

## SALT CRYSTALLIZATION AS DAMAGE MECHANISM IN MASONRY

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### Abstract

Salt crystallization is an important cause of weathering of building materials. It is thought that salt damage is a result of either crystal expansion due to hydration or the existence of crystallization pressure. Such a crystallization pressure should result in an increased solubility of the salt, i.e., a kind of supersaturation should be observable. We have studied the solubility of  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{SO}_4$  in pores and the bulk by using Nuclear Magnetic Resonance (NMR). It was found that sodium carbonate shows supersaturation in pores of 5 nm, indicating that a crystallization pressure of about 10.5 MPa exists. However, for sodium sulphate we do not observe supersaturation, which may be due to the fact that in all our experiments a meta stable phase is formed.

### Key Words

Salt, Crystallization, Supersaturation, NMR

### 1 Introduction

It is widely accepted that salts contribute to the deterioration of building materials. The process of salt weathering is not fully understood and more substantial knowledge is essential to avoid or repair damage of contemporary buildings and for improvement of preservation techniques for cultural heritage.

An example of typical salt damage is given in figure 1. In the left figure a typical example of efflorescence onto a masonry wall is shown. In this example at some places in the wall a surface layer was chipped off by the salt crystallization. In the right figure a laboratory experiment is shown also illustrating the chipping off. Similar examples can be found at many sites all over the world. In this paper we study the solubility of salts in porous media, which is believed to be closely related to the stress generated by the crystallization process.

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*Figure 1: Examples of crystallization damage to masonry. Left: a typical efflorescence in a masonry wall. Right: an example of chipping of a surface layer from a brick.*

## 2 Solubility, crystallization and stress

Two mechanisms for deterioration by salts have been proposed. The first is based on the assumption that expansion and shrinkage during hydration and dehydration processes, are responsible for the damage. The other is based on a model in which the crystallization pressure causes the damage. In this paper we focus on the latter approach, which will be discussed below in more detail.

In a pore a crystal can only adopt a size comparable to the pore size. When it is assumed that the pore has a cylindrical shape with radius  $r_p$  (see figure 2) the crystal adopts this radius and therefore has a certain curvature. Due to its own surface tension and this curvature an excess pressure develops in the crystal. This pressure is transmitted to the pore wall. As a consequence damage may be induced by crystallization. This excess pressure is given by (Scherer, 1999) and (Flatt, 2002),

$$P_c = \frac{-2 \gamma \cos \theta}{r_p} \quad (1)$$

in which  $\theta$  is the contact angle of the crystal with the pore. By thermodynamics this pressure can be related to the solubility of the salt, and hence (Scherer, 1999)

$$P_c = \frac{nRT}{v_c} \ln \left( \frac{C}{C_0} \right) \quad (2)$$

where  $C$  is the saturation concentration in the pore and  $C_0$  the saturation concentration in bulk solution,  $v_c$  is the molar volume of the salt,  $\gamma$  the surface tension,  $n$  the number of ions in the salt (3 for  $\text{Na}_2\text{SO}_4$  and 2 for  $\text{NaCl}$ ),  $R$  the molar gas constant and  $T$  the temperature in Kelvin. Given that  $\theta > 90^\circ$  equation 2 implies that the equilibrium solubility of a crystal in a pore is higher than the equilibrium solubility of a crystal in the bulk. This phenomenon is called supersaturation (Scherer 1999). We like to note that the term supersaturation is somewhat confusing, since usually this term is used for non equilibrium solutions when the solution concentration exceeds the saturation

concentration due to nucleation problems. In this case, however, it is used for the equilibrium situation.

There are two ways to induce supersaturation. The first is by drying: water evaporates and therefore the concentration of the salt increases (Pel et al. 2002). The second is by changing the temperature. The last way requires that there is a significant variation in the solubility with temperature. In this work we use temperature changes to induce supersaturation.

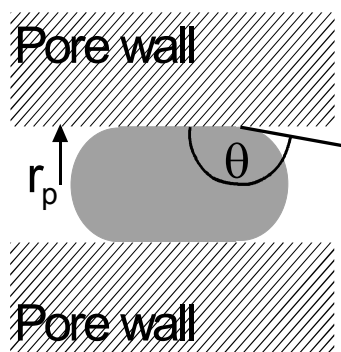


Figure 2 A crystal in a pore.

