A closer look at salt loaded microstructures

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Many walls of ancient buildings are covered with plaster layers. Amongst the most recurrent causes of damage of plasters and substrates are moisture and salt decay processes. To combat these salt problems, special salt resistant plasters have been developed for application on salt loaded substrates. However, experience in the field has shown that failures regularly occur on these special mortars, making the situation little transparent for end-users.
A European project called COMPASS has addressed this particular problem in a large number of plasters and renders in terms of their performance under severe salt load. This paper describes in more detail the relation that has been observed between salt transport and salt crystallization versus the microstructure (both permeability and composition) of both the plaster and the substrate. Field samples and laboratory tests are discussed. It is shown that the microstructure of both the plaster and the substrate do play a significant role in the transport and crystallization of salt.

Keywords: Renders, plasters, substrate, pore size distribution, halite (NaCl)

1   Introduction

Many walls of ancient buildings are covered with plaster layers. Being the "skin" of the masonry walls, plasters and renders are the most accessible elements and, therefore, have always been considered as the first protection element and the first component to be sacrificed when conditions are not suitable. It is in this role that plasters and renders have always played a major role in the protection of the built heritage.

Amongst the most recurrent causes of damage of plasters and substrates are moisture and salt decay processes. Although salt damage has been intensively investigated for several decades [Pühringer, 1983; Goudie & Viles, 1997; Charola, 2000; Lubelli, 2006], the mechanisms and factors that control the formation of salt crystals in porous media and the development of damage are poorly understood. A renewed interest in salt damage research has surfaced since the second half of the 20th century. The interest is probably due to the increase of large-scale salt damage hazards in the same period. The rise of the ground water level (due to e.g. irrigation and vegetation clearance), the increase in the salinity of ground water (caused by e.g. incursion of seawater), and the introduction of new sources of salts (originated by e.g. the used of de-icing salt and atmospheric pollution) are the main causes of the enhanced risk of salt damage.

To combat these salt problems, special salt resistant plasters have been developed for application on salt loaded substrates. These systems have been called "renovation mortars" by the European Committee for Standardization, who has set up a standard [EN 998-1: 2003] which defines them as "designed rendering/plastering mortars used on moist walls containing water soluble salts". They are meant to have a longer service life in the presence of salt and moisture. However, experience in the field has shown that these special mortars regularly fail, making the situation little transparent for end-users, with respect to the choice, case by case, of the most appropriate plastering mortar.

A European project called COMpatibility of Plasters And renders on Salt loaded Substrates (COMPASS) has addressed this particular problem. The consortium has made strong efforts to study a large number of plasters and renders in terms of their performance under severe salt load. This paper describes in more detail the relation that has been observed between salt transport and microstructure (both permeability and composition) of both the plaster and the substrate. A better understanding of this relation should eventually lead to a better prediction of how and where salt damage could occur.

2　Experience from the field

Within the COMPASS project partners from France, Spain, Portugal and the Netherlands have performed elaborate field investigations documenting salt damage on many different substrates, with a variety of plasters covering a range of climates. Besides collecting data, this work package also provided a large amount of damage pictures for the damage atlas made in the COMPASS project. Since salt damage is usually a process of years, the documentation of damage cases could not provide all information. Many times information on the substrate was scarce or not available; also the plaster used could not be traced back in many occasions. In such cases general descriptions were made or main components were described. To add to the complexity, the plasters often covered ancient buildings from which only limited sampling was allowed.

At the end of the project two case studies from Portugal, one case study from Spain, two case studies from the Netherlands and two well documented plasters from a field test in France have been analysed. This analysis consisted of a) documenting/photographing the general microstructure of the plaster, and the substrate if available, b) determining the location and morphology of salt present and c) determining the relative change of salt content over the depth of the plaster.

