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A DISCUSSION OF THE PAPER "DIFFUSION BEHAVIOUR OF CHLORIDE IONS IN CONCRETE" BY T. ZHANG AND O.E. GJØRV*

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The paper under discussion can be divided into two distinct parts. The first part deals with the Debye-Huckel theory and the second part with the electrical double layer both in relation to diffusion of chloride ion. In this discussion I would like to draw the attention to the possibility of simplifying the first and extending the second part to explain directly some of the observations on ion diffusion through cement based materials.

A) Simplification of the part on the Debye-Huckel theory: The Debye-Huckel theory is the first successful theory, though only for very dilute solutions, to explain the fundamental observation of Kholrausch on the concentration dependence of molar conductivity of ionic solution. The Debye-Huckel theory of course achieved much more than this. However, the relevance of molar conductivity to ionic diffusion can be extended beyond the Debye-Huckel range by going back to the Kholrausch's conductivity rule

$$\lambda_i = \lambda_o - \kappa\sqrt{c_i} \tag{1}$$

where λ_i and c_i are the molar conductivity and concentration of the ion in solution, λ_0 is the molar conductivity at infinite dilution and κ is a parameter. The above relationship is valid up to about 0.7 molar solution i.e. it covers sea water. However its range can be extended. Combining [1] with Nernst diffusion equation one easily gets the following relationship between diffusivity of an ion and its concentration in a solution (1):

$$D_i = D_o - \mathbf{K}\sqrt{c_i} \tag{2}$$

where D_i and D_0 are the diffusivity of the ion in concentration c_i and in infinite dilution and K is a parameter. To relate [2] to a porous material it has to be multiplied by $\varnothing$, the pore characteristics of the porous medium. This gives [3].

$$D_i = \theta D_o - \theta\mathbf{K}\sqrt{c_i} \tag{3}$$

The relationship [3] is strictly valid for diffusion across a thin section of a material. To apply this to a thick section it has to be averaged over all concentrations in the section. This gives [4] (2).

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$$D_m(c_o) = 1/c_o \int_o^{c_o} \theta D dc = \theta D_o - 2/3\theta \mathbf{K}\sqrt{c_o} \qquad (4)$$

where D_m is the measured diffusivity and c_0 is the concentration of the concentrated solution. The relationship of the type [4] has been found to be valid for the diffusion of $Ca(OH)_2$ through its solution (3), Li^+ and Na^+ through homoionic bentonite plugs (4) and recent results of chloride diffusion through thick mortar sections (5) all with correlation coefficients in excess of 0.95.

The equation [4] is valid for each type of ion. However, to get the diffusivity of a diffusant one has to take a weighted mean of anion and cation diffusivity. Most popular weighted mean is that due to Nernst:

$$D_{av} = 2D_C D_A/(D_C + D_A) \qquad (5)$$

where D_{av} is the weighted average diffusivity of the diffusant, D_C and D_A are the diffusivity of the cation and anion respectively.

B) Extension of the part on the double layer theory: For the ease of presentation it is necessary to recapitulate some of the empirical observations. Most of the diffusion work on cement paste has been carried out using diffusion-cells in which thin hardened paste barriers are inserted between moderately concentrated and very dilute solutions of the diffusants. At this stage it will be useful to consider an uni-univalent i.e NaCl diffusant.

Most authors have found that Na^+ ions have lower effective diffusivity, D_a., than the Cl^- ions (6). The situation is best illustrated by Fig.1 (7).

Higher D_a's of Cl^- ions means that more Cl^- ions move to the low concentration side than Na^+ ions. Obviously other ions are also moving at the same time to keep the electric charges balanced in the solutions on the either sides of the barrier. This means that Ca^{2+} ions move to the down-stream side and OH^- ions move to the up-stream side(8). It will appear that Ca^{2+} and OH^- ions can move in opposite directions without any imposed concentration gradients. It is obvious that the cement matrix strongly influences the process of ion diffusion through it.

