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Studying of salt diffusion behaviour in brick

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Abstract In this paper, an analysis of the diffusion behaviour of salts in fully saturated brick is presented. This paper extends the previous work to including more salt types and measurement data. Dependence of diffusion coefficient on temperature and other factors is discussed. Starting from the mathematical model which has been verified before, the obtained results are 2-fold: first the diffusion coefficients for different types of salts are given which are evaluated from measurements; moreover, dependence of temperature and ambient salt concentration on diffusion coefficient is presented.

Introduction

Brick is a common porous material used in building construction. Looking at its various ways of deterioration, it is clear that salt solute plays an important role [1]. In Mediterranean countries where the freezing and thawing action is not present or not severe, the most important cause of damage is salt crystallisation [2]. Due to high maintenance and repair costs, the deterioration of brick by salt attack should be predicted. Most important, modelling of the salt transport process must be performed.

Salt transport in brick is affected by a number of factors which are related to the characteristics of the brick, the composition of the salt solution and the environmental condition. When saturated at normal pressures the solute transport process is likely to be diffusion [3]. The diffusion process is commonly assumed to be governed by Fick's law. A fundamental parameter describing the resistance of the brick to the salt transport is the diffusion coefficient, D, which can vary with salt, salt concentration, ambient temperature and many other parameters. However, in practical experiments, D is often defined as constant because lack of the diffusion measurement data. Very often, techniques such as concentration profile, diffusion cell, electrical conductivity and destructive methods by drilling or grinding the sample are used to determine D [3–6].

Studying the literature of salt diffusion in brick, however, it is concluded that researches on this topic are lacking. Most of the related papers are limited primarily to specific applications with regard to diffusion behaviour of concrete. As concrete contains very fine pores, the measurement techniques which are commonly used for brick to determine D are time-consuming, and thus electrical methods are normally applied to accelerate the diffusion process. The process is then modelled by Nernst–Planck equation [7, 8]. As a result, the study method on diffusion in brick may be quite different from that on concrete.

In two previous papers, the transport of sodium chloride (NaCl) in brick was studied [9, 10]. During

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further testing of salt diffusion, it was shown that a change in a type of salt solution can significantly affect the rate of the salt diffusion into the brick. As there are many attacking salts found in brick such as NaCl, sodium carbonate (Na_2CO_3), calcium chloride ($CaCl_2$), etc, a more complete analysis of the diffusion behaviour of most commonly found attacking salts is presented in this paper. Moreover, prediction of the transport by diffusion of combined salt solution needs information of the diffusion process for each salt solution. Therefore, determination of the diffusion behaviour of each salt type solution in brick is important and this paper is concentrating on this research topic: diffusion of commonly found salts in fully saturated brick is analysed with diffusion cell measurements and numerical methods. Furthermore, effects on the diffusion process of various parameters are discussed with the verified mathematical model. As a representative sample of ceramic engineering brick, a new red brick manufactured commercially for buildings is selected in this work.

Experimental and mathematical model

Experiment

The diffusion cell method is adopted to determine the diffusion coefficient of salt which is displayed schematically in Fig. 1. Originally this porous diaphragm technique method was used for measurements of salt diffusion coefficients in aqueous solutions [4]. The thin membrane used in solution measurements has been substituted here with a saturated thin brick slice placed between two solution chambers α and β. The solutions on each side of the brick were maintained at a uniform concentration right up to the surfaces of the brick by mechanical stirring of the solutions. Provided certain conditions are satisfied, D can be estimated with a series of salt concentrations in chambers measured by monitoring increases in the electrical conductance as a function of time.

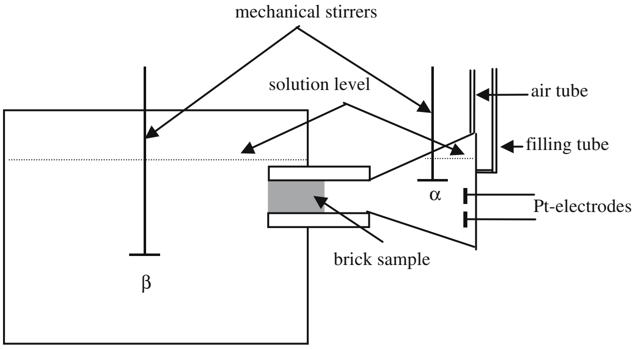

Fig. 1 Schematic picture of measurement equipment (not in scale)

