Combined wicking and drying of a NaCl solution in porous building materials

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Abstract. Salt weathering is a major cause of destruction of many valuable monuments. The salt damage of historical porous materials is mainly due to the crystallization of soluble salts due to drying. A special situation which occurs often in marine environments, the case where there is a permanent supply of sea water at one side of a material, whereas the other side is exposed to continuous drying in the open air. A well-known example is the historic city of Venice. Evaporation from the air exposed side provides a continuous moisture sink which is compensated by capillary suction, i.e., wicking of the sea water. As a result there will be a continuous flux of NaCl ions towards the surface. As soon as the concentration at the surface reaches the maximum solubility, crystallization will start which can give rise the damage. A simple analytic model was developed to describe this process. In order to verify this model non-destructive measurements were made of the moisture and ion transport during an experiment with limestone. In order to do so, we make use of a specially designed Nuclear Magnetic Resonance setup where we are able to measure quasi-simultaneously the ¹H and ²³Na content. Hence this method gives us the possibility for real-time monitoring of transport processes of the ions during experiments. It is seen that the concentration rise at the drying surface can be described by a simple analytic model.

1. Introduction

One of the main degradation mechanisms of porous building materials is salts crystallization. Dissolved ions can be advected along with moisture penetration into a porous material. The salt ions can accumulate and crystallizes in the pores and can as a result produce cracks, due to the build-up of the crystallization pressure. To get a better insight into the salt transport mechanism we looked at a special case, i.e., when a porous material is in contact with salt solution on one side and at the same time is exposed to drying conditions at the opposite side. This situation is often encountered in civil engineering constructions in marine environment, where typically a part of the construction in the (sea)water, as is also often seen in the historic city of Venice. As a result there will be a continuous flux of ions through the material towards the drying surface where it can give crystallization damage, both visual and mechanical. This continuous transport of a salt solution, combined with drying, is often referred to as wick action (see also Fig 1). Whereas this wicking can be identified quite simple in a marine environment, one should also think

of monuments in contact with natural groundwater. Ground water contains dissolved salts coming from natural sources such as dissolution of salt in soil, rock, and organic material, or human activities such as agricultural chemicals etc. Although the salt concentration might be very low, salts can still accumulate over many years or decades at the drying surface and give rise to damage and it is important to get more insight into this process.

Fig. 1. A schematic representation of combined wicking and drying of a masonry wall. The bottom of the wall is absorbing a salt solution, e.g., seawater, whereas at the same time the top of the wall side is drying. As a result there will be a continuous flow of ion towards the drying surface resulting in damage

In this study we have focused on wick action in the stable situation where the drying front stays at the top of the sample, i.e., the surface where the evaporation takes place. Hence the sample stays saturated and in this case we are able to come up with a simple analytic model of the ion transport. In order to limit the time scale of the experiment we have chosen to initially perform the experiments on a rather porous limestone. We have used Nuclear Magnetic Resonance (NMR) to measure both moisture and ion profiles non-destructively and quasi-simultaneously during wick action experiments. These experimental results have been compared to an analytic solution of the advection-diffusion equation describing the ion transport.

2. Theory

During wick action salt ions will move by two transport mechanisms, i.e., advection and diffusion. Advection is the process of ions moving along with the moisture flow. Hence this process will be determined by the drying conditions at the surface. Diffusion is dependent on the concentration gradient, i.e., diffusion tries to level off any concentration gradient. As a result the net ion flux through the material will be a competition of these two processes. As long as the sample stays saturated during the combined wicking and drying action, as we will assume in this study, the ion salt transport can be described by a combined advection-diffusion equation as given by (see, e.g., [[1-3]]):

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D_{\text{eff}} \frac{\partial c}{\partial x} - uC \right) \quad (1)$$

where C is the ion concentration, D_{eff} the effective macroscopic diffusivity of the ions within the porous material and u the macroscopic velocity of the liquid in the porous material, i.e., the Darcy speed. The macroscopic diffusivity of the ions within a porous material is related to the microscopic diffusivity of the ions through the pores by the

tortuosity. This equation will be valid as long as there is no crystallization taking place else a sink term has to be added to the right-hand side of this equation.

Therefore the right hand side is describing the total ion flux, consisting of the well-known diffusion, whereas the second part describes the advection of the ions along with the liquid flow. The competition of these two transport mechanisms can be characterized with a dimensionless number, i.e., the Peclet number. In this case, based on Eq 1. it can be defined as:

$$P_e = \frac{uL}{D_{eff}} \quad (2)$$

where L is a so-called characteristic length scale which, i.e., in this case it can be chosen as the length of the sample. In the case $Pe > 1$, advection will be dominant and there will be a built up of concentration peak. Whereas in the case of $Pe < 1$, diffusion is dominant and we expect a homogenous distribution of salt. This Pe-number was also found to be very useful in order to give an indication of the effect of poulticing, see e.g., [4]. In the case of drying as studied here, the boundary condition for ions at the drying surface is given by a no flux boundary, i.e., $q=0$, and hence i.e.;

