

Setting process of lime-based conservation mortars with barium hydroxide

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Abstract

This paper presents the effect of barium hydroxide on the setting mechanism of lime-based conservation mortars, when used as an additive material. The study focuses on the monitoring of the setting process and the identification of the mineral phases formed, which are essential for furthering the study of the durability of barium mixtures against chemical degradation. X-ray diffraction analysis (XRD), scanning electron microscopy (SEM) and thermal analysis (DTA–TG) were used to monitor the setting processes of these mixtures and identify new phases formed. The results suggest that barium hydroxide is evenly distributed within the lime and produces a homogeneous binding material, consisting of calcite (CaCO_3), witherite (BaCO_3) and barium–calcium carbonate [$\text{BaCa}(\text{CO}_3)_2$]. Finally, it was found that barium carbonate can be directly bonded to calcitic aggregates and therefore increases its chemical compatibility with the binding material.

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1. Introduction

Lime-based mortars are among the most widely used materials in architectural monuments [1,2]. Although they are particularly vulnerable to sulphur compounds and chemical degradation, traditional lime-based mortars are still widely used today in restoration works on stone monuments and historic buildings. Their incremental preference lies in their superior compatibility with the original mortars and building materials. In contrast, the use of cement-based mixtures, which have been used extensively in the past decades, is today under consideration [3–6]. It is apparent that the enhancement of the resistance of lime-based repair mortars against chemical degradation, and particularly against sulphur dioxide (SO_2) [7], would be crucial for the improvement of their performance, especially in urban environments.

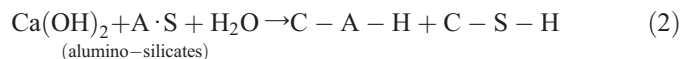
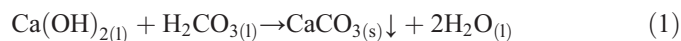
The sulphate resistance requirements were approached here through the addition of a material that could potentially fix and stabilize sulphate ions. Based on the literature of buildings conservation and the existing experience on stone, the material which was selected for this purpose was barium hydroxide [$\text{Ba}(\text{OH})_2$]. Barium carbonate, precipitated from barium hydroxide, was initially considered as an alternative consolidant for carbonate stones [8]. Moreover, barium hydroxide solutions have been used for the consolidation of sulphated marble surfaces, sculptures and wall-paintings, a procedure known as the ‘Florentine method’ [9]. The first step for the design and development of repair mortars consists of the detailed knowledge of their setting process, as well as the chemical and mineralogical composition of the resulting mixtures. It is known that all the above are affected principally by the raw materials within the binder fraction [10]. Moreover, the setting mechanism has a strong influence on the physical characteristics, strength and durability of the mixtures.

The setting mechanisms of typical lime and lime–pozzolan mixtures are well known and they are generally described by the

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dissolution of carbon dioxide (CO₂) in water, the carbonation reaction of calcium hydroxide (Eq. (1)), and the formation of hydrated phases (C–S–H, C–A–S) through the reactions between the lime binder and the pozzolanic material (Eq. (2)). The evaporation of water has a strong effect on the above processes, as the amount of water that remains controls the diffusion of carbon dioxide into the mortar and its dissolution in the pore water, as well as all the reactions that take place in the liquid phase [11–14].



In the case of barium hydroxide, the barium carbonate phase, which is formed through the carbonation of barium hydroxide, is considered a somewhat similar material to calcium carbonate, both being alkaline-earth carbonates with relatively low solubilities [15]. Stone consolidation literature suggests that when barium ions are in contact with calcium carbonate crystals, along with carbonation, a significant degree of exchange of barium ions for calcium ions is achieved. Therefore, the precipitated barium carbonate is directly bonded to the surface of calcium carbonate crystals and thus, the new mineral phase increases its adherence to the stone material [16,17].

Based on the above, this paper presents the effect of barium hydroxide on the setting mechanism of lime-based conservation mortars, when used as an additive material, and focuses on the monitoring of the setting process. The behaviour of barium hydroxide [Ba(OH)₂]–calcium hydroxide [Ca(OH)₂] mix is monitored in both binary pastes and mortar mixtures in order to find out whether it can play an active role within the mortar mass and produce, in a similar way to its consolidating action, a successful binding material. The results presented offer the necessary background for further study of the physical properties and durability of lime-based barium mixtures.

2. Experimental

2.1. Quality control of raw materials

The raw materials selected for the preparation of mortar mixtures consisted of: a) calcium hydroxide [Ca(OH)₂]; b) barium hydroxide octahydrate [Ba(OH)₂·8H₂O]; c) a medium fraction of ceramic fragments with grain size in the range of 0.125–2.0 mm diameter and; d) a calcitic sand with grain size in the range of 0.125–2.0 mm.

Calcium hydroxide and barium hydroxide were pure chemical products, provided by FLUKA and MERCK, respectively. Calcitic sand and ceramic fragments were commercially available materials and were obtained from local builders' supply firms in Greece.

Laboratory-prepared lime putty was used, rather than hydrated lime powder or commercially available lime putty, in order to ensure lime quality and provide greater repeatability

of future experimental tests and field applications. Pure, chemical calcium hydroxide and barium hydroxide were mixed individually with equal portions of water in order to produce homogeneous putties. The putties were left to mature for a period of 3 months.

