

Saline absorption in calcium silicate brick observed by NMR scanning

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**Saline absorption in calcium silicate brick
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Abstract

The absorption of a 4 M NaCl solution in calcium-silicate brick was investigated by nuclear magnetic resonance scanning. This method has the advantage that quasi-simultaneously both the moisture and the Na profile can be measured during absorption. It was found that during the absorption process the Na ions clearly stay behind and hardly any Na is present near the wetting front. This is caused by binding of the Na ions to the pore surface. It is shown that both the moisture and the Na profiles during absorption can be scaled using the Boltzmann-Matano transformation.

1. Introduction

Moisture and especially salt can give rise to the deterioration of porous building materials. Two major effect of salts are salt efflorence, which can cause both visual and structural damages, and the corrosion of steel in concrete structures, which can cause structural damages. Therefore a detailed knowledge of moisture and salt transport is essential for

understanding the durability of these materials.

For measuring the combined moisture and ion transport often destructive methods are used. These methods usually involve drilling or grinding of the sample, gravimetrically determining its moisture content, and chemically determining its salt concentration. These methods have the disadvantage of destroying the sample, which complicates any time-dependent measurements, and usually lack sufficient resolution (of the order of 10 mm).

It has been shown that Nuclear Magnetic Resonance (NMR) offers a powerful technique to measure the moisture profiles in a non-destructive way [1, 2, 3]. In this paper, NMR is also used to measure the Na content, thereby offering the possibility to measure the combined ion and moisture transport in a non-destructive way. First, we will present a short introduction on combined ion and moisture transport. Next, a comprehensive description will be given of our nuclear magnetic resonance apparatus that allows non-destructive quasi-simultaneous measurements of both moisture and Na profiles in porous building materials. Finally, some results of measurements on the absorption of a 4 M NaCl solution in a calcium silicate brick will be discussed.

2. Theory

If gravity is neglected, the isothermal transport of water and ions in a porous material for the one-dimensional problem considered in this paper can be described by nonlinear diffusion equations. The liquid moisture transport can be described by (e.g., see [4]):

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x} \left(D(\theta) \frac{\partial \theta}{\partial x} \right) \quad (1)$$

In this equation θ is the volumetric liquid moisture content, $D(\theta)$ (m^2s^{-1}) is the so-called isothermal moisture diffusivity. This moisture diffusivity describes the moisture transport by capillary action and is a function of the actual moisture content. Here the transport of water due to a salt gradient has been neglected. However, salts will have a direct influence on the capillary action, viscosity, and permeability and therefore on the moisture diffusivity.

In case of water absorption the ions will be transported by advection with the liquid and diffusion within the liquid. However, ions can be bounded chemically or physically to the pore surface, and hence a distinction will be made between free and bound ions. The ion

transport can be described by [4, 5, 6]:

$$\frac{\partial(\theta c_{\text{free}})}{\partial t} = - \frac{\partial}{\partial x} \left(\theta \left(c_{\text{free}} v_1 - D_h \frac{\partial c_{\text{free}}}{\partial x} \right) \right) - \frac{\partial c_{\text{bound}}}{\partial t} \quad (2)$$

In this equation c_{free} is the free ion concentration in the water and D_h is the hydrodynamic dispersion coefficient, v_1 is the liquid fluid velocity and c_{bound} the concentration of bound ions. In case of absorption the dispersion coefficient can be neglected [4].

The bound ion concentration is a function of the free ion concentration; a simple non-linear equilibrium isotherm was suggested by Freundlich [7]:

$$c_{\text{bound}} = K c_{\text{free}}^m \quad (3)$$

Here K and m are parameters which have to be determined experimentally. Note that Eq. 3 has been used for saturated porous media. Here it will assumed that this isotherm is also valid for unsaturated media.

3. Nuclear magnetic resonance technique

NMR is a magnetic resonance technique, where the resonance condition for the nuclei is given by:

$$f = \gamma B_0 \quad (4)$$

In this equation γ is the so-called gyromagnetic ratio and B_0 is the externally applied static magnetic field. The gyromagnetic ratio depends on the type of nucleus (see table 1).

