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ON THE APPLICABILITY OF FICK'S SECOND LAW TO CHLORIDE ION MIGRATION THROUGH PORTLAND CEMENT CONCRETE.

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ABSTRACT

From a strictly theoretical point of view Fick's second law could not be used to analyze the chloride ion migration data through cement based materials. The proper formalism would be an integrated one combining both Nernst and the electrical double layer theories. However Fick's second law could still be used, for concrete, purely on an empirical basis. To ascertain this possibility the chloride migration data, from a number of concrete samples, has been analyzed. The results indicate that the assumption of a constant chloride ion diffusivity, through a sample, is seldom satisfied. An increasing or a decreasing diffusivity with depth could be observed depending upon the history of the sample. The results call for further investigation. The technique of electro-assisted chloride diffusivity measurement has been commented upon. It seems that the use of the measured, by any method, chloride diffusivity data to calculate the long term chloride penetration depth in a structure is uncalled for and may give misleading predictions.

In the recent years much research work is being carried out on the chloride ion migration through cement based materials. In analyzing the collected data most of the workers use some form of Fick's second law. Now that a large amount of data has been collected it will be worthwhile to examine how far Fick's second law is valid for cement based materials i.e. cement mortar or concrete.

Fick's second law has the form

$$\frac{\delta C}{\delta t} = D.\frac{\delta^2 C}{\delta x^2} \quad \ldots\ldots\ldots\ldots (1)$$

This is of the parabolic type and the solution must be made to fit the boundary and the initial conditions. In the cement and concrete field the most commonly used solution of the equation 1 is the equation 2, where C_s is the chloride ion concentration of the sample at the surface which is in contact with the chloride solution; C_x is the chloride ion concentration of the sample at a depth $\mathbf{x}$; C_o is the initial chloride ion concentration of the sample, t is the length of exposure to the chloride solution in seconds, and erf is the error function which can be found in many mathematical tables.

$$\frac{(C_s-C_x)}{(C_s-C_0)}=erf\left[\frac{\mathbf{x}}{\sqrt{(4Dt)}}\right]\ldots\ldots.(2)$$

To use the equation 2, the sample, under investigation, is exposed to a concentrated chloride solution for a length of time. It is then sectioned at different depths and the chloride ion concentrations at different depths are estimated. The chloride ion concentrations are then plotted against their corresponding depths. The equation 2 is then used to calculate the effective diffusion coefficient, $D_{eff.Cl}$,of the chloride ion through the sample. This technique is known as the concentration profile technique. Variations of this basic technique, including electro-assisted migration of chloride ion, could be found in the literature.

Attention has recently been drawn to the fact that Fick's laws of diffusion are valid only for non-ionic materials [1]. For the ionic diffusants Fick's laws have to be modified to take account of Nernst equation which states that the diffusivity of an ion increases with dilution. A further modification has to be carried out to take account of the electrical double layer formation on the cement hydration products [2]. Some evidence has also been adduced in [2] to show that in a steady state migration of chloride ion, through cement pastes, the $D_{eff.Cl}$ increases with decreasing concentration of NaCl solution used to perform the experiment and a very large fraction, about 80%, of the migrating chloride ions get fixed up in the cement paste probably as Friedel's salt. It has also been shown that the migration of chloride ion is coupled with that of the cations in the sense that movement of one influences the movement of the other. Above also explained the calculated high activation energy of chloride ion diffusion [2]. Although most workers have treated the chloride penetration in concrete as a two component system actually it is a complex multi-component system i.e. at least calcium, sodium, hydroxyl and chloride ions take part in the process; even a single type of ion may move in two directions at the same time [2]. Question about the applicability of Fick's second law, without a large modification, to cement based materials then arises naturally.

