

Interaction of uranium with *in situ* anoxically generated magnetite on steel

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Abstract

In the high level nuclear waste repository concept, spent nuclear fuel is designed to be encapsulated in steel canisters. Thus, it is necessary to study the influence of the steel and/or its corrosion products on the behaviour of the radionuclides released from the fuel. In this sense, the main objective of this work is to contribute to the knowledge of the influence of the steel and/or its corrosion products on the uranium(VI) retention. To this aim, magnetite (Fe₃O₄) has been generated by anaerobic steel corrosion in an autoclave reactor at an overpressure of 8 atm of H₂(g). After characterisation by X-ray diffraction (XRD), the obtained corroded steel coupons were contacted, at two different H₂(g) pressures (1 atm and 7.6 atm), with a U(VI) solution. The evolution of the uranium concentration in solution is determined and a study of the composition of the coupons at the end of the experiments is carried out. The main conclusion obtained from this work is that magnetite generated on a steel coupon is able not only to retain uranium via sorption, but also to reduce hexavalent to tetravalent uranium in a higher extent than commercial magnetite, thus, providing an effective retardation path to the migration of uranium (and, potentially, other actinides) out of the repository.

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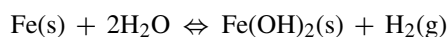
Keywords: Magnetite; Steel; Uranium; Spent nuclear fuel

1. Introduction

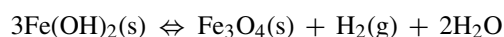
In the high level nuclear waste repository concept, spent nuclear fuel is designed to be encapsulated in steel canisters [1]. Besides constituting a physical barrier for an eventual groundwater intrusion, the steel canister or its corrosion products could act as an effective trap for the radionuclides released from the fuel via two different mechanisms: (1) decreasing the redox potential of the groundwater [2] and reducing the migration of most radionuclides, whose solubility under reducing conditions is much lower than that under oxidizing conditions; and (2) reducing the concentration in solution of a number of radionuclides via sorption [3]. On the other hand, it has to be considered that different types of steel would behave very differently in an aqueous environment.

In this sense, to estimate the actual impact of the canister on the radionuclides release and migration, its corrosion by the groundwater should be considered and, in particular, which phases are formed as a product of the corrosion, their sorption capacity, and their redox properties.

The intrusion of the groundwater might produce the anoxic corrosion of the iron [4–7]. Under these conditions, in a first step iron(II) is formed by the reaction of the iron with the hydrogen ion or directly by reaction with water:



These two reactions differ in their kinetics, but the direct reaction with water probably is the predominant one considering the concentration of the hydrogen ion in the groundwater [8]. The iron(II) hydroxide is a metastable solid that is transformed into magnetite through the Schikorr reaction:



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Magnetite is one of the main iron corrosion products under a reducing environment, which is the condition expected to prevail in a deep geological high level radioactive waste repository.

Different studies have been carried out to study the magnetite adsorption capacity for different elements. In particular, the sorption of some radionuclides has been studied, e.g. Tc(VII) [9], Np(V) [9], Pu(V) [10], U(VI) [5,11], Se(IV) and Se(VI) [12]. On the other hand, the semiconductor characteristics of magnetite points out its potential redox capacity, indicating that it could have an important role in the reduction of actinides released from the spent nuclear fuel. In this sense, reduction of uranium(VI) onto the magnetite surface has been observed in studies performed using commercial magnetite [2,13–15].

However, when considering the effect of the magnetite formed as a corrosion product of the canister in the migration of radionuclides, it should be considered the potential impact of the non-corroded iron that remains under the freshly formed magnetite, because it might influence the redox capacity of the corroded steel. According to Allen et al. [16] and Scott et al. [17], two different mechanisms control the deposition of uranium on mild steel: (1) incorporation into iron oxyhydroxides as uranium(VI) and (2) reductive precipitation of U(IV). In the reductive precipitation there are two mechanistic phases, an initial rapid reduction of uranium at the steel surface and a reductive precipitation of uranium by dissolved iron(II), co-precipitating uranium dioxide and iron oxyhydroxide phases onto the surface [16].

