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Discussion

Discussion of C. Li et al., “A review: The comparison between alkali-activated slag (Si + Ca) and metakaolin (Si + Al) cements”

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The recent paper of Li et al. [1] provides a timely overview of some important scientific areas related to alkali activation, and in particular the distinction between calcium-dominated (alkali-activated slag) and aluminosilicate-dominated (“geopolymer”) systems. For this reason it is a valuable contribution to the literature. However, there are some points in [1] which do require clarification, particularly with regard to the chemistry of slag and its relationship to dissolution behaviour.

The most important point requiring discussion is the comment (Section 2.1 of [1]) regarding phase separation in slag glasses, where it is stated that the slag will form “…two phases: a silica rich phase with composition close to SiO_2 and an alumina rich phase with composition close to $Al_6Si_2O_{13}$”, and citing the work of Aramaki and Roy [2]. However, it is important to note that the paper of Aramaki and Roy relates strictly to the binary Al_2O_3–SiO_2 system, in the absence of Ca. Phase separation into a silica glass and a mullite glass as described here is observed upon rapid cooling of molten kaolinite particles, as occurs during generation of fly ash in pulverised coal combustion [3], but will not happen in the presence of high levels of Ca. The phase diagram of the system CaO–Al_2O_3–SiO_2 at 1200 °C shows no coexistence between slag and mullite phases, with this coexistence only possible at 1400 °C below 12 mol% CaO, and at 1600 °C below 17 mol% CaO [4]. Blast furnace slags are much more Ca-rich than this, meaning that mullite formation will not occur within the range of temperatures expected in the operation of a blast furnace.

It should be noted that the authors of [1] are correct in noting that some compositional segregation in slag glasses is possible, in addition to the widely observed partial crystallisation during cooling [5,6]. However, the extent of segregation between Al and Si in calcium-rich slags will not be sufficient to result in the formation of a phase with a composition approaching that of mullite, because a high concentration of alkaline earth cations in an aluminosilicate melt or glass will cause aluminium to retain tetrahedral coordination [7] rather than taking the octahedral form observed in mullite.

A second, related point is that the image presented as Fig. 5 of [1] (which is an image reprinted from [8], a paper co-authored by the author of this discussion) is actually a representation of a glassy fly ash particle containing a polymerised silicate glass network with minor Ca and Na as network modifiers, not the much more depolymerised glassy structure of a high-calcium slag. The mechanism of dissolution of a slag glass will therefore be much less dependent on the breakage of Si–O–Si and Si–O–Al bonds than is the case for the fly ash particle represented by this diagram, which is important in understanding the relatively rapid reactions achievable in alkali-activated slag systems when compared to alkali activation of fly ashes.

Additional points worthy of brief note include:

- Table 1 of [1] appears to be an expanded version of a table developed originally by Roy in 1999 [9], with a selection of more recent literature cited. It is debatable whether the literature selected from the past decade in fact represents the most critical advances in the research field in this area — and although it is not the purpose of this Discussion to enter into a discourse in this area, it would certainly be remiss not to mention the extremely valuable 2006 book of Shi et al. [10] in a listing such as this.
- The ‘poly-sialate’ nomenclature depicted in Fig. 1 of [1] is of very limited value in the description of geopolymer gel structures, as it fails to allow for either non-integer Si/Al ratios or the formation of a three-dimensional gel network. Its use has thus been largely discontinued in the geopolymers literature. Also, the schematic diagram shown for the “sialate link” concept is chemically incorrect; the potassium cation would be associated most closely with an (negatively charged) oxygen atom, not the (positively charged) aluminium atom, similar to the well-known alkali cation positions associated with aluminosilicate zeolite frameworks.
- Regarding the influence of sodium silicate solutions (third paragraph of Section 4.1 of [1]), this paragraph does not present an accurate summary of the discussion in the book cited here ([11]; reference 10 of [1]). The role of a silicate solution in enhancing the strength of metakaolin-based geopolymers is primarily due to its role in directing microstructure via control of reaction kinetics [12], not specifically by changing aluminosilicate oligomerisation equilibria.
- Regarding the discussion of Al–O–Al bonds (first paragraph of Section 4.3 of [1]), it is extremely unlikely that these structures will be present in slag glasses, as the formation of Al(IV)–O–Al(IV) sites in aluminosilicates is strongly disfavoured and requires an Si/Al ratio very close to 1 [13,14], which is not the case in slags.

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So, the conclusion of this Discussion is that the review paper [1] does present useful descriptions and summaries of various aspects of the chemistry of alkaline activation of metakaolin and slag, but requires clarification in some areas where the information in the literature appears to have been misconstrued. Therefore, this Discussion has been intended to raise a few technical areas where the analysis presented in [1] is incomplete, with the aim of providing greater scientific clarity to the alkali activation research community.

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