
Chromate Removal by Dithionite-Reduced Clays: Evidence from Direct X-Ray Adsorption Near Edge Spectroscopy (Xanes) of Chromate Reduction at Clay Surfaces

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Abstract: Chromium(VI) in the environment is of particular concern because it is toxic to both plants and animals, even at low concentrations. As a redox-sensitive element, the fate and toxicity of chromium is controlled by soil reduction-oxidation (redox) reactions. *In-situ* remediation of chromium combines reduction of Cr(VI) to Cr(III) and immobilization of chromium on mineral surfaces. In this study, Fe-rich smectite, montmorillonite, illite, vermiculite, and kaolinite were examined to determine reactivity in sorption-reduction of Cr(VI). The clays were compared to forms that were reduced by sodium dithionite. Clays containing Fe(II) efficiently removed soluble Cr(VI) from solution. Chromium K-edge X-ray absorption near edge structure (XANES) suggested that clays containing Fe(II) reduced Cr(VI) to Cr(III), immobilizing Cr at the clay/water interface. Adsorption of Cr(VI) by the Fe(II)-containing clay was a prerequisite for the coupled sorption-reduction reaction. Sodium dithionite added directly to aqueous suspensions of non-reduced clays reduced Cr(VI) to Cr(III), but did not immobilize Cr on clay surfaces. The capacity of clays to reduce Cr(VI) is correlated with the ferrous iron content of the clays. For dithionite-reduced smectite, the exchangeable cation influenced the sorption reaction, and thus it also influenced the coupled sorption-reduction reaction of Cr(VI). The pH of the aqueous system affected both the amount of Cr(VI) reduced to Cr(III) and the partition of Cr(III) between aqueous and adsorbed species. A plot of pH *vs.* amount (adsorption envelope) adsorbed for the coupled sorption-reduction reaction of Cr by reduced smectite exhibited a similar pattern to that of typical anion-sorption.

Key Words: Illite • IMt-2 • Kaolinite • KGa-2 • Montmorillonite • Reduction • Smectite • Sorption • SWa-1 • SWy-1 • XANES

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