In this study, ordinary cylindrical shaped new red brick samples were used with different diameters and thickness. The brick is very permeable for both water and salt meaning that osmotic pressure cannot developed over them. This has been tested in our laboratory. The diffusion cell, including the conductivity cell, was kept at a constant temperature using a thermostatically controlled water-bath. Reliable temperature control is important because both the diffusion and the conductivity are very sensitive to temperature changes. The accuracy of the temperature control inside the diffusion cell was ± 0.05°C. The hydrostatic pressure generated by different solution densities in both chambers was equalized with different heights of the solution levels. The hydrostatic equilibrium was quickly reached in about 10–30 min when the solution level in chamber α (initially pure water) was 0.079–3.34 mm higher than that in chamber β depending on its concentration (0.1–6.16 mol/dm^3). This time period is much shorter than that required achieving quasi-steady-state condition (at least 10 h). A more detailed description of the measurement equipment and techniques were given at [4, 5].

Mathematical model

Mathematical equations of one-dimensional salt diffusion in a homogeneous isotropic brick is described by Fick's law as:

$$\frac{\partial C}{\partial t} = \frac{\partial C}{\partial x}\left(D\frac{\partial C}{\partial x}\right) \tag{1}$$

where C (mol m^{-3}) is the salt concentration in brick and D (m^2 s^{-1}) is the salt diffusion coefficient in brick.

The following initial and boundary conditions are applied in the diffusion cell measurement for two chambers and the sample:

$$C = C_{\alpha_0}, \quad C = C_0 \quad L > x > 0 \quad t = 0 \tag{2}$$

$$C = C_\alpha, \quad A\varepsilon D\frac{\partial C}{\partial x} = V_\alpha \frac{dC_\alpha}{dt} \quad x = 0 \quad t > 0 \tag{3}$$

$$C = C_\beta, \quad A\varepsilon D\frac{\partial C}{\partial x} = -V_\beta \frac{dC_\beta}{dt} \quad x = L \quad t > 0 \tag{4}$$

where α presents the chamber α, β the chamber β, L(m) the length of the brick sample, A(m^2) the area of the brick sample which is exposed to chambers, ε(m^3 m^{-3})

the porosity of the brick sample, $V_\alpha(\mathrm{m}^3)$ the volume of the chamber α, $V_\beta(\mathrm{m}^3)$ the volume of chamber β, $C_{\alpha_0}(\mathrm{mol\ m}^{-3})$ the initial salt concentration in chamber α, $C_0(\mathrm{mol\ m}^{-3})$ the initial salt concentration in brick, $C_\alpha(\mathrm{mol\ m}^{-3})$ the salt concentration in chamber α and $C_\beta(\mathrm{mol\ m}^{-3})$ the salt concentration in chamber β.

Equations 3 and 4 assume that the rates of the changes of salt contents in chambers are equal to the rates of diffusion flow of salt from the brick into the chambers. If the volume ratio of chamber β and chamber α is big in the sense that when equilibrium reaches the concentration in one of the chambers, say chamber β, changes small, then the boundary condition (4) at $x = L$ can be simplified as the following:

$$C_\beta = \mathrm{const}, \quad C = C_\beta \quad x = L \quad t > 0. \tag{5}$$

In our tests we assume Eq. 5 is satisfied throughout the whole test. This assumption will be discussed in the next section. As the diffusion starts, salt in chamber β diffuses through the brick sample to the chamber α. The salt concentrations in chamber α are measured at a series of time periods. The salt diffusion coefficient D in brick is then calculated from the measured data.

The diffusion coefficient D can be estimated as follows: assuming at time $t > t_0$, steady-state is reached, integrating Eq. 3 and collecting term gives the following formula which is used to estimate D:

$$\varepsilon D = \ln\left(1 + \frac{C_\alpha - C_{\alpha_0}}{C_\beta - C_\alpha}\right)\frac{V_\alpha L}{A(t - t_0)}. \tag{6}$$

As $C_\alpha \ll C_\beta$, Eq. 6 can be simplified as

$$\varepsilon D = \frac{C_\alpha - C_{\alpha_0}}{C_\beta}\frac{V_\alpha L}{A(t - t_0)}. \tag{7}$$

In [8], an approximated analytical solution for the diffusion cell measurement (Eqs. 1–3, 5) has been developed as

$$C_\alpha = C|_{x=0} = (C_\beta - C_0) + (C_{\alpha_0} - C_\beta)\exp\left(-\frac{t}{d}\right) + C_0 \tag{8}$$

where d is defined as

$$d = \frac{V_\alpha L}{\varepsilon A D} + \frac{L^2}{2D}. \tag{9}$$

Note that the characteristic number d is of the fundamental importance in determining the salt transport process in brick and thus in chambers. It has a time unit.

