Mechanisms of Ni²⁺ removal by green rust sulfate (GR_{SO4})

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Green rust (GR) minerals are Fe^{II} - Fe^{III} bearing layered double hydroxides [1] known to incorporate into their structure divalent metals, including Ni²⁺ [2]. In contaminated subsurface environments, removal of toxic metals such as Ni by co-precipitation would be a more effective and permanent method compared to adsorption. However, the efficiency of this process and how Ni incorporation may affect GR properties are still poorly understood. We quantified the removal efficiency of Ni²⁺ using co-precipitation with GR sulfate (GRso4), and assessed the morphological and crystallographic changes in the resulting solids.

GR_{SO4} was synthesized under strict anaerobic conditions from an initial Fe²⁺:Fe³⁺ solution ratio of 3 and in the presence of 0 to 500 mg L⁻¹ of Ni²⁺. The so formed GR_{SO4} was aged for up to 24 hours. The total ion mass balance was evaluated from the aqueous ion concentrations in the supernatant and the elemental compositions of the resulting solids as analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES). Potential variations in crystallographic properties as well as crystal shapes, sizes and polydispersity were characterized by X-ray powder diffraction (PXRD) and transmission electron microscopy (TEM) combined with energy dispersive X-ray spectroscopy (EDX) and selected area electron diffraction (SAED). Our results indicate a linear relationship between the excess Fe in the supernatant and the amount of Ni associated with the solids. Furthermore, Ni uptake is more efficient at higher initial aqueous Ni concentration and up to 87% of the initial aqueous Ni can be removed through co-precipitation with GR_{S04}. This is also supported by slight changes in the lattice parameters as calculated from the Le Bail refinement. Ni uptake increased with aging, indicating that other processes such as crystal growth and maybe even adsorption may enhance the overall Ni removal efficiency.

References: [1] Abdelmoula et al. (1998) *Hyperfine Interact.* **112**, 235–238. [2] Refait et al. (1990) *Hyperfine Interact.* **57**, 2061–2066.