

## Optimizing the use of magnetite from an iron mine for reduction of aqueous Cr(VI)

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### Introduction

Magnetite is an inverse spinel ferrite that contains in its structure both Fe<sup>3+</sup> and Fe<sup>2+</sup> [1], and may therefore act as a reducing agent. This behavior has been applied in remediation of contaminated water with oxidized metal species that upon chemical reduction become immobile [2]. In this paper we present an investigation using natural samples of this mineral from an Fe mine deposit in Mexico towards the reduction of Cr(VI) to Cr(III), with the final aim to understand the geochemical conditions of optimal performance for applying it to real pollution scenarios. The most important problem to solve for optimal implementation, is the rapid surface passivation of the mineral due to complete oxidation of superficial Fe<sup>2+</sup>, which results in very low Cr(VI) reduction yields.

### Methodology

Investigations were performed with magnetite of various particle sizes, both natural and synthetic. Batch experiments were performed with a solid concentration of 6 g L<sup>-1</sup> and concentrations of Cr(VI) of 5-10 mg L<sup>-1</sup> and up to 50 mg L<sup>-1</sup>. Mixtures of magnetites with low amounts of Fe (0) were also investigated, which presumably replenish superficial magnetite Fe(II) [3].

### Discussion of Results

The reduction capacity of magnetite increased with decreasing particle size, but the overall reduction rates and yields were relatively low. Small weight percentages of Fe (0) (1-5%) mixed with magnetite, which in the absence of magnetite showed no reduction capacity, significantly increased both rates and yields. We report the optimization of the magnetite/Fe (0) ratio as a function of particle size, and pH, and confirmed the surface-mediated reduction mechanism.

[1] Liu *et al.* (2006) *Mater. Lett.* **60**, 2979–2983.

[2] Kendelewicz *et al.* (2000) *Surf. Sci.* **44**, 55–60. [3] Coelho *et al.* (2008) *Chemosphere* **71**, 90–91.

## A unified surface structural model for ferrihydrite: Proton, electrolyte, and arsenate adsorption

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### Introduction

Ferrihydrite (FH) is a common hydrous ferric oxide nanomineral of 'young' formation in aqueous geochemical environments. Its small particle sizes (1.5-5 nm) [1, 2] expose a very high specific surface area at the mineral/water interface, and this may have considerable influence on the transport and fate of a variety of trace and major elements through diverse sorption processes. In particular, arsenate anions show a very high affinity for FH, and their fate in contaminated environments is almost invariably associated to Fe(III) oxide surfaces [3, 4]. The extremely small FH nanoparticles, which show high particle aggregation when dried, preclude experimental determination of important surface parameters for the thermodynamic description of its adsorption behavior. In the present work we have compiled eight sets of published acid-base surface titration data for synthetic preparations of FH across a wide range of particle sizes, and two sets of arsenate adsorption data, and unified their description through a face-distribution site-density model developed previously for goethite.

### Discussion of Results

We show that the surface proton charge behavior of FH in conjunction with its As(V) adsorption behavior may be adequately described using the affinity constants derived for goethite, by assuming the FH surface to be composed predominantly of a surface site configuration equal to that of the (010) goethite face (*Pnma* space group). Also, through the applied model the available specific surface area of each FH preparation in aqueous suspension may be successfully derived, showing values between 330 and 1120 m<sup>2</sup>/g. The implications of the results reported here are highly relevant for predictive purposes of FH surface reactivity in general.

[1] Murphy *et al.* (1976) *J. Colloid Interface Sci.* **56**, 270–283.

[2] Janney *et al.* (2000) *Clay Clay Min.* **48**, 111–119. [3] Arai *et al.* (2006) *ES&T* **40**, 673–679. [4] Slowey *et al.* (2007)

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