

Modeling of As fate governed by naturally occurring Mn-oxides under varying geochemical conditions

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Arsenic (As) contamination in groundwater poses serious environmental and human health risks. The transformation of arsenite (As^{III}), into less mobile and less toxic arsenate (As^{V}) enhance As sequestration from groundwater and reduces the risk [1]. Manganese (Mn) oxide minerals are known to oxidize As^{III} to As^{V} . Mn-oxides commonly occur as coatings and fine-grained aggregates of poorly-crystalline mineral phases in the natural environment. The oxidation process by Mn-oxides can be very rapid, compared to the direct oxidation of aqueous As^{III} by molecular oxygen [2].

A number of mechanisms for As^{III} oxidation by Mn-oxides have been suggested in the literature [3,4,5], of which most are complex and involve several simultaneous reactions. There is a general agreement that the first step in oxidation is adsorption of As^{III} onto either Mn^{IV} or Mn^{III} sites on Mn-oxide surfaces. This is followed by oxidation of sorbed As^{III} by either electron transfer or substitution [4]. The rate of oxidation reaction could differ between Mn^{IV} and Mn^{III} sites. Mn^{+2} ions are also produced in the oxidation step from the reductive dissolution of $\text{Mn}^{\text{IV/III}}$ oxides. Both, Mn^{+2} and As^{V} , could remain sorbed or form precipitates on the surface and passivate the surface sites, thereby inhibiting further As^{III} oxidation. Other ions, e.g., Fe^{+2} and phosphate, are also known to passivate Mn-oxide surface sites [1,6].

In this study, we have reviewed and translated previously proposed conceptual models into a process-based numerical model and evaluated the model against measured data [1].

[1] Wu, Y., et al. (2015) *J. of Colloid and Interface Science* **457**, 319-328. [2] Eary, L.E., et al. (1990) *ACS Symposium Series* **416**, 379-396. [3] Scott, M.J. and Morgan, J.J., (1995) *ES&T* **29(8)**, 1898-1905. [4] Nesbitt, H. W., et al. (1998) *GCA* **62(12)**, 2097-2110. [5] Ying, S. C., et al. (2012) *GCA* **96(0)**, 294-303. [6] Parikh, S.J., et al. (2010) *ES&T* **44(10)**, 3772-3778.