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Salt diffusion in brick structures

Part II *The effect of temperature, concentration and salt*

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This is our second article concerning salt diffusion measurements in porous brick materials. In the first article a method for measuring the rate of diffusion of salt in ceramic material was presented and applied to the measurement of diffusivity of NaCl in different brick materials. In this work the same method was applied to other water-soluble salts commonly found in building materials. The binary diffusion coefficients were measured for KCl, $NaNO_3$, $CaCl_2$, Na_2SO_4, $MgCl_2$ and Na_2CO_3. The result for the diffusivity of 0.05 molar salts in water in new Finnish red brick varied between $(0.271–0.544) * 10^{-5}$ cm^2/s at a temperature of 25 ± 0.05°C. The effect of temperature and concentration on the diffusivity of NaCl in new red brick was also measured. The rate of change of diffusivity as a function of temperature, concentration and the type of salt was very similar to that in free solutions. However, the values of the diffusion coefficients were lower in the porous medium than in solution. A mutual relation between the binary diffusion coefficient and the viscosity of the salt-water solution was observed in the porous brick.

1. Introduction

The presence of aqueous electrolyte solutions in the capillary pores of brick materials can under changing climate conditions cause deterioration of wall structures. Salts move in brick depending on its water content and they may be precipitated on the outer wall or concentrated under paint layers covering the surface of the brick. Different type of damage may appear in masonry walls due to these concentrating phenomena. Salt deterioration is known from the cold and arid areas of the antarctic to the hot and arid areas of Saudi-Arabia. It is also, common in marine climates [1–3]. This world wide problem has increased interest in understanding the salt transfer phenomena taking place with in a porous brick matrix [4, 5]. In particular the diffusion coefficients of different salts as a function of concentration and temperature are needed. These coefficients maybe used in a simulation program to predict moisture profiles in brick under different environmental conditions.

In part I of this work [6] a method for measuring the diffusion coefficient of salts in porous ceramic material under stationary conditions was presented and applied to the measurement of the diffusivity of NaCl in different types of brick materials. In this work the diffusion coefficient of sodium chloride was measured as a function of temperature and concentration. The binary diffusion coefficients were measured also for KCl, $NaNO_3$, $CaCl_2$, Na_2SO_4, $MgCl_2$ and Na_2CO_3. These water-soluble salts are often find in building materials in combination with NaCl.

2. Experimental

The diffusion coefficient measurements were made with a diffusion cell based on the, so called, porous diaphragm technique [7–9]. The equipment consisted of two salt solution containers (α and β) and the brick specimen in between them. The brick specimens used in the measurements were cylindrical with a thickness of 10 mm and diameter of 25 mm. The outer surface of the brick cylinders were lacquered in order to prevent leakage of the salt solution. The removal of air from the pores of the specimen was ensured by sucking the salt solution used in each experiment through the specimen with a vacuum pump.

The change of concentration in chamber α was measured by monitoring increases in the electrical conductance as a function of time. The conductivity cell, with platinum electrodes, was calibrated using standard KCl-solutions. The cell constant was 1.702 cm^{-1}. The diffusion cell, including the conductivity cell, was held at a constant temperature using a thermostated water-bath (±0.05°C). A schematic diagram showing the arrangement of the apparatus is included in a previous paper [6].

The volume of the β-chamber, V_β, was large (2200 cm^3) compared to the volume of the α-chamber, V_α (25 cm^3), and as a consequence its concentration was assumed to be constant during the experiment. The volume of the α-chamber was larger than the volume of the brick sample (effective volume 1 cm^3) because of the requirements of a stationary state. The hydrostatic pressures in both compartments were equalized in order to prevent hydrostatic flow.

The solutions on each side of the brick were maintained at a uniform concentration right up to the surface of the brick. This was ensured by mechanical stirring of the solutions on both side of the specimen. All the electrolyte solutions and the brick specimen where prepared as described in our earier paper [6]. The brick specimens used in these experiments were new Finnish red brick (NRB). Each individual brick specimen were taken from the same location of 10 mm from the surface of each sample brick. The porosity, ε, was determined by measuring the volume and the mass of the dry, and fully water-saturated brick specimen. The porosity was measured separately for each specimen.

3. Mathematical model and evaluation of *D*

The starting point to the mathematical model was isothermal binary salt diffusion in a fully saturated porous isotropic material. In these circumstances the mathematical model of diffusion can be expressed in one dimension as an empirical relation of Fick's first law applied in pseudo steady state conditions [7, 10]. This means that in each time moment the diffusive flux of substance, J, is not dependent of the space coordinate x, which means that there is a linear concentration profile inside the brick.

