

# Measurement of salt solution uptake in fired clay brick and identification of solution diffusivity

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## Abstract

Salt solution uptake rates in fired clay brick were measured with  $\gamma$ -ray to investigate the influence of salt on solution diffusivity for appropriate numerical analysis of salt solution transfer and crystallization in porous materials. NaCl and Na<sub>2</sub>SO<sub>4</sub> are the main salts confirmed in Hagia Sophia (Aya Sophia Museum), Istanbul, Turkey, and are used in this experiment. We identified solution diffusivity as a function of solution content by a numerical analysis of solution transfer. The main results are as follows. Solution uptake tests demonstrated that saturated solutions take approximately six times longer to attain a steady state than the time needed for pure water to obtain steady state. This was thought to be caused by the viscosity of the dissolved salts and the presence of crystallised salt in the material. We identified solution diffusivity by multiplying moisture diffusivity for pure water by a constant to reproduce the measured solution content in the cases where large amounts of efflorescence was observed at the material surface. In the case of a saturated solution of Na<sub>2</sub>SO<sub>4</sub>, which is considered the salt that most frequently precipitates into material, it was necessary to correct the solution diffusivity equation by considering the effect of in-pore salt precipitation.

Keywords: Solution diffusivity,  $\gamma$ -ray attenuation, fired clay brick, sodium salts

## 1. Introduction

Salt weathering is one of the main causes of the deterioration of brick masonry walls, which can be found at the Hagia Sophia (Aya Sophia Museum) in Istanbul (see photo 1). There are many sources of salt in the environment, including ground water, atmospheric deposition, and originally contaminated salts in the materials. In Hagia Sophia, atmospheric deposition and originally contaminated salts in the materials are assumed to be the main sources of salt that cause weathering of the structures.<sup>1</sup> In the Hagia Sophia case, there exist complex humid-dry and wet-dry cycles that complicate the deterioration process that comprises adhesion, dissolution, and infiltration processes that transfer salts from the sources in the environment. Therefore, the process is much more complex than when ground water is the main salt source. The objective of this study was to develop an analytical model of the simultaneous transfer of heat, moisture, and salt and the subsequent crystallisation and dissolution of the salt for reproducing the deterioration mechanism caused by these complex salt deterioration processes.

Salt, which exists in the dissolved phase or solid phase (crystal) in porous material, causes significant changes to the material properties of the surface it contacts. This is due to a rise in viscosity of the solution and the descent of vapour pressure of the salt solution and changing pore structure in the solid phase.<sup>2, 3</sup> Therefore, material properties conside-



Photo 1: Deterioration of the inner walls due to salt crystallisation at Hagia Sophia, Istanbul, Turkey

ring these effects of salt are needed to predict the real phenomenon appropriately.

In this research, we investigated the solution diffusivity, which is an important aspect that influences the transfer rate of dissolved salts. We conducted pure water and salt solution uptake tests on fired clay brick material.  $\text{Na}_2\text{SO}_4$  and  $\text{NaCl}$  are the main salts found in the walls of Hagia Sophia, and they were used in this experiment. The spatial distribution of the solution during the experiment was

quantitatively measured by a  $\gamma$ -ray attenuation apparatus. In addition, we characterised solution diffusivity as a function of volumetric solution content by a numerical analysis of the salt solution transfer process. This was done to investigate the effects of dissolved salt and salt crystallisation.

## 2. Methodology

### 2.1. Outline of solution uptake test

A salt solution uptake test of  $\text{NaCl}$  and  $\text{Na}_2\text{SO}_4$  was conducted to investigate the influence of dissolved salts and crystallised salts on solution transfer. Fired clay bricks with dimensions of  $3 \times 4 \times 10$  cm were used. An epoxy resin and aluminium film were applied to the surfaces of the bricks, with the exception of the top and bottom face ( $3 \times 4$  cm), to provide water and vapour proof seals and accomplish one-dimensional solution transfer. Specimen bricks were hung above a pure water/salt solution water bath. The bottom surface was exposed to the bath. The top surface was in contact with room air only. Initially, pure water uptake tests were conducted using specimen bricks in a dry condition. Subsequently, salt solution uptake tests were conducted with the same specimen that had been dried again. This process allowed for a comparison of the uptake of water vs salt solution. Experimental conditions during the experiments, such as the saturation ratio of the solution, the ambient temperature, and the room humidity are shown in *Table 1*.

