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EFFECT OF ALKALI FERROCYANIDES ON CRYSTALLISATION OF SODIUM CHLORIDE: PRELIMINARY RESULTS

Ameya Kamat^{1,2*}, Barbara Lubelli¹, and Erik Schlangen²

KEYWORDS

Crystallisation pressure, direct measurement, sodium chloride, sodium ferrocyanide, 3D microscopy

ABSTRACT

Sodium chloride (NaCl) is one of the ubiquitous soluble salts in the environment and is responsible for weathering of building materials. The salt weathering is attributed to the stress developed from crystallisation of these salts in pores of the building materials, with supersaturation as the driving force. In the last years, researchers have successfully mitigated the damage associated with the crystallisation of NaCl by the use of alkali-ferrocyanides (crystallisation inhibitors) in porous building materials. The observed mitigation of the damage has been attributed to lowering of the crystallisation pressure, possibly related to changes in the crystal habit and preferential crystallisation of the salt in the form of efflorescence instead of crypto-florescence. However, the effect of the inhibitor on the development of the so-called crystallisation pressure has not been studied in detail yet. In fact, direct measurement of this pressure is challenging and, until now, only a few experiments have been successful. In this research, an experimental set-up has been developed to directly measure the crystallisation forces of NaCl and the effect of ferrocyanide on these, while visualizing the crystallization process under a microscope. Some preliminary tests using this set-up have been carried out: these consisted in monitoring force evolution from a drop of solution with and without the inhibitor confined between two glass plates.

¹ Faculty of Architecture, Delft University of Technology, Delft, the Netherlands a.a.kamat@tudelft.nl

² Faculty of Civil Engineering and Geosciences, Delft University of Technology, Delft, the Netherlands

1 INTRODUCTION

Sodium chloride is one of the most common soluble salts responsible for weathering of (historic) building materials. Traditional building materials like mortars (plasters and renders) are particularly susceptible to the salt crystallisation induced damage. The damage is often associated with a progressive material loss. Current conservation practices are not completely effective and show limited durability. Moreover, they are scarcely compatible to the existing building fabric. Conservation and repair of the built cultural heritage is a challenging and an expensive task.

An innovative approach to mitigate salt crystallisation damage has been proposed in the last years, which makes use of crystallisation inhibitors [1]. Particularly, sodium ferrocyanide, an inhibitor of NaCl crystallisation, seems to be promising for the mitigation of NaCl-induced decay. Several laboratory studies show its effectiveness in mitigating damage and enhancing salt transport associated with sodium chloride crystallisation in porous building materials [2]–[4]. Recent studies showed an improved resistance to NaCl decay of lime mortar additivated with sodium ferrocyanide [5], [6]. The mitigation mechanism has been often attributed to increased advection of salt ions to the evaporating surface, favouring efflorescence instead of harmful crypto-florescence, and to changes of the crystal habit, from cubic to dendritic pattern. Moreover, SEM observations in the pores reveal formation of smaller crystals with a high nucleation density [7]. A high nucleation density can result in a higher consumption of supersaturation, which could potentially reduce the crystallisation pressure. However, all these hypotheses have not been experimentally validated yet.

Salt weathering is attributed to the development of stresses due to salt crystallisation in the pores of building materials [8]. Progressive damage occurs when the crystallisation stress (pressure) exceeds the tensile strength of building materials. Development of crystallisation stress is driven by supersaturation, meaning the concentration of the dissolved salt ions exceeds the equilibrium saturation threshold. The crystallisation pressure in large pores for NaCl can be approximated with the following equation [9] :

$$P \sim \frac{\nu RT}{V_m} \ln \left(\frac{m}{m_0} \right) \quad (1)$$

Where, R , T and V_m are the universal gas constant, temperature and molar volume of the crystal respectively. ν is the number of ions on full dissociation which for sodium chloride is equal to 2. The supersaturation $\frac{m}{m_0}$ is expressed as a molal ratio of the dissolved salt concentration to their equilibrium concentration. In the past, a few studies have focused on indirect quantification of pressure by measuring supersaturation [3],[4]. Recently, a few studies were successful in directly measuring the crystallisation force using mechanical experimental setups. In one study, crystallisation force was measured from an evaporating drop of NaCl solution confined between two glass plates using a rheometer [12]. In another study, a similar principle was used but the force was measured using two electromagnets [13]. Both the studies provide a direct experimental evidence of crystallisation stress measurement. However, a vast difference is observed in the range of crystallisation pressure

