Pergamon

CEMENT AND CONCRETE RESEARCH

Cement and Concrete Research 29 (1999) 1929–1935

Sorel's cement mortars
Decay susceptibility and effect on Pentelic marble

P. Maravelaki-Kalaitzaki[a,*], G. Moraitou[b]

[a]25th Department of Prehistoric and Classical Antiquities, Chania, Ministry of Culture, 21 Chalidon Str., Chania 73100, Greece
[b]Directorate for Conservation of Antiquities, Athens, Ministry of Culture, 4 Dioskouron Str., Athens 10355, Greece

Received 28 May 1999; accepted 7 September 1999

Abstract

To evaluate the decay susceptibility of mortars of magnesium oxychloride cement used for the restoration of blocks of Pentelic marble of the Athens Acropolis monuments, mineralogical and physicochemical analyses were performed on samples from different exposure conditions. The decay of mortars depends mainly on environmental influences. The observed decay forms and the responsible processes are: (1) expansion of mortars leading to break-up of the marble as a result of the carbonation of oxychloride phases; (2) disintegration of mortars exposed to washing and staining of marble due to the release of magnesium chloride; and (3) in mortars sheltered from rain action, efflorescence due to the sulfation of mortar constituents that yields hydrated sulfate salts of magnesium and calcium with different water molecules; their hydration, crystallization, and rehydration during microclimatic shifts imply volume changes and the release of corrosive solutions leading to formation of cracks and staining. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Magnesium oxychloride cement; Carbonation; Sulfation; Efflorescence; Cracks

1. Introduction

Magnesium oxychloride or Sorel's cement (MgO-$MgCl_2$-H_2O system) has four reaction products, which are designated by the number of $Mg(OH)_2$ moles appearing in its formula in relation to each $MgCl_2$ mole, as follows: $2Mg(OH)_2 \cdot MgCl_2 \cdot 4H_2O$ (F2); $3Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$ (F3); $5Mg(OH)_2 \cdot MgCl_2 \cdot 5H_2O$ (F5); and $9Mg(OH)_2 \cdot MgCl_2 \cdot H_2O$ (F9) [1–3]. According to the phase diagram, the ternary oxychloride phases are dependent on the $MgO/MgCl_2$ molar ratio and are unstable in water, dissociating to magnesium hydroxide and magnesium chloride solutions [4]. Form 3 (F3) and form 5 (F5) of oxychloride are the only ones stable at room temperature ($<100°C$) [5]. Sorrell and Armstrong [6] described the importance of MgO reactivity in the formation of the oxychloride phases.

Mortars based on magnesium oxychloride cement (MOC) were used on the Acropolis monuments and sculptures for restoring damaged marble from the end of the last century until 1975 [7]. MOC has been chosen by virtue of its resistance to accumulation of static charge and its attractive, marblelike appearance; compared to Portland cement it does not need wet curing and has high fire resistance, low thermal conductivity, and good resistance to abrasion. Magnesium oxychloride also bonds very well to a variety of inorganic and organic aggregates, such as marble flour, sand, and gravel, giving a cement that has high early strength [1].

Some difficulty has been encountered in the use of oxychloride cement, however, especially for exterior applications as in the case of the Acropolis monuments. Problems of dimensional instability, lack of resistance to weathering, scaling and staining of the adjacent marble, and finally the release of corrosive solutions were severe in some cases and are not well understood [8,9].

This study provides insights into the reasons for the disintegration and appearance of cracks in the Sorel mortars used for restoration of sculptures of Pentelic marble, as well as reasons for flaking and staining of marble. In addition, this paper reports on reaction studies both in out- and indoor environments for the system MgO-$MgCl_2$-H_2O and relates these data to the decay susceptibility of the oxychloride cements.

2. Materials and methods

Sampling of the Sorel cement mortars used for restoration purposes on the Acropolis monuments ensured representative samples of all different exposure conditions. The examined mortars were prepared at the time of use by mix-

---

* Corresponding author. Tel.: +30-821-44418; fax: +30-821-94498.
E-mail address: Noni.Maravelaki@keepka.culture.gr (P. Maravelaki-Kalaitzaki)

0008-8846/99/$ – see front matter © 2000 Elsevier Science Ltd. All rights reserved.
PII: S0008-8846(99)00197-0

ing caustic-calcined magnesia (MgO) and magnesium chloride with water excess, which was necessary for workability of the paste, along with calcite powder ($CaCO_3$) and sand [10]. Intensive efflorescence was noted on mortars used on areas protected from direct rain action, such as under porticoes, architraves, etc. In some cases the efflorescence extends to the adjacent marble.