Basic parameters

As the diffusion coefficients are not read directly from measurements, various measurement parameters may affect the accuracy. Statistical analyses are made in order to (1) test the significance of the dependent parameters and determine the dependence of the diffusion coefficient on the dependent parameters, (2) evaluate the diffusion coefficient D for different specimens for the same brick and salt, (3) estimate the diffusion coefficient D for different types of brick and (4) determine the diffusion coefficient D for different type of salts. Linear regression method was adopted.

To see the effect of the ambient temperature on diffusion coefficient, salt NaCl was selected as an example. Statistical study shows that D depends on the temperature. The relation is

$$D = 0.00033 \times T^2 + 0.006 \times T + 0.15 \tag{10}$$

where T = 8–25 °C.

It was also found that D depends on the ambient salt concentration, the relation is

$$D = 0.03912 \times C_{\mathrm{mean,\,ambient}}{}^2 - 0.12606 \times C_{\mathrm{mean,\,ambient}} - 0.498384 \tag{11}$$

where $C_{\mathrm{mean,\,ambient}}$ is the external solution mean salt concentration and

$$C_{\mathrm{mean,\,ambient}} = 0.05\,\mathrm{mol\,dm}^{-3} - 3.08\,\mathrm{mol\,dm}^{-3}.$$

Both Eqs. 10 and 11 are valid for the salt NaCl only. Furthermore, seven different types of salt diffusions were made in total. It is well-known that the major difficulty in determining D is the inconsistency for different specimens. To assess this effect by statistical analysis the estimated average D for different types of salts and bricks is reported in Table 1. Validation of these data is demonstrated in the following section.

Based on Table 1, a ranking can be obtained for some typical salt solutions for new red brick as

$$D_{\mathrm{CaCl_2}} < D_{\mathrm{NaCl}} < D_{\mathrm{KCl}}. \tag{12}$$

Table 1 Salt diffusion coefficient D (10^{-5} cm^2 s^{-1})

25 °C	NaCl	KCl	$CaCl_2$	Na_2CO_3	$NaNO_3$	Na_2SO_4	$MgCl_2$
New red				brick	0.499	0.544	0.321
0.271	0.425	0.291	0.305				

This sequence is the same as the increase of the relative viscosity $\eta_{\mathrm{rel}}(\mathrm{CaCl_2}) > \eta_{\mathrm{rel}}(\mathrm{NaCl}) > \eta_{\mathrm{rel}}(\mathrm{KCl})$. This mutual relation between the viscosity and the diffusivity was already recognized by Gordon [11], but in the absence of porous material.

This ranking of the diffusion coefficients is exactly the same as observed in pure electrolyte-water solutions in the whole concentration region at 25 °C from infinite dilution to the saturated solution [12]. The lagging motion of the cations will retard the drift velocity of the chlorides in the increasing order of K^+, Na^+ and Ca^{2+}. This ranking of diffusion coefficients is also very similar to that observed in porous compacted sodium bentonite (montmorillonite clay), where a clear correlation between the ionic radius and apparent diffusivities was observed. The divalent cations (Ca^{2+}, Sr^{2+}, Ba^{2+}) had lower diffusivities than monovalent cations (Na^+, K^+) of comparable unhydrated size. The diffusivities obtained suggest that the ion with the largest unhydrated radius suffers the greatest reduction in mobility while diffusing in clay in stead of pure water [13–15].

The ranking is not completely the same as reported in the literatures for concrete, which shows that [16–18]

$$D_{\mathrm{NaCl}} < D_{\mathrm{KCl}} < D_{\mathrm{CaCl_2}}. \tag{13}$$

This ranking is not quite comparable to our measurements because of the following reasons: first, the chloride concentration, instead of salt concentration, was kept constant in their measurements [16–18]. Second, difference in pore structures, pore sizes and the electrical double layer of the pore walls exists in brick and concrete. In the fine pores of concrete the diffusing ions are interacting more frequently with pore walls than in the case of diffusion in brick. Hence the well-known chemical chloride binding and surface diffusion may significantly interfere with the transport of the chloride ions [19]. Third, the diffusion coefficients in concrete have been measured with migration tests where ions are driven by applied electrical potential rather than by a concentration gradient like in our natural diffusion tests. The possibility of developed electroosmosis as a side effect in migration method could also be an explanation of the discrepancy [20, 21]. The diffusion behaviour of salts in concrete is also a more complex and complicated transport process than what can be described by Fick's law of diffusion [22].

