

Sodium sulphate test on lime-based mortars: attaining degraded material to test conservation products and assessing salt resistance

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Abstract

Four mortar mixtures were subjected to a sodium sulphate test, formulated to obtain degraded material for the further testing of conservation products and to estimate its salt resistance based on their hydric and hygric parameters. The ageing test involves cyclic conversion of thenardite-mirabilite. The cycle comprises of: the drying stage, salt absorption by capillarity, cooling and finally a total immersion in water. Water absorption by capillarity and microporosity determined by mercury porosimetry, were found to have a significant effect on the amount of salt absorbed consequently reflecting the induced damage. The experimental results support the theoretical view that micropores smaller than 0.1 μm in radius have a critical influence on the damage induced by sodium sulphate. Lime-metakaolin mortar proved to be extremely salt-susceptible in respect to lime mortar. The addition of linseed oil to both lime and lime-metakaolin mortar improved the salt resistance of both materials by granting hydrophobicity and restraining the absorption of salt. The ageing test used was successful in attaining lime mortar specimens to exhibit degradation patterns parallel to naturally exposed material, therefore can now be used for the testing of conservation products.

Keywords: sodium sulphate, lime, metakaolin, microporosity, hydrophobicity

1 Introduction

Salt damage is currently considered one of the main weathering processes of porous construction materials [1] and it is especially relevant in old buildings. Salt degradation progresses faster in old masonries because these are based on lime mortars, which are mechanically weaker than the porous materials in new buildings. One way to improve the strength and durability of air lime mortars is to partially replace air lime by other materials such as pozzolanas. Metakaolin is a promising pozzolanic material in this regard because it can grant higher mechanical strength than pure air lime mortar but not high enough to generate stress leading to failure of the original system [2].

Since liquid transport is one of the key factors influencing durability, materials that grant hydrophobic properties to mortars have become of great interest to the scientific community [3]. Research on the usage of traditional compounds to improve repairing mortars durability has also become of great interest [4, 5, 6] due to their harmless nature, compatibility with the traditional construction materials and cost-effectiveness.

Under the impossibility of sampling damaged materials from the historic buildings, *in situ* tests are the only means of evaluating the behaviour of the treatments in real field conditions. Nevertheless, the controlling of the variable parameters and the measuring conditions impose great difficulties in gathering reliable information [7]. This situation forces the investigations to simulate the testing of sound materials, which may not be quite representative of the onsite reality. The results obtained are limited in what concerns the evaluation of the treatment efficiency because there is an information lack about its action in the weathered material, which has different characteristics from the sound material. The contrast of properties is also expected to be lower in sound materials and therefore the harmful potential of the tested situations may result severely underestimated when compared to reality.

The values of the material properties, namely the hydric and hygric parameters (e.g. porosity, water capillary coefficient, pore size distribution, drying behaviour) are of utmost importance in the immediate action, namely in the cohesive properties and durability of the product. This aspect was the main goal for the formulation of the salt ageing test used in the present study.

Sodium sulphate was selected as the ageing salt due to its highly aggressive nature, to its worldwide occurrence in the architectural heritage and to its common use in building material durability studies [8, 9]. However, the definition of a testing protocol based on the action of sodium sulphate to produce a controlled artificial ageing has shown to be a more difficult task than it was initially expected because degradation is not a simple regular process. In fact, trying to induce slight modification of the

specimen through the action of sodium sulphate may destroy it completely within one or two cycles [10].

2 Experimental design

2.1 Materials

In the present study, four mortar types were designed and subjected to a sodium sulphate ageing test: lime mortar and lime with metakaolin to improve the mechanical strength; linseed oil was mixed in both reference mortars to grant hydrophobicity and investigate its salt resistance effectiveness.

Aerial dry hydrated lime in the form of powder (classified as CL90S) was used as the basic reference binder for all the specimens. Pure siliceous sand with controlled granulometry (0 to 4mm) was used as aggregate. The hereby-designated metakaolin corresponds to the burnt Czech clay shale Mefisto L05 described in [11]. The linseed oil used was extracted by the cold press method from flax seeds.

