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Determination of the Ion Diffusion Coefficient in Moisture and Salt Loaded Masonry Materials by Impedance Spectroscopy

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Summary

The presented work is part of a doctorate project dealing with ion transport in moisture and salt loaded masonry materials due to desalination processes (Buchwald [1]). One of the main subjects of the project was the determination of diffusion coefficients of salt ions in masonry materials such as brick, mortar and sandstone. Beside the usage of diffusion experiments the impedance spectroscopy has also be applied. It will be shown that the determined diffusion coefficients are very good comparable to those from diffusion experiments. Therefore the advantages and disadvantages of the method are discussed. Apart from this, the article presents the results due to the influence of water content on the ion diffusion coefficient in pore systems of different masonry materials.

1 Introduction

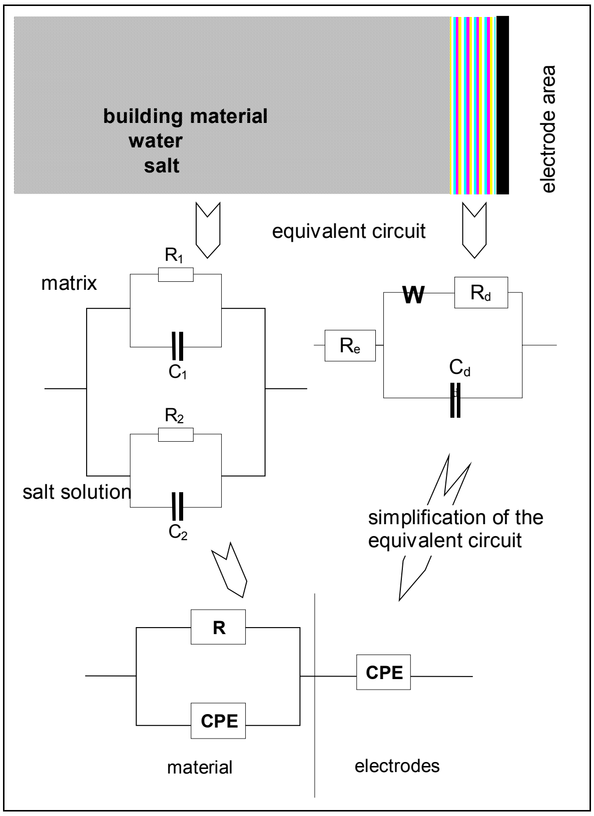
The existence and movement of water and damaging salts are at the origin of numerous types of decay observed in masonry. Salt migration can be subdivided at least into two processes based totally on different mechanisms. Ions of dissolved salts can be transported with the migrating water. The second transport mechanism is the ion diffusion driven by a concentration gradient. In practice these mechanism comes into play to remove dissolved ions from salt containing masonry by application of a compress. For the calculation of the duration of such a desalination process the knowledge about salt diffusion coefficient is necessary. The diffusion coefficient of the ion pair of Na^+ and SO_4^{2-} in fully saturated brick material were recently presented (Buchwald [2]). Nevertheless in reality the water saturation is much less than 100 %. Therefore the diffusion coefficient were determined by impedance spectroscopy measurements at lower water contents as well.

2 Impedance Spectroscopy

The method of impedance spectroscopy is widely used to measure electrical or dielectric properties of materials, coatings etc.. Apart from the direct interest in an electrical property, the usage of impedance spectroscopy will be successful if any changes of the physical or chemical properties lead to changes of the electrical properties as well. Therefore many research has been done to use impedance spectroscopy in civil engineering. A lot of investigation were reported about cement hydration (Gu [3], Ramachandran [4]) and structural parameter of hardened concrete (McCarter [5], Gu [6], Xie [7]). Impedance spectroscopic investigation were also be used to determine the diffusivity of alkali ions in zeolithe structures (Wassener [8]).