Validation and discussions

Validation

The measurements were divided into three groups in order to see validation and analysis results of the evaluated D in section "Basic parameters" based on the statistical analysis. The mathematical model has been validated [8, 9]. Note that the diffusion coefficient D is determined from the measurement by assuming the steady-state condition is achieved. Hence the determination of D depends on the measurement time duration. The longer the time duration is, the smaller the estimated error is achieved. However it is unrealistic to wait for too long time in each measurement. Theoretically, the steady-state condition is achieved when salt concentration changes in both chambers α and β are neglected. However, the diffusion cell measurement requires a concentration change in chamber α. Hence only quasi-steady-state condition is set on the sample.

In the Table 2 of [23], it was shown the estimation error of D can be neglected if the time required for reaching the quasi-steady-state conditions is less than 20% compared to the total measurement duration time. If the time t_0 represents the lower bound of the time required to achieve quasi-steady-state condition, all of our measurement duration time is longer than $5t_0$. The time t_0 also presents the time required for detectable salt quantities diffuse through the specimen. Hence in the following validation calculations, the analytical and the numerical results are applied when $t > t_0$.

Table 2 Specimen properties, group I

New red brick	A (cm^2)	L (cm)	ε (cm^3/cm^3)	V_α (cm^3)	V_β (cm^3)	$D \times 10^{-5}$ (cm^2 s^{-1})	C_{α_0} (mmol L^{-1})	C_β (mmol L^{-1})	C_0 (mmol L^{-1})
Group I, NaCl									
Sample 1 (8 °C)	4.83	1.04	0.223	23.51	2200.0	0.219	0.97	100.0	100.0
Sample 2 (13 °C)	4.83	1.04	0.223	23.51	2200.0	0.284	0.48	100.0	50.0
Sample 3 (18 °C)	4.83	1.04	0.223	23.51	2200.0	0.365	0.26	100.0	50.0
Sample 4 (25 °C)	4.83	1.04	0.223	23.51	2200.0	0.506	0.22	100.0	50.0

Dependence of D on temperature

Table 2 sumarizes briefly the sample properties in group I. Salt was chosen as NaCl. The corresponding calculated salt diffusion coefficients of NaCl from Eq. 10 and Table 1 are also presented in the same table. In this group, the variation parameter is the temperature. The lower bounds of the required time to reach the quasi-steady-state conditions were taken as 10, 10, 10 and 20 h and the measurement duration periods were 115, 111, 115 and 163 h. Thus the time required for reaching the quasi-steady-state conditions was less than 13% compared to the total measurement duration time in group I. This number is smaller than 20% which was suggested by Glass and Buenfeld [23] for guaranteeing the quasi-steady-state condition. In the following two groups, all of the measurement time duration fulfilled this requirement. We shall not present this here in order to save the space.

Validation results for group I are displayed in Fig. 2a–d. It can be seen that the calculated results agree with the measured results. To see the effect on salt transport of different temperatures, Fig. 3 demonstrates the salt distributions at time $t = 163$ h for sample 4 with different temperatures. The result shows that the higher the ambient temperature is, the faster the salt diffuses through the sample. Assume one side of the brick (sample 4 in group I) is exposed to the same environment as chamber β as shown in Table 2, Fig. 3 shows that after 163 h, the salt concentration in the other side is doubled with the ambient temperature at 25 °C compared to that with the ambient temperature at 8 °C. Therefore, in simulating salt diffusion in brick, temperature effect must be taken into account.

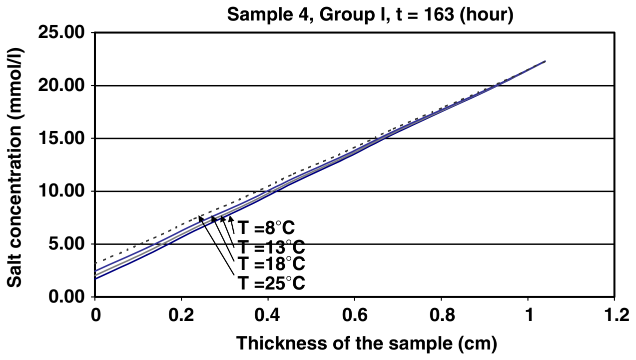

Fig. 3 Calculation of salt distributions for brick sample with different temperatures

