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Salt diffusion in brick structures

Part I *Measurements with NaCl*

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Salts causes surface damages and efflorescence for masonry walls. This has increased the interest to understand the salt transfer phenomena taking place in porous matrix. There is still however a lack of published transport data in the literature. Especially the diffusion coefficients of salts in different brick structures are lacking. In this work a method for measuring the rate of diffusion of salt in ceramic material is presented and applied to the measurement of diffusivity of NaCl in three different brick materials. Fick's first law of diffusion was applied to calculate the diffusion coefficients in a pseudo stationary state by means of linear regression analysis. The result for the diffusivity of 0.05 molar NaCl in water in new Finnish red brick was $(0.499 \pm 0.004) * 10^{-5}$ cm^2/s in the temperature of $25 \pm 0.05^\circ$C. The corresponding values for the old light brick and old dark brick was $(0.453 \pm 0.008) * 10^{-5}$ cm^2/s and $(0.337 \pm 0.009) * 10^{-5}$ cm^2/s respectively. The diffusion coefficients are given as an effective diffusion coefficients calculated with the porosity value measured to each of the specimen. The concept of salt diffusion and diffusion mechanism inside the porous matrix are also discussed.

1. Introduction

Crystallization of salts occurs on the surface of porous building materials as efflorences or near the surface as subflorences. This white, powdery scum of crystallized salts in connection with moisture and temperature changes affect the degradation of building materials like masonry walls in many ways [1, 2]. Three conditions must exist before efflorescence will occur. First, there must be water-soluble salts in the wall. Second, there must be sufficient moisture to render the salts into a soluble form and third, there must be a path for the salt solution to migrate through to the surface where the moisture can evaporate leaving the salt crystals on the brick wall [3]. For brick to retain its reputation as a material that is both durable and maintainance free, a greater understanding of the transport of aggressive salts in porous brick is necessary.

In aqueous solutions salts are transported by diffusion, migration, convection or thermal conduction. The mechanisms of salt transport in porous materials can be even more complicated including, in addition, capillary suction accompanied by physical and chemical binding of salts on the pore walls (adsorption and absorption). This may cause surface transport effects depending of the concentration of the salt solution in the pores of the brick. In all practical situations diffusion contributes to the transport of these ions into and in the brick structures.

In order to measure the effect of one particular transport process all other transport processes must be excluded experimentally, or mathematically. In the present paper we are interested only in binary salt diffusion processes occuring in porous ceramic brick materials. As a model salt we have chosen a very common efflorescent salt, sodium chloride, which has caused surface damages and decay of bricks [4, 5].

2. Binary salt diffusion

It is well known that diffusion is caused by the thermal motion of the atoms and molecules under a gradient of concentration, or more strictly speaking chemical potential, from a high concentration to a low concentration zone. The coefficient related to the rate of diffusion is called the diffusion coefficient, D. When only one electrolyte like NaCl is present, the highly mobile chloride and the slower sodium ions are constrained, by electrostatic forces, to move at the same rate. Because of these electrostatic requirements, the flux of NaCl is characterized by a single diffusion coefficient, an average between the diffusion coefficients of Na^+ and Cl^- ions [6].

Alternative names for binary diffusion often used in the literature are interdiffusion, mutual diffusion, heterodiffusion, chemical diffusion, concentration diffusion, electrolyte diffusion and salt diffusion [7]. This variety of different names may cause confusion but binary diffusion is fundamentally different from that of multi-component diffusion where the flux of one component is influenced by the concentration gradient of a second component. Instead of a single electrostatic attraction force tying one anion and one cation, there now is a myriad of attraction and repulsion forces tying together all the ions in the systems. When salt diffusion is taking place in a system of two components (N = 2) there exists only one independent diffusion flux and one diffusion coefficient. In a system of N components there are (N − 1) independent diffusion fluxes and $(N-1)^2$ different diffusion coefficients.

3. Theoretical

The mathematical theory of diffusion in isotropic substances is based upon the hypothesis that the rate of transfer of diffusing substance through unit area of a section is proportional to the concentration gradient measured normal to the section. This hypothesis is expressed in one dimension as an empirical relation

$$J = -D\frac{\mathrm{d}c}{\mathrm{d}x} \tag{1}$$

where J is the rate of transfer per unit area of section (mol $\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$), c is the concentration of diffusing substance (mol cm^{-3}), x is the space coordinate measured normal to the section (cm), D is the diffusion coefficient ($\mathrm{cm}^2\,\mathrm{s}^{-1}$).