In this work, samples of mortars and efflorescence were studied to detect chemical transformation of the MOC by various methods:

- The crystalline phases of different samples were identified by X-ray diffraction analysis (XRD) with a Siemens D500 automatic equipment (Siemens, München, Germany) coupled to a graphite monochromator for copper Kα radiation.
- Infrared spectroscopic analysis (FTIR) revealed the inorganic and organic compounds present in the mortar and efflorescence. For the FTIR analysis 1 mg of sample was homogenized with 0.2 g of KBr and the disks formed were examined in an FTIR spectrophotometer (Nicolet 20SXC, Madison, WI, USA) in an absorbance range between 4000 and 400 cm^{-1}. The minerals were identified according to Farmer [11].
- Environmental scanning electron microscopy (ESEM)/energy dispersive analysis (EDX) (Philips XL30, Eindhoven, The Netherlands) was used to examine the microstructure and the texture, and also was used for carrying out X-ray mapping.
- Thermal gravimetric analysis/differential scanning calorimetric analyses (TG/DSC, Netzsch Sta 1090, Selb, Germany) also were performed to verify the nature of mortar constituents by an appropriate analytical procedure. Samples were heated in static air atmosphere to a temperature of 1400°C at a rate of 10°C min^{-1} to simultaneously obtain the TG and DSC traces.

3. Results

The XRD pattern of an outdoor Sorel mortar sheltered from direct rain action is shown in Fig. 1. The major mineral phases identified in these mortars are calcite, magnesium oxychlorocarbonate [$Mg(OH)_2 \cdot 2MgCO_3 \cdot MgCl_2 \cdot 6H_2O$], and traces of F5 and F3. This result is consistent with previous studies indicating that F5 crystallizes more rapidly than the F3 phase; however, after a long period of time F5 is transformed into F3, which reacts rapidly with atmospheric CO_2 to form oxychlorocarbonate [5,12,13]. The infrared spectroscopic analysis also revealed magnesium chlorocarbonate as the main mineral phase followed by gypsum ($CaSO_4 \cdot 2H_2O$), epsomite ($MgSO_4 \cdot 7H_2O$), and potassium nitrate (KNO_3) (see also below).

