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Discussion

A discussion of the papers "A novel method for describing chloride ion transport due to an electrical gradient in concrete: Part 1 and Part 2" by K. Stanish, R.D. Hooton, M.D.A. Thomas[☆,☆☆]

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In these two papers, the authors have proposed and verified a novel phenomenological data fitting method to describe chloride ion profile in concrete samples subjected to so-called "migration tests"[1,2]. The authors commented that they could not find any other suitable explanation for the chloride ion profiles. In this context, I have some observations that may interest the authors and other workers in the field.

Consider the analogous case of water penetration in a dry soil. In this case, many of the complicating factors of chloride ion penetration, e.g., chloride binding by cement hydration products, effect of other ions, etc., do not occur. The authors also referred to this case in Eq. (8) of Ref. [1]. Soil physicists and hydrodynamists have studied this case rather extensively [3–5]. From these references, it can be found that the moisture profile can in general be divided into saturated and unsaturated parts. D'Arcy's law apply only to the saturated part of the sample. The penetration depths of both the saturated and unsaturated parts of the moisture profile individually obey a $\sqrt{t}$ rule, where t represents the exposure time [4,5]. For a bundle of straight glass capillaries of different radii, the dependence on the $\sqrt{t}$ rule follow directly from the Hagen–Poiseulle's equation. Consider the case of a bundle of horizontal glass capillaries of known size distribution. One end of this bundle is in contact with a water reservoir of shallow depth such that gravity does not play any part in the water flow. In an individual capillary, the length of water penetration, l, is given by:

$$l = (r\gamma/4\eta)^{0.5}t^{0.5} \tag{1}$$

where r is the radius of the capillary; γ and η are the surface tension and viscosity of water and t is the elapsed time of water penetration. From the known size distribution of the capillaries, it is easy to calculate how many of these capillaries will be water filled at a given time at a given distance from the water reservoir. From this value, one can also calculate what is the overall degree of saturation of the bundle at that time and distance. At the initial stage, a plot of these values will yield a decreasing moisture profile like Fig. 6 of Ref. [1]. The development and propagation of the saturated profile depend up on the pore characteristics, i.e., pore volume and size distribution of the pore spaces and their connectivity, of the porous material under study and *may take a long exposure time for its development*. A short time exposure always shows an unsaturated moisture profile. Thus, a decreasing moisture profile in an unsaturated sample does not depend on the specific properties of the solid matrix. A decreasing moisture profile appears both in a bundle of straight glass capillaries of different radii as well as in packed soil samples. Thus, a $\sqrt{t}$ dependence of penetration depth does not depend on diffusion only.

In the case of penetration of an electrolyte solution in a soil sample, one has to be very careful. If the soil sample contains significant amount of charged particles, like smectite, then the hydrodynamic permeability is not a material constant; it decreases with decreasing electrolyte concentration. This decrease is connected with the forma-

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tion of electrical double layers on the smectite particles. Even "Darcy's law is not exactly valid, inasmuch as the relationship between pressure drop and filtration velocity is no longer linear, even for a given porous medium and fluid (electrolyte)" (Ref. [3], p. 118–120). A number of workers (e.g., Ref. [6]) have shown that the cement hydration products are charged particles and their zeta potentials are of the order of -35 mV.

This brings me to water penetration in concrete samples. On earlier occasions, I have drawn attention to the fact that the main bulk of cement paste or concrete remains unsaturated even when the sample is stored under water for a long time. In a theoretical paper, I have shown that a mortar or concrete sample with a water/cement ratio of 0.5 will have a saturated outer layer of about 11 mm after one year of under water storage. The rest of the sample remains unsaturated [7]. Persson [8] gives extensive data on the unsaturated state of concrete samples that were stored under water for 450 days. Furthermore, the rate of penetration of the saturation front is insensitive to external water pressure. Best evidence for this last point is supplied by Collepardi [9]. Collepardi subjected concrete cylinders, of different water/cement ratios and different periods of underwater curing, to DIN 1048 (ISO 703) test. This test consists of subjecting concrete cylinders to 2 days at 1-bar water pressure followed by 1 day at 3-bar water pressure and finally 1 day at 7-bar water pressure. At the end of this test, the cylinder is split open longitudinally and the depth of water penetration is measured. The specification requires that the depth of water penetration should be less that 20 mm. Collepardi reports that a concrete with water/cement ratio of 0.50 requires only 2 weeks water curing to satisfy the specification, a concrete with water/cement ratio of 0.45 needs only 7 days and a concrete with water/cement ratio of 0.40 needs only 3 days curing. It is obvious that before the test, the saturation depths of concrete cylinders were much lower. My personal experience with this test method shows that for well-cured concrete samples with water/cement ratio below 0.50, the water penetration depth seldom exceeds 10 mm.

This brings me to the cases of chloride ion penetration in concrete samples. Stanish et al. have correctly stated, "In a porous media, the ions are only free to travel through the liquid-filled pore space. The ions cannot travel though the solid pore walls". Some of the difficulties of chloride ion penetration, like chloride ion binding, etc., can be avoided by determining the chloride ion profile in the expressed pore solution from different depths. Sergi et al. [10] have reported such chloride ion profile. That chloride ion profile also shows decreasing ion concentration with depth. It appears that decreasing chloride concentration may not be connected with chloride ion binding on the cement hydration products. In a chloride penetration test, the concrete sample was initially free or nearly so of chloride ion. Therefore, one would expect, by analogy with water penetration, a decreasing chloride profile at the initial stage of penetration. Only at longer time the saturated part of the ion profile will develop. The maximum time×volt parameter used by Stanish et al. [2] was 1080 V h. It might not be long enough to develop a saturation front of chloride ion in a water-saturated concrete sample.

The maximum water/cement ratio of the concrete sample used by Stanish et al. [2] was 0.45. Stanish et al. do not describe the pretreatment of their samples. From Collepardi's results and my own experience, I would not expect that the concrete samples were fully water saturated. In that case, the situation is more complicated by the presence of empty pore spaces. Most of the empty pore spaces will not allow chloride ion penetration through them. Furthermore, empty pore spaces will have only the adsorbed water layers on them. Cement hydration products are negatively charged. They will exclude negative chloride ions from the electric double layers on them. As a result, the adsorbed water layers in the empty pore spaces will remain nearly free from chloride ions. Thus, chloride ion penetration through the adsorbed water layers is very restricted and thereby further contributing to the decreasing chloride ion profile with depth.

As far as I understand, in deriving his equation, Tang (Eq. (5). Ref. [1]) assumed a fully saturated concrete sample. Tang also assumed that the ionic mobility, U, to be constant. In fact, U is related to the molar concentration, c, of an ion by an equation of the type $Y=A-B\sqrt{c}$ where A and B are two constants [11]. This concentration dependence is valid up to about 1 M concentration. Another unusual character of Tang's equation is its assumption of a constant diffusivity, D. Diffusivity, D, of an ion is related to its molar concentration, c, by an equation of the type $Y=A'-B'\sqrt{c}$ [11,12]. All these assumptions have contributed to the unusual shape of the Tang plot.

Migration test method has some other uncertainties, like production of OH^- ions at the cathode compartment and their comigration with Cl^- ions, etc. [13,14]. Unless the unsaturated state of the bulk of a concrete structure and other uncertainties are taken into consideration, the results of migration tests will be of little relevance to long-term chloride penetration in a concrete structure. This has already been observed in Denmark.

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