Equation 1 is known as Fick's first law and it is valid in a stationary state. In diffusion experiments this steady state diffusion is important and yields valuable information especially where diffusion through a porous ceramic brick sample of thickness 1, whose surfaces $x = 0$ and $x = 1$ are maintained at constant concentrations c_β and c_α, respectively [8].

The diffusion problem is usually solved with Equation 1 even if the concentration c_α is not constant but changes slower than the rate of change of concentration in the brick sample. This is called the pseudo-steady-state hypothesis and means that in each time moment the flux of substance J is not dependent on the space coordinate x. This means that we have a linear concentration profile in the brick expressed by the Equation 9

$$\frac{\mathrm{d}c}{\mathrm{d}x} = \left(\frac{c_\alpha - c_\beta}{1}\right) \tag{2}$$

If the volume of the chamber α is V^α and the cross sectional area of the porous brick is A, the change in the amount of diffusing substance in side α, as a function of time, is given by the equation

$$\frac{\mathrm{d}n^\alpha}{\mathrm{d}t} = V^\alpha\frac{\mathrm{d}c^\alpha}{\mathrm{d}t} = JA \tag{3}$$

By combining Equations 1, 2 and 3 we get

$$\frac{\mathrm{d}c^\alpha}{\mathrm{d}t} - \frac{D}{\xi}(c^\beta - c^\alpha) = 0 \tag{4}$$

where $\xi = V^\alpha 1/A$.

The solution of the differential Equation 4 with initial condition $c^\alpha(t_0) = c^{\alpha 0}$ is

$$\ln\left(\frac{c^\beta - c^\alpha}{c^\beta - c^{\alpha 0}}\right) = \frac{D}{\xi}t_0 - \frac{D}{\xi}t \tag{5}$$

where t_0 = time corresponding to the beginning of the stationary state

The diffusion coefficient, D, which describes the rate of diffusion can be solved from the Equation 5 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 we don't have any absolute values of D in porous brick materials. The common way to calculate ξ is to use a known diffusion coefficient measured in aqueous potassium chloride solutions. This calibration procedure must be criticized because it equalizes the diffusion in free water and in the porous brick materials giving a result comparable to salt diffusion in water. It is not obvious that the diffusion of salt in water is similar to that of diffusion of salt in water in porous brick materials.

In our experiments the parameter ξ has been 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 either by taking the porosity, ε, into account or not. In the former case we call the diffusion coefficient an effective diffusion coefficient, D_e, and in the latter case a geometrical diffusion coefficient, D_g. These coefficients are also called pore system (or solution) diffusion coefficient, D_p, and intrinsic diffusion coefficient, D_i, correspondingly [10, 11]. For example in the case of salt diffusion in new red brick ($\varepsilon = 0.225$ $\mathrm{m}^3/\mathrm{m}^3$) the value of D_g is ε times the value of D_e.

4. Experimental

We present here a method to measure the rate of diffusion of salt in ceramic brick materials. The method is based on the so called porous diaphragm technique introduced by Nothrop and Anson [12] and developed by McBain [13], Hartley [14] and Stokes [15]. Originally this method was used for measurements of salt diffusion coefficients in aqueous solutions. The thin membrane used in solution measurements have here been substituted with a brick sample (6–15 mm) wherein the diffusion coefficient are going to be measured. While in traditional solution measurements the membrane is assumed to be inert and have no effect to the diffusion coefficient in our measurements just the effect of the brick sample (membrane) on the diffusion coefficient is measured.

A diagram of the apparatus used to measure salt diffusion in bricks is presented in Fig. 1. It is based on equipment designed to measure the diffusion coefficient of salt through membranes by Garbarini *et al.* [9] and through bricks by Lempinen *et al.* [16] and the author [17]. In designing the diffusion cell attention has been focused on the geometrical structure, mechanical vibrations and temperature control of the cell. Also polarization effects on the electrodes and the leakage of electrolyte over specimen have been controlled.