Chemical composition of all raw materials used was studied in the solid state by scanning electron microscopy (SEM) coupled to energy dispersive X-ray analysis (EDX), and X-ray diffraction analysis (XRD).

2.2. Test specimens

The test specimens studied were divided into two groups, namely Binary Pastes and Mortar Mixtures.

Binary pastes, containing mixtures of lime putty with varying proportions of barium hydroxide and water, were initially prepared in order to determine the maximum amount of barium hydroxide that could be added to mortars without affecting their performance. These pastes were also used to study the new products formed during the setting and hardening of the lime binder, with different amounts of barium hydroxide added. Finally, the potential of using barium hydroxide as a binding material, on its own, was investigated by preparing a set of different binary mixtures of barium hydroxide with a very fine fraction (<0.063 mm) of calcium carbonate (limestone) and ceramic powder. The mixing proportions of all binary pastes prepared are given in Table 1.

Mortar mixtures were composed of lime putty, with aggregates, barium hydroxide and water. The determination of the maximum amount of barium hydroxide that could be used was based on the results of the first set of preparations, the binary pastes. The fraction of aggregates consisted of equal parts of calcitic sand and ceramic fragments in the range of 0.125–2.00 mm. The grain size distribution chosen was based on the recommendations proposed by BS EN 196-1 standard [18]. The amount of binder required for the given granular distribution of aggregates was determined from the density of

Table 1

Mixing proportions, expressed in parts per volume, of binary pastes, prepared by barium hydroxide (BaH), lime putty (CaH), fine calcium carbonate (Cc) and ceramic (Cer) powder in different proportions

No	Mixture code name	Mix proportions by volume				Water: binder ratio	Amount (%) of binder being replaced
		CaH	BaH	Cc	Cer		
1	CaH	1	–	–	–	0.5	0
2	CaH3BaH1	3	1	–	–	0.5	25
3	CaH2BaH2	1	1	–	–	0.5	50
4	CaH1BaH3	1	3	–	–	0.5	75
5	BaH	–	1	–	–	0.5	100
6	BaHCc10	–	9	1	–	0.5	10
7	BaHCc25	–	3	1	–	0.5	25
8	BaHCc50	–	1	1	–	0.5	50
9	BaHCer10	–	9	–	1	0.5	10
10	BaHCer25	–	3	–	1	0.5	25
11	BaHCer50	–	1	–	1	0.5	50

Table 2
Mixing proportions of mortar mixtures

Mixture	Aggregates		Binder	Binder: aggregate ratio	Ba(OH) ₂ (%)	Water:binder ratio	Flow value (mm)
	Calcitic	Ceramic					
LM-01	1	1	Lime	1:3	0	0.40	155±9
LM-02	1	1	Lime	1:3	0	0.80	>250
LM-03	1	1	Lime	1:3	0	0.55	200±15
LM-04	1	1	Lime+barium hydroxide	1:3	10	0.55	200±15
LM-05	1	1	Lime+barium hydroxide	1:3	25	0.55	200±15
LM-06	1	1	Lime+barium hydroxide	1:3	~15% (saturated solution)	0.55 (BaH saturated solution)	204±13

The amount of barium hydroxide that is presented on the table represents the amount of hydrated lime putty being replaced. All values in the table refer to volumes.

the lime putty and the volumetric porosity of the sand skeleton [19,20]. The calculated binder:aggregate ratio was 1:3 by volume. The mix proportions of the mixtures prepared are given in Table 2.

Based on the assumption that the role of the binder in mortar mixtures is to fill the voids between aggregate grains, all mix proportions are presented in terms of volume. The laboratory specimens were, however, prepared by weight, after taking the density of all components into account. The density of lime putty was found to be 1400 kg/m³, of barium hydroxide 1360 kg/m³ and of ceramic aggregates 2350 kg/m³.

The optimum amount of water required for the mixtures was determined through the measurement of the consistency of three different fresh mortar mixtures (LM-01, LM-02 and LM-03) containing different amounts of water, by flow test [21] (Table 2). A water:binder ratio of 0.55 was finally selected, which gave a mean flow value of 200 mm (LM-03 mixture).

For the preparation of mortar mixtures, barium hydroxide was added in the solid state in two different amounts. In the first two mixtures (LM-04, LM-05) barium hydroxide constituted 10% and 25%, respectively, of the total binder volume, by replacing equal volumes of lime putty. Water used in mixtures LM-04 and LM-05 was at room temperature (20 °C±2 °C). In a third mixture (LM-06), the water was replaced by an equal volume of a saturated solution of barium hydroxide, at a temperature of 80 °C. At this temperature, barium hydroxide hydrate reaches its maximum solubility and, therefore, maximum concentration in the solution [22]. This procedure aimed to simulate the actual consolidation process during the setting and hardening of fresh mixtures. The amount of barium hydroxide added to the mixture in this way was calculated as 15% v/v.

2.3. Curing conditions

Cubic (50 mm×50 mm×50 mm) and cylindrical shaped specimens of 60 mm height and 30 mm diameter were prepared. The specimens were initially stored at relative humidity of 90%±5%, and 20 °C±2 °C air temperature, for 7 days, followed by a period of 28 days at relative humidity of 65%±5% (20 °C±2 °C). After this period, the specimens were removed from the moulds, placed on a thick plastic grid and stored in the laboratory room until testing, at a temperature of 20 °C±2 °C and relative humidity of 50%±5%. Curing conditions were based on the directives described in the BS EN 4551-1 standard [23].

