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*Cement & Concrete Composites* **17** (1995) 3–8
Elsevier Science Limited
Printed in Great Britain

# Crystallization of Sodium Sulphate in Polymer Impregnated Plasters

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(Received 8 December 1993; accepted 18 June 1994)

***Abstract***

*The common occurrence and harmful effects of sodium sulphate make it a major cause of deterioration in plasters. The investigation conducted showed that a plaster composed of eminently hydraulic lime impregnated with water-repellent solutions (a perfluoropolyether or an oligomeric alkylalkoxysiloxane) or admixed with an acrylic latex is significantly more durable than plain plaster. In particular, the different modes of salt crystallization are discussed in relation to the microstructural properties conferred by the polymers, and to the thermohygrometric conditions of the system.*

*Keywords:* Plasters, crystallization of salts, durability, water repellent polymers, acrylic latex.

## INTRODUCTION

Plasters prepared with mortars containing inorganic binders (lime or hydraulic cements) act as an interface between the building and the environment and thus exert both an aesthetic and protective function. Their durability, and hence functionality, is however often compromised by the crystallization of salts on the surface and/or within the porous matrix, which results in the plaster crumbling or falling off the surface to which they have been applied. Of the salts contained in water absorbed by buildings, sodium sulphate is one of the most common and most harmful.[1–4] Here the results are presented of laboratory tests on sodium sulphate crystallization promoted in a variety of environmental conditions on specimens on mortars for plasters obtained using a hydraulic lime as binder. Special attention has been focused on the effect of polymers (added during mixing or impregnated in the pores by means of an evaporable organic solvent after hardening) on the microstructure as well as on the type of crystals formed, both factors that influence the degree of deterioration.

## EXPERIMENTAL

### Materials

A commercial eminently hydraulic lime was used as binder (Plastocem-Italcementi), having the following composition: CaO 53%, $SiO_2$ 5·7%, $Al_2O_3$ 4·5%, $Fe_2O_3$ 1·5%, $SO_3$ 1·5%, $Na_2O$ 0·65%, $K_2O$ 0·2%, L.o.I. 25·9%. The X-ray diffraction spectrum revealed the presence of $C_3S$ and $\beta$-$C_2S$ as the main crystalline components. Torre del Lago sand was used as aggregate[5] (siliceous, rounded grains, top size 2 mm). The latex was a 30% dispersion of acrylic polymer (Sikalatex Sika) in water. 'BSO 166' (ChemSpec), denoted as 'B', and 'Fluorobase cls' (Syremont), denoted with 'C', were used as water repellents. 'Fluorobase cls' is a 10% by weight solution of perfluoropolyether with an amidosilanic functional group; its molecular structure is characterized by an excellent stability to chemical and physical stresses: average molecular weight ranges from 800 to 1000. As the solvent evaporates (trichlorotrifluoroethane) so the water-repellent polymer is deposited on the pore surfaces to which it adheres by means of the terminal functional group amidosilane. 'BSO 166' is an alkylalkoxysiloxane with low molecular weight. Here a 10% by weight solution in ethyl alcohol was used. As the solvent evaporates, the oligomer in contact with the pore surfaces generates along with the moisture, reactions of hydrolysis and hence polymerization which lead to the formation of a silanic polymer with the strongly hydrophobic alkylic groups directed towards the exterior of the treated surface. The above materials were employed to prepare the four systems: NT = not treated system, B = hydrofobized system with 'B' solution, C = hydrofobized system with 'C' solution, and L = system with latex where the water/binder ratio by weight was 0·40 (for the L system it was 0·35); sand/binder ratio by weight was 3·5 and, for the L system, the latex/binder ratio by weight was 0·17.

## Methods

The mortars were prepared with an electromechanical rotary and revolutionary mixer in compliance with Italian Standards for hydraulic binders. Specimens 4 × 4 × 16 cm in size were prepared for testing mechanical properties after different ageing, absorption kinetics of the polymeric impregnating solutions and of the salt solutions, and crystallization cycles. The specimens were aged in air at 20°C and relative humidity of between 70% and 80%. Thirty days after casting, the specimens were impregnated with the polymeric solutions. Absorption was 6500 g/m$^2$ for 'C' and 3500 g/m$^2$ for 'B'. Crystallization tests were started after a further 60 days. Crystallization cycles consisted of placing specimens in a 200 g/litre $Na_2SO_4$ solution for 3 days and then leaving them to dry for one day at 60°C and relative humidity of 30% in a climatic chamber. The microstructure of the materials was characterized by observation under scanning electron microscopy (SEM), porosimetry using the mercury intrusion method and X-ray diffraction (CuK$\alpha$ radiation).