The binder/aggregate ratio used to prepare all mortar specimens is shown in Table 1. The amount of water was added in order to achieve 170 ± 5 mm consistency with the flow table test. Binder and aggregate were mixed in an automatic mortar mixer at low speed for 6 min. Water was then added and the mixture was blended for another 3 min. Linseed oil was added in 1.5 wt.% in respect to the binder weight, following the results obtained by [5] and was mixed with the mortar mixture before adding water.

The mortars were moulded in prismatic 40×40×160 mm casts using a jolting table to compact them. The specimens were demoulded after 1 day and the fresh young samples were cut in half to obtain 40×40×80 mm specimens. For the following 6 days the specimens were kept under high RH conditions (90 ± 10 %) and at 20 ± 5 °C. After this period, the mortar prisms were stored for 83 days in a room with controlled RH and T (60 ± 10 % and 20 ± 5 °C) lain on a 40×80 mm face over grid lined plastic shelves. Therefore, the prepared mortars were hardened for 90 days previously to carry out the tests. A more detailed description about the materials and sample preparation can be found in [12].

2.2 Test methods

The ageing test was elaborated based on a previous study with the aim of weathering stone specimens for further treatment [10] and in the present study it was applied on mortars and also used to test the durability of the hydrophobic mortars with linseed oil.

The samples were initially oven dried at 40 °C to constant weight and impregnated by capillarity with a 14 wt.% sodium sulphate solution at 40°C for 5 min. After the impregnation step, the samples were immediately placed in a climatic chamber at 5 °C temperature and 70 % RH, which is above the equilibrium humidity for the $\text{Na}_2\text{SO}_4 - \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ transition, during 60 min. The samples were then dried at 40 °C during 24 h and afterwards immersed in water at room temperature for 24h. This sequence of procedures corresponds to 73 h weathering cycle. Four samples were used for this test.

The selection of the time interval for the salt solution absorption was preceded by a pilot test with samples with the lateral surfaces unsealed in order to follow the salt solution front along the sample thickness. After 5 minutes the salt solution reached the following depth on each mortar type: Lime (L) – 32 mm; Lime + Oil (LO) – 11 mm; Lime - metakaolin (LM) – 20 mm; Lime-metakaolin + Oil (LMO) – 10 mm. These values already point out the hydrophobic effect in mortars with oil and the material thickness that becomes more exposed to the sodium sulphate action.

The goal of the immersion in water is to include a desalination stage to extract the salt in order to use the degraded material for further investigation of conservation treatments. In the previous study performed with stones [10] it was observed that the immersion in water stage was the one inducing the most severe degradation, regardless of the temperature of the immersion bath (20 °C and 40 °C). In this study the immersion in water was run at room temperature because it is technically more accessible and the degradation is faster as also concluded from the literature [13]: samples subjected to impregnation-drying tests showed no damage during drying at 105 °C and immersion at 50 °C after 7 ageing cycles. Degradation occurred only when immersion was done at 20 °C.

The environmental conditions, i.e., temperature and relative humidity, of the tests were selected based on the phase diagram of sodium sulphate presented in [14].

The amount of salt solution absorbed was registered after each cycle. The mass loss was also monitored after each cycle by measuring the mass remaining in the vessel used for the specimen immersion bath because the degradation expressed as loss of material occurred mostly during immersion in water.

Each mortar type was analysed with mercury intrusion porosimetry after the salt solution impregnation step of the cycle that preceded the most severe degradation or destruction of the material. Prior to this measurement the samples were dried at 40 °C. MIP was used in order to investigate the pore sizes involved in Na_2SO_4 crystallization. The measurements were performed in two specimens of each mortar type on 10 mm layers sampled from the surface of the 40 mm thick mortar specimens.

3 Results and discussion

Figure 1 presents the amount of salt solution absorbed per surface unit. L and LM mortars absorb the highest amount of salt solution as it was expected from the results of water absorption by capillarity. However, LM mortar absorbs a higher amount of salt solution than L mortar although the capillary coefficient is significantly lower. The same phenomena occurred with LMO mortar, which absorbs a similar amount of solution as L mortar on the first 3 cycles, although the capillary coefficient is remarkably lower.

