

THE EFFECT OF PORE SIZE ON ION MIGRATION IN CONCRETE DURING ELECTROCHEMICAL CHLORIDE EXTRACTION

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ABSTRACT. Electrochemical chloride extraction (ECE) is the removal of chlorides from the vicinity of the reinforcement leaving sound concrete intact. In a short period, 3 to 5 weeks, a high current, relative to other applications such as cathodic prevention or protection, is applied to the structure. Concrete shows a difference in pore size and pore size distribution before and after ECE treatment. Furthermore during ECE applications an increase in concrete resistance can be observed. An experimental study was conducted to investigate the influence of pore size on the resistance of artificial concrete pore liquid. The results showed that the resistance increases with decreasing pore size if a certain limit is exceeded. This limit appears to be related to the ion species and the concentration of the ions in the solution.

Keywords: Electrochemical chloride extraction, pore size, ion redistribution, migration, concrete resistivity

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INTRODUCTION

The two main causes of reinforcement corrosion are chloride and carbonated concrete. Electrochemical chloride extraction and its sister technique, re-alkalisation, are used to restore chloride contaminated or carbonated concrete. Both processes take advantage of the fact that migration of ions under an electrical field in concrete is much faster than diffusion. The chloride contamination through diffusion can thus be reversed in a short period of time. Migration and diffusion of a charged species such as chloride in concrete is dependent on a combination of factors. One of them might be the pore structure, because it is altered during electrochemical chloride extraction. It is difficult to examine the contribution of one single factor, such as the pore size, on ion migration in concrete, because concrete is a heterogeneous, reactive environment. Therefore, studies were conducted on thin membranes with known pore size in artificial concrete pore water and its components.

CHLORIDE CONTAMINATION THROUGH DIFFUSION

Chloride ions diffuse through concrete towards the reinforcement when the structure comes in contact with e.g. de-icing salts. During diffusion the cement binds chloride as Friedel's salt[1]. Fundamental equations of diffusion are Fick's 1st and 2nd laws. When Fick's law of diffusion is applied to ions in concrete it only applies to the diffusion of undissociated molecules, not ions such as chloride. Fick's 1st law applies only for steady state diffusion e.g. where the chlorides were cast in. The transport process under Fick's law is a simple diffusion process and cement is not an inert or fully open medium to diffusants (i.e. water). Therefore, the diffusion equations need to be modified. Only the pore characteristics allow the diffusants to pass through the sample and there are interactions between the diffusants and the cement. The formation of Friedel's salt and the adsorption of sodium ions by CSH will reduce the effective concentration gradients. The diffusion coefficient becomes an apparent diffusion coefficient for cement[2]. For ionic materials the influence of the electronic double layer and the fact that concrete reacts with the diffusants needs to be taken into consideration[3]. The concentration gradient of ions across a permeable barrier is generally accompanied by an electrical potential gradient. This electrical potential gradient hinders the diffusion of ions across the barrier and a membrane potential is formed[4].

CHLORIDE EXTRACTION THROUGH MIGRATION

Chatterji[5] suggested that ion transport through cement based material can properly be described only by using a combination of Nernst-Planck and the electrical double layer diffusion processes. Movements of positive and negative ions are coupled, which would explain the high activation energy of chloride diffusion. The high activation energy of chloride migration processes in concrete is considered to be an indication of other linked processes. These processes are the transport of positive and negative ions, the dissolution of cement hydrates and the migration of calcium and hydroxide in opposite directions, the maintenance of calcium in the double layer and the linked formation of Friedel's salt.

For a steady state diffusion there is a solution due to Planck. All ions present in the pore solution that have been generated at the electrodes will move towards the counter pole. This movement has to follow the mass transport law for electrolytes (Nernst-Planck), which states

that the total net flow is the addition of diffusion, migration and convection. The Nernst-Planck equation is expressed as follows:

$$J_j(x) = -D_j \frac{\partial C_j(x)}{\partial x} - \frac{z_j F}{RT} D_j C_j \frac{\partial \phi(x)}{\partial x} + C_j v(x) \quad (2)$$

Migration takes into account the movements due to the application of an electrical field. The migration term is also named the Nernst-Einstein equation. The diffusion coefficient in the Nernst-Einstein equation is a function of the electrolyte conductivity. In an ionic solution, a electrostatic field due to the other ions in the solution restricts the movements of ions. This restriction becomes particularly important when the diffusion occurs through a permeable barrier such as concrete across which there is a concentration gradient.