## RESULTS AND DISCUSSION

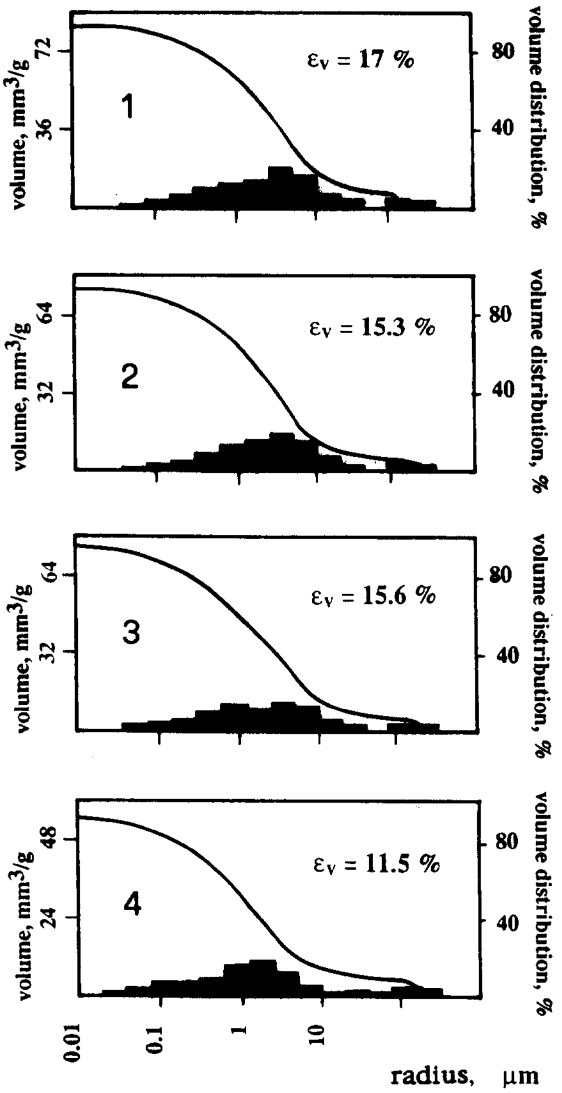


**Fig. 1.** Pore size distribution and cumulative curves of the four systems. 1 = NT; 2 = treated with 'B' solution; 3 = treated with 'C' solution; 4 = admixed with latex; $\varepsilon v$ = volume fraction of pores.

Figure 1 shows the cumulative curves and size distribution of the voids for the four systems examined. The untreated specimen (graph 1) displayed greatest porosity (17%) followed closely by the two specimens treated with the water repellents B (graph 2) and C (graph 3) (between 15 and 16%): this confirms that these substances tend to coat the pores without substantially altering their total volume. The system admixed with latex by contrast shows a much lower total volume of pores (11·5%), distributed moreover in the smaller size classes (graph 4). This finding was also substantiated by the capillary absorption of the sulphate solution measured after 3 and 72 h. The untreated system saturated almost straight away, attaining values of about 4500 g/m$^2$. By contrast the L system takes much longer to absorb considerably smaller amounts of solution (2000 g/m$^2$ after 72 h). Clearly the two systems treated with water repellents displayed much lower absorptions, only 200 g/m$^2$, approximately, after 72 h. Table 1 shows the compressive strengths of the four systems measured just before crystallization tests and after 5 and 10 cycles in the sulphate solution. The results are compared with the specimens aged for similar times in air and water, respectively. The strengths of NT, B and C are substantially similar at the start of the crystallization tests (11–12 MPa), whereas that of the L system is far superior. This is also because of the smaller proportions of water required in the mix to achieve equivalent workability, by virtue of the plasticizing effect of the latex itself. Regarding the