The general approach is to apply an electrical stimulus (sinus shaped voltage impulse) to the electrodes and observe the response (the resulting current). This is done over a wide frequency range. To discuss the electrical properties of the sample and the correlated properties as well it has to be construct a physical model of the system sample-electrodes. This will be transformed in to an equivalent circuit in which electrical circuit elements (resistance, capacitor etc.) symbolise the electrical behaviour of the whole system. Afterwards the parameters of the equivalent circuit elements were fitted to the experimental data using complex non-linear least squares (Macdonald [9]).

The used equivalent circuit and its derivation are shown in Picture 1. As first one can see the sample consist of the porous matrix material containing water and salt in the pore system. the sample is contacted to the electrodes, schematically drawn on the right side. The electrical behaviour of the sample material can be symbolise by a parallel circuitry of two RC-elements (parallel circuitry of an ohms resistance and a capacitor). This parallel circuitry can be replaced by a summarised one and the capacitor can be replaced by a CPE-element because of the non-ideal behaviour of real materials. The electrical behaviour of electrode zone has been simplified by a CPE as well.



Picture 1 Derivation of a equivalent circuit of moisture and salt loaded building materials

3 Materials

The investigated building materials include brick, mortar and sandstone. Beside these materials porous glass as a model material were used, which has a similar pore structure at different pore diameters. An overview about the porosity characteristics are given in Table 1. It can easily be seen, that the porous glass material represent a broad spectrum of porosity properties where the building materials can be inserted. The pore structure of the sandstone and the porous glass materials are similar. The porosity of the brick material is formed by small gaps mainly orientated in extrusion direction. The mortar contains two different kind of porosity, ones the capillaries and as second the big air holes.

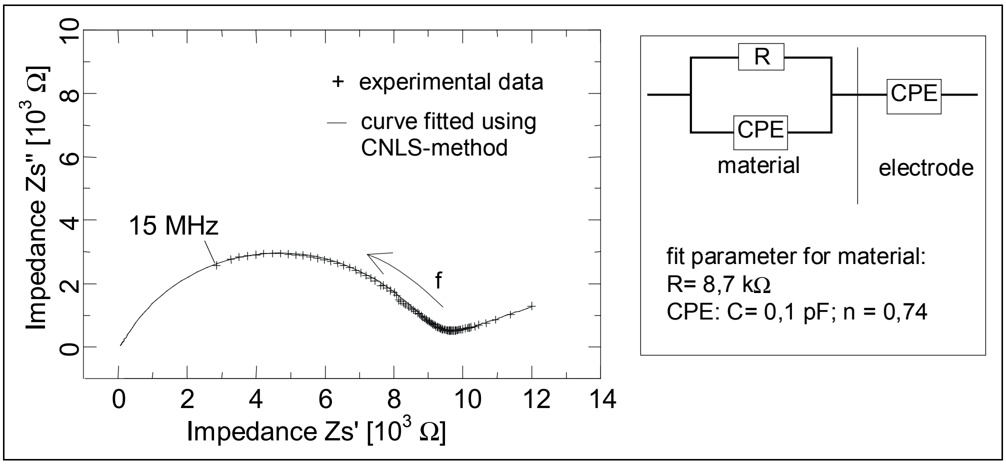
		bulk density [g/cm^3]	density [g/cm^3]	true porosity [vol.-%]	apparent porosity [vol.-%]	coefficient of water adsorption [kg/m^2√h]	permeability to gases [10^{-14} m^2]	medium pore diameter [µm]
brick	Z1	1.81	2.81	36	34	19	0.45	2
lime mortar	Mo	1.80	2.65	32	31	6	6.8	2 / 200
sandstone 1	S1	2.15	2.63	18	17	1...4	1...3	0.5
sandstone 2	S2	2.07	2.69	23	22	9...20	8...14	50
porous glass 1	P1	1.35	2.39	43	39	-	11.6	100
porous glass 2	P2	1.27	2.33	45	43	-	11.2	80
porous glass 3	P3	1.70	2.33	27	23	-	5...8	22
porous glass 4	P4	1.69	2.31	27	24	-	6.5	10
porous glass 5	P5	1.68	2.28	26	24	-	0.25	0.9

Table 1 Porosity characteristics of the used materials

4 Determined Investigations

Cylinder shaped samples with 18 mm in diameter and 5 to 35 mm thickness were used for impedance spectroscopy in a SI 1260 impedance analyser. The samples were impregnated with salt solution, mainly 0,01M Na_2SO_4. For best electrical contact between sample and electrode, silver coated gum were used to avoid artefacts due to surface resistance (Hwang [11]). After the measurement was done the next (lower) moisture content were fixed by microwave impulse drying. The so prepared sample has been measured again in the impedance spectrometer. The measurements were done in the frequency range 10 Hz to 15 MHz and using a voltage amplitude of 0,1V.