The NMR measurements reported in this paper were performed using a so-called spin-echo technique [8]. Assuming a single exponential decay, the magnitude of a NMR spin-echo signal is given by [8, 9]:

$$S \sim G \rho [1 - \exp(-TR/T_1)] \exp(-TE/T_2) \quad (5)$$

where G is the relative sensitivity of the nuclei in comparison to hydrogen, ρ the density, T_1 the spin-lattice (longitudinal) relaxation time, TR the repetition time of the spin-echo experiment, T_2 the spin-spin (transverse) relaxation time, and TE the spin-echo time. This

equation is valid if $T_1 \gg T_2$. As can be seen from Eq. 5, small T_2 values lead to a decrease of the spin-echo signal whereas, on the other hand, small T_1 values are preferred, as this parameter limits the repetition time (usually $TR \approx 4T_1$).

For the experiments described in this paper a home-built NMR scanner is used, which incorporates an iron-cored electromagnet operating at a field of 0.78 T. In table 1 the various parameters are given for the ions under investigation at 0.78 T. As can be seen from this table, the sensitivity of chloride is very low and therefore this ion was not considered in this study.

nucleus	γ MHz/T	relative sensitivity (-)	T_1 (ms)	T_2 (ms)	averages (-)	measurement time (s)
^1H	42.6	1.0	100	30	16	16
^{23}Na	11.3	0.093	20	6	128 × 16	26
^{35}Cl	4.2	0.0047				

Table 1: *The values of the various NMR parameters in the experiments at 0.78 T on calcium silicate brick for a 4M NaCl solution.*

In order to measure quasi-simultaneously both the moisture and the Na profiles, a specially designed RF circuit was incorporated, of which a schematic diagram is given in Fig. 1. Using two switches which are actuated by a step motor, the capacitors for the resonance frequency and for the impedance matching can be changed. In this way the resonance frequency of the tuned LC-circuit can be toggled between 33 MHz for the moisture measurements and 9 MHz for the Na measurements.

In order to compensate for the lower relative sensitivity of Na with respect to H, a larger number of averages is needed to obtain a comparable signal-to-noise ratio. Fortunately, the relaxation time T_1 for Na is smaller, which allows a higher repetition rate. In addition, the magnitude of T_2 of the Na ions allows to use a CPMG pulse sequence [9]. By averaging over 16 consecutive spin-echoes of the CPMG sequence, the signal-to-noise ratio is increased but the measurement time is not. The actual experimental parameters are given in table 1.

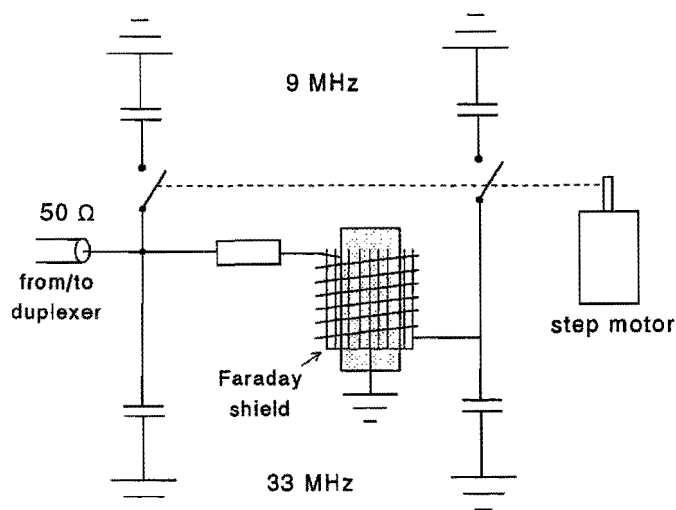


Figure 1: Schematic diagram of the electric resonance circuit of the NMR insert. Using a step motor both the capacitors for the impedance matching and for the resonance frequency can be changed. In this way, the LC-circuit can be tuned to the NMR resonance frequency of water (33 MHz) or that of Na (9 MHz at 0.78 T).