**Table 1.** Compressive strength (MPa)

| | *Cycles number or corresponding time* | *Air* | *Water* | *Sulphatic solution* |
|---|---|---|---|---|
| NT | 0 | 11·7 | — | — |
| | 5 | 14·9 | 18·0 | 5·0 |
| | 10 | 15·0 | 19·4 | 0·0 |
| B | 0 | 11·3 | — | — |
| | 5 | 12·9 | 11·8 | 10·5 |
| | 10 | 12·0 | 12·2 | 6·8 |
| C | 0 | 12·2 | — | — |
| | 5 | 11·9 | 11·5 | 12·1 |
| | 10 | 11·8 | 12·9 | 6·5 |
| L | 0 | 31·3 | — | — |
| | 5 | 31·6 | 31·8 | 32·0 |
| | 10 | 32·0 | 31·5 | 30·7 |

**Fig. 2.** SEM micrography. Efflorescence on the NT specimen in still air ( × 140).

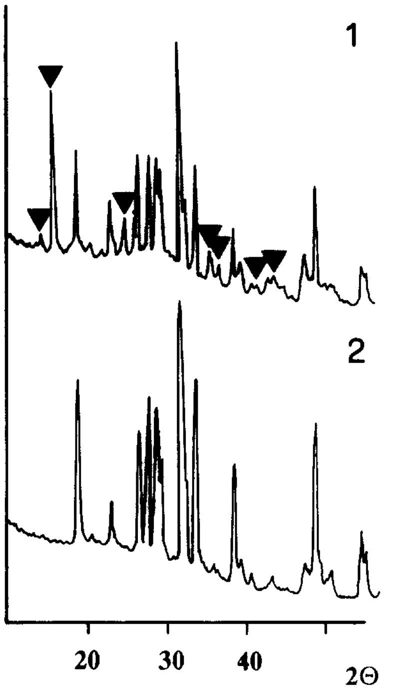


**Fig. 3.** X-ray diffraction patterns of efflorescence of NT specimen. 1 = after 10 min; 2 = after 30 min; ▼ = mirabilite peaks.

untreated specimens, NT, when exposed to air for the same time as the cycles, strengths increased slightly with time, whereas when subjected to wetting/drying cycles strengths were enhanced considerably (18 MPa after five cycles and almost 20 MPa after 10). The latter behaviour can be attributed to the continuing hydration process of the hydraulically active binder. On the other hand the two polymer treated systems that are impervious to water did not display substantial variations.[6]

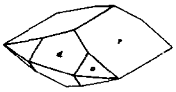
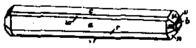
Tests with the sulphate solution produced a very different response. After just five cycles the untreated specimen showed a drastic decline in mechanical properties due to expansive effect of the salt, while after 10 cycles it disintegrated altogether. The polymer impregnated systems stood up fairly well for the first five cycles but after the 10th cycle they began to show clear signs of deterioration (flaking), which reduced their strength by about half.

The system L warrants separate discussion, in that its properties remain practically unchanged in all the test conditions. This behaviour can presumably be attributed for the most part to the elastic response conferred by the latex that enables the system to withstand stresses of this type.[7–9]

To justify the above findings a microstructural investigation (SEM and XRD) was carried out on the tested systems.

Some NT specimens were placed with a 4 × 4 cm face in contact with the saturated sodium sulphate solution in still air (temperature 25°C, relative humidity 70%). Within 24 h lots of crystals had formed as much as 20 mm thick (Fig. 2). The X-ray spectrum of the efflorescence (Fig. 3, graph 1) revealed the presence of both the decahydrate (mirabilite) and anhydrous (thenardite) forms, in keeping with what is reported in the literature concerning efflorescences appearing on buildings.[10,11] The salient physico-mineralogical characteristics of the two crystal forms, useful for discussion purposes, are shown in Table 2. When the diffraction spectrum was repeated after a few hours on the same samples it was observed that the peaks of the decahydrated phase had attenuated drastically (Fig. 3, graph 2). Clearly the mirabilite is to be regarded as an unstable phase in the test conditions at hand and tends to convert into the anhydrous form of the sulphate. This transformation manifests itself as a flouring of the decahydrated crystal's surface as shown in Fig. 4.

