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TRANSFORMATION OF MAGNETITE TO GOETHITE DURING Cr(VI) REDUCTION UNDER ALKALINE pH CONDITIONS

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Cr is one of the major contaminants in the tank waste discharged from REDOX process which was used extensively in DOE sites to extract Pu and U through redox reactions. It is desirable to reduce Cr(VI) to Cr(III) since the oxidation state of Chromium usually determines its solubility, mobility and its fate in the environment. Magnetite is a major Fe(II) containing mineral in Hanford sediments and has the potential to reduce and immobilize Cr(VI). The objective of this study was to investigate Cr(VI) reduction/immobilization by synthetic magnetite under alkaline pH conditions similar to what have found in high level waste at the Hanford site.

Cr(VI) REDUCTION BY SYNTHETIC MAGNETITE UNDER ALKALINE pH CONDITIONS

In acid and neutral pH conditions, Cr(VI) was all removed from the solution phase. Under alkaline pH, less than 10% Cr(VI) was reduced and removed from solution. Comparing Cr(VI) reduction at three pH conditions, Cr(VI) reduction was fastest and most significant at acid pH, slightly slower but complete reduction at neutral pH and least significant at alkaline pH. The inhibition of Cr(VI) reduction at alkaline pH are probably controlled by the following three processes.

Sorption

Under alkaline pH conditions, limited Cr(VI) reduction by synthetic magnetite may be due to limited or no sorption at high pH, since Cr(VI) sorption is strongly pH dependent, and weak under alkaline condition. Therefore, Cr(VI) sorption is not likely to play a major role in Cr(VI) removal in the alkaline pH conditions of the present study. However,

Cr(VI) reduction was still observed at pH conditions at which Cr(VI) sorption is not likely. This suggests that sorption may not necessarily be the first step before reduction can occur as suggested in earlier studies.

Oxygenation

Ferrous iron oxygenation is rapid in neutral to alkaline pH conditions. The half life for the ferrous iron is only a few seconds at pH greater than 7.5 (Kieber and Helz 1992). The reaction of Fe(II) with O₂ at 25°C and pH 8 is a factor of 20-10 faster than that with Cr(VI) at 0.01M and 0.7 M ionic strengths, respectively, while the rates are similar at pH 7 and 7-14 times slower at pH 6 (Pettine *et al.* 1998). At alkaline pH conditions, O₂ will be even more reactive than Cr(VI) in oxidizing Fe(II). Dissolved O₂ could convert magnetite to maghemite/goethite removing material for reaction with Cr(VI), thus Cr(VI) reduction will be limited by the available Fe(II) not oxidized by O₂ in the system.

Passivation layer formation

Another possibility of limited reduction at alkaline pH is due to passivation of the magnetite surface by maghemite and goethite formation (as discussed in the next section). It is not known to what extent goethite precipitates might have coated the magnetite particles, passivating the surfaces against further Cr(VI) reduction.

The XAS measurements indicated that Cr(III) was associated with the solid phase after reduction of Cr(VI). Cr was sorbed or precipitated as Cr(III) in octahedral coordination with a Cr-O distance of 1.99 Å and a Cr-Cr/Fe distance of 3.05 Å. The Cr-O distance measured in the presence of magnetite is similar to that of the Cr-containing precipitates formed in the homogeneous system, but the Cr-Cr/Fe distance is slightly larger than what was measured for the precipitates in the homogeneous system. This may be due to heterogeneous precipitation on the magnetite surface in the present system. But in the homogeneous system, Cr-Fe forms coprecipitates. The Cr:Fe ratio is different in these two types of environments and the differences in the Cr:Fe ratio may lead to different Cr-Cr/Fe distances, as suggested by (Hansel *et al.* 2003) that Cr mole fraction increase will cause the expansion of Cr-Cr/Fe bond.

MAGNETITE TRANSFORMATION UNDER ALKALINE pH SOLUTIONS

It is generally accepted that Maghemite, a structural polymorph of hematite, is the most common weathering product of magnetite. In the present study, in addition to maghemite formation, XRD and TEM analyses showed that a prominent goethite phase was also formed from magnetite under alkaline pH conditions and the intensity of goethite peaks in the XRD patterns increased with increased amounts of NaOH (Fig. 1). TEM micrographs of magnetite reacted with NaOH (Fig. 2) show needle shaped crystals coexisting with apparently residual cubic magnetite. This appears to be the first physical evidence of goethite formation directly from magnetite. The differences in the crystal structure of magnetite and goethite make epitaxial goethite formation unlikely. The possible mechanism is through the dissolution and re-precipitation process. Magnetite dissolves under alkaline pH conditions, releases Fe²⁺, forms Fe(OH)₂ and Fe(OH)₂ was oxidized by Cr(VI) or O₂ to form goethite.

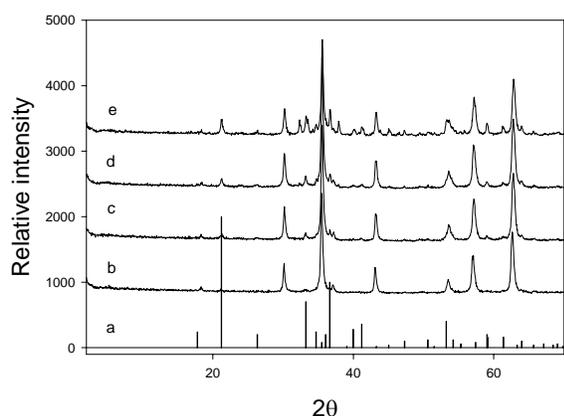


Figure 1. XRD of synthetic magnetite at different NaOH concentrations in the presence of $1 \text{ mmol L}^{-1} \text{ Na}_2\text{CrO}_4$. Goethite formed in all NaOH treatments and relative intensity increased with increased NaOH concentration. a) Theoretical pattern of goethite, plotted from a standard Powder Diffraction File 1993 database; b-e. 0, 0.1, 0.5, 2 mol L^{-1} NaOH treatment, respectively.



Figure 2. TEM micrograph showing goethite formation in magnetite system in 2 mol L^{-1} NaOH in the presence of $1 \text{ mmol L}^{-1} \text{ Na}_2\text{CrO}_4$.

The study showed that magnetite is not efficient in reducing and removing Cr(VI) at alkaline pH conditions, due to oxygenation and the passivation of magnetite and goethite formation. The passivation layer formation has important implications in *in situ* remediation project. However, formation of goethite may enhance the removal of metal contaminants in the downstream of waste plumes.

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