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Discussion

Reply to the discussion by John L. Provis, Claire E. White, Jannie S. J. van Deventer on the paper “Study of ion cluster reorientation process of geopolymerisationreaction using semi-empirical AM1 calculations” by Y. Zhang et al.

Zhang Yunsheng*

Jiangsu Key laboratory for Construction Materials, Southeast University, Nanjing, 211189, PR China

The comments on our paper are appreciated. They address some issues which are very significant to better understand the ion cluster reorientation process of geopolymers at a molecular level. The authors of both the paper and the discussion are aware that, although it is not easy, it is desirable to study the possible pathways involving the synthesis of geopolymers by the application of a range of experimental techniques and quantum chemistry theory. Of course it is not at all unusual for different researchers to reach somewhat differing conclusions; this is not necessarily a negative thing. In fact, such differences may pave the way to a better overall understanding of the novel type of inorganic cementious materials-geopolymer by the community at large. In this spirit, the authors present the following responses to the issues raised in the discussion of their article.

The discussion states that the selection of Si and Al species, upon which the calculations are based on, is controversial and needs to be improved. The higher alkalinity (approximately $pKa=15.7$) than the realistically used one in geopolymer synthesis is needed to obtain the $HOSi(OM)_3$ species that are modelled. I accept this viewpoint. In fact, we had measured pH values in the fresh geopolymer pastes. It is about 14, which is a little lower than $pKa=15.7$. The chemical status of $Si(OH)_4$ in MOH solution of $pH=14$ is not reported in the public literature. Babushkin [1] showed that more than 97.47% of $Si(OH)_4$ exists as $HOSiO_3$ anion that will participate in ion-pairing reaction with alkali metal cation $M+$ (M represents Na or K) to form $HOSi(OM)_3$ species in strongly alkaline solution ($pH>14$). Although a difference exists between $pKa=15.7$ and the realistic one ($pH=14$), it should be reasonable to assume that in strongly alkaline geopolymeric pastes most of the $Si(OH)_4$ exists as $HOSi(OM)_3$ species, but the percentage of $HOSi(OM)_3$ species is lower than 97.47%.

Another point raised is there is no evidence for the existence of deprotonated aluminate species such as $Al(OH)_3O^{2-}$ in alkaline solution, let alone the triply deprotonated. Firstly I thank the discussion authors very much for pointing this out. When we performed the modelling, the same situation was also encountered. No documented literature involved the state of $Al(OH)_4$ anion in alkaline solution could be found, so, in order to make the calculation, it was assumed that $Al(OH)_4$ anion exists as $HOAl(OM)_3$ species in MOH solutions by considering a similar role as Si. Further modelling will be carried out by using $OH–Al^{-}(OM)_2–O–Al^{-}(OM)_3$ or others as the Al species.

The final issue raised was that the reactions were treated at a reasonably low level of theory — AM1 semi-empirical modelling framework. High-level methods including in some cases the inclusion of solvation effects should be used. In our research group, *ab inito* method is recently employed to calculate the reaction energies involving the dissolution-reorientation and polycondensation process of geopolymers.

As said by the discussers, the reorientation process in the paper is analyzed according to thermodynamic theory, rather than a kinetic one. As suggested, we will further improve the calculation results by using the transition state theory and calculation of potential energy surfaces. I believe that the interpretation of the results with regard to reaction pathways could be improved in the near future.

Reference

[1] V.T. Babushkin, G.M. Matveyev, O.P. Mchedlov-Petrossyan, Thermodynamics of Silicates, Springer-Verlag, Berlin, 1985 pp 276–281.

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* Tel.: +86 25 52090640; fax: +86 25 52090667.
E-mail address: zhangys279@163.com.

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