**Table 2.** Main characteristics of anhydrous and decahydrate form of sodium sulphate

| | *Anhydrous* | *Decahydrate* |
|---|---|---|
| Chemical formula | $Na_2SO_4$ | $Na_2SO_4 \cdot 10H_2O$ |
| Mineral name | Thenardite<br>Orthorhombic | Mirabilite<br>Monoclinic |
| Crystal structure |  |  |
| Water solubility (25°C g/litre) | 500 | 150 |
| Specific volume ($mm^3/g$) | 327 | 680 |

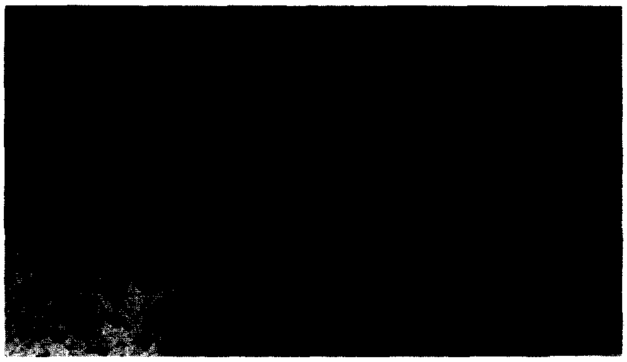


**Fig. 4.** SEM micrography. Mirabilite → thenardite transformation on the surface of the NT system ( × 300).

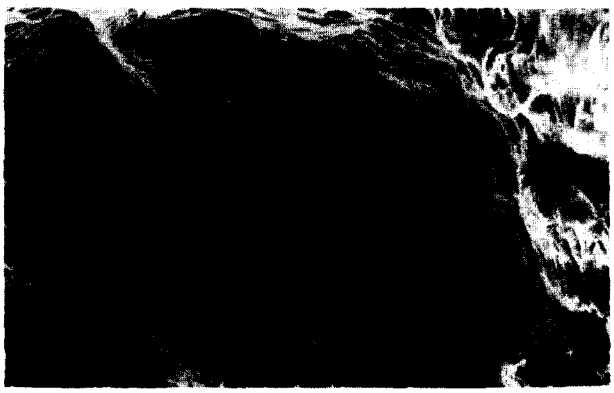


**Fig. 5.** SEM micrography. Coat of anhydrous (thenardite) form on the NT system ( × 700).

**Fig. 6.** SEM micrography. Mirabilite crystals formed after five crystallization cycles in the decohesioned surface in the NT system ( × 4000).

The surfaces of specimens subjected to forced hot and dry air circulation (temperature 60°C, relative humidity 30%) (Fig. 5 — NT system for example) in the climatic chamber became well coated with salt, the anhydrous form of the sulphate. The new formations on the surface can give rise, in the course of the cycles, to some degree of decohesion of the outer layer, with detachment of sand grains and/or cement matrix. However, much more deleterious is the decay which takes place in the bulk of the material where crystallization produces a decline in compressive strength, as already discussed with reference to Table 1.

Figure 6 shows a number of (monocline) mirabilite crystals that formed after five crystallization cycles on a fresh decohesioned specimen of the NT system. Here the presence of the decahydrated form of the salt is related to the local hygrometric conditions of the bulk (extremely high degree of saturation and considerable porosity) that is furthermore protected from the outside because of the extremely rapid formation of the salt coating as seen in Fig. 5. The conditions of the bulk of the systems rendered hydrophobic by polymer impregnation differ radically. Significant signs of deterioration are only observed around the 10th cycle (Table 1) and only brought about by a small number of cracked surfaces.

Figure 7 shows that the damage is caused by the formation of a few large crystals ('wedge' effect) of the anhydrous form (orthorhombic) of the sulphate. Here crystallization differs substantially from the untreated specimen because the matrix absorbs the solution to a lesser degree and its circulation (which in the untreated specimen causes the flow towards the surface and hence its coating as well as the large number of crystal nuclei) is slowed down considerably, being water repellent. Thus, the salt solution can only work its way into existing cracks produced, for instance, by shrinkage or casting in successive stages, which because of their size are not sufficiently protected by the water repellents, thus creating suitable sites for the formation of a limited number of (anhydrous) orthorhombic crystal seeds.

The system admixed with latex proved the most resistant to the stresses of a series of crystallization cycles in the sulphate solution (Table 1).