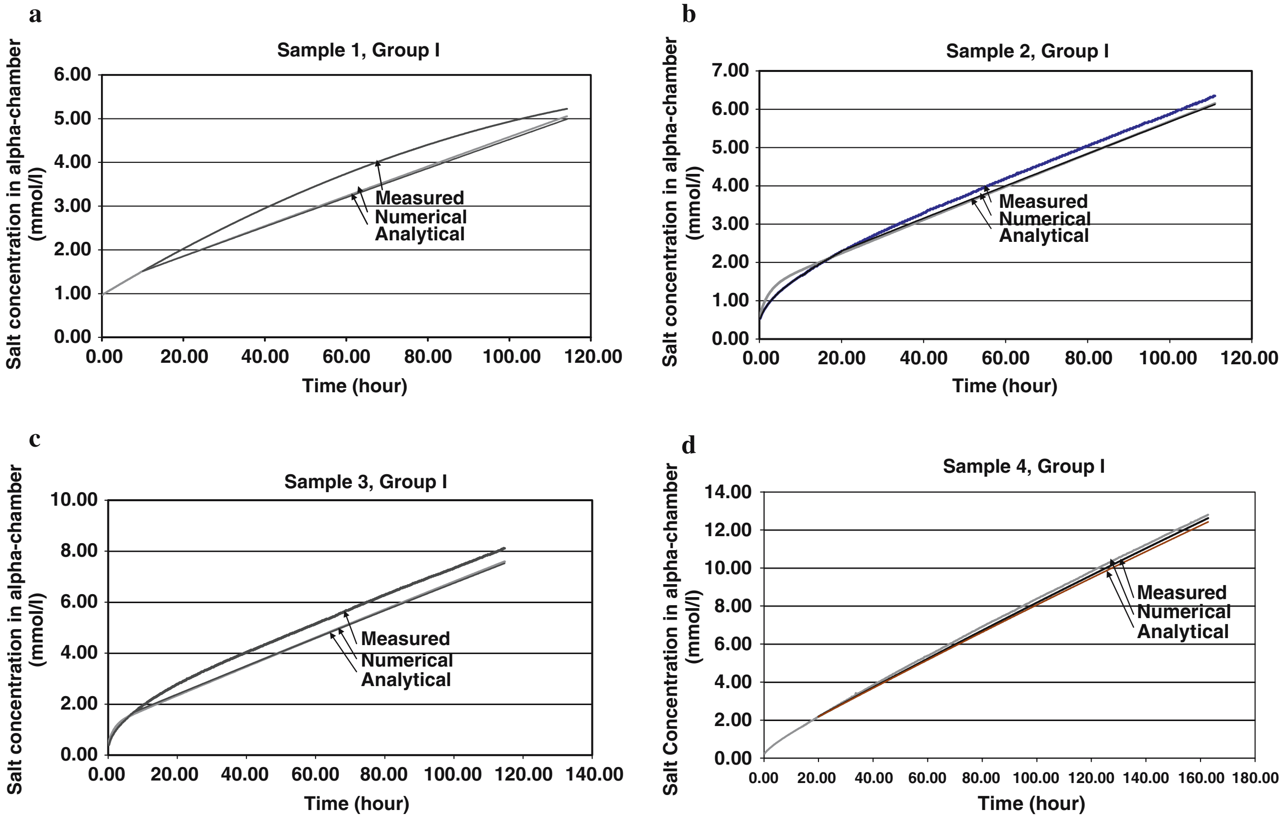

Fig. 2 Calculation of salt concentrations in chamber alpha for (**a**) sample 1, (**b**) sample 2, (**c**) sample 3, (**d**) sample 4, group I

Table 3 Specimen properties, group II

New red brick	A (cm^2)	L (cm)	ε (cm^3/cm^3)	V_α (cm^3)	V_β (cm^3)	C_{α_0} (mmol L^{-1})	C_β (mmol L^{-1})	C_{α_0} (mmol L^{-1})
Sample 5 (KCl)	4.83	1.04	0.231	23.51	2200.0	0.48	100.0	100.0
Sample 6 ($CaCl_2$)	4.83	1.04	0.231	23.51	2200.0	0.03	100.0	50.0
Sample 7 (Na_2CO_3)	4.83	1.04	0.231	23.51	2200.0	0.17	100.0	50.0
Sample 8 ($NaNO_3$)	4.83	1.04	0.231	23.51	2200.0	0.18	100.0	50.0
Sample 9 (Na_2SO_4)	4.83	1.04	0.231	23.51	2200.0	0.28	100.0	100.0
Sample 10 ($MgCl_2$)	4.83	1.04	0.223	23.51	2200.0	0.12	100.0	50.0