The diffusion cell, including the conductivity cell, was kept at a constant temperature using a thermostatically controled water-bath. Reliable temperature control is important because both the diffusion and the conductivity are very sensitive to temperature changes. The

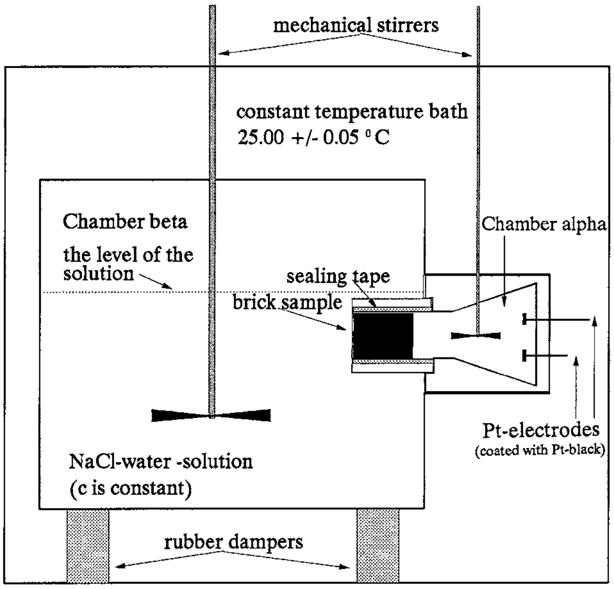

Figure 1 Schematic of the apparatus for diffusion studies in brick.

accuracy of the temperature control inside the diffusion cell was ±0.05°C. The thickness of the cylindrical brick specimen, of diameter of 25 mm, could be varied between 3–20 mm. In order to prevent leakage over the specimen the outer surface of the brick cylinder was lacquered prior to cutting to the final dimensions. The brick samples immersed in solution was installed with the help of sealing teflon tape in between the two chambers α and β. The removal of air from the pores of the specimen was ensured by sucking the salt solution used in the experiment through the specimen with a vacuum pump.

The volume of the beta chamber V_β was large (2200 cm^3) compared to the volume of the alpha chamber V_α (25 cm^3) because its concentration is assumed to be constant during the experiment. Also the volume of chamber alpha was larger than the volume of the brick sample (1 cm^3 effective volume) because of the requirements of stationary state. The water levels in both compartments was equalized in order to prevent hydrostatic flow.

It is essential according to the boundary conditions that the diffusion process occurs solely in the brick sample. This means that the reservoirs of the solutions on each side of the brick must be maintained at a uniform concentration right up to the surface of the brick. This is ensured by mechanical stirring on both side of the specimen.

The change of concentration in chamber α was measured by monitoring increases in the electrical conductance as a function of time. The conductivity cell was calibrated with standard KCl-solutions. The cell constant was 1.702 cm^{-1}. The platinum electrodes used was coated electrochemically with platinum black deposition in order to minimize the electric polarisation effects and to improve the repeatability of the measurements. The dependence of conductivity from the frequency of AC was negligible in the frequency region of 500 Hz to 20 kHz.

All the solutions of sodium chloride in water were prepared by weighing taking account the appropriate buoyancy corrections. The p.a. grade NaCl (Merck, pro analyse) was dried 5 days before weighing with an accuracy of 0.001%. The water used was ion exchanged (Milli-Q) water and its conductance 2 μS/cm was substracted from the conductivity results. The brick samples were purified by boiling 12 pieces at a time in a stainless steel kettle in two litres of distilled water. Boiling duration was 1 hour. After that, the water was changed twice and the brick samples were left in two litres distilled water for seven days. Brick samples were dried in the oven at 105°C until their weight was constant. Samples were kept in exicator prior to use.

The meaning of the purification process was to remove all impurities from the samples including soluble salt remains which may have penetrated to the brick under storage and transportation or drilling and cutting of the samples (tap water cooling). This is a standard procedure used in our laboratory [18] and no indication that this would have altered the measured diffusion coefficient or porosity have been discovered.