CONCRETE RESISTIVITY

The ions in the pore water transport electrical current, hence the resistivity is a measure of the continuity of the pore solution through which chlorides migrate[6,7]. Andrade[8] and Bamforth[9] suggest measuring the resistivity of concrete as an indication of chloride permeability. The use of conductivity (reciprocal of resistivity) of concrete for measurements of chloride permeability has also been suggested[10]. Dry concrete acts as electrical insulator; its resistivity (oven-dry) is approximately 109Ωm, but moist concrete acts as conductor with a resistivity of approximately 50 Ωm[11]. Resistivity may be obtained by dividing the IR voltage drop across the specimen by the average current density and the specimen thickness[12]. Andrade[13] proposed a mathematical formula for the calculation of the chloride diffusivity in concrete related to its resistivity. The resistivity of blended cement is higher than resistivity of OPC concrete[14], because of smaller pores. For the same reason carbonation increases the electrical resistivity and water adsorption of concrete[15].

EXPERIMENTAL PROCEDURE

Concrete specimens were subjected to ECE treatment for a period of 40 days. The concrete pore size distribution was analysed prior to and after the ECE treatment at various depths. It was noted that the pore size and distribution had changed due to ECE. An experimental study was then conducted to investigate the influence of pore size on migration of ions during ECE. The diffusion and migration of ions in concrete is a complex interaction of a multitude of factors such as concentration of migrating species in different layers of the concrete, physical properties of the concrete, etc. It is thus not possible to investigate the influence of one single parameter on ion migration using real concrete. The composition of concrete pore water and the range of concentrations of individual species can be reproduced for laboratory investigation[16]. The concentrations of ions used in this investigation are given in *Table 1*.

Table 1 Concentration of Ions in Artificial Concrete Pore Solution

Name (chemical abbreviation)	Concentration [g/l]
Potassium hydroxide (KOH)	2.0
Sodium hydroxide (NaOH)	0.3
Calcium hydroxide (Ca(OH) ₂)	0.1
Sodium chloride (NaCl)	2.5
Artificial concrete pore water	Sum of above components

The pore size of concrete and cement paste is reported to be between 0.003 and 1.000 μm for young cement pastes and between 0.003 and 0.1 μm for mature cement pastes[17]. Instead of concrete a material with known pore size - *Whatman*[®] *Anopore* filter membranes with 0.02, 0.10 and 0.20 μm pore diameter - were used to investigate the influence of pore size on migration.



Figure 1 Experimental Set-up

The experimental set-up is shown in Figure 1. An impermeable Perspex[®] membrane with a $\text{Ø}35\text{mm}$ hole in the centre was glued into a crystallisation dish to form two compartments and the hole was covered with a permeable filter membrane and sealed. Migration of ions was therefore possible only through the membrane. Two platinum electrodes with an electrode area of 1cm^2 were placed at a distance of 2cm from each other, separated only by the membrane or plain solution in case of the measurements without membrane. The filter membrane is very thin compared to concrete cover, but one thin membrane can represent concrete, because during impedance the migration of species is reversed at high frequencies. One membrane (filter membrane) does, therefore, have the same effect as multiple membranes (or concrete).

The electrical resistance of the system reflects the reactions of an electrode system. The resistance of the solution (R_s), the evolving double layer on the electrodes (R_p) and the capacitance of the electrode (C) give the total resistance or impedance[18]. The capacitance is constant, but the solution resistance and the resistance of the double layer depend on the concentration of the ions in the solution. Impedance Z and resistance are obtained the same at high frequencies when reactions at the electrode do not take place. The impedance measurements of the influence of membranes in artificial concrete pore solution were conducted with a Schlumberger SI 1260 Impedance/Gain Phase Analyser and SI 1286 Electrochemical Interface.

EXPERIMENTAL RESULTS AND IMPLICATIONS

The impedance measurements showed, for different electrolytes, an increase in resistance when a membrane was introduced between the electrodes. This effect was observed at low and at high frequencies.

The results of the impedance measurements of the artificial concrete pore solution are displayed in *Figure 2*. The resistance significantly increases below a certain frequency. This can be attributed to the build up of a double layer and the occupation of free sites on both electrode surfaces by the adsorption and subsequent reactions of ions. This effect is even more significant during ECE as a direct current is applied. This results in an instantaneous formation of a reactive layer on the surface with a corresponding increase in resistance. Therefore, resistance/resistivity measurements under a direct current source always contain an element of error due to the build up of the double layer and do not truly reflect the migration properties of ions in the concrete.