Dependence of *D* on salt

Table 3 presents the sample and chamber properties in group II. Different types of salt solution were selected, see Table 1 for the diffusion coefficients. Temperature is kept at 25 °C. Validation results are displayed in Fig. 4a–f. To see the effect on salt transport of different salt solution, Fig. 5 demonstrates the salt distributions

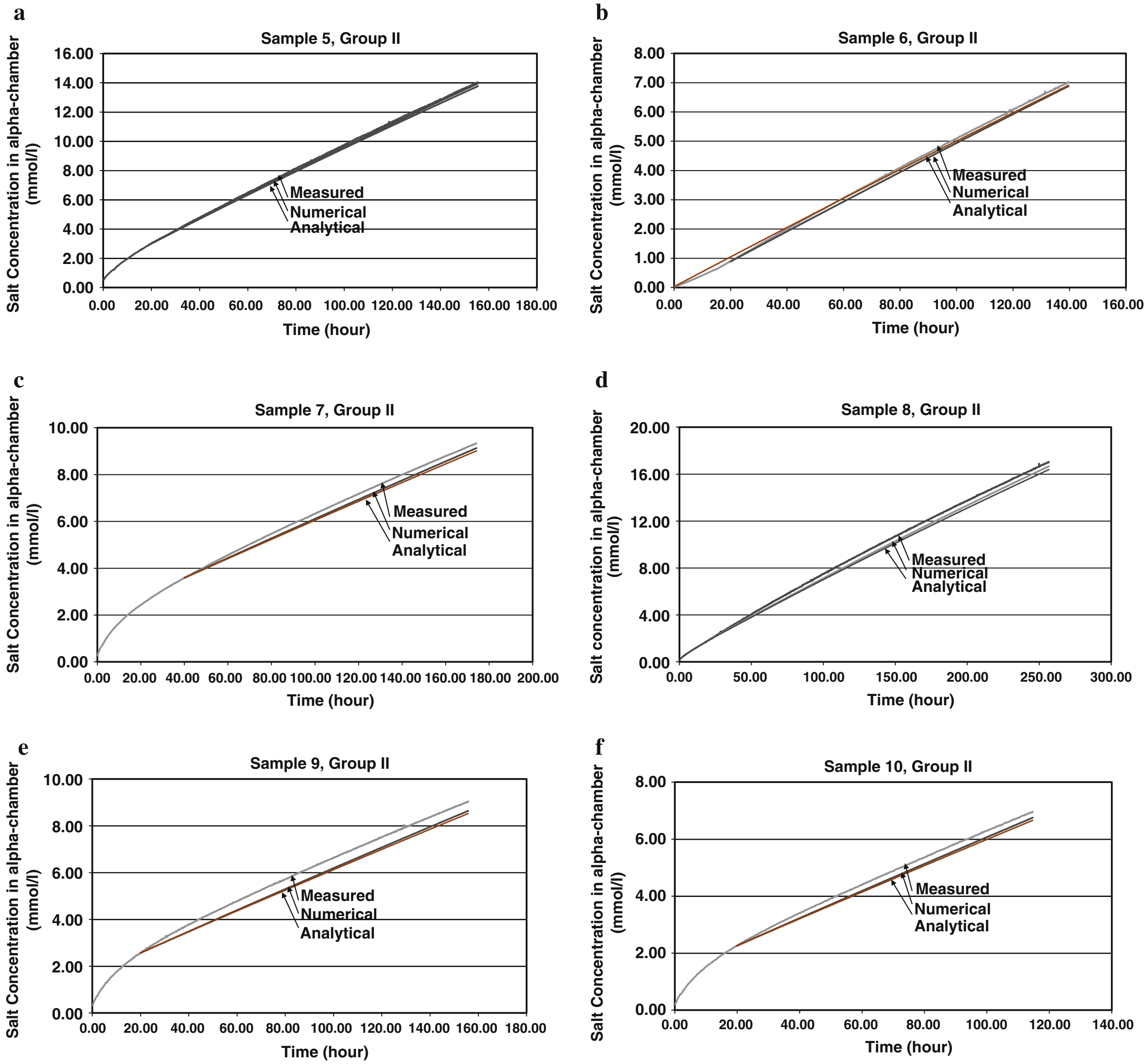

Fig. 4 Calculation of salt concentrations in chamber alpha for (**a**) sample 5, (**b**) sample 6, (**c**) sample 7, (**d**) sample 8, (**e**) sample 9, (**f**) sample 10, group II

