Salt Transport and Crystallization in Plaster Layers: a Nuclear Magnetic Resonance Study

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Abstract

The durability and performance of specially developed restoration plasters or renders, are not always as good as expected. Salt crystallization is one of the causes of the observed degradation processes. To understand these processes in more detail, we investigated whether transport in the plasters depends on the masonry material. The transport of salt and moisture during drying of some plaster/substrate systems is followed with a Nuclear Magnetic Resonance technique. The observed differences in drying behaviour can be related to differences in pore structure between the plaster and substrate. For a good performance of the plaster a proper matching of its pore-size distribution with that of the masonry is required.

Keywords: Salt crystallization, plasters, renders, deterioration, NMR.

Salztransport und Kristallisation in Putzschichten: Eine NMR Studie

Zusammenfassung

Die Beständigkeit und die Eigenschaften von eigens hergestellten Restaurierputzen und -mörteln sind nicht immer so gut wie erwartet. Salzkristallisation ist eine der Ursachen der beobachteten Schadensmechanis-men. Um diese Vorgänge auch in Einzelheiten besser zu verstehen, untersuchten wir, ob der Transport in der Putzschicht vom darunter liegenden Mauerwerk beeinflusst wird. Der Transport von Salz und Wasser wurde während des Austrocknens von Systemen bestehend aus Putz und Untergrund mit Hilfe der magnetischen Kernspinresonanz (NMR) untersucht. Die beobachtbaren Unterschiede beim Austrocknen können mit den unterschiedlichen Porengefügen von Putz und Untergrund in Verbindung gebracht werden. Die Putzschicht kann die ihr zugewiesene Aufgabe nur erfüllen, wenn ihre Porengrößenverteilung auf die des Untergrunds abgestimmt ist.

Stichwörter: *Salzkristallisation, Innenputz, Außenputz, Zerstörung, NMR*

1   Introduction

Restoration plasters are used both for decorative and protective reasons. The choice of plasters or renders, suitable for long-time protection, is a delicate conservation problem. Even if specially developed plasters are used, their performance is not always satisfactory [1]. The durability of a plaster and its protective potential strongly depends on its transport properties for salt and moisture. Although salt damage has been intensively investigated for several decades [2, 3], the mechanisms and factors that control the formation of salt crystals in porous media and the development of damage by crystal growth are poorly understood. A better understanding of the movement of water and ions during drying and salt crystallization in plasters is required to understand the salt damage and for developing better formulations. It is known that the fluid transport is influenced by the pore sizes of the single medium [4]. Apart from this, it is important to know whether the salt transport in the plaster-substrate system also depends on the substrate material. Until now the recommendations for the application of plasters did not take the influence of substrate materials into account [5].

In the present work we examine whether large differences in the pore structure of the plaster and the substrate influence the transport properties of salt solutions. To answer this question we use a Nuclear Magnetic Resonance (NMR) imaging technique. NMR gives us the possibility to monitor quantitatively moisture and salt profiles in the plaster/substrate systems. In these experiments profiles are obtained during one-dimensional drying of the materials. First, we will explain the NMR method, and introduce the materials we used. Next, we will discuss the results of drying and water transport in these materials. Further, we will investigate how the salt moves in these materials. Finally, we will discuss the possible consequences for salt weathering.

2   Method

Nuclear Magnetic Resonance (NMR) imaging is a non-destructive method for quantitative mapping of certain chemical elements in materials. Using a home-built NMR scanner, designed for the imaging of the building materials [6], it is possible to follow the distribution of water and dissolved sodium in time during wetting [7] or drying [8].

To obtain the water and Na signal from a sample by NMR it is necessary to pick up the radio frequency (RF) signals at the resonance frequency of the H and Na nuclei. This frequency, often called Larmor frequency, is determined by the magnitude of the applied magnetic field B:

$$v_i = \frac{1}{2\pi} \gamma_i B \qquad (1)$$

where the index i characterizes the H or Na nucleus, v_i is the Larmor precesion frequency, and γ_i is the gyromagnetic ratio of the nucleus ($\gamma_H/2\pi$ = 42.58 MHz/T; $\gamma_{Na}/2\pi$ = 11.27 MHz/T).

