Structural diversity and heterogeneity of Fe(III)-precipitates formed by Fe(II) oxidation in water

ANDREAS VOEGELIN, ANNA-CATERINA SENN,
RALF KAEGI AND STEPHAN HUG

Eawag, Swiss Federal Institute of Aquatic Science and Technology, Switzerland (andreas.voegelin@eawag.ch)

The oxidation of dissolved Fe(II) by O_2 in water induces the precipitation of nanoparticulate Fe(III)-precipitates that profoundly impact the fate of co-transformed major and trace elements. Initially motivated by studies on As removal from groundwater and As dynamics in paddy fields, we started to investigate how phosphate, silicate and Ca affect the formation and structure of Fe(III)-precipitates [1-4].

Our results show that Fe(III)-precipitates formed by Fe(II) oxidation in near-neutral water over a wide range of conditions relevant for natural water resources can be described as mixtures of three types of precipitates (whose exact composition and structure itself depends on formation conditions): (i) amorphous (Ca-)Fe(III)-phosphate, (ii) poorly crystalline lepidocrocite, and (iii) ferrihydrite-type precipitates. During Fe(II) oxidation, only (Ca-)Fe(III)-phosphate precipitates as long as dissolved phosphate is present in solution. If the initial Fe(II) concentration is high enough to deplete dissolved phosphate, (Ca-)Fe(III)-phosphate formation is followed by the precipitation of ferrihydrite-type precipitates in silicate-containing solutions or poorly crystalline lepidocrocite in silicate-free solutions. In closed systems in which dissolved Fe(II) is completely oxidized, this precipitation sequence leads to the formation of nanoscale Fe(III)-precipitate particles whose heterogeneous internal composition and structure reflect the sequential formation of different precipitate types. This intra-particle heterogeneity should be taken into account when assessing the structure of Fe(III)-precipitates using bulk techniques, but also when investigating the reactivity of Fe(III)-precipitates and their impact on trace elements.

These findings contribute to a better understanding of the effect of water chemistry on the structure and reactivity of Fe(III)-precipitates and serve as a basis for future work on the impact of Fe oxidation products on nutrient and contaminant dynamics at environmental redox interfaces and their effective use in water treatment or remediation.

[1] Voegelin et al., *Geochim. Cosmochim. Acta* **74**: 164, 2010. [2] Kaegi et al., *Geochim. Cosmochim. Acta* **74**: 5798, 2010. [3] Voegelin et al., *Geochim. Cosmochim. Acta* **117**: 216, 2013. [4] Senn et al., in review.