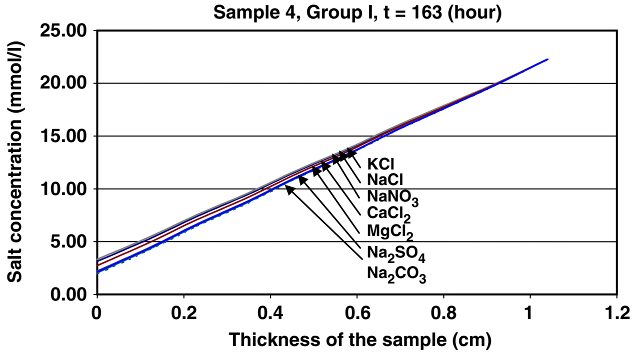

Fig. 5 Calculation of salt distributions for brick sample with different salt solutions

at time $t = 163$ h for sample 4 with different salt solution. Differences are clearly shown in the figure.

Dependence of *D* on concentration

Table 4 shows the sample and chamber properties in group III. The varied parameter here is the salt concentration in chamber β, or the ambient salt concentration. NaCl is chosen as the salt example. Temperature is kept at 25 °C. Dependence of the ambient salt concentration on the measured salt diffusion is demonstrated in Eq. 11. Validation results are displayed in Fig. 6a–d. Assume one side of the brick (sample 4 in group I) is exposed to the same environment as chamber β as shown in Table 4, Fig. 7 shows that after 163 h, the salt concentration distributions for sample 4 with four different salt diffusion D's evaluated from the measurements. The difference is very little. Therefore, in many practical diffusion problems the ambient concentration dependence of diffusion coefficient can be ignored for simplicity when dealing with salt diffusion in brick.

Measurement parameters

The validation of the diffusion cell measurements requires that the volume of the chamber β is big enough in such way that when the system reaches an equilibrium stage, the change of salt concentration in β can be ignored. The influence of this parameter is determined by actually both the volume β and the salt concentration in β. If Eq. 4 is used instead of the simplified Eq. 5, the final salt concentrations in β are 599.9, 1999.9, 6159.9 and 99.7 mmol L^{-1} which corresponding to 600.0, 2000.0, 6160.0 and 100 mmol L^{-1}. Thus Eq. 5 is a good approximation. The result also demonstrates that the volume of β is big enough in our diffusion cell measurement.

Conclusions

This paper presents a study of salt diffusion in new red brick with different types of salt solution. The most important conclusion to be drawn is the diffusion coefficients obtained from measurements and statistical analysis which are most valuable for building scientists. The analytical and numerical data are compared with the measurement data. Good agreement is achieved. Second, ambient temperature plays an important role in salt diffusion process. The dependence on temperature of the diffusion coefficient for NaCl was constructed in this paper. Third, with the verified mathematical model, the effects on determining diffusion coefficient of measurement parameters were studied. It is worth mentioning that these data have been verified by many experiments which have not shown in this paper due to the space limitation.

The measured binary diffusion coefficient for NaCl varied with concentration according to the Eq. 11. In most of the practical research work in brick structures, D can often be defined as constant for simplicity. As we can see from the validation figures presented in this paper, the constant D gives a satisfactory result. In our previous work, dependence of D on salt concentration has been studied also. Based on some of other measurements, a concentration dependent D is estimated with the help of statistical analysis [24]. The

Table 4 Specimen properties, group III

New red brick	A (cm^2)	L (cm)	ε (cm^3/cm^3)	$D \times 10^{-5}$ ($cm^2\ s^{-1}$)	V_α (cm^3)	V_β (cm^3)	C_{α_0} (mmol L^{-1})	C_β (mmol L^{-1})	C_0 (mmol L^{-1})
Sample 11	4.83	1.04	0.223	2200.0	0.454	23.51	1.70	600.0	600.0
Sample 12	4.83	1.04	0.223	2200.0	0.415	23.51	14.14	2000.0	1000.0
Sample 13	4.83	1.04	0.223	2200.0	0.481	23.51	157.21	6160.0	3080.0
Sample 14	4.83	1.04	0.223	2200.0	0.499	23.51	11.56	100.0	50.0