$$D_{eff} \frac{\partial C}{\partial x} + uC = 0 \quad (3)$$

Whereas, the flux boundary condition at the wicking surface, where the salt solution is absorbed is given by:

$$q_{surface} = uC_0 \quad (4)$$

where C_0 is the concentration of the salt solution being absorbed at the wicking surface. As we have in our experiment a constant boundary condition, we can assume that in first order the liquid flow is constant, i.e., $u = \text{constant}$. As also the concentration of the absorbed salt solution is constant, i.e., $C = C_0$, we can in this case solve the differential equation giving the concentration $c(x,t)$ as a function of time and position, i.e. [6];

$$C(x, t) = a(t)e^{-\frac{D_{eff}}{u}x} + C_0 \quad (5)$$

Where $a(t)$ is a constant which is a function time. Hence this solution tells us that the concentration in the sample can be described by a simple exponential decay. In addition it indicates that characteristic width of the salt concentration peak, given by $4D_{eff}/u$ and hence is determined by the ratio of the liquid velocity and diffusivity.

3. Materials and methods

In order to reduce the time scale of the experiment in this study we have chosen biomictic lime stone from Sardinia. It has a porosity of 0.34 (m^3/m^3), a pore size with the maximum distribution of around 1.6 μm and has only very minor magnetic impurities. For the experiments we used cylindrical samples with a diameter of 20 mm and length of 100 mm, which were drilled out of a larger block. After rinsing the sample in clean water, the sample was dried at 40°C until constant weight. The experiments were started with samples, which were vacuum saturated with distilled water. In order to perform 1D experiment the specimens were isolated on the sides with an epoxy coating. The experimental setup is given in Fig. 2. The sample holder is a Teflon cylinder with a reservoir at the bottom and air flow inlet and outlet at the top to provide drying at the top of the sample. The bottom of the sample is in contact with a 1m (mole/kg) NaCl solution. In order to maintain a constant

level the pump is controlled by using an electrical sensor (max fluctuations in the order of 3 mm). To induce drying, the top of the sample is exposed to a constant air flow of 10 L/min at approximately 0% relative humidity. A plastic evaporation shield has been added as to separate the drying and absorption part, i.e., to limit the influence of the drying on the bath concentration.

Fig. 2. A schematic representation of the setup for measuring the combined wicking and evaporation using NMR. With an electronic level control and a pump the reservoir level is kept constant.

Both the moisture and Na-content are measured using Nuclear Magnetic Resonance (NMR) [5]. Using NMR we are able to non-destructive and quantitatively measure the moisture and Na-content at a fixed position, with a 1D-resolution in the order of 2 mm for hydrogen and 6 mm for Na. Hence every point represents an average over 2 to 6 mm. A stepper motor was used to move the sample holder vertically inside the NMR as to be able to measure the moisture and Na profiles over the complete sample. Measuring both a moisture and Na-profile takes in the order of 3 hours. The total experiment lasted up to 40 days.

4. Experimental results

The results of the combined wicking and evaporation experiment are given in fig 3. Although the NaCl concentration profiles were measured every 3 hours, here we have given the profiles every 5 days for the first 40 days of the experiment, reflecting the slow process. As can be seen from these NaCl profiles the concentration near the surface slowly increases, whereas the concentration of the back remains constant at 1 m (mole/kg),

reflecting the constant concentration of the inflow and of the reservoir. On the other hand we do not see the concentration rising to the saturation concentration of 6.1 m as expected for NaCl. Indeed if we inspect the profiles closer, the NaCl concentration rises from almost 0 at the position 4 mm outside of the sample, i.e., in the air, to maximum 4 m at the position 4 mm inside the sample. This gradual increase near the surface is due to 1D-resolution of the NMR, which is averaging each measurement point over 6 mm as explained previously. Hence the 1D resolution is smoothening the real concentration profile within the sample, and the maximum concentration reached within the sample, i.e., the top, will be higher. In order to correct for this problem, we have fitted the model as derived (see Eq. 5) to each individual profile. The results are also given in figure 3. As can be seen each profile can be approximated well by an exponential decay function. We can also see that the interpolation with $x=0$ indicates that the maximum salt concentration of 6 m is reached after 40 days, which could also be seen from crystals forming at the top of the sample.

Fig. 3. The measured Na-concentration profiles as determined by NMR during wick action of a sample of 100 mm in length. Dry air is blown over the top of the sample at $x=0$, whereas a reservoir of 1m NaCl is supplied at $x=100$ mm. The profiles are given for every 5 days for a total time of 40 days.

5. Conclusions

Wick action in combination with evaporation at the top of a sample can be described by an analytic model, which only takes into account the liquid speed and the diffusivity. The measured concentration profiles match well with a simplified model and hence can give us more insight into the time scales and profiles seen in practice. NMR has been shown to be an effective method to measure the concentration profiles during wick action over a long time and non-destructively.

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