

Speciation and Crystal Chemistry of Fe(III) Hydrolyzed in the Presence of SiO₄ Ligands

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Beamline(s): X23A2

The hydrolysis and condensation mechanisms of Fe(III) in aqueous solutions have received considerable attention in the past decade. The nature and structure of the resulting solids strongly depend on the nature and concentration of the ligands present during hydrolysis. For instance, Fe(III) chloride and nitrate lead to the formation of β -FeOOH and α -FeOOH respectively. Complexing ligands such as PO₄ or natural organic matter strongly limit the polymerization of Fe(III), dimers and trimers typically being the largest Fe species.¹⁻³ Despite their relevance in environmental as well as industrial processes, the influence of the potentially strongly complexing SiO₄ ions on the Fe hydrolysis has not been studied in detail at the molecular scale. The present study describes the results obtained on beamline X23A2 at the NSLS for Fe-Si systems with a Si/Fe molar ratio between 0 and 4, and pH values ranging from 3 to 10.⁴ All samples were prepared by adding NaOH to FeCl₃-Tetra Ethyl Ortho Silicate mixtures ([Fe] = 0.2 M) until the desired pH was reached (3, 5, 7 and 10). The suspensions were then centrifuged and the residue freeze-dried. Fe K-edge measurements were performed in the transmission mode. Standard data treatment was done using the software suite developed by Michalowicz.

The presence of SiO₄ ligands largely affects the polymerization of iron. The total number of Fe neighbors (between 5.5 and 2) is sensitive to the Si concentration. However there is no linear trend between these two parameters. The total number of neighbors decreases sharply at low Si/Fe (<1), reaches a minimum at Si/Fe = 1, and increases again for higher Si/Fe ratios, without, however, reaching the initial (i.e. without Si) value. This trend is observed at all 4-studied pH values. This shows that SiO₄ ligands have an inhibiting effect on the polymerization of Fe(III). However, this effect is weaker than in the case of phosphate or organic ligands. The analysis of linkage types between Fe atoms revealed an interesting feature. For the low Si/Fe ratios, the decrease of the total number corresponds to a decrease of the number of all linkage types: edge (Fe-Fe around 3 Å), double corner (Fe-Fe around 3.45 Å) and single corner (Fe-Fe around 3.85 Å). The increase of the total number from Si/Fe = 1 is predominantly due to an increase of the number of edge linkages. For those samples, the number of double corner linkages remains low and single corner linkages are not detected anymore. This suggests the presence of two growth regimes for Fe species in Fe-Si systems. At low Si/Fe, the presence of corner linkages is indicative of a three-dimensional growth, whereas at high Si/Fe, the predominance of edge linkages suggests a two-dimensional, sheet-like growth, systems at Si/Fe around 1, where complexation by Si causes the Fe polymerization to reach a minimum, representing a crossover between these two regimes. Additional FT-IR and ²⁹Si NMR results support these findings and in particular the existence of Fe-O-Si bonds within the precipitates.^{5,6}

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