which can be attributed to the contact area measurements. In addition to the force measurements, the crystallisation pressure strongly depends on an accurate determination of the contact area between the growing crystal and the substrate. Estimation of the contact area is challenging owing to an uneven crystal profile [13]. Moreover, since contact area is a dynamic parameter, in-situ area measurement is necessary to increase the reliability of the results.

In this paper, as a first step, the adopted measurement principles from [12], [13] have been used as starting point to develop an experimental setup to measure crystallisation force. Some preliminary results are reported, focusing on sodium chloride solution, with and without the addition of sodium ferrocyanide decahydrate ($\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$) as the inhibitor. A preliminary study to measure the contact area using 3D microscopy is presented. This will be eventually extended to in-situ measurement of the contact area. Finally, suggestions are given for further improvements to the developed setup.

2 MATERIALS AND METHODS

2.1 Experimental setup

The experimental setup is designed to measure the force exerted by a growing crystal confined between two planes. The setup consists of two parts: 1. Assembly of glass plates and 2. The force measurement device. The schematic of the setup is presented in Figure 1.

Glass slides are used as confining planes owing to their smooth surface, transparency and known wetting properties with NaCl solutions. A standard microscope slide (75x25x1 mm) acts as the base plate (test surface) where the salt solution droplet is placed. Two microscope slides with a 1000 ± 5 μm thickness are glued to the base plate to create a gap of 1000 ± 5 μm and support the cover glass. The cover glass (10x10 mm) is positioned on these supports such that the bottom surface of the glass plate touches the top surface of the droplet at the start of the experiment. The cover glass is around 170 μm thick and acts as a low weight rigid plate.

The force measurement device is made of two aluminium beams (150 x 20 mm) with a depth of 80 mm. The bottom beam is fixed. The top beam is supported by a hinge on one side and a variable screw on the other side. The screw allows to change the distance between the two beams. On the underside of the top beam, a low profile force sensor is attached. This is done on the hinged side of the setup so that the distance between the screw and the force sensor is maximized. This ensures a finer control of the vertical movement of the force sensor for each tread rotation of the screw. In this setup, a calibrated high sensitivity piezo-resistive force sensor (Honeywell) with a maximum capacity of 5N has been used. The load actuator of the sensor is composed of a rigid material with a negligible deformation, allowing a reliable force signal. The glass slide assembly including the drop is placed on the lower beam such that the force sensor is exactly above the cover glass of the glass assembly. The force sensor is lowered using the screw until the actuator is in contact with the cover glass. The force sensor is connected to an amplifier, which is in turn connected to a computer. Data is continuously acquired at an interval of 1 sec.

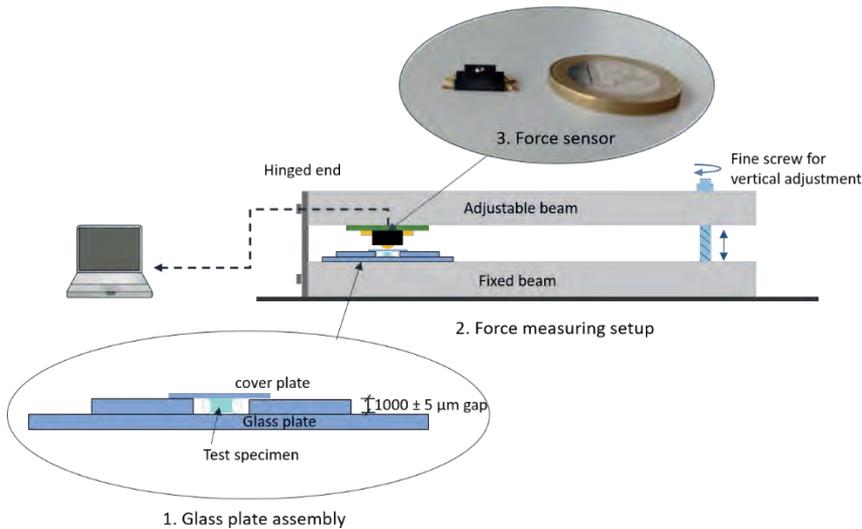


Figure 1: Scheme of the experimental setup. Enlarged view of the glass plate assembly and the force sensor is presented for clarity.

