Characterization of Green Rust Sulfate Transformation Products Associated with Hexavalent Chromium Remediation

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Due to its rapid reduction of CrO_4^{2-} and the stability of the Cr (III)-substituted Fe (III) oxide byproducts of this reaction [1], green rust sulfate [$Fe^{II}_4Fe^{III}_2(OH)_{12}SO_4 \cdot 2H_2O$] is a strong candidate for treatment of groundwater contamination by CrO_4^{2-}. Previous studies [1] have characterized the iron oxide byproducts of this reaction under variable conditions and have determined that the identity of these byproducts exhibits a strong dependence on the reaction kinetics (and therefore [CrO_4^{2-}]). However, the effects of [CrO_4^{2-}] on the reaction byproducts in the absence of other factors has not been investigated.

In this study, after synthesising green rust sulfate using a modified coprecipitation method [2], approximately 30 mg of green rust were oxidized to completion in CrO_4^{2-} solutions varying in concentration from 33.3 µM to 1.33 mM. Samples of solid obtained after 24 hours and 7 days were then analyzed using XRD and EXAFS techniques at the ANKA synchrotron facility. These techniques revealed that all CrO_4^{2-} was reduced to Cr (III) and the composition of all reacted samples included ferrihydrite and goethite. Although there are significant differences after 24 hours, all samples are virtually identical after 7 days, where a solid composed of 70% ferrihydrite and 30% crystalline Fe (III) oxide (of variable composition) was observed. Based on these results, we have hypothesized that because green rust sulfate has multiple reaction sites, different reaction mechanisms produce goethites with variable amounts of Cr (III)-for-Fe (III) substitution. Goethite domains with high levels of substituted Cr (III) [3] then transform into Cr (III)-ferrihydrite.

[1] Skovbjerg, Stipp, Utsunomiya & Ewing (2006). *Geochimica et Cosmochimica Acta* 70, 3582-3592.

[2] Ruby, Géhin, Abdelmoula, Génin & Jolivet (2003). *Solid State Sciences* 5, 1055-1062.

[3] Schwertmann, Gasser, & Sticher (1989). *Geochimica et Cosmochimica Acta* 53, 1293-1297.