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ION TRANSPORT AND CRYSTALLIZATION IN FIRED-CLAY BRICK: A NMR STUDY

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Abstract

Salts are widely recognized as a major cause of the loss of many historical objects, such as masonry, statues, and other artwork. To obtain information about the mechanisms underlying these damage processes we have studied the moisture and ion transport within two types of fired-clay brick: a modern type produced in the Netherlands and an old fired-clay brick from the city of Venice in Italy
The time evolution of NaCl saturated samples of fired-clay brick during drying was measured using Nuclear Magnetic Resonance. The moisture content and amount of dissolved Na ions were measured quantitatively as a function of position. The NaCl concentration profiles obtained from these data reflect the competition between advection to the surface and redistribution by diffusion. For both types of brick, the fast drying Dutch fired-clay brick and the slow drying Venice fired-clay brick, an accumulation of NaCl at the drying surface is observed in the experiments.

Key Words

Drying, crystallization, NMR, EPD

1 Introduction

Salts are widely recognized as a major cause of the loss of many historical objects, such as masonry, statues, and other artwork. While a material is drying, salt crystallization may occur at the surface, i.e., efflorescence, or just under the surface (subflorescence), where it may cause structural damages, e.g., delamination, surface chipping, or desintegration with consequent loss of detail, either carved or painted. Also many contemporary buildings and civil structures suffer from salt-induced damage processes. Salt weathering can therefore be considered as a common hazard with significant cultural and economic implications. Hence salt damage has been intensively investigated for several decades, e.g., Evans (1970), Goudie and Viles (1997), Wellman and Wilson (1965), and Lewin (1980). For a long time the development of

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realistic models for combined moisture and ion transport hardly made any progress, mainly because of the lack of adequate and reliable experimental data. However, using NMR techniques (Gummerson et al 1979 and Pel et al 2000) non-destructive measurements of the moisture and ion profiles in bricks is possible, offering new possibilities to approach this problem.

In this paper we focus on the one-dimensional drying of two types of fired-clay brick saturated with a NaCl solution: a modern type produced in the Netherlands and an old fired-clay brick from the city of Venice in Italy. First we will discuss the moisture and ion transport during the drying. The NMR method and set-up for measuring non-destructively the moisture and Na distribution during drying is explained in section 3. The results concerning measured moisture and ion transport will be discussed in section 4.

2 Moisture and ion transport

In figure 1 a schematic representation is given of the drying process of a sample saturated with a salt solution. During the drying process moisture will be transported to the drying surface. The ions will be transported by advection with the moisture and diffusion within the moisture.

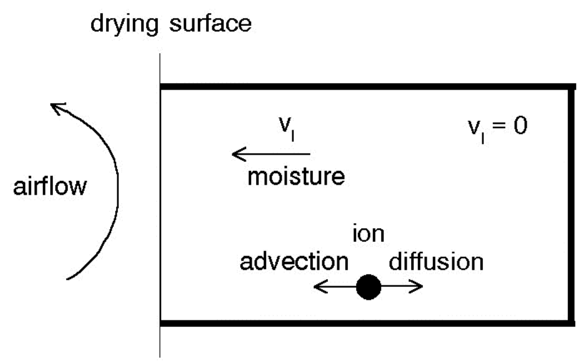


Figure 1: A schematic diagram of the one-sided drying of a sample saturated with a salt solution. v_l is the moisture fluid velocity

Initially the ions will be transported by advection to the drying surface. As a consequence a salt peak will built up and a salt concentration profile will develop. But as soon a concentration gradient develops diffusion will start to level off the accumulation. Hence 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. This competition between advection and diffusion can be expressed in a so-called Peclet number, Pe, which in this case can be defined as (see, e.g., Huinink et al 2002):

$$Pe = \frac{h\,L}{\theta_m D_c} \qquad (1)$$

h is the drying rate [$m^3\ m^{-3}\ s^{-1}$];
L is the length of the sample [m];
θ_m is the maximum moisture content by capillary saturation [$m^3\ m^{-3}$];
D_c is the diffusion coefficient of the ions in the moisture in a porous material [$m^2\ s^{-1}$].

If during drying Pe<<1 diffusion will be the dominant proces and the ion concentration profiles will remain homogeneous whereas if Pe>>1 the advection will be dominant and accumulation will take place at the drying surface. If this accumulation reaches the saturation concentration any additional advection will result in crystallization.

