Available online at www.sciencedirect.com
ScienceDirect
Geochimica et Cosmochimica Acta 71 (2007) 835–843
Geochimica
www.elsevier.com/locate/gca

Effects of *in situ* biostimulation on iron mineral speciation in a sub-surface soil

Joseph W. Stucki [a,*], Kangwon Lee [a], Bernard A. Goodman [a], Joel E. Kostka [b]

[a] *University of Illinois at Urbana-Champaign, Department of Natural Resources and Environmental Sciences, Urbana, IL 61801, USA*
[b] *Florida State University, Department of Oceanography, Tallahassee, FL 32306, USA*

Received 24 May 2006; accepted in revised form 2 November 2006

Abstract

The *in situ* alteration of Fe redox states in subsurface soils by bacteria, otherwise known as bioreduction, may play a key role in the immobilization of hazardous redox active metals such as U, Tc, and Cr. The objective of this study was to characterize changes in Fe mineralogy occurring in a subsurface soil as a result of biostimulation in order to evaluate the bioremediation potential of this approach. Biostimulation was achieved by injecting glucose into the soil through a small well next to a sampling well. Cores taken from the sampling well were analyzed by variable-temperature ^{57}Fe Mössbauer spectroscopy. Results revealed that biostimulation resulted in an overall loss of Fe from the system and major changes in the distribution of its oxide and oxyhydroxide mineral forms. Compared to the non-biostimulated soil, the spectral components assigned to goethite were greatly diminished in intensity in the samples that had been biostimulated, whereas the hematite component was appreciably increased. The Fe(II):Fe(III) ratio in the non-oxide phase (aluminosilicate clay minerals) also increased, indicating that the bioreduction processes in the soil also affected the redox state of Fe in the constituent clay minerals.

1. Introduction

Intense efforts are underway to remediate radionuclide contaminated soils by stimulating the growth of indigenous bacteria to promote the *in situ* immobilization of U, Tc, Cr, and other harmful metals generated from nuclear power and weapons production (Kukkadapu et al., 2001; Senko et al., 2002, 2005; Petrie et al., 2003; Fredrickson et al., 2004; Istok et al., 2004; North et al., 2004; Michalsen et al., 2006). To stimulate bacterial activity in the sub-surface soils, a carbon source such as ethanol, acetate, or glucose can be injected into the soil through a small-diameter well. The reducing environment created by bacterial activity affects all redox-sensitive constituents in the soil, including the ubiquitous Fe-bearing minerals, and impacts synergistic relationships among these minerals and the target radionuclides in the system. Iron is by far the most abundant redox-active metal in the soil and cycling between Fe(II) and Fe(III) is a prominent factor affecting chemical processes in soils, especially where large periodic changes in water contents occur (Ponnamperuma, 1972). The oxidation state of Fe thus provides a valuable indicator of the redox status of the soil and greatly influences redox processes.

Among the Fe-bearing minerals in soils, the most common are aluminosilicate clay minerals and iron oxides or oxyhydroxides (Schwertmann, 1988). The oxidation state of structural Fe in the clay minerals alters the physical-chemical properties of their surfaces (Stucki, 2006) and reducing environments greatly enhance the dissolution potential of the Fe oxides, which generally control the levels of Fe in solution. The particular Fe oxide mineral phase also influences the chemical behavior of other elements in the system. For example, Dodge et al. (2002) reported that when U is co-precipitated with maghemite, magnetite, or goethite, the uranium species are oxyhydroxides and are

* Corresponding author. Fax: +1 217 244 7805.
E-mail address: jstucki@uiuc.edu (J.W. Stucki).

0016-7037/$ - see front matter © 2006 Elsevier Inc. All rights reserved.
doi:10.1016/j.gca.2006.11.023

readily dissolved in concentrated HCl, whereas with lepidocrocite and ferrihydrite the uranium species resist dissolution. If U is co-precipitated with green rust, it is in the U(IV) form. Upon exposure to air, both U and green rust are oxidized rapidly, which converts green rust to magnetite and remobilizes the U. Understanding how the Fe minerals are affected by biostimulation in soils thus can give key insight into the behavior of targeted redox-active species. It also aids in the development of reliable theoretical models as valuable tools for predicting the fate of U in contaminated soils. At present, the utility of such models is marginalized because of the lack of reliable information about the behavior of Fe minerals in the system.

