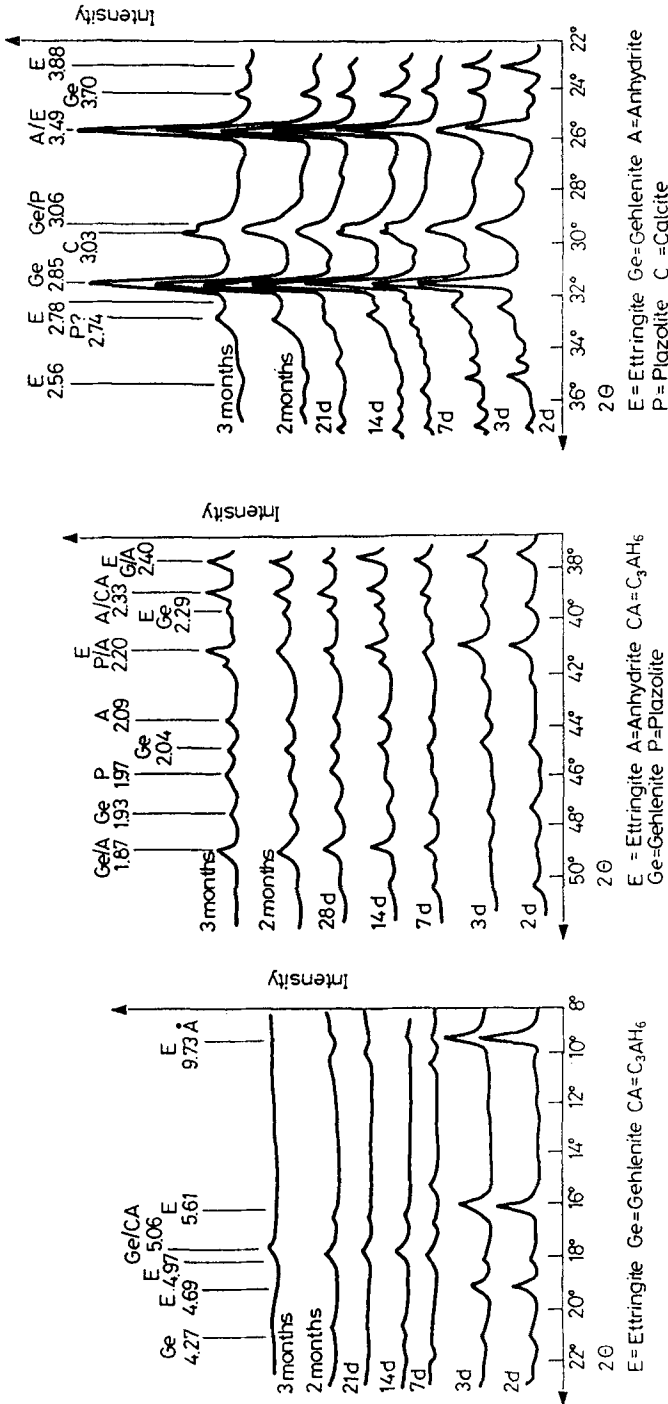


Fig. 6 Changes in composition of SSC95-53 at various ages

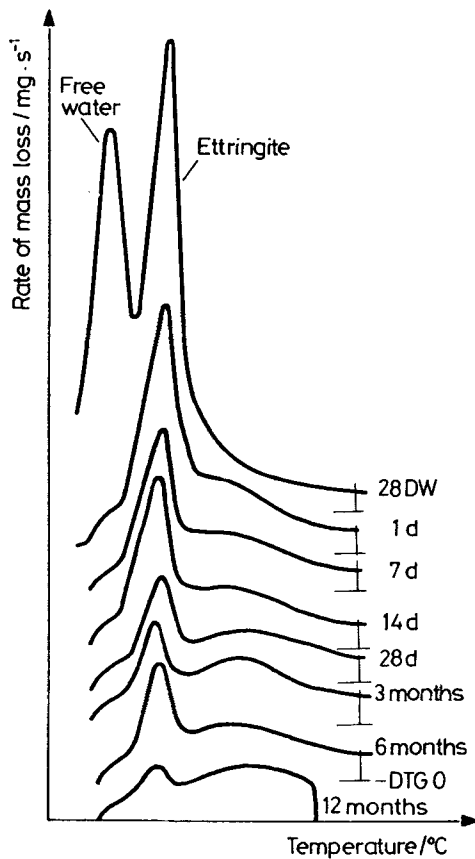


Fig. 7 Change in shape of DTG curve for SSC95-11

The shape of the DTG curve also changed during the decomposition period, although clear identification of the products was not possible. Figure 5 shows the changing shape, where approximate comparison is possible, since all curves were obtained from similar sized samples. The large peak due to ettringite reduced greatly between 21 and 28 days and could not be detected at 5 months. A change in shape at higher temperatures is shown once decomposition had occurred. This effect could be due to plazolite formation or the change in the nature of the CSH structure.

The other two drying regimes at 95°C continued the trend discussed for lower temperatures, [1] but in this case the effects were greatly accelerated; SSC95-53 showed no evidence of ettringite after 7 days. Figure 6 illustrates the change in the XRD pattern of SSC95-53, which does indicate some decomposition products. Anhydrite is shown to increase, however, other peaks are less well defined. Plazolite and C_3AH_6 are both possibilities. Synthetic ettringite

stored under the same conditions showed evidence of the presence of C_3AH_6 , which exhibits a main peak at 5.16 \AA and this could be a possibility for SSC95-53, but other peaks coincide with those for other compounds, notably $CaSO_4$. The rate of decomposition of SSC was rapid and it is suggested that, as with synthetic ettringite under the same conditions [4], drying and decomposition had occurred simultaneously. The main decomposition product was $CaSO_4$. Plazolite and C_3AH_6 are likely to have been formed also and it is possible that a substantial amount of ettringite exists in the dried form at a reduced water content, such that it exhibits no XRD pattern and the main DTG peak is also absent.

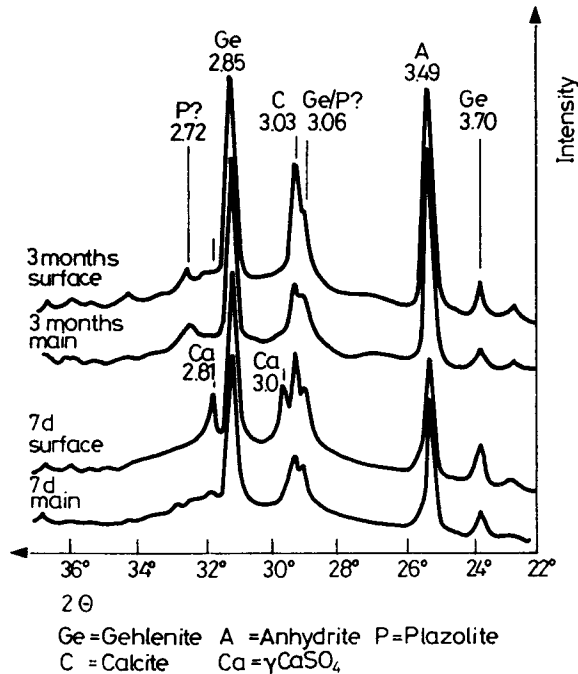


Fig. 8 Sections of XRD patterns from SSC95-53 comprising main and surface samples

SSC95-11 showed a rapid drop in ettringite content after only 1 day, but from that time the decrease was more gradual and peaks only completely disappeared from the XRD pattern after 9 months. Figure 7 shows the reduction in the main DTG peak due to ettringite and the disappearance of the free water peak, a small ettringite peak still occurs after 12 months. The effect of the background CSH response can also be seen from this series of curves. No evidence of any decomposition products was found from XRD. The anhydrite peak did not increase. In the case of SSC95-11 decrease in ettringite seems to be simply due to drying, similar to synthetic ettringite prepared under similar conditions. Since the main DTG peak was still observed but XRD gave virtually no pattern, it is likely that the ettringite had dehydrated to between 9 and $12H_2O$ [2].

Rehydration of dried samples

It had been noted that on rehydration, water could be replaced into the structure of previously dried synthetic ettringite [3]. Therefore, it was considered likely that this would also occur during rehydration of SSC samples if the reduction in ettringite content was due to drying. Samples of SSC95-53 and SSC95-11 were placed in distilled water and tested for ettringite content up to approximately one week.

