Pergamon

Cement and Concrete Research 30 (2000) 1005–1006

CEMENT AND
CONCRETE
RESEARCH

Discussion

A discussion of the papers "Concentration dependence of diffusion and migration of chloride ions. Part I and 2" by Luping Tang ☆

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Received 6 December 1999

Dr. Tang has to be congratulated for collecting a large number of equations and relevant data from different textbooks on solution electro-chemistry. In themselves, they are very useful. It is obvious that all we may ever hope to achieve is to determine the apparent diffusivity of different ions. However, questions still remain as to the relevance of these equations, etc., to ion transport processes through cement-based materials. Do they give any indication as to the rates of transport of different ions through different types of cements, or long-term penetration of ions in real-life concrete, etc.? In the following, I will discuss some of these questions. For the ease of presentation, I shall take up diffusion and electro-migration separately.

Steady state diffusion: This is the simplest case to analyze. I shall concentrate mainly on alkali halide diffusants; some references will be made to alkaline earth halide. In the experimental set-up, a comparatively thin membrane of cement-based materials is interposed between a concentrated and a very dilute solution of the chosen diffusant. Only some workers measured the diffusivity of both anions and cations simultaneously. Others measured the diffusivity of one ion only. In Portland cement-based materials, the diffusivity of a halide ion is much higher than that of an alkali ion and this difference increases with the decreasing water/cement (w/c) ratio and decreasing alkali halide concentration on the upstream side [1–3]. In an ordinary Portland cement paste of w/c = 0.4 D_{Cl}/D_{Na} is about 10. The diffusivity of a halide ion is higher when the counter ion is an alkaline earth ion than when it is an alkali ion. Observing these differences Atkinson and Nickerson commented "This means that the diffusion process cannot be envisaged as being the same diffusion mechanism as in free liquid simply constrained by the pore structure since the diffusibility should then be the same for all the ions" [3]. Some authors attributed the above differences to an electronegative character of cement paste. However, in the case of slag–Portland cement paste, the diffusivity of alkali and halide ions is identical, i.e. the simple electronegative character of cement paste does not explain the known facts [1]. Furthermore, clay-plugs, which also form electronegative semimembrane, behave differently depending up on the presence or absence of $CaCO_3$ [4,5]. Quigley has shown that in the same clay bed, D_{Cl}/D_{Na} is 1 in $CaCO_3$ free layer and 3 in the layer containing $CaCO_3$. The diffusivity of both Na^+ and Cl^- ion is higher in the layer containing $CaCO_3$. Thus, the presence of calcium salt affects the diffusivity of Cl^- by a factor of about 5 or more and is more important than the electronegative nature of the membrane.

Higher D_{Cl} through Portland cement-based materials means that more Cl^- ions move to the downstream side than alkali ions, i.e. OH^- moves upstream to maintain the charge balance. Measurements of OH^- ion concentrations in up and downstream solutions show that OH^- ions move mainly to the upstream side. This movement could not be attributed to the high concentration of OH^- ion inside the paste. A similar OH^- movement occurs when pure C_3S paste is used as the barrier [6]. Similarly, Ca^{2+} ions move downstream to maintain the charge balance in downstream solution. This transport of Ca^{2+} is unusual. Phenomenologically, there is no concentration gradient for Ca^{2+} ion. The concentration of Ca^{2+} in the pore solution is about 3 mmol/l. However, a Ca^{2+} ion concentration of above 8 mmol/l has been measured in the downstream solution. Apparently, Ca^{2+} ions can move to a higher concentration solution, defying the second law of thermodynamics. Neither Fick's laws nor its Nernst–Planck variant predicts these transport of OH^- and Ca^{2+} ions. It means that somewhere in the Portland cement paste, there is a concentrated solution of Ca^{2+} ion. A phenomenological analysis of Atkinson and Nickerson's work indicates this Ca^{2+}-rich solution resides at the surface of cement hydration products [7]. This indication seems to have gone unnoticed among cement workers.

Note that the experiment was set up to study the transport of alkali and halide ions through Portland cement paste but

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☆ Cem Concr Res 29 (1999) 1463–1474.

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PII: S0008-8846(00)00247-7

turned up to be coupled transport of four ion types. In the transport of the halide ion, only a small fraction is accompanied by alkali ions; most is accompanied by Ca^{2+} ion. This Ca^{2+} ion accompaniment increases the diffusivity of the halide ion. The diffusivity of halide ion gradually increases, within the paste barrier, as Ca^{2+} ion accompaniment increases. Thus, the measured diffusivity of halide ion is a weighted average of varying diffusivity along its diffusion path. A large part of halide transport is intimately connected with the counter movement of OH^- ion.

The above deliberations only means that it is illogical to set up Nernst–Planck or any other equations only for alkali and halide ions. Logically, a Nernst–Planck equation has to be set up for each of the four coupled ions, taking into consideration the direction of their individual movement. These four equations have to be solved simultaneously. The mathematical difficulty is formidable; this is particularly so as the transference numbers are changing all along the diffusion path length. The main physical difficulties are in the unknown path lengths and concentrations of Ca^{2+} and OH^- ions.

The movement of Ca^{2+} and OH^- in opposite directions means that $Ca(OH)_2$ is being dissolved during the experimentation. This dissolution changes the pore structure and that at best only a quasi-steady state is achieved.

The most important characteristic of normal penetration of ions in Portland cement-based materials, is that all the ions, except for OH^-, move in one direction, i.e. from upstream to downstream. Only OH^- moves in the opposite direction. This characteristic differentiates it from electro-migration tests.

Unsteady state: In the unsteady state migration of ions in concrete, all the above uncertainty still remain. Unlike steady state diffusion, in the unsteady state experimentation, the penetrating halide ion accumulates in the sample. This accumulation brings about further uncertainty.

Electro-Migration tests: The most important characteristic of the migration test is that all the cations move in one direction and all the anions move in the opposite direction. This means the movements of anions and cations are decoupled from each other. The only condition that remains is that of the overall electroneutrality of the system. Furthermore, during the testing, cations like Na^+ and Ca^{2+} get discharged to form corresponding metals. These metal atoms then react with water, forming OH^- ions. These OH^- ions then migrate along with Cl^- ions. These OH^- ions react with $C_3A \cdot CaCl_2 \cdot 12H_2O$ that has formed earlier within the sample forming $C_3A \cdot Ca(OH)_2 \cdot 12H_2O$ and Cl^- ions. Freshly released Cl^- ions migrate to the anode. This Grotthuss-like transport increases the apparent diffusivity of Cl^- ion through the cement-based materials. The absolute magnitude of this Grotthuss-like transport increases with decreasing Cl^- ion concentration. The applied electric potential has another effect on the ion conductance through porous materials. With increasing voltage, ions are progressively forced to follow the paths of least resistance, i.e. through larger pores and shortest paths thereby increasing the apparent diffusivity of Cl^- ion. This effect has no counterpart in solution electrochemistry. Taking all the above factors together, it is not obvious what relevance this type of test offers to unaided diffusion of ions through cement-based materials.

The unsaturated state of mass concrete: The discussions above indicate that the application of unmodified equations of solution electrochemistry and migration are inappropriate for the evaluation of ion penetration through cement-based materials. None of them gives any indication how different types of cement affect the diffusivity of an ion. However, the most important fact is that bulk of a good quality concrete is unsaturated. In the case of a good quality concrete stored under water, only a few centimetre thick outer layer is saturated and the rest is unsaturated. All the equations proposed so far assume a saturated concrete and as such, is of no value for a long-term evaluation of a real-life concrete.

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