2.2 Specimen preparation

Bulk solution of sodium chloride (NaCl) was prepared using pure analytical grade crystalline sodium chloride and demineralised water. To compare results with the literature [12], [13], a concentration of 5.54 m (0.9 times the saturation concentration at 20°C) was selected. To study the effect of the inhibitor on pressure development, a 3 m NaCl solution was chosen as the control solution. This concentration was selected to ensure complete solubility of the inhibitor in the salt solution. Reagent grade (Sigma Aldrich) sodium ferrocyanide ($\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$) was used as inhibitor. NaCl solution additivated with inhibitor was prepared by first dissolving 0.01 m $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$ in demineralised water. NaCl was then added to this solution such that the concentration of NaCl was 3 m.

2.3 Experimental procedure

The test area (base plate) was first cleaned using demineralised water followed by ethyl alcohol to get rid of impurities. A drop from the respective bulk solutions was placed using a standard Pasteur pipette. The weight of the drop was measured using a 3 decimal precise weighing scale. The volume of the specimen was calculated approximately by considering the solution density reported in literature [14]. The cover glass was cleaned on both surfaces also using demineralised water and ethyl alcohol and carefully placed on the glass supports using precision tweezers. The contact of the specimen with both the plates was visually checked. The glass assembly was then placed inside the force measuring device and the force sensor was lowered using the screw. The force sensor was lowered until a confining force (pre-stressing) of 0.8 g was applied. This ensured a complete contact between the force sensor actuator and the cover plate as well as confinement of the drop between the glass plates. This force is later subtracted from the measured forces. The specimen is exposed to lab conditions where the relative humidity (RH) is maintained always

below the equilibrium humidity of NaCl ensuring (75%) crystallisation conditions. The environment is continuously monitored using a temperature and RH sensor. The total duration of the experiment is around 5 hours.

At the end of the experiment, the crystal habit is observed using 3D-profiling high resolution digital microscope. 3D profile of the crystal is reconstructed from multiple 2D slices automatically acquired at different focal lengths with a vertical pitch of 7.5 μm . This allows to quantify spatial features of the final crystal in all 3 dimensions.

3 RESULTS AND DISCUSSIONS

Four sets of drops were independently tested using the developed experimental setup. Table 1 shows the weight and the calculated volume of the drops.

Specimen	Weight (g)	Assumed density (g/ml)	Calculated volume (μl)
5.54m NaCl	0.043	1.181	36.4
3m NaCl_1	0.037	1.105	33.4
3m NaCl_2	0.032	1.105	28.9
3m NaCl +0.01m In	0.035	1.105	31.7

Table 1: Volume approximation of the specimens.

The force development during crystallization of a nearly saturated salt solution (5.54 m NaCl) is presented in Figure 2. At the start of the experiment, the measured force decreases until it reaches a constant value. This corresponds to the balancing of capillary forces developed between the glass plates due to the liquid-glass interface. The negative sign shows the presence of attractive forces, i.e. the glass plates are pushed closer to each other. Once mechanical equilibrium is reached, the forces remain constant. A peak is observed around 350 minutes, which corresponds to the salt crystal pushing the cover glass. A sharp change in the direction of force is observed indicating repulsive forces relative to the glass plates. The ambient exposure conditions (temperature and relative humidity) remain stable with no anomalies observed. Visual observations show the crystal touching the cover glass. Therefore, it can be reasonably concluded that the sharp peak in the force measurement is due to salt crystallisation. These results are comparable to those reported by Koudelková et al.[13]. The experimental conditions used by Koudelková et al. are also comparable to the experiment used in this study to great extent. Only notable differences are the size of the specimen ($\sim 9\mu\text{l}$) and the gap between the glass plates (500 μm).