The diffusion in brick was modelled by the following diffusive equation [6];

$$\frac{dc^{\alpha}}{dt} - \frac{D}{\xi}(c^{\beta} - c^{\alpha}) = 0. \tag{1}$$

The solution of the differential Equation 1, with initial condition $c^{\alpha}(t_0) = c^{\alpha 0}$ is

$$\ln\left(\frac{c^{\beta} - c^{\alpha}}{c^{\beta} - c^{\alpha 0}}\right) = \frac{D}{\xi}t_0 - \frac{D}{\xi}t. \tag{2}$$

where, c^{x} = the concentration of the salt in chamber x, t = diffusion time, t_0 = time corresponding to the beginning of the stationary state, $\xi = V^{\alpha}1/A$, V^{α} = the volume of the α-chamber, 1 = the thickness of the brick sample, A = the diameter of the brick sample.

The diffusion coefficient, D, which describes the rate of diffusion can be solved from Equation 2 with the experimental results $\ln[(c^{\beta} - c^{\alpha})/(c^{\beta} - c^{\alpha 0})] = f(t)$. The material parameter, ξ, can not be solved from the diffusion experiment because the lack of absolute values of D in porous brick materials [6]. The geometric thickness of the brick sample, 1, is not necessarily the same as the routes the salt ions have to travel through the sample. This difference is caused by the tortuous diffusive pathways within porous medium (tortuosity, τ) and the form of the pores (constrictivity, δ).

In our experiments the material parameter ξ has been taken as a constant and evaluated from the measurement of geometry (1/A) of the specimen and the measurement of the volume V^{α}. The cross section area A is calculated by taking the porosity ε of each specimen into account. We call the resulting diffusion coefficient an effective diffusion coefficient, D_e, which is also called the pore system (or solution) diffusion coefficient, D_p [11, 12].

4. Results and discussion

4.1. The calculation of results

The measured quantity in a diffusion experiment was the electric potential (U) of the conductivity cell in α-chamber, $U = f(t)$. The voltage differences were then changed to the conductivity values (K) with known correlation, $K = f(U)$. With the help of measured calibration curve, $c = f(K)$, the measured conductivity values were finally changed to the corresponding concentration values as a function of time, $c = f(t)$. After reaching the pseudo-stationary state Equation 2 was applied to the experimental results. In this particular measuring geometry the pseudo-stationary state was reached in about 40–100 hours depending on the experiment and especially the initial state of the brick specimen (salt concentration). The change of concentration, c^{α}, (in the α-chamber with time) in two typical experiments are given in Figs 1 and 2.

The fitting of the measured data from these experiments with Equation 2 are shown in Figs 3 and 4. The

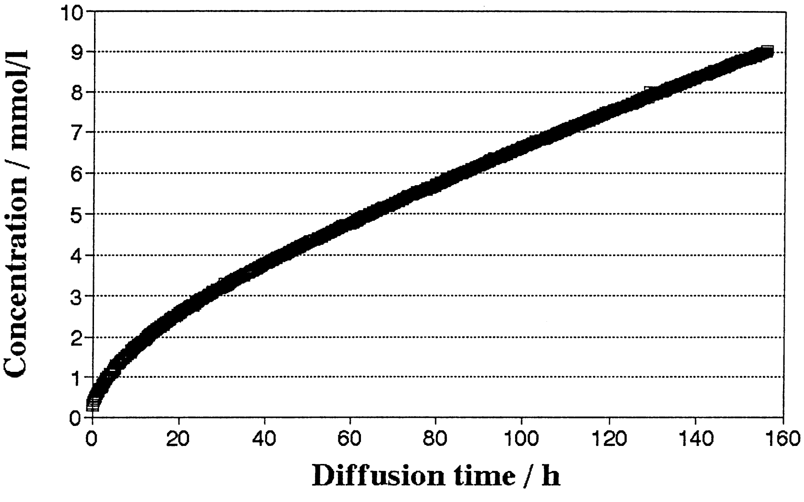

Figure 1 The rate of change of concentration in chamber alpha, $c^{\alpha} = f(t)$. $c(\mathrm{Na_2SO_4}$ in brick, $t = 0) = 50$ mmol/l. Measurement NS01P1.