The field samples were analysed at Delft University of Technology using an Environmental Scanning Electron Microscope (ESEM) equipped with an Energy Dispersive X-ray system (EDX). The ESEM used is a tungsten XL30 by FEI and the EDX system is by EDAX with a super ultra thin window (version 3.3) and a resolution of 128.0 eV. ESEM analysis was chosen to minimize preparation and damage to the samples. As soluble salts were expected to be present,

preparation techniques using water have been avoided. This eliminated the possibility of making thin sections, as a set-up for non-water based preparation is not available in our laboratory. The only preparation of the samples consisted of dry cutting using a non-cooled circle blade. This provided a smooth enough surface to do semi-quantitative analysis for salt profiling.

In each case study a sample from a deteriorated area and, usually higher on the wall, a sample from a non-deteriorated area was collected. From each sample the outer region has been analysed, i.e. the section closest to the surface of the render (or plaster). To be able to compare the EDX results amongst each other the arbitrary choice was made to detect the presence and amount of the following chemical elements: Na, Mg, Al, Si, S, Cl, K, Ca and Fe. Oxygen was deliberately left out since the signal of oxygen is usually disturbed in ESEM environment due to the presence of water vapour. The analyses have typically been collected using 15-20 kV accelerating voltage for a minimum of 60 seconds live counting time at a magnification of 250x. For statistical purposes, five parallel cross-sections are analysed within an area of 10 mm wide. Measurements have been performed in depth direction every 2 mm for at least the outer 20 mm perpendicular to the outer surface of the plaster.

Two case studies will be discussed here to illustrate the observations found in the analyses.

Test field Dieuze – Terrassane render

In France, our partner LRMH[1] has a test site for renders. The test site is located in Dieuze at Les Salines Royals de Dieuze, Bâtiment de la Délvrance (Figure 1). The building dates back from the 17th century and was devoted from the very beginning to the storage of salt (halite, NaCl).

Figure 1: Test site of LRMH at Dieuze. Left: platform for salt transfer, East side; middle: test wall with renders, West side; right storage of salt against wall, inside.

From this test site, two samples have been taken from a Weber et Broutin Terrassane render. This render is a commercially available product in France. The main components are Portland cement, sand and a mass water repellent. The samples contained only render material; no material of the brick based wall was attached to the samples.

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One sample was a non-deteriorated render, the other was deteriorated. The deteriorated sample showed a crack parallel to the surface at a depth of about 7 mm. According to the case study assessment performed by LRMH, the render suffers from cracking due to initial shrinkage and slight granular disintegration. No analysis has been performed to determine the type of salt present, but since the storage facility is for halite, it is assumed that this is the major salt present.

Results by ESEM indicate that in the non-deteriorated sample hardly any salt is visible. In the deteriorated sample, the presence of salt increases with depth (Figure 2). It is noted that the salt is seen crystallized in relatively small crystals; the crystals are not really filling pores but seem to be stuck to solid render matrix.
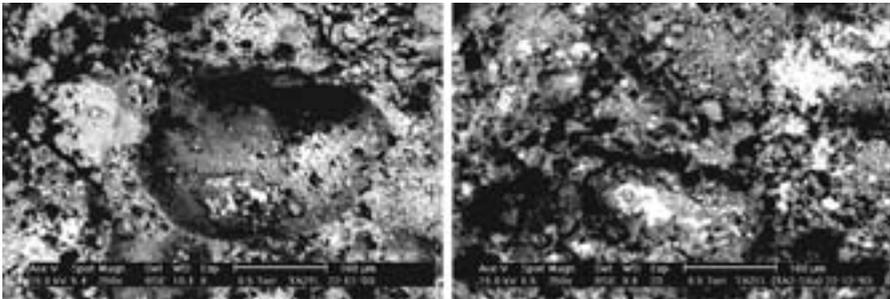

Figure 2: *Increase in salt content going deeper into the render of the deteriorated sample. 10 mm depth (left), 15 mm depth (right).*

When the salt distribution is analysed by EDX, a profile can be determined as is shown in figure 3. EDX element analyses have only been made per image, not for individual concentrations of components within an image. Furthermore, the results are compared relative to each other[2] under the assumption that the render material has a constant signal over the depth. In figure 3, both Na and Cl are plotted to determine whether or not the result is mainly halite, or other components are present. The error bars indicate the variations found along the five parallel measurement lines.

