12th International Congress on the Deterioration and Conservation of Stone
Columbia University, New York, 2012

COMPARISON OF SALT DECAY SUSCEPTIBILITY OF NHL REPAIR MORTARS UNDER DIFFERENT TESTING CONDITIONS

Davide Gulotta,[1] Margherita Bertoldi,[1] Cristina Tedeschi[2] and L. Toniolo*[1]

[1]*Dipartimento Chimica, Materiali e Ingegneria Chimica "Giulio Natta", Politecnico di Milano,*
Milan, Italy
[2]*Dipartimento di Ingegneria Strutturale, Politecnico di Milano, Milan, Italy*

* Reference author: lucia.toniolo@polimi.it

Abstract

In the present work, the salt decay susceptibility of commercial products for the preparation of restoration mortars is presented. Four commercial NHL ready-mixed mortars and two commercial NHL binders have been selected among the most diffused product in the Italian market for the preservation of the architectural heritage. The salt susceptibility has been tested according to two standard protocols by RILEM TC: salt resistance of the hardened mortars on cubic specimens(modified version of MS-A2); and durability test of three-leaf wallettes (MS-A1). In both cases, a sodium sulphate solution was employed to contaminate the specimens (steady T and RH regime). The damage evolution was recorded during the tests and the final decay of the mortar cubic specimens was evaluated as mass variation, while the wallettes degradation was measured by meansof a laser profilometer. The results of the two methods applied on the same mortars are not always in accordance for what concerning damage rate and extent, confirming the crucial importance of choosing the most suitable crystallization test conditions for a reliable assessment of durability. The evaluation of salt susceptibility is confirmed to be a complex issue, which depends on a number of concomitant parameters but the results of the study showed the relevance of the microstructural characteristics in the damage occurrence.

Keywords: salt decay; crystallization test; natural hydraulic lime; repair mortar; damage evaluation.

1. Introduction

Salt crystallization is widely recognized as a major cause of decay of porous materials of the architectural heritage (Goudie and Viles, 1997, Charola, 2000, Steiger and Siegesmund, 2007). When historic masonries are considered, surface scaling, cracking, granular disintegration, powdering and loss of adhesion of the mortar joints are the main degradation patterns related to the presence of soluble salts (Doehne, 2002). In such cases the restoration of the bricks/mortar system integrity is required. In recent years, natural hydraulic limes, NHL according to UNI-EN 459-1 technical standard (UNI-EN, 2002), have been widely employed in the preservation of the built heritage activity. NHL are commercially available both as anhydrous binders and a as components of ready-mixed mortars. These latter, in particular, represent a particularly

advantageous alternative to traditionally prepared mortars, as they only require to be added with water followed by simple mixing operation.

On the other hand, when new materials are introduced in heterogeneous and aged systems, as historic masonries usually are, they are subjected to the same potentially harmful environment affecting the original ones and can suffer of similar decay mechanisms. Despite their increasing diffusion, commercial NHL products are often not adequately supported by a complete knowledge of the specific compositional features and of the performances at work of the hardened mortars. In such way, the fulfilment of the compatibility requirements (Maravelaki-Kalaitzaki et al., 2005, Rodrigues and Grossi, 2007) and the evaluation of the resistance to damaging agents, especially in term of salt decay behaviour, can hardly be achieved. As a consequence, the overall durability of the conservative intervention cannot be properly assessed.

Four commercial NHL ready-mixed mortars and two commercial NHL binders for the conservation of historic masonries were selected among the most diffused product in the Italian market. All the products are classified by the manufacturers as totally cement-free, with a minimum content of soluble salts, based on NHL binders and designed for the preparation of bedding mortars. The present study reports a comparison of the durability results of the hardened mortars respect to salt decay as indicated by two standard protocols by RILEM TC (RILEM, 1998). Uni-directional sodium sulfate crystallization tests have been preliminary performed according to a modified version of the RILEM MS-A2 on cubic mortar specimens. The RILEM MS-A1 three-leaf wallettes have been prepared and studied as well, in order to take into account the influence of a porous substrate and to better simulate the real application condition of a restoration mortars in a masonry system. Mass variation has been employed as a damage indicator of the mortars' cubic specimens while the damage evolution of the wallettes has been recorded an monitored by means of laser profilometry. The durability results of the two protocols have been compared. Moreover, an attempt has been made in order to correlate the salt susceptibility with specific compositional, microstructural and mechanical characteristics of each mortar in order to identify the most significant parameters influencing the damage.