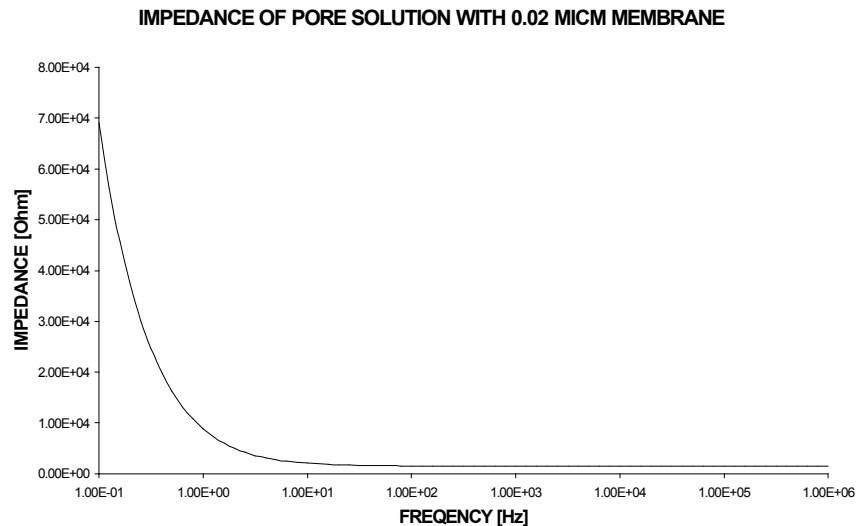


Figure 2 Results of Impedance Measurements for Artificial Concrete Pore Solution

During ECE ions are removed from the bulk concrete. Hydroxide and chloride form water and chlorine at the anode and cations precipitate at the pore walls near the cathode once their maximum solubility is exceeded. Thus these ions do not take part in the migration process and fewer ions carry the current, which results in increasing resistivity during ECE.

Concrete acts a membrane and due to the build up of a concentration gradient across the membrane, i.e. the reinforcement and the anode, a potential gradient develops, which is caused by the non-uniform distribution of charged species. This potential is called the membrane potential and contributes to the increase of the resistance and was observed where a DC current was applied between two electrodes separated by membranes. Two effects can be observed, first, the initial resistance of the system is different due to different pore size of the membranes and second, with time the resistance increases slightly. To analyse the influence of the parameter of pore size it is important to use only the impedance measurements that represent the resistance of the solution. This is equivalent to the part of the impedance, which is parallel to the horizontal in *Figure 2*.

The relative increase of resistances (percent) of the different solutions is plotted against the pore sizes in *Figure 3*, the resistance of the solution without membrane was thereby taken as 100%. It can be seen that with decreasing pore size the resistance of the system increases. A linear relationship best describes the relationship between pore size and resistance for the pore solution and calcium hydroxide and for the remaining three solutions a logarithmic relationship gives a good approximation of the influence of pore size on resistance.

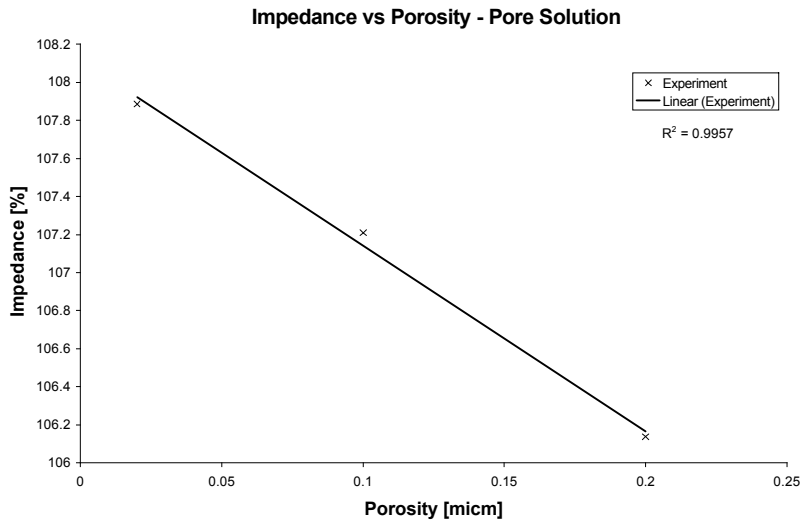


Figure 3 Relationship between Impedance and Pore Size of Membranes

The impedance measurements are based on four points on the vertical, but only for three points, the membrane, the pore sizes (horizontal) are known – not for the measurements without membrane. To find the pore size where migration remains unhindered, the graph has to be extrapolated to reach the horizontal.

The results of this analysis are shown in *Figure 5* and *Figure 4*. The resistance remains unhindered for a pore size of larger than 4 μm for NaCl and larger than 10 μm for sodium hydroxide. It is not possible to isolate and investigate the influence of one type of ion because a cation is always accompanied by an anion to satisfy the electroneutrality condition. It appears that the coupled migration of sodium and hydroxide requires more space than the coupled migration of sodium and chloride. *Figure 4* shows to be a logarithmic plot, but the data in *Figure 5* is plotted on a normal scale. It becomes apparent that the logarithmic graph gives a better fit when the data is extrapolated, because the curve approximates better to the known