In order to develop the method and find the optimum measuring conditions both the effect of thickness of the brick sample and the effect of initial salt concentration in the brick on the binary salt diffusion coefficient was investigated. The thickness of the brick specimen was varied from about 6–15 mm. In the beginning of the experiment the specimen was immersed either in the pure water (chamber α) or in the sodium chloride concentration c_b. Concentration $c = 0.5 * c_\beta$ was used also.

The effect of different porous materials on the diffusion coefficient of sodium choride was measured also. The new red brick (NRB), the old light brick (OLB) and the old dark brick (ODB) specimen have been used in the experiments. The porosity have been determined by measuring the volume of the specimen and the mass of the fully saturated brick specimen.

5. Results and discussion

5.1. The effect of initial concentration and thickness of sample

With the help of the calibration curve $c = f(K)$ the measured conductivity (K) values were changed to the corresponding concentration values as a function of time. The rate of change of concentration (chamber α) calculated from the conductivity data is given in Fig. 2. After reaching the pseudo-stationary-state the Equation 5 can be applied to the experimental results. In our measuring geometry this took about 20–60 hours depending on the experimental conditions.

The fitting of the measured data with the Equation 5 is shown in Fig. 3. The fittings were done with the least squares method. The best fitting from the whole fitting region was find on the basis of the correlation coefficient. In a successful experiment which included about 500–700 measured datapoints (measurements of seven days) the correlation coefficient was better than 0.9995.

In Fig. 4. the diffusion coefficients are given as a function of diffusion time calulated from Equation 5, where the values of $c^{\alpha 0}$ and t_0 are taken from the

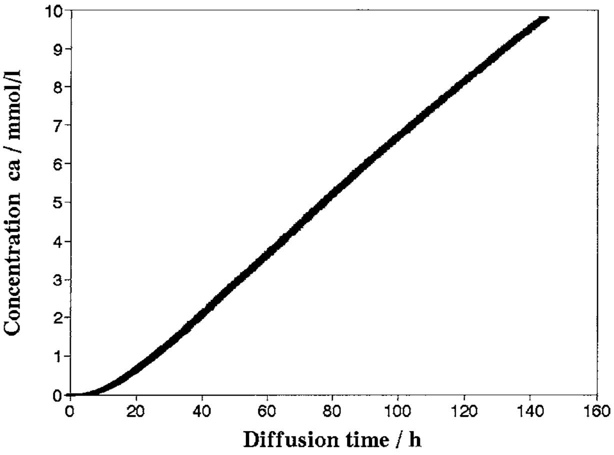

Figure 2 The rate of change of concentration in chamber alpha, $c^\alpha = f(t)$.

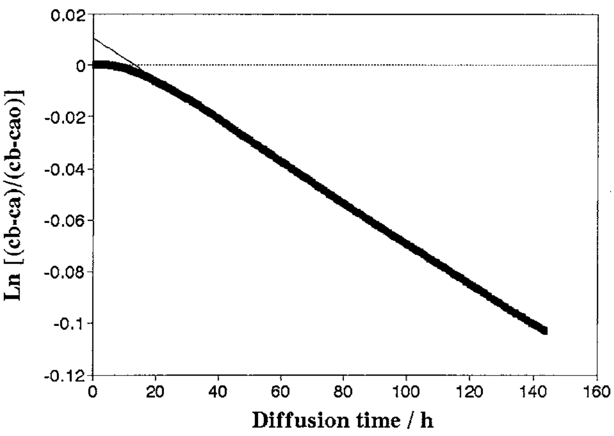

Figure 3 The least-square fitting ($t = 25$ h–144 h) of the measurement na01pc, $r = 0.99991$.

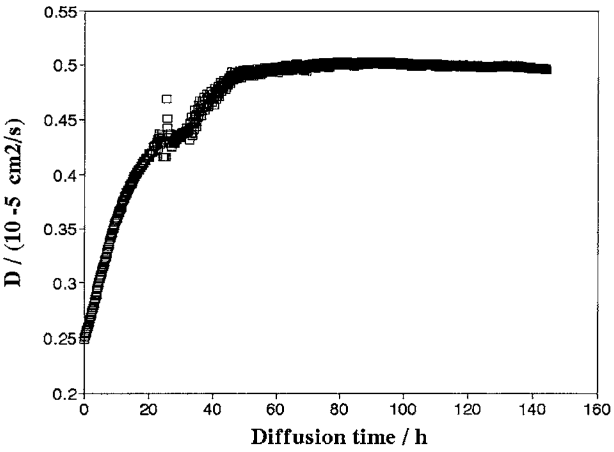

Figure 4 The diffusion coefficients calculated from equation 5, $D = f(t)$.

beginning of the stationary state. After the diffusion reaches the stationary state the value of the diffusion coefficient become constant.