The sample, a calcium-silicate brick cylinder with a length of 90 mm and a diameter of 20 mm, was placed inside a closed teflon holder to prevent evaporation. In order to perform quantitative measurements, special attention was given to the impedance matching of the NMR insert. To reduce the effects of variation of the dielectric permittivity by a changing moisture content in the sample, a Faraday shield was placed between the tuned circuit of the probe head and the sample [10]. The quality factor of the LC circuit was chosen rather low ($Q \approx 40$), to suppress the effects of Eddy currents, that are generated by the RF field within the (electrically conducting) NaCl solution. Although these effects were found to be very pronounced in the reservoir with the NaCl solution, they appeared to be negligible within the porous material itself. A constant magnetic field gradient of up to 0.15 T/m was applied using Anderson coils, giving a one-dimensional resolution for both water and Na of the order of 2 mm. The spin-echo experiments were performed at a fixed frequency, corresponding to the centre of the RF coil. No attempt was made to switch the gradients during the individual pulse sequences.

For an absorption experiment, a volume of water or a NaCl solution is put on top of the sample. While the liquid is being capillary absorbed by the sample, 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 and the Na concentration in that region is measured. After these two measurements the sample is moved in the vertical direction by a computer controlled step motor with a resolution of 0.25 mm and the moisture and Na concentration are measured again. This procedure is repeated until a complete moisture and Na profile have been measured. A time stamp is given to each measurement point.

4. Results

In order to be able to determine the effect of ions on the transport of moisture, first an absorption experiment was done with pure water. The moisture transport during absorption can be described by Eq. 1 and the initial condition $\theta=\theta_0$ for $x>0$ at $t=0$ and boundary condition $\theta=\theta_{cap}$ at $x=0$ for $t>0$. Here θ_0 is the initial moisture content of the dry sample and θ_{cap} is the capillary moisture content, which is the maximum moisture content under atmospheric conditions. Under these conditions the Boltzmann-Matano transformation [11] $\lambda=x/\sqrt{t}$ can be applied. This reduces the nonlinear diffusion equation (1) into an ordinary differential equation:

$$2\frac{d}{d\lambda}\left(D(\theta)\frac{d\theta}{d\lambda}\right)+\lambda\frac{d\theta}{d\lambda}=0 \quad (6)$$

Hence all profiles can be related by a simple \sqrt{t} scaling. The resulting profiles for pure water after the transformation are given by the crosses in Fig. 2. As can be seen all profiles collapse onto one single master curve. This indicates that the liquid moisture diffusivity is not a function of the position and supports the modeling of the moisture transport by a diffusion equation.

In case of water absorption, an exponential relation between the moisture diffusivity and the moisture content, $D(\theta)=D_0\exp(\beta\theta)$, is commonly assumed for all porous materials [2, 3, 12, 13]. The results of simulations based on such a relation are denoted by the solid curves in Fig. 2. As can be seen these computer simulations give an adequate description of the observed moisture profiles.

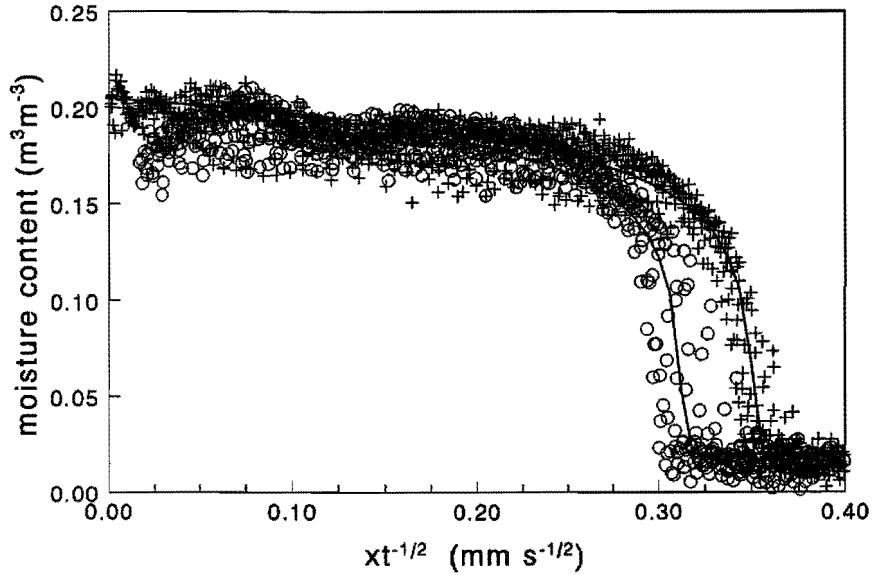


Figure 2: Boltzmann-Matano transformation of the measured moisture profiles during absorption: (+) pure water and (O) 4 M NaCl solution. The solid curves represent the Boltzmann-Matano transformation of simulated moisture profiles based on an exponential relation between D and θ : $D(\theta) = D_0 \exp(\beta\theta)$.