2. Materials and methods

2.1 Commercial products

Four ready-mixed commercial mortars (named M1, M2, M3, M4) and two commercial binders (named B1 and B2) specifically designed for restoration purpose have been selected. All products are defined as based on NHL, classified as cement-free and with a minimum content of soluble salts. The commercial materials are supplied by BASF, Italcementi, Kerakoll, Kimia and Tassullo. The aggregate used for mortars preparation (mixed with B1 and B2) is a standard quartz-siliceous sand.

2.2 Mortars preparation

Mortars preparation has been performed according to the indications of the technical data sheet provided by the suppliers. NHL anhydrous binders have been mixed with the standard aggregate (B/A ratio 1:3; weight/weight) and a fixed amount of water. Ready-mixed mortars powders have been simply added with the required amount of water. Mixing operations have been performed with a mechanical mortar mixer

according to European technical standard (UNI-EN, 2005).4x4x16 cm prismatic specimens have been casted in demountable steel mould, compacted by mechanical vibration and stored at 20°C - 90% RH for 48 hours. Specimens have been then removed from the mould, cured at 20°C - 90% RH for 60 days, and divided into 4 cm cubes by means of a diamond wheel cutter.

Three-leaf wallettes specimens (approx. 250x200x120 mm) have been prepared with traditional fire-clayed red bricks as porous substrates (Fig. 1a). Each wallette consists of three courses of bricks with two horizontal bed joints and a vertical one The mortars have been laid between the brick's surface, let to harden at 20°C - 90% RH for 48 hours and the wallettes have been finally stored at 20°C - 90% RH for 60 days.

2.3 Crystallization test

Cubic mortar specimens have been dried at T = 60°C until constant weight and the initial weight has been recorded. The four lateral faces of the specimens have been sealed in order to allow evaporation through the upper surfaces alone. A saturated Na2SO4 water solution (anhydrous Na_2SO_4 reagent grade, Fluka) has been added until an imbibitions depth of 1 cm from the bottom of the specimens. The imbibition phase has been carried out for 2 hours at 20°C and followed by the storage of the specimens in a dessicator for 22 hours at t = 20°C and RH 80% to promote mirabilite crystallization (Flatt, 2002). The complete imbibition/crystallization cycle (2 hours imbibitions +22 hours crystallization) has been repeated four times a week (week cycle) and then specimens have been dried at 60°C. Debris and loose particles have been removed by brushing the upper surface and the mass variation of the specimens has been measured. The week cycles have been repeated until a significant damage of the evaporation surfaces has been has been developed by most of the mortars.

The wallettes have been imbibited through their lower side with a 10% (w%) Na2SO4 solution (anhydrous Na_2SO_4 reagent grade, Fluka), stored over a layer of dry gravel and sealed in a plastic container. In such way the upper side alone has been available as an evaporation surface exposed to the laboratory environment (20°C and 50% R.H.). Each crystallization cycle has been prolonged for four weeks. At the end of the cycle the upper surface of the wallettes has been brushed to remove all the efflorescences and detached materials prior to the profilometry measurements; de-mineralised water was added inside the sealed box in order to promote further crystallization (Fig. 1b) and a new 4-weeks cycle has been started.


Fig. 1. Three-leaf wallette before the crystallization test (a) and stored in a plastic container at the beginning of a new crystallization cycle (b).

3. Results and discussion

3.1 Commercial products characterisation

The complete characterisation of both the anhydrous commercial products and the related hardened mortars has been reported in a previous work (Gulotta et al., 2009) and here summarized in Tab. 1. The hydraulic behaviour of the commercial products mostly relies on the presence of di-calcium silicate as larnite, which is the main hydraulic compound in M2, M3, M4 and in binder B2. In binder B1 larnite is present together with portlandite while in M1 it cannot be traced and portlandite is the only binding compound detected by XRD. As far as the aggregate fraction is concerned, the one of M1 and M2 is the most heterogeneous and includes both quartz-siliceous sand and carbonate minerals. M3 aggregate fraction has calcite prevalent respect to dolomite and minor quartz; while the one of M4 is eminently carbonate and almost entirely composed of dolomite.