The diffusion coefficients were measured with different initial concentrations of the specimen c^t (Table I). The initial concentration of the specimen did not have any statistically significant influence on the diffusion coefficient. Standard deviation in the mean (standard error) in the case of measurements started with $c^t = 0.1$ M was smaller than in the case of initial concentration $c^t = 0$. In the latter case each of the measurements took three extra days in order to get the diffusion coefficient. This result is resonable because the initial concentration of the specimen should not have any influence to the stationary state of the measurement. Only the stationary state is reached faster and more accurately when the specimen is initially immersed to the higher sodium chloride concentration $c^t = 0.1$ M. The same result was even more clearly found by starting the measurement with specimen concentration of $0.5 * (c_\alpha + c_\beta)$. By doing so we saved valuable measuring time.

TABLE I Diffusion coefficients $D_e/10^{-5}$ cm^2/s of 0.05 M NaCl at 25°C measured with two different initial concentrations of brick samples

New red brick	$\varepsilon = 0.225$	$l = 0.616$
Measurement	D_e ($c^t = 0$)	D_e ($c^t = 0.1$)
1.	0.421	0.446
2.	0.492	0.464
3.	0.543	0.491
4.	0.548	0.528
D (mean)	0.501	0.482
Std. error	0.030	0.018

ε = porosity (m^3/m^3).
l = thickness of the brick (cm).
c^t = initial concentration of the brick (mol/dm^3).

The salt diffusion coefficient was measured by using brick specimens of different thickness 1 (Table II). The thickness of the new red brick specimen did not have any significant influence on the diffusion coefficient. The observed deviation in the measured diffusion coefficients did not follow the thickness of the specimen. The reproducibility of the measurements done with thin brick specimen (6 mm) was worse compared to the measurements made with thicker specimen (10 mm and 15 mm) as could be seen by comparing the standard errors of the diffusion coefficients. The deviation is more probably explained by the heterogenity of the different specimen. In thin specimen the heterogenity of the ceramic brick is more likely to be observed.

Specimens of the same thickness taken from different parts of the brick could have different diffusivity. In order to improve the reproducibility and accuracy of the measurements the specimen were taken from the same location 10 mm from the surface of each brick. The

TABLE II Diffusion coefficients $D_e/10^{-5}$ cm^2/s of 0.05 M NaCl at 25°C measured in red brick samples of different thickness

New red brick		$\varepsilon = 0.225$	$c^t = 0.1$
Measurement		l	
D_e	0.616	1.032	1.521
1.	0.548	0.504	0.508
2.	0.491	0.496	0.495
3.	0.510	0.484	0.489
4.	0.446	0.507	0.503
D_e (mean)	0.499	0.498	0.499
Std. error	±0.02	±0.005	±0.004

ε = porosity (m^3/m^3).
l = thickness of the brick (cm).
c^t = initial concentration of the brick (mol/dm^3).

porosity of each specimen was measured separately. In all of the measurements cylindrical samples, 10 mm thick, and of the same initial salt concentration of 0.1 mol/cm^3 (chamber β) was used.

5.2. The effect of brick materials

The measured diffusion coefficients are given in Table III. The coefficients are given as an effective diffusion coefficients (D_e) calculated with the porosity value (ε) measured for each of the specimen. The effect of the different ceramic materials on the diffusivity is given in Table III, also. The biggest diffusion coefficients were measured in new Finnish red brick. In old light brick the diffusion is faster than in old dark brick.

The measured porosity values at temperature of 25°C are presented in Table IV together with the porosity values of different brick materials given in the literature [19]. In Table IV the literature values of porosities are obtained by mercury intrusion porosimetry (MIP) whereas our values were measured with capillary saturation of water. The measured porosities are still consistent with the literature values especially because our results present effective porosity values. By effective porosity we mean a measure of the volume fraction of brick accessible to the diffusing ions. The variations of the porosities are largest in old dark brick specimens as expected. The differencies in measured porosity values means that each sample must be measured individually for porosity in order to get an accurate effective diffusion coefficient.

