Pergamon

Cement and Concrete Research 33 (2003) 85–91

CEMENT AND CONCRETE RESEARCH

Physicochemical study of the alteration surface of concrete exposed to ammonium salts

Raoul Jauberthie[a,*], Frank Rendell[b]

[a]Laboratory GRGC Matériaux, INSA, 20 Av. des Buttes de Coësmes, CS 14315, 35043 Rennes, France
[b]University of East London, Longbridge Road, Barking, London, RM8 2AS, UK

Received 20 October 2001; accepted 9 July 2002

Abstract

The storage of chemicals in concrete silos often presents durability problems due to chemical attack, the high concentration encountered inevitably causes severe conditions. The aim of this paper is to examine the physicochemical changes that occur in concrete exposed to ammonium salts, notably ammonium sulphate and nitrate, which are noted for their aggressivity. The modification to mortar surfaces is examined with X-ray diffraction (XRD) and with SEM. Mortar immersed in ammonium sulphate is covered with gypsum needle-like crystals and undergoes rapid cracking when removed from the solution and washed. In the case of mortars immersed in ammonium nitrate solutions, there is rapid decalcification, accompanied by strength loss, due to the solubilization of calcium. It is also observed that the mortar surface is covered with rhombic calcite, which is attributed to the reaction between liberated calcium and CO_2 in the water.

Keywords: Durability; SEM; X-ray diffraction; Sulphate; Nitrate

1. Introduction

In previous works, the deterioration of concrete in sulphate environments, solutions of sulphuric acid and ammonium sulphate was studied [1–3]. The modification of the pore structure, due to chemical dissolution or precipitation [4] in the cement-rich skin of the mortar [5], plays a key role in the kinetics of the deterioration. The reaction between certain ammonium salts and concrete has long been recognised as potentially aggressive, ammonium chloride, sulphate and carbonate being considered the most harmful, whereas ammonium carbonate, oxalate and fluoride being harmless [6]. Most codes, e.g. EN 206, would consider concentration in excess of 60 mg NH_4^+/l as an extreme exposure condition. Ammonium compounds are found to occur in sewage, typically 30 mg NH_4^+/l; certain industrial wastewater and sludge treatment processes will have concentrations up to 500 mg NH_4^+/l. The most severe conditions that are likely to exist are found in the storage silo where an ammonium compound is stored in bulk [7].

In this paper, the action of two solutions of ammonium salts on cement mortars is considered: ammonium sulphate and ammonium nitrate. The mortars are manufactured with two different Portland cements (ordinary Portland cement [OPC] and sulphate resistant Portland cement). The mortars are stored in the ammonium solutions and every 4 weeks are washed under a water jet. The modifications to the superficial layer of the mortars during immersion are examined with SEM/EDS and by X-ray diffraction (XRD).

2. Methodology

2.1. Test samples

An experimental programme is conducted with the aim of observing the deterioration of OPC mortars immersed in ammonium sulphate solution and ammonium nitrate solution. The mortars used in the test are standard mortars conforming to EN196; the aggregate/cement ratio being 3.0 and the aggregate type being a standard sand conforming to ISO 679. The first cement type used (referenced as

---

[*] Corresponding author. Tel.: +33-2-23-23-83-14; fax: +33-2-23-23-83-96.

E-mail address: Raoul.Jauberthie@insa-rennes.fr (R. Jauberthie).

0008-8846/03/$ – see front matter © 2003 Elsevier Science Ltd. All rights reserved.
PII: S0008-8846(02)00929-8

Cement I) is an OPC—CEM 1 52.5 manufactured in Lafarge at Saint-Pierre-La-Cour (France). The second cement type used (referenced as Cement II) is a sulphate resisting cement—CEM 1 52.5 PM (PM—suitable for marine works, i.e. sulphate resisting), manufactured in Lafarge at Le Havre (France). An analysis of the cement types is summarised in Table 1. Table 2 shows the potential mineralogical composition of Cements I and II, this being calculated by the Bogue equations [8] using the oxide analysis set out in Table 1.

