



Environmental deterioration of ancient and modern hydraulic mortars

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Abstract

Little is known about the nature and durability of hydraulic mortars in ancient buildings. Furthermore, the characterisation of the type of binder is important in order to proceed to the design of conservation interventions. A procedure has been set up to identify the type of binder used in historic hydraulic mortars. A number of mortars has been sampled from historic buildings, on which analyses have been performed to verify the set up methodology and evaluate their deterioration due to environmental deposition. Being sulphation one of the most important mechanisms of degradation found on historical buildings, SO₂-exposure tests were performed on different replicas of hydraulic mortars. The formation of sulphur containing species, such as gypsum, ettringite and thaumasite, has been studied in controlled conditions. The results obtained prove that the sulphation occurs on hydraulic mortars, depending on the composition of the binder.



1 Introduction

The occurrence of gypsum formation on masonry due to environmental effects is very dangerous in the case of cement mortars, concretes and hydraulic binders in general, since two damaging reactions are likely to take place in the presence of gypsum, leading to the formation of ettringite and thaumasite. This research project was initiated from the concern on the role of environmental pollution in the deterioration of ancient and modern hydraulic mortars (pozzolan as well as cement-based). An understanding of the impact of the environment on such mortar types is of great importance as the number of monuments from the 19th and 20th century that need restoration in all European countries is increasing. Understanding of future behaviour and environmental impact is of utmost importance to decide how to deal with the hydraulic mortars used in current restoration sites.

The emphasis was put on the study on sulphation of hydraulic mortars due to environmental effects with the aim of clarifying 1) which phases contained in cement mortars are more reactive; 2) if pozzolanic mortars are affected by environmental sulphation; 3) if environmental sulphation can produce expansive ettringite; 4) if environmental sulphation and carbonation can produce thaumasite in cement and lime-pozzolan mortars; 5) what is the change of the porous system and (water and CO₂) diffusion properties of the mortars due to those reactions.

Therefore, these problems were afforded within a EC-Project on "Environmental Degradation of Ancient and Modern Hydraulic Mortars (EDAMM)", with the following objectives: 1) to improve scientific understanding of the decay mechanisms in hydraulic mortars used for historic masonry-work due to environmental action; 2) to improve scientific understanding of the parameters of mortars responsible for the type and speed of degradation due to atmospheric deposition; 3) to identify the environmental effects in existing historic buildings where hydraulic mortars were used; 4) to simulate the sulphation process on different types of hydraulic mortars in a laboratory chamber; 5) to study the change of physical properties of the hydraulic mortars with increasing degradation due to atmospheric pollution in view of evaluating compatibility with other masonry materials.

2 Methodology

2.1 Structure of the research

Research was structured around two main axes: (a) characterisation and analysis of mortars sampled from existing historical buildings in Belgium, Italy and Spain. Two categories of materials have been sampled: original mortars and mortars used for restoration. Aim of this part has been (i) the identification of the changes and new formations that occurred at the surface of the samples due to

environmental exposure and (ii) the development of a procedure for the identification of mortar types, with emphasis on the recognition of the hydraulic mortars and their origin. The comparative study of the water-vapour and CO_2 diffusion properties of ancient and early 20th century hydraulic mortars was also part of this research, to study their effect on deterioration; (b) preparation of laboratory samples, in order to study the effect of sulphation, with special focus on ettringite and thaumasite formation. Aim of this part of the research has been to determine if, and under which conditions, formation of ettringite and thaumasite can take place. Moreover, the effect of sulphation on the pore structure and diffusion properties of the samples has also been studied.

2.2 Materials and compositions used for the laboratory samples

The pastes have been synthesised with pure reagents in stoichiometric amounts. The composition of each paste as well as the corresponding hydration products are given in Table 1. To produce the mortars destined to the study of sulphation, two types of pozzolans were used: one synthetic, made of pure reagent SiO_2 gel and $\text{Al}(\text{OH})_3$, and one natural. Furthermore, one synthetic OPC mortar (M1) was obtained with the use of the above synthesised pastes (P6). For the production of the other mortars (for thaumasite studies as well) commercially available materials were used. Their chemical composition is shown in Table 2.

