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Discussion

Reply to the discussion by S. Chatterji of the paper "Electrostatic repulsion between particles in cement suspensions: domain of validity of linearized Poisson–Boltzmann equation for nonideal electrolytes"☆

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We thank Dr. Chatterji for his interest and compliments [1] about our paper [2].

Dr. Chatterji mentions the difficulty that he has in "utilising even the standard DLVO methodology". So do we, to the extent that Dr. Chatterji means estimating the electrostatic force by a Poisson–Boltzmann-type approach. As we stated in our paper: "....It (*our treatment of the electrostatic force*) remains however limited by the continuum mean field framework in which such approaches are anchored. The limitations of mean field theory are particularly apparent on close approach (~2–5 nm). Finite size effects of the ions is perhaps the most immediate to come to mind. However, important deviations from continuum theory only appear important for polyvalent ions [5], and this results essentially from ion correlation effects."

Dr. Chatterji is concerned that no electric double layer will develop on the dissolving grains because of the absence of a stable surface. It appears to us that for some readers, a clarification may be necessary here. The issue Dr. Chatterji is raising lies in the pertinence of assuming the equilibrium of electrochemical potential between the surface and the bulk, as is done in Eq. (1) of our paper. An issue which we had already mentioned: "A word of caution must be made with respect to hydrating cement suspensions, since these are not at full chemical equilibrium and that the ionic composition evolves with time."

The hypothesis underlying Eq. (1) allows, with the knowledge of the bulk concentration of electrolyte, the surface potential to be calculated from the distribution of ions as a function of the distance for the charged interface. When two surfaces approach, ions are in excess with respect to their equilibrium concentration, and an osmotic pressure results, which leads to a repulsive force between surfaces with similar potentials.

The question raised by Dr. Chatterji pertains to how to deal with a situation in which this equilibrium condition is not reached. As mentioned in our paper, we believe that this assumption is valid for snapshots where the input of ionic composition and surface charge are needed: "However, locally one might still reach an equilibrium condition in which ions have the same chemical potential in the bulk as close to the reacting surfaces. Over time, the nature of the exposed surfaces changes, so that the potential changes and that other ionic compositions will match this equilibrium requirement..."

We presume that Dr. Chatterji remembers reading these words of caution but would like to be informed of why we think this might be so or what might be done to evaluate electrostatic interactions if the hypothesis is questionable.

First of all, it appears necessary to remind the reader that owing to the typical range of ionic composition of the aqueous phase of cementitious suspensions, the Debye length is small on the order of 0.7 nm. About twice that distance is the range where ion concentration is affected by the surface charge.

The issue is not so much whether over such distances, equilibrium establishes quickly or not, but whether there is a larger range diffusion gradient from the surface into the bulk. In such a case, the bulk concentration of electrolytes will actually underestimate the concentration with which the equilibrium may be considered to be established locally. Presuming that one has a reliable measure of the surface potential, this implies that the electrostatic force would be overestimated from our calculation.

Nägele [3] has already given some of these questions consideration. He used three regions to describe the

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evolution of the zeta potential versus time for a Portland cement:

(i) the first corresponds to the "vigorous" early reaction and no zeta potential exists;
(ii) in the second region, a nonequlibrium theory can be used to describe the zeta potential evolution (around 5 to 120 min); and
(iii) for longer times (> 120 min), the standard equilibrium theory can be used. In fact, the differences between the equilibrium and nonequilibrium zeta potential are always small (on the order of 1–3 mV) and are therefore within experimental error for most zeta potential measurement methods, apart for the first few minutes.

Dr. Chatterji raises another point of concern about the charge of various phases. It is an unfortunate fact that much of the early literature dealing with the surface charge or rather zeta potential, of cement particles was based on methods that require conditions far from reality and can be the source of many artefacts and misinterpretation (electrophoeresis). Results from different groups were not always in agreement, as stated in Reference 13, quoted by Dr. Chatterji. For methods allowing more realistic conditions, such as electro-osmosis, efforts to calculate an accurate zeta potential from the data (i.e., taking into account surface conductivity) were not often made [4]. More recent techniques, such as electroacoustics, appear better suited for cement suspensions [5]. However, even in this case, there are serious difficulties in obtaining reliable values of zeta potential, a fact we have already described [6]. What does appear quite clearly, however, is that the true zeta potentials are smaller than some early studies have led the cement community to believe (no more than 10 mV in absence of organic admixtures; [5,6]).

With such potentials and ionic strengths, the conclusion is that electrostatic repulsion is not an important process. That is in the early stages of hydration. As hydration layers build up, the dispersion force that causes the agglomeration is expected to decrease [7]. However, in parallel, ion correlation forces cause the cohesion of C–S–H bearing surfaces. These are short-range attractive electrostatic forces and are specific to multivalent ions [8,9]. As we mentioned in our paper, the role of these forces is not considered in our treatment.

Dr. Chatterji asks what potential must be used to calculate electrostatic repulsion at the initial stages of hydration? As stated above, the work of Nägele [3] indicates that equilibrium and nonequilibrium zeta potentials are the same within experimental error apart for the first few minutes. Hence, the very first minutes of hydration cannot be tackled within the framework we presented. However, beyond these few minutes, equilibrium approaches appear reliable. The most reliable values of potential values, then, are probably those determined by electroacoustic methods, but are still to be used with caution. The magnitudes are small and lead to the conclusion that electrostatic repulsion is not important. However, electrostatic attractions, whether from ion correlation forces or surface charge inhomogeneity, are topics that need to be considered in terms of their contribution to the cohesion of agglomerates. It is also quite possible that small amount of organic admixtures may contribute to decreasing this cohesion by the homogenisation of surface charge, thus, by reducing attractive forces rather than introducing repulsive ones.

The issue about the exact positioning of the plane of origin is also unclear to us. The zeta potentials that most people use, including us, are potentials at some "shear plane" at a certain distance from our hydrating surface. It is very unlikely to be directly at the particle's surface and is difficult to thus locate. This position of the charged plane has larger implications in stability calculations for adsorbed superplasticizers, as discussed elsewhere [5,10]. This issue is a challenge for the future, and we hope that molecular modelling might bring some elements of answers to such questions in the not too distant future.

Concerning the question about how the number density of cement hydration products will affect the electrostatic repulsion, we must first stress that, as we already indicated, C–S–H particles will tend to introduce ion correlation forces, which are responsible for the cohesion of C–S–H.

Concerning the Reference 14 quoted in Dr. Chatterji's discussion paper, its contribution is an evaluation of the electrostatic repulsion in concentrated dispersions to take into account the field of more than one neighbouring particle. As the authors illustrate themselves in one of their figures, this becomes increasingly less relevant as ionic strength increases, leaving two body interactions quite suitable for discussing electrostatic repulsion in cement suspensions, given their high ionic strengths and low surface charges (as measured by electroacoustic methods). Thus, this leaves the role of particle size, which can be addressed through the long-standing Derjaguin approximation.

We thank Dr. Chatterji for his interest and challenging questions. We hope to have given answers he will be satisfied with.

Finally, we would like to state that we have very much enjoyed joining the restricted club of the "Chattterji discussions" in such illustrious company as Professors Scherer, Uchikawa, Buenfeld, and Monteiro!

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