A siliceous sand conforming to CEN EN 196-1, ISO 679 was used in all the mortars, this sand having rounded grains and a silica content of at least 90%. The French standard mortar mix, with a water-to-cement ratio of 0.5, was batched in accordance with NF P 15-411. The test samples $40 \times 40 \times 160$ mm^3 were made according to the following protocol:

- Mortar was compacted in two equal layers using a vibrating table.
- The samples were then conserved at 100% RH, 20 °C for 24 h before striking.
- The samples were stored in an air-conditioned room (20 °C, 50% RH) until their mass was stabilised.

A first series of samples were then immersed in 0.25 mol/l ammonium solutions for a period of 2 years under static conditions. The size of the bath in which the samples were stored was $120 \times 120 \times 240$ mm^3. At the end of each month, the samples were removed from the bath and washed with a water jet, the solution in the bath was not changed. A second series is stored in the same solution but without washing.

3. Physicochemical study

3.1. Visual observations

Fig. 1 shows the layout of the samples in the solutions after 4 months of exposure to the ammonium solutions. The following observations were noted.

Table 1
Chemical composition of the cements (%) used in the tests

Cement	I	II		I	II
Insoluble	0.2	0.1	SO_3	3	2.75
SiO_2	19.7	21.5	S^-	<0.01	<0.01
Al_2O_3	4.9	3.6	Cl^-	0.01	0.02
Fe_2O_3	2.8	4.25	CO_2	1.9	0.1
TiO_2		0.17	Free CaO	1.4	0.45
Mn_2O_3		0.1	Active alkalines		0.3
CaO	64.5	64.9	Loss on ignition	2.7	1.1
MgO	0.9	0.75			
K_2O	0.9	0.26	Gypsum content	5	3.8
Na_2O	0.2	0.1			

Table 2
Mineralogical composition (%) for the Portland cements I and II

Composition	I	II	Composition	I	II
C_3S	79.84	73.19	C_3A	9.10	2.5
C_2S	2.22	10.50	C_4AF	9.41	13.78

3.1.1. Ammonium nitrate solution

- There was a white deposit on the surface of the ammonium nitrate solution and a similar, but very light, deposit on the surface of the samples.
- Cracking during washing (Series 1) did not occur until after 1 year. No cracking was observed in the samples that were not washed (Series 2).