When the applied magnetic field is homogeneous, the nuclei in the whole sample are at resonance, and a signal from whole sample is obtained. To achieve spatial resolution it is necessary to excite the nuclei in a limited volume of the sample. This is done by making the resonance condition position dependent by superimposing a constant magnetic field gradient G on the main magnetic field B_0.

$$B = B_0 + Gx \qquad (2)$$

where x is a position in the sample along the direction of the magnetic field gradient G.

Quantitative analysis is possible since the intensity of the received signal is proportional to the density of the nuclei ρ:

$$S = k\rho \cdot \left[1 - \exp\left(-TR/T_1\right)\right] \cdot \exp\left(-TE/T_2\right) \quad (3)$$

In this equation k is a proportionality constant, T_1 and T_2 are physical parameters (nuclear relaxation times) and TR and TE are experimental parameters, which are explained elsewhere [9,10]. In general, TR and TE are chosen in such a way that $TR >> T_1$ and $TE < T_2$.

The main magnetic field (B_0) and the gradient (G) used in our experiments were 0.7 T and 0.33 T/m, respectively. The resulting spatial resolution was 1 mm. To determine the H and Na profiles over the whole sample, the sample was moved in the x direction by means of step-motor [11], see Fig. 1. With our equipment is possible to measure H and Na quantities only in the liquid phase. During the acquisition of the profiles the RF frequency is switched in such a way that H and Na signal can be recorded quasi-simultaneously [7,11].
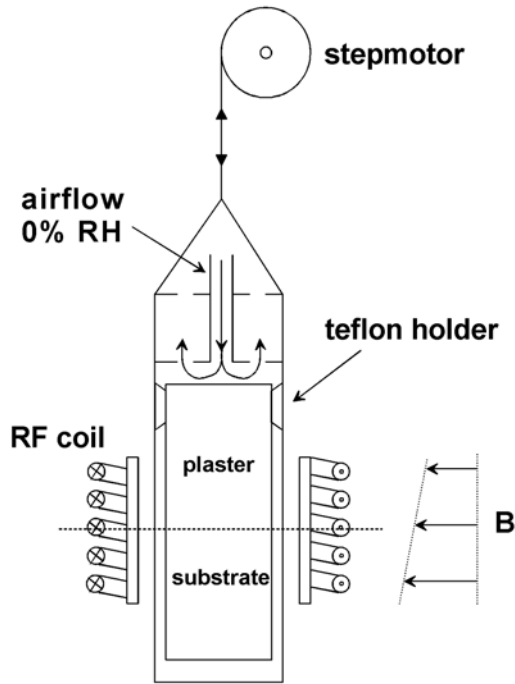
Figure 1: Experimental setup for drying experiments. The teflon holder with the sample is moved in the vertical direction by means of the step-motor. The signal from the nuclei precessing around the magnetic field B is received by the RF coil.

The samples had a cylindrical shape with the diameter of 19 mm and total length of 50 mm. They were sealed on all sides except at the top (the plaster/air interface). Therefore, the drying and salt transport can be considered as quasi 1D process. The dry air is blown over the top of the sample.

3 Materials

We have measured two different plaster-substrate systems. Bentheimer sandstone and calcium-silicate brick (or sand-lime brick) are used as substrates. The plaster was lime based: lime:cement:sand = 4:1:10 (v/v). These materials were selected because their pore-size distributions differ significantly, see Table 1. The Bentheimer sandstone has the largest pores, calcium-silicate brick has both large and small pores. The plaster has a typical pore size smaller than the pores of the Bentheimer sandstone and larger than smallest pores of the calcium-silicate brick. Initially all samples were saturated with pure water or a NaCl solution.