The purpose of the current study was to narrow that gap by characterizing changes in Fe mineralogy occurring in a biostimulated soil using variable-temperature Mössbauer spectroscopy. The objective was to investigate how Fe minerals are affected by biostimulation in the U-contaminated soils. This is by no means a straightforward exercise, since several Fe-containing phases could be present and a considerable fraction of the Fe could be of a poorly crystalline or amorphous nature. The overall Fe concentrations are, moreover, only about 5–6 mass % of the soil. These mineral forms are, therefore, difficult to identify by conventional X-ray powder diffraction.

2. Materials and methods

The samples used were obtained from contaminated and biostimulated subsoils at the US Department of Energy (DOE) Field Research Center (FRC) at Oak Ridge National Laboratory, Tennessee. These soils were contaminated with varying amounts of U and Tc, among other elements, over a period of more than two decades and have been investigated through a series of single-well, push-pull tests to determine the feasibility of using in situ biostimulation as a means for radionuclide immobilization. Studies (Petrie et al., 2003; Istok et al., 2004; North et al., 2004) found that indigenous Fe-reducing bacteria responded to injection of electron donors (acetate, glucose, or ethanol) by catalyzing the reduction and immobilization of U(VI) in the soil. The mineralogy and redox state of Fe in the surrounding soil minerals are believed to play an important role in this process. In order to characterize these changes in the Fe minerals more completely, parallel samples to those investigated by Petrie et al. (2003) and North et al. (2004) were submitted to analysis by variable-temperature Mössbauer spectroscopy. The samples selected were: (1) FWB302 taken from an uncontaminated background area; (2) FWB032-01-05 taken from the contaminated subsoil (without biostimulation) in push-pull well identified by Istok et al. (2004) as FW32; and (3) FB45-01-42 taken from the glucose biostimulated subsoil in a nearby well labelled FB45 by Istok et al. (2004). The reader should consult Petrie et al. (2003) and North et al. (2004) for further information about these samples. A limited number of analyses were also performed on cores removed from wells labelled FW27, FW31, FW33, and FW34, which were located near well FW32.

After sampling, care was taken to protect the samples from the atmosphere and from significant bacterial activity by enclosing them in Ar purged tubes at the site, then freezing them to 77 K in liquid nitrogen (see description by North et al., 2004). Samples were kept frozen until used, then inert atmosphere techniques were used in order to minimise changes in oxidation state during laboratory handling (Stucki et al., 1984). No attempt was made to dry or homogenize samples by grinding or extensive mixing; sub-samples were selected for study by manually removing large (predominantly quartz) grains by eye under a N_2 atmosphere. Samples were analyzed for Fe(II) and total Fe using the 1,10-phenanthroline method of Komadel and Stucki (1988), which, unlike the commonly used Ferrozine method (Stookey, 1970; Lovley and Phillips, 1986), is reliable for the quantitative determination of the different oxidation states of Fe in both silicate and oxide minerals.

2.1. Mössbauer spectroscopy

Mössbauer spectra were acquired in transmission mode using a Web Research (Edina, Minnesota) spectrophotometer equipped with a Janis (Wilmington, Massachusetts) Model SHI-850-5 closed cycle refrigerator (CCR) cryostat. This cryostat is capable of reaching

Table 1
Temperatures at which magnetic hyperfine interactions are observed for Fe oxides and oxyhydroxides as sextet lines in the Mössbauer absorption spectrum (from Stevens et al., 1983; Murad and Johnston, 1987; Murad, 1988)

Iron oxide/ oxyhydroxide	Magnetic ordering temperature (K)	Hyperfine magnetic field, B_{hf} (T)	Temperature (K) of Mössbauer spectrum
Hematite	955	51.8 at 295	298
		53.5[a], 54.2	77
		53.3[a], 54.2	4.2
Magnetite	850	49.2, 46.3, and 45.1	298
Maghemite	743–985	50.0	298
		52.6	77
		52.6	4.2
Goethite (well crystallized)	393	38.2	298
Goethite (poorly crystallized)	<77	50.0	77
		50.6	4.2
Lepidocrocite	<77	45.8, 52.5	4.2
Ferrihydrite (6-line)	<77	49.3, 50.0	4.2
Ferrihydrite (2-line)	<77	46.5	4.2

[a] Above the Morin transition temperature.