The profile shown in figure 3 does only show Na and Cl levels present in the sample. It is assumed that it represents a halite profile when the Na and Cl levels behave similarly. When the two elements do not behave similar, it must be concluded that other phases play a role. In the profile of the non-deteriorated sample, it can be seen that hardly any halite is present. This does agree with the absence of any damage. The deteriorated sample shows higher levels of salt. The peak in the profile at about 7 mm depth corresponds well with the position of the crack observed macroscopically.
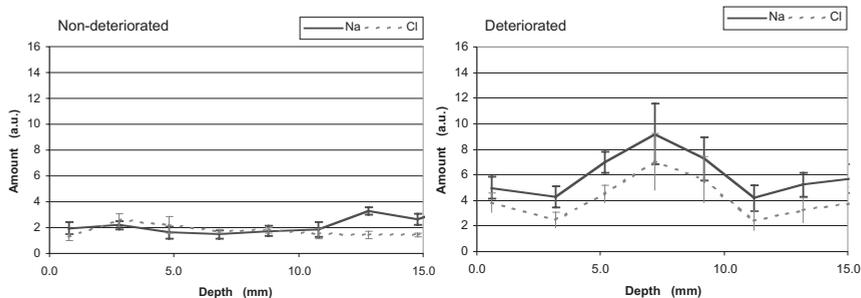
2 *In arbitrary units (a.u.)*

Figure 3: Salt profiles as found in Terrassane render. Left non-deteriorated sample; right deteriorated sample. Error bars indicate variation based on five parallel line measurements.

Church Velsen – indoor lime based plaster

Another field investigation discussed here has been performed by TNO: the Engelmundus church, situated in Velsen, the Netherlands. The plaster is in the interior of the church and suffers from peeling of the paint layer, sanding, scaling and crumbling of the plaster. The discussion in the remaining part of this section focuses on a non-deteriorated sample, which is shown in figure 4a. This sample is interesting because of its multi-layer nature.

In figure 4b, the EDX profile is given for the elements sodium and chloride. Actually, it is not known what kind of salt is present in this sample. Considering the profiles of both sodium and chloride, the presence of halite may be assumed. This is based on the relative similar behaviour of the levels of sodium and chloride. Further analysis of the EDX sodium profile appears to reveal that the salt content is related to the microstructure of the layers, see e.g. the change in salt content going from mortar to the plaster layer. The change in microstructure from the fired clay brick to the plaster corresponds to a sharp difference in the relative concentration of salt across the interfaces between both microstructurally different materials.

Of course, it should be realized that the analyses are based on the assumption of the presence of halite. In reality, this does not need to be the case. In the profiles, this would emerge from a deviation in the similar trend between sodium levels and chloride levels. An example of this effect is shown in the brick part of the sample. Here, sodium keeps increasing at larger depth of the sample while the chloride level remains the same. This indicates other salts being present or difference in composition of the brick itself.
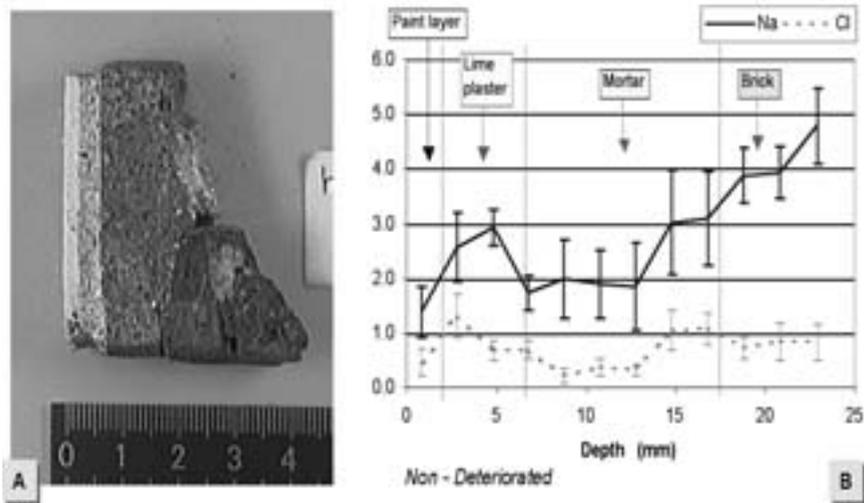
Figure 4: Cross-section of a non-deteriorated sample from Engelmundus church (a), with corresponding sodium and chloride profiles through the various layers (b).