### 3 Materials and Methods

Considering the fact that the supersaturation will show up in the solubility, one actually wants to measure the solubility inside the pores without disturbing it. Measurement of the solubility of a salt solution inside a porous material is not far from trivial, especially when the solubility exceeds the bulk solubility. We have used Nuclear Magnetic Resonance (NMR) to measure the salt concentration inside the pores. To our knowledge we are the first to present solubility measurements inside porous materials using this technique.

With NMR nuclei can be probed selectively at a resonance condition  $f = \gamma B$ , where  $f$  is the resonance frequency,  $B$  the applied magnetic field and  $\gamma$  the gyromagnetic ratio (42.5 MHz/T and 11.25 MHz/T for hydrogen and sodium, respectively). The NMR scanner is home built (Kopinga et al. 1994), based on an iron cored electromagnet generating a 0.8 T magnetic field. It is equipped with a resonant circuit, to transmit the radio frequency used to excite the nuclei and to receive the NMR signal from those nuclei, incorporating a Faraday shield for quantitative measurements. The time decay of the NMR signal (relaxation) gives additional information. All measurements presented in this paper were done with settings such that only ions and water in solution were measured. Ions in the crystals and water in crystal water cannot be detected.

Table 1 Overview of the damaging salts (Weber 1985)

Na <sub>2</sub> SO <sub>4</sub>	NaCl
CaSO <sub>4</sub>	CaCl <sub>2</sub>
MgSO <sub>4</sub>	
3 CaO Al <sub>2</sub> O <sub>3</sub> 3CaSO <sub>4</sub> 32 H <sub>2</sub> O	
Mg(NO <sub>3</sub> ) <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>
Ca(NO <sub>3</sub> ) <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>
5 Ca(NO <sub>3</sub> ) <sub>2</sub> 4NH <sub>4</sub> NO <sub>3</sub> 10 H <sub>2</sub> O	Ca <sub>2</sub> CO <sub>3</sub>

It is useful to know which salts are responsible for the damages observed, and which of those can be used in the NMR experiments. A list with the most damaging salts can be found in (Weber 1985) and is shown in table 1. Since our scanner measures Na, only Na containing salts can be studied. Because we want to create supersaturation by temperature changes in the range 0 - 40°C we have chosen to study sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) and sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>). NaCl is not used in the experiments because in the temperature range 0 - 40°C the solubility varies only slightly.

To obtain an unambiguous value for the concentration  $C$  in the pores (Eq. 2) we want to use a porous material with one known dominant pore size and measure the solubility inside. A model porous material (Nucleosil) was used because it has pores of a well determined size, instead of a broad pore size distribution as most building materials have. The samples were saturated with a solution, saturated at 40°C, and then cooled to 2°C. After nucleation had occurred the samples were heated slowly, such that equilibrium was always guaranteed.

## 4 Results

Measurements on Na<sub>2</sub>CO<sub>3</sub> were done in the bulk and in Nucleosil samples with 5, 10, and 12 nm pores. The results are presented in figure 3. As can be seen the bulk concentration is in agreement with the known phase diagram (Lide 1998). The solution in the 5 nm pores clearly shows supersaturation, as does the solution in the 10 and 12 nm pores. Using equation 2 and a supersaturation ratio  $C/C_0 = 2.4$  (10°C) deduced from these data, the pressure on the pore wall generated by the crystal in 5 nm pores is estimated to be 10.5 MPa. In the 10 and 12 nm pores this is approximately 7 MPa.

Solubility measurements on Na<sub>2</sub>SO<sub>4</sub> in bulk and in pores of 5, 10, and 30 nm are presented in figure 4. The bulk follows the solubility of the metastable Na<sub>2</sub>SO<sub>4</sub>·7H<sub>2</sub>O crystal. Within our experimental accuracy the solubility inside the pores does not deviate from the bulk behavior. No supersaturation or subsaturation is observed. These measurements suggest that the Na<sub>2</sub>SO<sub>4</sub>·7H<sub>2</sub>O phase of sodium sulfate has a contact angle of about 90° and cannot cause significant stresses in a porous medium.