Table 1: Pore sizes measured by mercury-intrusion porosimetry.

	nanometer pores	micrometer pores	volume ratio
Bentheimer sandstone		(30 ± 15) μm	
calcium-silicate brick	(12 ± 10) nm	(20 ± 10) μm	1:1
plaster		(0.5 ± 0.4) μm	

4 Results

4.1 Drying

First, we studied the drying behaviour of plaster/substrate systems, which were saturated with water alone. In all studied cases the water escapes from the sample via the plaster/air interface, which is located at x = 0. In Fig. 2 the water profiles of the Bentheimer/plaster system were plotted at different stages of the drying process. This figure shows that Bentheimer sandstone dries faster than the plaster. During the first 10 hours of the drying process the sandstone dries homogeneously. During the first 8 hours the plaster remains saturated. It starts to dry when the water content in the Bentheimer sandstone has reached a value below 0.1 m^3/m^3.

This behaviour can be understood as follows. During drying water tends to remain in the pores with the highest capillary pressure, P_c, these are the smallest pores according to Laplace's equation [4]:

$$P_c \approx \frac{2\gamma}{r} \qquad (4)$$

In this equation γ is the surface tension of the air-water interface ($\gamma = 0.072$ N/m for water) and r is the pore radius. Air penetration in pores filled with water is only possible when the pressure difference between air and water exceeds the capillary pressure. Therefore, the resistance against air invasion is smallest in the widest pores. Bentheimer sandstone has bigger pores than the plaster (Table 1) and therefore dries first.
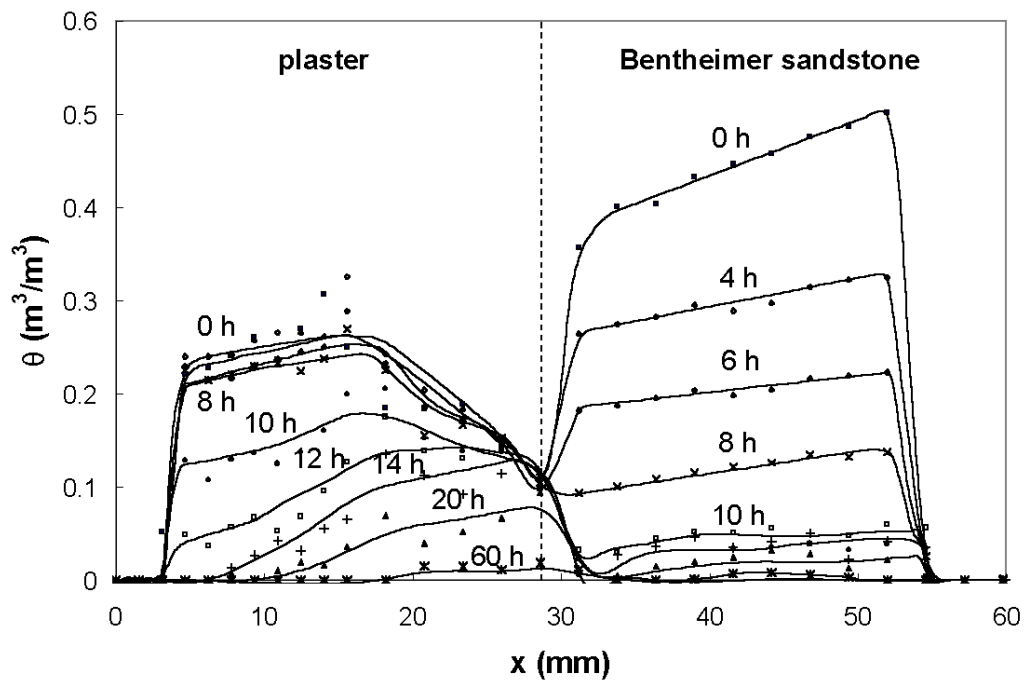
Figure 2: Water distribution in the plaster/Bentheimer sandstone system during drying. The dry air is blown over the top of the sample (x = 0) with a flow of 0.1 l/min. The samples were initially saturated with water. The Bentheimer sandstone clearly dries faster than the plaster. The solid curves are guides to the eye.
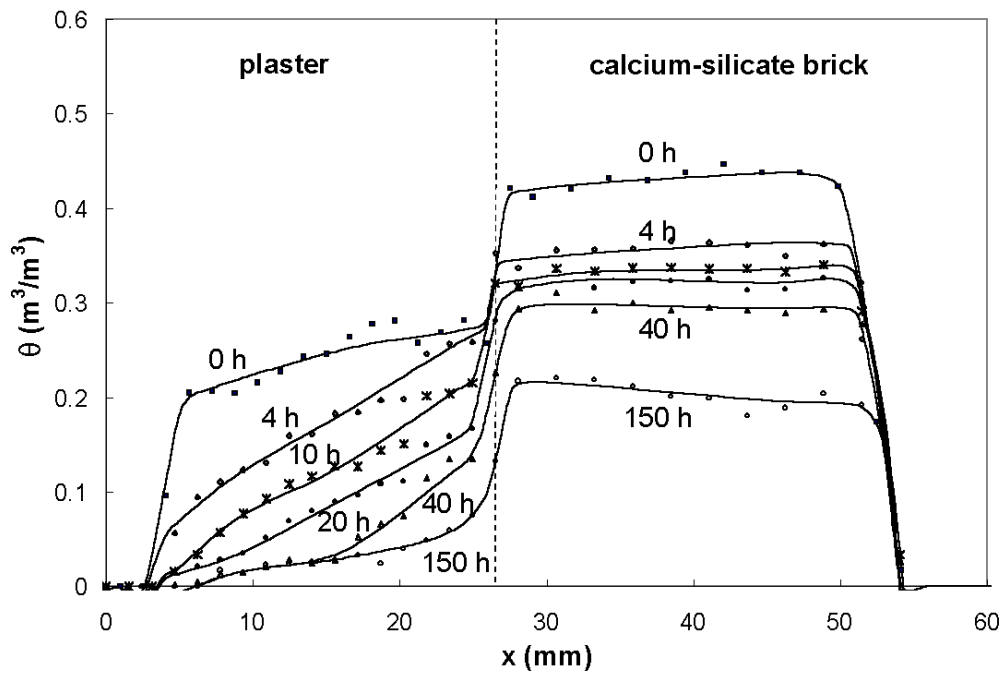
Figure 3: Water distribution in the plaster/calcium-silicate brick system during drying. The dry air is blown over the top of the sample (x = 0) with a flow of 0.1 l/min. The samples were initially saturated with water. The plaster dries faster than the calcium-silicate brick. The solid curves are guides to the eye.