3 Nuclear Magnetic Resonance

In a Nuclear Magnetic Resonance (NMR) experiment the magnetic moments of the nuclei are manipulated by suitably chosen radio frequency fields, resulting in a so-called spin-echo signal. The amplitude of this signal is proportional to the number of nuclei excited by the radio frequency field. NMR is a magnetic resonance technique, where the resonance condition for the nuclei is given by:

$$f = \gamma B_o \tag{2}$$

f is frequency of the radio frequency field [Hz];
γ is the gyromagnetic ratio (γ = 42.6 MHz/T for ^{1}H, 11.3 MHz/T for ^{23}Na)
B_O is the externally applied static magnetic field [T].

Because of this condition the method can be made sensitive to one type of nuclei and therefore to hydrogen (and thus to water) and sodium.
For the experiments described here a home-built NMR scanner is used, which incorporates an iron-cored electromagnet operating at a field of 0.78 T. In order to perform quantitative measurements a Faraday shield is placed between the tuned circuit of the probe head and the sample (Pel 1995, TPM 2004).
The sample, a fired-clay brick cylinder with a length of 40 mm and a diameter of 20 mm, was placed inside a closed teflon holder to prevent evaporation. A constant magnetic field gradient of up to 0.3 T/m was applied using Anderson coils, giving a one-dimensional resolution of the order of 2 mm for both water and Na. The spin-echo experiments were performed at a fixed frequency, corresponding to the centre of the RF coil.

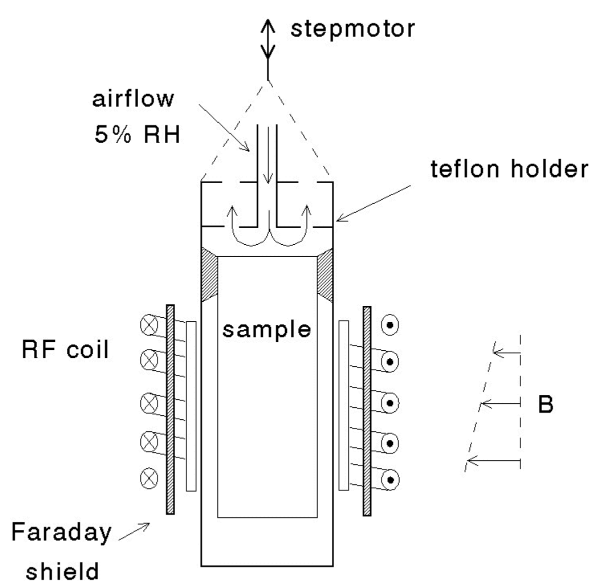


Figure 2: A schematic diagram of the NMR set-up for measuring the moisture and Na distribution during drying

The experimental set-up is given in figure 2. The sample is moved vertically through the magnet with the help of a step motor. It is sealed at all sides, except for the top over which air with a relative humidity of 5% is blown. In this way a one-dimensional drying process is created.

While the sample is drying, first the moisture content in the small region of the sample near the centre of the RF coil is measured. Next, the frequency is changed from 33 MHz (^1H) to 9 MHz (^{23}Na) and the Na concentration in that region is measured. After these two measurements the sample is moved in the vertical direction by the step motor and the moisture and Na concentration are measured again. The measurement time for the moisture content was 1 minute whereas it took 4 minutes to measure the Na content with a similar signal to noise ratio. This procedure is repeated until a complete moisture and Na profile has been measured. A time stamp is given to each measurement point. Measuring an entire Na concentration profile takes typically 3 hours whereas only measuring a moisture profile takes typically 1 hour. Since the typical time of a drying experiment is in the order of days, the variation of the moisture and ion profiles during a single scan can be neglected. With NMR settings used in these experiments only the Na nuclei in the solution are measured, i.e., no signal is obtained from NaCl crystals.

4 Experiments

The experiments where performed on two types of fired-clay brick, a modern type produced in the Netherlands (Dutch fired-clay brick) and an old fired-clay brick from the city of Venice in Italy (Venice fired-clay brick).

4.1 Moisture transport

First the drying of both types of fired-clay brick was measured of a capillary saturated sample with water. The results of the measurements are given in figure 3.