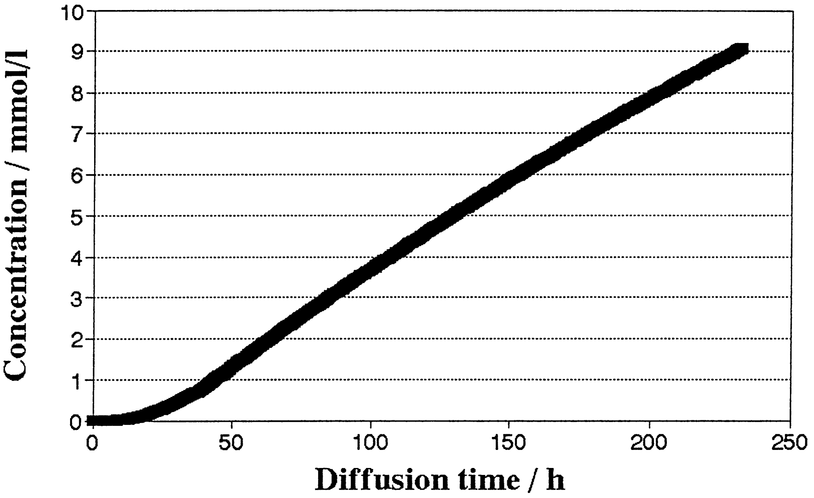

Figure 2 The rate of change of concentration in chamber alpha, $c^\alpha = f(t)$. $c(\mathrm{Na_2CO_3}$ in brick, $t = 0) = 0$ mmol/l. Measurement NC01P1.

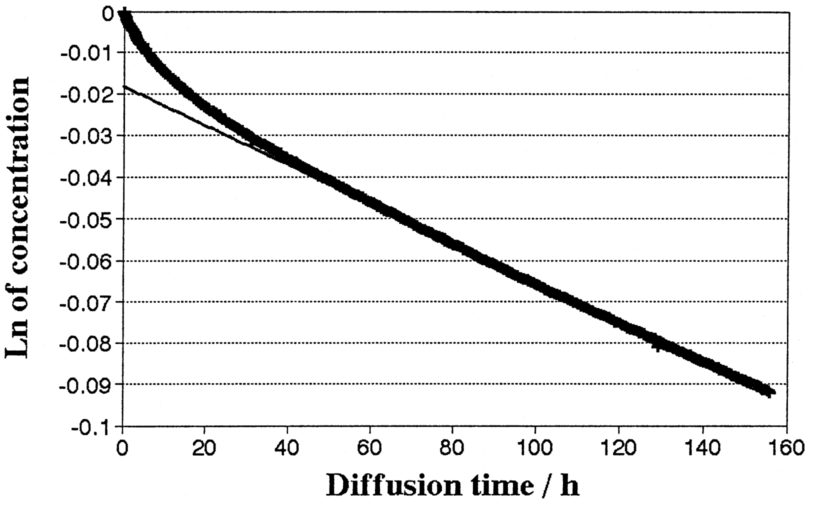

Figure 3 The least-square fitting ($t = 66$ h–156 h) of the measurement NS01P1, $\mathrm{Ln}[(c^\beta - c^\alpha)/(c^\beta - c^{\alpha 0})] = f(t)$, $D = (0.289 \pm 0.0002) * 10^{-5}$ cm^2/s, $r^2 = 0.9998$.