If plotted in the complex impedance plane (Nyquist-plot), the IS-data form a depressed arc in the high-frequency zone which goes over in a straight line at lower frequencies. A typical curve of a salt and moisture impregnated sample is shown in Picture 2. The bulk resistance R is then found as the interception of the high frequency-arc and the real axis using the indicated equivalent circuit (Picture 1) for fitting the experimental data.



Picture 2 Nyquist plot and equivalent circuit of a typical sample (f-frequency; Circuit elements: R-resistance, CPE-constant phase element with C-capacity and n- arc-depressing factor).

The conductivity σ_{eff} of the material can then be determined using R and the geometry h (thickness of cylinder) and A (area of cylinder):

$$\sigma_{eff}=\frac{h}{R\,A} \qquad (1)$$

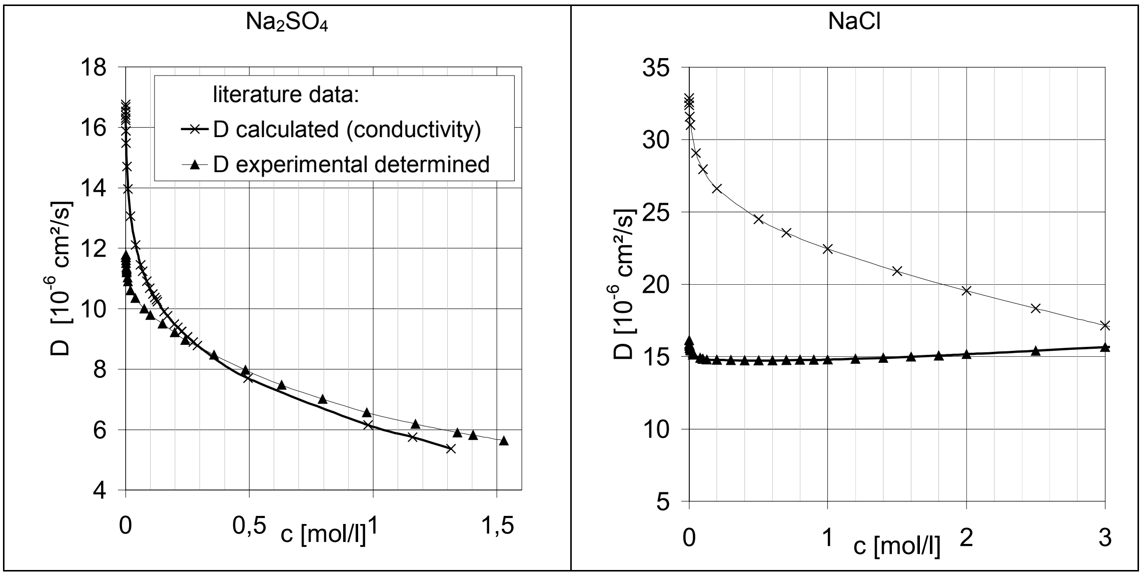
Using Nernst-Einstein-relation, the diffusion coefficient D_{eff} can be calculated from σ_{eff} and the salt concentration in the sample c_{salt} (Kudo [11]):

$$D_{eff}=\sigma_{eff}\frac{kT}{z_i^2 F e c_i} \qquad (2)$$

k: Boltzmann constant
T: Temperature
z: charge number
F: Faraday constant
e: electron charge

Looking at literature data of Diffusion coefficients of salt ions in free solutions determined in diffusion experiments and calculated from measured conductivity, a discrepancy will be seen. Picture 3 shows these data for the salt solutions Na_2SO_4 and NaCl (Lobo [12]). Looking on the left diagram, one can see an decreasing diffusion coefficient with increasing concentration of the salt solution. Both curves from conductivity and from diffusion experiment are quit similar but not identically. The sodium chloride shows a different behaviour. The diffusion coefficient from diffusion experiments increase with concentration. These effects can be due to ion pair building for example (Bockris [13]).