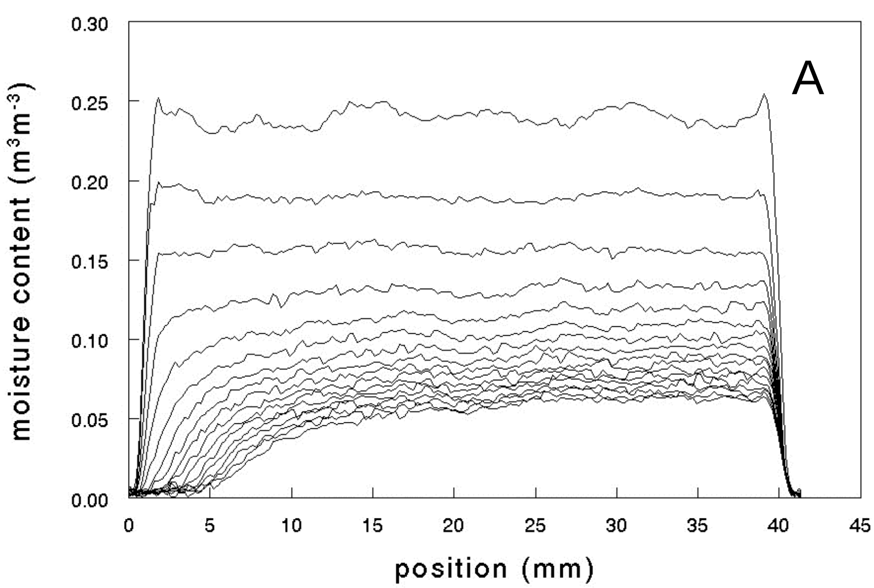


Figure 3A: The measured moisture profiles during drying of a Dutch fired-clay brick sample of 40 mm length. The time between subsequent profiles is 1 hour. The drying surface is at 0 mm.

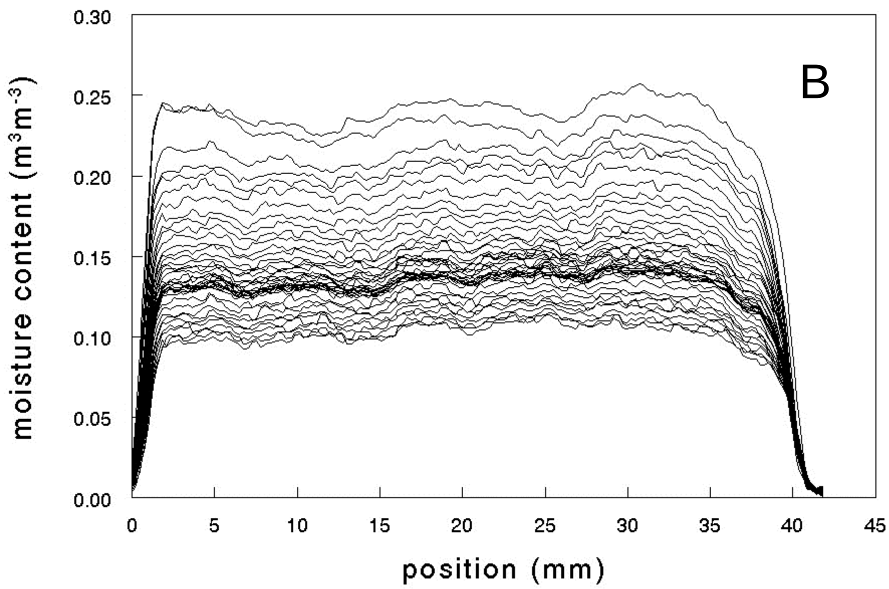


Figure 3B: The measured moisture profiles during drying of a Venice fired-clay sample of 40 mm length. The time between subsequent profiles is 1 hour. The drying surface is at 0 mm.

A clear difference in drying behaviour is observed. For the Dutch brick the drying is initially externally limited and almost flat moisture profiles are observed. After 4 hours the surface becomes dry and a receding drying front is seen entering the material, and hence the drying is internally limited. For the Venice brick only a very slow drying is observed and within the measurement time no drying front is observed. In figure 4 the drying curves are given for both experiments, i.e., the average moisture content as a function of time. Here also clearly the different drying behaviour of the two types of fired-clay brick can be seen.