In this sense, the objective of this work was to elucidate the effect of the freshly formed magnetite as a corrosion product of the steel on the U(VI) concentration in solution as well as to establish if there is an effect of the steel that remains non-corroded.

2. Experimental

2.1. Materials

Commercial magnetite was supplied by Aldrich, with a purity of 98%, a particle size $<5 \mu\text{m}$ and $1.58 \pm 0.01 \text{ m}^2 \text{ g}^{-1}$ surface area. The X-ray diffractogram showed a small percentage of Iron(III) oxide [13].

The carbon steel coupons had dimensions of $30 \text{ mm} \times 30 \text{ mm} \times 1 \text{ mm}$. A semi-quantitative chemical analysis of the surface was carried out by an Energy Dispersive Spectrometer (EDS, Jeol 1200 EX-II), the composition was: Fe 97 wt% and C 3 wt% (high carbon steel). The coupons were cleaned

through different steps: (a) pickling in 10% HCl, (b) washing in distilled water and ethanol in order to remove the oxide film air-formed, and (c) immersed in a $5 \times 10^{-4} \text{ mol/dm}^3$ NaHCO_3 and 0.01 mol/dm^3 NaCl solution which had been previously deaerated with H_2 during 2 h.

The corroded carbon steel coupons were obtained by the procedure described by Blackwood et al. [18]. The coupon and the solution used in the third cleaning step explained above were transferred to a steel autoclave which was brought to the optimum operating conditions for anaerobic corrosion of carbon steel: $P(\text{H}_2) = 8.4 \text{ atm}$ and $T = 90^\circ \text{C}$. The time taken to reach the operating temperature was less than 1 h and the coupons were exposed to the corrosive environment for 54 days.

After this time, the coupons were removed from the autoclave reactor and a standard sample was characterised by XRD (Bruker D-5005). Magnetite was identified by means of XRD, although the existence of other amorphous phases cannot be discarded [19].

At the end of the experiments, solid phase surfaces were examined by XPS. Spectra were recorded on a PHI Perkin-Elmer ESCA Multianalyzer 5500 using an Al $K\alpha$ X-ray source (1486.6 eV). The error in the determination of the photoelectron energies was $\pm 0.2 \text{ eV}$.

2.2. Experimental procedure

In all the experiments, 200 cm^3 of the test solution were put in contact with the solid phase. Aliquots (1 cm^3) were taken periodically, immediately filtered through a $0.22 \mu\text{m}$ pore size filter and acidified by adding a small volume of concentrated HNO_3 . The uranium concentration in solution was determined by ICP-MS (Perkin-Elmer Elan 6000).

All the experiments were performed at room temperature and in 0.01 mol/dm^3 ionic strength (NaCl). Two different reactors were employed depending on the H_2 overpressure under which the tests were carried out (1 atm or 7.6 atm). An orbital stirrer was used to keep a continuous stirring of the solution.

$\text{H}_2(\text{g})$ with $\text{CO}_2(\text{g})$ 0.015% was bubbled continuously into the reactors during the experiments at 1 atm. $\text{H}_2(\text{g})$ was used to avoid the intrusion of oxygen in the system while the $\text{CO}_2(\text{g})$ in the gas stream was added to form a pH buffer in solution. In the experiment with H_2 overpressure, since it was not possible to perform gas bubbling, NaHCO_3 was added to the initial solution.

The pH of the solutions was monitored by means of a calibrated combined-glass electrode. Redox potentials were measured with a platinum electrode and the measurements were

Table 1
Summary of the experimental conditions employed in the different tests

Test	Solid	[U] ₀ (M)	$\log p(\text{CO}_2)$	Pressure (atm)	pH _f	pe _f
A	Commercial magnetite	7.3×10^{-5}	-3.82	1	8.1	0.8
B	Corroded coupon	1.1×10^{-5}	-3.82	1	8.1	-1.2
C	Corroded coupon	7.6×10^{-6}	$2.5 \times 10^{-4,a}$	7.6	7.3	^b

^a $[\text{NaHCO}_3]$.

^b Not measured due to the experimental set-up employed.

presented against the Ag/AgCl(s) and KCl saturated reference of the combined glass electrode.