If ones want to compare the diffusion coefficient determined by these two methods one have to take into account this behaviour especially if dealing with different concentrated salt solutions. A concentration correction factor plays this role in the presented work.



Picture 3 Diffusion coefficient D of Na2SO4 and NaCl in free solution, experimental values and calculated values from measured conductivity {literature data (Lobo [12])}

5 Results

5.1 Comparison between results from diffusion experiment and from impedance spectroscopy

The absolute values of D_{eff} for all materials at 100% water saturation measured by impedance spectroscopy are given in Table 2.

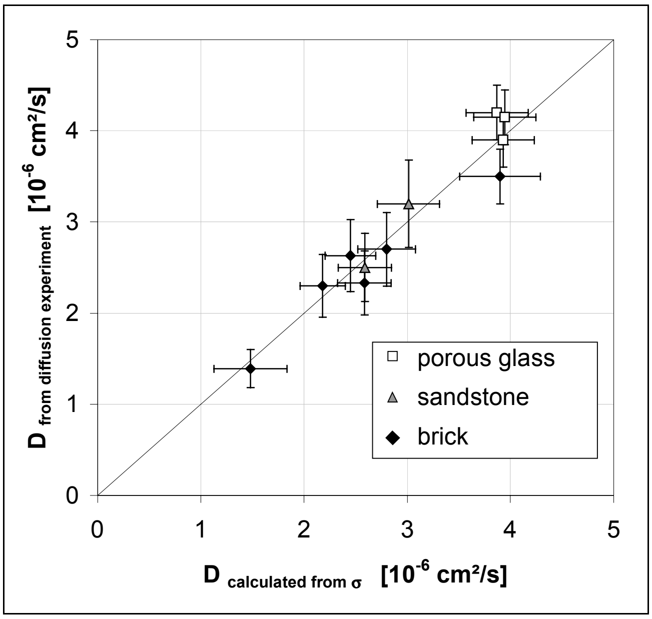
	Z1	Mo	S1	S2	P1	P2	P3	P4	P5
D_{eff} [10^{-6} cm²/s]	2.1	4.8	3.1	2.3	3.9	3.9	2.1	2.5	3.9

Table 2 Diffusion coefficient of 1M Na_2SO_4 in fully saturated material by impedance spectroscopy

Looking on the diffusion coefficients in the porous glasses, one can see that P1, P2 and P5 show the same value. That means the diffusion coefficient are not influenced by the pore diameter as long as the pore structure are similar. P3 and P4 which has a lower content on porosity has also an lower diffusion coefficient. But a different pore volume itself has no direct influence on the diffusion coefficient as it can be seen if comparing the diffusion coefficient of brick (Z1) and mortar (Mo). Both of them have an comparable pore volume but a rather different pore morphology. For further discussion see (Buchwald [1], Buchwald [14]).

The values in Table 2 correspond with the diffusion coefficients which are determined by diffusion experiments (Buchwald [1]). Picture 4 shows the comparison.

