Assessing the capabilities of the ternary CaO-K$_2$O-SiO$_2$ phase diagram to predict real life process behavior with respect to the recent database development

Emile ATALLAH[1,2], Françoise DEFOORT[1], Alexander PISCH[2]

[1] Université Grenoble Alpes, Commissariat à l'Energie Atomique et aux Energies Alternatives (CEA), Laboratoire d'Innovation pour les Technologies des Energies nouvelles et les Nanomatériaux (LITEN), F-38000 Grenoble, France
[2] Université Grenoble Alpes, CNRS, Grenoble INP, SIMaP, 38000 Grenoble, France

Thermodynamic equilibrium simulations have become a widely used tool to better understand and predict the chemical reactions of specific elements in certain applications. More specifically, the ternary CaO-K$_2$O-SiO$_2$ phase diagram was widely used as a prediction tool in the glass and ceramic industries, and more importantly in the biomass thermochemical valorization techniques (combustion and gasification). More than 90% of biomass ash are composed of calcium, potassium, and silica oxides; hence, their behavior governs the ash behavior of the feedstock in the reactor. For instance, high alkali-silicate contents can form ash in the liquid phase that reacts with the bed materials to cause agglomeration in a fluidized bed, and can sinter in a furnace and block the reactor. Consequently, failure to understand the behavior of the CaO-K$_2$O-SiO$_2$ system can cause serious catastrophic operational problems.

CaO-SiO$_2$ and K$_2$O-SiO$_2$ sections are well studied in literature, especially near the pure SiO$_2$ region [1]. However, liquidus is not accurate and data for CaO-K$_2$O region are totally absent in literature due to K$_2$O volatilization that poses several problems on its synthesis and measurements [2–3]. As a result, the main aim of this work is to present the recent development in the thermodynamic database of this system, highlighting the differences between GTOXID and FTOXID databases. Then, ternary phase diagram calculation and process simulation are compared against equilibrium P-XRD findings of ash samples from a 50-50 mixture bark – straw mixtures in combustion at 1000°C. This aims to assess the weaknesses in the database and help to direct the further improvements that are needed.

The two major ternary phases K$_2$Ca$_2$Si$_2$O$_7$ and K$_2$Ca$_6$Si$_4$O$_{15}$, which were found experimentally at equilibrium, were totally absent from GTOXID database. Despite their presence in FTOXID database, the existing tie lines were found to be contradicting with the experimental results. Besides, K$_2$CaSiO$_4$, reported to be at equilibrium in the database, was absent in all experiments. Process simulation at equilibrium also showed contradicting results with experiments. For instance, K$_2$Ca$_2$Si$_2$O$_7$ was found to be destabilized by magnesium, phosphorous, and chlorine in the process simulation. In addition, different concentrations were found between the predicted phases in the thermodynamic simulation and those found experimentally at equilibrium. Consequently, even the most recent database needs further improvement. The ternary phases of interest should be synthesized and their thermodynamic properties should be measured to remodel this system more effectively.

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