

RESISTANCE OF SUPERSULFATED CEMENT TO STRONG SULFATE SOLUTIONS

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Abstract

One of the principal uses of supersulfated cement has been for structures exposed to sea water and sulfate bearing ground waters. The resistance to such environments has been related to the absence of calcium hydroxide and the combination of much of the free alumina into ettringite during hydration. This paper reports the resistance of SSC to sulfate solutions in which ettringite has been decomposed.

Prism samples were subjected to initial water storage at 25°C for both 28 days and 6 months. Samples were also cured for 6 months at 95°C and at both 11% and 100% R.H. The control samples of 28 days were compared with the 6 months samples of a more mature undecomposed SSC paste. After curing the prisms were measured and all the samples were immersed in three sulfate solutions (0.7M Na₂SO₄, 0.7M MgSO₄ and saturated CaSO₄), and water at the same time. Measurements of linear expansion over 6 months were carried out. Core and surface material following immersion was examined by DTG and XRD.

The study indicated that SSC is resistant to sodium and calcium sulfate solutions. Strong magnesium sulfate solutions decomposed the samples under all conditions. A possible mechanism for this attack is suggested.

Keywords: ettringite, mechanism of supersulfated cement (SSC), resistance of SSC

Introduction

Previous investigations into the stability of supersulfated cement [1] (SSC) under different conditions of temperature and relative humidity have been reported [2]. One of the principal uses of supersulfated cement has been for structures exposed to sea-water or sulfate bearing ground waters, since the cement has generally shown superior resistance to such environments. This resistance has been related to the absence of calcium hydroxide (Ca(OH)₂) and the combination of much of the free alumina into ettringite during hydration [3, 4]. The purpose of this study was to investigate the resistance of supersulfated cement (SSC), in which the ettringite had been decomposed, to sulfate solutions.

There has been debate for several years on the appropriate methods which should be used for the investigation of the sulfate resistance of cements. Because degradation takes some time, often years, methods of accelerating the reactions have

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been developed [5, 6]. The traditional method involves the soaking of specimens in strong sulfate solutions and the measurement of the resultant linear expansion. This method has received some criticism for its unrealistic nature and indeed does seem inappropriate for a study of the complex mechanisms involved in sulfate attack. However, as a quick and simple indicator of sulfate resistance, it can still be regarded as a significant method. Since the intention of this paper is to establish whether the decomposition of ettringite would dramatically alter the resistance of SSC, the traditional soaking method was considered the most convenient.

Thermal methods in general have often been used for analysis of cements, although TG/DTG has been less popular than differential thermal analysis (DTA). Ben-Dor [7] presented an interesting review of thermal methods that have been applied to cement science. During TG /DTA of hydrated cement, mass losses occur through dehydration, dehydroxylation and decarbonation of the cement compounds [8]. These losses occur in temperature ranges which can be compared to known compounds in order to help in identification of the phases present. The additional use of a more direct identification method, such as X-ray diffraction, provides a significant technique for the analysis of cements [9].

Experimental

SSC paste prisms, nominally 12.5x12.5x100 mm and 12.5 mm cubes were exposed to strong solutions of the three most common ground-water sulfates. These were 0.7M Na_2SO_4 , 0.7M MgSO_4 and saturated CaSO_4 . Similar samples were exposed to distilled, deionised water (also used for sulfate solution preparation) as a control. For the maintenance of reasonably stable exposure conditions, a ratio of 100 to 1 as volume of solution to volume of specimens was used and the solutions were stirred continually. A volumetric titration method [10] was used occasionally to check that the sulfate concentration was maintained. Saturation of the CaSO_4 solution was indicated by the constant presence of the solid material.

Attack by sulfate was monitored by the measurement of the linear expansion between indentations in the ends of the prism using a frame mounted dial gauge and also by visual assessment of both cubes and prisms. Selected mineralogy testing was carried out on some of the cubes to establish the nature of any decomposition products.