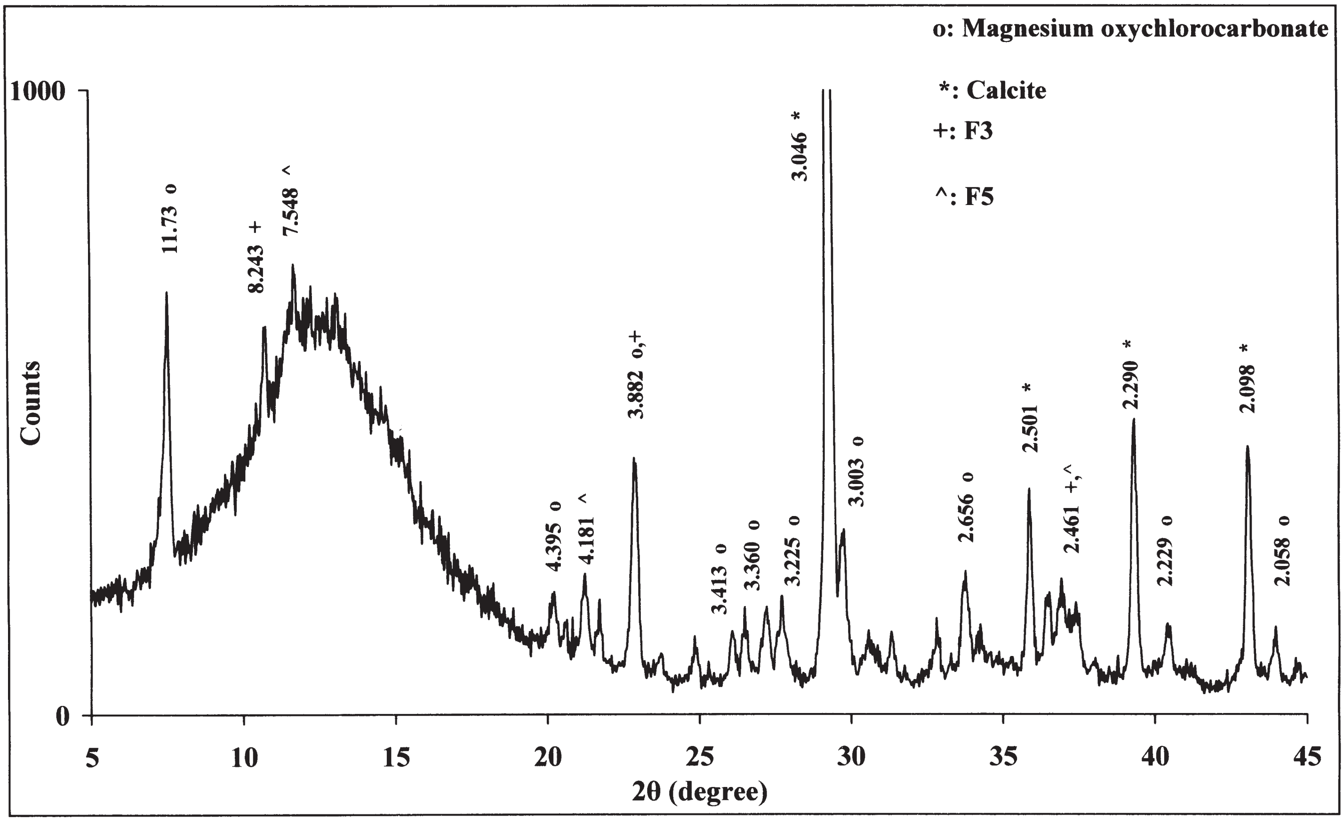

Fig. 1. XRD pattern of an outdoor mortar sheltered from direct rain action, with calcite (5-0586), magnesium oxychlorocarbonate (7-0278), and traces of F5 (according to Deng and Zhang [18]) and F3 (7-0412).

In Fig. 2, the curves a and b show the results of XRD analysis of the efflorescence formed on the previous Sorel cement mortar. In the first case gypsum and calcite were detected (a), while the second efflorescence (b) consists mostly of hydrated magnesium sulfate salts, such as hexahydrite ($MgSO_4 \cdot 6H_2O$) and starkeyite ($MgSO_4 \cdot 4H_2O$). This fact clearly indicates that sulfates in the MOC pastes are associated with environmental influences.

XRD analysis of Sorel cement mortars used for sculptures displayed in the museum revealed F3 as the main mineral phase; oxychlorocarbonate, calcite, and traces of F5 were also seen. Thermogravimetric analysis also showed evidence of dehydroxylation of magnesium hydroxide in the range of 382 to 450°C, as well as decomposition of magnesium carbonate and calcium carbonate at 548 and 744°C, respectively.

Infrared spectroscopic results are also in accordance with the XRD and unlike previous outdoor mortars, sulfates were not detected in indoor samples. Fig. 3 shows the infrared spectra of Sorel cement mortars exposed in outdoor (a) and indoor (b) environment. In both spectra in Fig. 3 strong ab-

