

Green rust composition effect on reactivity with toxic metals and chlorinated solvents

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Green Rust (GR) minerals can form in iron-rich, reducing environments and could have played a key role in early Earth history [2]. They are also promising reactants for remediation of toxic compounds in contaminated soils and aquifers [1]. GR minerals belong to the family of layered double hydroxides, consisting of Fe^{2+} - Fe^{3+} hydroxide sheets that sandwich interlayer anion, water and occasionally monovalent cations. The anions in the interlayer, most commonly sulphate, carbonate or chloride, determine the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in the hydroxide layer and hence GR stability and its reduction capacity. It has been shown that ion substitution in the hydroxide layer, e.g., Fe^{3+} by Al^{3+} , leads to changes in GR structure and size [3]. Less is known however, about how such compositional changes affect GR reactivity with toxic metals and chlorinated solvents

In this study, the reductive capacity of Al^{3+} substituted GR (Al-GR) minerals, with either interlayer Cl (GRCl) or SO_4 (GRSO₄), toward common organic (carbon tetrachloride, tetrachloroethylene) and inorganic (chromate) groundwater contaminants was evaluated. Pure GR and Al-GR, with a range of molar Al:Fe ratios, were synthesised by Fe^{2+} oxidation at pH held constant at 7.0. Characterisation with high resolution microscopy and X-ray diffraction showed that Al substitution altered the particle size and crystallinity of both GRCl and GRSO₄, owing to the difference in ionic radius between Fe^{3+} and Al^{3+} . The changes in Al-GR morphology and structure, coupled with varying Fe^{2+} fractions in the structure, led to substantial differences in reactivity toward the target contaminants. This new insight is relevant for designing better catalysts while understanding the implications GR minerals for in-situ remediation.

[1] Erbs et al. (1999) *Environ. Sci. Technol.* 33: 307.

[2] Halevy et al. (2017) *Nat. Geosci.* 10: 135.

[3] Aissa et al. (2004) *Hyperfine Interact.* 156/157: 445.