Table 1. Composition of the studied pastes

Ref.	Anhydrous and hydrated phases
P1	$\text{C}_3\text{S} + \text{H}_2\text{O} \rightarrow \text{C-S-H (I)} + \text{CH}$, $w/s = 0.45$
P2	$\text{C}_3\text{S} + \text{SiO}_2 \text{ (amorphous)} + \text{H}_2\text{O} \rightarrow \text{C-S-H (I)} + \text{C-S-H (II)}$, $w/s = 0.77$
P3	$\text{C}_3\text{A} + \text{H}_2\text{O} \rightarrow \text{C}_3\text{AH}_6$, $w/s = 0.6$
P5	$\text{C}_4\text{AF} + \text{H}_2\text{O} \rightarrow \text{C}_3 \text{ (A,F)} \text{H}_6$, $w/s = 0.3$
P6	synth.HOPC (70% $\text{C}_3\text{S} + 12\% \text{C}_3\text{A} + 12\% \text{C}_4\text{AF} + 6\% \text{gypsum}$), $w/s = 0.5$

The studies on thaumasite formation in hydraulic mortars when interaction of such materials with SO_2 is forced, were performed on four types of mortars: Hydraulic Lime Mortars (MT1), Lime-Pozzolan Mortars (MT2), Ordinary Portland Cement Mortars (MT3) and White Portland Cement Mortars (MT4). After curing, mortars used in the thaumasite formation study, were carbonated until the total transformation of portlandite into calcium carbonate. Finally they were submitted to accelerated sulphation by exposing the samples to 300 ppm SO_2 , 25°C and 95% R.H. for 2 days. Subsequently, the 50% of the sulphated samples were kept in a chamber with 0.3ppm SO_2 as pollutant and 0.50 l min^{-1} flow gas velocity, at 5°C and 95% H.R. for 6 and 12 months. The other half of the sulphated samples were conserved partially immersed in water at 5°C for 4



and 9 months. At those ages mortars were characterized by the techniques described in the following section. The composition of the binder as well as the binder to sand ratio (B/S) and water content (w/s) of the mortars are presented in Table 3.

Table 2. Chemical analysis of the raw materials

	OPC I-45A	WPC	Hydraulic Lime	Segni Pozzolan	Hydrated Lime	Sand
L.O.I.	1.66	0.82	22.66		24.45	0.05
I.R.	0.57		0.17*		0.02	0.40
SiO ₂	20.44	24.34	21.22*	51.65	0.39	98.92
Al ₂ O ₃	3.07	1.98	6.32	16.23	1.10	0.18
Fe ₂ O ₃	4.08	0.37	1.80	7.55	0.20	0.06
CaO	66.43	67.6	45.20	8.87	73.82	0.0
MgO	0.94	0.55	1.34	4.21	0.0	0.28
SO ₃	2.90	2.78	0.98		0.0	0.0
Na ₂ O		0.05		1.45		
K ₂ O		0.10		5.54		
SiO ₂ sol.			9.66**			
I.R.			17.13**			

* alkaline fusion attack ** cold acidic attack

Table 3. Composition of the studied mortars

Ref.	Binder type of the mortars used for the study of the effects of sulphation
M1	70% C ₃ S + 12% C ₃ A + 12% C ₄ AF + 6% gypsum, B/S = 1/3, w/s = 0.5
M2	Ordinary Portland Cement, B/S = 1/3, w/s = 0.5
M3	Lime + natural pozzolan, L/P/S = 1/1/6, w/s = 0.8
M4	Lime + synthetic pozzolan (lime : SiO ₂ gel : Al(OH) ₃ = 1:0.5:0.5)
Binder type of the mortars used for the study of thaumasite formation	
MT1	Hydraulic Lime, B/S = 1/1, w/s = 0.6
MT2	Lime & Pozzolan, L/P/S = 1/1/6, w/s = 0.8
MT3	Ordinary Portland Cement, B/S = 1/3, w/s = 0.5
MT4	Mineralised White Portland Cement, B/S = 1/3, w/s = 0.5

2.3 Methods

Physical characterisation was performed using a Mercury Intrusion Porosimeter. To identify the matrix composition X-ray diffraction (XRD), infrared spectroscopy (FTIR) and thermal analysis (DTA-TGA) were used. Furthermore, ion chromatography (IC) for ion quantification was also performed along with

SEM-EDX analyses for single particle identification. The diffusion of CO_2 at different sample water contents was measured using a Wicke and Kallenbach-like diffusion cell coupled to an infrared absorption analyser (Van Balen et al.¹).

To simulate the sulphation on artificial samples, a weathering chamber realised in the previous STEP Programme (contract CT90 0107) was used. After exposure, the samples were analysed using a Ion Chromatograph Dionex (4500i) for the quantitative determination of the ions SO_4^{2-} and SO_3^{2-} . Since the quantification of sulphite is important for a correct interpretation of the reactions taking place at the material surface, special precautions were adopted to avoid the oxidation of sulphite into sulphates during analysis, following a methodology set up specifically (Gobbi et al.²), by one of the participants. The identification of the salts formed, with particular attention to ettringite and thaumasite, were investigated by X-ray diffraction (XRD), infrared spectroscopy (FTIR) and scanning electron microscopy (SEM-EDX and TEM).