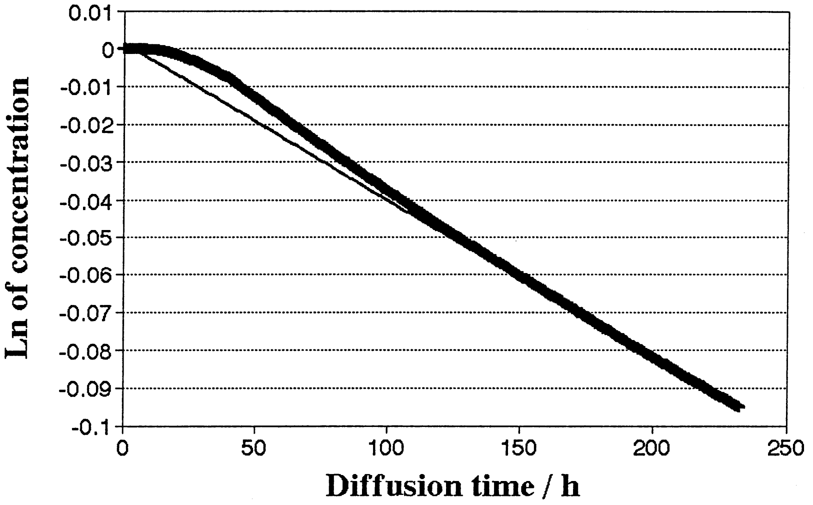

Figure 4 The least-square fitting ($t = 175$ h–232 h) of the measurement NC01P1, $\mathrm{Ln}[(c^\beta - c^\alpha)/(c^\beta - c^{\alpha 0})] = f(t)$, $D = (0.273 \pm 0.0001) * 10^{-5}$ cm^2/s, $r^2 = 0.9999$.

fittings were done with the least squares method. The best fit from the whole fitting region was determined on the basis of the coefficient of determination, r^2, the square of the Pearson product-moment correlation coefficient, r [13]. In a successful experiment, which included 480 measured datapoints (measurements of 10 days) the coefficient of determination was typically better than 0.9990 (correlation coefficient better than 0.9995).

In Fig. 5. the calculated values of diffusion coefficients from Equation 2, are represented as a function of diffusion time, where the values of $c^{\alpha 0}$ and t_0 are taken

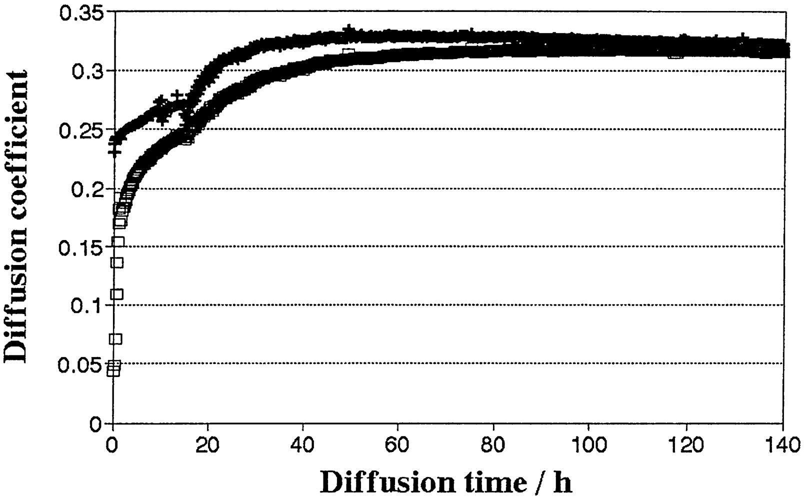

Figure 5 The diffusion coefficients (10^{-5} cm^2/s), calculated from the Equation 2, $D(\mathrm{CaCl_2}) = f(t)$. □ ≡ $c^{\alpha 0}$ and t_0 taken from the beginning of the measurement; + ≡ $c^{\alpha 0}$ and t_0 taken from the beginning of the stationary state.

either from the beginning of the stationary state or from the beginning of the measurement. As can be seen the choosing of the time $t = t_0$ can be somewhat arbitrary, but in the former case the constant, and correct, diffusion coefficient is reached earlier.

It should be noted that the diffusion coefficients are given as an effective diffusion coefficient (D_e), calculated with the porosity value (ϵ) measured for each of the specimen and without any correction term to the geometrical thickness of the brick sample (tortuosity, τ).

4.2. Effect of salt

The measured diffusion coefficients in different salt-water-solutions are given in Table I. The measured binary effective diffusion coefficients of 0.05 molar salts in water in new Finnish red brick varied in between $(0.271\text{–}0.544) * 10^{-5}$ cm^2/s at 25 ± 0.05°C.

The biggest diffusion coefficients were measured for the alkali metal electrolytes (valency ratio for cation-anion is 1–1). After these mono-valent electrolytes, came the alkaline-earth metal electrolytes (2–1). The smallest diffusion coefficients were measured for the bi-valent anion alkali metal electrolytes (1–2). The diffusion coefficients measured decreased in the order of KCl, NaCl, $NaNO_3$, $CaCl_2$, $MgCl_2$, Na_2SO_4 and Na_2CO_3. This variation of the diffusion coefficients is very similar to that observed in pure electrolyte-water solutions in equivalent conditions or in infinite dilution calculated with the Nernst Hartley equation [10] as illustrated in Fig. 6. The manner of the decrease of the diffusivity is very similar to the increase of the viscosity of the same electrolytes under the same conditions (p, T, c).

