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Citation for published version (APA):

Pel, L., Huinink, H. P., & Kopinga, K. (2002). Ion transport and crystallization in inorganic building materials as studied by nuclear magnetic resonance. *Applied Physics Letters*, 81(15), 2893-2895.
<https://doi.org/10.1063/1.1512329>

DOI:

[10.1063/1.1512329](https://doi.org/10.1063/1.1512329)

Document status and date:

Published: 01/01/2002

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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- The final published version features the final layout of the paper including the volume, issue and page numbers.

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Ion transport and crystallization in inorganic building materials as studied by nuclear magnetic resonance

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(Received 14 June 2002; accepted 13 August 2002)

Salt weathering is a major cause of deterioration of buildings and monuments of cultural heritage. We have determined the underlying moisture and ion transport within a representative building material by measuring the time evolution of NaCl-saturated samples during one-sided drying using nuclear magnetic resonance. The measured NaCl concentration profiles reflect the competition between advection to the surface and redistribution by diffusion. By representing the measured moisture and NaCl profiles in an efflorescence pathway diagram (EPD) the crystallization is also taken into account. The pathways followed in the EPD indicate that for historical objects in general, crystallization at the surface cannot be avoided. © 2002 American Institute of Physics.
[DOI: 10.1063/1.1512329]

Buildings and monuments of cultural heritage are under constant threat from their environment. Salts are widely recognized as a major cause of the loss of many historical objects, such as statues, buildings, and other artworks.^{1–4} While such porous materials are drying, salt crystallization may occur at the surface (that is, efflorescence) or just below the surface, where it may cause structural damage, for example, delamination, surface chipping, or disintegration, with consequent loss of detail. Salt weathering can therefore be considered as a common hazard with significant cultural and economic implications. It has to be mentioned that salt weathering also plays an important role in various geophysical deterioration processes.²

Although salt damage has been intensively investigated for several decades, 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 evaporation and salt crystallization in porous materials is required to explain salt damage for different materials and conditions and to develop methods to mitigate this problem. For a long time, the development of realistic models for combined moisture and ion transport made hardly any progress. In geology, no consensus exists as yet about the way in which salts induce the stone decay. The critical issue is not the formulation of transport equations and constitutive relations, but the lack of adequate and reliable experimental data. Only recently, technological developments have created the opportunity to solve this problem.

Nuclear magnetic resonance (NMR) imaging techniques allow the imaging of specific nuclei spatially, as in medical imaging. The first application of NMR imaging to building materials was reported by Gummerson.⁵ Imaging of building materials is complicated, as in general these contain many magnetic impurities: Fe and Mn, for example. These impurities generate large magnetic field gradients in the material, causing a fast dephasing of the nuclear magnetic moments,

resulting in a very short nuclear relaxation time,⁶ which hampers the study of fluids in these materials with standard NMR equipment. However, by using a specially adapted NMR setup it appeared possible to measure the moisture distribution in these materials in a quantitative way with a high spatial resolution.⁷ As NMR can also selectively detect other nuclei, such as Na, this makes it possible to study the salt transport in materials, for instance, during drying.

In this study we focus on the salt transport during the drying of a salt-contaminated material, as this induces crystallization at the surface of the material. Here we consider single-sided drying of a material saturated with a NaCl solution. The apparatus used in this study has an iron-cored electromagnet generating a field of 0.8 T. Anderson gradient coils generate a constant gradient of 0.3 T, resulting in a one-dimensional resolution of the order of 1 mm. A Faraday shield has been added to suppress the effect of dielectric changes.⁷ By an electrically operated switch the tuned circuit of the insert can be toggled between 33 MHz for hydrogen or 8.9 MHz for Na imaging. The cylindrical sample with a diameter of 20 mm is moved vertically through the magnet with the help of a step motor. This sample is sealed at all sides except the top, over which air with a relative humidity of 5% is blown. In this way a one-dimensional drying process is created. It takes 60 s to determine the moisture content at one position. Due to the lower relative NMR sensitivity of Na it takes 4 min to measure the Na content with a comparable signal-to-noise ratio. Because of the NMR echo times used in the experiments ($TE = 205 \mu\text{s}$) only the Na nuclei in the solution are measured, that is, no signal is obtained from NaCl crystals. Hence, the NaCl concentration in the solution can be calculated from the Na signal and the moisture signal. Measuring an entire NaCl concentration profile for a sample with a length of 45 mm takes about 3 h. Since the typical time of a drying experiment is several days, the variation of the concentration profile during a single scan can be neglected.