After drying the same sample was used for an absorption experiment with a 4 M NaCl solution. The measured moisture and Na profiles are given in Fig. 3. This figure shows that for water still very steep wetting fronts occur. The resulting moisture profiles after the Boltzmann-Matano transformation are represented by the circles in Fig. 2. For this solution still all profiles collapse onto one master curve. However, the absorption process is slightly slower, due to the presence of the ions.

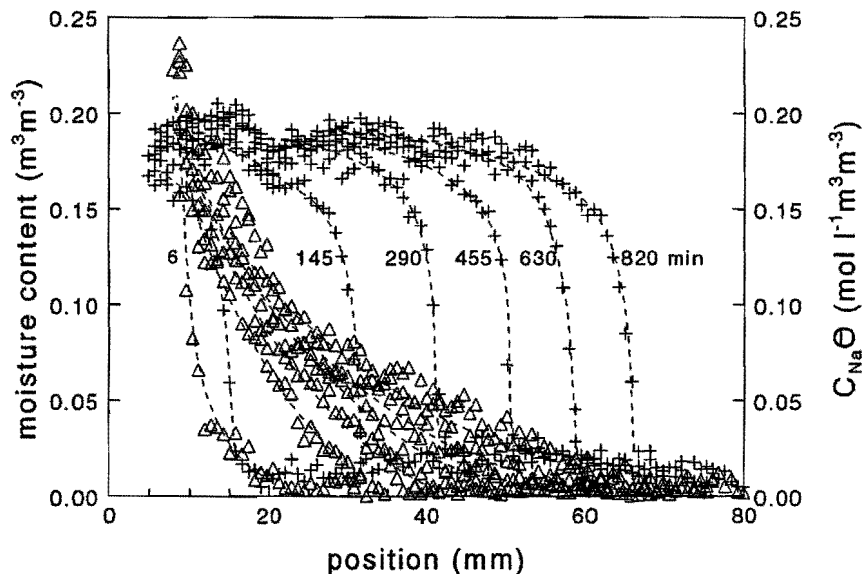


Figure 3: *The moisture (+) and Na profiles (Δ) measured during the absorption of a 4 M NaCl solution. The dashed curves through the points are meant as guides to the eye, whereas the times are given as an indication of the elapsed time. (For sake of clarity, only every second measured profile has been plotted).*

For moisture a sharp wetting front is observed. However, the Na profiles clearly lag behind the moisture profiles. Almost no Na is observed near the wetting front. Moreover, the Na concentration does not seem to exceed $0.2 \text{ mole l}^{-1} \text{ m}^3 \text{ m}^{-3}$, although the reservoir has a concentration of 4 M and therefore the maximum Na content would be expected to be $0.8 \text{ mole l}^{-1} \text{ m}^3 \text{ m}^{-3}$ at the boundary. This effect is caused by the interaction of the Na-ions with the pore surface.

The present NMR measurements are insensitive to Na that is bound to the pores and hence only the free Na content is measured. Using various NaCl solutions with different concentrations the relation between the free and bound ion concentration was determined for capillary saturated calcium silicate samples. The actual NaCl solution present in the samples

was checked by independent gravimetric measurements where the total amount of NaCl was compared with the volume of the absorbed solution. The results, together with a fit of the Freundlich isotherm (Eq. 3) with $K=2.4 \text{ mole l}^{-1}$ and $m=0.45$ are given in Fig. 4. This figure shows that for a 4 M NaCl solution only 1.25 M is present as free ions in the sample, whereas 2.75 M is bound to the pore wall. This relation found from the NMR measurements on Na is very similar to results reported for the Cl binding isotherm in concrete (see, e.g., [5])