The changes in the samples dimensions were measured with a caliper (resolution of 0.01 mm) after wetting and drying. No differences were detected on the samples dimensions but the method used to measure it is of low precision. The linear hydric coefficient of a lime and lime-metakaolin mortar has been determined [15]: the coefficient of a LM mortar between the dry state and the capillary water saturated state was almost two times higher than for the lime mortar. The mortar used in this study has lower metakaolin content (25 wt.% of binder weight) compared to that of [15] (50 wt. %) but given the important effect that the addition of metakaolin can have on the hydric expansion, this property can have an important influence on the absorption by capillarity and on the degradation process of lime-metakaolin mortars.

Therefore, the capillary absorption result can be misleading e.g. due to reaction between metakaolin and water, which tends to cause swelling and lower the capillary absorption. This is not expected with the salt solution, hence the higher absorption.

The amount of salt solution absorbed during ageing is increasing progressively for both reference and hydrophobic mortars, which means that the water-repellent effect decreases during ageing.

Table 1: Mortars composition, hydric and hygric properties. The values correspond to the average \pm standard deviation.

Mortar code	Composition (L - Lime; M - Metakaolin; S - Sand)	Open porosity ^a [%]	Capillary coefficient ^b [$\text{kg}\cdot\text{m}^{-2}\cdot\text{h}^{-0.5}$]	Drying index ^c
L	L:S(1:3)	32.0 \pm 0.2	28.5 \pm 0.42	0.70 \pm 0.01
LO	L:S (1:3) + Oil	34.4 \pm 0.6	3.95 \pm 1.66	0.63 \pm 0.03
LM	L:M:S (0.75:0.25:3)	34.4 \pm 0.1	13.4 \pm 0.30	0.53 \pm 0.03
LMO	L:M:S (0.75:0.25:3) + Oil	32.4 \pm 0.5	1.98 \pm 0.04	0.57 \pm 0.02

^a Open porosity test was performed with 4 samples according to [16].

^b Sorptivity corresponds to the slope of the curve representing the weight gain per unit surface area as a function of the square root of time and was calculated with 3 samples according to [17].

^c The evaporation curve was determined with 4 samples according to [18] at 40 \pm 5% relative humidity and the drying index was calculated according to [19] which is also described by [20] in English.

Figures 2 and 3 show, respectively, the mass loss and the aspect of the mortars during ageing. On the 8th cycle L mortar showed severe damage throughout the total sample thickness whereas degradation of LO mortar was limited to a layer of the surface. LM and LMO mortar were severely cracked after 2 and 5 cycles, respectively.

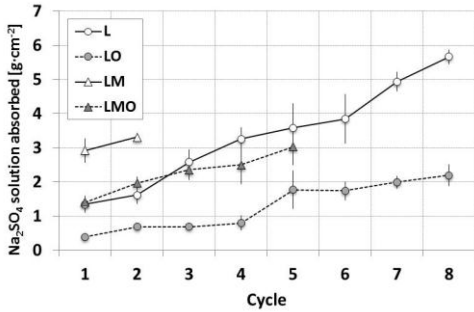


Figure 1: Salt solution absorbed by the samples during ageing.

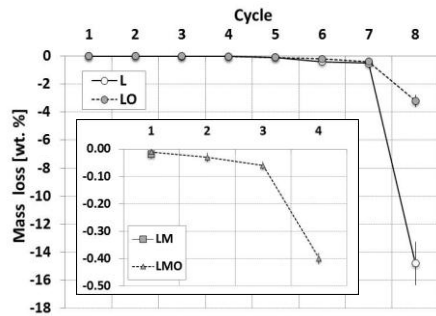


Figure 2: Mortars mass loss during ageing.