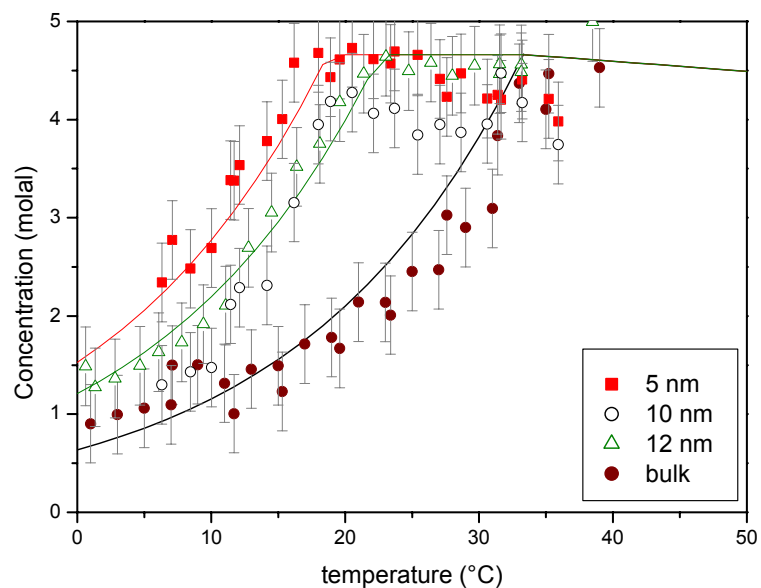


Figure 3: Measured solubility of  $\text{Na}_2\text{CO}_3$  in the bulk and in pores of 5, 10, and 12 nm. The solid line reflects the phase diagram for the bulk reported in the literature.

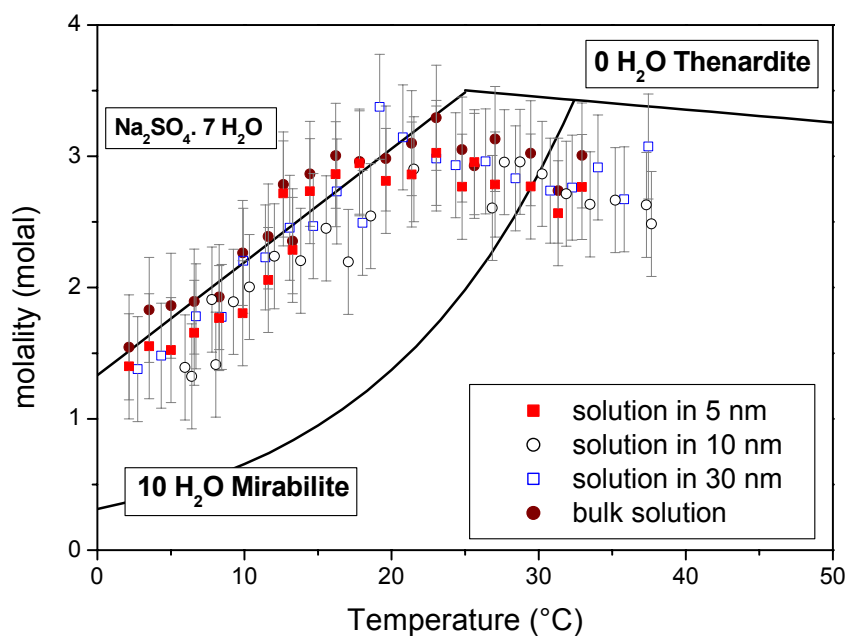


Figure 4 Measured solubility of  $\text{Na}_2\text{SO}_4$  in the bulk and in pores of 5, 10, and 30 nm.

## 5 Conclusions and Outlook

Sodium carbonate clearly shows supersaturation in pores of 5, 10, and 12 nm under equilibrium conditions. The pressure generated by the salt can be estimated as about 10.5 MPa. Sodium sulfate crystallizes in a known metastable phase, of which the solubility is not influenced by the pore size. This suggests that the metastable sodium sulfate phase does not transmit pressure to the pore wall.

Further studies will be done to obtain a more quantitative verification of the theory, i.e.  $\ln(C/C_0)$  should be inversely proportional to the pore size, see equation 1 and 2. Further work will be done with sodium sulfate to grow the stable phase  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  inside the pores and to see whether or not a pressure builds up.

As a subsequent step we will perform similar measurements on masonry and other building materials.

## 6 Acknowledgements

Part of this research was supported by the Dutch Technology Foundation (STW), the Priority Program Materials Research (PPM), and the Center for Building and Systems TNO-TUE. The authors wish to thank Hans Dalderop and Jef Noijen for their experimental help.

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