A very interesting comparison can be made by presenting the reciprocal η_0/η of the relative viscosities of the salt-water solutions as a function of salt type and temperature (Fig. 7). Only the η_0/η-value of 0.05 M $NaNO_3$ is not in the falling curve of the reciprocal of relative viscosity. A minor deviation from the falling curve is measured also for solution of 0.05 M Na_2SO_4.

TABLE I Diffusion coefficients $D_e/10^{-5}$ cm^2/s of different salts ($c_{\mathrm{mean}} = 0.05$ M) in new red brick at 25°C

KCl	D_e	D_e (mean) ± SE_m	D_w
1.	0.541		
2.	0.547	0.544 ± 0.002	1.896[a]
3.	0.544		1.994[i]
NaCl			
1.	0.495		
2.	0.508		
3.	0.510	0.499 ± 0.004	1.504[b]
4.	0.502		1.611[i]
5.	0.484		
6.	0.491		
7.	0.502		
$NaNO_3$			
1.	0.426		
2.	0.424	0.424 ± 0.001	1.471[cd]
3.	0.424		1.568[i]
4.	0.421		
$CaCl_2$			
1.	0.322		
2.	0.319	0.321 ± 0.001	1.140[e]
3.	0.321		1.335[i]
$MgCl_2$			
1.	0.306		
2.	0.304	0.305 ± 0.002	1.057[f]
3.	0.304		1.250[i]
4.	0.301		
5.	0.311		
Na_2SO_4			
1.	0.290		
2.	0.290	0.291 ± 0.001	1.024[g]
3.	0.292		1.230[i]
4.	0.295		
5.	0.289		
Na_2CO_3			
1.	0.266		
2.	0.274		
3.	0.273	0.271 ± 0.001	1.000[h]
4.	0.270		1.162[i]
5.	0.272		
6.	0.268		
7.	0.270		

D_w = literature value in water at 25°C in 0.05 M. [a][14], [b][15], [c][16], [d][17], [e][18], [f][19], [g][20], [h][21].

[i] D_w at infinite dilution calculated with the Nernst Hartley equation.

SE_m = standard error of the mean [13].

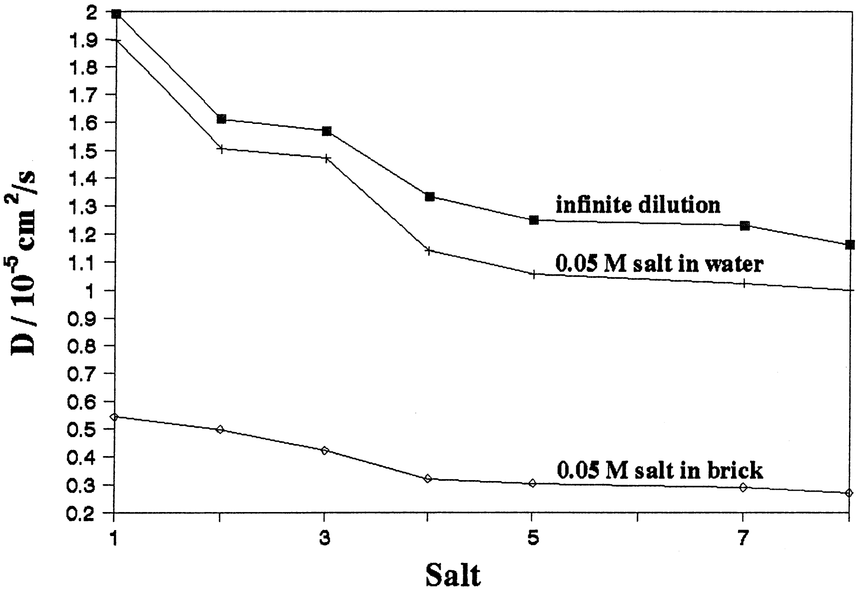

Figure 6 The diffusion coefficients of different salts (10^{-5} cm^2/s). Measured in new red brick at 25°C and literature values [14–21] in the absence of porous medium. 1 ≡ KCl, 2 ≡ NaCl, 3 ≡ $NaNO_3$, 4 ≡ $CaCl_2$, 5 ≡ $MgCl_2$, 6 ≡ Na_2SO_4, 7 ≡ Na_2CO_3.