3 Main results obtained

3.1 Mortar identification procedure

The identification of the mortar type presents important difficulties, because, on the one hand, the initial mortar constituents have reacted, making recognition of the process very difficult; on the other hand, the products of the hydration of lime and pozzolans or of cement-based materials are quite similar.

The methodology developed and tested within the EDAMM Project, in order to make this identification possible, is summarised in Fig. 1. It consists of the following operations:

1. Visual analysis, aiming in the general description of the unknown samples;
2. Optical microscopy, aiming in the identification of the aggregate and the study of the binder;

On the basis of the results yielded by the aforementioned techniques, further analyses can be performed (X-ray Diffraction, chemical analysis consisting on a pozzolanicity test or the determination of the soluble silica content, DTA/TGA) in order to confirm the conclusions drawn after the first two steps.

3.2 Diffusion properties of original and restoration hydraulic mortars

3.2.1 Historical buildings

The Mercury Porosimetry analysis (MIP) highlighted that the total porosity of the cement-based mortars is much lower than of the lime-pozzolan ones. However, no conclusions can be made relatively to their respective pore structure. Indeed, if the pozzolan mortars seem to have a concentration of pores around $1\mu\text{m}$, the cement-based mortars sampled cannot be classified. Some have very fine pores, while some others are characterized by pores much bigger than $1\mu\text{m}$ as well. The obtained hygroscopic curves (isotherms) were in good



agreement with the conclusions obtained by MIP. Indeed, the hygroscopicity of the lime-pozzolan mortar is relatively higher than this of the cement- and cement-based mortars, especially at humidity levels less than 90%. The modern hydraulic mortars present a very similar behavior until this level and it is only at very high relative humidity that they start differentiating between them.

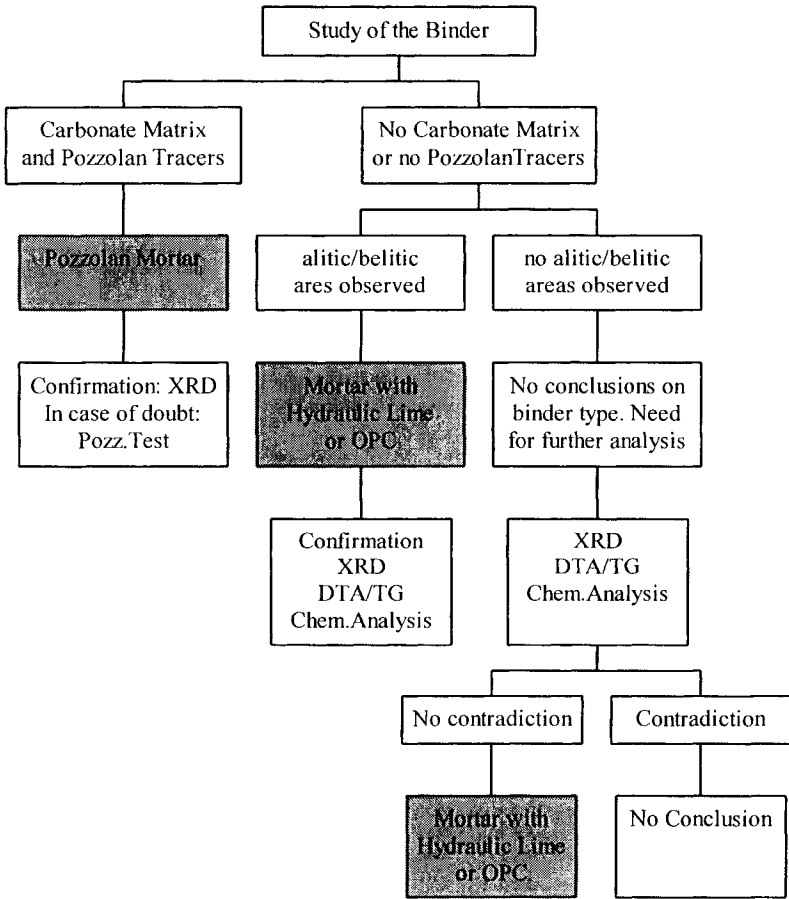


Figure 1. Flow chart for binder identification

Concerning CO₂ diffusion, the difference in the behavior of cement- and cement-based mortars in comparison to the pozzolanic mortar tested is clear. Diffusivity within the cement matrix is practically hindered at high relative humidity, while it still occurs within the lime-pozzolan mortars. This result is compatible with the materials' different pore systems: the cement-based materials have finer pores than the lime-pozzolan ones.