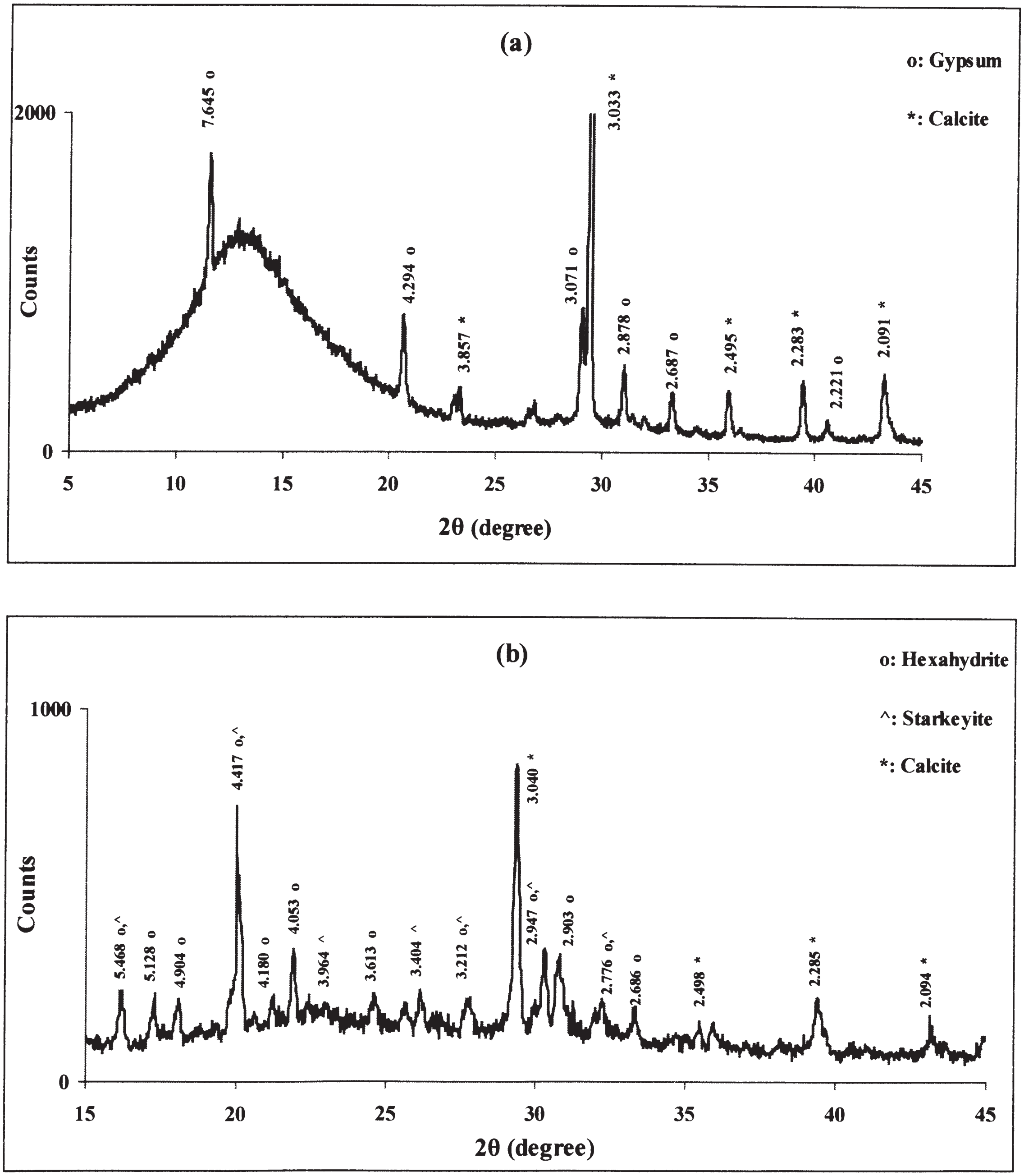

Fig. 2. XRD patterns of the efflorescence formed on (a) an outdoor mortar with gypsum (6-0046) and calcite (5-0586) and (b) an indoor sample with calcite (5-0586), hexahydrite (24-0719), and starkeyite (24-0720).