The total porosity values of the hardened mortars range between 21,42% of B2 and 34,26% of M4. The four ready-mixed mortars show a limited variation, with the lower porosities belonging to M2 and M3. If the median pore radius is considered, M1 is characterised by a particularly fine porosity with a significant pore concentration in the micro-pores and meso-pores range. The mortars prepared with the commercial binders (B1 and B2) have a rather mutually comparable porosity, which is slightly lower than those of the ready-mixed ones, and a quite similar median pore radius.

Tab. 1. Summary of the main compositional, microstructural and mechanical characteristics of the initial anhydrous commercial products and of the final hardened mortars.

	ANHYDROUS COMMERCIAL PRODUCTS								HARDENED MORTARS		
Sample	Binder NHL class	XRD results							Porosity [%]	Median pore radius [μm]	Compressive strength [MPa]
		P	L	F	C	D	M	Q			
M1	5	++	-	+++	+	-	++	+++	30,37	0,05	9,57
M2	5	-	++	+	+++	-	+	++	26,48	0,16	10,06
M3	3,5	-	++	-	+++	+	-	++	27,08	0,43	8,84
M4	5	-	+	-	++	+++	-	+	34,26	0,66	4,39
B1	3,5	+++	+++	-	+	-	-	++	22,59	0,27	4,70
B2	5	-	++	-	+++	++	-	++	21,42	0,20	7,38

+++ = dominantly present, ++ = present, + = traces, - = not detected
P = portlandite, L = larnite, F = feldspar, C = calcite, D = dolomite, M = muscovite, Q = quartz

The average compressive strength values of the samples after 60 days curing define three groups: the highest strength is shown by M1, M2 and M3 which all reach at least 8,5 MPa; M4 and B1, on the other hand, have the lowest final resistance; B2 has an intermediate behaviour.

The results highlight that for all the ready-mixed mortars a clear correlation between the NHL binder class and the final mechanical behaviour cannot be established, while in the case of B1 and B2 the 60 days strength results are rather in accordance with the binder classes they belong to.

Finally, it has to be pointed out that mortar M2 showed an unexpected presence of slag fragments within the hardened binder's matrix after the petrography analysis. Despite the manufacturer's indication, it cannot be defined as a proper natural hydraulic lime based product.

3.2 Salt crystallization test: cubic specimens

Seven week cycles have been performed in order to obtain significant damage in most of the mortars. The salt crystallization over the mortars' surfaces takes place according to two main patterns which can be observed during the initial cycles: elongated and powdered crystals can be formed all over the evaporation surfaces (M1), as well as a non homogeneous white veil due to the salt accumulation just beneath the mortars surface (M4). As the imbibition/crystallization cycles proceed, the former pattern gives rise to massive granular disintegration. The salt accumulation of the latter one leads to the progressive cracking of the mortars, with delamination and scaling of the external material. In all cases, further analyses have been conducted in order to characterize the efflorescences coming out from the substrate. Sodium sulfate is confirmed to be the only soluble salt present, thus excluding any potential contribute of the mortars' composition itself to salt formation.

The damaging rate is reported in Fig. 2, in which the percentage mass variation (100% corresponds to the initial mass of the samples) is plotted against the crystallization cycles.