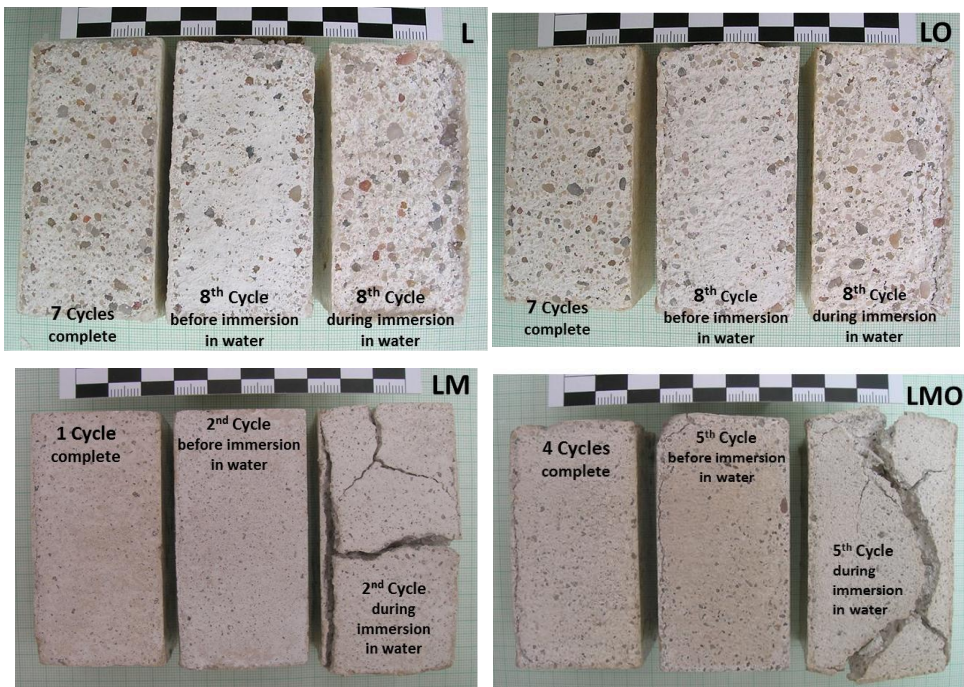


Figure 3: Aspect of mortar specimens during ageing (scale above the specimens shows 1mm intervals).

The mass variation during ageing is rather low during all cycles except for L and LO mortars on the 8th cycle after which full crumbling and severe surface damage, respectively, is noticed. During the previous ageing cycles the material loss of L and LO mortars is mostly assigned to powdering and sanding. After 6 to 7 cycles L mortar seems properly aged for the testing of conservation products as it exhibits moderate powdering and sanding.

On the 8th cycle the L mortar loses a layer of ca. 10-15 mm thickness on both top (in contact with the salt solution) and bottom part, although on the 1st salt absorption stage the solution front only reached 31 mm. The remaining material part is very fragile and it is the resin used to seal the lateral surfaces that sustains it (this is not clear in Figure 3). The reason for the integral damage is probably assigned to salt diffusion during the immersion stage. LO mortar loses only a top layer of 4-6 mm thickness, which reveals the protective effect of oil addition by restraining salt transport.

LM and LMO mortars are the most affected by the salt ageing test: destruction occurs on the 2nd and 5th cycle, respectively. The damage was not evidenced in terms of weight loss but the samples did suffer considerable deformation and cracking during immersion as shown in Figure 3. Higher tensile strengths usually result in more durable materials to salt weathering. Therefore, the crystallization pressure developed in mortars with metakaolin has to be much higher than in mortars with lime because the tensile strength of lime-metakaolin mortar is around 98% higher (1.65 MPa) than that of lime mortars [10].

Taking into account that the tensile strength is a macroscopic quantity and a high crystallization pressure in a single pore does not necessarily cause damage, two additional conditions must be met according to [21]. First, a sufficiently large fraction of the pore wall needs to be in contact with the growing crystal that generates stress. Second, the stress generated by the growing crystals must be large enough to propagate existing flaws in the material. That is, the crystals generating the stress must propagate through a volume of the material sufficiently large compared to the flaw sizes.

The higher hydric expansion coefficient of lime-metakaolin mortar in respect to lime [15] can possibly lead to a higher susceptibility of crack formation.

The thin section of not aged LM mortar analysed by optical microscopy and SEM did not show cracks, as was also the case for L mortar [12]. Therefore, in LM mortar, one cycle is sufficient to generate micro-flaws through the porous structure of the material leading to its destruction on the 2nd cycle.

It was observed that the cooling stage promoted hair-like cracks on the surface, probably due to the hydration distress caused by the supersaturation in respect to mirabilite as the sample temperature decreases. Under the conditions the cooling stage was performed (rapid cooling from a sodium sulphate solution at 40 °C) it is possible that the heptahydrate phase forms rather than the decahydrate as reported in older and recent literature [22]. However, another study [23] using nuclear magnetic resonance to measure Na_2SO_4 solubility in bulk and in pores of 5, 10 and 30nm has suggested that the heptahydrate phase cannot cause significant stress in a porous medium because no supersaturation or subsaturation is observed.