Drying experiments were performed on various types of fired-clay brick. These bricks show almost no adsorption of

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FIG. 1. NaCl concentration profiles measured during drying of a fired-clay brick sample of 45 mm length after 0, 1, 3, 6, 9, 12, and 15 days.

ions at the pore wall. In all drying experiments, with the drying rates used in this study, it was observed that the moisture profiles were almost homogeneous, and within the time of these experiments, that is, up to 14 days, no receding drying fronts were observed. We attribute this to the wetting properties of the NaCl solution. In Fig. 1, an example for a drying experiment of a 3 M NaCl solution is shown. During the initial drying, Na ions are advected to the surface (position 0 mm) and the NaCl concentration slowly increases to 6 M, which is the saturation value for a NaCl solution. At this point additional advection will result in crystallization at the top of the sample, which is observed as a white efflorescence. From this point on the NaCl concentration profile in the sample starts to level off until the total sample is at 6 M. During a drying experiment there will be a competition between advection, which transports ions to the top of the sample and thereby causes accumulation, and diffusion, which levels off any accumulation. For the drying of a porous material a Peclet number can be defined as:⁸

$$Pe \equiv \frac{hL}{\theta_m D}, \quad (1)$$

where h [$\text{m}^3 \text{m}^{-2} \text{s}^{-1}$] is the drying rate, L [m] the length of the sample, θ_m [$\text{m}^3 \text{m}^{-3}$] the maximum fluid content by capillary saturation, and D [$\text{m}^2 \text{s}^{-1}$] the diffusion coefficient of Na in the porous material. For $Pe \ll 1$ diffusion dominates and the ion-profiles will be uniform, whereas for $Pe \gg 1$ advection dominates and ions will be accumulated at the drying surface.

In Fig. 2 the drying curve, that is, the average saturation S_{avg} ($S = \theta/\theta_m$) as a function of time, is plotted for the experiment shown in Fig. 1. We have used a value of D of the order of $1 \times 10^{-9} \text{ m}^2 \text{s}^{-1}$ to estimate the Peclet number.⁹ Initially the drying rate gives rise to $Pe \approx 3$, corresponding to the accumulation of the 6 M peak at the surface, whereas after two days $Pe \approx 0.7$, corresponding to the leveling off of

FIG. 2. Time dependence of the average saturation S_{avg} in the sample (Δ) and that of $C_{\text{avg}} S_{\text{avg}}$, which represents the total amount of NaCl present in the solution ($\square$) for the experiment corresponding to Fig. 1.

the NaCl profile. In Fig. 2 the time dependence of $C_{\text{avg}} S_{\text{avg}}$ (C_{avg} is the average salt concentration in the solution) is also plotted. This quantity is proportional to the total amount of dissolved ions in the solution (observed by NMR), since in our experiments the water is uniformly distributed within the sample, in which case $(CS)_{\text{avg}} = C_{\text{avg}} S_{\text{avg}}$. Initially this amount decreases rapidly, indicating that salt is crystallizing at the top. As the drying rate decreases also the crystallization rate decreases. A second kink in $C_{\text{avg}} S_{\text{avg}}$ is observed after about 11 days, when the sample is homogeneous at 6 M. At this point the crystallization rate becomes proportional to the drying rate.

