

Structure investigation of Cr(III)-Fe(III)-oxyhydroxides

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Chromium is an important anthropogenic contaminant and its transport in the natural environment can be strongly affected by the occurrence of iron minerals. Cr(VI) can be reduced by iron minerals to Cr(III), which is less toxic and mobile. Chromium(III) (oxy)hydroxide and mixed Cr(III)-Fe(III)-(oxy)hydroxides are known to have very low solubilities and therefore are likely to be the fate-controlling phase of Cr(III) in natural environments. However, due to their X-ray amorphous properties, little is known about their actual structure. This study involves synthesis Cr(III)-Fe(III)-(oxy)hydroxides of different composition, and the use of TG-DTA, FTIR, HRTEM, X-ray absorption spectroscopy (XAS), and pair distribution function (PDF) analysis to evaluate their solid solution properties and their structure. The results provide new information on the speciation of Cr and remediation methods based on the reduction of Cr(VI) to Cr(III).

TG-DTA results show that the Cr end member has a higher water content than the Fe end member, and show two stages of weight loss probably related to loss of structural water and/or hydroxyl groups. For Cr-Fe-(oxy)hydroxides, as Cr content decreases, the temperature for dehydration decreases and the temperature for dehydroxylation increases. Weight loss and chemical analysis give a possible chemical formula of Cr(OH)₃·3H₂O for the Cr end member. Temperature resolved *in situ* X-ray diffraction study shows that the Cr end member converts to crystalline Cr₂O₃ at around 420°C. XAS and PDF analysis show that the Fe end member is similar to nanocrystalline 2-line ferrihydrite with an average particle size of 2 nm, and the Cr end member sizing around 1 nm is likely to be amorphous. Results show these compounds are not simply physical mixtures of the end members because chemical substitution across the whole series was observed.

Structural investigation of Fe(II) adsorption on hematite (0001) and (1 $\bar{1}$ 02)

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Iron (hydr)oxides play a key role in iron biogeochemical cycling and act as one of the most important natural scavengers of numerous contaminants primarily via adsorption reactions. Therefore, biological availability and transport of Fe and aquatic contaminants is strongly influenced by stability and surface reactivity of iron oxides. The adsorption of Fe(II), a highly soluble and common aquatic species, significantly impacts the stability and surface reactivity of ferric (hydr)oxides [1]. However, there is still limited molecular scale understanding of Fe(II) binding modes and surface reaction pathways.

In this study, the structure of hematite (0001) and (1 $\bar{1}$ 02) surfaces are determined after reaction with Fe(II) using synchrotron based crystal truncation rod (CTR) X-ray diffraction. The results show surface bound Fe occupies crystallographic lattice sites on both hematite surfaces. However, the geometry of adsorbed Fe complexes is different on different surface, which highlights the importance of surface structure of underlying substrate. On both substrates the average Fe-O bond lengths of surface bound Fe are characteristic of Fe(III). These observed Fe-O bond lengths provide indirect evidence of oxidation of Fe(II) after adsorption, which is consistent with recent studies indicating Fe(III) oxides are effective oxidants for dissolved ferrous ion [2, 3, 4]. Overall, the structural understanding of incipient Fe(II) adsorption on iron oxides will result in an improved understanding of how Fe(II) affects structure, stability and reactivity of iron oxides.

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