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The Formation of Meta-Stable Sodium Sulphate Heptahydrate During Drying as Studied by NMR

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Abstract

Salt weathering is a major cause of deterioration of porous building materials. Of the salts responsible, especially sodium sulfate is seen as very damaging. However many questions arise concerning which sodium sulfate phase will crystallize out during salt weathering. In this study we focused on the crystallization during isothermal drying of a sample saturated with a sodium sulfate solution. As the material is drying moisture will leave and hence the salt concentration will rise until the maximum solubility is reached. From that point on crystals will be formed. Using NMR we have measured quasi simultaneously both the moisture and Na profiles during drying. These experiments have been performed at various temperatures and concentrations. In our NMR experiments we observe the formation of a metastable phase of sodium sulfate, the heptahydrate crystals.

Keywords

Crystallisation, drying, porous media, sodium sulphate heptahydrate, NMR

1. Introduction

The sodium sulfate phase diagram is shown in Fig.1. There are three crystalline phases known for sodium sulfate: the anhydrous phase Na_2SO_4, also called thenardite, and two hydrous phases: Mirabilite, $Na_2SO_4*10H_2O$, also called decahydrate and heptahydrate, $Na_2SO_4*7H_2O$, which is a metastable phase.

During crystallization a pressure is built up in the pores, causing damage of material. The magnitude of this pressure is strongly dependent on crystal properties and morphology. From this point of view is very important which type of sodium sulfate crystal phase is formed.

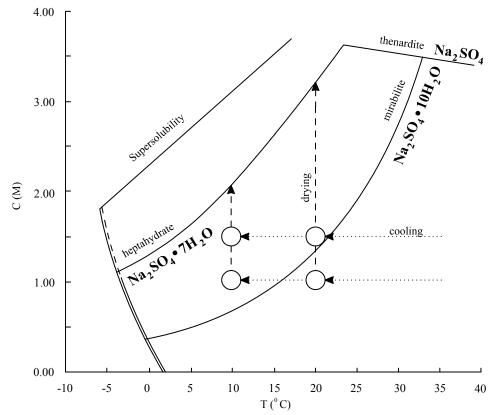

Fig. 1: The sodium sulfate phase diagram. The performed drying experiments are indicated. First, the system is cooled down from 35°C till a certain temperature. Then drying is started and ion and moisture profiles are measured by NMR.

By Rijniers [1] heptahydrate formation during cooling inside of isolated brick was observed and shown that the crystallization pressure of heptahydrate is considerably smaller then the decahydrate one. But in literature on salt damage the heptahydrate phase is neglected in the damaging mechanisms.

We have focused on the crystallization during isothermal drying of a sample saturated with a sodium sulfate solution to find out which type of sodium sulfate crystals is formed in drying.

2. Methods and Materials

For our experiments the NMR of magnetic field 0.78 T is used. The sample, a small cylinder with a length of 40 mm and diameter of 20 mm, is placed in a teflon holder of which the upper side is open (teflon hardly contains any hydrogen). A dry air with of RH 5 % and temperature 20°C is blown over the sample with airflow of approx 0.5 m/s, thus creating a one-dimensional drying experiment.

A coil, which forms part of a tuned LC circuit, is placed around the sample for creating and receiving the radio frequency fields. For sodium it is 8.1 MHz and echo time is 340 μs. The defined magnetic field gradient, generated by the gradient coil, is vertically oriented, giving a resolution of 2 mm. After capillary saturation with sodium sulfate solution, sample is sealed and cooled till a certain temperature. Then drying is started and sodium profiles are measured.

3. Results

For the drying measurements we have used fired clay brick with porosity of 25 %, and calcium silicate brick, porosity of 80 %.

The resulting profiles are given in Fig.2. As can be seen as soon as the drying is started there is an accumulation near the surface. This indicates that Peclet number is lager than one for these experiments. The concentration near the surface increases until the maximum concentration for heptahydrate is reached. From this point any additional advection will result in the formation of meta-stable heptahydrate crystals. As can be seen further during the time of these experiments no transformation into mirabilite is observed.

The formation of heptahydrate was also observed for calcium silicate brick. Indeed in 97 % of the 28 drying experiments was observed the formation of heptahydrate.