### 2.2. Measurement set-up of volumetric salt solution content

The time evolution and spatial distribution of the volumetric content of the pure water/salt solution in the material

Number of specimen	Test 13	Test 14	Test 17
Salt	NaCl	Na <sub>2</sub> SO <sub>4</sub>	
Saturation ratio at 20°C	100%	100%	20%
Temperature (°C) Relative humidity (%)	20.5°C, 40–48%	20.5°C, 40–48%	20.5°C, 43–44%

Table 1: Experimental conditions

during the uptake process was experimentally measured using  $\gamma$ -ray attenuation. Volumetric solution content  $\psi_{sol}$  [m<sup>3</sup>/m<sup>3</sup>] was evaluated using  $\gamma$ -ray transmission of the material during the experiment in equation 1:

$$\psi_{sol} = -\frac{1}{\rho_{sol}\mu l} \ln \frac{I}{I_0} \quad (1)$$

where  $\rho_{sol}$  is the density of solution [kg/m<sup>3</sup>],  $\mu$  is the mass attenuation coefficient [cm<sup>2</sup>/g],  $l$  is the thickness of specimen [cm], and  $I_0$  and  $I$  are the intensity of  $\gamma$ -ray radiation of material at dry state and at the time of experiment [cps], respectively.  $\mu$  is the specific value of a radioisotope, and the value of the water of americium is 0.2059. Prior to the experiments, the mass attenuation coefficient,  $\mu$  of the salt solution was identified from the measured values of the  $\gamma$ -ray transmission of an acrylic water container filled with a salt solution. Figures 1 and Figure 2 show the schematic representation of the measurement set-up and the mass attenuation coefficient of the salt solutions, respectively. The identified mass attenuation coefficients of the salt solutions, which depend on salt concentration and the type of salt used, were utilised to calculate the volumetric salt solution content.

### 2.3. Fundamental equations for dissolved salt and moisture transfer

The fundamental equations for dissolved salt and moisture transfer which are

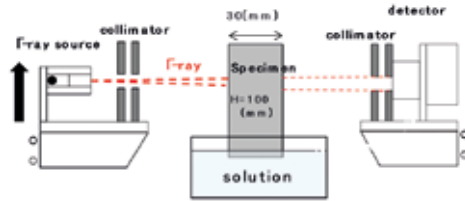


Figure 1: Schematic representation of the measurement set-up

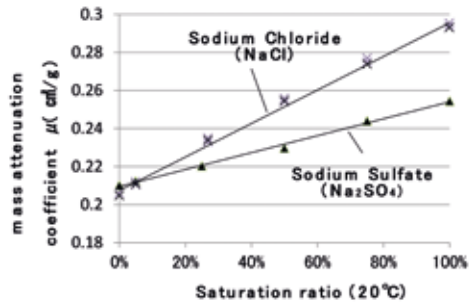


Figure 2: Mass attenuation coefficients of the salt solutions

used to identify the solution diffusivity are shown. The Boltzmann transformation method is also an effective method for the determination of solution diffusivity when gravity can be neglected.<sup>4,5</sup> In this research, we conducted a numerical analysis of the salt solution and moisture transfer that included the effect of gravity.<sup>6,7</sup> We identified the solution diffusivity  $D_{sol}$  in Eqn. (2) using time change of measured volumetric solution content distribution. For this research, we assumed that the salt crystallisation and salt diffusion due to the salt concentration

gradient did not occur during the absorption of the solution. In addition, we assumed that dissolved salt moved by advection only. Under these assumptions, the mass balance of liquid phase which consists of liquid phase water and dissolved salt ions, is expressed by equation (2):

$$\frac{\partial \rho_{sol} \psi_{sol}}{\partial t} = \nabla \cdot D_{sol} \left( \nabla \psi_{sol} - \frac{\partial \psi_{sol}}{\partial \mu_o} g \right) \quad (2)$$

where  $D_{\psi_{sol}}$  is the solution diffusivity in function of solution content [kg/ms],