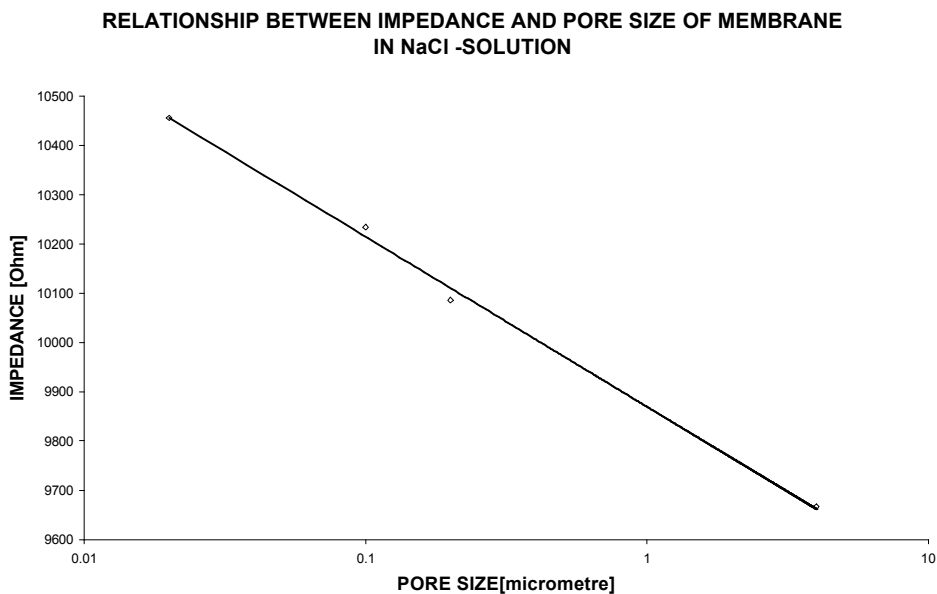


Figure 4 Migration Properties of Sodium Chloride Solution

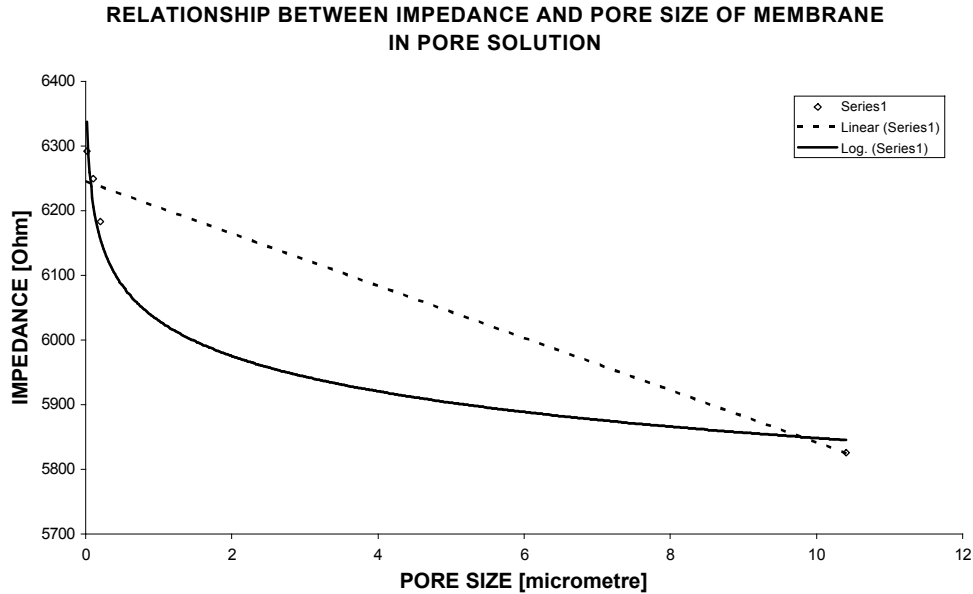


Figure 5 Migration Properties of Artificial Concrete Pore Solution

values of pore sizes. The logarithmic relationship can, however not be used to find the minimum pore size, because it would give unrealistically high values for minimum pore sizes (100 μm for calcium hydroxide and 1000 μm for pore solution). If a linear relationship is used for extrapolation a minimum pore size of 10.41 μm for calcium hydroxide and 6.48 μm for plain pore solution is obtained. Potassium hydroxide can migrate undisturbed through pores with a pore size of 1 μm whereas calcium hydroxide requires a much wider space although its concentration was much less compared to potassium hydroxide.

CONCLUSIONS

From the study a number of conclusions can be drawn.

1. The diffusion of charged species such as chloride or hydroxide and their corresponding cations are related to their electrical properties, interactions with the diffusive medium and interactions with each other.
2. During ECE the pore size and the pore distribution of concrete change.
3. Amongst other factors, the change in pore size, if it falls below a certain limit, will influence the migration properties of the species and change the resistance of the system.
4. However, this limit is different for different ions and it varies with concentration. Further work is recommended to consider the effects of changing pore size for the migration of ions in concrete.

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