2.4. Monitoring the setting process

Mineralogical analysis of the binary pastes and mortar mixtures was carried out by XRD after 1 day, 28 days and 12 months setting times, in order to determine the products that were formed in each case, as a function of time. Samples were drilled from a layer 10–15 mm thick, from both cylindrical and cubic specimens (corresponding to binary pastes and mortar mixtures respectively). X-ray diffraction analysis of the samples was performed on a Siemens D-500 Diffractometer using the Cu-K_α radiation ($\lambda=1.5406 \text{ \AA}$) with a graphite monochromator in the diffraction beam, at 1.2 kW (40 kV, 30 mA). Spectra were collected in the range of 2–60° 2 θ , with a step of 0.03°/s. The identification of the setting products was performed using the Siemens Diffract, EVA-1 software. The diffraction patterns of the setting products were also analysed using the Search–Match software [24] in order to extract additional quantitative data on the concentration of each crystal phase in the sample. All measurements were carried out in triplicate ($n=3$).

The setting process was monitored by studying the mixtures under a JEOL 5310 scanning electron microscope, coupled to an Oxford EDX analyser. The analysis was achieved using the INCA/ISIS microanalysis suite. Freshly fractured surfaces of both binary and mortar mixtures, as well as thin sections of the mortar mixtures cured for 1 year, were examined. The samples were initially placed in acetone for 2 h and then in an oven, at 80 °C for 22 h. Fractured surfaces were coated with carbon for examination in SEM, while samples for thin sections were impregnated with epoxy resin.

Thermogravimetric analysis was additionally used to determine the phases formed in the binary pastes and mortar mixtures after a one-year setting and hardening period. Analysis was carried out on a Perkin-Elmer Diamond TG/DTA unit, using samples (20–25 μg) taken from a batch (4–5 g) collected from a layer of 10–15 mm thickness. Measurements were performed in static air with a heating rate of 10 °C/min in the range of 30–1000 °C, in triplicate ($n=3$).

3. Results and discussion

3.1. Raw materials

Chemical analysis of the calcium hydroxide powder showed that no impurities were present that could affect the quality and performance of the produced lime putty. The X-ray diffraction

Table 3

Semi-quantitative results calculated from the XRD patterns of binary pastes, after 12 months, using Crystallographica Search–Match software

Samples	Relative concentration of phases (%)									
	Ptl		Bh		Cc		W		A	
Setting period (months)	1	12	1	12	1	12	1	12	1	12
CaH	44	26	nd	nd	51	70	nd	nd	5	4
CaH3BaH1	37	22	3	nd	3	7	57	71	nd	nd
CaH2BaH2	39	18	4	nd	1	3	56	79	nd	nd
CaH1BaH3	16	9	4	nd	nd	nd	80	91	nd	nd
BaH	nd	nd	4	nd	nd	nd	96	100	nd	nd

The mineral phases identified are portlandite (Ptl), calcite (Cc), barium hydroxide hydrate (Bh), witherite (W) and aragonite (A).

analysis of the same powder showed that only crystalline portlandite $[\text{Ca}(\text{OH})_2]$ was present. The chemical analysis of the barium hydroxide powder revealed barium compounds >99%. Its diffraction pattern gave the crystalline form of barium hydroxide octahydrate $[\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}]$ as the predominant phase. The anhydrous form of barium hydroxide and the barium carbonate were also identified as secondary minerals, albeit in a very low amount. Sand consisted of calcite with less than 2% alumino-silicate impurities, and therefore could be characterised as calcitic. Chemical analysis of the ceramic fractions between 0 and 500 μm showed that the ceramic mass was slightly calcareous and potassium rich. Quartz, plagioclase, illite–montmorillonite, K-feldspars and hematite were the main minerals matched in the diffraction pattern.

3.2. Setting of binary pastes

Binary pastes served as ‘pure’ systems, free from the effect of aggregates, in order to monitor the formation of the setting products. The relative concentrations (%) of the phases

identified in the binary pastes, at different setting periods, are given in Table 3. These values are only semi-quantitative, as the precision of the results is reduced when strong peaks overlap the weaker peaks of other phases. Calcite and a small portion of aragonite are the two carbonate phases (CaCO_3) formed during the carbonation of lime putty (Fig. 1). A considerable amount of portlandite $[\text{Ca}(\text{OH})_2]$ was identified in all of the samples containing lime, even those with a setting period of 12 months (Table 3). In contrast, non-carbonated barium hydroxide was identified only in those samples analysed after a setting period of 1 month, while after 12 months, all $\text{Ba}(\text{OH})_2$ in the BaH paste was transformed to BaCO_3 (Fig. 2). Witherite (BaCO_3), formed by the carbonation of barium hydroxide, was the main product in the binary pastes, as shown in the diffractograms of the CaH2BaH2 binary paste, in Fig. 3. In the same paste, barium–calcium double carbonates $[\text{BaCa}(\text{CO}_3)_2]$ were also identified, although with difficulty, as its main peaks have the same 2-theta position as those of witherite. This consists of the promising evidence that the favourable barium–calcium carbonate could have been formed during the setting of the mortar mixtures.

The high reactivity of barium hydroxide, in comparison to calcium hydroxide, as illustrated by the XRD data, is also evident in the thermal analysis (DTA/TG) results (Fig. 4). The thermal analysis diagrams describe the thermal transformations (μV) and weight changes (%) attributed to the dehydration, dehydroxylation and decomposition of carbonates that take place during continuous heating of the samples. The weight loss values (%) of the binary pastes, at different temperature ranges, are summarised in Table 4.