It is during the immersion stage that the degradation expressed as loss of material is evident. The loss of small amounts of surface material during the first ageing cycles immediately after immersion in water can partially be attributed to the cementing effect of sodium sulphate [24]. No particle detachment occurs during the cooling and drying stage as the accumulated salts are simultaneously filling the micro-cracks developed.

When the specimen is submerged in water the dissolution of the cementing salts produces an immediate loss of material surface, even before the precipitation of hydrated phases could commence, as also described in another experimental study [25]. Therefore, surface powdering and sanding occurs as soon as the specimens are submerged because of the immediate dissolution of the salts accumulated at the surface.

The severe cracking phenomena along the specimen thickness takes several hours to occur and can be assigned to the hydration distress, which takes longer time to develop. In the previous study [10], severe degradation of the stone samples also occurred when performing the immersion in water at 40 °C, but the process was less destructive and occurred at a later cycle. It has been recently shown that thenardite alone can inflict substantial damage to building stones in both cyclic total immersion and continuous partial immersion tests without involving mirabilite precipitation [25]. Therefore, the observed degradation can be partially attributed to the cementing effect of salt crystals.

According to [13] noticeable damage can commence once enough salt has accumulated in the porous network. This is due to the fact that salt crystals themselves should act as a confining barrier by occupying and narrowing down the pore spaces, thereby preventing unrestrained crystal growth as well as increasing the chances of confining newly precipitating crystals and thus of crystallization pressure [26]. In this study the water immersion stage contributes to salt extraction but at the same time induces hydration distress. Therefore, it can be inferred that the observed abrupt damage that occurs at a determined cycle for each mortar is not solely assigned to the accumulation of salt but rather develops once the generated flaws reach the threshold of the material resistance.

The MIP technique was used to investigate the pore sizes involved in Na_2SO_4 crystallization. Figure 4 presents the pore size distribution of the samples before and after ageing. The salt loaded samples studied were aged until the cycle that precedes its severe degradation in order to investigate the porometry of the aged specimens. Table 2 presents the porosity, microporosity and density obtained with MIP as well as the amount of salt solution absorbed by the specimens before performing the measurement. Microporosity is defined in this study as the percentage of the porosity expressed in pores less than $1\mu\text{m}$ radius. According to [27] pore sizes under $1\mu\text{m}$ facilitate crystallization damage as also concluded in the previous experiment with limestone [7].

Mortars with oil present higher porosity and less micropores because the triglycerides present in the oil hydrolyse to glycerol when mixed with the alkaline lime based materials [6] and this reaction has a similar effect to that of the saponification (formation of air bubbles), causing air entrainment and shifting the main pore diameter to higher sizes [12].

Mortar L exhibits a trimodal distribution with the main pore volume maxima located at ca. $0.46\mu\text{m}$ showing a small percentage of pores within the region $0.04 - 0.08\mu\text{m}$ and $12.5 - 71.8\mu\text{m}$. The latter pore range is probably assigned to shrinkage cracks and it is through these that water moves faster by capillary transport [28]. LO mortar also shows pores within this size range, however the pores in LO mortar are lined with hydrophobic non-polar hydrocarbon molecules, which prevent the water and salt solution absorption. The pore structure of LM and LMO mortars is mostly constituted of pores below $1\mu\text{m}$ in size. This is due to the presence of hydraulic phases such as CSH (calcium silicate hydrate) [29].

L and LO mortars showed a significant porosity decrease after the 7th cycle solution absorption: 22 and 11 % reduction, respectively. The porosity decrease was considerably higher for L mortar, which is in accordance with the higher amount of salt solution absorbed. A relevant percentage of the porosity decrease in L mortar is assigned to pore sizes below $1\mu\text{m}$ (28 %). LM and LMO mortars did not show significant changes in the porosity values but the microporosity after ageing was slightly higher (1 % increment).