The apparatus for TG/DTG, incorporates a small furnace and a sensitive electronic balance. The equipment used in this study was a Stanton Redcroft TG 760 balance with a Universal Temperature Programmer and Balance Control Unit. The DTG was obtained from a Linseis N42 derivative unit with N31 pre-amplifier. The information was recorded on a Linseis multipen flatbed chart recorder. The sample is suspended in the microfurnace from the sensitive electro-balance. As the temperature is raised the balance measures mass changes while a thermocouple, situated approximately 0.5 mm below the sample holder, measures the temperature. The balance in the TG 750 is of the 'null-point' variety, which has the advantage of maintaining the same sample position within the furnace throughout the analysis. This improves the accuracy of temperature measurement. The voltage produced is amplified and also input to the derivative unit to allow simulta-

neous recording of TG and DTG. This particular apparatus allows the heating of samples of up to 100 mg from ambient temperature to 1000°C at heating rates between 1 and 99°C min⁻¹ in steps of 1°C min⁻¹.

Results and discussion

Preparation of samples

It was decided to study the change in resistance of SSC paste in which ettringite had been reduced a) by decomposition and b) by drying. Therefore paste samples were prepared at a water : cement ratio of 0.27 and then stored in water for 28 days at 25°C. One set of samples was then cured for 6 months at 95°C and 100% RH and another set for 6 months at 95°C and 11% RH. Mineralogical analysis after these periods confirmed the previously obtained results. An example is reproduced here for SS95-100 of the XRD and DTG curves. These curves are shown in Figs 1 and 2.

In addition, these two series were compared with samples cured for 28 days in water at 25°C and samples stored for 6 months at 25°C and 100% RH. The 28-day series provided a control and the 6 month series gave a useful indication for a more mature undecomposed SSC paste. These samples would also indicate whether any free alumina was available to cause sulfate expansion. After the curing periods, the prism lengths were measured and all samples were immersed in the three sulfate solutions and water at approximately the same time.

Initially, it had been intended to also include 0.7M K₂SO₄. However, at this concentration the solution tended to form a gelatinous precipitate. From previous results [11] it had been noted that surface carbonation had occurred in many of the paste samples. It was decided to abandon testing in potassium sulfate and to distribute the samples amongst the remaining solutions. This allowed two series of samples for

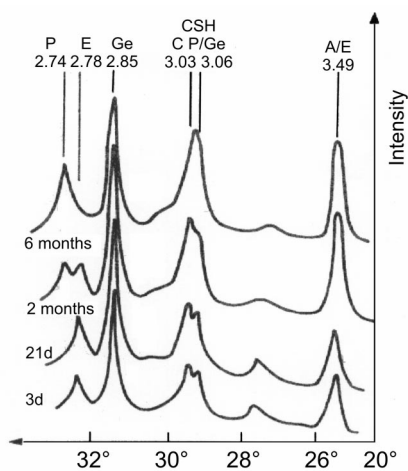


Fig. 1 XRD patterns for SSC95-100RH sample

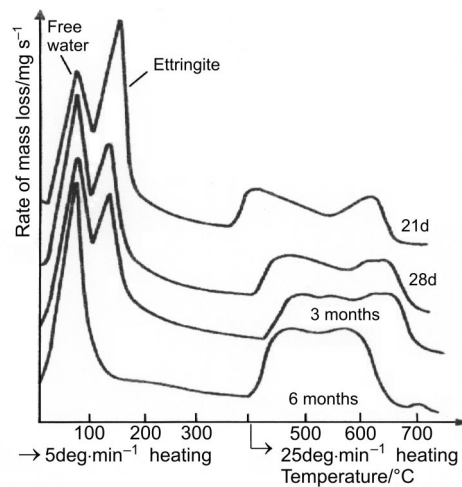


Fig. 2 DTG curves for SS95-100RH

each set of conditions; (1) with the original surface removed and (2) with the carbonated surface retained. For each of the conditions 'SSC95 - 100S', 'SSC95 - 11S', 'SSC25 - 100S' and 'SSC28 DWS'**, both with and without the surface, at least two prisms and four cubes were studied.

Resistance to sodium sulfate and calcium sulfate solutions

Samples from SSC95 - 100S, SSC25 - 100S and SSC28DWS showed no significant expansion or visible signs of attack after 9 months in calcium or sodium sulfate solution. Samples from SSC95 - 11S showed an initial expansion, which the water control sample (SSC28DWS) confirmed as simply due to rehydration of the dried specimens, with no subsequent expansion or attack. The linear expansion with time is shown in Fig. 3. It was noted that the ettringite was fully restored in these samples.