The peaks in the range of 80–120 °C correspond to the evaporation of the naturally absorbed water, humidity and the melting of barium hydroxide hydrate $[\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}]$ in its water of crystallisation [22]. The small peak at 250 °C is attributed to the dehydration of chemically-bound water in the

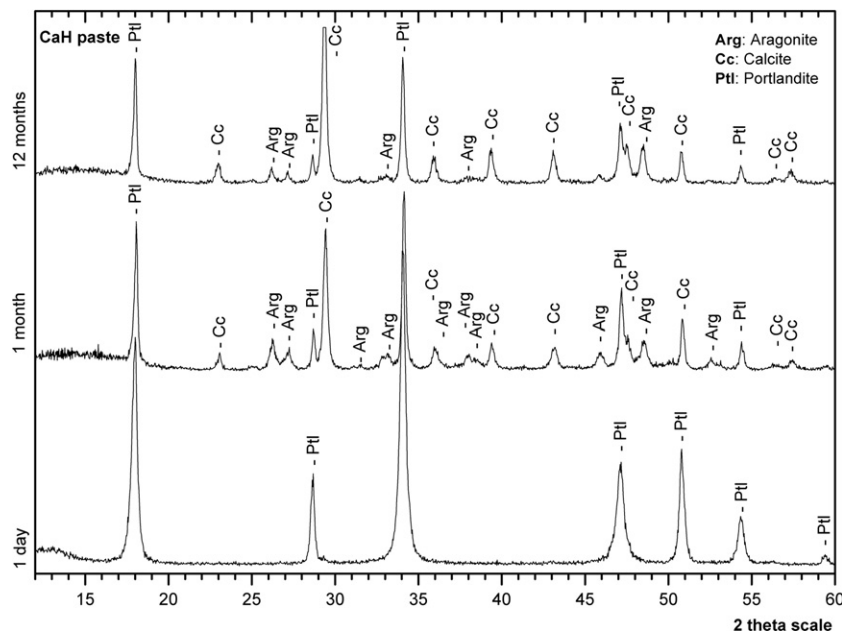


Fig. 1. Diffraction patterns of pure lime binder (CaH paste) after setting for different time periods.

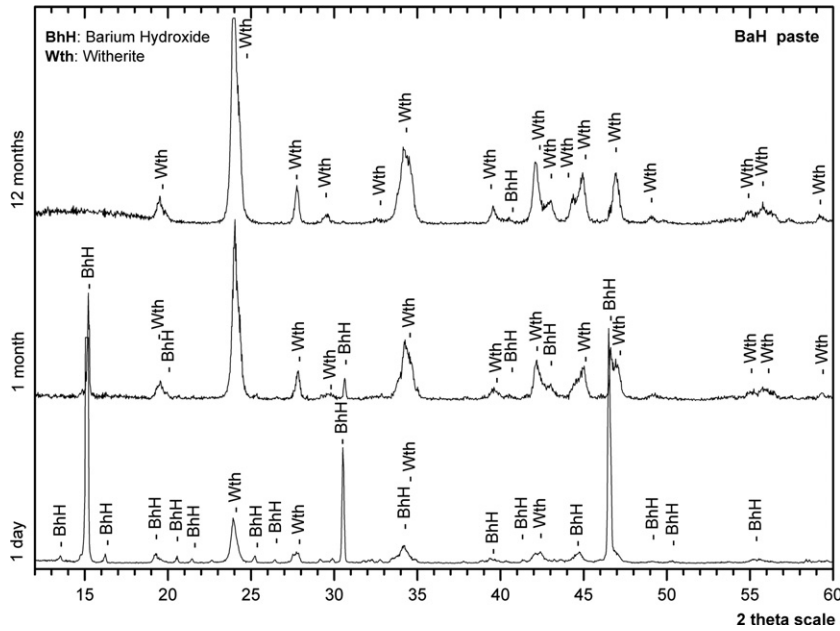


Fig. 2. Diffraction patterns of barium hydroxide (BaH paste) after setting for different time periods.

barium hydroxide [Ba(OH)₂] phases. Dehydroxylation reactions for barium hydroxide and calcium hydroxide take place at 350 °C and 400 °C, respectively. Finally, decomposition of carbonate phases is observed at 700 °C for calcite (CaCO₃) and at 800 °C for witherite (BaCO₃) [25] (Figs. 5 and 6). In sample CaH₂BaH₂, thermal transformations in the region 425–650 °C correspond to the decarboxylation of both calcite and barium–calcium carbonate.

Mineralogical (XRD) and thermal analysis results showed that the carbonation of barium hydroxide is much faster than the carbonation of lime. The main peak of barium hydroxide [Ba(OH)₂·8H₂O] disappeared after a setting period of 3 months. In

practice, this means that since carbonates are less soluble than hydroxides, the amount of Ba²⁺ ions that could be potentially leached in the initial period of setting, is reduced.