The calcium-silicate brick/plaster system behaves quite differently, as can be seen in Fig. 3. Initially the brick and the plaster dry simultaneously. However, between 4 and 40 hours after the beginning of the drying process, the calcium-silicate brick dries much slower than the plaster. After 40 hours the plaster has become almost dry, while after 150 hours a significant amount of water is still present in the brick.

This behaviour is consequence of the two dominant pore sizes present in the calcium-silicate brick, which dimensions are an order of magnitude smaller and bigger, respectively, than the pore sizes of the plaster, see Table 1. During the first 4 hours the bigger pores of the brick dry out. Also the plaster dries to some extent. The most important feature of the drying process is that after a sufficiently long time (150 h) the small pores of the brick still contain water, while the plaster is nearly dry. Again, this can be explained from the capillary pressure, see eq. (4). Air prefers to invade the widest pores, which are, at this stage of the drying process, only available in the plaster layer.

Our drying experiments demonstrate that an equivalent plaster layer behaves differently on different substrates. Since in both cases the plasters applied had the same formulation, we can conclude that the substrate is of great importance for the transport behaviour in a plaster. This difference in water transport may influence the salt transport and crystallization.

4.2 Salt Transport and Crystallization during Drying

The combined transport of water and salt in the plaster/Bentheimer system was also studied. Initially the sample was saturated with a 4 M NaCl solution. The water profiles are presented in Fig. 4. The sample dries in a similar way but slower than in the case of pure water (Fig. 2). The drying of Bentheimer sandstone is faster than drying of plaster, which in 66 hours of drying remains almost fully saturated. In Fig. 5 the Na concentration profiles are shown. In connection with the water transport, differences in the salt transport in the plaster and the Bentheimer sandstone can be observed. During the first 16 hours the salt concentration in the Bentheimer sandstone remains uniformly distributed. The NaCl concentration does not exceed the initial concentration of 4 M. The data points show a rather large scatter, a result of the low NMR signal from the Na nuclei. During drying of the Bentheimer sandstone, the amounts of H_2O and Na in the liquid phase decrease and the signal to noise ratio decreases. In the plaster the salt concentration increases from 4 M to around 6 M. The NaCl distribution in the plaster is not uniform, but a concentration peak develops at the drying face. At this stage, crystallization at the plaster/air interface is visually observed.

Since the sodium concentration in the Bentheimer sandstone remains constant during the first 10 hours of drying, the same fractions of salt and water leave the stone. The water evaporates at the plaster/air interface while the salt remains in the plaster material. Because of this, the salt concentration in plaster increases till the saturation value of 6 M. After reaching the saturation concentration, the salt crystallizes mainly close or at the plaster/air interface.

5 Conclusions

In the present work we have shown that NMR imaging is a useful technique for non-destructive measuring of salt and water profiles in building materials during drying. The two plaster/substrate systems tested, in which only the substrate differed, showed different drying behaviour, which can be related to pore size differences between the plaster and the substrate. The layer with the widest pores always dries first. Therefore, the drying behaviour of a plaster/substrate layer depends on the pore size distributions of both the plaster and the substrate.