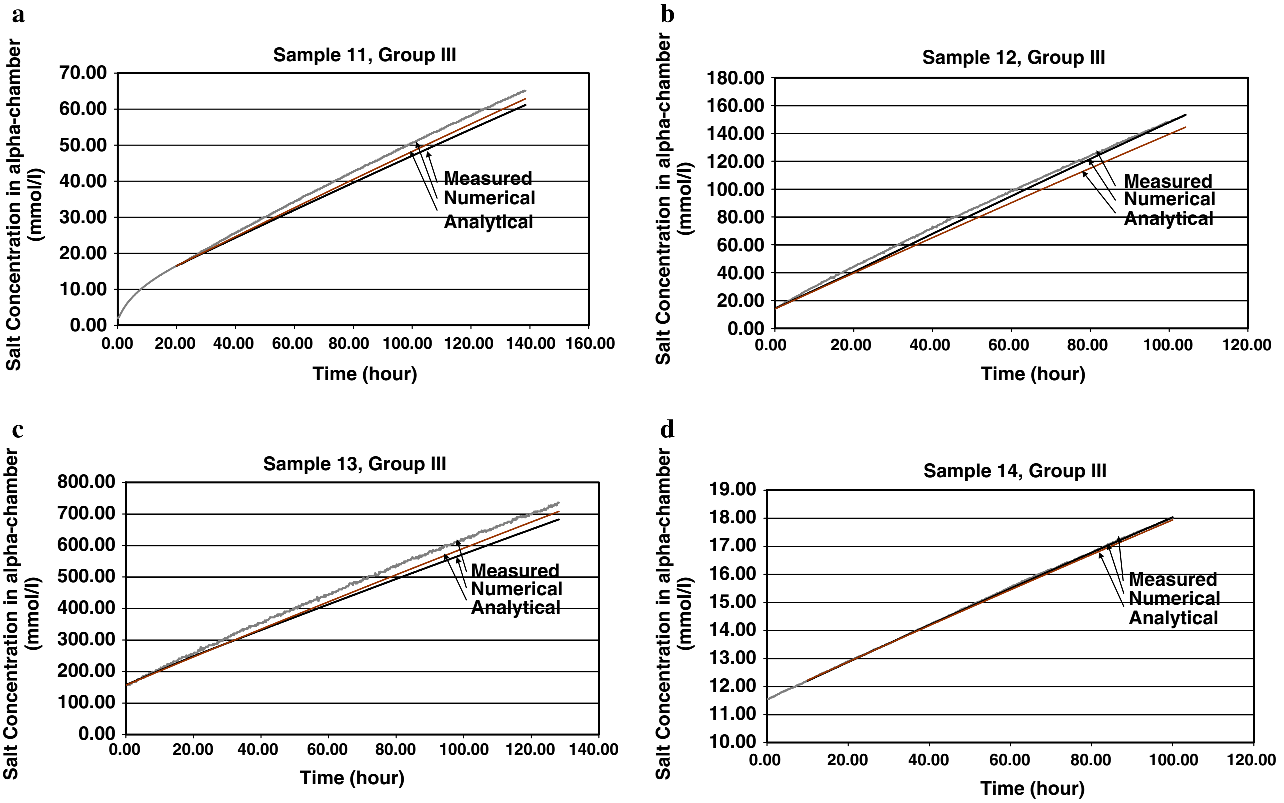

Fig. 6 Calculation of salt concentrations in chamber alpha for (**a**) sample 11, (**b**) sample 12, (**c**) sample 13, (**d**) sample 14, group III

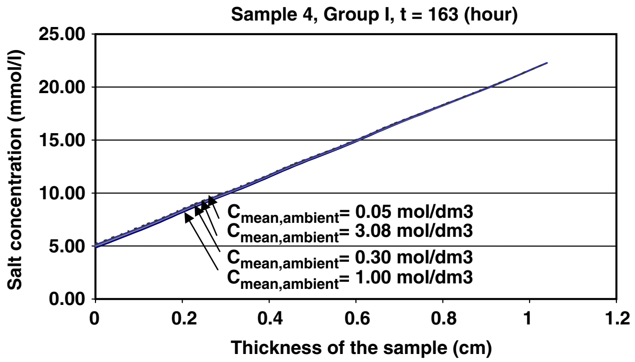

Fig. 7 Calculation of salt distributions for brick sample with different mean salt concentrations

function of D shown in [24] is an inverse function of the salt concentration. The result is consistency with the measurement made by Andrade and Whiting [25] for concrete.

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