Resistance to magnesium sulfate solution

All samples showed rapid expansion and extensive decomposition in 0.7M MgSO₄ solution. Figures 3 and 4 show the linear expansions found for these samples. For the two 25°C series, the two curves in each figure represent mean values for samples with and without the carbonated surface. Figure 5 shows similar curves for SSC95 - 100S, but the deterioration caused the ends of these samples to become dislodged at a relatively early stage. Figure 6 presents the curves for each of the SSC95 - 11S samples to illustrate the large variation in the level of expansion which occurred between these samples. The values for expansion shown on all of these curves are extremely high.

The two 25°C - stored series showed similar rates of expansion, which began almost immediately on immersion. SSC95 - 100S showed similar degradation behav-

** The nomenclature SSC95 - 100S refers to SSC stored at 95°C and 100% RH. SSC28 DWS refers to SSC cured for 28 days in water at 25°C

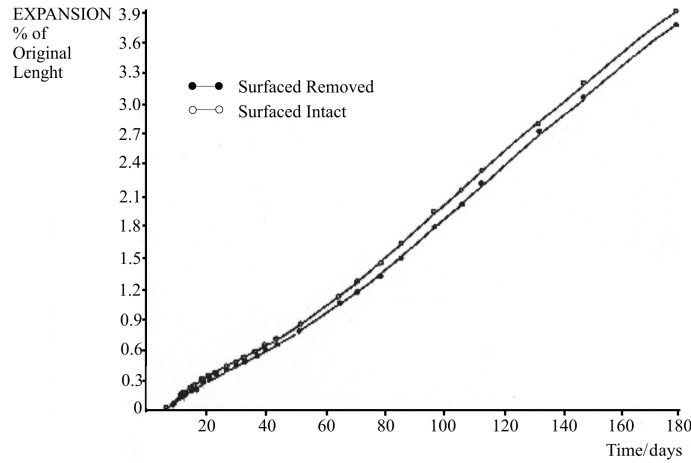


Fig. 3 Linear expansion of prisms of SSC stored at 25°C at 100RH then exposed to 0.7M MgSO₄

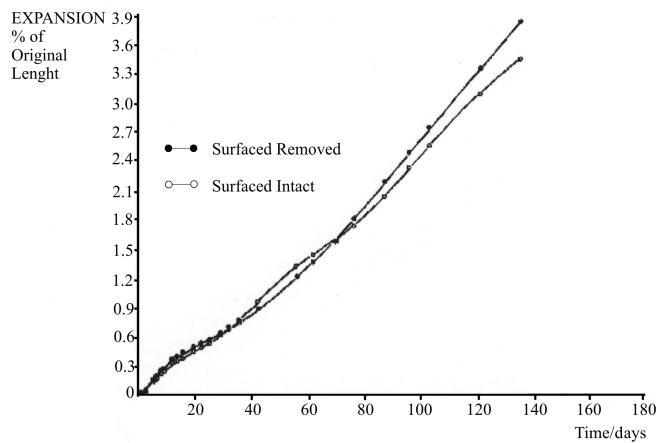


Fig. 4 Linear expansion of prisms of SSC cured for 28 days in water at 25°C and subsequently stored in 0.7M MgSO₄ for times shown on the graph (SSC28)

ious but showed less tolerance to the movement, such that the ends were dislodged. The four samples from SSC95 - 11S showed a high variability but in general exhibited smaller length changes than in other series.

Figures 7 and 8 are photographs of specimens immersed for approximately 5 months in the MgSO₄ solution. These show clearly that the reaction takes place at the surface and gradually progresses into the main body of the sample. The first sign of attack was always shown as a splitting at the corners and edges of the prisms and cubes, which opened further as decomposition progressed. This pattern is consistent with a surface expansion causing splitting when constrained by the main body of the

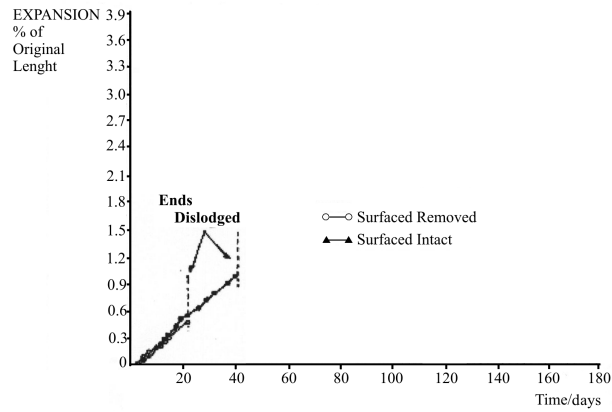


Fig. 5 Linear expansion of prisms of SSC stored at 95°C at 100% RH, exposed to 0.7M MgSO₄