3.2.2 Laboratory tests

Diffusivity tests were also carried out on the laboratory specimens. The difference in the pore structure is reflected in the diffusivity properties of the specimens. As in the case of the sampled mortars, water -vapour diffusion is more important through a lime-pozzolan than a cement-based matrix. Furthermore, the diffusion resistance increased after exposure in the weathering chamber for both mortar types, probably due to their carbonation.

3.3 Sulphation of hydraulic mortars

3.3.1 Historical buildings

XRD data show how gypsum is one of the main phases present in the mortar samples collected on historical buildings in Belgium, Italy and Spain. The presence of gypsum is otherwise attributed to the sulphation reaction occurring at the sample surface, between the atmospheric deposition and the calcium salts present in the binder of the mortar sample. This underlines how the sulphation process already found in carbonate-based material, such as lime mortars, also occurs in both pozzolan and cement mortars. The optical observations confirm the XRD analyses. In fact, a large quantity of microcrystalline gypsum degrades the structure of the sample, as well as substituting the carbonate matrix, surrounding carbonaceous particles of atmospheric deposition and forming strongly degraded areas. Such reactions are most evident on the atmosphere-exposed face of the samples, while their concentrations are markedly reduced in the innermost layers, where the structure appears less damaged. Spongy spherical particles (cenospheres), emitted by the incomplete combustion of fossil fuels and deposited on the exposed surface of the samples are also found by SEM-EDAX.

The data obtained by ion chromatography show that the SO_4^- ion is the most abundant anion alongside NO_3^- and Cl^- . This finding highlights how sulphation is the most important degradation process occurring on hydraulic mortars. Moreover, half of the samples present small amounts of sulphite, a result that confirms how the sulphation mechanism occurs by: 1) direct deposition of SO_4^- , 2) deposition of SO_2 and its subsequent oxidation into sulphate at the surface of the mortar.

NO_3^- , in concentrations ranging from traces to 38060 ppm, is the final product of oxidation-hydration process of NO_x present in the atmosphere. NO_3^- and SO_4^- , typical components of industrial and urban emissions are clearly more abundant in the samples collected from urban sites, compared to suburban, rural and marine sites.

Chloride, being present in both industrial emissions or as a main component of marine aerosol, cannot be considered a typical tracer. In fact, Cl^- is abundant in the samples from urban sites, in some marine sites and also in some rural sites.

The IC results also reveal the presence of considerable amounts of organic anions: acetate, formate and oxalate (in order of abundance). These ions



constitute an important fraction of the carbon compounds present in the atmospheric aerosol. Formates and acetates, present in considerable quantities in our samples, can derive from the deposition of either primary pollutants or secondary pollutants due to photochemical reactions in atmosphere and/or after deposition. Finally, the presence of oxalates on monuments and historic buildings is still the subject of controversy, reported in the literature as being due to a number of different mechanisms: (a) the transformation of organic materials (oils, waxes, etc.) used in the past as protective and/or aesthetic treatments; (b) biological weathering: lichens in fact produce oxalic acid which reacts with the underlying carbonate component, leading to the formation of calcium oxalate monohydrate and dihydrate (whewellite and weddellite); (c) deposition of primary pollutants due to the incomplete combustion of fossil fuels and secondary pollutants forming from the photochemical oxidation of olefin compounds.

3.3.2 Laboratory tests

The sulphur species formed on the paste and mortar specimens exposed to 0.3 ppm of SO₂ for 6 and 12 months have been found to be partially soluble and partially insoluble.

In all the exposed samples, the soluble S-species were found as sulphites and sulphates: a significant increase in the SO₄⁼ concentration was observed, along with considerable quantities of sulphite, confirming the hypotheses on sulphation mechanism advanced from the results obtained on historical buildings. In all the exposed samples, the insoluble S-species were quantified by treating the samples with strong cationic resin with H cycle (Gobbi et al.³) and in the aluminate paste samples (P3) identified as ettringite. By FTIR analyses was also evidenced the C-S-H decomposition, highlighting a competition between the carbonation and sulphation processes.

