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# Influence of concentration change of calcium ions over time on their diffusion through sandstone

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**Abstract.** Diffusion is one of the most important salt transport mechanisms. The knowledge of the rate of transport of ions in the pore system of building materials is thus of primary importance for their service life prediction. In this paper, the transport of  $\text{Ca}^{2+}$  in sandstone Mšené was studied as a model system; two types of experiment were performed: a) without addition of  $\text{Ca}^{2+}$  ions for the achievement of original initial concentration and b) continuous addition of  $\text{Ca}^{2+}$  ions. The experiment was performed under laboratory conditions in a two-side plexiglass box at the ambient temperature of  $(20\pm 2)$  °C for a period of 426 hours. Calcium concentrations were analyzed chelatometrically.

## 1. Introduction

Calcium ions are able to destruct concrete and other building materials. The chemical reactions involved can form complex salts. It is therefore interesting to study the transport of calcium ions ( $\text{Ca}^{2+}$ ) in porous building materials. The transport is most often realized by diffusion that is driven by a concentration gradient of migrating particles. They diffuse through a bulk mobile phase stagnating in pores, so that there is practically no interaction between the particles and the inner walls of the pores. However, particles may be adsorbed on these walls and diffuse on the surface while staying adsorbed. This particle migration in the adsorbed state is called surface diffusion. Surface diffusivity depends both on the diffusing particles and on the substrate and it is more complicated to determine it than the standard (bulk) diffusivity [1]. Diffusion has been mostly studied in gas-solid systems, while liquid-solid systems have been less frequent.

However, both diffusion modes are influenced by many factors as temperature, humidity, biological agents, concentration of diffused ions and their mutual interactions [2-3]. For this reason, there is necessary to study these effects in simple experiments for a better understanding of the intensity of individual factors on diffusion rate. Setting the laboratory conditions under which the experiment is conducted is also important.

In this paper we present a pilot study of through-diffusion experiments of calcium ions ( $\text{Ca}^{2+}$ ) in aquatic solutions for sandstone under different laboratory conditions. We compare the effects of original calcium concentration and equilibrium concentration during the experiment on diffusion effectivity of calcium ions.



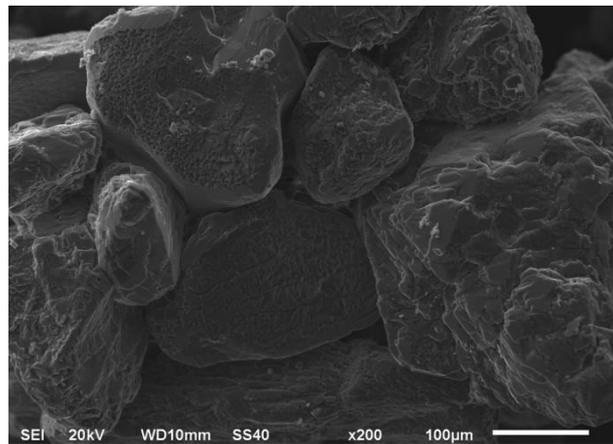
## 2. Studied materials

Sandstone from Mšené, Czech Republic, was used as a model sample. It is siliceous rock, containing 99% of quartz and traces of kaolinite. Fundamental parameters of the rock are shown in Table 1. The sample is unimodal and its pore system is formed by voids between individual clasts. The mean pore diameter is 37  $\mu\text{m}$ . The nature of sample is well observable by SEM (Figure 1).

$\text{CaCl}_2$  (99% purity) from Lach-Ner Ltd. was used in the experiment. Powdered  $\text{CaCl}_2$  was dissolved in distilled water. The concentration ( $C_0$ ) was chosen on the base of preliminary experiment as 4 g  $\text{l}^{-1}$ .

**Table 1.** Basic properties of the studied sandstone.

Quantity	Value
Porosity	28.2 %
Pore volume	0.1393 $\text{cm}^3 \text{g}^{-1}$
Specific surface area	0.44 $\text{m}^2 \text{g}^{-1}$
Compressive strength	8.7 MPa



**Figure 1.** SEM image of Mšené sandstone.

## 3. Experimental setup

Two boxes made of plexiglass were used in the experiment (Figure 2). The following description is the same for both the boxes. Initially dry sandstone samples of disk shape ( $d = 5 \text{ cm}$ ,  $h = 1 \text{ cm}$ ) were sealed with silicone in a circular aperture cut in the plexiglass panel splitting the box into two chambers. One of the chambers (chamber 1) was filled with 500 ml of distilled water, while the other one (chamber 2) was filled with calcium solution of a desired concentration. The box was closed by a plexiglass lid. The box was placed on a table at ambient temperature ( $20 \pm 2$ )  $^{\circ}\text{C}$  for a period of 426 hours.