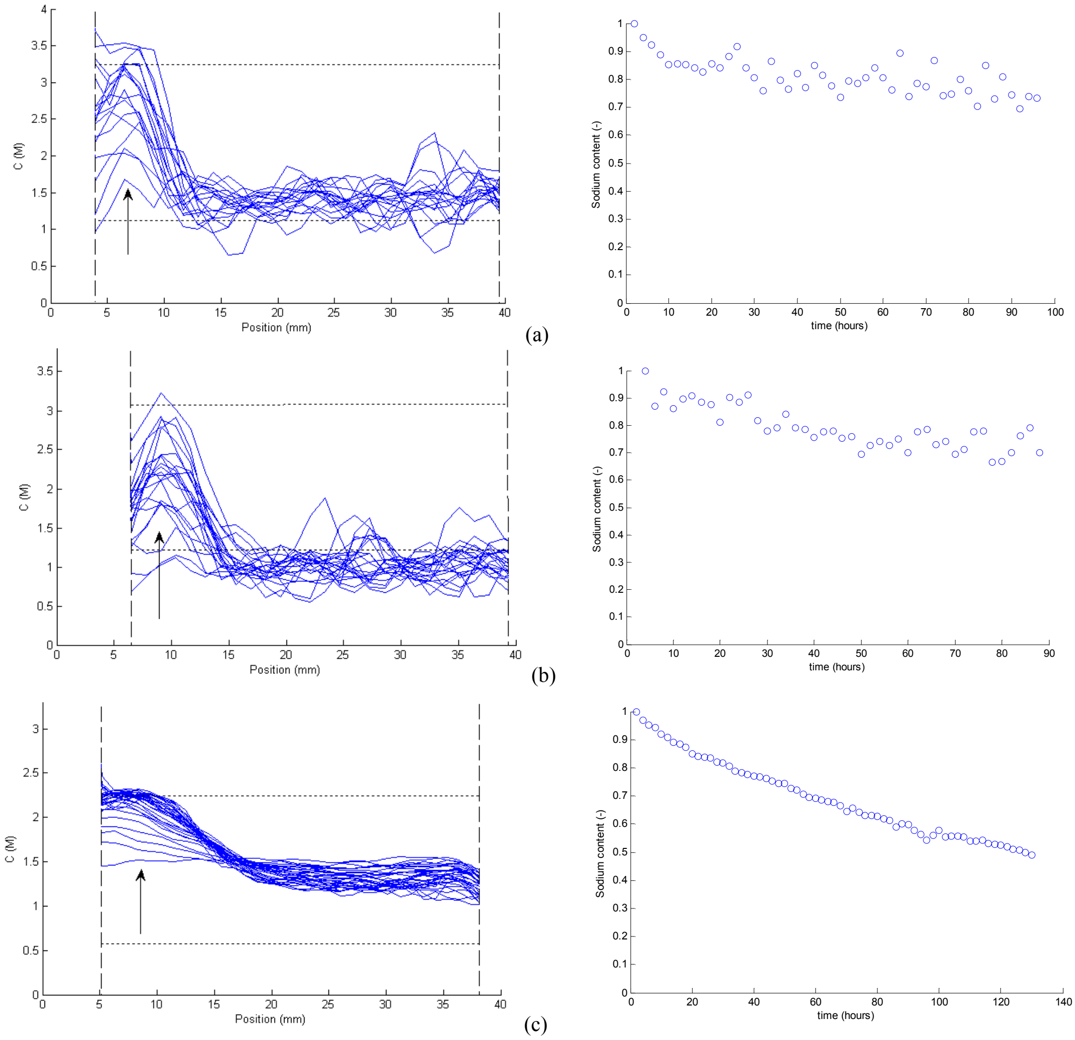

Fig. 2: Drying measurements performed for the fired clay brick, saturated with 1.5 M sodium sulfate solution and drying temperature of 20°C, pictures (a); 1 M and 20°C, pictures (b); and 1.5 M and 10°C, pictures (c). Left pictures indicate concentration of sodium sulfate solution in the sample. Dashed horizontal lines, from down-to-up correspondingly, show Mirabilite and heptahydrate lines in accordance with phase diagram. Time between each profile is 4 hours. Arrow shows evolution of time. Right pictures show the evolution of sodium content in the solution, which brick is saturated with, indicating crystallization processes.

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