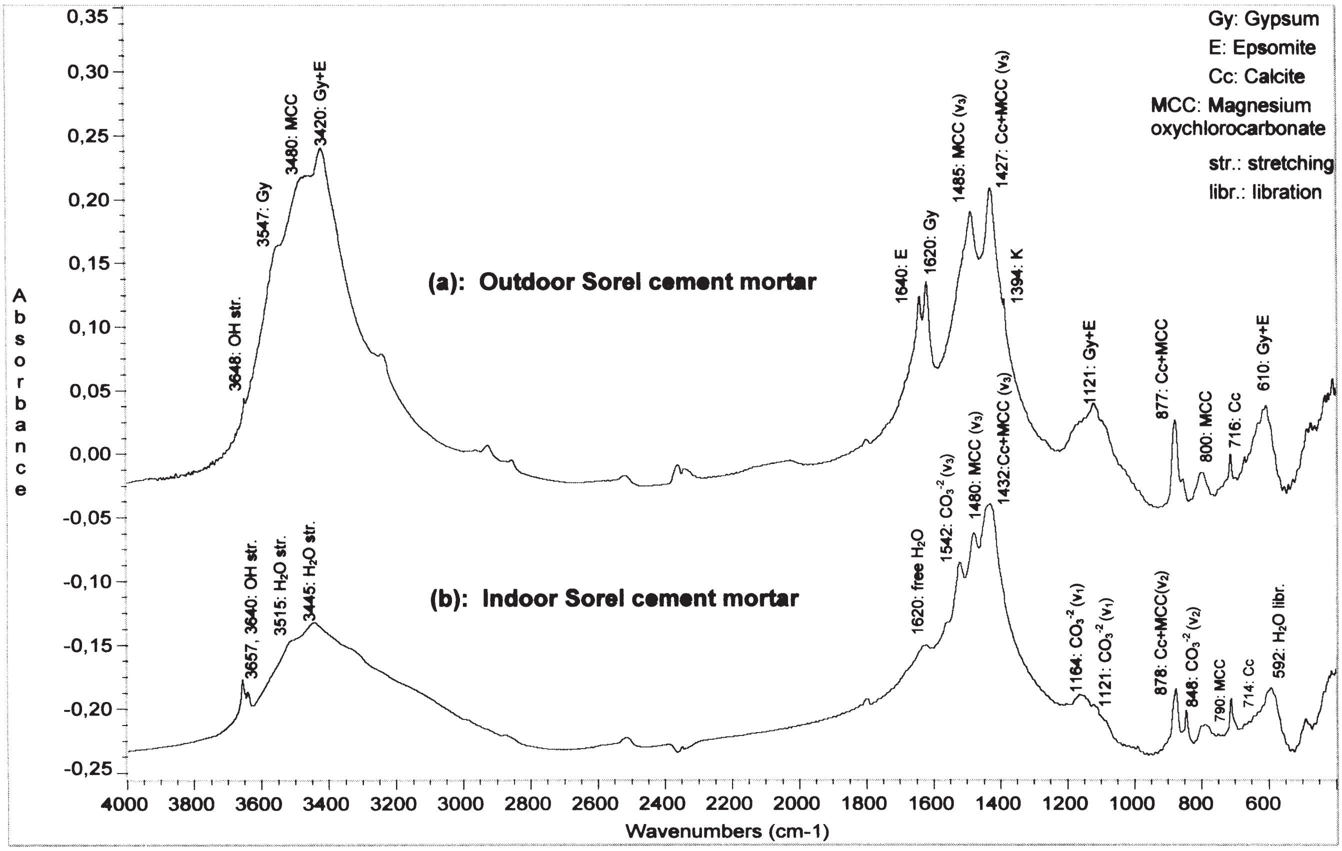

Fig. 3. Infrared spectra of (a) an outdoor Sorel cement mortar with gypsum (Gy), epsomite (E), calcite (Cc), magnesium oxychlorocarbonate (MCC), and (b) an indoor mortar with calcite (Cc) and magnesium oxychlorocarbonate (MCC), as well as OH-H_2O stretching vibrations and H_2O librations ascribed to oxychloride form F3.

sorption bands of the CO_3^{-2} internal modes can be observed, such as the distinct doubling of both ν_1 (at 1164 and 1121 cm^{-1}) and ν_2 (at 878 and 848 cm^{-1}), as well as the extra components of ν_3 (at 1542 and 1480 cm^{-1}), which do not exist in the spectra of ionic monocarbonates (e.g., in the spectrum of calcite). All previously mentioned additional bands could be accounted for by an assumption of two distinct CO_3^{-2} ions in the structure (Fig. 3b) [14]. The study of the spectral range 3700 to 3400 cm^{-1} allowed the attribution of OH and H_2O stretching vibrations along with the H_2O librations at 1620 and 592 cm^{-1} at the F3. The sulfate ion present in the outdoor sample displayed a group of intense stretching fundamentals near 1100 cm^{-1} and two or more bending modes near 600 cm^{-1} (Fig. 3a). The differences arising between the two spectra in the above regions suggest that sulfuric attack in outdoor exposed samples yields sulfate salts.

Further evidence concerning the composition of these mortars came from the ESEM micrograph and the ESEM-EDX maps of the elements Ca, Mg, and Cl, which are related to the detected mineral phases in the matrix (Fig. 4). The ESEM micrograph of the mortar (Fig. 4a), along with the distribution of Ca (Fig. 4b), testify that calcitic aggregates were embedded in the microcrystalline matrix of the binder. The magnesium and chlorine distributions in the binding material (see Figs. 4c and d, respectively) verify the magnesium oxychloride form detected in this mortar. In particular, in the lower part of Fig. 4c and among the calcitic aggregates, the magnesium accumulation suggests that either magnesium hydroxide or magnesium carbonate or both were present.

Mortars located on areas exposed to intensive rain action also were examined by X-ray diffraction. Calcite, barite, hydromagnesite [$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$], and quartz ($SiO_2$) were detected, as shown in Fig. 5. Hydromagnesite resulted from carbonation of the oxychloride phases after additional leaching of magnesium chloride. The aggregates used in these mortars contain calcite and quartz, while barite was been added in the initial paste to improve the resistance of MOC to water [15].

4. Discussion

The above analytical examinations clearly indicate the mechanism of the conversion of oxychlorides to new phases. The more stable of the oxychlorides, F5 and F3, were transformed into oxychlorocarbonate, which is much