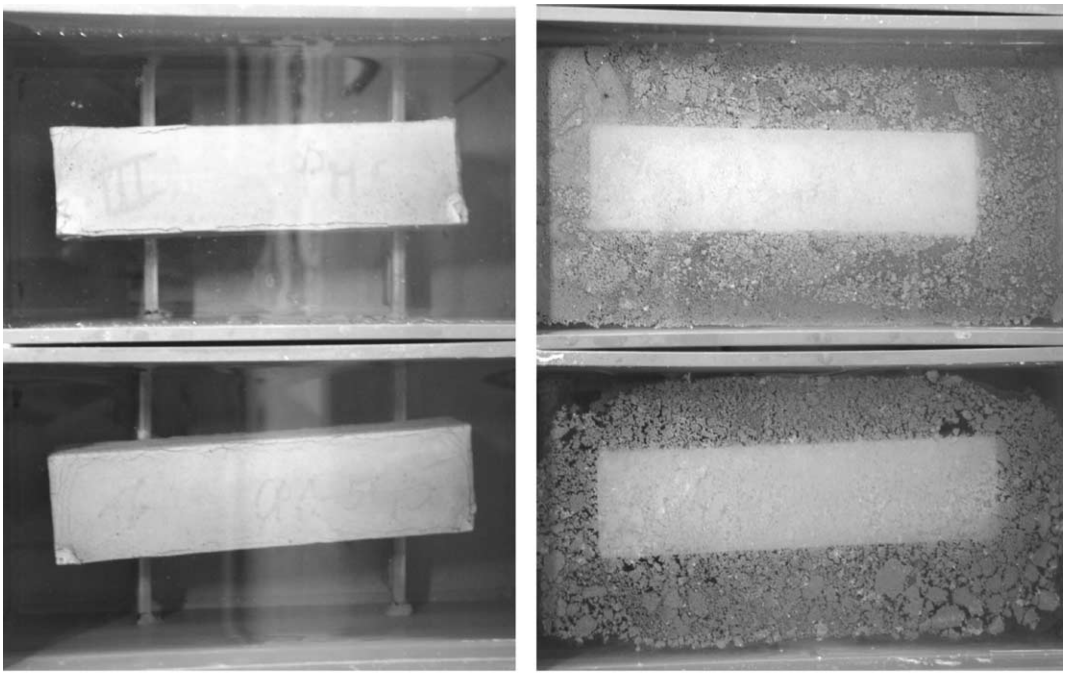
3.1.2. Ammonium sulphate solution

- In the ammonium sulphate solution, needle-like crystals were found on the periphery of the bath and covering the mortar sample.
- In the case of the samples that were not washed (Series 2), the needle-like crystals continued to grow. When washed (Series 1), most of these crystals were destroyed and cracking occurred.
- The initial pH in the baths was of the order of 6, the rate of increase depended on the cement type: relatively rapidly (CEM II) or slowly (Cement Fondu). Crystallisation starts at a pH of the order of 8.5; the value then remains stable.
- The mortar, in the sulphate solution, developed cracks parallel to the edges of the samples.

3.2. Analysis of surface deposits

The deposits formed on the surface of the mortar samples (Series 2) were carefully removed by scraping, care being taken not to remove any of the mortar matrix. These deposits were ground to a powder and analysed by XRD. The diffraction diagrams were obtained by step scanning the powder sample, the X-ray wavelength being CuKα. Fig. 2 shows the diagrams relating to the surface deposits for samples immersed in ammonium sulphate and Fig. 3 relates to those from the mortar immersed in ammonium nitrate.

The surface deposit found on the two mortar samples immersed in ammonium sulphate is of a needle-like form. The XRD analysis (Fig. 2) shows that gypsum ($CaSO_4 \cdot 2H_2O$) is the only phase present. The Miller Indices for the atomic planes are noted on the diffraction diagram. The intensities do not correspond to the ICDD powder diffraction files (PDF) [9], this being due to the form of the mineral which, even after grinding, had an elongated axis. The intensities for the planes (020) and (040) are abnormally high and for others are abnormally weak. This is a consequence of the orientation of the crystals in the sample; the elongated



Ammonium sulphate

Ammonium nitrate

Fig. 1. Mortar samples in ammonium solution after 4 months of exposure.

c-axis of the crystals' unit cell being parallel to the face of the sample in the diffractometer.

The XRD analysis of the surface formations found on the mortars immersed in ammonium nitrate solution (Fig. 3) consists of calcite ($CaCO_3$) with a small quantity of another form of calcium carbonate, vaterite, (μ-$CaCO_3$). The solid phase that was found on the liquid surface of the bath containing the ammonium nitrate solution was also found to be a mixture of calcite and vaterite. The scanning electron microscope micrographs of the surface deposits found on the surface of the mortars exposed to ammonium sulphate are shown in Fig. 4.

SEM examination of the needle-like crystals formed in contact with ammonium sulphate shows an almost perfect crystal, often with a hexagonal section with side widths of the order of 20 μm and an elongation of up to 5 mm. These crystals are similar to trapezoidal Haüy gypsum, with faces developed in the planes (010), (110) and (103).