SSC95-53 provided evidence for combined dehydration and decomposition at 53% RH. SSC95-11 showed a return of ettringite peaks, but with a trace of gypsum, indicating the possibility of some decomposition. SSC95-53 showed no return of the peaks due to ettringite upon rehydration. This implies that, after the maximum storage period, the decomposition was complete. The XRD trace from the SSC95-53 rehydrated sample was almost identical to that for the SSC95-100 sample after 9 months (Fig. 3). It is likely therefore that the decomposition of SSC95-53 was similar to that of SSC95-100. Plazolite shows reduced intensity XRD peaks after drying, but which are restored by rehydration. This in turn suggests that ettringite in SSC is inherently unstable at 95°C, which could also explain why the SSC95-11 sample showed some decomposition while other samples at lower temperature and 11% [4] did not.

Previous results [1] and these tests confirm the suggestion that at both 50 and 75°C with 11% RH, the apparent ettringite content was reduced by drying, whereas at 53% RH a combination of drying and decomposition had occurred. At 95°C, ettringite in SSC sample became unstable, but storage at 11% RH could possibly delay but not prevent the decomposition.

Carbonation during storage

It is traditional during study of cement pastes to remove the surface layer of samples prior to mineralogical and microstructural analysis, to avoid possible unrepresentative sampling. This had been carried out for all of the samples previously discussed. Despite the inclusion of soda lime in the storage containers, synthetic ettringite had shown carbonation decomposition. It was, therefore, decided to examine the mineralogy of the SSC surfaces for carbonation.

The surface layers removed were very shallow and quantification could not be carried out accurately. The surfaces were simply scraped to a depth of about 0.5–1.0 mm using a sharp scalpel. At 100% RH the surface skin was slightly lighter in colour than the main body of the sample. This facilitated removal of this layer, but at lower humidities, the distinction was less certain. XRD and DTG traces of material removed in this way were compared to the main sample traces at similar ages. It is noted that in no case would the sample surface be regarded as 'dusty' due to a friable layer.

For the samples at high temperatures and high relative humidities the situation was complicated by the decomposition of ettringite, which reduced the ettringite content simultaneously with any carbonation reaction. However, several surface samples showed large calcite peaks and reductions in ettringite relative to the main body of the SSC paste. The increase in calcite peaks seemed larger than would be expected, if caused by decomposition of ettringite.

This trend is illustrated in Fig. 8, it shows a section of the XRD trace for SSC95-53, at 7 days and 3 months compared to the main sample. Carbonation had occurred, but had modified the decomposition reaction. Calcite was produced, but γ -CaSO₄ (ASTM2-0134) was also evident as an intermediate stage in the formation of anhydrite. Results suggest that surface carbonation of the SSC pastes had occurred, but due to the arbitrary nature of the sampling method, it was not possible to evaluate this consistently. The large relative intensity of some of the calcite peaks could indicate carbonation of other phases e.g. CSH.

References

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Zusammenfassung — Unter Anwendung relativer Luftfeuchten von 100, 53 und 11 % wurde bei 95°C die Stabilität von supersulfatierem Zement (SSC) untersucht. Vorangehende [1] Untersuchungen bei 25, 50 und 75°C unter den gleichen Feuchtigkeitsbedingungen berichteten über die Stabilität von Ettringit, eines der ersten Hydratationsprodukte. Bei 95 wurde für alle Feuchtigkeitswerte die Zersetzung von Ettringit festgestellt, die bei 100 % relativer Feuchtigkeit am schnellsten verläuft. Mittels TG und Röntgendiffraktion wurden die Hydratationsprodukte von Zementleim bei einem Wasser/Zement-Verhältnis von 0.27 bestimmt.

Während des Zersetzungs-/Dehydratationsprozesses wurde die Bildung von Hydrogranat und Plazolit registriert. Unter Einsatz destillierten Wassers wurden nach Lagerung für die Dauer bis zu 9 Monaten Rehydratationsuntersuchungen an den Produkten durchgeführt und die Proben auf den Gehalt an Ettringit untersucht. Man schloß, daß Ettringit bei 95°C in SSC von Natur aus instabil ist.