
Interaction of Synthetic Sulphate " Green Rust" with Phosphate and the Crystallization of Vivianite

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Abstract: Because layered Fe(II)Fe(III)-hydroxides (Green rusts, GRs) are anion exchangers, they represent potential orthophosphate sorbents in anoxic soils and sediments. To evaluate this possibility, two types of experiments with synthetic sulphate-interlayered GRs ($\text{GR}_{\text{SO}_4} = \text{Fe}^{2+}_4\text{Fe}^{3+}_2(\text{OH})_{12}\text{SO}_4 \cdot x\text{H}_2\text{O}$) were studied. First, sorption of phosphate in GR_{SO_4} was followed by reacting suspensions of pure GR_{SO_4} synthesized by oxidation of Fe(II) with an excess of Na_2HPO_4 (pH 9.3).

Second the possible incorporation of phosphate in GR during formation by Fe(II)-induced reductive dissolution of phosphate-containing ferrihydrites was examined in systems containing an excess of Fe(II) (pH 7). With excess phosphate in solution, GR_{SO_4} initially sorbed phosphate in the interlayer producing a basal layer spacing of 1.04 nm, but only ~ 50% of the interlayer sulphate was exchanged with phosphate. This GR slowly transformed to vivianite within months. In the Fe(II)-rich systems, reaction with synthetic ferrihydrites produced GR_{SO_4} similar to that produced by air oxidation. Reaction of Fe(II) with phosphate-containing ferrihydrites initially produced amorphous greenish phosphate containing precipitates which, after 3– 4 h, crystallized to GR_{SO_4} and vivianite. In these solutions, stable phosphate-free GR_{SO_4} can form since precipitation of vivianite produced low phosphate activity. Consequently, in both systems GR or amorphous greenish precipitates act as reactive intermediates, but vivianite is the stable end-product limiting phosphate concentration in solution. It is also inferred that $\text{Fe}(\text{OH})_2$ is an unlikely phosphate sorbent in mixed Fe(II)-Fe(III) systems because GR phases are more stable (less soluble) than $\text{Fe}(\text{OH})_2$.

Key Words: Anion Exchange • Fe(II)Fe(III)-hydroxides • Green Rust • Layered Hydroxides • Phosphate • Vivianite

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