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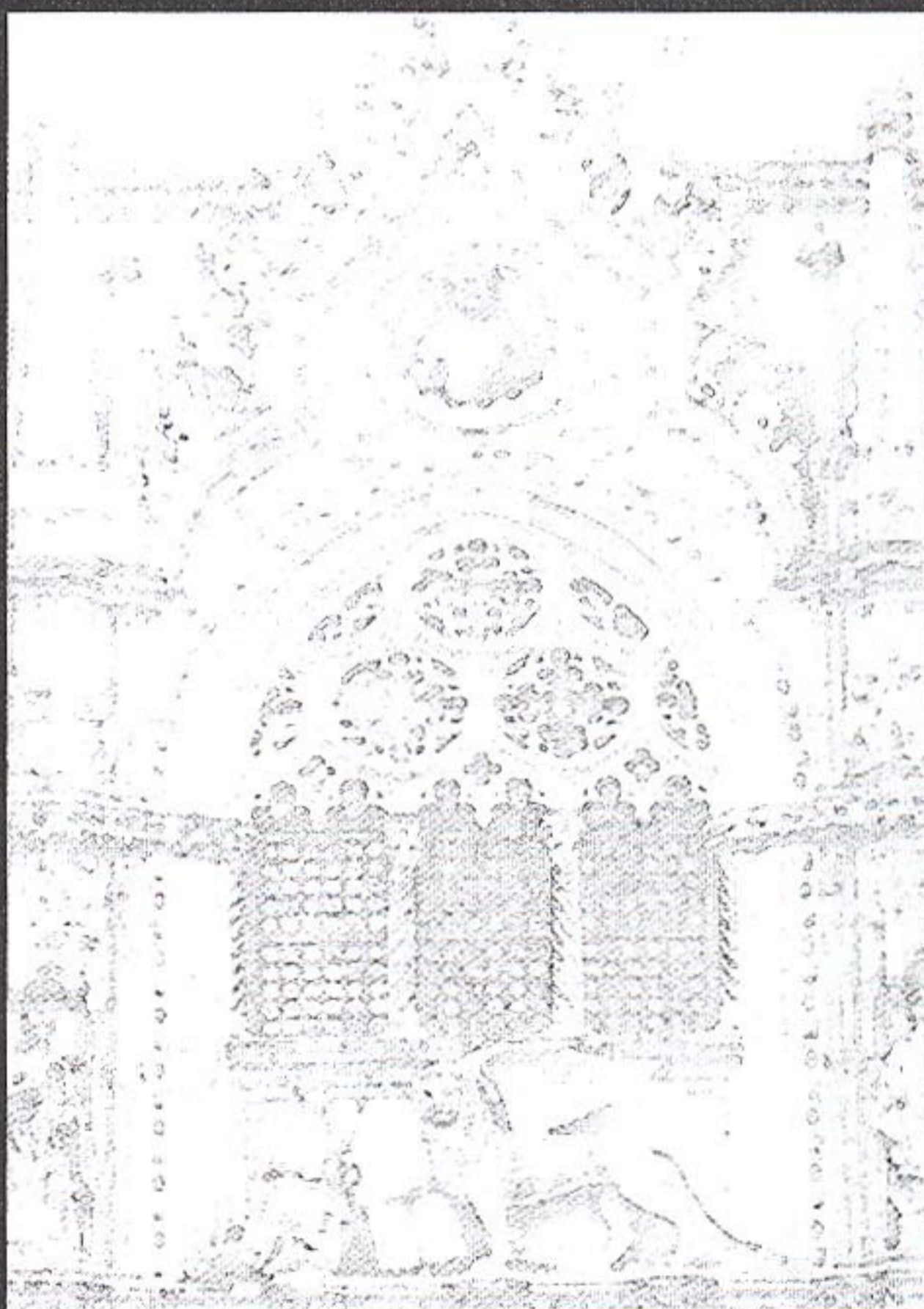


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VENICE JUNE 19-24, 2000

ELSEVIER

Proceedings of the



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**Istituto
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A COMPARATIVE STUDY OF MORTARS CONTAINING BARIUM HYDROXIDE ($\text{Ba}(\text{OH})_2$). APPLICATION ON MONUMENT'S CONSERVATION

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Abstract

The purpose of this project is to study the potential effect of barium hydroxide $\text{Ba}(\text{OH})_2$ as an additive material to the durability and the characteristics of the mortars used in conservation.

In order to study the potential effect of barium hydroxide on repair mortars two series of specimens have been prepared, the one containing lime, cement, sand and barium hydroxide and the other lime, cement and sand.