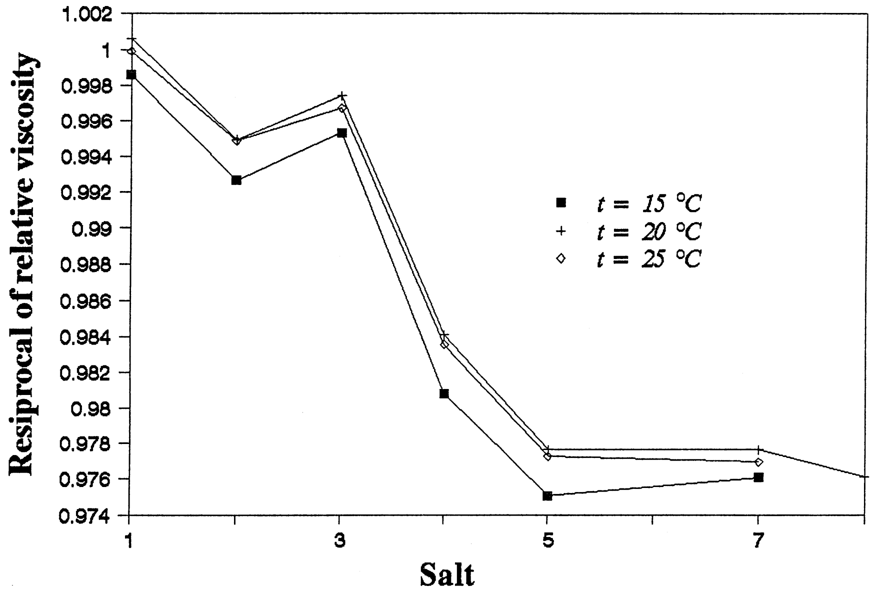

Figure 7 The reciprocal values of relative viscosities (η_0/η) in different electrolytes at (15–25)°C. 1 ≡ KCl, 2 ≡ NaCl [22], 3 ≡ $NaNO_3$, 4 ≡ $CaCl_2$, 5 ≡ $MgCl_2$, 6 ≡ Na_2SO_4 [23], 7 ≡ Na_2CO_3 [24], w = 0.05 mol/kg.

This mutual relation between the viscosity and the diffusivity was also observed by Onsager and Fuoss [24] in absence of the porous material. In this work the same relation was observed to also be valid in the presence of porous material (Figs 6 and 7).

4.3. The effect of the concentration

In order to simulate the effect of different environmental conditions on the diffusivity of the salt, the effect of temperature and concentration on the diffusivity of NaCl in new red brick was measured. The concentration dependence of the diffusion coefficient is given in Table II. The concentration region from 0.1 M to saturated salt solution was measured with four different NaCl concentrations. The measured binary effective diffusion coefficients in new Finnish red brick varied between (0.415–0.499) $*\ 10^{-5}$ cm^2/s at the temperature of 25°C.

The variation of D_e for NaCl is clearly smaller as a function of concentration than the variation of D_e as a function of different salts remaining closely to that of NaCl in free solution at 25°C, (Fig. 8). The values of diffusion coefficients of NaCl are about three times smaller in red brick than in free solution over the whole concentration range. It is worth emphasizing that the measured D_e is an integral value [26, 27] of D_e from the concentration region of the β-chamber to the pure water in the α-chamber.

4.4. The effect of temperature

The measured diffusion coefficients as a function of temperature are given in Table III. As was expected

TABLE II Diffusion coefficients $D_e/10^{-5}$ cm^2/s of NaCl in new red brick at 25°C as a function of concentration

Measurement	D_e	D_e (mean) ± SE$_e$
$c_m = 0.05$		
1.	0.495	
2.	0.508	
3.	0.491	
4.	0.510	0.499 ± 0.004
5.	0.502	
6.	0.484	
7.	0.502	
$c_m = 0.30$		
1.	0.452	
2.	0.455	0.454 ± 0.001
3.	0.457	
$c_m = 1.00$		
1.	0.414	
2.	0.422	0.415 ± 0.004
3.	0.409	
$c_m = 3.08$		
1.	0.492	
2.	0.467	0.481 ± 0.006
3.	0.486	
4.	0.491	
5.	0.471	

c_m = mean concentration (mol/dm^3).
SE$_m$ = standard error of the mean [13].

