Kinetics of Fe (III) mineral crystallization in the presence of Si at alkaline conditions

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Fe (III) minerals are ubiquitous in diverse near-surface environments, where they exert important controls on trace species transport. In alkaline environments such as the glass-steel interface in geological HLW disposal sites with cement plugging and grouting, Fe minerals are closely associated Si that may affect their structure and reactivity. While it is well-known that Si retards Fe mineral crystallization, there is currently an overall lack of quantitative information on the rates of crystallization of stable Fe minerals in the presence of Si at alkaline conditions. Kinetic data may be useful in predicting Fe mineral crystallization in these environments, which may have implications in the dissolution rates of vitrified waste and the transport of radioactive contaminants.

Batch synthesis experiments of Fe-oxides/oxyhydroxides in the presence of varying amounts of Si were conducted at a constant pH of 10 and at 50°C to 80°C. Samples extracted at different reaction durations were characterized using powder XRD. The proportion of different phases in the product were estimated from XRD data using Rietveld refinement and plotted as a function of time to derive kinetic parameters.

Results show the rapid precipitation of metastable ferrihydrite ($5Fe_2O_3 \bullet 9H_2O$) at high pH. At all temperatures, the presence of Si generally delays the appearance of crystalline phases. With increasing Si, the percentage and crystallization rate of goethite (α-FeOOH) decrease, while those of hematite (α-Fe_2O_3) increase then drastically drop at Si concentrations greater than 5×10^{-4} M Si. Apparent activation energies for goethite increase with increasing Si, indicating the inhibition of goethite crystallization. On the other hand, apparent activation energies for hematite show that hematite crystallization is promoted at low Si concentrations but is then eventually inhibited at higher concentrations. The influence of Si on Fe mineral crystallization may be explained by its effect on the dissolution and aggregation of the ferrihydrite precursor, which are crucial steps in goethite and hematite formation, respectively.