

Effects of Isomorphic Substitution on Hexavalent Chromium Reduction by Green Rust

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The Fe (II, III) layered double hydroxide mineral green rust sulfate (GRSO₄) is a proven reagent for reductively transforming hexavalent chromium, but the long-term stability of the byproducts of this reaction is under debate. Our previous work (Thomas et al., unpublished) suggested that reductive transformation of hexavalent chromium at concentrations characteristic of contaminant plumes produced an amorphous Cr (III) hydroxide product at the surface of the green rust particles via an internal electron conduction mechanism. Although the particles successfully remove the chromium from solution, Cr (III) is susceptible to oxidation in soils via existing manganese redox cycles. From a remediation standpoint, the preferred byproduct of this reaction is therefore a less soluble Cr (III)-bearing byproduct such as Cr (III)-substituted goethite.

We hypothesise that cation substitution (e.g., with Al, Mg, Zn) in GRSO₄ can theoretically slow electron conduction within GRSO₄ crystals because these cations are unlikely to change oxidation states. This in turn may favor an interlayer sulfate exchange with chromate, leading to the production of Cr (III)-substituted goethite. We tested this here by synthesizing GRSO₄ with 5% molar substitutions of Zn, Mg, Al and combined Mg/Al and Zn/Al. These particles were reacted with chromate solutions and then characterised with X-ray diffraction and transmission electron microscopy. Initial observations show goethite as the main product, with low crystallinity. This potentially could be due to Cr incorporation, as well as the presence of the substituted cations.