TABLE III Diffusion coefficients $D_e/10^{-5}$ cm^2/s of 0.05 M NaCl in new red brick as a function of temperature

Measurement	D_e	D_e (mean) ± SE$_m$
$t = 8$°C		
1.	0.223	
2.	0.214	
3.	0.215	0.218 ± 0.002
4.	0.221	
$t = 13$°C		
1	0.277	
2.	0.284	0.277 ± 0.004
3.	0.270	
$t = 18$°C		
1.	0.369	
2.	0.359	0.364 ± 0.004
3.	0.364	
$t = 25$°C		
1.	0.495	
2.	0.508	
3.	0.491	0.499 ± 0.004
4.	0.510	
5.	0.502	
6.	0.484	
7.	0.502	

SE$_m$ = standard error of the mean [13].

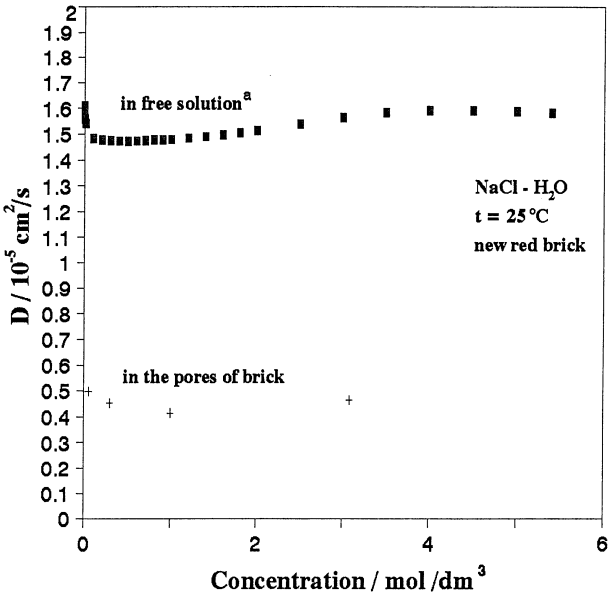

Figure 8 The diffusion coefficients of NaCl as a function of concentration. ^{a}literature values [28].

diffusivity increased as a function of temperature. The first order polynomial fit in porous brick in 0.05 molar NaCl-H$_2$O-solution fitted from our measurements in the temperature range of $t = (8–25)$°C can be expressed in the form of equation $D_e/(10^{-5}\ \text{cm}^2/\text{s}) = 0.0167t + 0.0718$. This equation can be compared to the first order polynomial fit of $D/(10^{-5}\ \text{cm}^2/\text{s}) = 0.0323t + 0.709$ in 0.05 M NaCl-H$_2$O-solutions fitted from the literature values [28] in the temperature range of $t = (0–35)$°C. The coefficients of determination for the best fits were $r^2 = 0.990$ (in brick) and $r^2 = 0.996$ (in free water), respectively. This linear dependence between diffusion coefficient and temperature can be seen in Fig. 9. In porous brick the rate of change of diffusivity as a function of temperature was only slower than in free water. It is difficult to compare these measured diffusion coefficients, D_e (NaCl) $= f(c, t)$ with the literature values because of the relative lack of published diffusion measurement data in brick materials.

5. Conclusions

The binary diffusion coefficients measured for KCl, NaNO$_3$, CaCl$_2$, Na$_2$SO$_4$, MgCl$_2$ and Na$_2$CO$_3$ in new Finnish red brick varied between $(0.271–0.544) * 10^{-5}$ cm^2/s. The coefficients given are mean values of measurements for the diffusion of salt from the concentration region of 0.1 mol/dm^3 to the pure water ($c_{\text{mean}} = 0.05$ M) at (25 ± 0.05)°C. The measured values were calculated using the porosity value (ϵ) measured to each of the specimen.

The measured diffusion coefficients for NaCl in new Finnish red brick varied as a function of concentration between $(0.415–0.499) * 10^{-5}$ cm^2/s over the concentration range $c_{\text{mean}} = (3.08–0.05)$ M at 25°C. The measured diffusion coefficients for NaCl in new Finnish red brick varied between $(0.218–0.499) * 10^{-5}$ cm^2/s over the temperature range of $t = (8–25)$°C.

