Available online at www.sciencedirect.com

ScienceDirect

Geochimica et Cosmochimica Acta 186 (2016) 71–90

Geochimica et Cosmochimica Acta

www.elsevier.com/locate/gca

Fe hydroxyphosphate precipitation and Fe(II) oxidation kinetics upon aeration of Fe(II) and phosphate-containing synthetic and natural solutions

B. van der Grift [a,b,*], T. Behrends [c], L.A. Osté [b], P.P. Schot [a], M.J. Wassen [a], J. Griffioen [a,d]

[a] Copernicus Institute of Sustainable Development, Faculty of Geosciences, Utrecht University, P.O. Box 80115, 3508 TA Utrecht, The Netherlands
[b] Deltares, P.O. Box 85467, 3508 AL Utrecht, The Netherlands
[c] Department of Earth Sciences, Faculty of Geosciences, Utrecht University, P.O. Box 80021, 3508 TA Utrecht, The Netherlands
[d] TNO Geological Survey of the Netherlands, P.O. Box, 80 015, 3508 TA Utrecht, The Netherlands

Received 6 August 2015; accepted in revised form 19 April 2016; available online 27 April 2016

Abstract

Exfiltration of anoxic Fe-rich groundwater into surface water and the concomitant oxidative precipitation of Fe are important processes controlling the transport of phosphate (PO_4) from agricultural areas to aquatic systems. Here, we explored the relationship between solution composition, reaction kinetics, and the characteristics of the produced Fe hydroxyphosphate precipitates in a series of aeration experiments with anoxic synthetic water and natural groundwater. A pH stat device was used to maintain constant pH and to record the H^+ production during Fe(II) oxidation in the aeration experiments in which the initial aqueous P/Fe ratios ($(P/Fe)_{ini}$), oxygen concentration and pH were varied. In general, Fe(II) oxidation proceeded slower in the presence of PO_4 but the decrease of the PO_4 concentration during Fe(II) oxidation due to the formation of Fe hydroxyphosphates caused additional deceleration of the reaction rate. The progress of the reaction could be described using a pseudo-second-order rate law with first-order dependencies on PO_4 and Fe(II) concentrations. After PO_4 depletion, the Fe(II) oxidation rates increased again and the kinetics followed a pseudo-first-order rate law. The first-order rate constants after PO_4 depletion, however, were lower compared to the Fe(II) oxidation in a PO_4-free solution. Hence, the initially formed Fe hydroxyphosphates also affect the kinetics of continuing Fe(II) oxidation after PO_4 depletion. Presence of aqueous PO_4 during oxidation of Fe(II) led to the formation of Fe hydroxyphosphates. The P/Fe ratios of the precipitates ($(P/Fe)_{ppt}$) and the recorded ratio of H^+ production over decrease in dissolved Fe(II) did not change detectably throughout the reaction despite a changing P/Fe ratio in the solution. When $(P/Fe)_{ini}$ was 0.9, precipitates with a $(P/Fe)_{ppt}$ ratio of about 0.6 were formed. In experiments with $(P/Fe)_{ini}$ ratios below 0.6, the $(P/Fe)_{ppt}$ decreased with decreasing $(P/Fe)_{ini}$ and pH value. Aeration experiments with natural groundwater showed no principal differences in Fe(II) oxidation kinetics and in PO_4 immobilisation dynamics compared with synthetic solutions with corresponding P/Fe ratio, pH and oxygen pressure. However, aeration of groundwater with relative high DOC concentrations and a low salinity lead to P-rich Fe colloids that were colloidally stable. The formation of a Fe hydroxyphosphate phase with a molar P/Fe ratio of 0.6 can be used for predictive modelling of PO_4 immobilisation upon aeration of pH-neutral natural groundwater with an $(P/Fe)_{ini}$ ratio up to 1.5. These findings provide a solid basis for further studies on transport and bioavailability of phosphorus in streams, ditches and channels that receive anoxic Fe-rich groundwater.

---

[*] Corresponding author at: Deltares, P.O. Box 85467, 3508 AL Utrecht, The Netherlands. Tel.: +31 623478769.
E-mail address: bas.vandergrift@deltares.nl (B. van der Grift).

http://dx.doi.org/10.1016/j.gca.2016.04.035
0016-7037/

Keywords: Iron; Kinetics; Oxidation; Phosphate; Precipitation (chemistry); Redox conditions; Groundwater; Aeration; Colloids; Fe hydroxyphosphates; Aqueous solution

---

1. INTRODUCTION

The chemistry of phosphate in aquatic systems is often controlled through interactions with iron (Fox, 1989; Mayer and Jarrell, 2000). Under oxidising conditions, aqueous phosphate has a strong affinity to associate with Fe oxyhydroxides (Filippelli, 2008). Association with Fe oxyhydroxides may include adsorption, surface precipitation, formation of solid solutions and co-precipitation (van Riemsdijk et al., 1984; Fox, 1989; Dzombak and Morel, 1990; Ler and Stanforth, 2003; Griffioen, 2006; Voegelin et al., 2010). Iron associated PO_4 can be solubilised under reducing conditions due to reductive dissolution of Fe oxyhydroxides (Mayer and Jarrell, 2000). However, under anoxic conditions, mobilisation of PO_4 can be limited due to formation of Fe(II)-phosphate minerals such as vivianite (Roden and Edmonds, 1997; Heiberg et al., 2012). Redox transformations of iron in natural environments thus exert a strong influence on the mobility of PO_4.