$\mu_o$  is the water chemical potential [J/kg], and  $g$  is the gravitational acceleration [m/s<sup>2</sup>]. In this paper, the literature values of solution density for NaCl solution and Na<sub>2</sub>SO<sub>4</sub> solution at 20 °C are used.<sup>8</sup> We identified the solution diffusivity  $D_{sol}$  used in equation (2) as  $\nabla \psi_{sol}$ . The sorption isotherm for the material was identified from the literature.<sup>9</sup>

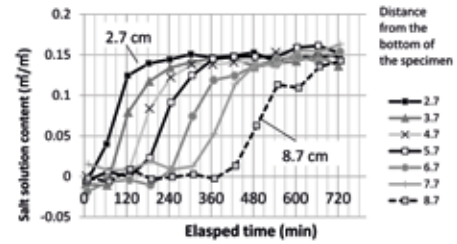
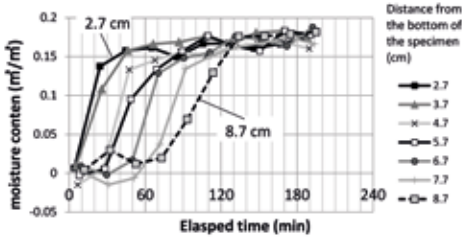


Figure 3: Change in the spatial distribution of the volumetric solution content used in TEST 13 (Left: pure water, Right: NaCl saturation)

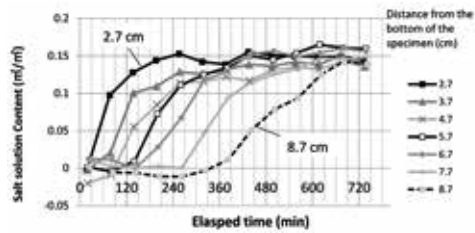
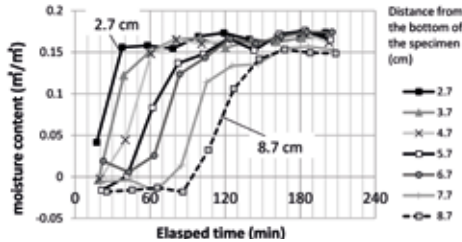


Figure 4: Change in the spatial distribution of the volumetric solution content used in TEST 14 (Left: pure water, Right: Na<sub>2</sub>SO<sub>4</sub> saturation)

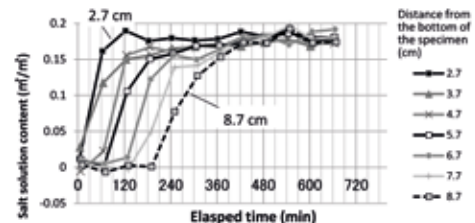
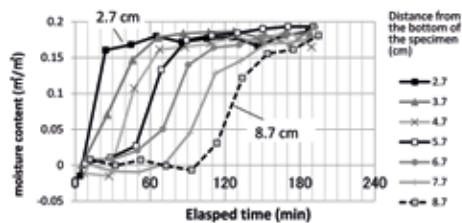


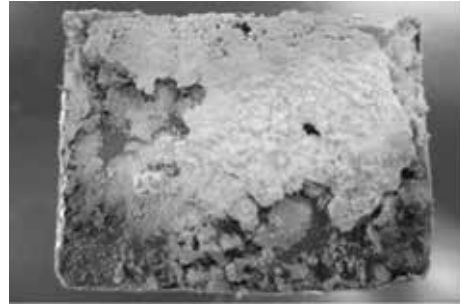
Figure 5: Change in the spatial distribution of the volumetric solution content used in TEST 17 (Left: pure water, Right: Na<sub>2</sub>SO<sub>4</sub> 20%)