Chemicals used in this work were of analytical grade and supplied by Merck. All solutions were prepared with bidistilled water from a Millipore Corp. Milli-Q system.

The experimental conditions are summarized in Table 1.

3. Results and discussion

Fig. 1 shows the evolution of the uranium concentration versus initial uranium concentration ratio with time in experiments A and B. As it can be seen, the uranium concentration in solution seems to decrease at a similar rate in both cases. However, after more than 20 days, the main trend observed is that much lower uranium concentrations are obtained in the experiment with the corroded coupon (experiment B) than in the experiment with commercial magnetite (experiment A).

The presence of zero-valent iron below the magnetite surface in experiment B might account for an increase of the electronic density at the surface and, therefore, might facilitate the electronic transference, causing a preferential oxidation of the structural iron in front of the experiment conducted in the absence of steel. On the other hand, there is strong evidence that partial dissolution of metallic iron occurring from beneath the surface oxide layer can result in a release of iron to the solution [16,17]. Subsequently, the oxidation of aqueous Fe(II) sorbed to the material drives further reductive precipitation of U(IV) from solution [16,17,26].

The ability of metallic iron to reduce U(VI) under anoxic conditions has been a matter of study by several authors [20,21] due to the feasibility of installing reactive barriers to remediate uranium contaminated groundwater. The main result is that Fe⁰ is very efficient in reducing U(VI), not only under reducing but also under anoxic conditions. Actually, the precipitation of amorphous UO₂ in solution after addition of metallic iron to a U(VI) solution has been demonstrated [22].

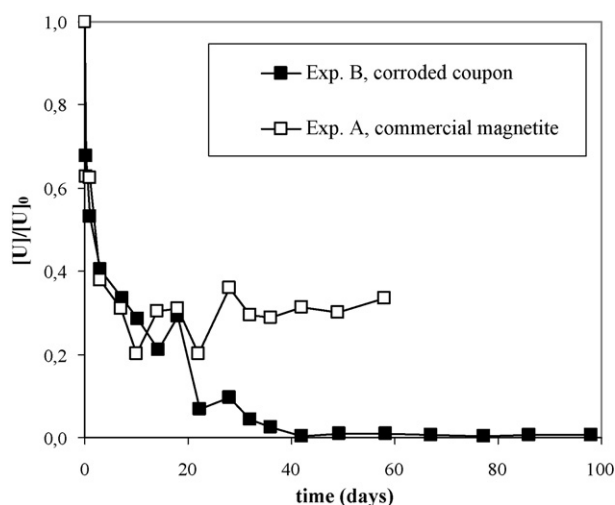


Fig. 1. Evolution of the uranium concentration vs. initial uranium concentration ratio as a function of time in experiments A and B.

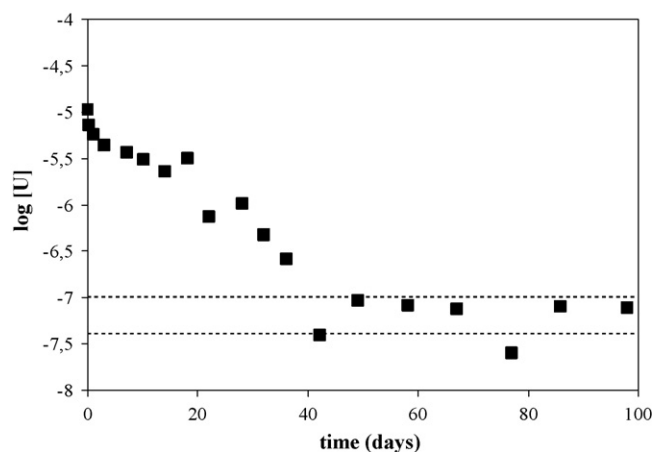


Fig. 2. Variation of the uranium concentration in solution in experiment B (black points). Dotted lines represent the range of uranium concentrations obtained at the end of experiments of amorphous UO₂ precipitation [22].

