

The effect of aluminium on green rust sulphate structure and reactivity

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Green rust (GR), an Fe^{II}-Fe^{III} layered double hydroxide, has been widely investigated as a potential reductant for toxic metals and chlorinated solvents in contaminated soils and aquifers. As GR reduces the contaminant, GR itself is oxidised to Fe (oxyhydr)oxides, which themselves also have high potential for pollutant trapping. It is useful to know the effect of aluminium in this process because Al is omnipresent in nature and because of its ionic similarities to Fe^{III}, it frequently substitutes for Fe^{III} in minerals. While Al effects on the structure and composition of Fe (oxyhydr)oxides have been reported, little is known about the impact of substituted Al on GR reactivity and its transformation to Fe^{III} phases.

We synthesized GR at constant pH 7, by oxidizing a solution of FeSO₄, with and without dissolved Al. A suite of techniques (i.e., X-ray diffraction, transmission electron microscopy, synchrotron based pair distribution function analysis, transmission Mössbauer spectroscopy) was applied to characterise the synthesised (Al-)GR compounds and oxidation products following reaction with chromate. The results showed that Al substitution in GR dramatically reduced the crystallinity of GR and the stacking coherence of its hydroxide layers, leading to almost 6 fold smaller Al-GR particles compared with pure GR. The smaller size and hence higher surface area, combined with the lower crystallinity, lead to higher chromate reduction rate for Al-GR, compared with pure GR. This showed that although electron hopping might have been impaired by substituted Al in Al-GR, this had little effect on its reductive capacity. Indeed, a higher total amount of chromate was reduced with Al-GR, while for pure GR, the formation of a reaction rim inhibited complete chromate reduction, i.e., GR oxidation. These results are essential for predicting GR formation, stability and reactivity in natural settings and they also open new avenues for GR particle modification, for designing more reactive compounds for contaminant reduction.