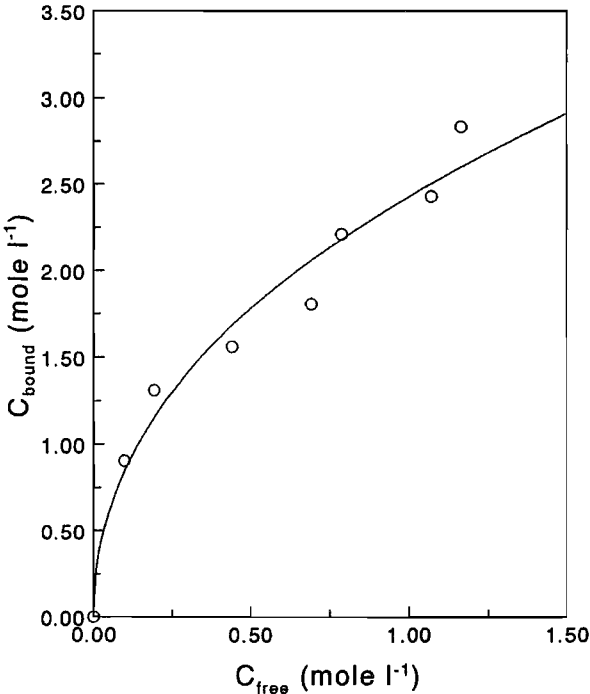


Figure 4: *The bound Na content in various capillary saturated calcium silicate samples versus of the free Na content in these samples determined from NMR measurements. The solid curve indicates the equilibrium Freundlich isotherm with $K=2.4 \text{ mole/l}$ and $m=0.45$.*

In case of absorption with the initial condition $c\theta=0$ for $x>0$ at $t=0$ and boundary condition $c\theta=c\theta_{cap}$ at $x=0$ for $t>0$, where $c=c_{free} + c_{bound}$, and neglecting the hydrodynamic dispersion, the Boltzmann-Matano transformation can also be applied, now giving:

$$2\frac{d}{d\lambda}\left(c_{free}D(\theta)\frac{d\theta}{d\lambda}\right)+\lambda\frac{d(\theta c_{free})}{d\lambda}+\lambda\frac{dc_{bound}}{d\lambda}=0 \quad (7)$$

Hence in the case of non-saturated absorption of a salt solution also the ion profiles are related by \sqrt{t} scaling. The resulting profiles after such scaling, both for moisture and Na, are given in figure 5. Indeed all profiles for Na collapse on a single master curve. This indicates that the ion transport can be described by a nonlinear diffusion equation during the initial absorption and, moreover, that the binding process is equal throughout the sample. These scaled profiles clearly show that almost no Na is transported directly with the wetting front.

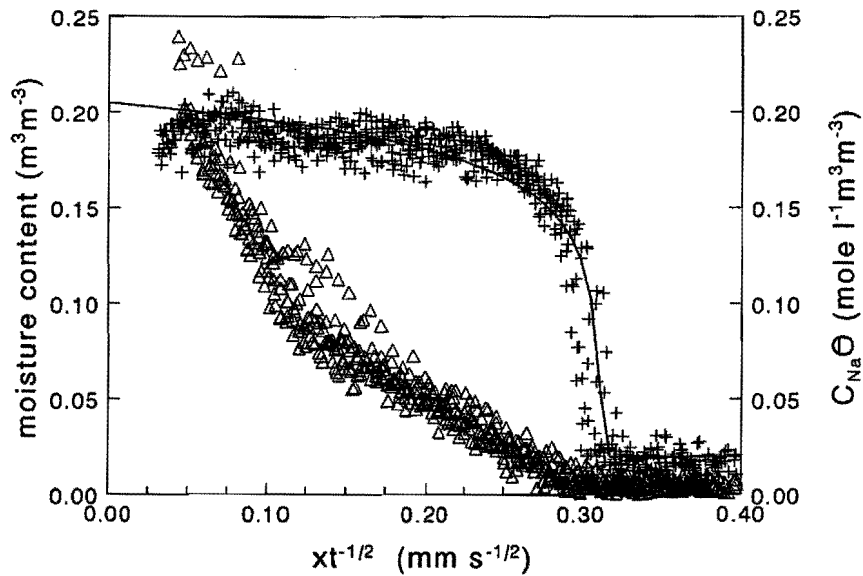


Figure 5: Boltzmann-Matano transformation of the measured moisture (+) and Na profiles (Δ). The full curve represents the Boltzmann-Matano transformation of simulated moisture profiles based on an exponential relation between D and θ : $D(\theta)=D_0 \exp(\beta\theta)$.

