

Release of chromite nanoparticles and their alteration in the presence of Mn-oxides

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ABSTRACT

The discovery of chromite nanoparticles in silicates of ultramafic rocks may change our approach on the environmental risk assessment of mine waste associated with chromitite mining. This experimental study shows for the first time that the alteration of Cr-rich silicates results in the release of chromite nanoparticles and that their interaction with oxidizing Mn-oxide nanoparticles causes the dissolution of chromite and Mn-oxide nanoparticles and the precipitation of Fe³⁺- and Cr³⁺-hydroxides. Transmission electron microscopy (TEM) in combination with ultra-microtomy, centrifugation, chromatography, ICP-MS, and UV-VIS is used to characterize release and alteration of chromite nanoparticles and the concentrations and speciation of Cr aqueous species. Alteration of clinocllore grains containing chromite nanoparticles results in the release of the nanoparticles and their attachment to Si-bearing Al-hydroxide colloids. Chromite nanoparticles with the end-member composition FeCr₂O₄ are synthesized, and their interaction with Mn-oxide nanoparticles (hausmannite, Mn₃O₄), Fe²⁺-silicates (chamosite, [(Fe_{3.9}Mg_{0.62}Al_{0.48})Al(Si₃Al)O₁₀(OH)₈] and organic matter is studied over a period of six to nine months in suspensions of pH = 5. The interaction of chromite and hausmannite nanoparticles is facilitated by the aggregation of the nanoparticles and dissolution-precipitation processes. Processes on the surfaces of the hausmannite nanoparticles include the reductive dissolution of the substrate (reduction of Mn³⁺ to Mn²⁺ by Fe²⁺ species) and its replacement by amorphous or nanocrystalline Cr³⁺-bearing Fe³⁺-hydroxides. Processes on the surfaces of the chromite nanoparticles involve the attachment of hausmannite nanoparticles, the oxidative dissolution of the substrate (oxidation of Fe²⁺ and perhaps Cr³⁺ by Mn³⁺ species), its replacement by an amorphous or nanocrystalline Mn-bearing Cr³⁺-hydroxide matrix and the formation of the Cr³⁺-hydroxides bracewellite and grimaldite within the latter matrix. Analyses of the suspensions indicate only minor amounts of Cr⁶⁺ in the suspensions (<5 µg kg⁻¹) suggesting that formation or occurrence of Cr⁶⁺ species can be limited in complex geochemical and mineralogical systems even in the presence of hausmannite nanoparticles.

Keywords: Chromite, nanoparticles, alteration, manganese oxide, hexavalent chromium, TEM, colloids, mine waste