3 The effect of the substrate

When a plaster or render needs to be applied on a masonry substrate, the choice for a specific type of plaster is often based on practical considerations like ease of workability, nice and easy finishing capabilities and experiences with the plaster/render material from previous projects. However, the effective influence of the substrate is hardly taken into account, or at least not quantified. Due to the influence of the substrate properties even salt transport is influenced, or so it seems from the previous section. Therefore, it is necessary to adjust the plaster choice to the properties of the substrate. It should be no surprise that the behaviour of a plaster can be completely different when applied onto two totally different substrates.

In fact, this principle was already demonstrated by Groot [Groot, 1993] for mortar-brick combinations. He showed that part of the wet mortar is being sucked into the capillary pores of the brick, thereby improving the bond between brick and mortar. As a consequence, the pores are finer near the interface of the mortar and brick as compared to the pores in the mortar further away from the mortar-brick interface.

Later, Wijffels [Wijffels, 1996] showed the effect of this process on a plaster that is applied in two layers. This work clearly shows that the plaster layer applied on the substrate has a finer overall pore size distribution than the pores of the outer plaster layer applied on top (Figure 5).
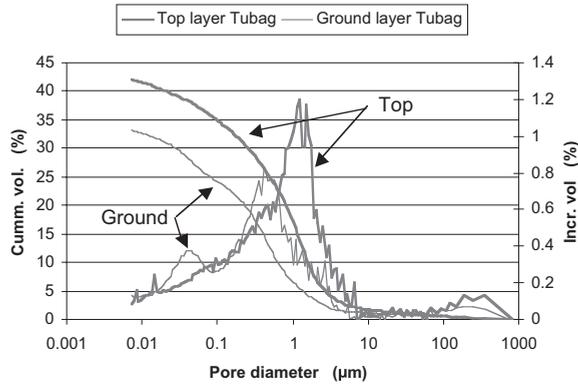
Figure 5: Pore size distribution of first and second plaster layer applied right after each other [Wijffels, 1996]. Tubag is a commercial name of a trass-lime based plaster with a mass water repellent.
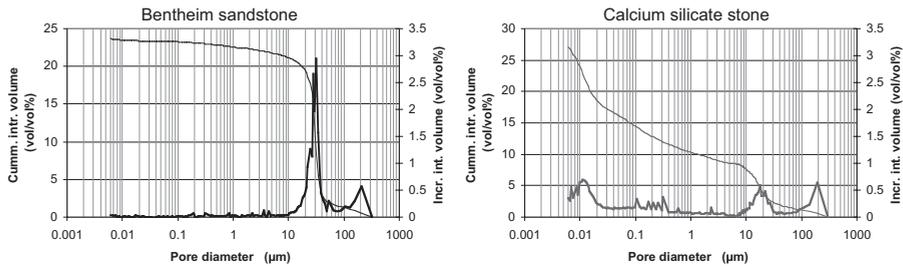

Figure 6: Pore size distributions of Bentheim sandstone (left) and a calcium silicate brick (right).

In the COMPASS project, in preliminary experiments, a single plaster was applied on two extreme substrates: a Bentheim sandstone and a calcium silicate brick. The pore size distributions of these substrates are shown in figure 6 as determined by mercury intrusion porosimetry (MIP).