The physical and mechanical properties of the specimens have been studied as well as their durability to various decay agents through an accelerated ageing process. X-ray diffraction (X-RD), scanning electron microscopy (SEM/EDAX) and infrared spectroscopy (FTIR) have been used for the examination and characterization of the specimens. In addition, porosimetric measurements and microscopic observation were carried out.

The comparative study of the two series of mortars indicates that the addition of barium hydroxide increases the durability of the mortars to decay agents such as soluble salts and acid attack.

Key Words: mortars, barium hydroxide, conservation, repair, durability.

1. Introduction

The aim of this paper is the study of barium hydroxide $\text{Ba}(\text{OH})_2$ as a constituent in conservation mortars, taking into account the bibliographic references concerning the advantages and disadvantages of its use both as a consolidant for limestone (Lewin, 1974) and as additive material in cement (Lambropoulos, Parisakis, 1996), as well as the presentation and analysis of the following issues:

- a. The appearance and the setting of the mortars
- b. Their physical characteristics and mechanical properties
- c. The formation of barium compounds and
- d. The durability of the mortars to various decay agents.

For this purpose three types of mortars were selected containing both lime putty and white Portland cement.

Tests and measurements were carried out on several specimens according to the procedure de scribed as follows.

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2. Experimental

2.1 Samples preparation

The raw materials utilized for producing the mortar mixtures consisted of: a) lime putty (L), b) white Portland cement (C), c) calcareous sand (S) and d) barium hydroxide (B). These are typical commercially available materials and were obtained from local suppliers in Athens-Greece. The sand and the cement were previously sieved using sieves with 2mm diameter.

The different compositions of the mortar specimens that were studied are shown on table 1 (tab. 1).

Table 1: The compositions of the mortars studied

Compositions	SAa	SAb	SCa	SCb	SDa	SDb
Lime	1	1	4	4	1	1
Cement	0	0	1	1	1	1
Sand	1	1	6	6	6	6
Barium hydroxide	1	0	4	0	1	0

The above compositions are commonly used in conservation, for example in repointing of walls and joint mortars, and they have well-known properties as they were studied by Peroni S. and others (Peroni, 1981). Also, they are recommended by international standards such as ASTM C270 [1].

For the preparation of the mortars all materials were measured by volume and the following procedure was followed: sand was mixed first with pre-water, lime putty, cement and final water to a consistency that could be placed in the moulds. Barium hydroxide when used, was mixed first with lime putty.

The mixture was vibrated and compressed into the moulds in order to avoid the formation of internal voids. All specimens were cubic with 5cm edge and were allowed to cure at 90-95% relevant humidity (RH) for seven days and then were stored at 50-60% RH for twenty eight days. The curing and storage were completed at ambient temperature (20-25 °C). The specimens were thirty five days old when they were subjected to the accelerated ageing procedure and to other tests.

All tests and measurements were carried out on at least five specimens from each composition.

2.2 Methodology

The suggested methodology for the study of mortars used in conservation refers to both their physical and mechanical properties (Holmstrom, 1981; Bouineau, 1981). The tests that were carried out concern the following properties:

- Workability
- Setting time
- Volume change upon setting
- Colour and hardness
- Porosity
- Water absorption and capillary rise

- Compressive strength.

The estimation of the workability, setting time and colour of the specimens was carried out by visual observations during the setting of the specimens. The three dimensions of all the specimens were measured after seven and thirty days of their production. The measurements of the porosity, water absorption and capillary rise of the specimens was based on NORMAL proposed methodology [2]. Finally, compressive strength measurements were carried out using the ELOT/EN 196.1 standards [3] on seven and thirty days old mortar specimens.

For the durability determination of all the mortars against various decay agents, the specimens were subjected to accelerated ageing cycles with soluble salts and acid attack. In each cycle five specimens of every composition were used. The ageing cycles were determined according to RILEM proposed methodology [4]:

- Specimen drying at 105 °C for 22 hours
- Specimen weighing after obtaining room temperature
- One hour immersion of the specimens in soluble salts or acid solution respectively
- Specimen drying at 105 °C for 22 hours
- Weighing of the specimens after obtaining room temperature.

The soluble salts selected for the experiments were: NaCl 14% w/w and Na₂SO₄ 14% w/w and the acid solutions were formed with HNO₃ 0,1M and H₂SO₄ 0,1M.

At the end of the cycles, tables of the specimens' weight change were made as well as diagrams presenting the percentage of the specimens' weight change after each cycle.

In addition, X-ray diffraction (X-RD), scanning electron microscopy (SEM/EDAX) and infrared spectroscopy (FTIR) have been used for the examination and characterization of all specimens.