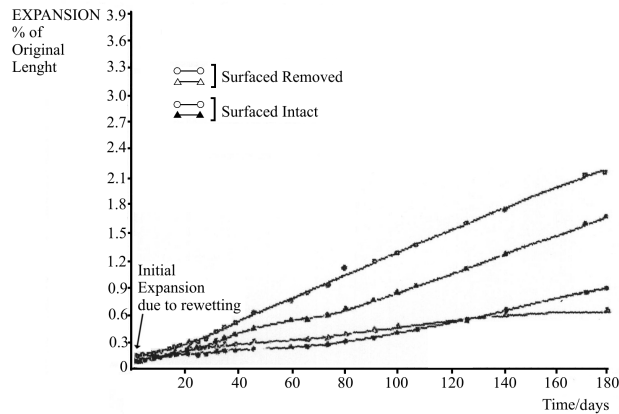


Fig. 6 Linear expansion of prisms of SSC stored at 95°C at 11% RH, exposed to 0.7M MgSO₄

sample. Outward movement of this surface would allow rapid ingress to the next layer, which would itself expand causing progressive inward reaction. Figure 10 shows this effect very clearly for a cube in which one face had become dislodged after 2 months. The darker central core in this photograph was largely unattacked. One of the prisms from SSC95 - 100S failed laterally but it was considered that this was not caused directly by expansive attack forming a crack but that the sample must have contained a flaw which behaved similarly to two external faces, which were then pushed apart. Large needle crystals were visible even by eye and were confirmed by XRD to be gypsum. On attempting to break another prism from the same series by hand, it was noted that, despite extensive surface damage, the central core retained considerable strength. Figure 9 shows that the samples from SSC95 - 11S gave a slightly different pattern of decomposition. Initially, a surface 'rippling' effect was observed, which was later followed by degradation which gave a spalling effect re-

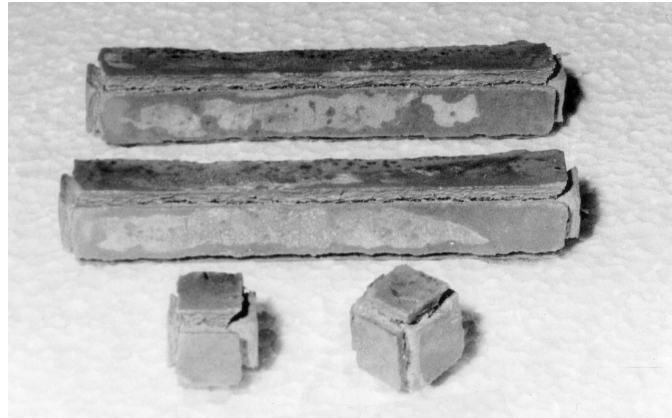


Fig. 7 Samples of SSC25–100S after storage in $MgSO_4$ solution



Fig. 8 Samples of SSC95–100S after storage in $MgSO_4$ solution

sembling an eruption from below the surface. This suggests a slightly different mechanism and could account for the lower levels of expansion.

XRD and DTG analyses were carried out on several samples from both the expanded surface material and the central core. The surface contained large amounts of gypsum which, apart from gehlenite, was the only significant crystalline solid; no ettringite was found in any surface sample. The unattacked cores resembled the original material before immersion, except that ettringite rehydration had occurred in the SSC95 - 11S specimens. Therefore ettringite was decomposed during $MgSO_4$ attack of those sample in which it was still present but disruption also occurred in samples which did not contain ettringite. This indicates that, although ettringite is attacked by $MgSO_4$ solution, the attack of the main constituent CSH is the overriding cause of the degradation and expansion.