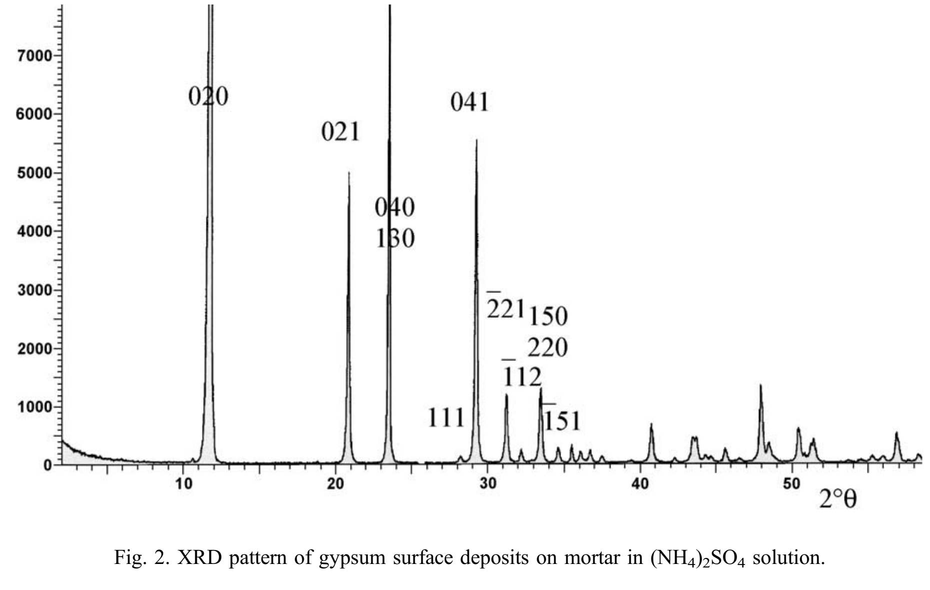


Fig. 2. XRD pattern of gypsum surface deposits on mortar in $(NH_4)_2SO_4$ solution.

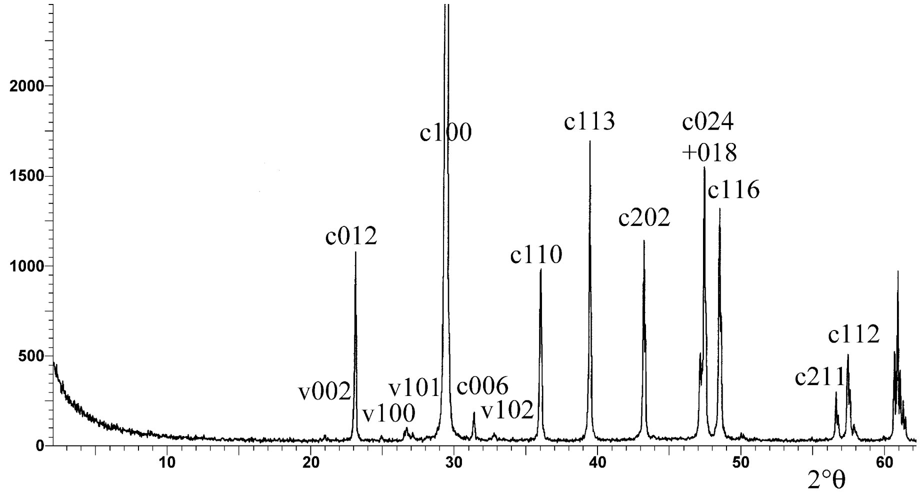


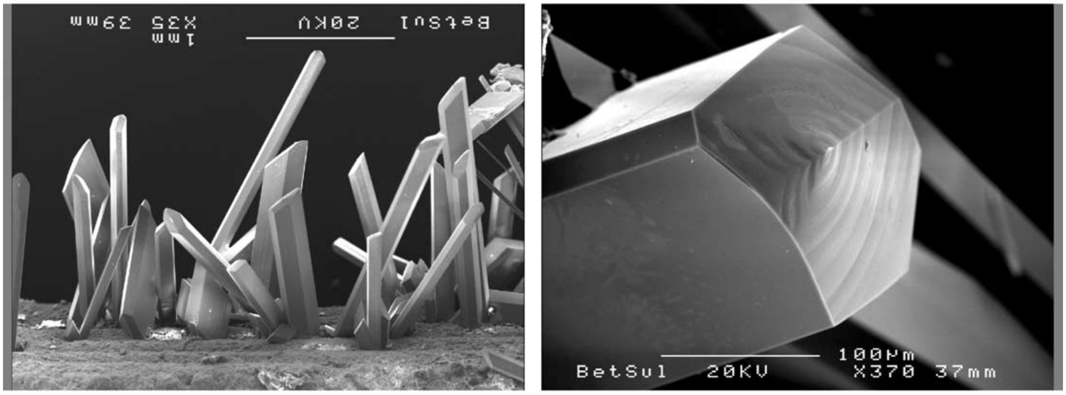
Fig. 3. XRD pattern of calcite (c) and vaterite (v) surface deposits on mortar in NH_4NO_3 solution.