3. Results

The results deriving from the study of the physical and mechanical properties of the mortar specimens of all compositions as well as from the ageing cycles can be summarized as follows.

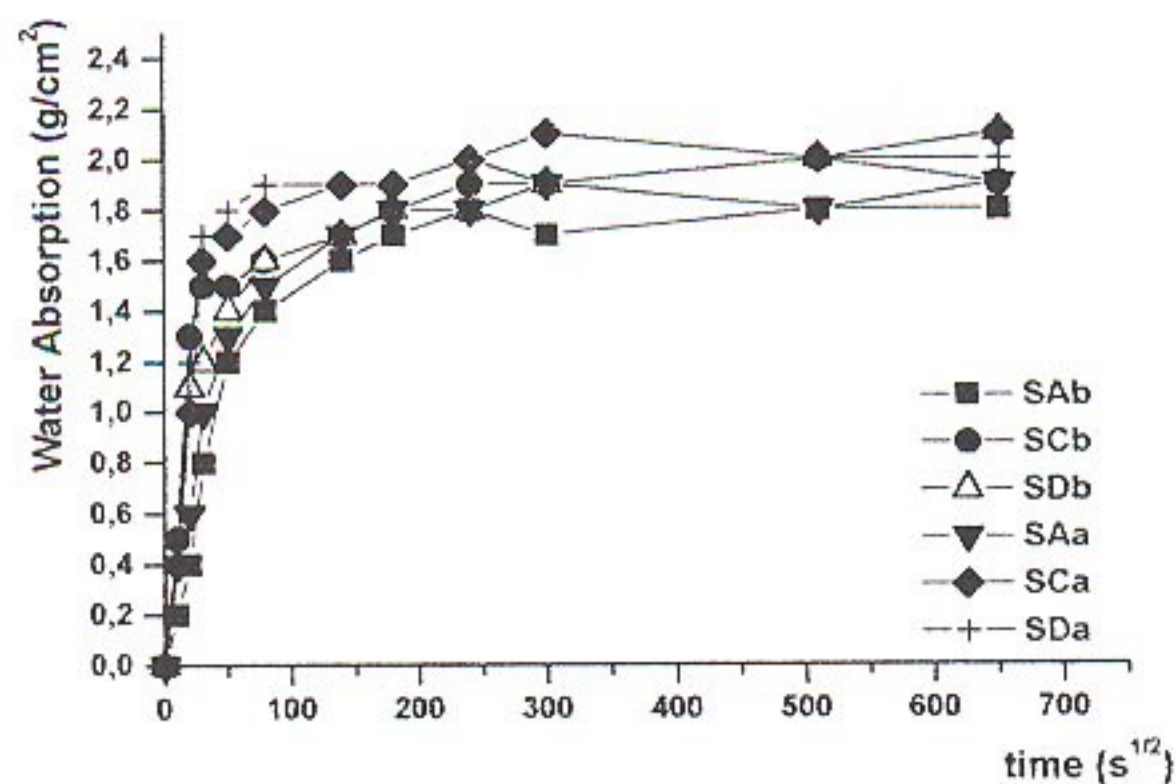
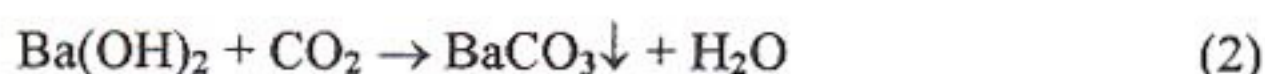
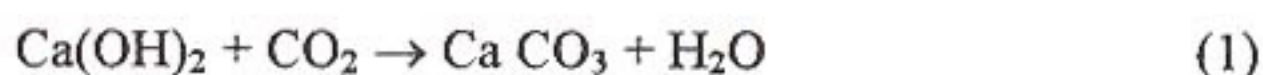


Figure 1: Water absorption by capillary rise of the mortars

The compositions SC and SD have presented similar workability, which was around twenty to thirty minutes. The workability of composition SA was about forty minutes.

As it was anticipated the setting time of the specimens containing white Portland cement, compositions SC and SD, begins earlier than in type SA specimens. After three days of curing all the mortars of every composition appear to have a solid structure. Measurements of their pH were taken at regular intervals in order to determine the setting time of each composition. The pH rates for type SC and SD mortar specimens after thirty five days were stabilized around 7,5 whereas the rates for type SA specimens were bigger than 8.

The reduction of the pH rate is due to the reactions that take place during the setting of the mortars. The main reactions concerning calcium and barium hydroxide are presented below (1) (2):



The colour of all the mortar specimens that did not contain barium hydroxide had a beige-ochre shade. The ones containing barium hydroxide were much more whiter.