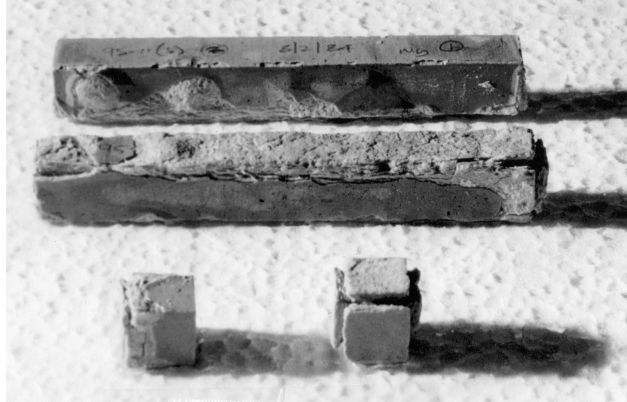


Fig. 9 Samples of SSC95-11S after storage in $MgSO_4$ solution

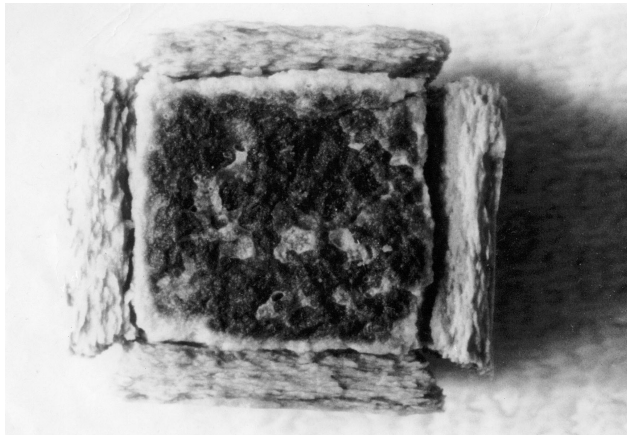


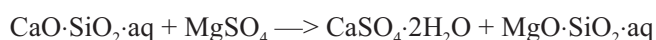
Fig. 10 A cube from $MgSO_4$ solution showing the layered nature of the decomposition

Discussion of the sulfate resistance of SSC

The results of this study indicate that SSC is resistant to sodium and calcium sulfate solutions even when the ettringite has been decomposed. This might be expected, since one of the decomposition products is calcium sulfate, which implies that the alumina-bearing phases produced, mainly hydrogarnets, are not available for subsequent reaction with sulfate ions.

All samples are rapidly decomposed by the strong magnesium sulfate solution irrespective of whether ettringite is present or not. The only effect of previous decomposition is the lower tolerance of SSC95 - 100S to the expansion process. This could be related to the weakening of the paste structure by decomposition.

The actual mechanism of the attack of the $MgSO_4$ solution is unclear, but it appears that in common with Portland cements, it is the magnesium ion that is responsible for the initiation of the reaction. For Portland cement, attack by magnesium is considered to be due to the combination of hydroxyl ions into $Mg(OH)_2$, which, being less soluble than $Ca(OH)_2$, precipitates out, causing a lowering of the pH. This causes CSH to liberate $Ca(OH)_2$ in order to restore the pH, but which then combines to produce more $Mg(OH)_2$ if the source of magnesium is continuous. If the magnesium hydroxide is not allowed to build up into a protective layer, this process continues to decompose the CSH. In the case of SSC, no crystalline $Mg(OH)_2$ was detected, which suggests that the mechanism was not exactly the same. However, the magnesium ion does seem to be extracting calcium from the CSH which then combines with the sulfate to form large quantities of gypsum. This causes expansion and softening of the paste. If the magnesium does not combine into $Mg(OH)_2$, there is the possibility of the formation of a weak magnesium silicate hydrate, which has been discussed as an ultimate product during the sulfate degradation of Portland cement [3]. For example:



Overall, the results suggest that the decomposition of ettringite under the storage conditions used, did not substantially affect the resistance of SSC to sulfate solutions.

Conclusions

- SSC is resistant to sodium and calcium sulfate solutions under all the conditions examined here, even when all the ettringite has been decomposed.
- All samples studied, rapidly decomposed in strong magnesium sulfate solutions, whether ettringite was present or not.
- A carbonated surface layer did not reduce the attack, but the lower strength of SSC at 95°C and 100% RH in which ettringite is decomposed, reduced its tolerance to the expansion reaction.
- It is suggested that magnesium ions are responsible for the attack and the decomposition of calcium silicate hydrate.
- The results suggest that the decomposition of ettringite under the conditions used did not substantially affect the resistance of SSC to sulfate solutions.

Symbols

SSC	supersulfated cement
CSH	calcium silicate hydrate
RH	relative humidity

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