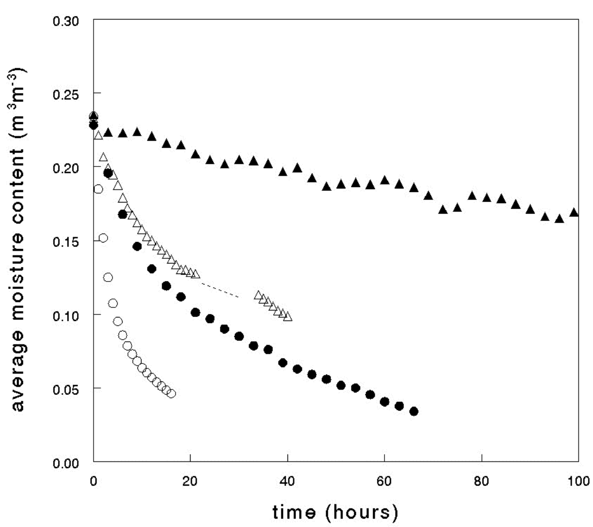
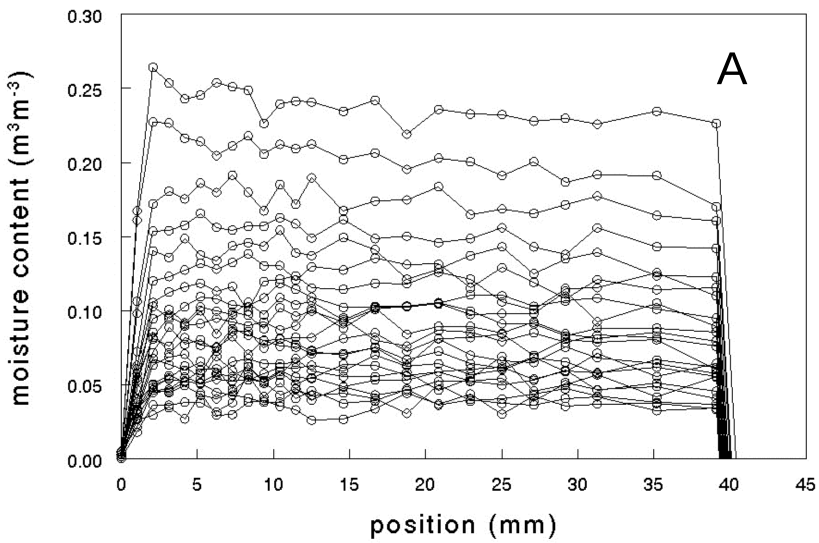


Figure 4: The drying curve, i.e., the average moisture content as a function of time, for the experiments given in figure 3 and 4. ○ Dutch-fired clay brick and △ Venice fired-clay brick capillary saturated with water. ● Dutch fired-clay brick saturated with 1 M NaCl and ▲ Venice fired-clay brick saturated with 3 M NaCl.

4.2 Moisture and ion transport

Next the samples were rewetted with a NaCl solution: Dutch fired-clay brick with 1 M and Venice fired-clay brick with 3 M. The results for the measured moisture and Na concentration profiles are given in figure 5 and 6. Figure 5 shows that in this case for the Dutch fired-clay brick the moisture distribution within the sample remains homogeneous during this drying experiment, i.e., no longer a receding drying front is observed. We attribute this to the wetting properties of the NaCl solution. For both types of brick due to the presence of the NaCl the drying rate decreases strongly. This can be observed clearly in the drying curves, which are also plotted in figure 4.