The hardness of all the specimens was almost the same for all the compositions and was determined about 5,5 of the Mohs scale. The hardness of the specimens of type SA, which do not contain cement, was estimated at 3-3,5 of the Mohs scale.

The values of the porosity are presented on table 2 (tab.2). These values are close to the ones of historic lime mortars, in the range of 30-45% by volume (Schafer, 1993). The values of water absorption by capillary rise and compressive strength measurements of all specimens are presented on figures 1 and 2 (fig. 1) (fig. 2).

Table 2: Open porosity of the mortars

Mortars	Porosity
SAa	33,7
SAb	32,8
SCa	36,2
SCb	35,1
SDa	36,2
SDb	35,6

The compressive strength results show that there is no big difference between the durability of the mortars containing barium hydroxide and those that do not. Furthermore, these results are very close to the ones referred in the bibliography (Peroni, 1981).

All the specimens did not show any shrinkage and volume change upon setting because the conditions during their curing were very stable and the water had evaporated at a slow and regular rate.

The results that derive from the completion of the accelerated ageing cycles with soluble salts and acid solutions are presented on figures 3 and 4 (fig. 3) (fig. 4).

The results after the soluble salts cycles show that the specimens containing barium hydroxide are more durable than their corresponding ones, they had held out for three more cycles and their appearance was better. In both series of mortars, with and without barium hydroxide, an increase of their weight of about 15% was observed due to the penetration

and crystallization of the soluble salts into the pores of the specimens. The ageing cycles with the soluble salts have caused exfoliations, blistering and efflorescence on the surface and the body of the specimens before their total destruction (fig.5).

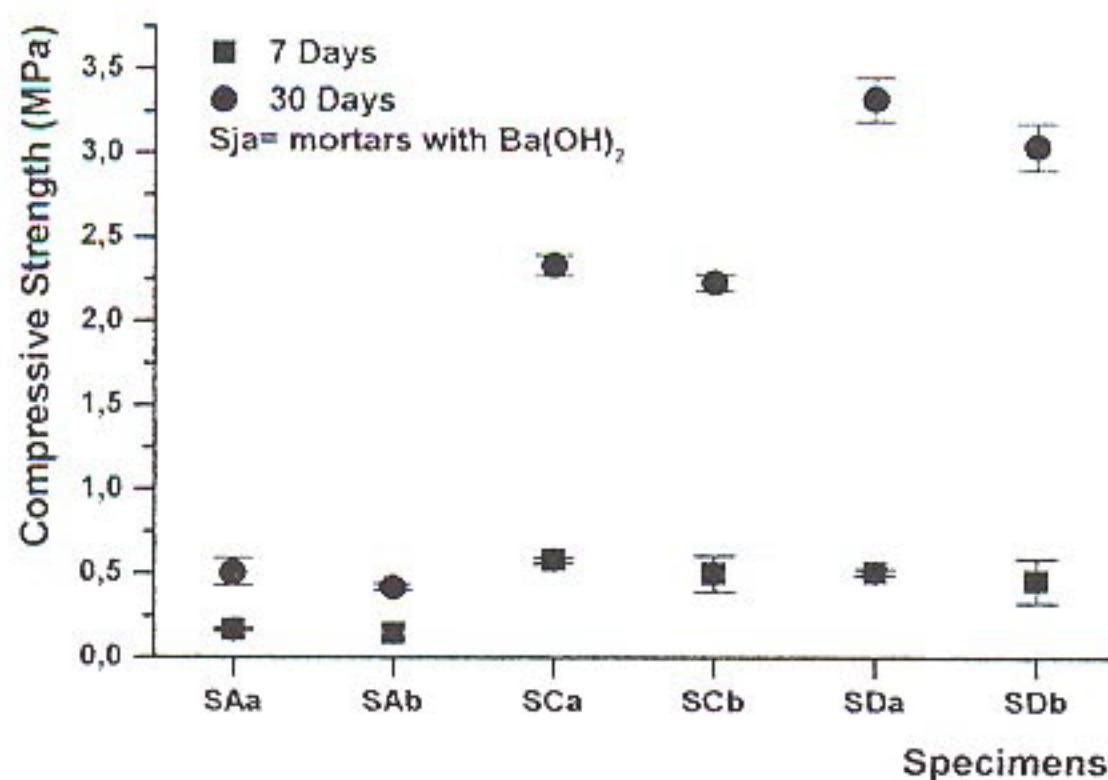


Figure 2: The variation of the compressive strength values during the setting of the specimens.