Another reason to question the applicability of Fick's second law to concrete is its probable unsaturated state. Any large volume of a good quality concrete is, almost by definition, unsaturated due to the self-desiccation of cement and the relative humidity can fall as low as about 80% (3). As a result of this self-desiccation a large part of the pore space, especially the important large pores, will be empty. This unsaturation can easily be seen by taking a core from any structure, even from the under-water parts, and splitting it longitudinally. Only the outer few cms. of the core will have a wet look and the rest of the length will have a dry look. This has been recognised by ISO/DIS 7031 test method. In this test method concrete cores or cylinders are subjected to a uni-directional water pressure of up to 700 kPa and water penetration is visually measured after splitting the sample. In good quality concrete water penetration is seldom more than about 10 mm. The empty pores will not allow chloride ions to migrate through them easily i.e. chloride ion will have a low apparent diffusion coefficient through self-desiccated concrete.

In the following investigation the concentration profile data from a number of samples from independent laboratories have been collected. The samples included both laboratory made, comparatively small sized, cylinders which were stored under water from 24 hours on until tested. Other samples were from long cores from existing structures. In the second instances only the parts of the cores farthest from the outer surfaces were used to determine the chloride ion migration characteristics. Each laboratory stored their samples in a 2.86 N NaCl solution for 56 days to allow for chloride ions to penetrate the samples. The concentration profiles were then independently fitted to the equation 2. The concentration profiles fitted reasonably well. Using reported C_s, C_o, C_x values and the equation 2, the $D_{eff.Cl}$ values were then calculated for each measurement points of each sample and plotted against the corresponding depths. It was expected that if unmodified Fick's second law was applicable then each sample would have its own constant, within the experimental accuracy, $D_{eff.Cl}$ value.

Figs. 1 to 4 show the general types of $D_{eff.Cl}$ vs-depth curves observed during this investigation. Figs.1 and 2 refer to small laboratory made cylinders which were never allowed to dry. Fig.3 refers to a long core taken from an existing structure.

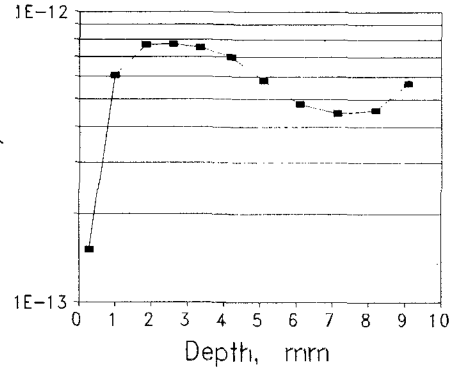

Figure 1. Calculated Diffusion coefficient - Depth relationship in a laboratory made mortar sample.

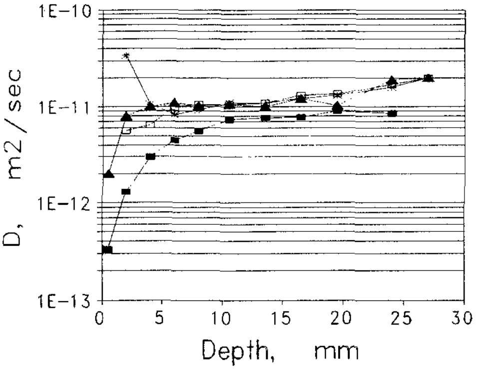

Figure 2. Calculated Diffusion coefficient - Depth relationships from different concrete samples.

Figs.1 and especially 2 show that $D_{eff.Cl}$ values increase, rather, rapidly between the first and second measurement depths followed by a slow increase. These results could be rationalized by the formation of a large amount of Friedel's salt, within first few mm. of the samples [2]. This lowered the concentration of chloride ions in the pore liquids and hence increased the diffusivity of chloride ions as is demanded by Nernst equation.

Fig.3 shows that the diffusivity first decreases, rather sharply and then attain a more or less steady value. Other cores showed slowly increasing diffusivity after the initial drop. The large lowering of diffusivity between the first and second measurement points may be attributed to the unsaturated state of the cores from existing structures. Only the outer parts of these cores could have become saturated during the exposure to NaCl solution and allowed for a higher rate of chloride migration. It is obvious that both Figs.1 and 2 and Fig.3 could not be attributed to a single cause.