The decrease in microporosity is due to salt crystallizing in and closing the pores. Regarding L and LO mortars, changes in larger pore sizes, between 10 and $100\mu\text{m}$ were also measured. They may be related not only to crystallization of salt partially filling the large pores but also to modifications in the porous structure (cracking). However, no clear shift towards bigger pore radii is registered in samples subjected to the salt crystallization test. Only LM mortar shows a significant increment of the main peak that can be related to modifications in the porous structure (micro-cracking) due to damage development. In this mortar the salt seems to precipitate preferentially in the pore size range between 0.04 and $0.3\mu\text{m}$.

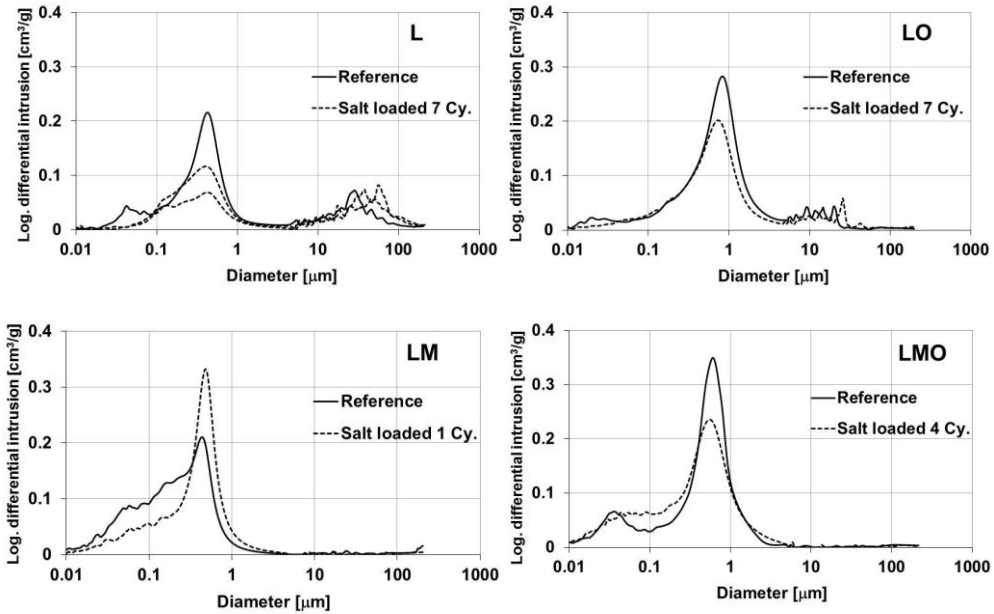


Figure 4: Pore size distribution of reference mortars and salt laden mortars. Only one curve from the two measurements performed in two different specimens is shown since both curves were very similar, except for L mortar aged specimens.

Table 2: Mortar properties determined with MIP of reference and salt laden samples and amount of salt solution absorbed before performing the analysis. Microporosity is defined in this study as the percentage of the porosity expressed in pores less than 1 μm radius.

Mortar code		Porosity [%]	Micro-porosity <1 μm) [%]	Density [g/cm ³]	Amount of salt solution absorbed [wt. %]
L	Reference	32.0 ±0.5	74 ±0.5	1.88 ±0.01	–
	Salt – 7 Cy.	24.9 ±5.1	58 ±2.1	2.15 ±0.10	6.3 ±0.9
LO	Ref.	37.0 ±0.2	69 ±0.2	1.69 ±0.05	–
	Salt – 7 Cy.	33.1 ±2.9	68 ±0.6	1.87 ±0.06	2.7 ±0.7
LM	Ref.	32.9 ±0.4	89 ±0.3	1.78 ±0.02	–
	Salt – 1 Cy.	31.3 ±1.4	90 ±0.2	1.84 ±0.05	4.1 ±1.1
LMO	Ref.	34.9 ±0.6	85 ±0.0	1.69 ±0.03	–
	Salt – 4 Cy.	34.4 ±1.7	86 ±0.3	1.71 ±0.03	3.1 ±0.8

The salt cementing effect is well expressed on the density values of the salt laden material that increases for all mortar types.