The precision in each of the successful diffusion experiment was very good. The standard error, SE, varied in between $\pm(0.0001–0.0003) * 10^{-5}$ cm^2/s. The reproducibility of the experiments was good, also. The standard error (deviation) of (in) the mean, SE$_m$, [13, 29] varied in between $\pm(0.001–0.006) * 10^{-5}$ cm^2/s depending on the series of the experiment (Tables I–III). The diffusion coefficients measured were in accordance with the diffusion coefficients measured for NaCl previously [6]. The result for the diffusivity of NaCl measured in the same conditions was $(0.499 \pm 0.004) * 10^{-5}$ cm^2/s. No other

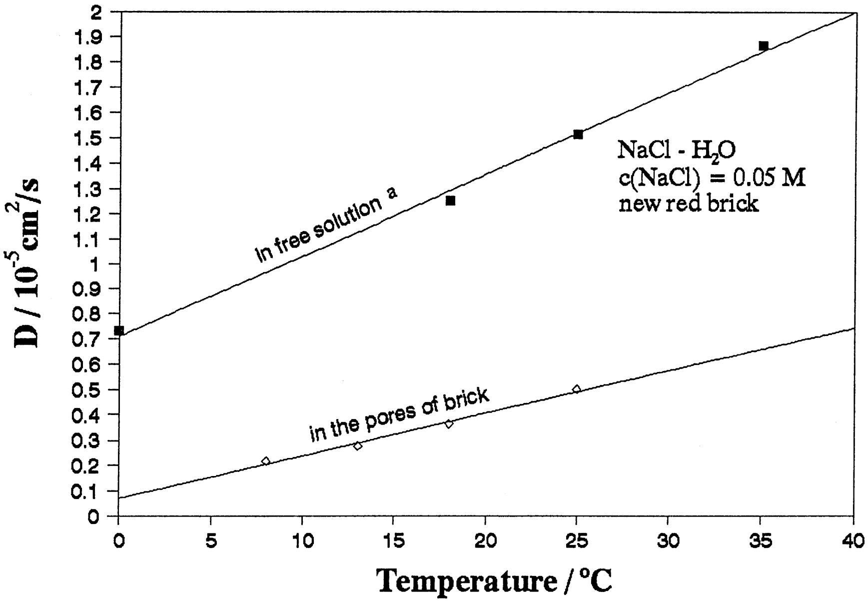

Figure 9 The diffusion coefficients of NaCl as a function of temperature. Datapoints and first order polynomial fits. ^{a}literature values [28].

literature values measured for porous brick was found.

The rate of change of diffusivity as a function of the concentration, temperature and the type of diffusing salt was very similar to that measured in free solution. Only the values of diffusion coefficients were smaller in porous medium than in free water. The difference of diffusivity of salt in porous media compared to free water is mainly caused by the geometrical properties of the medium and the precence of the fluid-solid interface.

Geometrical properties include the cross sectional area of medium accessible to diffusive ions (porosity, ϵ), the form of the pores (constrictivity, δ) and the tortuous diffusive pathways within porous medium (tortuosity, τ) [30]. All these effects have to be taken into account in comparing the values of the diffusion coefficient. In our measurements only the porosity of the brick sample was taken into account. It would be necessary to know a lot more about the fine structure of the porous brick medium in order to include the other possible parameters.

The deterioration of brick structures and other porous building materials are result of various factors affecting the material; salts, humidity, temperature, rainwater, pollutants etc. Water can affect disintegration of the porous materials in the same way as salts, because absorbed water causes temperature dependent volume changes. The deterioration is due to a combination of salt and water interactions. It is important to distinquish between decay by water and decay by salt even if their influence is often linked together. For example moisture content in a saline material is usually higher than in salt free material. Salts are observed also to decrease capillary suction and evaporation in a porous material. Theoretical models to calculate moisture and salt transport in brick structures have been proposed [31]. In all practical situations diffusion contributes to the transport of salts into and in the brick structures. The diffusion coefficients measured in this and previous [6] work maybe used in a simulation program to predict moisture and salt profiles in brick structures.

At this moment we are using our measured diffusion coefficients for simulation work in new Finnish red brick (NRB), which is a porous engineering brick manufactured commercially for house building etc. We are studing salt diffusion by means of diffusion cell measurements and mathematical methods. The mathematical methods involve analytical, and numerical simulation, of the diffusion process in combination with measurement data in different environmental conditions. By that way we try to understand the effect of salt diffusion in the complex interaction of different mechanisms in the decay process of brick structures. The decay mechanisms in porous building materials due to salts are presented in the report of C.B. Nielsen [31].

Our measuring program is still going on with the closed capillary method [32, 33] applied to the diffusion coefficient measurement in porous brick structures. Previously this method has only been applied to the diffusion measurements in aqueous solution [34]. Our goal is to compare the diffusion coefficients measured with the closed capillary method to these results measured in this work using the diaphragm method.

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