On top of the substrates, a home made plaster was applied consisting of pure lime : Portland cement : river sand in the volume ratio of 4 : 1 : 10. When measuring the pore size distribution of plaster samples taken from the different substrates, it was found that the pore size distributions of the plasters were not identical, see figure 7. Typically, the calcium silicate brick has an extra peak around 25 µm pore size. Furthermore, the fine pores of the calcium silicate brick start at a smaller pore size than the Bentheim sandstone (c. 0.9 µm versus c. 1.5 µm).
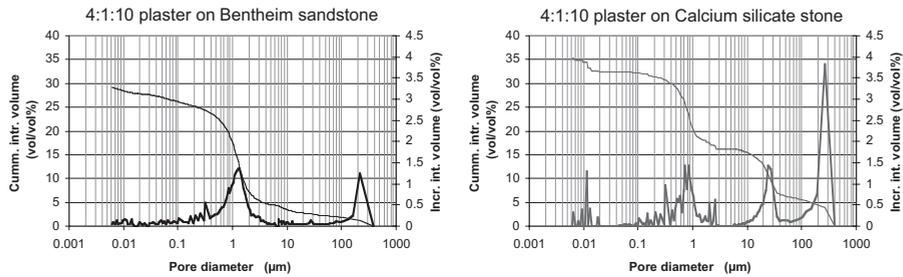
Figure 7: Pore size distributions from identical plasters applied on two different substrates: on Bentheim sandstone (left), on calcium silicate brick (right).

In the preliminary tests, the plaster layers were intended to be one layer plaster systems. However, in the application process the material was applied in two steps. Even though the time difference between the two steps was less than one minute, two regions inside the plaster system could be determined by NMR techniques, see figure 4 [Petković, 2004].
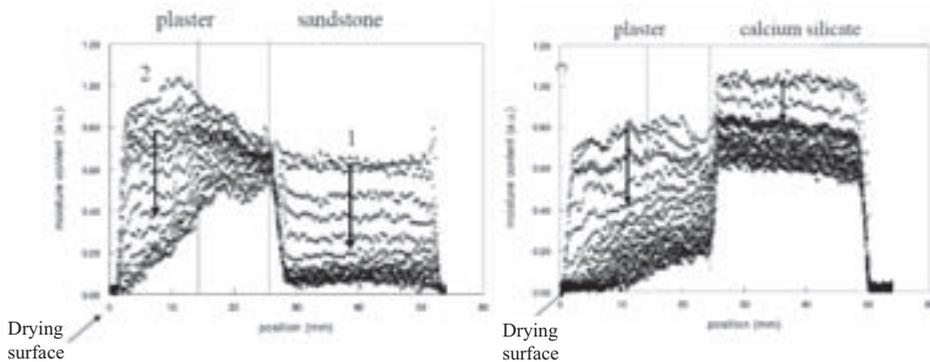

Figure 8: Results of drying experiments in NMR setup: plaster on Bentheim sandstone (left), plaster on caclium silicate stone (right) [Petković, 2004].

Summarizing the effects shown in this section, the work of Wijffels and Petković clearly shows that the substrate does have a significant influence on both pore size distribution and transport properties of the plaster applied on top of the substrate.

4   Evaluation of plasters

One of the objectives within the COMPASS project was to evaluate restoration plasters in case of application on salt loaded substrates. To do so an accelerated salt crystallization test ("COMPASS-TEST") has been developed within the consortium. This test allows assessing the

behaviour of plasters in contact with salt loaded substrates and reproduces common failures they may develop. The test shows how quick and how far salts migrate in a substrate/plaster system and where they accumulate until eventual degradation. In the next paragraph, a brief summary of the test procedure is provided.

The COMPASS-TEST

Detailed description and background information of the COMPASS-TEST can be found in Lubelli [2006] and Wijffels & Lubelli [this issue]. In short, the test procedure is described as follows. The test specimens are cut in small sizes ($5 \times 2 \times 2$ cm) and are sealed on all four lateral sides with epoxy resin. The small sizes reduce the test periods while still maintaining sufficient surface for a sound evaluation of damage. These specimens are dried at 60 °C until constant weight.