Structural characteristics of the porous brick materials are given in Table V. From these literature values can be seen that small pore size means high inner surface area and high porosity values. These structural characteristics dosn't unequivocally explain the diffusivity variations between different brick materials. The diffusivity seems not to increase as a function of porosity of the specimen exept in old dark brick where both the diffusivity and porosity are the smallest. To explain the observed differencies in diffusion coefficients more knowledge of the materials structure is required. For example measured tortuosity and constrictivity values for each brick specimen should clarify the discovered fluctuations in diffusivity. We are still looking for ways to measure or estimate these parameters.

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

Measurement	D_e	D_e (mean)
Brick	$l = 1.0$	$c^t = 0.1$
Old light brick		
1.	0.445	0.453 ± 0.008
2.	0.469	
3.	0.446	
Old dark brick		
1.	0.319	0.337 ± 0.009
2.	0.344	
3.	0.348	
New red brick		
1.	0.495	0.499 ± 0.004
2.	0.508	
3.	0.491	
4.	0.510	
5.	0.502	
6.	0.484	
7.	0.502	

l = thickness of the brick (cm).
c^t = initial concentration of the brick (mol/dm^3).

TABLE IV The measured porosity values ε of different brick materials at 25°C (m^3/m^3)

Measurement	ε	ε (mean)
New red brick ε (lit) = 0.238		
1.	0.257	0.225 ± 0.009
2.	0.205	
3.	0.207	
4.	0.208	
5.	0.247	
6.	0.223	
Old light brick ε (lit) = 0.324		
1.	0.297	0.292 ± 0.004
2.	0.290	
3.	0.283	
4.	0.284	
5.	0.304	
Old dark brick ε (lit) = 0.120		
1.	0.162	0.177 ± 0.012
2.	0.203	
3.	0.122	
4.	0.201	
5.	0.153	
6.	0.195	
7.	0.205	

ε (lit) = mean literature value [19].

TABLE V Structural characteristics of the porous brick materials [19] and diffusion coefficients (10^{-5}) in them (in 0.05 M NaCl at 25°C)

Brick material	OLB	NRB	ODB
Volume (mm^3/g)	181	119	52
Density (g/cm^3)	1.8	2.0	2.3
Pore size[a] (nm)	40	994	7959
Surface area (m^2/g)	10.9	0.4	0.18
Porosity (m^3/m^3)	0.324	0.238	0.120
Diffusivity[b] (cm^2/s)	0.453	0.499	0.337

OLB = old light brick.
NRB = new red brick.
ODB = old dark brick.
[a]Mean value of distribution.
[b]Measured in this work.

6. Conclusions

The result for the diffusivity of NaCl in water in new Finnish red brick was $(0.499 \pm 0.004) * 10^{-5}$ cm^2/s. The coefficient obtained is a mean value of 7 measurements for the diffusion of NaCl from the concentration region of 0.1 mol/dm^3 to the pure water ($c_{\mathrm{mean}} = 0.05$ M) at the temperature of 25°C. The measured value is calculated by using the porosity value (ε) measured for each of the specimens and without any correction term for the geometrical thickness of the brick sample (tortuosity). The corresponding values for the old light brick and old dark brick was $(0.453 \pm 0.008) * 10^{-5}$ cm^2/s and $(0.337 \pm 0.009) * 10^{-5}$ cm^2/s respectively.

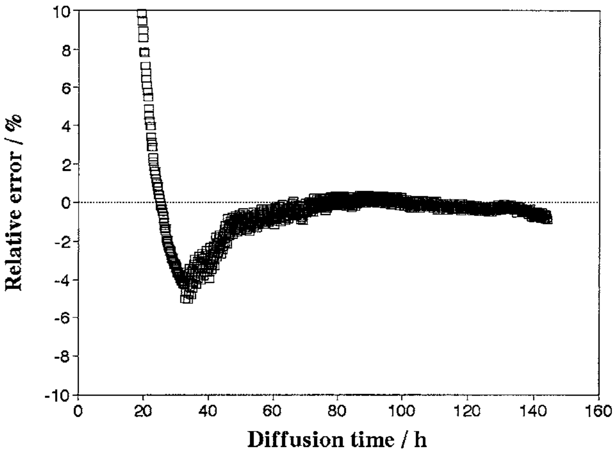

Figure 5 The relative fitting errors related to the estimation of concentration c^{α}.