Measurements on salt loaded systems indicate that the salt transport and accumulation is connected to by the drying behaviour of the plaster/substrate system. When the plaster has small pores compared to the substrate, most salt accumulates in the plaster. So far, salt transport was investigated only for the plaster/Bentheimer system. However, when the plaster has the larger pores, as for the plaster/silicate-calcium brick system, it is expected that a significant amount of salt will crystallize within the substrate itself. In this particular case first the plaster dries and the substrate stays wet. Most of the salts present in the substrate will be deposited at the plaster/substrate interface. To confirm this hypothesis salt transport experiments on plaster/calcium-silicate system are underway.
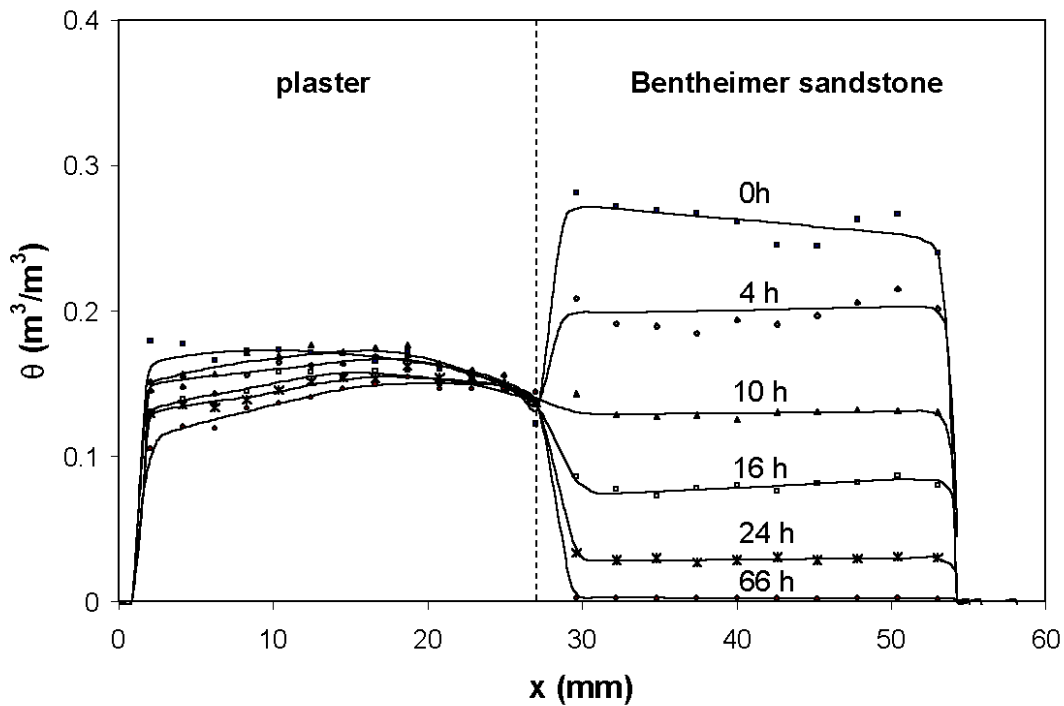
Figure 4: Water distribution in the plaster/Bentheimer sandstone system during drying. The dry air is blown over the top of the sample (x = 0) with a flow of 3 l/min. The samples were initially saturated with a 4 M NaCl solution. The solid curves are guides to the eye. The drying behaviour is similar as in figure 2.
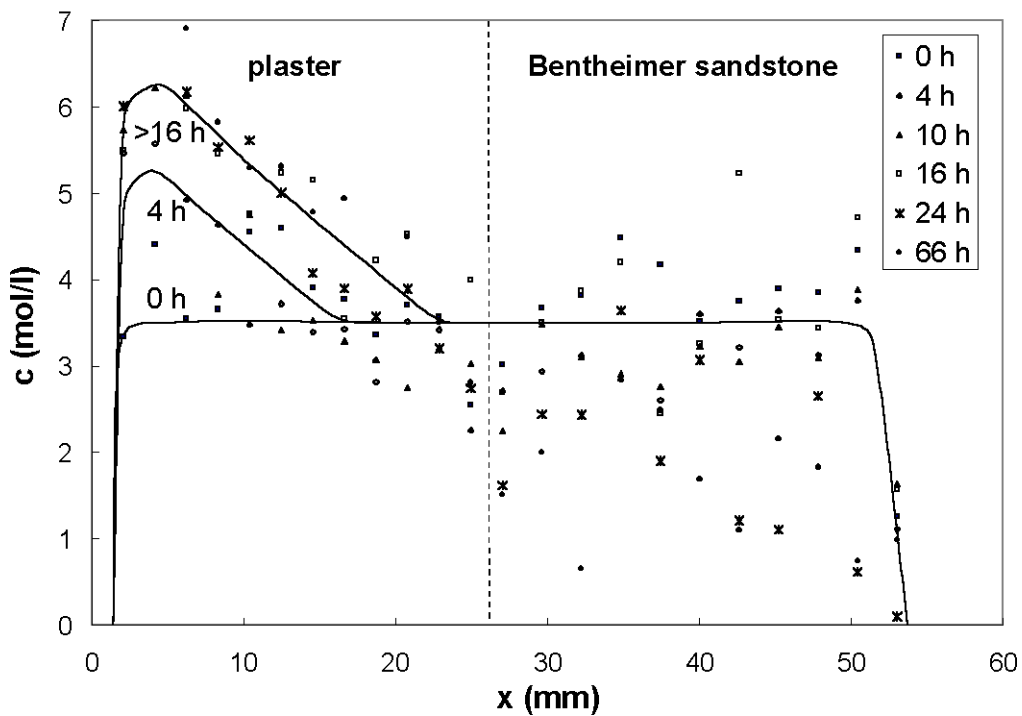
Figure 5: NaCl concentration in the plaster/Bentheimer sandstone system. The samples were initially saturated with a 4 M NaCl solution. During drying a peak in the NaCl concentration develops in the plaster, while the concentration in Bentheimer sandstone remains uniform and does not exceed the initial concentration of 4 M. The scatter of the data for the Bentheimer sandstone is due to the bad Na signal to noise ratio of the Na data.

Acknowledgements

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