The study of binary pastes (pastes 6–11 in Table 1) of barium hydroxide with ceramic and calcium carbonate powder proved that barium cannot act as a binding medium on its own. The majority of the specimens produced were not able to retain their shape and they collapsed during de-moulding and handling for storage. However, it was observed that binary pastes consisting of barium hydroxide and calcium carbonate powder exhibited a moderate cohesion, which allowed BaHCc-mixtures to be de-moulded and retain their shape. The above phenomenon could

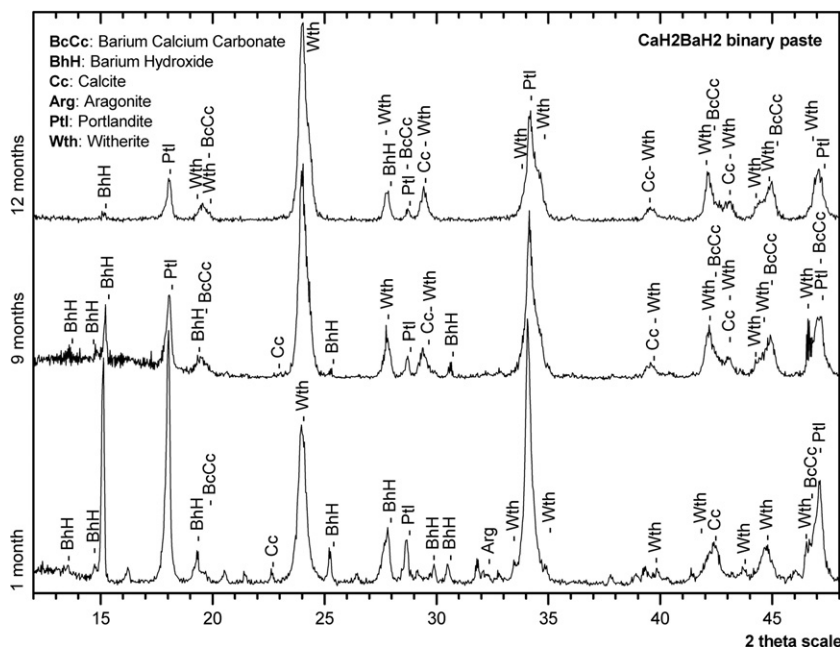


Fig. 3. Diffraction patterns of CaH₂BaH₂ paste after setting for different time periods. The paste initially contained equal parts of calcium and barium hydroxides.

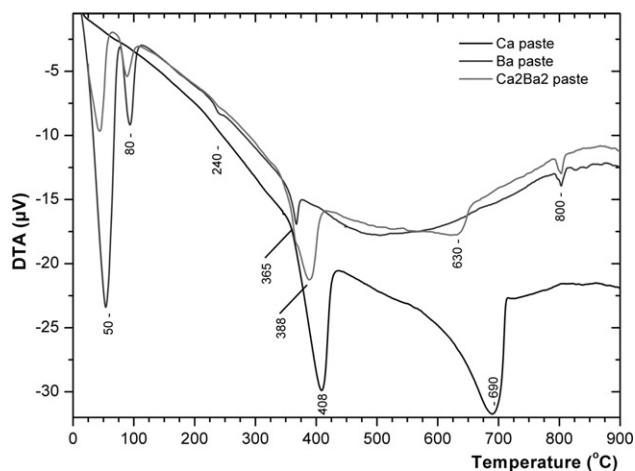


Fig. 4. Representative thermal analysis diagrams of binary pastes cured for 12 months.

be linked to the identification of $[\text{BaCa}(\text{CO}_3)_2]$ in the diffraction patterns of the above pastes and the concentration of barium around the calcitic crystals. This assumption was strengthened by the later examination of LM mixtures in SEM (Figs. 7 and 8).

Ceramic pastes have exhibited even lower cohesion. The initial cohesion and plasticity of the wet paste have been gradually decreased and finally disappeared by the evaporation of water and the carbonation of barium hydroxide. In this case, examination under the SEM showed that barium carbonate formed individual crystals and conglomerates, playing the role of inert inclusions.

3.3. Setting of mortar mixtures

The mineralogical composition results of the binding material of LM mixtures, was quite similar to those derived from the study of binary pastes. The main phases identified in the diffraction pattern of the reference mixture (LM-03) were calcite and aragonite (CaCO_3), portlandite [$\text{Ca}(\text{OH})_2$] and a small amount of quartz. Calcite is produced by the carbonation of the lime binder, while portlandite is attributed to the non-carbonated lime binder. Calcite and witherite (BaCO_3) were the main products identified in the mixtures that contain barium hydroxide hydrate (LM-04, LM-05 and LM-06) resulting from the carbonation of calcium hydroxide and barium hydroxide

Table 4
Thermal analysis (DTA/TG) results of binary pastes at 12 months

Temperature range (°C)	<80	80–120	120–450	450–750	750–950	Total
Samples	Weight loss (%)					
Ca	0.58	0.22	7.70	30.13	nd	38.63
Ca3Ba1	2.21	0.24	7.32	15.60	3.86	29.23
Ca2Ba2	9.77	1.55	5.48	6.50	4.68	27.98
Ca1Ba3	10.26	1.46	3.01	4.11	4.72	23.56
Ba	24.03	3.00	0.51	nd	4.22	31.76

Values correspond to the weight loss (%) of samples at different temperature ranges.