Next, the samples are contaminated at room temperature by either a 10 wt.% NaCl solution or a 10wt.% Na_2SO_4 solution. The contamination is performed by immersion (up to 2 mm) the bottom side of the sample into the salt solution. The intention is to moisten the entire brick substrate and only the substrate. In our case, this situation was obtained after five minutes of immersion. The specimen is then weighed and its bottom surface is wrapped so no evaporation can take place through this side.

Next, the specimen is placed in a climatic cabinet, where it is alternating between two conditions. A complete cycle takes 24 hours, 16 hours at 40 °C/15% RH and 8 hours at 20 °C/ 50% RH. When at least 80% of the moisture content is evaporated, the specimen is contaminated with a new load of salt using the same procedure as before.

At the end of a cycle before renewed contamination, visible damage (nature and location) is recorded, in addition to photographic documentation. Typically after 5 complete cycles, even if no damage to the plaster has occurred, the sample is sliced. The salt content in each slice is deduced from hygroscopic moisture content measurements at 95% RH, as described in RILEM TC 127-MS [RILEM, 1998]. The hygroscopic moisture content is then plotted against the depth, as an indication of the salt distribution along the substrate/plaster system.

Detailed evaluation of the COMPASS-TEST

The COMPASS-TEST has been performed on a wide range of restoration plasters of the European market and, as a comparison, on common mix-designs based on lime and cement. The test has been performed using a fired clay brick with a fairly coarse pore system as substrate. Most of its pores are in the range of 5 – 15 µm. The tested plasters and their main characteristics are presented in table 1. The porosity has been determined by mercury intrusion porosimetry (Micromeritics PoreSizer 9320). Water absorption coefficient (WAC) by capillary suction is calculated on the basis of EN 1925 [CEN, 1999]. Sodium chloride has been used as the contaminating salt solution.

Material	Main components	Porosity (vol%)	WAC (kg/m²√h)
Fire clay brick		36.7	14.30
Home made TNO	Lime – blast furnace slag cement – sand	23.7	5.04
Home made LNEC	Air lime – cement – sand	24.7	7.27
Jahn plaster M60	Portland cement – light aggregates	50.3	0.70
Trass lime Tubag	Trass – lime – mass water repellent	42.8	1.96
Strasserville MEP SP	Trass – lime – mass water repellent	41.0	0.30
Remmers Funcosil	Portland cement – light aggregates – mass water repellent	44.2	0.20
Lafarge Mortiers Parlumiere	Portland cement – sand – mass water repellent	38.6 – 44.5	0.34
Weber et Broutin Terrassane	Portland cement – sand – mass water repellent	56.0 / 68.4	0.57

The characterisation of plasters is ordinarily done like presented in table 1. First thing to remember is that these numbers are averaging a sample property. To illustrate this point the difference between pore size distribution and porosity is shown based on two examples, see figure 9. Even though both plasters have identical total porosities (both 40.1 vol.%), the pore size distributions are completely different. This point should be kept in mind when trying to explain trends in the plaster performances.
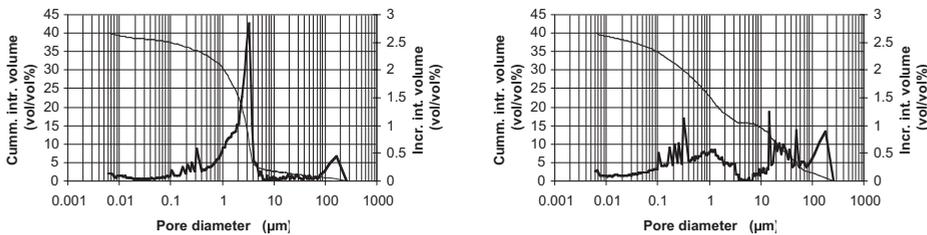

Figure 9: Two plasters with identical porosity values, but completely different built up of their pore size distributions. Left: A gypsum-lime plaster with water repellent; right: Weber et Broutin Terrassane render (N.B. Neither of the examples are from the COMPASS-evaluation test described here.)