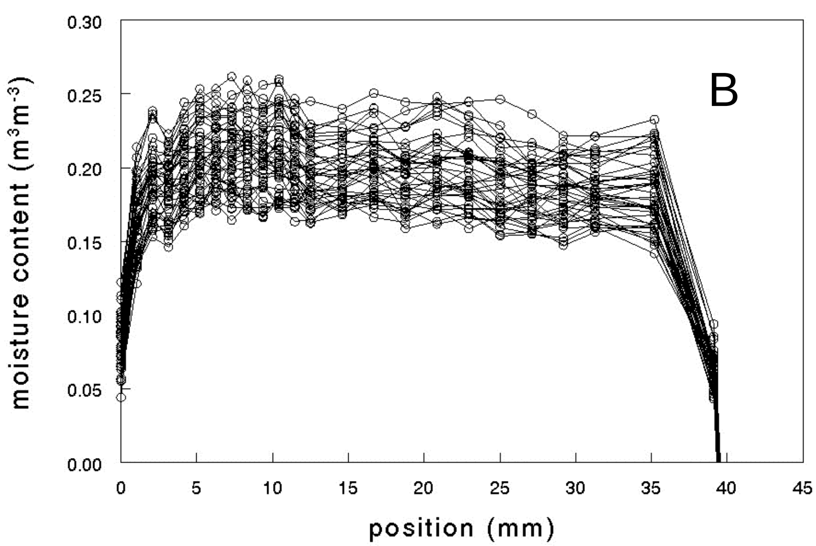
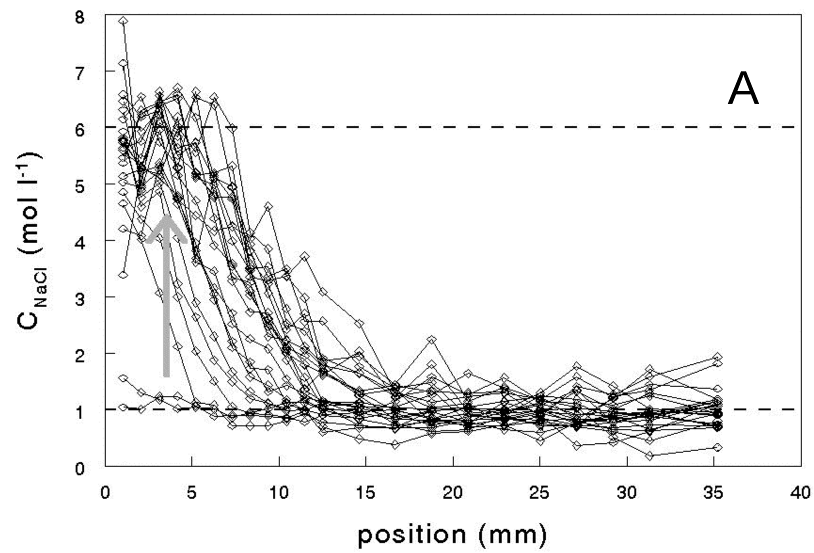


Figure 5: Moisture profiles measured during drying of a fired-clay brick sample of 40 mm length with a NaCl solution: A) Dutch fired-clay brick, 1 M NaCl and B) Venice fired-clay brick, 3 M NaCl. The time between subsequent profiles is 3 hours. The drying surface is at 0 mm.

In figure 6 the corresponding NaCl concentration profiles of Fig. 5 are plotted. Inspection of this figure shows that for both types of fired-clay brick after the start of the drying process Na ions are advected to the top and a peak develops just below the drying surface. As can be seen the NaCl concentration increases to 6 M, which is the saturation value for a NaCl solution. At this point any additional advection will result in crystallization at the top of the sample, which is observed indeed as a white efflorescence.



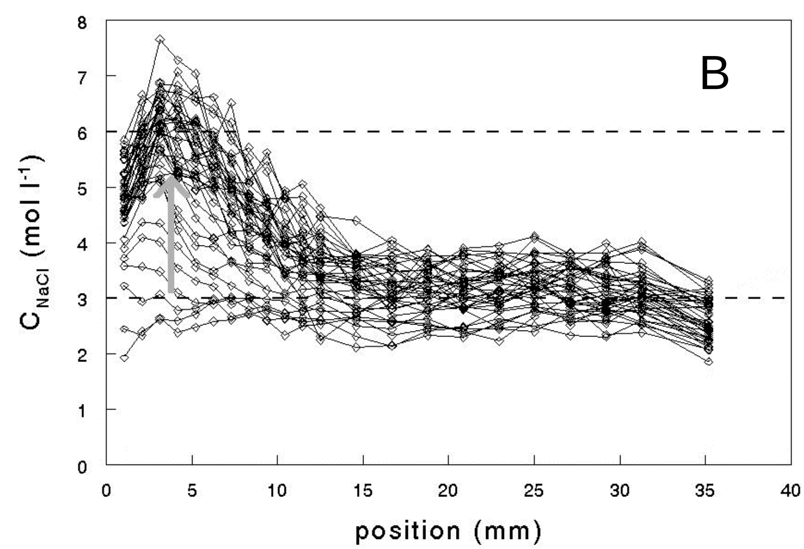


Figure 6: NaCl concentration profiles measured during drying of a fired-clay brick sample of 40 mm with a NaCl solution: A) Dutch fired-clay brick, 1 M and B) Venice fired-clay brick, 3 M. The time between subsequent profiles is 3 hours. The drying surface is at 0 mm.