Lowland areas, like the Netherlands, typically have redox-reactive aquifers containing anoxic Fe(II)-rich groundwater (Frapporti et al., 1993; Griffioen et al., 2013). When Fe(II)-rich groundwater enters surface water, Fe(III) precipitates are formed at the groundwater-surface water interface upon oxygenation of the anoxic groundwater (Vanlierde et al., 2007; Baken et al., 2013, 2015b; van der Grift et al., 2014). The formation of Fe oxyhydroxides during groundwater exfiltration is expected to be accompanied by the immobilisation of aqueous phosphate due to its association with the Fe precipitates (Griffioen, 1994; Baken et al., 2015a). The release of PO_4 to surface water following PO_4 leaching from heavily fertilised agricultural fields to groundwater and the extent of PO_4 retention at the redox interface are of major importance for surface water quality (Schoumans and Chardon, 2014; Baken et al., 2015b). Based on field data, Van der Grift et al. (2014) proposed that the formation of Fe(III) phosphate precipitates can be an important natural immobilisation mechanism for aqueous PO_4 during flow of groundwater into surface water. This may reduce the PO_4 load from agricultural land to surface water. Consequently, formation of Fe(III) phosphates at redox interfaces might be a major control on the PO_4 transport in the continuum from land to sea and on the bioavailability of PO_4 in natural waters that drain anoxic aquifers. Detailed insight into the chemical stoichiometry and the kinetics of formation of Fe(III) phosphate phases during oxygenation of anoxic, Fe and PO_4 containing groundwater is therefore of great interest.

Precipitation of Fe(III) from PO_4 containing aqueous solutions is expected to lead to the formation of Fe hydroxyphosphates (Stumm and Morgan, 1970) with variable P/Fe ratio according to the stoichiometry:

$$rFe^{3+} + PO_4^{3-} + (3r-3)OH^- \rightarrow Fe_rPO_4(OH)_{3r-3}(s) \qquad (1)$$

where $1/r$ is the stoichiometric molar P/Fe ratio of the Fe hydroxyphosphate. The solubility constants for mineral phases have been reported for $r = 1$ (strengite) by Nriagu (1972) and later by Iuliano et al. (2007), for $1/r = 0.66$ (tinticite) by Nriagu and Dell (1974) and for $1/r = 0.4$ by Luedecke et al. (1989). Pratesi et al. (2003) described the existence of an amorphous Fe hydroxyphosphate, santabarbaraite, with a $1/r$ value of 0.66 but no solubility data were presented. Iron(III) phases with high P/Fe ratios have been identified in natural systems such as lakes (Buffle et al., 1989; Lienemann et al., 1999; Gunnars et al., 2002) as well as estuarine or lake sediments (Tessenow, 1974; Hyacinthe and Van Cappellen, 2004). Precipitation of these phases has also been reported as a mechanism for PO_4 removal from wastewater (Stumm and Sigg, 1979; Luedecke et al., 1989; Fytianos et al., 1998).

Formation of Fe hydroxyphosphates induced by Fe(II) oxidation at near-neutral pH has been investigated in various studies (Einsele, 1934; Tessenow, 1974; Lienemann et al., 1999; Mayer and Jarrell, 2000; Matthiesen et al., 2001; Gunnars et al., 2002; Griffioen, 2006; Kaegi et al., 2010; Voegelin et al., 2010, 2013; Senn et al., 2015). Phosphate uptake per oxidised Fe was found to be limited to a P/Fe molar ratio of ≈0.5–0.6 under varying experimental conditions regarding initial Fe(II) and PO_4 concentrations, pH and background electrolytes, (Tessenow, 1974; He et al., 1996; Gunnars et al., 2002; Voegelin et al., 2013). This suggests the formation of a single type of Fe hydroxyphosphate phase at initial aqueous P/Fe ($(P/Fe)_{ini}$) ratios larger than ≈0.5. A limited number of studies indicate that P-rich precipitates with molar P/Fe ratio of 0.5–0.6 can form in the beginning of Fe(II) oxidation even when the $(P/Fe)_{ini}$ is less than 0.5 (Einsele, 1934; Tessenow, 1974; Deng, 1997; Gunnars et al., 2002; Voegelin et al., 2013). As a consequence, the P/Fe ratio in the solution progressively decreases when precipitates form which are relatively enriched in P. By using TEM and XAS, Voegelin et al. (2013) showed that, in solutions with $(P/Fe)_{ini}$ less than 0.5, early formation of amorphous Fe hydroxyphosphates is followed by the formation of short-range ordered ferrihydrite-type precipitates in silicate-containing solutions or poorly-crystalline lepidocrocite in silicate-free solutions when the solution becomes depleted in PO_4. The sequential precipitation of Fe hydroxyphosphates followed by precipitation of Fe oxyhydroxides during Fe(II) oxidation indicates that formation of Fe hydroxyphosphates with a P/Fe ratio around 0.5–0.6 is either kinetically controlled or Fe hydroxyphosphates with a P/Fe ratio around 0.5–0.6 are the thermodynamically favoured precipitates in the initial stage of homogeneous nucleation due to low surface energies (Navrotsky et al., 2008). The molar P/Fe ratio in precipitates was also around 0.5–0.6 in studies on As removal in presence of PO_4. This finding has been used to rationalize variations in the efficiency of As removal techniques from drinking water in areas with different groundwater chemistry (Roberts et al., 2004; Hug et al., 2008). Since the P/Fe ratios in the Fe hydroxyphosphates seem to vary to a small extent for several experimental