Some of the crystals are twinned and the cleavage plane (010) is clearly seen in the crystal shown in Fig. 4d. The development of these crystals seems in all points to be similar to the naturally occurring larger crystals, which indicates that their growth takes place from a limited number of germs. The cations Ca^{2+} can migrate in a solution over a relatively long distance (the pH of the solution being almost neutral), thus developing the crystal faces. The SEM observations of an internal section of the sample are shown in Fig. 5.

A specific monocrystal X-ray analysis (Laüe) of gypsum (similar to that shown in Fig. 4) taken from the surface of the mortar confirms that the *c*-axis is elongated; the parameters determined show that the structure is monoclinic:

a : general aspect (x35)

b : crystal extremity (x370)



c : growth of a crystal (x1200)

d : cleavage plane (x300)

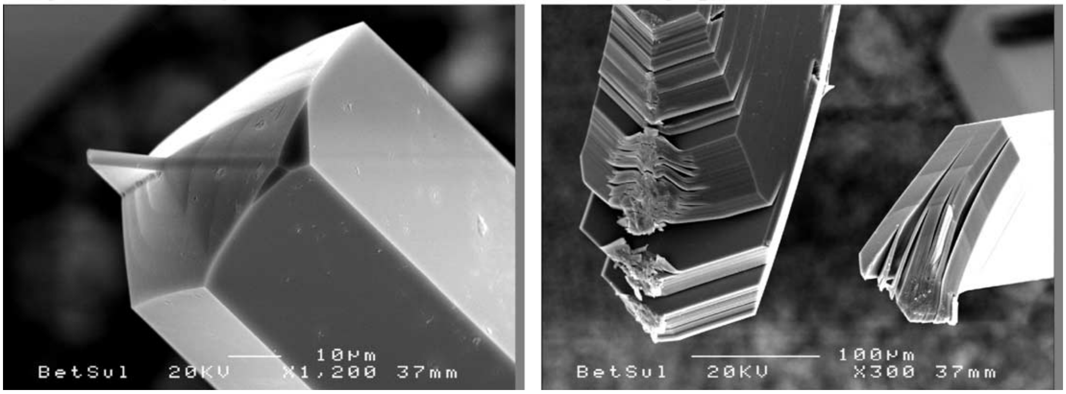


Fig. 4. SEM micrographs of gypsum found on the surface of the samples immersed in $(NH_4)_2SO_4$ solution.

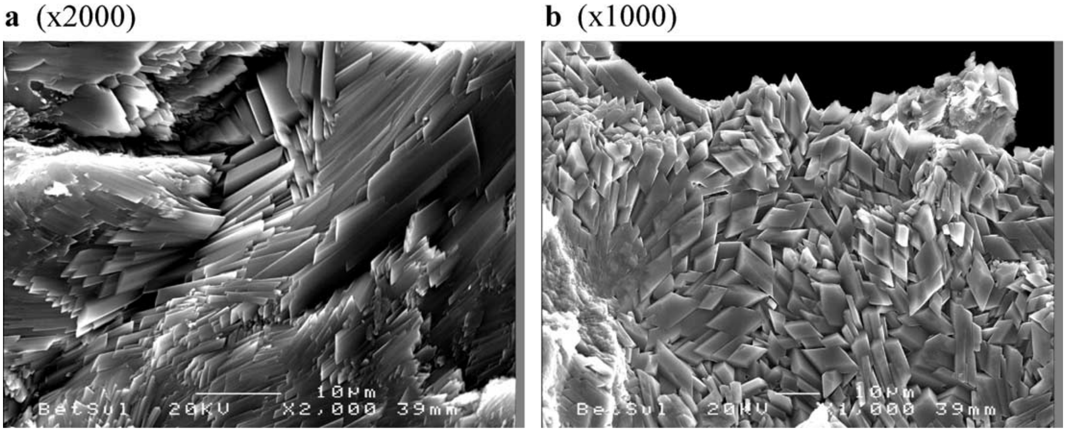

a (x2000) **b** (x1000)

Fig. 5. SEM micrographs of gypsum in the interior of the samples immersed in $(NH_4)_2SO_4$ solution.

$a = 0.567(1)$ nm, $b = 1.523(3)$ nm, $c = 0.625(1)$ nm and $\beta = 114.3(2)°$. These values are in close agreement to the ICDD PDF values (0.56776 nm, 1.52079 nm, 0.62845 nm and 114.09°).

