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Discussion

Discussion of Y. Zhang et al., “Study of ion cluster reorientation process of geopolymerisation reaction using semi-empirical AM1 calculations,” Cem Concr Res 39(12): 1174–1179; 2009

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ABSTRACT

We provide a brief discussion of some issues related to a recent paper published in Cement and Concrete Research.

The recent paper of Zhang et al. [1] touches on a number of issues which are worthy of comment, as well as bringing a need for clarification in some areas. The desire to understand the process of formation of geopolymers at a molecular level is certainly shared by the authors of this discussion, and so it is heartening for us to see that researchers are addressing this important problem by the application of a range of experimental and theoretical techniques. However, as we will discuss in more detail below, we are not convinced that some of the data presented in [1] are sufficiently accurate to justify the conclusions reached by the authors of that paper.

The main difficulty in applying the calculations presented by Zhang et al. [1] to the formation of geopolymers is to do with the selection of the species upon which the calculations are based. The fundamental building blocks used in the calculations are $HOSi(OM)_3$ and $HOAl(OM)_3^-$, where M is Na or K. In effect, this means that it is assumed that all silicate monomers are triply deprotonated, and the reactions modelled involve condensation of these species with expulsion of MOH to form dimers and trimers which contain no more than a single proton.

The problem here is therefore very straightforward: the third pKa of $Si(OH)_4$ is believed to be around 15.7, and the second-final pKa of the dimer $Si_2O_7H_x^{-(6-x)}$ is 15.8 [2]. This means that this is approximately the pH which must be reached before the triply-deprotonated species modelled in [1] become the predominant silicate species present in solution. At such a high alkalinity, the fact that pH scale is defined in terms of hydrogen ion concentrations becomes problematic, so it becomes more convenient to work on a pOH scale, where $pOH = 14.0 - pH$ (at 25 °C). A pOH of around -1.7 gives $a_{OH} \sim 50.1$, which is equivalent to approximately a 19.3 m (mol/kg H_2O) solution of NaOH at 25 °C, taking into account the increase in the activity coefficient in highly concentrated NaOH solution [3]. This is a much higher concentration than would realistically be used in a geopolymer synthesis, and is approaching the solubility of NaOH in water at 25 °C.

The situation with regard to aluminate in [1] is unfortunately even further from the reality of the solution chemistry of this ion. A major review in 2001 stated that “[t]here is no evidence for the existence of deprotonated aluminate species such as $Al(OH)_3O^{2-}$ in alkaline solution” [4] — let alone the triply-deprotonated (quadruple negatively charged) species proposed in [1]. A small extent of dimerisation of aluminate (similar to reaction 3 in [1]) has been hypothesised to occur in alkaline solutions at concentrations of several molal $NaAl(OH)_4$ [5,6], but this is understood to only involve fully protonated aluminate monomers reacting to form a species similar to $Al_2O(OH)_6^{2-}$, not the highly deprotonated form described in [1].

A secondary issue is that the reactions are treated at a reasonably low level of theory, via the AM1 semi-empirical modelling framework. This is not in itself a problem, except that comparable reactions (but with more realistic degrees of protonation) have previously been modelled using high-level Hartree–Fock methods, including in some cases the inclusion of solvation effects, which are seen to significantly influence the energetics of the reaction processes. Such investigations include (but are not limited to) the papers [7–9]. While it is not always necessary (or even desirable) to use the highest levels of theory in molecular modelling, it would seem essential, when reporting the results of a lower-level investigation, to at least provide some sort of comparison with the results of higher-level studies, either to validate

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or to provide an estimated error bound on the lower-level computations. It is also important to note that the discussion in [1] of reactions taking place 'in NaOH solution' or 'in KOH solution' are not strictly accurate; the computations do not in fact take into account the presence of a solution phase at all. To describe such effects, either an implicit or explicit solvent model would be required; the computations presented are in the gas phase.

In the discussion of potential reaction pathways, the authors of [1] also implicitly assume that the geopolymer formation process is under strict thermodynamic, rather than kinetic, control, meaning that the lowest-energy reaction product is assumed to always be formed. However, it is well known that the X-ray amorphous geopolymer binder is metastable with respect to zeolite crystals and other ordered aluminosilicate phases [10,11], and therefore kinetic control and/or cluster size effects [12] will be critical in determining the actual reaction pathways. The results presented in [1] do not provide such insight, and cannot therefore be claimed to predict the most probable reaction pathways; insight from transition state theory and the calculation of potential energy surfaces would be required to provide such information.

So, in summary, the conclusion of this discussion is that the results presented in [1] display a somewhat inaccurate analysis of the reaction processes which lead to geopolymer formation. The idea behind [1] is certainly a good one: using molecular models to deconvolute the complex processes involved in geopolymer synthesis is an admirable aim, as it will provide the fundamental understanding necessary for the optimisation and wider use of these materials. However, the selection of species to be modelled, the lack of comparison with higher-level computations, and the interpretation of the results with regard to reaction pathways, could each be improved.

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