Effects of Aging on Hexavalent Chromium Reduction by Green Rust Sulfate: Kinetics and Reversibility

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Due to its high reactivity and ease of synthesis, green rust sulfate (GR_{SO4}) has been extensively researched as a potential reagent for *in situ* reductive remediation of soil and groundwater contaminants, especially hexavalent chromium, Cr (VI). In short-term, lab-based tests, GR_{SO4} has a high reductive capacity for Cr, but due to the longer lifetimes of remedation projects, there is concern that lab-based studies are inadequate indicators of real-world performance. For example, upon prolonged exposure to groundwater, the reagent's surface area, crystallinity and chemical composition can dramatically change with aging time, which can impact its reactivity and reaction mechanism.

In this study, we performed lab-scale batch reduction of hexavalent chromium by differently aged GR_{SO4} to determine if and how aging affects the reaction pathways and the stability of the reaction products. GR_{SO4}, both pure and with substitutions of Al, Mg and Zn, were synthesized by co-precipitation and then aged for 24 hours and 55 days. Subsequently, batch reduction reactions in the presence of 0.67 mM Cr (VI) were carried out over seven days, The reaction products were then exposed to synthetic δ-MnO_2 to evaluate the vulnerability of Cr (III) in the products to re-oxidation. Mg-substituted GR_{SO4} was the most effective reagent tested, as it consistently produced the most stable Cr (III) reaction products (between 2 and 10% of Cr (III) re-oxidised by δ-MnO_2). However, aging significantly decreased the reactivity of all reactants tested, as well as the stability of the Cr (III) precipitates. In summary, this indicates that GR_{SO4} reagents may not be suitable for use in long-term Cr (VI) remediation projects.