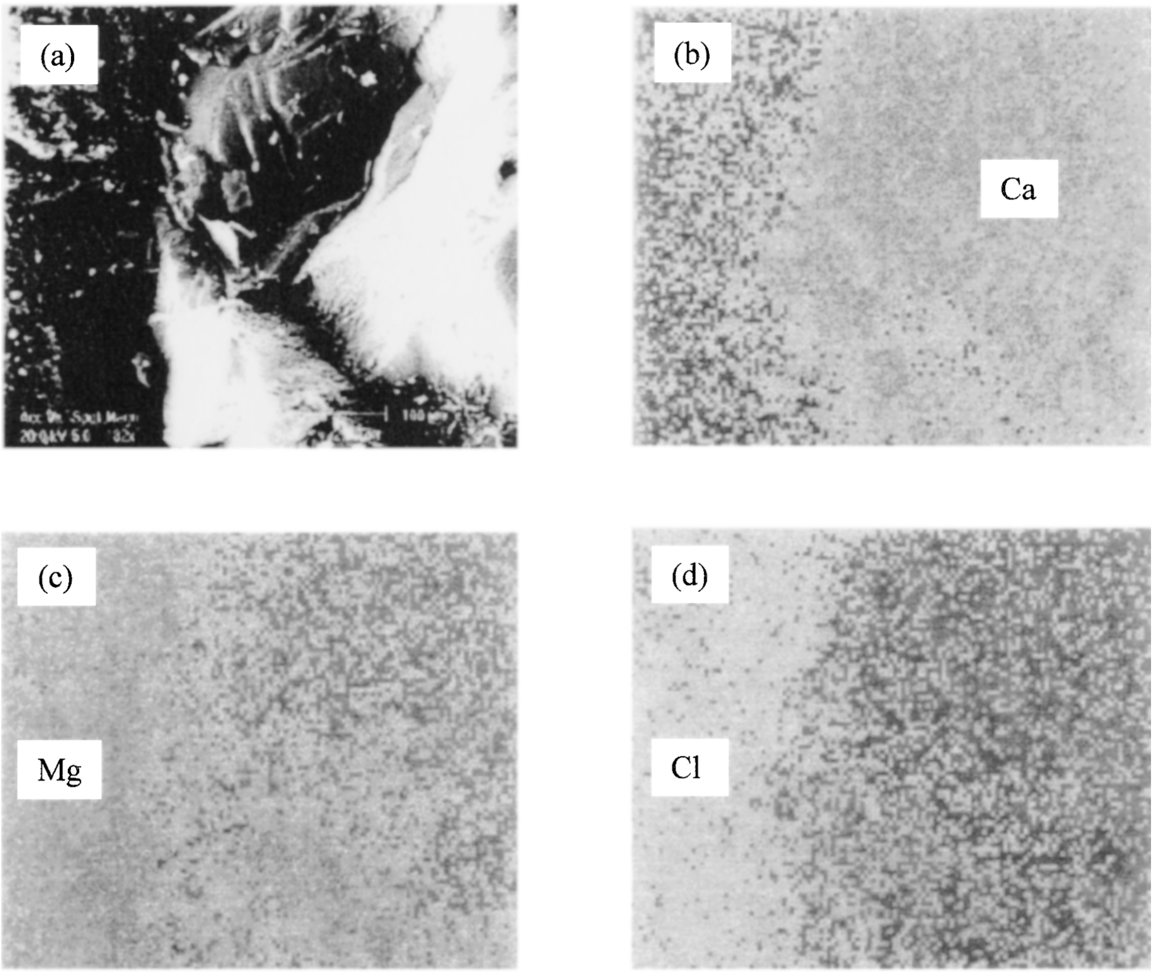

Fig. 4. (a) ESEM micrograph of an indoor mortar, along with ESEM-EDX maps in the same area of (b) Ca, (c) Mg, and (d) Cl.

less soluble in water than either of the oxychlorides and also protects the material from rapid attack by creating a surface coating [5,12,13]. Previous studies also indicated that the formation of oxychlorocarbonate is very temperature- and humidity-dependent and is favored at humidity greater than 60% [5]. This fact explains why oxychlorocarbonate is abundantly present in outdoor samples, while in indoor samples the F3 predominates among the detected mineral phases.

The carbonation, however, induces a structural rearrangement sufficiently capable of increasing the volume and producing stress that causes cracks [16], as was extensively noticed in areas where Sorel mortars were used. In addition, carbonation, which cannot be inhibited even in indoor environment, causes both compositional gradients to mortars and disruptive effects in adjacent structures.

Sorel mortars exposed to excessive washing were also subject to carbonation, resulting in hydromagnesite after additional leaching of magnesium chloride. As a result the binder is progressively removed and the mortar becomes weakened and crumbles, even if hydromagnesite, being less soluble than oxychlorides, might alone confer stability against the aggressive environment. Moreover, the washed-out magnesium chloride migrates to adjacent areas, causing staining of the surface [15,17].

Despite the fact that F5 is transformed after a long period of time into the other stable phase F3, traces of F5 were detected in Sorel mortars not directly exposed to rain action. The detection of F5 in our samples can be explained by the increased stability of F5 under high pH value conditions [18], which is the case here because of the addition of calcitic powder for the preparation of Sorel mortars.

Disintegration of mortars and staining of marble observed in outdoor areas sheltered from wetting are associated with the presence of magnesium and calcium hydrated sulfates; the latter arise by reaction of mortar constituents with atmospheric SO_2. Migration of excess magnesium chloride to the surface due to either inadequate mixing or inherent shortcomings of the constituents of MOC pastes may additionally form efflorescence or a deliquescent layer.

The damage induced by the salts discussed above is regarded as arising through volume changes that occur on crystallization, when crystals are deposited from solution or when they absorb water and change hydration state. The microclimate and especially the relative air humidity and tem-