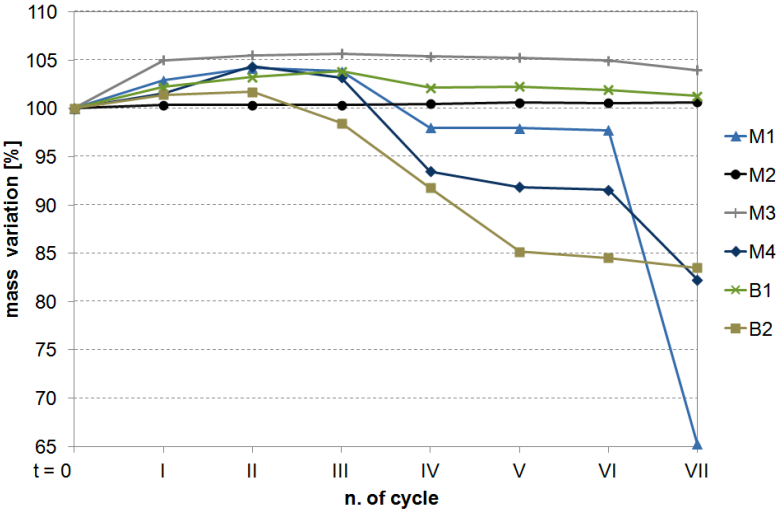

Fig. 2. Damaging rate of mortars' cubic specimens during the uni-directional salt crystallization test.

The first two cycles corresponds to the initial salt accumulation within the mortars' porosity. No damage still occurs during this stage and in all cases a mass increase is detected ranging from extremely limited (M2) to significant values (M3). During the subsequent cycle, three samples, namely M1, M4 and B2, start to show a mass decrease due to the ongoing mortar damage. B2, in particular, is characterized by a rather steady degradation rate, which tends to slightly slowing down during the final cycles. M1 and M4, on the contrary, show an increase in the damaging rate in the last cycle, which is particularly evident for M1 and determines the worst final performance in terms of durability. The initial major salt uptake of mortar M3, respect to all others, does not give rise to significant mass variation during the subsequent stages. This means that after a certain amount of salt solution is penetrated within the porous substrate, this last is able to let it crystallize without damage and the specimen remains almost stable during the remaining cycles. Minor variations, if compared to those of M1, M4 and B2, can be observed in B1, which only shows a slight mass decrease due to limited damage since the third cycle. Among all mortars tested, M2 is the only one showing no variations at all, neither during the first stage nor as the crystallization/dissolution proceeds. This indicates that the salt solution penetration within the mortar is almost completely inhibited.

The photographic documentation of all specimens at the end of the test is shown in Fig. 3. A clear correlation between the mass variation and the final damage level to the naked eye can be observed. The main degradation features of the mortars are described as it follows, according to decreasing extent of the final damage:

- the massive granular disintegration of M1 has lead to a dramatic loss of material;
- M4 and B2 both show significant damage and the loss of material is mostly

located on the edges of the specimens;

- B1 has minor damage mainly occurring on the edges; M3 only shows a minimal loss of material from the upper side edges, while the central area of the evaporation surface is almost undamaged;
- M2 does not show any damage at all.

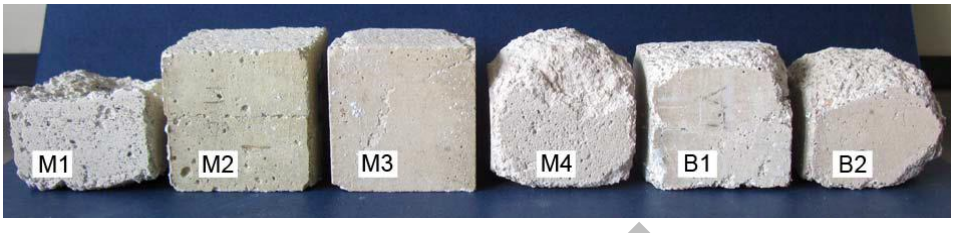

Fig. 3. Photographic documentation of the damage level of mortars' cubic specimens at the end of the uni-directional salt crystallization test (seven weekly cycles).

3.3 Salt crystallization test: wallettes

Eight crystallization cycles have been performed in order to obtain significant damage in most of the wallettes. The damage evolution has been monitored by means of a laser profilometer: the profile pattern of each wallette has been recorded at the end of every cycle along a fixed direction (transversal direction, crossing three bricks and two horizontal bed mortar joints); profiles of the same wallette collected at subsequent cycles have been then compared and analysed; the differences between the initial profile and the following ones has been ascribed to the damage occurrence.