As regards the ageing cycles with the acid solutions, the mortars that contained barium hydroxide showed greater durability than the ones without barium hydroxide, concerning mostly their appearance, volume change and loss of material. At the end of the cycles the porosity of the specimens had increased and the bonding material had deteriorated under the influence of the acid solution (fig. 6). The increase of the specimens' weight mainly at the beginning of the experiments is due to the formation of sulfuric and nitric salts as a result of the reactions between the acid and the components of the mortars. The formation of these compounds was anticipated and their presence was verified by infrared spectroscopy (FTIR) and X-ray diffraction (X-RD) analysis.

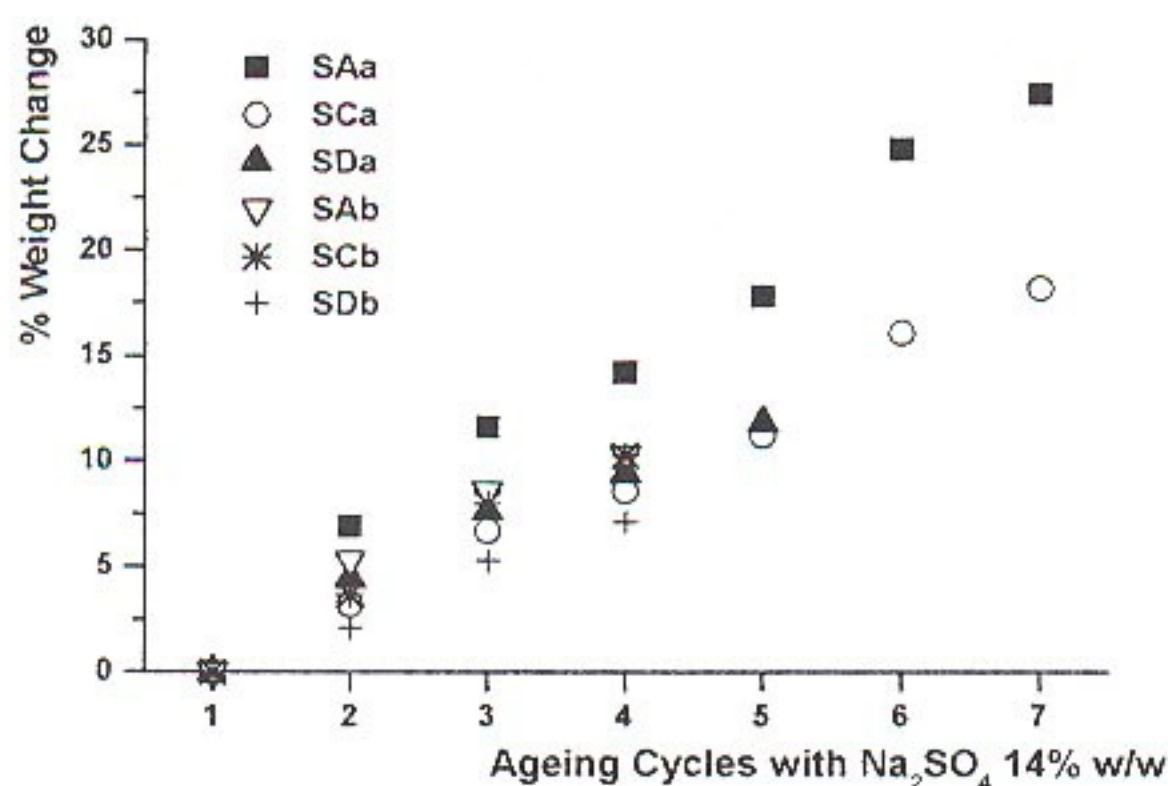


Figure 3: The %weight change of mortars specimens during the ageing cycles with Na_2SO_4 .

The analytical methods of infrared spectroscopy and X-ray diffraction were used for the characterization of the mortars and especially for verifying the formation of the barium compounds, witherite (BaCO_3) and barite (BaSO_4), to the matrix of the mortars (fig. 9). The

samples for the analysis were taken from two different points of the specimens, one near the surface, 1cm from the surface, and the other from the centre of the specimen, 2,5cm from the surface.

The analysis showed that barium carbonate (BaCO_3) is formed in both cases. This is very encouraging because it shows that the added barium hydroxide reacts with the calcareous material of the mortar, forming stable compounds.