Although the drying rate of the Venice fired-clay brick, and hence the advection of the ions, is much lower than for the Dutch fired-clay brick, still an accumulation is observed. That indicates that in this type of fired-clay brick not only the moisture transport is slower but that also the ion diffusion is decreased.

4.3 Efflorescence Pathway Diagram

In order to account for the crystallization occurring at the drying surface and to get an indication of the Peclet number, we have plotted the data resulting from the drying experiment shown in Figs. 5 - 6 in a so-called Efflorescence Pathway Diagram (EPD) (Pel 2002), which is given in Fig. 7. In an EPD the total amount of dissolved NaCl present in the solution, $C_{avg}S_{avg}$, is plotted against the average moisture saturation, S_{avg} (with the NMR no signal is obtained from NaCl crystals).

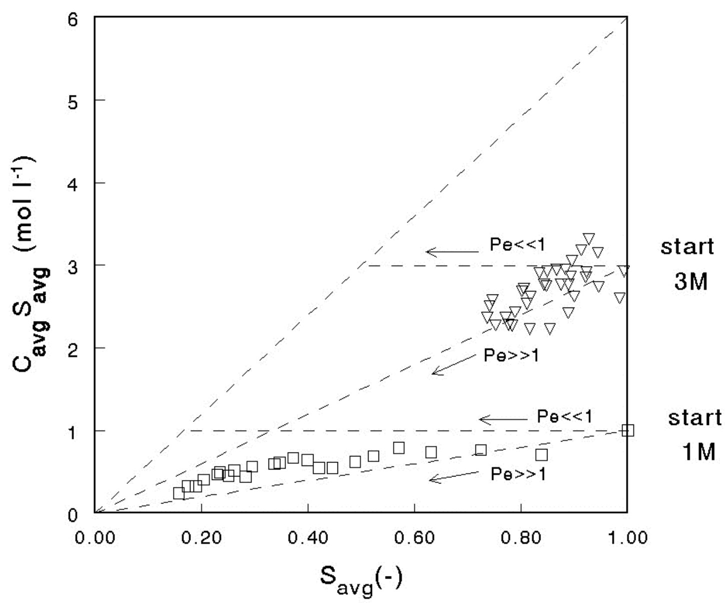


Figure 7. Efflorescence pathway diagram: $C_{avg}S_{avg}$, which represents the total amount of NaCl present in the solution, as a function of the average saturation S_{avg}. The data correspond to the drying experiment plotted in Figs. 5 -6.

In this diagram two limiting situations can be distinguished:

- Very slow drying, i.e., Pe << 1. In this case the ion profiles remain homogeneous and for some time no crystallization will occur. The average NaCl concentration slowly increases until the complete sample has reached 6 M. From this point on any additional drying will result in crystallization.
- Very fast drying, i.e., Pe >> 1. In this case ions are directly advected with the moisture to the top of the sample and a 6 M peak will build. If the rate of crystallization is high enough, i.e., if there are enough nucleation sites at the top to form crystals, the average NaCl concentration in the solution in the sample itself will remain constant at nearly the initial concentration.

As can be seen the EPD's of the two types of brick indicate that in these experiments the Pe>>1, and hence an accumulation will take place at the drying surface, as is also observed. As for the Venice fired-clay brick Pe>>1, this also indicates that the Na-

diffusion is decreased strongly in comparison to the Na diffusion in the Dutch fired-clay brick. This decreased diffusion in combination with the slow drying rate makes that for the Venice fired-clay brick still advection is dominant during this drying experiment.

5 Conclusions

The NMR measurements on combined moisture and ion transport during drying prove to be a powerful tool to study salt weathering. These experiments reflect the competition between advection to the surface and redistribution by diffusion. From the experiments is clear that the drying rate is the key parameter in the salt crystallization process. However care has to be taken as also the ion diffusion can decrease in a fired-clay brick. Hence also for a 'slow' drying Venice fired-clay brick an accumulation at the surface is observed as in this type of brick also the diffusion is strongly decreased for ions.

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