5. Conclusion and discussion

The water and ion transport during absorption of a 4 M NaCl solution in calcium-silicate brick was measured and has been shown to be described by nonlinear diffusion equations. The present experiments clearly indicate that the Na ions are not transported directly with the water, due to the binding of Na ions to the pore surface. This effect has also been reported for Cl during saline absorption in concrete (see, e.g., [14]). The direct cause of this binding has not yet been investigated for calcium silicate brick.

Some preliminary simulations were made of the binding effect on the Na transport. Fig. 6 shows the moisture and the Na-profiles that were simulated using the experimentally determined equilibrium Freundlich isotherm (see Fig. 4). It is obvious that in this simulation a sharp Na front is formed, which is clearly not in agreement with the experimental results (see Fig. 5). Therefore a simulation was also performed in which a relaxation time of 1 hour was added to the equilibrium Freundlich isotherm, i.e.,

$$c_{\text{bound}} = K c_{\text{free}}^m (1 - e^{-t/3600}) \quad (8)$$

The result is also plotted in Fig. 6. As can be seen, the simulations using this non-equilibrium isotherm correspond much better with the experimental results. However, the simulation does not reproduce the experimental profile for Na near the wetting front. Nevertheless, the results suggest that also a non-equilibrium Freundlich isotherm has to be determined in order to describe the absorption of Na correctly.

Although almost no Na ions are measured at the wetting front the presence of the ions in the solution decreases the absorption rate of the moisture. It might well be that salt has a clogging effect of the pores, thereby reducing the permeability and so decreasing the absorption, as was also suggested by Nilson and Tang [6]. However, more experimental evidence is needed to clarify this point.

The present study was limited to Na, since in the present NMR setup the sensitivity for Cl is too low. A simultaneous measurement of Na and Cl would give more information on the binding mechanisms and the interaction with the pore surface. This will therefore be the subject of a future study in a new 4.7T NMR scanner, where we intend to measure quasi-simultaneously the moisture, Na, and Cl profiles.

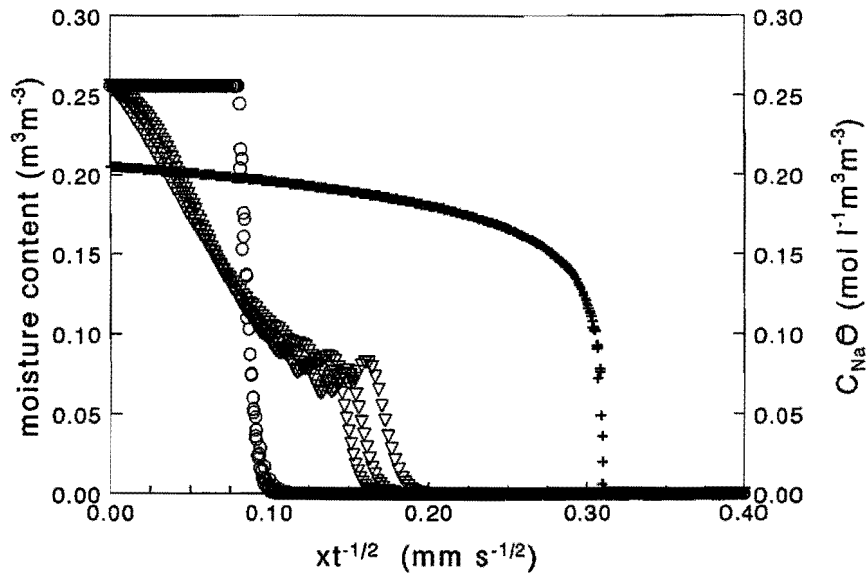


Figure 6: Boltzmann-Matano transformation of the simulated moisture (+) and Na profiles (o) using the equilibrium Freundlich isotherm (see Fig. 4) and the simulated Na profiles (∇) with an additional relaxation time of 1 hour (see Eq. 8).

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