Various experiments were performed with different salt concentrations (i.e., 1, 3, and 5 M), and different airflow rates over the samples. Instead of representing all these experiments by graphs like Figs. 1 and 2, we will now introduce the efflorescence pathway diagram (EPD), as plotted in Fig. 3. In an EPD the total amount of NaCl present in the solution $C_{\text{avg}} S_{\text{avg}}$, that is, the amount directly measured by NMR, is plotted against the average saturation S_{avg} . In this diagram two limiting situations can be distinguished. First, in the case of very slow drying (i.e., $Pe \ll 1$), the ion profiles stay homogeneous and for some time no crystallization will occur. The average NaCl concentration slowly increases (line A) until the complete sample has reached 6 M. From this point on any additional drying will result in crystallization (line B). The other extreme situation occurs in case of very fast drying of the samples (i.e., $Pe \gg 1$). Now ions are directly advected with the moisture to the top of the sample and a 6 M peak will build up with a width so small that the average concentration is not significantly affected. If the rate of crystallization is high enough, that is, if there are enough nucleation sites at the top, the average NaCl concentration in the solution in the sample itself will remain constant at

FIG. 3. Efflorescence pathway diagram: $C_{avg} S_{avg}$, which represents the total amount of NaCl present in the solution, as a function of the average saturation S_{avg} . (a) EPD for the experiment plotted in Fig. 2. Indicated are the points corresponding to the profiles plotted in Fig. 1(b). (b) The EPD for all experiments performed on fired-clay brick: 5 M $\square$, 3 M ∇ , $\square$, $\diamond$, $+$, $\circ$ and 1 M $\square$, $\diamond$, $\triangle$.

nearly the initial concentration (line C). From any point within the region bounded by the lines A–C only moisture removal will result in an increase of the NaCl concentration. A decrease of $C_{avg} S_{avg}$ can only take place by crystallization. This requires that ions are transported to a region with a local concentration of 6 M peak, that is, the drying surface in our experiments. Because the transport is driven by evaporation, crystallization always involves a (small) change of S_{avg} .

For the experiment shown in Figs. 1 and 2 the corresponding pathway is plotted in Fig. 3(a). This pathway indi-

cates that during the first 9–12 days a peak in the NaCl concentration is present and salt will crystallize at the top; that is, there is salt efflorescence. Thereafter the concentration in the sample is 6 M. In Fig. 3(b) all pathways are plotted for the experiments performed with the various samples starting at initial homogenous concentrations of 1, 3, and 5 M. In a few experiments indeed the boundary line of $Pe \gg 1$ is followed. This indicates that the salt crystallization is indeed fast enough and is not a limiting factor; that is, there are enough nucleation sites in this type of material. During these experiments with NaCl no supersaturation (i.e., concentrations higher than 6 M) is found. In contrast to the experiments for 3 and 5 M, it is possible to follow the $Pe \ll 1$ boundary line for 1 M.

The NMR measurements on combined moisture and ion transport during drying in combination with the EPD prove to be a powerful tool to study salt weathering. The EPD diagrams reflect the competition between advection to the surface and redistribution by diffusion, but also take into account the crystallization. The EPDs indicate that in general, crystallization at the surface cannot be avoided. However, it is evident that the drying rate is the key parameter in the salt crystallization process. When historical objects are preserved indoors, where the climatological conditions can be controlled easily, the relative humidity has to be kept as constant as possible and airflow around the object should be prevented. However, outdoor monuments and buildings are frequently exposed to wind and fluctuations of the relative humidity. In order to mitigate the problem of crystallization one should try to eliminate the source of the salts or try to prevent crystallization, for example, by a salt inhibitor.

A part of this project was supported by the Dutch Technology Foundation (STW) and TNO Building and Construction. We also like to thank Prof. P. C. F. Bekker, who initiated this research, for his ongoing encouragement and Dr. E. F. Kaasschieter for carefully reading this manuscript.

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