Fig.4 shows the chloride ion penetration data in a 24 years old marine structure (4). The curve A shows the measured chloride concentrations at different depths. From this data the authors of the paper calculated a single diffusion constant that fitted the data best (curve C). The estimated chloride profile is shown by the smooth curve B. (Curves A and B refer to the concentration axis). From the figure it can be seen that the estimated and the measured values fitted reasonably. This degree of fitness is quite common in the concrete field. The observed divergence is generally attributed to the scatter of the measured data. However, when the reported C_s (0.18%) and C_x values were used to calculate point by point diffusion coefficients they showed increasing diffusion coefficient with depth as can be seen from the curve D. It again emphasises that a trend has been missed in the usual analysis. It is surprising that this increasing trend is visible even after 24 years of exposure to a tropical marine environment.

The most interesting and important point is that all the above results show very little evidence of a constant diffusivity for chloride ion. However the development of the equation 2 is based on the assumption of a constant diffusivity of the diffusant. Thus there is a fundamental contradiction between the results and the basic assumption of unmodified Fick's second law when applied to concrete.

It seems to be a common practice among the laboratories to ignore the first couple of offensive data points and analyzed the rest using the equation 2. From the above results it appears that the above practice leaves some important information aside and may even give some misleading diffusivity values.

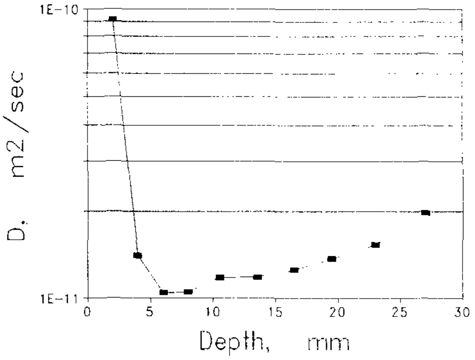

Fig.3. Calculated Diffusion coefficient - Depth relationship in a core taken from an existing concrete structure.

The present author would like to draw the attention of workers in the field to this pit fall. As it takes only a couple of minutes for the computers to plot the diffusivity values at individual measurement points it will be preferable to get plots like Fig.1 to 4 and report them.

From the above results it is obvious that Fick's second law could not be used, even on a purely empirical basis, to rationalize the chloride migration data through concrete.

In this context a few points on the measurement technique based on the electrically assisted ion migration will be in order. In this technique the movements of anions and cations are decoupled in the sense that they move in opposite directions as against their coupled migration in the same direction in the natural diffusion. During testing the cations will discharge at the cathode and react with water forming corresponding hydroxides. The hydroxyl ions thus formed will migrate along with chloride ions in contrast to their movement in opposite directions in the natural diffusion [2]. This co-migration of OH^- and Cl^- in the same direction will also interfere with the kinetics of Friedel's salt formation. At the later stages of the measurement the hydroxyl ion will accumulate and will be the main current bearing ion as it has a higher mobility than the chloride ion. All the above factors act together and may give a misleading diffusion coefficient. At least one should be aware of these factors and try to evaluate their effects and correct for the deviations where necessary. There seems to be very little discussion on these points in the literature.

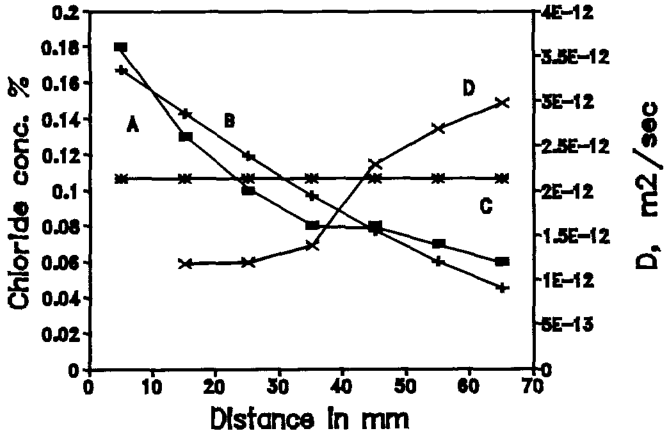

Figure 4. Chloride ingress in a 24 year old marine concrete.

Any attempt to predict the long term penetration depth of chloride ion in any existing structure, on the basis of the present day measured diffusivity ,by any method, may be very uncertain. A similar inference could be drawn from the results of an investigation on the chloride ion penetration in existing structures carried out by the Norwegian Road Directorate (5).

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