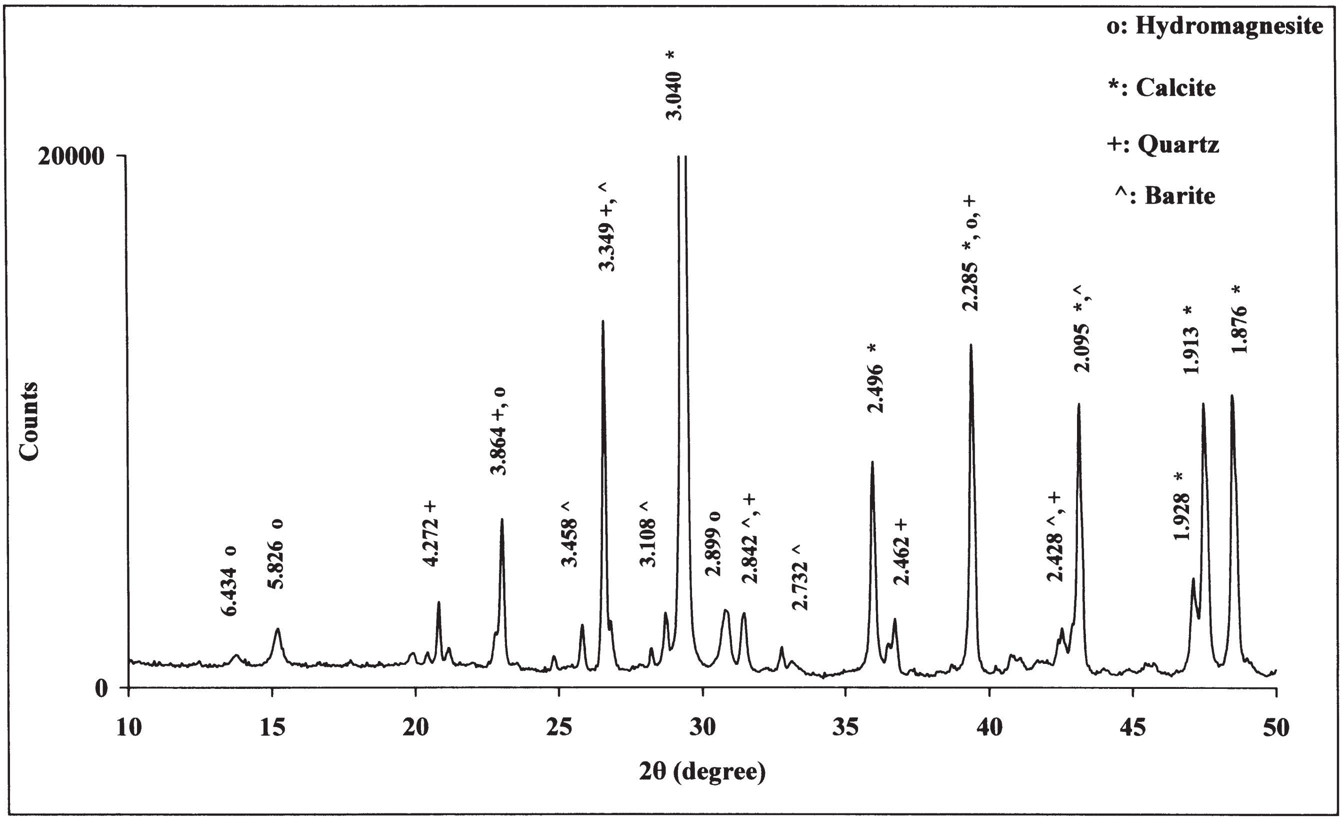

Fig. 5. XRD pattern of mortar exposed to intensive washing with calcite (5-0586), barite (24-1035), hydromagnesite (25-0513), and quartz (33-1161).

perature determines if hydration, crystallization, and rehydration of soluble salts occurs.

Gypsum, epsomite, and hexahydrite migrate to the masonry surface where they precipitate when the ambient relative humidity becomes lower than the equilibrium relative humidity of the saturated solution of the concerned salt phase in the system [19]. The equilibrium relative humidity of epsomite (e.g., 90% at 20°C) suggests that it precipitates easily and crystallizes on the surface [20]. In dry air conditions, epsomite may lose molecules of water and convert to the closely related minerals hexahydrite and starkeyite.

The calcite detected in the efflorescence may originate from hydration and the subsequent carbonation of calcium oxide found as an impurity in the magnesia. It must be emphasized that calcite formation is sufficiently inhibited by the magnesium ion, which is rich in the matrix [21]. Other sources of calcite could be either secondary reactions between soluble salts, originating both from the surrounding environment (e.g., marine spay) and the mortar constituents, or deposition of recrystallized calcium carbonate coming from dissolution of the adjacent marble [22].

The mineral phases identified above evidence a carbonation and sulphation effect on the Sorel cement mortars, enhancing their decay susceptibility. Moreover, corrosive solutions released from interactions of mortar and environment can cause further deterioration in the marble.

5. Conclusions

In Sorel cement mortars an excessive volume change is encountered after the carbonation of the ternary oxychloride phases into oxychlorocarbonate. Although the layer of oxychlorocarbonate serves to slow the leaching process, this transformation induces enough stress to provoke cracks both to mortar and to the adjacent marble, even in structures maintained indoors.