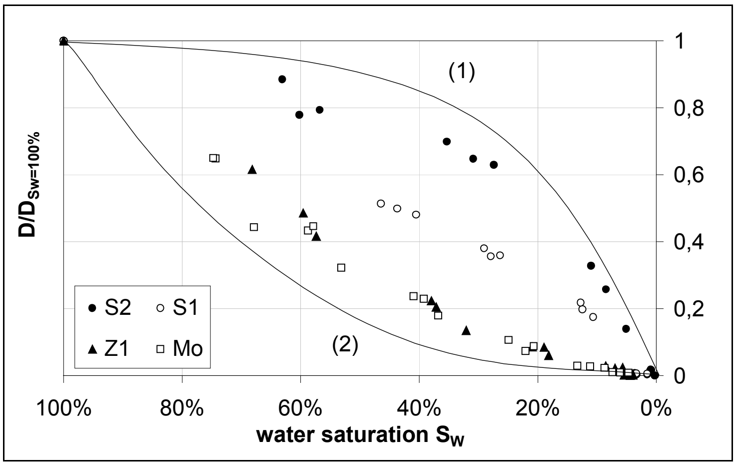
Each method contains advantages and disadvantages. The most recommendable advantage of the impedance spectroscopy compared to diffusion experiments is the quick and easy measurement, where all moisture degrees are measurable on only one sample. On the other side incorrect electrode contact leads easily to measurement artefacts. Additional errors occur in the high frequency zone, if the electrical behaviour of the material reaches the same order of magnitude then cable and stray immitance's (high conducting materials). Could these errors excluded, the impedance spectroscopy is an excellent method to determine the conductivity and therefore the ion diffusion coefficient of moisture and salt loaded materials.



Picture 4 Comparison of diffusion coefficients of 1M Na_2SO_4 determined in diffusion experiment as well as by impedance spectroscopy

5.2 Influence of moisture content on the diffusion coefficient

Starting from 100% water saturation the diffusion coefficient decreases with decreasing moisture content. Looking on Picture 5 one can see the relative diffusion coefficient of the masonry materials in relation to moisture content. The influence of the water saturation on the diffusion coefficient seems to be almost linear down to about 30 %. Afterwards the diffusion coefficient of the brick and the mortar decreases less rapidly and comes to almost zero. The diffusion coefficient of the two sandstone’s, which decreased less at high water saturation, show a more rapid decreasing at lower moisture contents. Similar behaviour of sandstone were reported by Rust [15]. Other authors found exponential or linear relation between D and S_W in soils (Romkens [16], Porter [17]).



Picture 5 Relative values of diffusion coefficients in relation to water saturation of different masonry materials

All curves can be expressed by the following potential relation:

$$D_{eff}=\frac{D_{Lsg}}{\tau} S_w{}^n \tag{3}$$

D_{Lsg}: diffusion coefficient in free solution
τ: tortuosity
S_w: water saturation
n: saturation exponent

Using equation (3) it can be seen that there are 2 typical groups of curves formed by the data. The decreasing of D_{eff} in brick (Z1) and mortar (Mo) is more rapidly at higher moisture contents then in sandstone S1 and S2. This is expressed by the saturation exponent n. Mortar and brick have exponents higher than 1, the sandstone lower than 1. Table 3 contains the exact values of n and τ. The tortuosity gives a summarised information about the pore structure of the material. One can interpret it as the lengthening factor of the diffusion path way.

	ZI	**Mo**	**S1**	**S2**
n	1,6	1,6	0,8	0,6
τ	2,96	1,83	2,17	2,57

Table 3 Parameter n and τ of the investigated materials

The saturation exponent and therefore the curve shape is influenced by the water distribution in the pore system. Picture 5 shows beside the experimental data two schematic curves. They correspond to two model cases dominates by the pore structure:

(1) The loss of water in the pore system leads to decreasing of the inner water film thickness. The remaining salt solution is higher concentrated than before. As known an shown in Picture 3 the diffusion coefficient of Na_2SO_4 decreases with increasing concentration. Therefore the effective diffusion coefficient decreases.

(2) But if the loss of water leads to interruptions of the inner water film and water isles appear, the ions have to diffuse a much more longer way through the intact water film. That means additionally to the decreasing of the diffusion coefficient due to concentration changes the effective diffusion coefficient decreases because of lengthening the diffusion path way.

Following these cases, one can conclude that the behaviour of brick Z1 and mortar Mo is dominated by case (2) whereas that of sandstone S1 and S2 is dominated by case (1).

In summary it could be introduce an useful measurement technique to determine the ion diffusion coefficient in moisture and salt loaded masonry materials. Few results were presented and compared to results from diffusion experiments. The influence of the moisture content on the ion diffusivity were discussed more in detail. It could be shown that the pore morphology dominates the water distribution in the pore system and therefore the ion diffusivity.

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