### 3. Results and discussion

#### 3.1. The time evolution of water / salt solution content distribution

Figures 3 and 4 show the change in the spatial distribution of volumetric solution content during TEST 13 (Left: pure water, Right: NaCl saturated solution) and TEST 14 (Left: pure water, Right:  $\text{Na}_2\text{SO}_4$  saturated solution), respectively. Since we assumed that the change in the concentration of salt solution would be very little during the solution uptake tests, constant values of the mass attenuation coefficient of the solution for each experimental condition were used to calculate the volumetric solution content. The moisture uptake rate of the specimens was variable. The specimens reached a near steady state in approximately two to three hours after the beginning the absorption of the pure water. The uptake rate of the saturated solutions of both NaCl and  $\text{Na}_2\text{SO}_4$  were significantly smaller than that of pure water, as it took approximately 12 hours for saturated solutions to reach a steady state. In addition, the uptake rate of the saturated solutions at upper locations on the specimens (7.7 cm and 8.7 cm from the bottom) became gradually slower. This tendency was assumed to be due to gravity or salt crystallisation within the material during the uptake process. This was significant in case of  $\text{Na}_2\text{SO}_4$ . Figure 5 illustrates the change in the spatial distribution of the solution in the specimen that absorbed the  $\text{Na}_2\text{SO}_4$  solution with a saturation ratio of 20%. The salt solution uptake rate was twice the rate of pure water, with a decreasing uptake rate at the upper locations of the specimen not seen. Photo 2 shows a comparison of salt crystallisation at the upper surface of the specimen after enough time had passed to allow crystal growth dissipation. In the case of the saturated solution of NaCl, salt precipitation on the surface began during the

solution uptake process and continued approximately 5 days after the solution uptake experiment. On the other hand, in the case of the  $\text{Na}_2\text{SO}_4$  saturated solution, efflorescence was not confirmed during nor after the uptake test.  $\text{Na}_2\text{SO}_4$  easily crystallised within the specimen because  $\text{Na}_2\text{SO}_4$  can change phase at a higher in relative humidity than NaCl. In the case of the  $\text{Na}_2\text{SO}_4$  solution with



TEST 13 NaCl sat.



TEST 14  $\text{Na}_2\text{SO}_4$  sat.



TEST 17  $\text{Na}_2\text{SO}_4$  20%

Photo 2: Salt crystallisation at the upper surface of the specimen

the saturation ratio of 20%, salt crystals emerged at the top surface. When we conducted the same experiment at a lower relative humidity (about 25%), the process of crystallisation of the 20% Na<sub>2</sub>SO<sub>4</sub> solution was similar to that observed in the Na<sub>2</sub>SO<sub>4</sub> saturated solution, TEST 14 (see Photo 2). Therefore, a small difference in the concentration of the solution, ambient temperature, or ambient humidity may affect the crystallisation behaviour of Na<sub>2</sub>SO<sub>4</sub>, which may increase the solution uptake rate.

### 3.2. Identified solution diffusivity

In this research, solution diffusivity was approximated by the exponential function  $D\psi_{sol} = C_1 e^{C_2 \psi_{sol}}$ , and the fixed values  $C_1$  and  $C_2$  were determined by matching the solution uptake tests. Figure 6 shows the comparison between the measured values and the calculated values

used to identify the solution diffusivity in the cases of pure water and a saturated solution of NaCl. The calculated values agree with experimental values in both cases. Therefore, we concluded that the solution diffusivity can be found by multiplying the moisture diffusivity of pure water by a constant. Figure 7 illustrates the comparison between the measured values and the calculated values of solution content in the case of the Na<sub>2</sub>SO<sub>4</sub> solution. In the case of a 20% saturated solution, the calculated values of solution diffusivity can be found by multiplying the moisture diffusivity of pure water by a constant. Generally, the results correspond with the measured values (see Figure 7, Right). Alternatively, in the case of the saturated Na<sub>2</sub>SO<sub>4</sub> solution, it was difficult to replicate the measured values by simply changing the solution diffusivity to that of pure water (see Figure 7, Left). This discrepancy is thought to be due to the difference of crystalli-