Calcium concentrations in distilled water, as well as the residual concentrations were measured in both boxes. The initial concentration (4  $\text{g.l}^{-1}$ ) was decreased during the time. However, the calcium chloride solution was continuously adjusted to its initial concentration (4  $\text{g.l}^{-1}$ ) in only one of the model boxes at each measurement (the experiment b). In the second box (the experiment a) the calcium chloride concentration was allowed to decrease during the whole time of experiment. The calcium concentrations in chamber 1 and chamber 2 were then compared for the entire experimental time.

#### 4. Chelatometrical measurement of calcium concentration

Chelatometrical measurement of calcium concentration was done according to [4]. A 0.05 M solution of chelaton III was used to measure the calcium amount. Namely, 500  $\mu\text{l}$  of a 5 M solution of KOH was added to a specific amount of the monitored sample from chamber 1 or 2 and colored by murexid red indicator [5]. Then chelaton III was dropping to the sample using an automatic byrette. When the titration was finished, the solution had violet color. The amount of titration reagent was used for the calculation of the calcium concentration according to equation 1:

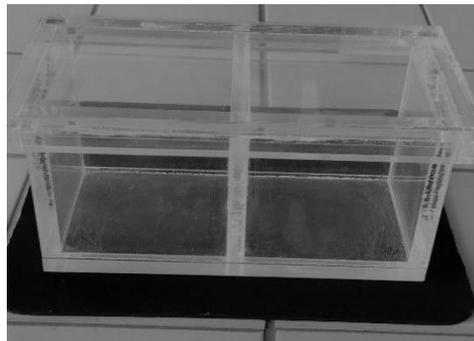
$$c = \frac{V_{ch}M_{ch}M_{Ca}}{V_{sam}}, \quad (1)$$

where  $c$  is the calcium concentration ( $\text{mg}\cdot\text{l}^{-1}$ ),  $V_{ch}$  is the volume of used chelaton (ml),  $M_{ch} = 0.05$  is its molarity,  $M_{Ca} = 40 \text{ g}\cdot\text{mol}^{-1}$  is the calcium molar mass, and  $V_{sam}$  is the volume of analyzed aquatic sample (ml).

The number of moles of calcium was calculated according to equation 2:

$$n = \frac{cV}{M_{Ca}}, \quad (2)$$

where  $V$  is the volume of chamber 1 or 2 (0.5 l).