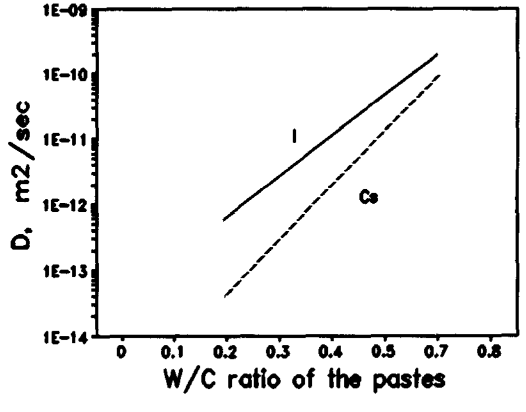

FIG. 1.

Dependence of Cs and I ion diffusivity on the w/c ratios of cement pastes (7).

Increasing difference in the D_a's of Na^+ and Cl^- ions with decreasing w/c ratio (Fig.1) indicates an increasing Ca^{2+} ion transport with the decreasing w/c ratio. With lowering w/c ratio the average pore size becomes increasingly narrow and the surface/volume ratio of the diffusion channels increases. A combination of this knowledge with the increasing Ca^{2+} transport with lowering w/c indicates that Ca^{2+} concentration in the solution at the pore surface is high as against bulk pore solution. One may also infer that the cations diffuse mainly along the pore surfaces and the anions through the bulk pore solution; although some cations also diffuse through the bulk pore solution.

The hydrated cement particles are negatively charged so that there will be an excess positive ions in the double layer and it is more concentrated than the bulk solution (9). Negatively charged Cl^- ions are in the bulk solution. In these double layers divalent Ca^{2+} ions tend to collect preferentially; although Na^+ ions will also be there. The high Ca^{2+} concentration at the pore surfaces could be identified with the high calcium concentration in the double layer solution. The high concentration of Ca^{2+} in the double layer will cause a diffusion of Ca^{2+} ions to the down-stream side along with Cl^- ions. Diffusion through both the double layer and bulk solutions follow [4]. The intrinsic diffusivity of ions in the double and bulk solutions are different. However, they are forced to diffuse together to keep electroneutrality of the sample which means that high diffusivity of Cl^- ion in the bulk solution will be retarded and low diffusivity of positive ions in the double layer will be accelerated.

Three scenarios may be considered:

i) The paste has no free $Ca(OH)_2$ e.g. blast furnace slag cement paste, and the double layer contains mainly Na^+ ions. In this case, for the same ionic charge on the cement particles, the molar concentration of the double layer is highest and Na^+ diffusivity is the lowest. In this case both Na^+ and Cl^- ions have the same low diffusivity via [5] (10).

ii) The paste contains $Ca(OH)_2$ e.g. Portland cement paste, and hence the double layer contains both Ca^{2+} and Na^+ ions. Since each Ca^{2+} ion replaces two Na^+ ions the average molar concentration of the double layer is lowered and the average diffusivity of the positive ions is increased. In this case the retarding action of the positive ions on Cl^- ion diffusivity is lowered. Other things remaining the same, the diffusivity of all the ions is higher than in case (i). However, as Na^+ is only a part of total positive ions the increase in its D_a is lower than that of Cl^- ion. This also explains deference in the diffusivity of Fig.1.

iii) The paste contains $Ca(OH)_2$ the double layer contains mainly Ca^{2+} ions i.e. the case of $CaCl_2$ diffusion through Portland cement paste. In this case, other things remaining constant, the molar concentration of the double layer is the lowest and the double layer diffusion is highest. The diffusivity of Cl^- ion is also the highest (8).

Notice that the above inferences are independent of the pore characteristics of the pastes. Different alkali ions will have different κ values in [2] so their diffusivity will also differ. There is a fly in the ointment though. A quick literature survey showed that up to the present time all models, including the present discussion, proposed for chloride penetration in concrete have implicitly assumed concrete to be fully saturated. However, all real-life structure made with a concrete of w/c ratio of 0.6 or lower remain unsaturated for a long time, except for outside few centimetres, even when stored under water (11). Lower the w/c ratio longer the concrete remains unsaturated and thinner is the outer saturated layer. Model for a saturated concrete is hardly relevant for an unsaturated concrete.

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