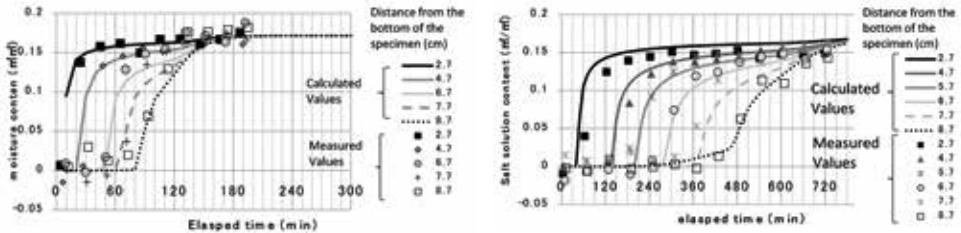


Figure 6: Comparison between the measured and calculated values of the volumetric solution content used in TEST 13 (Left: pure water, Right: NaCl sat)

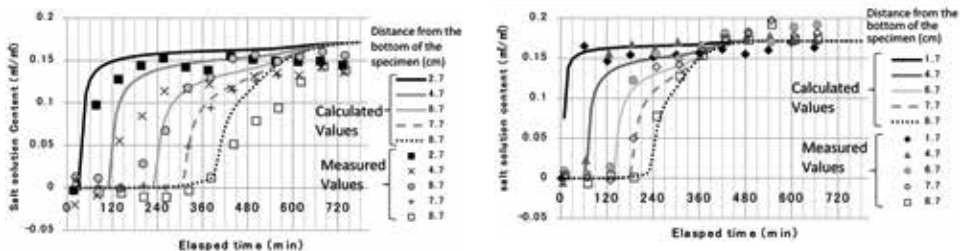


Figure 7: Comparison between the measured and calculated values of the volumetric solution content used in TEST 14 and 17 (Left: Na<sub>2</sub>SO<sub>4</sub> sat, Right: Na<sub>2</sub>SO<sub>4</sub> 20%)

sation behaviour within the specimen. Therefore, the solution diffusion model including a reduction of effective porosity due to salt crystallisation is necessary for reproducing the measured values in the case of the  $\text{Na}_2\text{SO}_4$  saturated solution. The Boltzmann data transformed with the Boltzmann variable  $\lambda = x \cdot t^{-1/2}$  obtained from the measured values of the saturated  $\text{Na}_2\text{SO}_4$  solution are shown in *Figure 8* as a reference to demonstrate that the consideration of in-pore crystallisation

is required. The relationship of solution content and  $\lambda$  is not able to be formalised as one function because the data scattered, especially at high moisture content. *Figure 9* shows the identified solution diffusivity,  $D_{\text{sol}}$  as a function of solution content. The influence of salt on solution diffusivity is so large that the value for the saturated solution of NaCl is 0.17 times smaller than that of pure water. In addition, a higher solution concentration causes smaller solution diffusivity. This