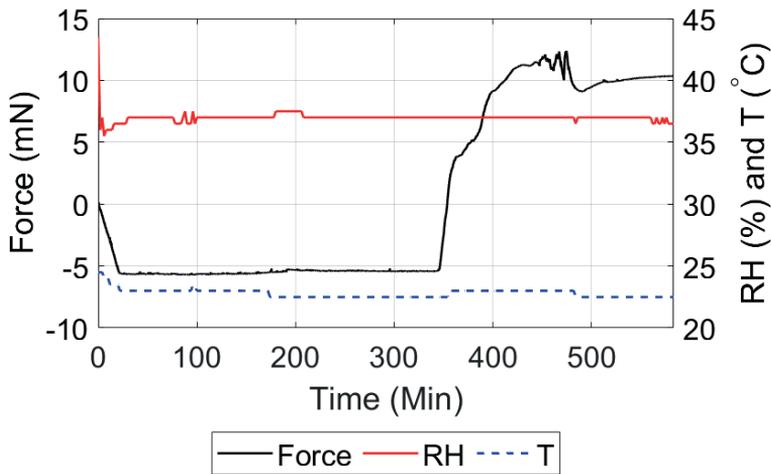


Figure 2: Force measurement from 5.54 m NaCl droplet.

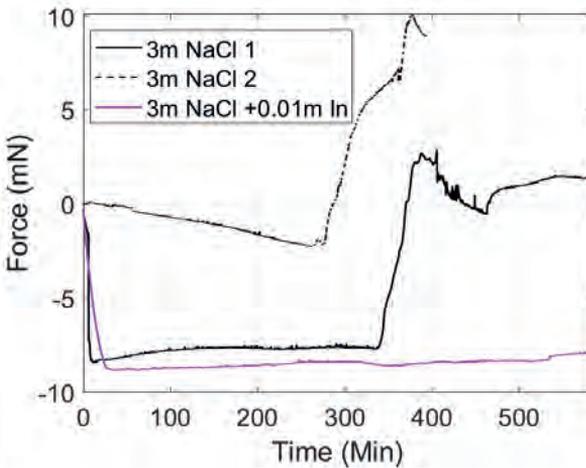


Figure 3: Comparison of force evolution in specimens with and without the inhibitor

A comparison of the force development in salt solution drops with and without the inhibitor is presented in Figure 3. Both 3m NaCl control specimens show a sharp peak, indicating a force imposed on the top glass plate due to crystallisation. Differently, no crystallisation force was measured in the drop containing the inhibitor. In case of the control specimens, microscopic observations at the end of the experiment show that the halite crystals have grown in their cubic equilibrium habit against the glass surface (see Figure 4 (a)). The crystal adheres to the cover plate and the height of the final crystal is greater than the initial gap between the glass plates (Figure 4 (c)). On the contrary, the specimen with the inhibitor exhibits a dendritic efflorescence like pattern (See Figure 4 (b)). The spread of the crystal

growth in the horizontal direction is more dominant than the vertical direction, similar to what reported in [15]. Microscopic observation show that there is limited crystal growth in the vertical direction (around $500\ \mu\text{m}$) (Figure 4 (d)). Salt creeping allows the crystals to escape the confined area in the horizontal direction. The dominant horizontal crystal growth is not able to activate the sensor and as a result, no forces are measured. It can be argued that the initial gap of $1000\ \mu\text{m}$ could be too large for the inhibitor additivated samples to grow in the vertical direction and actuate the sensor. The setup can be thus improved by lowering the gap between the glass plates.

Figure 3 also shows a difference in the results of two control specimens, especially in the initial period of capillary attraction. This could be because of the inaccuracies in replicating the same volume of droplet, as seen in Table 1. However, the total force increase due to crystallisation is around $11\ \text{mN}$ in both the cases. In comparison to that, the increase in force for $5.54\ \text{m NaCl}$ is around $17\ \text{mN}$ (Figure 2). A higher contact angle is obtained for higher concentration of salt solution. This causes a taller drop which is confined by the cover glass. As a result, a higher contact area is available at the start of the experiment for the salts to crystallise against the cover glass and could explain the higher peak force. However, more investigation is required to come to a conclusion.