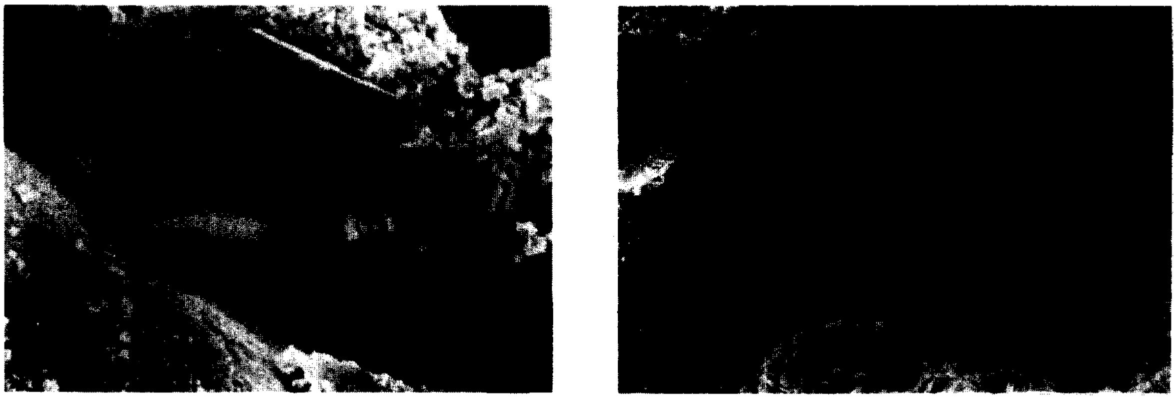


**Fig. 7.** SEM micrography. Thenardite crystals in cracks on the B (left) and C (right) systems ( × 840).

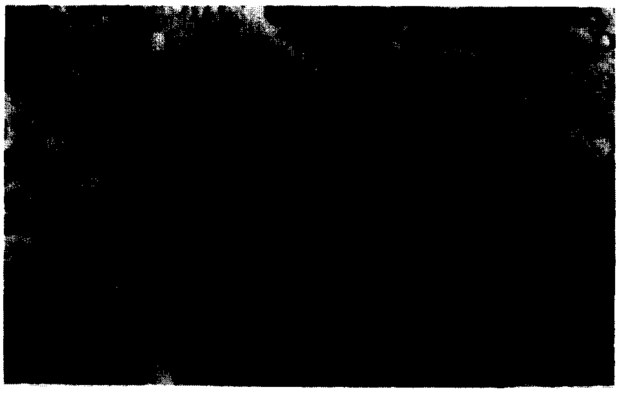


**Fig. 8.** SEM micrography. Thenardite crystals on the L system ( × 1250).

Examination under the SEM revealed in fact (Fig. 8) the presence of a small number of orthorhombic seed crystals, usually ill-formed and smaller than those observed in the polymer impregnated systems. The superior mechanical properties and 'elasticity' of the matrix containing latex can reasonably be regarded as the main reasons that prevent deterioration from setting in.[7–9]

## CONCLUSIONS

(1) Sodium sulphate is capable of producing significant deterioration in a plain hydraulic lime based plaster after just a few crystallization cycles. In this case decahydrated (mirabilite) crystals form that are also more deleterious because they have higher specific volume than the anhydrous form (thenardite).

(2) Impregnation with water-repellent substances provides an effective barrier against the penetration of the sulphate solution provided the plaster is perfectly sound. Should discontinuities be present (such as cracks caused by shrinkage or applications performed in successive stages) then these need to be filled prior to treatment. This may be a valid solution when renovating plasterwork in historical buildings. In fact it is the existence of cracks not adequately protected by the water repellents that allow the crystallization of the sodium sulphate in the anhydrous form. The few seed crystals that do form tend to develop into large crystals that act as a wedge in the matrix, thus compromising the properties of the plaster.

(3) Undeniably the systems admixed with latex yield the best results. Their superior mechanical properties, also related to the fact that they are not so porous and that the polymer confers a certain elasticity, enable them to better withstand the stresses produced by the formation of sodium sulphate crystals in the anhydrous form but smaller than those observed in the systems described above. The plaster admixed with latex can thus be regarded as the best option when designing new plasters.

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