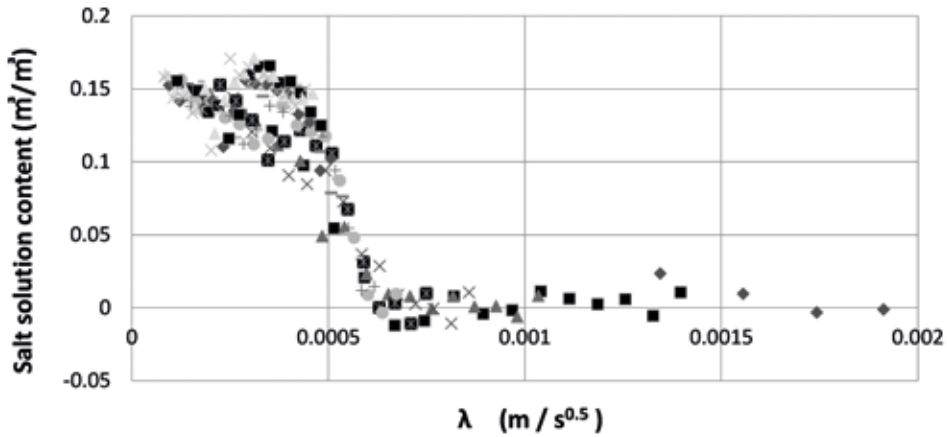


Figure 8: Boltzmann transformation of the measured solution content of the saturated  $\text{Na}_2\text{SO}_4$  solution

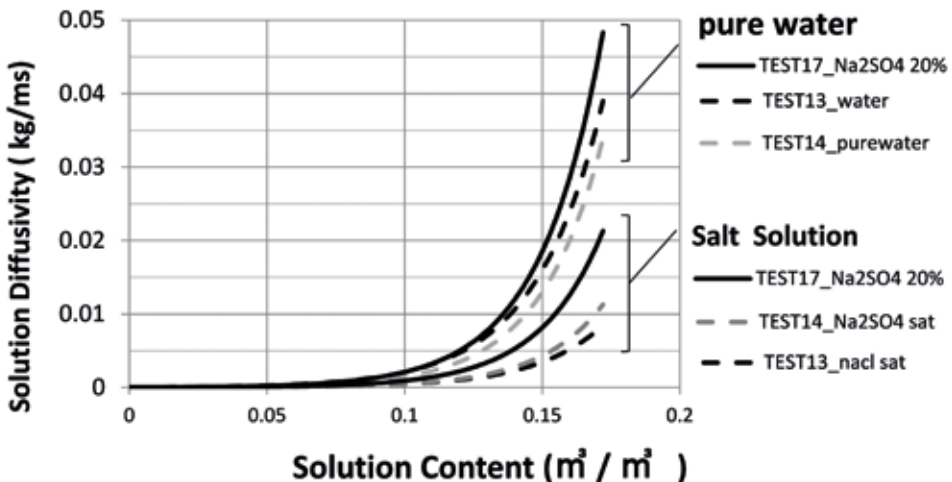


Figure 9: Identified solution diffusivity  $D_{\text{sol}}$  as a function of solution content

result can be explained by the rise in viscosity. From these results, we concluded that the moisture diffusivity model requires the consideration of both viscosity and in-pore crystallisation.

#### 4. Conclusions

We conducted a solution uptake test of two kinds of sodium salts ( $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$ ) which are believed to affect the deterioration of the inner walls of Hagia Sophia. Fired clay brick was used to investigate the influence of salt on solution diffusivity. The influence of salt on solution diffusivity is significant due to its viscosity and salt deposition characteristics. The uptake rate of a salt solution is, at most, approximately six times slower than that of pure water. It was observed from significant change of moisture behaviour that  $\text{Na}_2\text{SO}_4$  easily crystallises in the material compared to  $\text{NaCl}$ . A numerical analysis of dissolved salt moisture transport was also conducted to identify solution diffusivity as a function of solution content. The solution diffusivities for the saturated solution of  $\text{NaCl}$  and the 20% saturated solution of  $\text{Na}_2\text{SO}_4$  can be found by multiplying the moisture diffusivity of pure water by a constant including saturation degree of solution. The solution diffusivity model takes into account the change due to salt crystallisation, which is required to predict salt solution transfer with the influence of pore clogging, especially in the case of the high concentration  $\text{Na}_2\text{SO}_4$  solution.

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