As a significant example, in Fig. 4 is reported the graphical elaboration of a selection of the profile results of mortar M1. The blue profile describes the surface pattern prior to any crystallization (indicated as T0) and shows an irregular cross-section of the wallette, in which the two mortar joints can be easily identified being slightly in relief respect to the contiguous bricks.

After the first crystallization cycle the first degradation already occurs to both the lateral bricks and the mortar joints (height decrease), while the central brick highlights a height increase. This is due to a blistering effect induced by salt crystallization taking place just below the brick surface. As a matter of fact, as it can be observed at the end of the following cycles (cycle III), a massive loss of material takes place in this location due to delamination and detachment of brick scales. The damage of the remaining section proceeds at a lower but more constant rate respect to the central area and blistering can also be detected in joint 2. The major damage of the mortar joints takes place at the end of the fifth cycle (corresponding to a five months test duration). At the end of the test, after eight cycles, joint 2 doesn't show any further loss of material, while joint 1 appears extremely decayed due to massive granular disintegration and scaling occurred in the meanwhile.

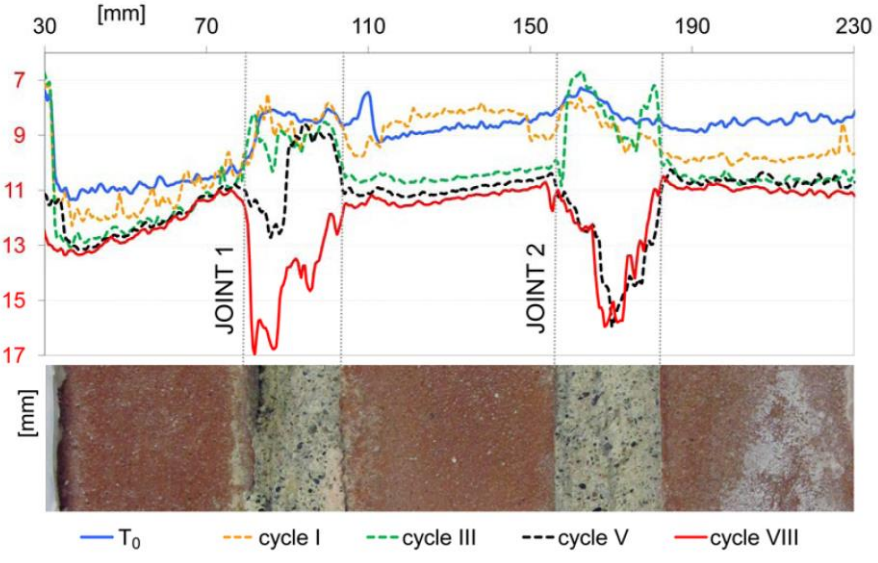

Fig. 4. Graphical elaboration of the profilometer results of mortar M1 and (below) photographic documentation of the superficial area of the wallette on which the profiles have been acquired. The upper border of the image indicates the measuring line followed by the profilometer.

The areas defined by the T0 profile (upper limit) and by the subsequent profiles collected after each crystallization cycle (lower limit) have been calculated in the two regions indicated by the vertical dotted line in Fig. 4. These values have been used to monitor the damage rate of the mortar joints. The initial salt accumulation phase, which preceded the damage of the cubic specimens previously discussed, does not take place. As a matter of fact, the damage of the joint occurs since the first crystallization cycle in most of the wallettes.M2 and M3 are the only exceptions as they both begin to show some degradation from the subsequent cycle. M2, M3, M4 and B1 are subjected to a rather constant damaging rate, while M1 reaches a sort of "critical point" at the end of the fifth cycle, when massive degradation takes place due the granular disintegration and scaling of the mortar.

The final damage extent values allow to classify the mortars according to three classes of resistance to salt decay:

- M1 shows the worst final result, with significant loss of material from the joint, which dramatically increases after the fifth crystallization cycle;
- M2 and B2 are characterised by a medium-level damage and by quite mutually similar damaging rates especially during the first cycles of the test;
- M3, M4 and B1 show the best durability result, as they only develop very limited damage. M4 and B1, in particular, develop most of the damage during the first cycles. After the salt has reached the evaporation surfaces of the wallette, the subsequent crystallization/ dissolution cycles seem to be much less effective in inducing further damage. As a consequence, the damaging rates tend to slow down and to become quite steady.