From the two different uranium deposition models described by Allen et al. [16], U(VI) incorporation into iron oxyhydroxides or reductive precipitation of U(IV)), in experiment B, the presence of zero-valent iron below the magnetite surface may account for a decrease in the redox potential of the system, which would be low enough to produce the reduction of U(VI) to U(IV) and to produce a lower uranium concentration in solution than in the experiment with commercial magnetite. The uranium concentrations obtained in this experiment could be low enough to precipitate amorphous uranium dioxide (see Fig. 2). Actually, the uranium concentrations at the end of the experiment B (around 10⁻⁷ mol/dm³) are very similar to the ones obtained in experiments of amorphous UO₂ precipitation (dotted lines in Fig. 2), between 5 × 10⁻⁸ mol/dm³ and 10⁻⁷ mol/dm³ [22], pointing to the possibility that the combination coupon/magnetite is able to reduce U(VI) to U(IV) and to precipitate amorphous UO₂.

In order to detect the presence of uranium(IV) on the corroded coupon surface, XPS spectra of the surface of the solids at the end of experiments A and B were recorded and are presented in Fig. 3. The aim of the XPS study of the surfaces was to determine the oxidation state of the uranium that is present on the surface of the coupon. In this sense, the U4f_{7/2} peak is the most useful because it has been reported (see Table 2) that the binding energies for U(VI) and U(IV) are different; the values for U(VI) are approximately 382.0 eV while the values for U(IV) are lower than 381 eV. In experiments A and B, the shifting of the U4f_{7/2} peak until energies of 381.5 eV and 381.3 eV, respectively indicates the presence of a certain percentage of U(IV)

Table 2
Binding energies (eV) reported for the U4f_{7/2} peak in U(IV) and U(VI) oxides by different authors

	Allen et al. [23]	Chadwick [24]	Wersin et al. [25]
UO ₂ (eV)	380.1	380.7	380.8
UO ₃ (eV)	381.9	381.9	382.4

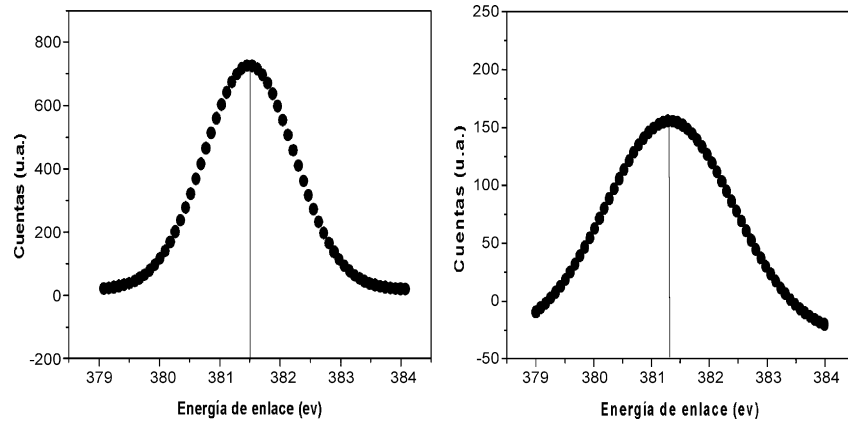


Fig. 3. U(4f) peak at the end of experiments A (left) and B (right).

on the surface of the solids and would corroborate the conclusion deduced from the study of the uranium concentrations in solution. This result would indicate that although sorption onto magnetite is likely to be responsible for the initial removal of U from solution, some subsequent surface reduction of U(VI) to U(IV) occurs, forming a solid UO_2 precipitate.

The XRD technique was used to identify the solid phases present at the end of the experiments on the coupons; it could corroborate the conclusions deduced from the evolution of the uranium concentration in solution and from the XPS study of the surface of the solids. XRD could actually help to identify the mechanism of uranium deposition according to the two mechanisms described by Allen et al. [16] and Scott et al. [17]. In this sense, in the experiment at high H_2 pressure (experiment C), the diffractogram gave, together with different iron corrosion products such as magnetite, lepidocrocite and hematite, the characteristic peak of the amorphous UO_2 phase (see Fig. 4).

This result clearly indicates that the reduction of U(VI) occurs on the surface of the corroded carbon steel coupon and gives confidence to the assumptions used to explain the evolution of the uranium concentration in solution. This result would reinforce the conclusion that uranium deposition onto the corroded coupon proceeds via a mechanism of reductive precipitation.