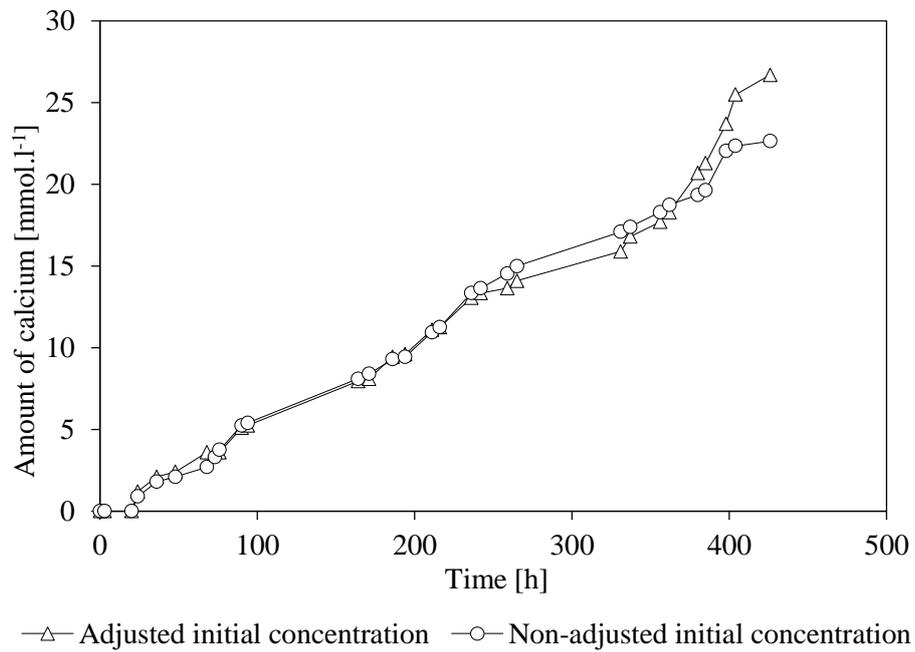


**Figure 2.** The plexiglass box (2 pieces) used in the experiment.

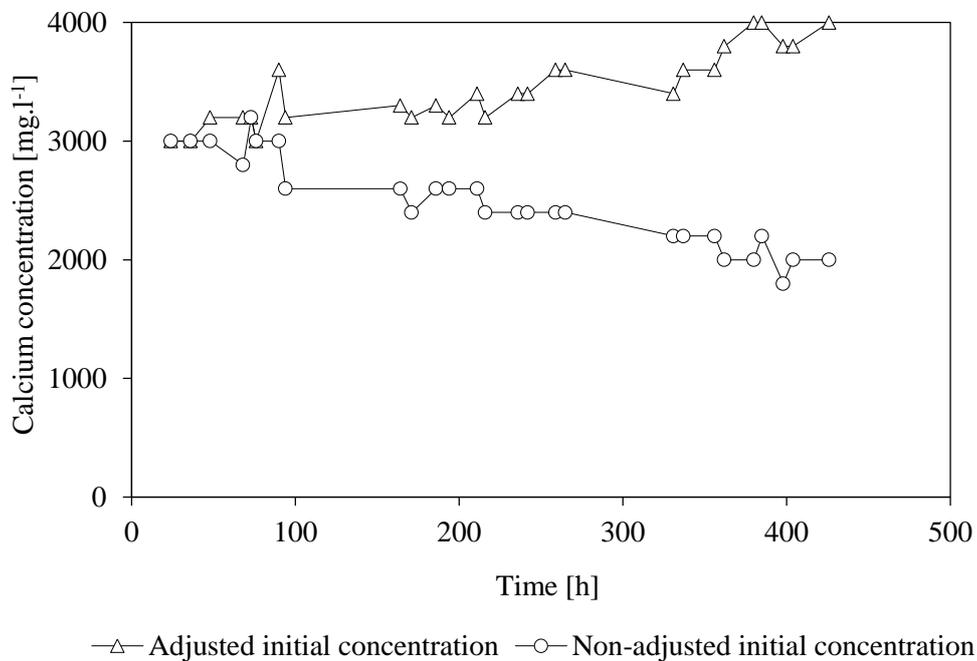
#### 5. Results and discussion

The results of the measurement of cumulative calcium concentration in chambers 1 and 2 as a function of time are plotted in Figures 3 and 4, respectively. Diffusion started in both boxes after 20 hours. It is evident, that calcium diffused similarly in both boxes at the start of the experiment. The diffusion was observed during the whole time of the experiment. In the experiment b), after first measurement calcium was added into one box for increasing the actual calcium concentration up to the initial concentration  $C_0$  ( $4 \text{ g}\cdot\text{l}^{-1}$ ). This process was repeated at each measurement when it was necessary. The measurements indicated that diffusion of calcium was again very similar in both boxes with exception to the last measurement (Figure 3). In the experiment a) the initial concentration was decreasing during the time to one half, compared to the original value, at the end of the experiment (Figure 4). These changes did not though have any effect on diffusion.

We can assume that the concentration available for the accumulation processes and the number of filled binding sites was not a principal factor affecting the diffusion rate. Unfortunately, we cannot compare our results with data from any other studies because they are not available.



**Figure 3.** Cumulative calcium concentration in chamber 1 as a function of time.



**Figure 4.** Actual calcium concentration measured in chamber 2 as a function of time.

## 6. Conclusions

In this paper, through diffusion of calcium in sandstone was studied in two experimental setups (adjusted and non-adjusted initial concentration during the experiment). The amount of calcium ions diffused into distilled water was similar for both model boxes for the whole time of the experiment. Therefore, besides diffusion as the main driving force of ion transport also other processes (e.g. capacity of calcium accumulation in the sample and gradual release of calcium ions from sandstone) had a significant influence on the amount of diffused ions.

## Acknowledgement

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