The deterioration of the crystal structure is pronounced to a depth of 2 or 3 mm. Microanalysis (EDS linked to SEM) shows the presence of sulphur only in fissures and pores. The crystal form (Fig. 5) is different from that found on the exterior of the sample; they are much smaller and interlocking, however, the chemical composition confirms that they are gypsum.

It has previously been shown by XRD that mortar in contact with ammonium nitrate solution is covered with a layer of calcium carbonate. The SEM micrographs of the crystals are shown in Fig. 6.

The chemical composition of the crystalline surface deposit was confirmed as calcium carbonate by microanalysis. The crystals of calcite and vaterite are very small and

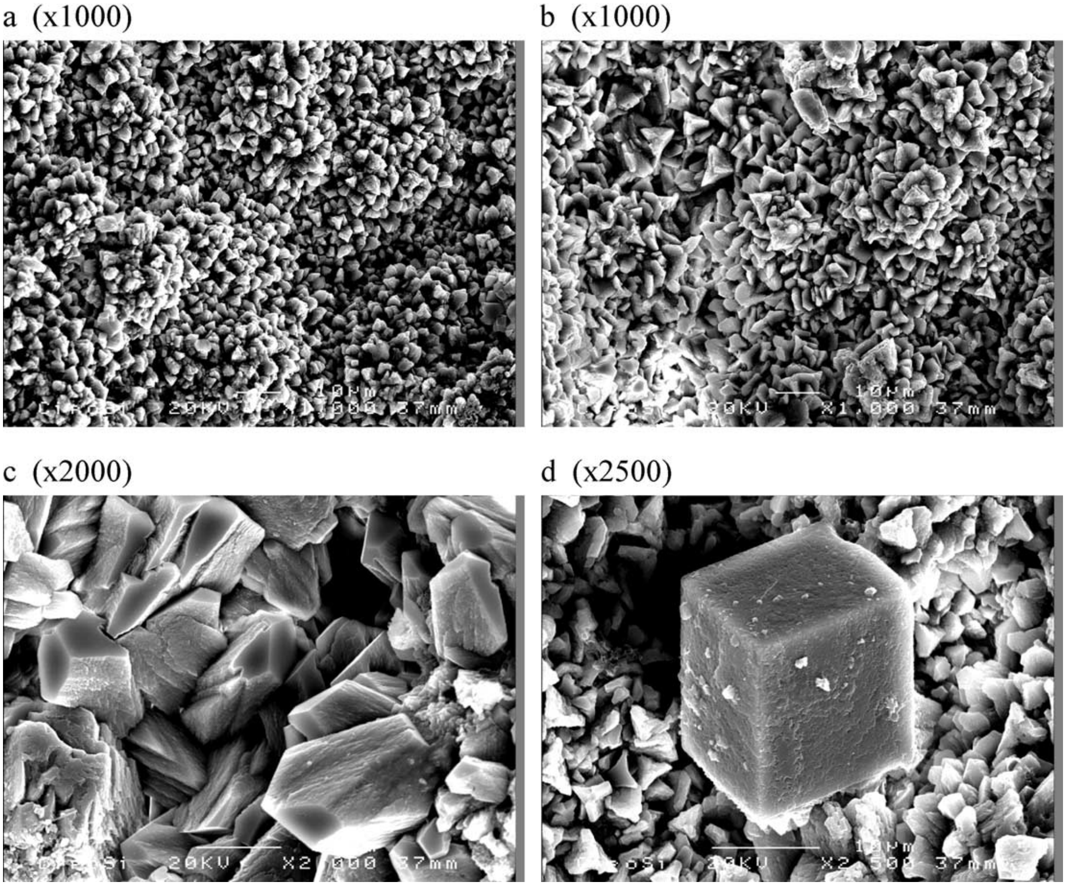

a (x1000) b (x1000) c (x2000) d (x2500)

Fig. 6. SEM micrographs of superficial calcite deposits on the samples immersed in NH_4NO_3 solution.

of the order of several micrometers (see Fig. 6a and b), the development planes of the crystals are rarely well defined, and only a few rhomboids are visible (Fig. 6d). The composition of the white deposit formed on the liquid surface of the ammonium nitrate bath was also confirmed as being calcite by microanalysis.