A typical result as it is documented from the COMPASS-TEST is given in figure 10. Here a plaster is shown on top of the fired clay brick substrate at the end of the test, after five cycles of contamination. Sodium chloride has been transported through the plaster, in this case the homemade TNO plaster, and efflorescence is shown at the outer surface/top side of the plaster. No cracks are visible in the sample.
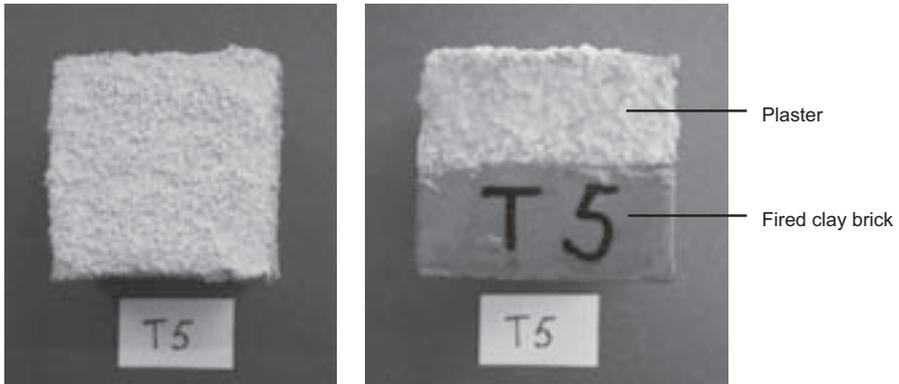
Figure 10: Final result after COMPASS-TEST for home made TNO plaster. View of topside (left), view of side (right).
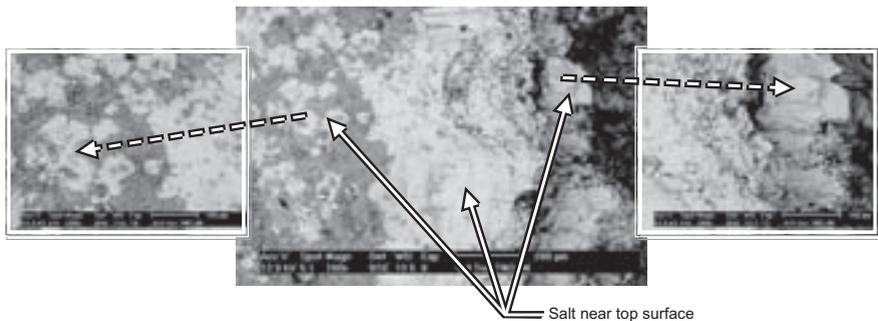

Figure 11: Halite efflorescence on the home made TNO plaster as seen by electron microscopy, showing at least three different crystal habits of the salt.

Besides this macroscopic observation, the microstructure and efflorescence can also be studied at a microscopic level. Observing the same halite efflorescence using a Philips XL30 ESEM, the salt efflorescence then appears as shown in figure 11. The salt is present as patches, which form a continuous layer at the surface, while the most outer salt crystals on the topside of the plaster/salt crust are oriented like small standing crystal columns. Hence, within a short distance (less than 1 mm), the morphology and distribution of the halite efflorescence shows at least three different habits (see centre image of figure 11).

