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Discussion

A discussion of the paper "Electrostatic repulsion between particles in cement suspensions: domain of validity of linearized Poisson–Boltzmann equation for nonideal electrolytes" by R.J. Flatt and P. Bowen[☆]

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I would like to congratulate the authors of this paper. This is one of the most interesting papers I have read for a long time. The authors have gone away from the usual practice of treating pore solution as ideal and symmetrical electrolytes. Instead, they have treated them as noninteger symmetric electrolytes. This has allowed the authors to approach the real world situation more closely. The authors' detailed calculations showed that in the potential range + 10– − 30 mV, the interparticle repulsion remains unaffected by the improved calculation. A deviation from standard calculation shows only above + 10 mV. This is very fortunate for practicing cement technologists. The zeta potential of cement grains in a freshly made paste is about + 10 mV. With time, zeta potential gradually decreases and finally becomes about − 35 mV. This change is connected with the gradual change in the chemistry of the pore solution. In alkali hydroxide solution, it is also − 35 mV [1]. The high negative potential also occurs in ready-mix concrete samples, especially when either a plant does not properly clean the mixer or uses wash water for the next batch. This wash water is often high in alkali hydroxide content.

However, I have some difficulty in utilizing even the standard DLVO methodology. Perhaps, the authors may help remove my misgivings. At this very onset, I would state that the aim of the following discussion is to clear some of my misgivings.

It appears to me that the development of an electric double layer around a particle depends on its having a stable, at least very slowly changing, surface. Dissolving grains do not have stable surfaces. If this assumption is correct, then, hydrating cement grains cannot have electric double layers around them. That the cement grains are always hydrating, even in the so-called dormant period, can be seen in the heat evolution curves [2], in the ongoing net volume shrinkage of the cement pastes [3,4], and in electron microscopic studies of cement pastes made with freshly ground cements [5,6]. The situation of carbonated or partly hydrated cement samples is different. These samples show alternate high and very low chemical reactivity [7,8]. One may therefore assume that in a normal cement paste, the anhydrous cement grains themselves have no electric double layer around them. Incidentally, many of the blending materials, like silica fume pozzolans, have very low reactivity in cement paste [9,10]. Especially, silica fume particles (even ground silica particles) absorb hydroxyl ions very fast and form charged particles [11]. Silica particles can have either positive or negative zeta potential depending upon the Ca^{2+}/M^{1} ratio of the ambient solution.

Above also means that electrical double layers form around cement hydration products. The mean density of cement hydration products is significantly lower than that of anhydrous cement. The hydration products are packed randomly around the hydrating cement grains. These factors make the hydrated layer porous and thicker than one would normally expect. The hydrated layer grows with time. Furthermore, the zeta potentials of cement hydration products are also uncertain. Calcium aluminate hydrates, both cubic and hexagonal, have zeta potentials of about + 60 mV in water and NaOH solutions [12]. The effect of calcium hydroxide solution on them is not known. C–S–H has a zeta potential of + 35 mV in saturated calcium hydroxide solution [13] and − 35 mV in 0.1 N NaOH solution. The zeta potentials of other hydration products, like etteringite, monosulphate, and $Ca(OH)_2$, are not known.

My misgivings are the following:

- What potential should I use to calculate the electrostatic repulsion at the initial stages of hydration?

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- Where should I place the solid–liquid interface boundary? And how is this interface located?
- It is known that the electrostatic repulsion decreases with increasing concentration of finely divided dispersed phase [14]. How will the number density of cement hydration products effect the electrostatic repulsion?

I hope that Drs. Flatt and/or Bowen will have time to help me out of my misgivings.

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