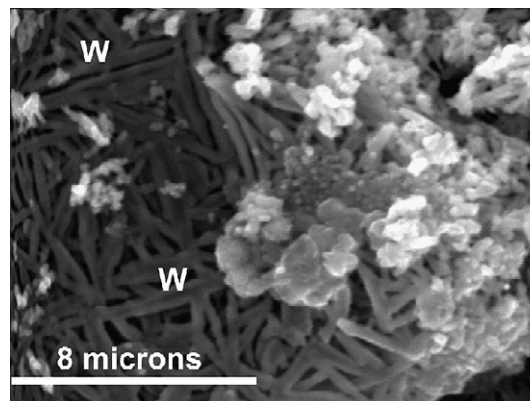


Fig. 5. Photomicrograph of BaH paste after setting period of 12 months. Elongated crystals of witherite (W) are formed through an amorphous conglomerate.

(Eq. (3)) respectively, along with portlandite and some small amounts of quartz or clay minerals.



The presence of barium–calcium carbonate $[\text{BaCa}(\text{CO}_3)_2]$ was also indicated in samples LM-05 and LM-06, although its main peaks overlay with those of witherite. Calcite was the predominant phase of calcium carbonate identified in the XRD patterns, followed by aragonite. The interpretation of the XRD patterns, which correspond to different setting periods showed that concentration of aragonite is gradually reduced with time and transformed to calcite.

The evaluation of XRD patterns and thermogravimetric diagrams suggests that the carbonation of barium hydroxide is much faster than that of lime, as was expected from the results of the binary pastes. The main diffraction peak of barium hydroxide hydrate $[\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}]$ at 15° is not present after a three-month setting period in all mixtures. In addition, DTA/TG diagrams do not show any peaks attributed to barium hydroxide. The fast transformation of barium compounds to the carbonate form increases their chemical stability and contributes to the lower amount of barium ions that could be potentially leached out of the binder mass, if exposed to the environment.

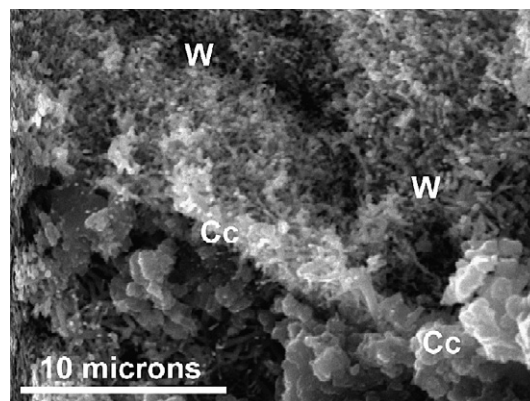


Fig. 6. Photomicrograph of CaH₂BaH₂ paste. Witherite crystals (W) are surrounded by very small hexagonal calcite crystals (Cc).

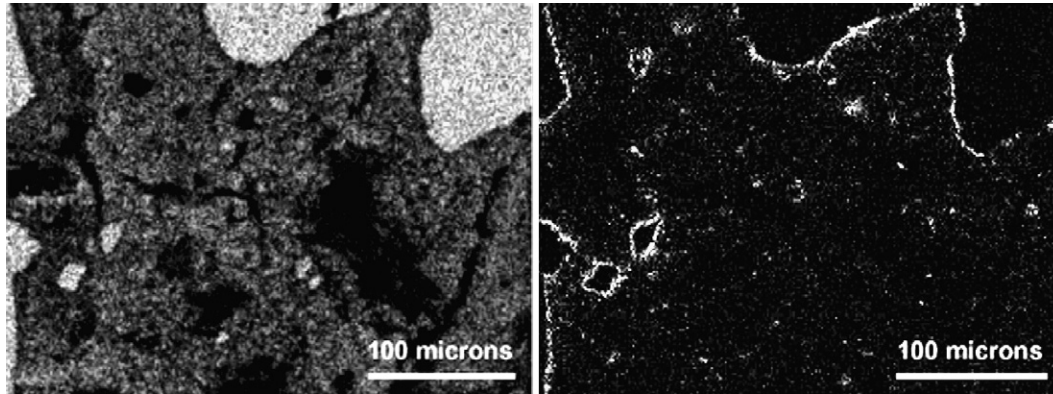


Fig. 7. X-ray maps of calcium (Ca^{2+}) left, and barium (Ba^{2+}) ions, right, in a thin-section of mixture LM-05. An increased concentration of barium ions is observed around calcitic grains.

Examination of freshly fractured surfaces under SEM, and thermal analysis of the binder fraction, verified the development of calcium silicate hydrate phases (C–S–H) with the typical needle-like crystals, which resulted from the reaction of lime with the ceramic material. Moreover, the formation of hydrated aluminosilicates, such as gismondine ($\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$) was indicated in the diffraction patterns of all mixtures.

Examination of the thin sections of LM mixtures under SEM and X-ray element-mapping showed that barium ions (Ba^{2+}) were evenly distributed through the binder matrix (Fig. 7). However, a more detailed examination of thin sections in higher magnification and linear scanning at the calcitic grains–binder interface areas (Figs. 8 and 9) revealed that barium ions increased their concentration around calcitic grains and reached their maximum values at the surface of calcitic grains. The relative concentration of barium and calcium ions around the calcite particles, as shown in Fig. 9, shows that barium ions are also present inside the mass of calcitic particles in a depth profile of 2–3 mm, but their concentrations gradually decreased to zero after this limit.