It was noted that samples immersed in the sulphate solution cracked during the monthly washing (Series 1). This cracking occurred rapidly, within minutes, during the washing process and was localised along the edges and the corners of the sample. SEM examination of the crack sites, taken after washing, failed to indicate the formation of any new phases. In the case of samples that had been cracked and reimmersed in the solution, gypsum crystals were found in the cracks.

In the case of the samples immersed in ammonium nitrate solution, initially no cracking was observed during the washing cycles. However, after a 1-year immersion period, cracking was observed to occur during the washing cycle. This delay in the onset of the phenomenon may be explained by the much slower kinetics involved in the nitrate reaction.

4. Discussion

The type of OPC (ordinary or sulphate resisting) does not seem to have an effect on the degree of mortar deterioration suffered during exposure to ammonium nitrate or sulphate solutions.

A sparse superficial deposit of needle-like gypsum crystals covers the surface of mortar immersed in ammonium sulphate. The Ca^{2+} ions pass into solution and combine with the SO_4^{2-} ions to form gypsum. The germs for the crystal growth are probably zones of portlandite; this explains the sparse covering of the crystals over the surface. With the relatively low solubility of gypsum at a neutral pH (0.24 g/l), this formation of gypsum crystals is possible.

The surface deposits found on the mortars exposed to ammonium nitrate solution are identified as small crystals of calcite. These deposits are also found on the liquid surface in the bath. The calcium ions pass into solution and combine with CO_3^{2-} ions in the solution to form calcite. As in the previous case, the occurrence of crystals is sparse and again the germs for the crystal formation are probably zones of portlandite. However, the quantity of carbon dioxide dissolved in the solution is small, and when this is consumed the reaction can only continue at the air–solution interface where CO_2 is absorbed by diffusion. The solubility of calcium nitrate is high, 120 g/l, explaining why crystallisation of this phase does not occur, only the calcium carbonate precipitates (solubility 0.0014 g/l) if CO_3^{2-} ions are present.

The samples stored in ammonium sulphate for several months become covered with the surface coating of needle-like gypsum crystals; if the sample is washed immediately after removal from the solution, rapid cracking is observed. The samples immersed in the ammonium nitrate did not initially exhibit cracking during washing, however, the phenomenon was observed in samples after a 1-year immersion period; this suggests that the reaction kinetics are much slower in this case.

The mechanisms involved in the ammonium salt–cement paste reactions are discussed by Torrenti et al. [10]. They propose that ammonium in a basic environment dissociates into ammonium gas and leads to the dissolution of portlandite according to the following reaction:

$$Ca(OH)_2 + 2NH_4NO_3 \rightarrow Ca^{2+} + 2OH^- + 2H^+ + 2NH_3 + 2NO_3^-$$

Torrenti et al. [10] consider the equilibrium between ammonium (NH_4^+) and aqueous ammonium (NH_{3aq}) and raise the following points:

- When the pH <9.25 ammonium NH_4^+ is the dominant species in the solution.
- When the pH >9.25 ammonium NH_{3aq} is the dominant species in the solution.
- There is an equilibrium between aqueous and gaseous ammonium dependent on partial pressure and concentration.
- In the confined conditions (interstitial solution in the cement paste), the gaseous ammonium will not cause cracking of the material or be liberated. Therefore, the gaseous ammonium can be disregarded.

In our studies, a series of samples was conserved in a bath of ammonium nitrate for 2 years (Series 2). While in the bath no cracking was apparent, additionally, when the samples were transferred to a water bath (no washing and no agitation of the water), no cracking occurred. These observations are in agreement with the views of Torrenti et al. [10].

Within the voids, the NH_{3aq} is in a partial or total gaseous form due to the high pH; this may be responsible for the swelling. In a previous 6-month study of mortars swelling due to ammonium sulphate solution [11], it was noted that a maximum swelling of 0.3 mm/m occurred. This swelling was totally reversed, at the end of the test, when the samples were immersed in water. In these tests, it was also noted that there was a smell of ammonium gas when the samples were fractured in strength testing. In both of these studies, no new crystal phases were identified in the mortar matrix, thus adding weight to the argument that gaseous ammonium contributes to the sample swelling.