4. Conclusions

The results of the durability test of mortar cubic specimens highlight quite different behavior of the commercial products for what concerning damaging rate, decay patterns and damage location.

At the end of the test, granular disintegration and delamination were observed on most of the specimens, while some of them only showed superficial crystallization and in one case no damage at all has been observed. The mass variation seems to be a reliable damage indicator and provides results which are supported by the naked eye observation of the final damage extent. The compositional heterogeneity of the commercial products gives rise to quite different microstructural and mechanical characteristics of the hardened mortars. It is therefore difficult to identify a single specific parameter, which mostly affects the salt susceptibility. However, the presence of a particularly fine porosity is confirmed to be a weakening factor respect to salt decay, while, on the other hand, the presence of a high amount of hydraulic compounds seems to generally improve the mortar resistance.

The salt susceptibility test of wallettes are more representative of the real application conditions of the restoration materials, but the presence of the brick porous substrates indeed introduces a further heterogeneity factor. In particular, the brick porosity strongly influence the migration of the salt solution as well as the evaporation front, which is no longer taking place on the mortar surface alone. Consequently, part of the damage occurs at the expenses of the brick and this contribution must be properly considered within the test result. Moreover, the use of a 10% Na2SO4 solution provided once instead of a saturated one with continuous feeding determines a much slower damage evolution respect to the cubic specimens. The laser profilometer seems to be able to record the variations of the wallettes as a result of the salt crystallization effect. Being the testing condition very different respect to those of the cubic specimens test, the final results are not always in accordance with those. In particular: whereas the extremely low resistance of M1 is always detected by both the test procedures; the very good result of M2 is not confirmed when the mortar is coupled with the brick substrate; both M3 and B1 always show only limited damage while the general performance of M4 slightly improves in the wallettes test, due to the bricks contribution.

Crystallization test still remains fundamental procedures to preliminary assess the behavior of hardened materials at work with respect to durability. The test methodology should be properly chosen according to final application conditions and considering that the more heterogeneous the materials/systems to be tested are, the more potential variation in the final results obtained with different procedures have to be expected. In all these cases, a large number of specimens is highly desirable in order to obtain reliable results.

References

Charola, A. 2000. Salts in the deterioration of porous material: an overview. *Journal of the American Institute for Conservation*, 39, 327-343.

Doehne, E. 2002. Salt weathering: a selective review. In: Siegesmund, S., Weiss, T. N. & Vollbrecht, A. (eds.). *Natural Stone, Weathering Phenomena, Conservation Strategies and Case Studies*. Geological Society, 51-64.

Flatt, R. J. 2002. Salt damage in porous materials: how high supersaturations are generated. *Journal of Crystal Growth*, 242, 435-454.

Goudie, A. & Viles, H. 1997. *Salt weathering hazards*, Chichester John Wiley.

Gulotta, D., Toniolo, L., Binda, L., Tedeschi, C., Van Hees, R. & Nijland, T. G. 2009. Investigation of commercial ready-mixed mortars for architectural heritage. *Proceedings of the 11th Conference on Structural Repairs and Maintenance of Heritage Architecture*. Tallinn, Estonia, 22-24 July. WIT Press, 231-241.

Maravelaki-Kalaitzaki, P., Bakolas, A., Karatasios, I. & Kilikoglou, V. 2005. Hydraulic lime mortars for the restoration of historic masonry in Crete. *Cement and Concrete Research*, 35, 1577-1586.

RILEM TC 127-MS. 1998. Tests for Masonry Materials and Structures. Materials and Structures, 31, 2-19.

Rodrigues, J. D. & Grossi, A. 2007. Indicators and ratings for the compatibility assessment of conservation actions. *Journal of Cultural Heritage*, 8, 32-43.

Steiger, M. & Siegesmund, S. (eds.). 2007. Special issue on salt decay. *Environmental Geology*, 52, 185-420.

UNI-EN 459-1. 2002. Building Lime - Definitions, specification and conformity criteria.

UNI-EN 196-1. 2005. Methods of testing cement - Part 1: Determination of strength.