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Study of the interaction between U(VI) and the anoxic corrosion products of carbon steel

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Abstract

The objective of this study was to investigate the removal mechanism of U(VI) from groundwater by magnetite as the main product of anoxic steel corrosion. For this purpose, a systematic sequence of batch experiments was conducted to focus the active role of magnetite in the reduction of U under different conditions. Results indicated that under anoxic conditions U(VI) was sorbed at the magnetite surface, whereas under reducing conditions at different H_2(g) pressures, U was present in tetravalent form as amorphous UO_2.

1. Introduction

Many countries that generate high level radioactive waste consider disposal in deep geological repositories to be the best waste management option. The aim of these repositories is to isolate the radioactive waste from the human environment for long periods, until it presents no significant hazard (Chapman and McCombie, 2003). In the high-level radioactive waste repository concept, spent nuclear fuel is designed to be encapsulated in C steel canisters which represent the first physical barrier to radionuclide migration. Carbon steel is preferred in most European repository concepts (Sweden and Finland include an outer shell of Cu, Spain, France, Belgium and others use only the cast Fe canister), because of its tendency to corrode uniformly, while stainless steel is prone to localized corrosion, making it difficult to predict breaching time. The release of radionuclides can occur, a few hundred years after the emplacement, due to canister failure as a result of Fe corrosion (Hoch et al., 1997) and penetration of groundwater into the canister leaching the spent nuclear fuel.

Uranium dioxide is the main component of spent nuclear fuel. Under reducing conditions, U is present in its tetravalent state, and it oxidizes to U(VI) under oxidizing conditions produced in the repository by the radiolysis of water. Nevertheless, the

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redox conditions in the vicinity of the canister are expected to be reducing and thus the corrosion of the canister steel in contact with groundwater will proceed anoxically.

In anoxic conditions, magnetite (Fe_3O_4) has been identified as a final corrosion product on steel surfaces. The redox reaction for the transformation of Fe to magnetite is as follows

$$Fe(s) + 4H_2O = Fe_3O_4(s) + 4H_2(g) \quad (1)$$

For this reason, the study of the radionuclide retention role of magnetite is an issue of crucial importance for the performance assessment of canisters used for spent nuclear fuel which contain Fe. The interaction between the magnetite and radionuclides has been studied by several authors who reported that this interaction can be attributed to a sorption process: Cs (Granizo and Missana, 2006; Rovira et al., 2004a), Sr (Rovira et al., 2004b), Mo (Rovira et al., 2006), Pu (Duro et al., 2004; Powell et al., 2004) and Se (Martínez et al., 2006). The effect of magnetite in the reduction of several transition metals was reported by White and Peterson (1996). These authors conducted experiments in the acidic pH region and observed that magnetite has important reduction effects on Cr(VI), Cu(II), V(V) and Fe(III), due the presence of Fe(II) contained in its structure. Furthermore, U(VI) reduction by structural Fe(II) has also been reported (Charlet et al., 1998; Liger et al., 1999; O'Loughlin et al., 2003; Behrends and Van Cappellen, 2005; Jeon et al., 2005). In the case of the interaction U/magnetite Grambow et al. (1996) showed partial reduction of U in saline solution. El Aamrani et al. (1999) and Missana et al. (2003) reported good evidence for surface mediated partial reduction of U(VI)–U(IV) under anoxic conditions. Dodge et al. (2002) suggested that U was associated with magnetite as U (oxy)hydroxide [$UO_2(OH)_2$]. Recently, Scott et al. (2005) have reported the reduction of U(VI)–U(IV) on the surface of magnetite in the presence of O_2 in solution.

However, to the authors' knowledge, the interaction between U(VI) and magnetite under reducing conditions at different H_2 pressure has not yet been studied, H_2 pressures as high as 15 atm are not excluded in the performance assessment of a granitic repository which is the preferred option of Sweden and Finland (Liu and Neretnieks, 2002). The effect of solid surfaces on the reduction of U(VI)–U(IV) in the presence of $H_2(g)$ was studied in several investigations during the second half of the last century (Forward and Halpern, 1953; Balaceanu et al., 1958; Bunji and Zogovic, 1958). In general, though, no reduction is observed in the absence of a solid surface. From these studies it can be concluded that the reduction of U(VI)–U(IV) by $H_2(g)$ catalyzed by an active solid surface is the most probable reaction. Hence, there is sufficient evidence that magnetite can play an active role in the potential reduction of radionuclides in the high H_2 pressure conditions generated by the anoxic corrosion of Fe.

In the present paper, the study of the interaction between U(VI) and commercial magnetite is undertaken firstly under reducing conditions, at different $H_2(g)$ overpressures and secondly by using $N_2(g)$ bubbling to account for anoxic (but not reducing) conditions.

2. Experimental

2.1. Materials

2.1.1. Solids

The commercial magnetite (powder) used in this study was supplied by Aldrich, with a purity of 98% and particle size less than 5 μm. Surface area was determined by the BET-method (Brunauer et al., 1938), the value obtained was $1.58 \pm 0.01\ m^2\ g^{-1}$. The X-Ray Diffractogram of the commercial sample gives the same pattern as a magnetite anoxically generated on steel (Rovira et al., 2007).

In the experiments, 200 cm^3 of test solution were put in contact with weighed amounts of magnetite. Once the solid phase was introduced into the reactors, aqueous samples (1 cm^3) were taken periodically allowing U analysis using an ICP-MS Perkin–Elmer Elan 6000 and Fe analysis by the ferrozine method (Gibbs, 1976). Samples were immediately filtered through a 0.22 μm pore size filter and acidified by adding a small volume of concentrated HNO_3. All the experiments were performed at room temperature. Two different reactors were employed depending on the H_2 pressure under which the tests were carried out. Careful and continuous stirring of the reactors was ensured by means of an orbital agitator.

2.1.2. Solutions

The Chemicals used in this work, $UO_2(NO_3)_2 \cdot 6H_2O$, NaCl and $NaHCO_3$ were of analytical grade and supplied by Merck. All solutions were prepared