The phenomenon of rapid sample cracking during washing under a water jet (Series 1) involves a dynamic situation and therefore cannot be explained by the previous hypothesis.

When the mortar sample is in the bath, the interstitial solution has a high pH and the gaseous ammonium will not cause cracking or be liberated. When the sample is taken from the bath and immediately placed under a water jet, there will be a rapid reduction in pH close to the surface, the NH_{3aq} or NH_{3gas} in this zone converts to NH_4^+ thus provoking a reduction in interstitial pressure. The rapid kinetics involved at the surface does not allow time for the core to decompress, and therefore, a stress gradient builds up close to the surface. The tensile stresses induced in the surface zone manifest themselves as cracking at the points of stress concentration, notably at the edges of the prisms.

5. Conclusions

Ammonium salts are known to produce significant damage to concrete. This study demonstrates that solutions of ammonium nitrate and ammonium sulphate produce different superficial deposits and mechanisms of deterioration. The nitrate produces a formation of carbonate at the surface and a decalcification of the mortar occurs due to the high solubility of calcium nitrate. The sulphate solution produces a surface deposit of needle-like gypsum crystals having low solubility. Severe mortar deterioration takes place when OPC mortars are washed after immersion in ammonium sulphate solution. This takes the form of rapid cracking due to surface shrinkage, and is possibly linked to the release of ammonium gas from the cement matrix. Both of the ammonium salts studied are capable of causing significant damage to concrete.

Ammonium nitrate produces rapid decalcification, with possible implications as to the depassivation of reinforcement. Ammonium sulphate causes strong sample swelling, which will inevitably weaken the cement matrix, and this deterioration is rapidly accentuated by surface washing. It is therefore suggested that cleaning by jetting should not be used on concrete exposed to ammonium sulphate.

Acknowledgements

We wish to thank Prof. Olivier Guillou, Director of “Chimie Inorganique des Lanthanides” and Florence Le Dret for their efforts and assistance with the laboratory work and analyses.

References

[1] R. Jauberthie, I. Robu, Ch. Lanos, F.X. Mortreuil, J.P. Camps, Caractérisation par diffraction X de l’attaque superficielle de pâtes de ciment en milieu sulfatique, J. Phys. IV 8 (1998) Pr5-519–Pr5-523.
[2] R. Jauberthie, Ch. Lanos, M. Temimi, M. Laquerbe, F. Rendell, Concrete damage due to sulphate attack, Proceedings of Second International Conference on Concrete under Severe Conditions, Tromso, Norway, vol. 1, E & FN Spon, London, 1998, pp. 232–241.
[3] R. Jauberthie, M. Laquerbe, F. Rendell, Dégradation de mortiers sous différents milieux sulfatiques, Ann. Bâtim. Trav. Publics 4 (1999) 21–28.
[4] F. Rendell, R. Jauberthie, J.P. Camps, The influence of surface absorption on sulphate attack, in: R.K. Dhir, M.J. McCarthy (Eds.), Proceedings of Creating with Concrete, Concrete Durability and Repair Technology, Dundee, Thomas Telford, London, 1999, pp. 197–208.
[5] P.C. Kreijger, The skin of concrete: Composition and properties, Mater. Struct., Res. Test. 17 (100) (1984) 275–283.
[6] J. Biczok, Concrete Corrosion and Concrete Protection, 8th ed., Akademiai Jiadl, Budapesta, 1972.
[7] New Civil Engineer, 5th July 2001.
[8] R.H. Bogue, La chimie du ciment Portland, Edition Eyrolles, Paris, 1952.
[9] Powder Diffraction Files, Joint Committee on Powder Diffraction Standard, International Centre for Diffraction Data, 1601 Park Lane, Swarthmore, PA 19081, USA.
[10] J.M. Torrenti, O. Didry, J.P. Ollivier, F. Plas, La dégradation des bétons, Hermes Sciences Publications, Paris, 1999, pp. 27–29.
[11] F. Rendell, Le comportement des bétons dans les systèmes d’assainissement, Thèse No d’ordre D00-01 INSA Rennes France, January 2000.