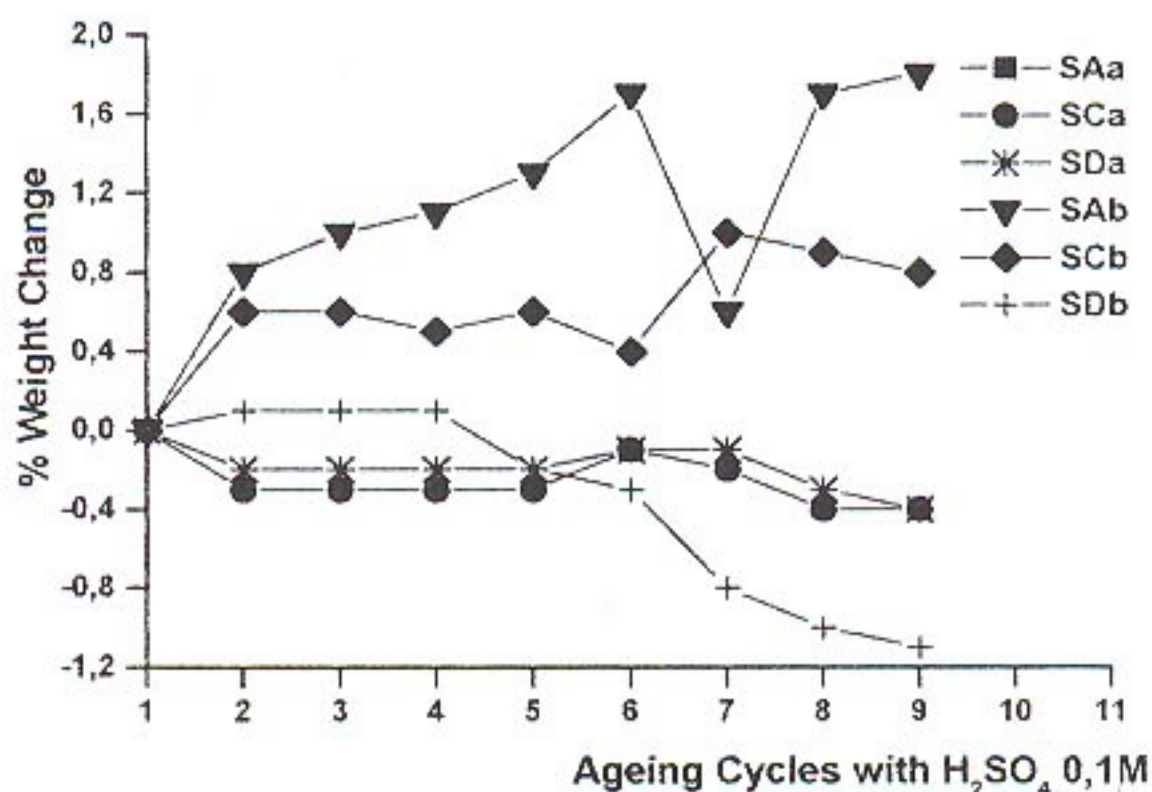
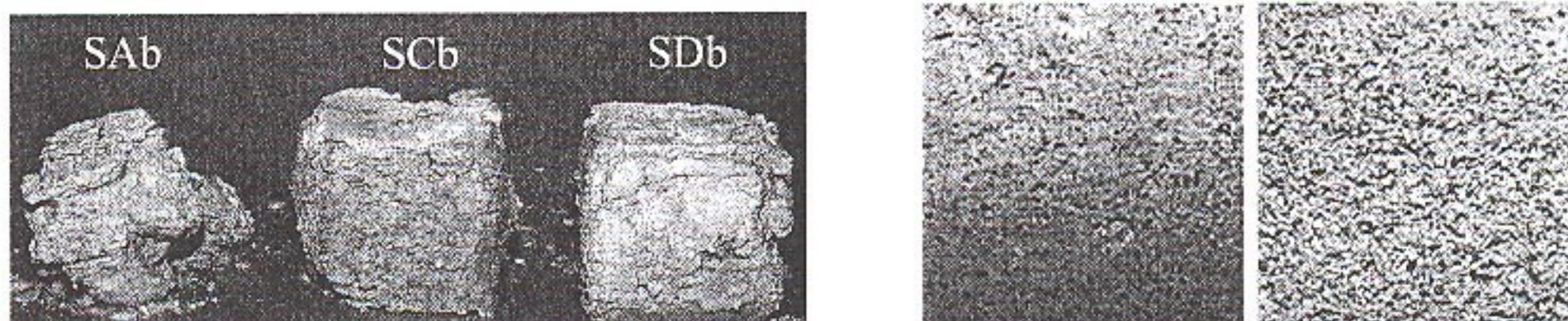


Figure 4: The %weight change of mortars specimens during the ageing cycles with H_2SO_4 .



Figures 5,6: The specimens after the ageing cycles with Na_2SO_4 and the surface of SDa (left) and SDb (right) after the ageing cycles with H_2SO_4 .

