Pergamon

Cement and Concrete Research 30 (2000) 1331

CEMENT AND CONCRETE RESEARCH

Discussion

Reply to the discussion by Carmen Andrade of the papers "Concentration dependence of diffusion and migration of chloride ions. Part 1 and Part 2"☆

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Received 2 June 2000

The author thanks Dr. Andrade for having given him an opportunity to further discuss the decisive parameters influencing chloride transport in concrete. There are indeed four main factors: (1) the parameter K_T describing the effect of counter electrical potential, (2) the ratio of cation velocity to anion velocity β_v, (3) the friction coefficient f which reflects the ionic interaction, and (4) the activity coefficient γ.

The first two parameters, K_T and β_v, are related to the drift velocities of cations and anions. The apparent difference between these two is that K_T is related to $(v_+ - v_-)$, while β_v is related to v_+/v_-. Mathematically, these two parameters are different, but they are related each other by Eq. (30) in Part 1 of the papers.

The last two parameters, friction coefficient f and activity coefficient γ, have completely different physical meanings. The friction coefficient has the nature of a transport property while the activity coefficient has the nature of a thermodynamic property [1]. There really is very little relationship between the two: the former describes the resistance to movement, while the latter describes the chemical potential as a driving force in the diffusion process.

The definition of friction coefficient has been given as Eq. (6) in Part 1. The concept of friction coefficient is not new, but comes from Newman's book [2], as already referred in the papers. As well known, both effective and apparent diffusion coefficients involve not only the nature of materials transport property, but also the nature of test methods and conditions. This is the main reason why the values of chloride diffusion coefficient scatter very much in the literature. It has been found that, for a concrete material, different methods and test conditions can result in a similar friction coefficient [3]. Therefore, friction coefficient is a core parameter, which well reflects the transport property of concrete. This can be easily seen by rewriting Eq. (6) into $D_{-+} = D_{-0}/f$, where D_{-+} is "the diffusion coefficient of anions with the interaction of cations," as described in Part 1. This diffusion coefficient is what we need for describing the transport property of materials, but it cannot be directly used in Fick's equations. We have already been confused with many diffusion coefficients. To avoid the further confusion, the author prefers the concept of friction coefficient — a reciprocal of D_{-+}.

The classical orthodox activity coefficient γ appears in the chemical potential μ in the form of a logarithmic scale: $\mu = \mu_0 + RT\ \ln(\gamma c)$, which can be found in any classical chemistry textbook. It arises in a diffusion function following a gradient of the chemical potential, in the form of $(1 + \partial \ln\ \gamma / \partial \ln\ c)$. In a concentration range from 0 to 1 mol/l, the activity coefficient of NaCl only changes from 1 to 0.68, as Dr. Andrade reported [4]. The maximum absolute value of $\partial \ln\ \gamma / \partial \ln\ c$ cannot be larger than 0.1, as shown in Fig. 3 in Part 2 of the papers. Thus, the influence of activity coefficient on ion transport is limited. This has also been demonstrated by Marchand et al. [5] from their numerical approach.

References

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☆ Cem Concr Res 30 (8) (2000) 1329.

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PII: S0008-8846(00)00355-0