Besides efflorescence, cracks are also observed regularly in the COMPASS-TEST. A typical example is shown in figure 12a: a crack at the interface plaster/substrate. In this case, no efflorescence is visible on the outer surface of the plaster. The plaster shown here is the trass lime Tubag plaster with a mass water repellent. Observation by ESEM shows the internal story. The salt (halite) can be observed in a small band just below the interface plaster/brick (see figure 12 b and c) Beyond this band of salt, more towards the top surface of the plaster, salt

cannot be detected anymore, as has been confirmed by EDX analysis. In this case the mass water repellent is completely blocking the transport of salt through the plaster.
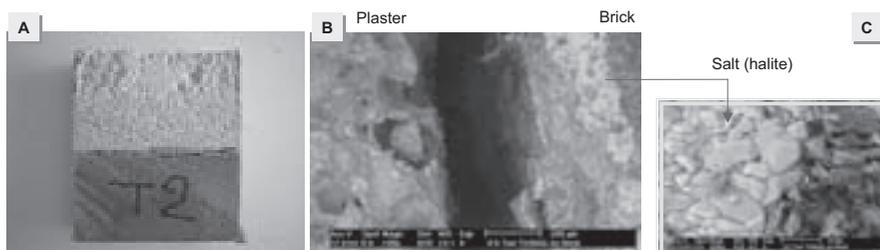

Figure 12: Final result after COMPASS-TEST for a trass lime Tubag plaster with a mass water repellent. Macroscopic view (a). ESEM observations: plaster/brick interface (b), detail of salt crystals (c).

At the end of the COMPASS-TEST, a salt profile through the plaster-brick system can be obtained through the use of hygroscopic moisture content (HMC) measurements. Such a salt distribution graph is shown in figure 13a for the home made TNO plaster. The patches of halite salt that were already shown in figure 11, increased in number per ESEM image when scans were made going from the middle of the plaster towards the top surface of the plaster, see figure 11 b and c. This increase in salt content was also confirmed by EDX analysis.
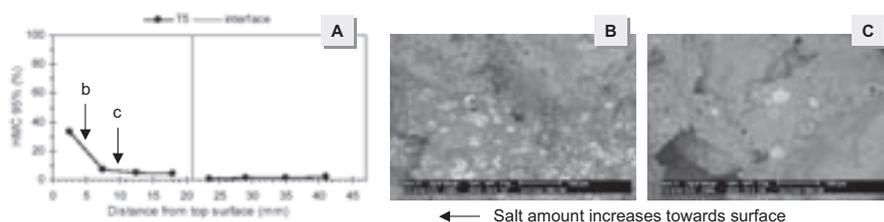

Figure 13: Distribution of salt (halite) over the plaster thickness as determined by HMC (a) and observations by ESEM (b and c). The locations of ESEM images are indicated in the HMC graph.

Comparing the COMPASS-TEST with field samples
When salt distributions are compared between the COMPASS-TEST and the field samples, it is noted that the field samples show damage with much less salt present than in the accelerated tests. Naturally the salt loading is increased significantly in the COMPASS-TEST to accelerate the evaluation period. However, in case of the field samples the salt content has not accumulated up to these high levels from the COMPASS-TEST, and yet damage does occur in the field.
Furthermore it is noted in both cases that the larger pores are not completely filled by salt

crystals. In fact, the damage observed in the COMPASS-TEST almost always did not show any salt present in the crack. It should be pointed out that cracking does not only occur over an interface like shown in figure 12, but can also be observed in the plaster system itself.

5   Conclusions

Based on the microstructural information the following conclusions can be drawn:
- The pore structure of a plaster or render is influenced by the pore structure of the underlying substrate material/masonry.
- Salt shows a tendency to crystallize at locations where the pore structure changes. In general these are locations where the pore structure changes from fine porous to coarse porous.
- Analysis of damaged field samples do in general not show pores being completely filled with salt crystals to initiate the damage. This observation holds for pores larger than 10 μm.
- The pore structure can even slightly alter by applying one plaster in multiple application steps.
- General characteristics of microstructure like total porosity does not take into account the possible heterogeneity at the microstructural level.
- The COMPASS-TEST gives new insights in salt transport, salt distribution and salt crystallization.
- The hygroscopic moisture content analysis after the COMPASS-TEST provides a quick and non-expensive addition for the salt distribution information, as has been confirmed by ESEM and EDX analysis.
- The transport of salt can be hindered or even stopped by using water repellent.
- Damage in the field occurs at much lower salt contents than is used in the COMPASS-TEST

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