Pergamon

Cement and Concrete Research 30 (2000) 1007–1008

CEMENT AND CONCRETE RESEARCH

Discussion

A reply to the discussion of the papers "Concentration dependence of diffusion and migration of chloride ions. Part 1 and Part 2" by S. Chatterji☆

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Received 22 February 2000

Dr. Chatterji has to be thanked for his discussion on the complex of ion transport through cement-based materials. There indeed exist many unclarified phenomena in regard to the movement of ions in the pore solution. It is noticed that Dr. Chatterji has tried to explain some experimental observations by introducing the characteristics of electrical double layer [1,2]. As Dr. Chatterji has already realized in his discussion, the mathematical and physical difficulties are formidable when quantifying the movement of ions inside the pore solution. A simple approach is to take concrete as a "black box," and just to study the input and output ions. In this way, the complicated feature of pore structure could be lumped in a single or few parameters. The constants K_{Tm} and f in my papers are such lumped parameters, the former describes the difference in drift velocity between cations and anions, and the latter describes the friction between ions.

1. Difference in apparent D_+ and D_-

It is a clear fact that apparent D_+ is less than D_-, or the flux of selected alkali ions is less than that of chloride ions in a diffusion test. Parameter K_{T} in my papers gives a quantitative description of the difference in D_+ and D_-. It should be noted that K_{T} includes two effects: one, K_{T0}, caused by the source solution, and another, K_{Tm}, caused by the membrane potential, the latter is, in fact, a quantified expression of what Dr. Chatterji called "double layer characteristics." For D_{Na} and D_{Cl}, for instance, my theoretical calculation is $D_{\mathrm{Na}}/D_{\mathrm{Cl}} = 0.24$ (see Table 4 in Part 2 of my papers), which is in good agreement with the experimental values reported by Ushiyama and Goto [3] ($D_{\mathrm{Na}}/D_{\mathrm{Cl}} = 0.27$) and by Goto and Roy [4] ($D_{\mathrm{Na}}/D_{\mathrm{Cl}} = 0.2$). I do not know how Dr. Chatterji could conclude a ratio of $D_{\mathrm{Na}}/D_{\mathrm{Cl}}$ 0.1 ($D_{\mathrm{Cl}}/D_{\mathrm{Na}} = 10$ in his discussion). In his previous paper [1], Dr. Chatterji reported an average diffusion coefficient of $D_{\mathrm{Na}} = 1.4$ and $D_{\mathrm{Cl}} = 8.2 \times 10^{-8}$ cm^2/s, which corresponds to a ratio of $D_{\mathrm{Na}}/D_{\mathrm{Cl}}$ 0.17. It is observed that in their experiment [1], the increase in Na^+ concentration at a 3-day interval varied from 0.94 to 0.32 (see Table 1 in Ref. [1]). The value of $D_{\mathrm{Na}}/D_{\mathrm{Cl}}$ reported in Ref. [1] might, therefore, involve a large uncertainty. Nevertheless, the less flux of Na^+ must be compensated by some other cations to keep the electro-neutrality in the downstream solution. Ca^{2+} is the first candidate because the solubility of $CaCl_2$ is much larger than $Ca(OH)_2$. More experimental investigations are, however, needed to quantify the effect of $Ca(OH)_2$ leaching on chloride transport.

2. Difference in apparent D_{diff} and D_{mig}

It has been found that apparent diffusion coefficient from a migration test, D_{mig}, is normally larger than that from a diffusion test, D_{diff}. A quantitative explanation to this phenomenon has been given in my papers. In my opinion, the larger D_{mig} is mainly attributed to the disappearance of the effect of K_{T} in a migration test due to a strong external electrical field.

In his discussion, Dr. Chatterji attributed the above phenomenon to the release of chloride ions from the earlier bound state. According to his explanation, the chloride flux in a downstream cell should be significantly larger than that in an upstream cell, because D_{mig} is almost double as large as D_{diff} [5]. However, Truc et al. [6] recently reported that the fluxes of chloride ions measured from both the downstream and the upstream cells under a steady state migration

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☆ Cem Concr Res 30 (2000) 1005–1006.

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PII: S0008-8846(00)00242-8

are quite comparable. Therefore, the release of earlier bound chlorides may be the reason for a lower chloride binding capacity in a migration test, but not be the reason for the large difference in D_{diff} and D_{mig}.

3. Material property and real life concrete

An apparent diffusion coefficient determined by simply using Fick's law or the Nernst–Planck equation involves both material property and environmental condition. This is why different test methods or the same method under different test conditions results in different values of diffusion coefficient. What we are doing is, in fact, to differ material property from the "apparent" coefficient and to establish relationships between different diffusion coefficients, so as to minimize confusions and make use of data from different test methods.

It should be kept in mind that exposure conditions vary very much in reality. Complicated mechanisms of ion transport and lack of methods or models for characterization of the real exposures are big obstacles in predicting chloride penetration into a real life concrete. Proper laboratory test methods and understandings of transport mechanisms are, anyhow, prerequisite. There is a long way to go before we could accurately predict chloride penetration into a real life concrete, especially under unsaturated conditions. However, it is still valuable to test and model concrete under a saturated condition as the first step to the goal.

References

[1] S. Chatterji, M. Kawamura, Electrical double layer, ion transport and reactions in hardened cement paste, Cem Concr Res 22 (1992) 774–782.

[2] S. Chatterji, Transportation of ions through cement based materials: Part 3. Experimental evidence for the basic equations and some important deductions, Cem Concr Res 24 (1994) 1229–1236.

[3] H. Ushiyama, S. Goto, Diffusion of various ions in hardened Portland cement paste, Proceedings of 6th Intl Congr Chem Cem, Moscow, Russia, 1974, pp. 331–337.

[4] S. Goto, D.M. Roy, Diffusion of ions through hardened cement pastes, Cem Concr Res 11 (1981) 751–757.

[5] J. Arsenault, J.P. Bigas, J.P. Ollivier, Determination of chloride diffusion coefficient using two different steady state methods: Influence of concentration gradient. Proceedings of RILEM Intl Workshop on Chloride Penetration into Concr., St. Rémy-lès-Chevreuse, France, 1995, pp. 150–160.

[6] O. Truc, J.P. Ollivier, M. Carcasses, A new way for determining the chloride diffusion coefficient in concrete from steady state migration test, Cem Concr Res 30 (2000) 217–226.