Sorption pores (pore size diameter less than $0.1\ \mu\text{m}$) are mostly related to the presence of hydraulic phases such as CSH [29] and according to [30] pore radius smaller than $0.1\ \mu\text{m}$ facilitate the crystallization damage. In the present study, the micropores of LM mortar, that are not present in the reference L, lie within the range of $0.04 - 0.3\ \mu\text{m}$. Therefore, this pore size range seems to be the culprit behind the observed salt crystallization damage. Other studies have pointed pore radius smaller than $0.5\ \mu\text{m}$ [24] and between 0.5 and $5\ \mu\text{m}$ [31] as the micropores that facilitate the crystallization damage.

It can be concluded that the observed damage in all mortar types is mostly related to the pore size distribution and water absorption by capillarity. The open porosity and drying behaviour of the materials tested do not seem to play such an important role since they are relatively similar. However, it is noteworthy that only the lime-metakaolin mortars (LM and LMO) developed a significant amount of salt efflorescences during drying, which is contradictory since these materials show lower drying index in respect to the lime mortars. However, the drying curve of lime mortars is characterized by a straight line meaning the drying rate remains constant during the total drying process whereas for lime-metakaolin, the drying rate does not drop in the beginning, later it does.

It can be inferred that the evaporation in lime mortars more rapidly retracts to the interior, not giving time for the development of salt efflorescences. In lime-metakaolin mortars the retraction of the moisture front progresses more slowly at the beginning, therefore salt efflorescences can develop. Thus, the drying behaviour of lime-metakaolin mortars should account for a higher salt resistance of these materials by promoting the development of salt efflorescences but it was proved to be negligible compared to the other physical properties.

4 Conclusion

It can be concluded that the mass variation during the applied ageing process is not a good indicator for monitoring the mortar degradation because the damage is not clearly evidenced in terms of the weight loss. This is possibly due to the fact that sodium sulphate induces a structural degradation, i.e., in the bulk of the sample, whereas the loss of material is only sensitive to the processes of surface degradation. Therefore, the collapse of the materials at a determined cycle is drastic because the propagation of cracks, with the consequent reduction of the materials resistance, has the character of a cumulative and exponential process and the specimen disintegrates once the threshold of the material resistance is reached. The MIP results in the cycle that precedes the material breakdown already show accumulation of damage, which is in accordance with the degradation mechanism observed. The evolution of the salt solution absorption proved to be a better method to follow the mortar ageing because it reveals the progressive degradation (formation of cracks) of the material expressed as a faster capillarity absorption rate.

The observed damage in all materials can be attributed to the double attack of thenardite (during drying) and mirabilite (during cooling and possibly during immersion) although in this study visible damage is only registered during cooling and water immersion stages.

After 6 to 7 cycles L mortar seems properly aged and useful for the testing of conservation products as it exhibits moderate powdering and sanding. LM mortar manifested itself as a very salt-susceptible mortar by being destroyed on the 2nd cycle.

In the present study it has been shown that the replacement of 25 wt. % of lime by metakaolin has a negative effect on the material resistance towards cycles of thenardite-mirabilite. Although the mechanical strength is improved by metakaolin addition, the microporosity is significantly higher than in the L reference. This is probably the cause for the salt-susceptible degradation of lime-metakaolin mortars because in a smaller sized pore the pressure developed by crystal growth is higher than in larger pores. This factor is so important that not even the addition of oil to lime-metakaolin, which significantly reduces the salt solution absorption, was able to attain the same level of salt resistance as the lime mortar. Further tests should be performed with a mix design with less metakaolin content (e.g. 16.8 wt. % [9]), which does not alter the pore size distribution in respect to the reference and probably decreases the hydric expansion.

The present ageing method proved to be promising to produce weathered mortar and to test its salt resistance. The fact that a complete desalination is difficult to achieve after ageing should be taken into account for the testing of conservation products.

Acknowledgements

The present study was supported by the Czech national project MK ČR NAKI DF11P01OVV008 entitled “High Valuable and Compatible Lime Mortars for Application in the Restoration, Repair and Preventive Maintenance of the Architectural Heritage” and by the Research Development Plan RVO 68378297 at the Centre of Excellence of Telč, built with the support from the EC, from the Czech Ministry of Education, Youth and Sports (CZ.1.05/1.1.00/02.0060). The authors are grateful to Dr. Krzysztof Niedoba for helping with MIP measurements.

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