In addition to the disruptive action of carbonation (especially on Sorel cement pastes sheltered from wetting), a physicochemical action of secondary salts, such as gypsum, epsomite, hexahydrite, and starkeyite, also affected the monuments. Both oxychlorides and mortar aggregates when linked to sulfurous gases are partially transformed to hydrated sulfate salts with different water molecules. Their hydration, crystallization, and rehydration according to microclimatic shifts imply volume changes and the release of corrosive solutions, leading to formation of cracks and staining.

Mortars that are in prolonged contact with water release magnesium chloride and therefore weaken and crumble. Migration of magnesium chloride to mortar surface or adjacent areas causes efflorescence and staining. Hydromagnesite forms from carbonation of the remaining binder; although being less soluble than oxychlorides, it could not prevent their disintegration.

Acknowledgments

We are grateful to Drs. D. Papageorgiou and A. Papageorgiou of TITAN Cement Industry, in Athens, for the ESEM-EDX and TG-DSC measurements. We also thank Drs. V. Kilikoglou and V. Psyharis of the National Center for Scientific Research "Dimokritos," in Athens, for facilities in FTIR and XRD analyses.

References

[1] S. Sorel, On a new magnesium cement, Compt Rend 65 (1867) 102–104.
[2] T. Demediuk, W.F. Cole, H.V. Heuber, Studies on magnesium and calcium oxychloride cement, Aust J Chem 8 (2) (1955) 215–233.
[3] W.F. Cole, T. Demediuk, X-ray, thermal and dehydration studies on magnesium oxychlorides, Aust J Chem 8 (2) (1955) 234–251.
[4] L. Urwongse, C. Sorrell, The system MgO-$MgCl_2$-H_2O at 23°C, J Am Ceram Soc 63 (9/10) (1980) 501–504.
[5] M.C. Ball, Reactions of compounds occurring in Sorrel's cement, Cem Concr Res 7 (1977) 575–584.
[6] C.A. Sorell, C.R. Armstrong, Reaction and equilibria in magnesium oxychloride cement, J Am Ceram Soc 59 (1/2) (1976) 51–54.
[7] Th. Skoulikidis, E. Papakonstantinou, A. Galanos, Y. Doganis, Study for the restoration of the Parthenon, Athens: Ministry of Culture, Committee for the Preservation of the Acropolis Monuments, vol. 3, 1994.
[8] P. de Henau, M. Dupas, Study of the alteration in Acropolis monuments, in: Proceedings of Second International Symposium on the Deterioration of Building Stone, Athens: Ministry of Culture, 1976, pp. 319–325.
[9] A. Moraitou, Meyer cement and its effect on the Propylaea marble, in: Study for the Restoration of Propylaea, Athens: Ministry of Culture, Committee for the preservation of the Acropolis monuments, vol. 1, 1994, pp. 475–578.
[10] D. Dimitriadis, The state of conservation of the west freeze of Parthenon, technical report, Athens: Archive of the Committee for the Preservation of the Acropolis Monuments, 1968, Reference No. 141-28/1/1969.
[11] V.C. Farmer, The infrared spectra of minerals, Mineralogical Society, Monograph 4, London, 1974.
[12] L. Walter-Levy, Neutral chlorocarbonate of magnesium, Compt Rend 205 (1937) 1405–1407.
[13] L. Walter-Levy, Contribution to the study of halogenocarbonates of magnesium, Compt Rend 206 (1938) 1898–1900.
[14] W.B. White, The carbonate minerals, in: V.C. Farmer (Ed.), The Infrared Spectra of Minerals, Mineralogical Society Monograph 4, London, 1974, pp. 265–266.
[15] D.S. Hubel, A new inorganic cement and adhesive, Industrial and Engineering Chemistry 29 (2) (1937) 123–132.
[16] M.D. de Castellar, J.C. Lorente, A. Traveria, J.M. Tura, Cracks in Sorel's cement polishing bricks as a result of magnesium oxychloride carbonation, Cem Concr Res 26 (8) (1996) 1199–1202.
[17] A.S. Bhist, S.P. Singh, Problem of stain appearance at high humidity on stone sculptures joined with Meyer's cement, Conservation of Cultural Property in India 12 (1979) 17–20.
[18] D. Deng, C. Zhang, The effect of aluminate minerals on the phases in magnesium oxychloride cement, Cem Concr Res 26 (8) (1996) 1203–1211.
[19] I.S. Evans, Salt crystallization and rock weathering: a review, Rev Géomorph Dyn 19 (1970) 153–177.
[20] L. Greenspan, Humidity fixed points of binary saturated aqueous solutions, J Res Nat Bur Standards, A Phys Chem 81A (1977) 89–96.
[21] R.L. Folk, Natural history of calcium carbonate, J Sed Petrology 44 (1974) 40–53.
[22] A.E. Charola, S.Z. Lewin, Efflorescences on building stones—SEM in the characterization and elucidation of the mechanisms of formation, Scan Electr Microscopy 1 (1979) 378–386.