It is worthwhile to emphasize that the measured D_e is a mean value or integral value of D_e in the concentration region of 0 to 0.1 mol/dm^3 of NaCl. The diffusion coefficient is a function of concentration. This can be seen very clearly by simulating the concentration of chamber α with a constant least-square fit value of $0.499 * 10^{-5}$ cm^2/s. The relative fitting error of the simulation is presented in Fig 5. The fitting error is at minimum in the middle of the measurement where the measured D_e is valid.

It is difficult to compare the results with literature values because of the lack of publised diffusion measurement data. Only two different references could be found. Nielsen [1] has measured the salt diffusion coefficients of NaCl in red brick in two different concentration of NaCl at room temperature. The values given are $(2.8 \pm 0.7) * 10^{-5}$ cm^2/s in about 5 M NaCl and $(1.9 \pm 0.3) * 10^{-5}$ cm^2/s in about 2.5 M NaCl aqueous solutions. The diffusion coefficients Nielsen has measured differ too much from our results. Their values are even higher than found in pure salt solutions [20, 21]. The high values could be explained due to greater diffusion rates on surfaces than in bulk solutions of brick capillaries. The standard error given there is also large compared to our results. The other measured literature value for diffusion coefficient of NaCl in red brick found was $0.217 * 10^{-5}$ cm^2/s. This was measured in 0.5 mol/dm^3 NaCl solution in room temperature [16]. This diffusion coefficient is too small but close to our result $0.499 * 10^{-5}$ cm^2/s measured in red brick in 0.05 mol/dm^3 NaCl solution at the temperature of 25°C. For old light brick and old dark brick we could not find any diffusivity values in literature.

The diffusion coefficient of NaCl in water in concentration of 0.05 mol/dm^3 and at a temperature of 25°C is $1.500 * 10^{-5}$ cm^2/s [22]. Compared to diffusion coefficient measured for NaCl in bulk water our results for NaCl in different brick materials are very reasonable $(0.337–0.499) * 10^{-5}$ cm^2/s. The difference of diffusivity of salt in porous medium is mainly caused by the smaller cross sectional area of solution (porosity ε), the form of the pores (constrictivity δ), the longer routes the salt ions have to travel (tortuosity τ) [23] and the interaction of salt with the medium (interface coefficient γ) [16]. 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 samples was taken into account.

The concept of the binary salt diffusion coefficient in free water solution and on the other hand in porous materials like a ceramic brick needs also discussion. This discussion of salt diffusion, which is often ignored in the literature, is needed because of the very different circumstances of diffusing ions in pores and in the free solution. In contrast to molecules and ions in the bulk, those occluded in the pore interior, both in the adsorbed state on pore surfaces or in the confined fluid state, are under the influence of the overlapped interaction force field exerted by the pore walls as explained by the double layer theory [24–26]. This fact must have some kind of contribution to the diffusion mechanism of diffusing ions and molecules in the pores.

An important parameter for the contribution of pore surface to the diffusivity of salt is the ratio of the pore size to the diffusing species and solvent molecules. In the measurements of Takahashi *et al.* [27] the diffusion resistance of nickel nitrate increases rapidly in pores of silica plates of diameter <5 nm with decreasing pore diameter. The pore-diffusion coefficient in the micropores was measured to be even less than 0.01 of the diffusion coefficient in an unbounded system (in our measuring system only less than 0.3). An interesting question is also the meaning and the effect of the surface diffusion on the measured diffusion coefficient values and its relation to the charge and concentration of the diffusing ions.

At this moment we are measuring the concentration and temperature dependence of the diffusion coefficient of NaCl in ceramic brick. We are also measuring the diffusion coefficients of different electrolytes in brick and will compare them to the diffusivity of NaCl.

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