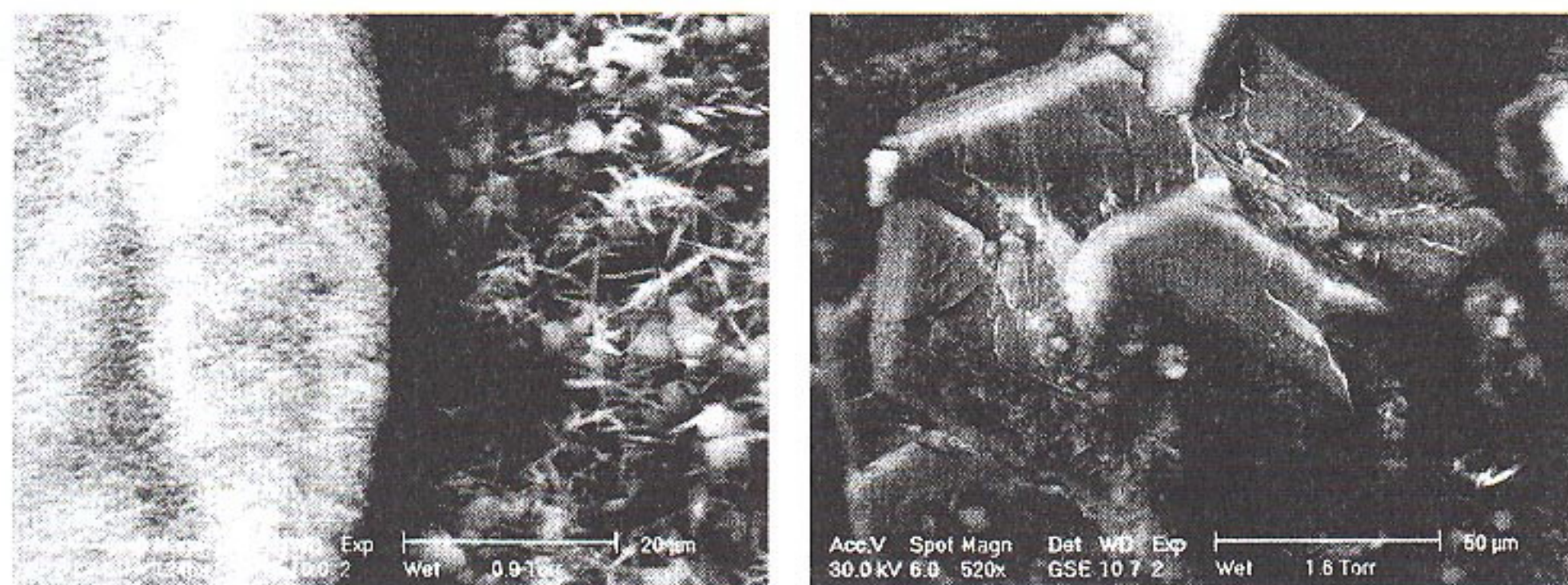
The results from the scanning electron microscopy (SEM/EDAX) show that there is a homogeneous distribution of barium and lime throughout the mass of the mortars (fig. 7) (fig. 8).

4. Conclusions

From the evaluation of the results it can be concluded that the appearance and the physical properties of the mortars containing barium hydroxide meet the requirements of repair mortars. Cracks, exfoliations and shrinkage are not observed during and after the setting of the mortars as referred in the references (Skoulikidis, 1996). Special care is required for the curing conditions so that the conversion of barium hydroxide to barium carbonate (see reaction 1) could take place throughout the mass of the mortars. These conditions have an effect on the physical and mechanical properties of the specimens.

The X-ray diffraction and scanning electron microscopy (SEM/EDAX) verify the formation of barium carbonate (BaCO_3) and barium sulfate (BaSO_4) in the entire mass of the specimens as well as the complete absence of barium hydroxide (Ba(OH)_2). This is very encouraging because it is proved that the curing conditions mentioned in paragraph 2.1 have promoted the reaction of barium hydroxide with the carbon dioxide of the air.

The main advantage of adding Ba(OH)_2 to repair mortars is the formation of barium sulfate which has the following properties (tab. 3).



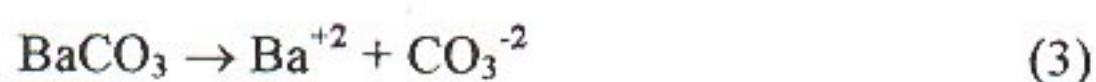
Figures 7,8: Left figure shows the distribution of barium ions (probably BaCO_3) and cement fibers. The right figure shows a crystal of BaSO_4 .