In mixture LM-06, where barium hydroxide was added as a saturated solution at 80 °C, the setting process involved an additional stage. Barium hydroxide precipitated from solution

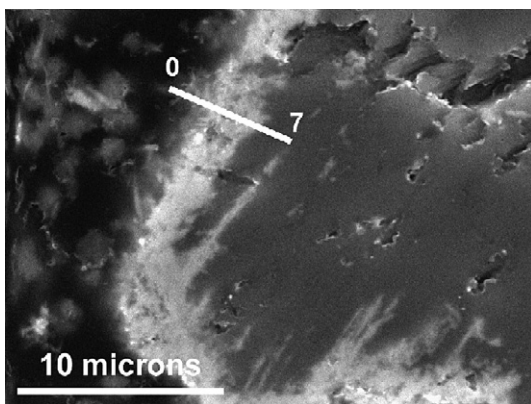


Fig. 8. Thin-section of LM-05 mixture under scanning electron microscope. The whitish area around the calcitic grain indicates the exchange of calcium and barium ions on the surface layer and the formation of a barium–calcium carbonate solid solution.

in the initial stage of mixing, due to the cooling of the solution. The precipitated barium hydroxide has small crystal size and is evenly distributed in the lime mass. The ion capacity of the solution is reduced as it reaches room temperature. When the solution reaches room temperature, barium ions react with carbon dioxide to form barium carbonate. Because of their high specific surface area, the precipitated barium hydroxide crystals also react with carbon dioxide and form barium carbonate. Depending upon the size of the initial particles, unreacted barium hydroxide may remain in the core. During the setting and curing of mixtures, no micro-cracks nor any other defects on the specimens, were observed.

The interpretation of all the above results indicates that two phenomena take place during the setting of barium mortars. At the interface around calcitic particles, calcium ions leave the calcite crystal, creating vacant places in which barium ions diffuse in a depth of *ca.* 2 μm (Fig. 9). In the mass of lime binder, barium ions co-precipitate with calcium ions and form a solid solution of barium carbonate in calcium carbonate, as evidenced from the predominant peaks of calcite and witherite which appear in binder

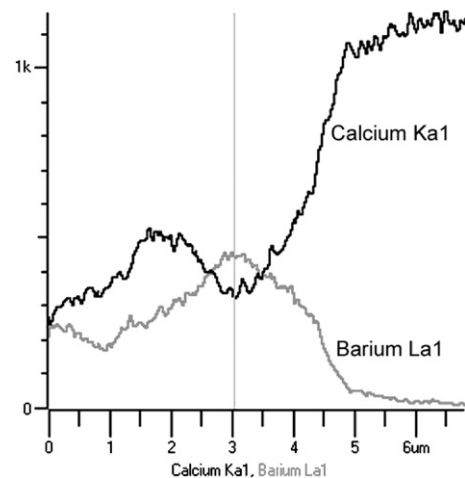
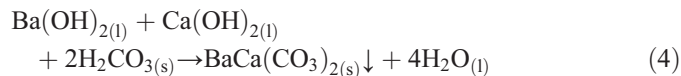


Fig. 9. Line-scan at the interface zone between calcitic grains and binding material. The binder consists of 75% v/v of calcium hydroxide and 25% v/v of barium hydroxide. The vertical line in the spectrum indicates the surface of the calcitic grain.

diffraction patterns. Furthermore, X-ray diffraction analysis provides evidence that barium–calcium carbonate is also formed within the binder. The formation of the above phase can be derived either by the diffusion of barium ions into the calcite lattice (replacement) or through the co-precipitation of barium–calcium carbonate during the carbonation process (Eq. (4)):



The formation of the solid solution described above offers a new matrix, which is rich in barium carbonate around calcitic particles, and new barium carbonate crystals may be directly bonded. Therefore, it acts as a bridge between calcitic aggregates, barium phases and lime binder, contributing to the formation of a more homogeneous microstructure. This is in accordance with similar observations in calcitic stone consolidation [8,16,17].

The formation of barium phases within the mass of lime binder could be beneficial to the durability of conservation mortars. Compared to calcite ($K_{sp}=6.9 \cdot 10^{-9}$ at 25 °C), witherite is less soluble in water ($K_{sp}=1.6 \cdot 10^{-9}$ at 25 °C). Moreover, in a polluted environment the reaction of carbonates with sulphur dioxide leads to the formation of gypsum (CaSO_4) ($K_{sp}=2.4 \cdot 10^{-5}$ at 25 °C), which is easily dissolved in rainwater and barium sulphate (BaSO_4), a compound of very low solubility ($K_{sp}=1.08 \cdot 10^{-10}$ at 25 °C), even in acidic environments [15]. Thus, the amount of the binding material dissolved and washed out of the mortar matrix could be reduced and, therefore, damage to conservation mortars minimized.

4. Conclusions

Based on the results of the experimental work presented above, it could be safely proposed that barium hydroxide may be used as an additive material to lime-based conservation mixtures. It was found that barium hydroxide can be mixed with lime putty to create a homogenous matrix in repair mixtures, without causing any defects.

The setting and hardening of lime–barium mortars, is described by the carbonation of both calcium hydroxide and barium hydroxide, the precipitation of calcite (CaCO_3) and witherite (BaCO_3), as well as the formation of the barium–calcium carbonate phase [$\text{BaCa(CO}_3)_2$]. It was also found that the carbonation of barium hydroxide is much faster than that of calcium carbonate.

The co-precipitation of barium and calcium carbonates leads to the formation of a barium carbonate in calcium carbonate solid solution. Its formation is more pronounced in areas around calcitic grains of diameter below 100 μm . The small grains act as nuclei and support Ca^{2+} – Ba^{2+} exchange reactions with the binding material. The above mechanisms result in the chemical compatibility of barium hydroxide with the lime binder.