3.4 Thaumasite formation on hydraulic mortars

Thaumasite formation in hydraulic mortars and concretes is a current subject of research because it presents some aspects scarcely defined in bibliography (Aguilera⁴). The main objective of this part of the project was to reproduce the formation of thaumasite in real samples by means of simulation tests carried out on mortars kept in an environmental chamber. SO₂ interacts with materials and as a consequence of this accelerated sulphation process, samples fix sulphur species. The amount of sulphate and sulphite ions detected in the mortars is given in Table 4. Gypsum crystals were seen on MT1 surface and syngenite crystals on the MT2 surface. In MT3 and MT4 no new phases were observed but some sulphur species were fixed as analyzed by EDX. MT1, MT3 and MT4 samples exposed to further SO₂ interaction in chamber, show substantial amounts of gypsum and few calcite crystals on their surfaces after 6 months. At this age MT2 surface appears covered by a thick and very well developed layer

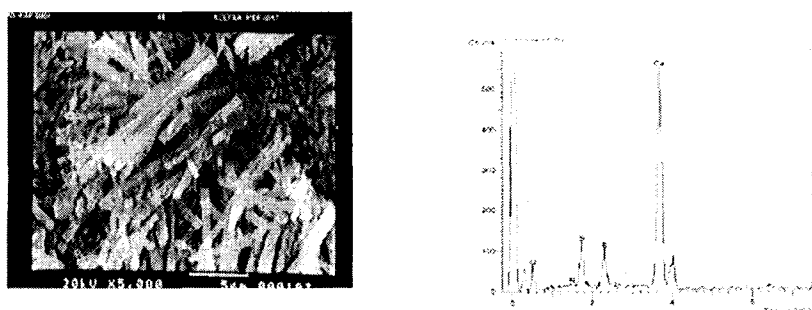
of syngenite crystals. After 12 months MT1 and MT2 samples show a very important microstructural modification at the surface; additionally they do not respectively contain gypsum/syngenite. At the same time an increase in the absorption bands due to CO_3 vibrations, can be seen in the FTIR spectra of these samples. MT3 and MT4 contain a lot of gypsum at 12 months of exposure; in MT3 some needles, similar to the thaumasite ones, can be observed at this age. The evolution of the total porosity of the specimens is shown in Table 5. On the basis of these results, it seems that mortars MT1 and MT2 reduced the total porosity, while mortars MT3 and MT4 underwent a small increase.

Table 4. Amount of ions in mortars after accelerated sulphation

IONS	MT1	MT2	MT3	MT4
SO_3^- (mg/g)	3,817	3,182	1,891	1,565
SO_4^- (mg/g)	5,972	7,48	7,974	7,871

Table 5. Total porosity evolution

Time of exposure	MT1(cc/g)	MT2 (cc/g)	MT3 (cc/g)	MT4 (cc/g)
Non exposed	0,142	0,134	0,069	0,066
6 months	0,128	0,117	0,076	0,074



**Figure 2. MT3, 9 months of conservation.
Thaumasite crystals and EDX analysis.**

The evolution of the other half of the sulphated samples (conserved partially immersed in water at 5°C for 4 and 9 months), was very different because there was no further SO_2 -material interaction. Thaumasite or thaumasite-ettringite solid solution crystals were identified on the surfaces of MT1, MT3 and MT4 after 4 months of conservation. In MT3 and MT4 the amount of those phases increases with time (Fig. 2). MT2 contains some syngenite and gypsum in the surface after 4 months of conservation and evolves with time in such a way that after 9 months it just contains some gypsum.



4 Conclusions

On the basis of the results obtained within the Project “Environmental deterioration of ancient and modern hydraulic mortars”, the following conclusions can be drawn:

1. A methodology for the identification of the mortar type and the distinction between lime-pozzolan and cement-based binders was developed and tested.
2. The pore structure of lime-pozzolan mortars is much more “open” and built up with pores of wider diameters than the cement-based mortars. This factor controls the water-vapour diffusivity through the matrix. The porous system is one of the factors explaining the durability of ancient hydraulic mortars.
3. Sulphation reaction occurs on hydraulic mortars due to the deposition of atmospheric SO_2 . These results are particularly important as cement mortars were used in 19th and 20th century monuments as well as in restoration works.
4. The interaction of hydraulic mortars with atmospheric SO_2 produces sulfur compounds that often evolve towards gypsum formation. In presence of alkaline ions (in lime pozzolan mortars for example) the evolution could lead to syngenite crystalization. Subsequently, gypsum may react with calcium carbonates and silicates generating thaumasite.
5. The formation of thaumasite or thaumasite-ettringite solid solution by interaction of atmospheric SO_2 with hydraulic lime mortars or cement mortars, has been reproduced in laboratory.

Acknowledgments

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