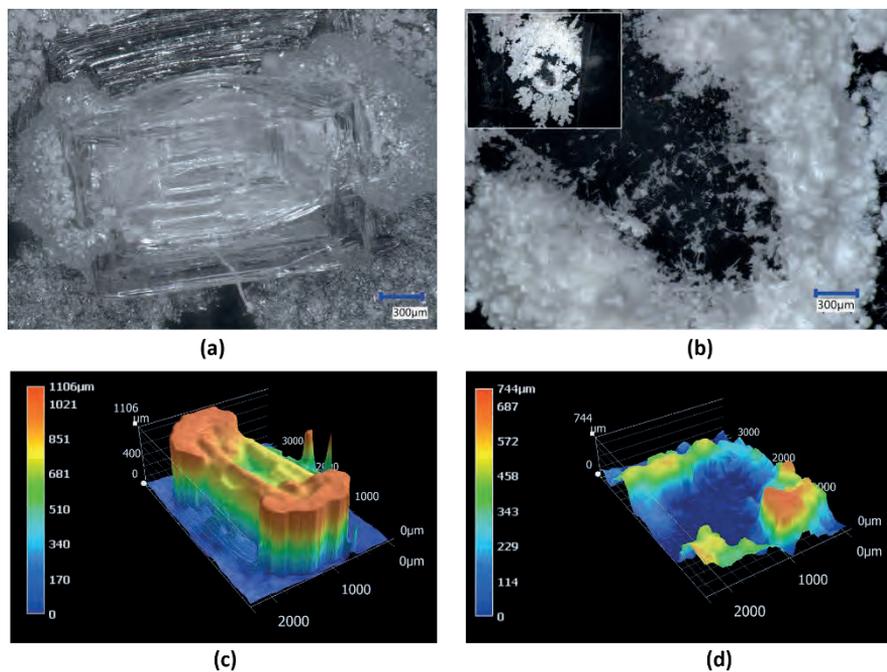


Figure 4: (a) Micrograph of $3\ \text{m NaCl}$ (b) Micrograph of $3\ \text{m NaCl} + 0.01\ \text{m In.}$ Inset: a low magnification micrograph to show the degree of spread (c) 3D reconstruction of $3\ \text{m NaCl}$ (d) 3D reconstruction of $3\ \text{m NaCl} + 0.01\ \text{m In.}$

In order to calculate the crystallisation pressure, the force obtained from Figure 3 has to be divided by their respective contact areas. 3D reconstruction of the crystal volume from stacked 2D images is presented in Figure 4. It can be observed that the crystal surface is not flat but composed of crests and troughs. A higher crystal growth is observed along the outer edges (rim formation) than the interiors as reported by [16]. Thus, the contact area can be difficult to quantify from a 2D micrograph. However, a high resolution 3D reconstruction provides the necessary information over the crystal depth to accurately quantify the contact area. As a next step, the current experimental setup will be integrated with the 3D profiling digital microscope. This will allow visualisation and 3D acquisition of crystal growth in-situ, simultaneously with force evolution. The contact area between the crystal surface and the cover glass at the moment the peak force is reached can then be calculated.

4 CONCLUSIONS AND OUTLOOK

The study provides a proof of concept and a working prototype to measure crystallisation forces from bulk solutions using simple force sensors. The results obtained by the preliminary experiments show forces measured due to initial capillary attraction followed by an instantaneous increase in force at the time of crystallisation. These are comparable to literature findings.

The current setup seems to work well for pure sodium chloride drops, thanks to their cubic crystal habit. In case of drops with the inhibitor, the growth in the horizontal direction dominates the vertical growth due to creeping of salts. As a result, the sensor cannot be actuated to measure crystallisation forces. This suggests that the gap between the two glass plates should be reduced in order to confine the dendritic crystals.

The crystal morphology observed at the end of the experiment clearly exhibits an uneven crystal surface making the contact area calculation challenging from a single 2D micrograph. However, thanks to a high resolution 3D reconstruction from multiple slices acquired at different focal lengths, sufficient information is available to accurately calculate the contact area. As a next step, a 3D profiling digital microscope will be integrated with the current setup to acquire in-situ crystal profile

An additional sensor will be added to monitor the weight of the droplet. In this way, the changes in concentration and supersaturation can be estimated.

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