References

[1] A. Moropoulou, A. Bakolas, K. Bisbikou, Investigation of the technology of historic mortars, *J. Cult. Herit.* 1 (2000) 45–58.

- [2] J. Hughes, J. Valek, Mortars in historic buildings, A Review of the Conservation, Technical and Scientific Literature, Historic Scotland, Edinburgh, 2003.
- [3] C. Rodriguez-Navarro, E. Hansen, W.S. Ginell, Calcium hydroxide crystal evolution upon aging of lime putty, *J. Am. Ceram. Soc.* 81 (11) (1998) 3032–3034.
- [4] A.W. Hendry, Masonry walls: materials and construction, *Constr. Build. Mater.* 15 (2001) 323–330.
- [5] M.J. Mosquera, D. Benitez, S.H. Perry, Pore structure in mortars applied on restoration. Effect on properties relevant to decay of granite buildings, *Cem. Concr. Res.* 32 (2002) 1883–1888.
- [6] J. Lanás, J.I. Alvarez, Masonry repair lime based mortars: factors affecting the mechanical behavior, *Cem. Concr. Res.* 33 (2003) 1867–1876.
- [7] T. Yates, Mechanisms of air pollution damage to brick, concrete and mortar, in: P. Brimblecombe (Ed.), *Air Pollution Reviews: The Effects of Air Pollution on the Built Environment*, Imperial College Press, London, 2003, pp. 107–132.
- [8] S.Z. Lewin, N.S. Baer, Rationale of the barium hydroxide–urea treatment of decayed stone, *Stud. Conserv.* 19 (1) (1974) 24–35.
- [9] M. Matteini, In review: an assessment of Florentine methods of wall paintings conservation based on the use of mineral treatments, in: S. Cather (Ed.), *The Conservation of Wall Paintings*, The Getty Conservation Institute, Los Angeles, 1991, pp. 137–148.
- [10] J. Schafer, H.K. Hildsford, Ancient and new lime mortars — the correlation between their composition, structure and properties, in: M.J. Thiel (Ed.), *Conservation of Stone and Other Materials*, Proceedings of the International RILEM/UNESCO congress, 29 June–1 July, Paris, 1993, pp. 605–612.
- [11] K. Van Balen, D. Van Gemert, Modelling lime mortar carbonation, *Mater. Struct.* 27 (1994) 393–398.
- [12] Y.F. Houst, F.H. Wittmann, Influence of water content and porosity on the diffusivity of O_2 and CO_2 through HCP, *Cem. Concr. Res.* 24 (1994) 1165–1176.
- [13] Y.F. Houst, F.H. Wittmann, Depth profiles of carbonates formed during natural carbonation, *Cem. Concr. Res.* 32 (2002) 1923–1930.
- [14] A.E. Charola, F.M.A. Henriques, Hydraulicity of in lime mortars revisited, in: P. Bartos, C. Groot, J.J. Hughes (Eds.), *Historic Mortars: Characteristics and Tests*, Proceedings of the International RILEM workshop, 12–14 May, Paisley, 1989, pp. 95–104.
- [15] E. Hansen, E. Doehne, J. Fidler, J. Larson, B. Martin, M. Matteini, C. Rodriguez-Navarro, E.S. Pardo, C. Price, A. de Tagle, J.M. Teutonico, N. Weiss, A review of selected inorganic consolidants and protective treatments for porous calcareous materials, *Rev. Conserv.* 4 (2003) 13–25.
- [16] J. Terada, Rhombohedral crystals of Ba–Ca and Sr–Ca double carbonates, *J. Phys. Soc. Jpn.* 7 (1952) 432–434.
- [17] J. Terada, Crystal structure of the Ba, Sr, and Ca triple carbonates, *J. Phys. Soc. Jpn.* 8 (1953) 158–164.
- [18] BS EN 196-1, Methods of Testing Cement — Part 1: Determination of Strength, British Standard Institution, 1995.
- [19] Technical Advice Note (TAN) — 1, Preparation and Use of Lime Mortars, The Scottish Lime Centre, Historic Scotland, Edinburgh, 2003.
- [20] R. Hayen, K. van Balen, D. van Gemert, The influence of production processes and mortar compositions on the properties of historical mortars, in: P.H. Bischoff, J.L. Dawe, A.B. Schriver, A.J. Valsangkar (Eds.), *9th Canadian Masonry Symposium—Spanning the Centuries with Masonry*, New Brunswick, 2001, URL: <http://www.nrc.ca/irc/fulltext/mortar/>, (accessed on September 2003).
- [21] BS EN 1015-3, Methods of Test for Mortar for Masonry — Part 3: Determination of Consistence of Fresh Mortar (By Flow Test), British Standard Institution, 1999.
- [22] M.P. DiBello, L.J. Manganaro, E. Aguinero, Barium Compounds, *Encyclopedia of Chemical Technology*, vol. 3, Wiley and Sons Pub, 1992, pp. 909–931.
- [23] BS 4551, Methods of Testing Mortars, Screeds and Plasters — Part 1: Physical Testing, British Standard Institution, 1998.
- [24] Crystallographica Search–Match Software, Version 2.1.1.1, Oxford Cryosystems 1996–2003, available at: www.crystallographica.co.uk.
- [25] R.C. Mackenzie, *Differential Thermal Analysis*, Academic Press, London, 1970.