Table 3: Physical and mineralogical properties of barium and calcium compounds (Phillips; Hatzioannou, 1985)

Mineral	Chemical formula	Crystal structure	Specific gravity	Solubility (Ksp)
Calcite	CaCO_3	Hexagonal	2,71	$6,9 \cdot 10^{-9}$
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Monoclinic	2,31	$2,4 \cdot 10^{-5}$
Witherite	BaCO_3	Orthorombic	4,29	$1,6 \cdot 10^{-9}$
Barite	BaSO_4	Orthorombic	4,50	$1,5 \cdot 10^{-9}$

It can be seen that barium sulfate is less soluble than calcium sulfate. This is an important advantage for the durability of the mortars to acid attack, specially by SO_x which are the main pollutants in industrial areas and big cities. The evaluation of the results of the experiments, which concern the accelerated ageing cycles with sulfuric acid and sodium sulfate leads also to the same conclusion.

Barium and calcium carbonate are crystallized under the same crystal structure, hexagonal and rombic. The presence of barium carbonate is positive, because it does not cause any problems to the structure and appearance of the mortars and could lead through its solutions (see reaction 3) to the formation of barium sulfate, engaging the SO_4^{-2} ions that come from rain water or capillary rise. This reaction could take place during the immersion of the specimens to the Na_2SO_4 solution (see reaction 4).



In general, it seems that greater durability to decay agents such as soluble salts and acid attack can be achieved by using barium hydroxide mainly due to the chemical stability of BaSO_4 and the similar crystalline properties of BaCO_3 with CaCO_3 .

Further studies about the formation of barium compounds, in various conditions, should be carried out taking into account the requirements for repair mortars.

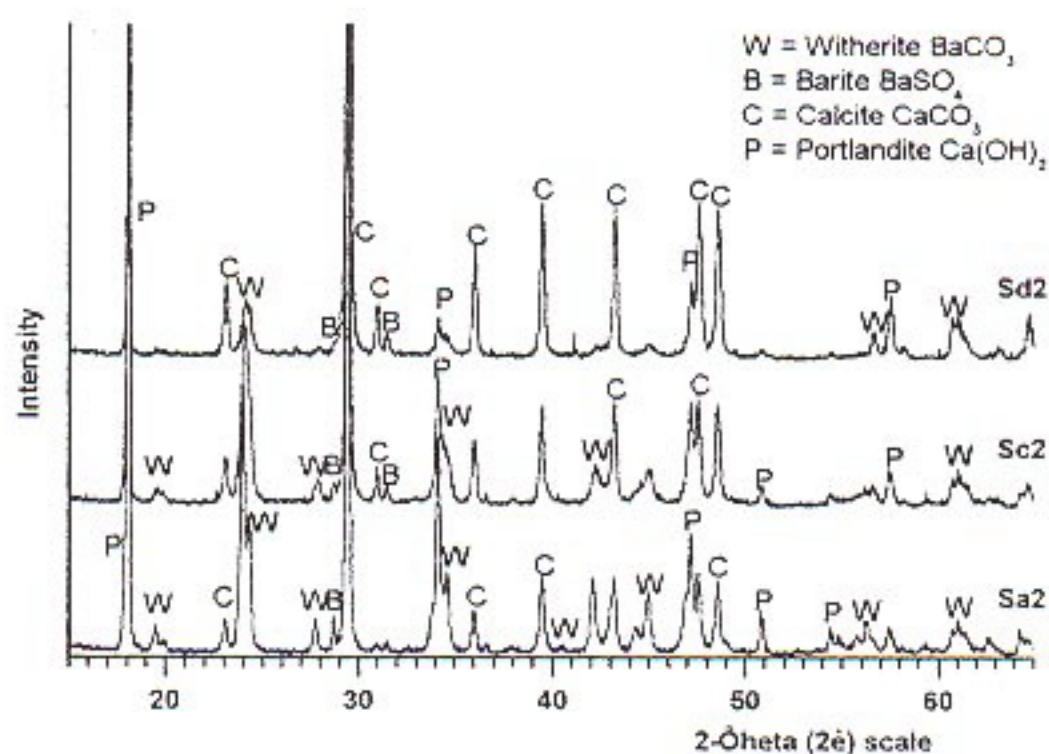


Figure 9: X-ray Diffraction results from samples taken from the centre of the specimens, 35 days old.

Standard Specifications for testing methods

- [1] ASTM C 270 – 97a, Standard Specifications for Mortar for Unit Masonry
- [2] Normal – 11/85, Assorbimento d' Acqua per Capillarita, Coefficiente di Assorbimento Capillare
- [3] EL0T/EN 196.1, Methodi Dokimis Tsimentou- Prosdiorismos Antoxon (Methods for testing cement – Compressive strength determination)
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