This sample was analysed by using SEM in an attempt to find UO_2 particles on the surface of the coupon, which were expected to be of nanometric scale, according to O'Loughlin et al. [14]. In spite of the fact that very small particles observed on the corroded coupon could be identified as uranium dioxide, a visual identification was complicated due to the presence of different iron corrosion products (see Fig. 5). However, from the uranium mapping made by EDS it was possible to conclude that uranium was almost homogeneously distributed on the surface of the corroded coupon, as it is shown in Fig. 6.

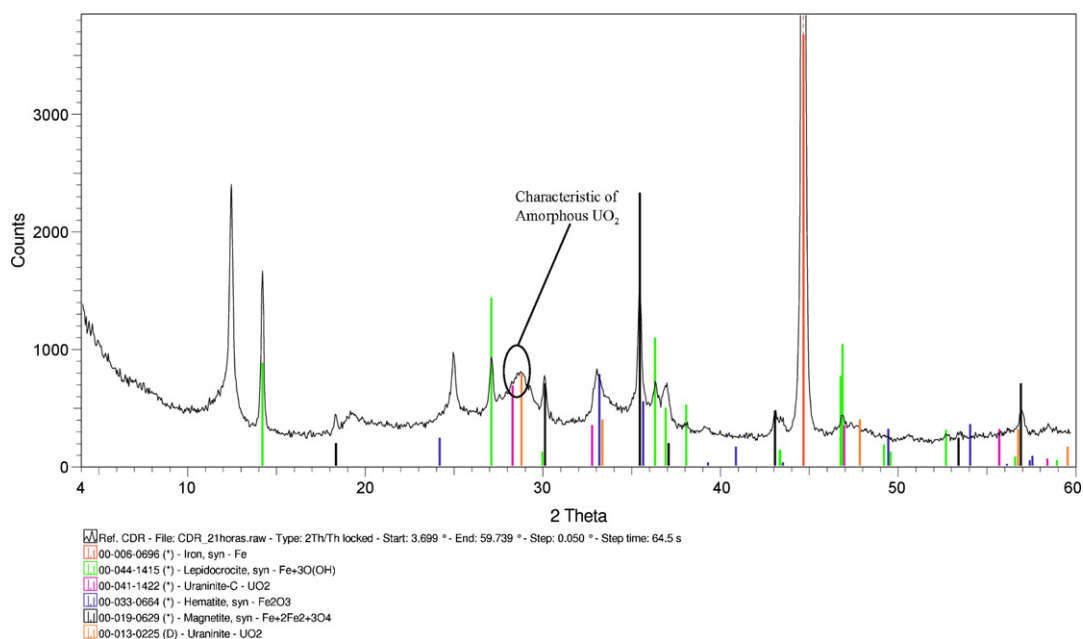


Fig. 4. X-ray diffractogram of the corroded carbon steel coupon at the end of experiment D.

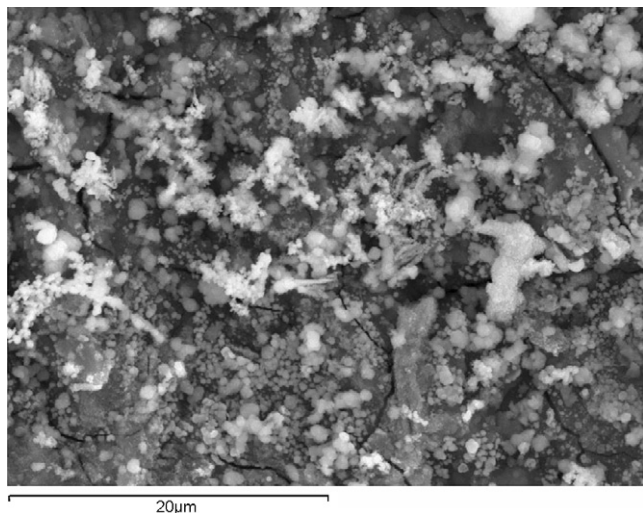


Fig. 5. Microphotograph of the surface of the corroded coupon. The smallest particles could be related to a uranium phase.

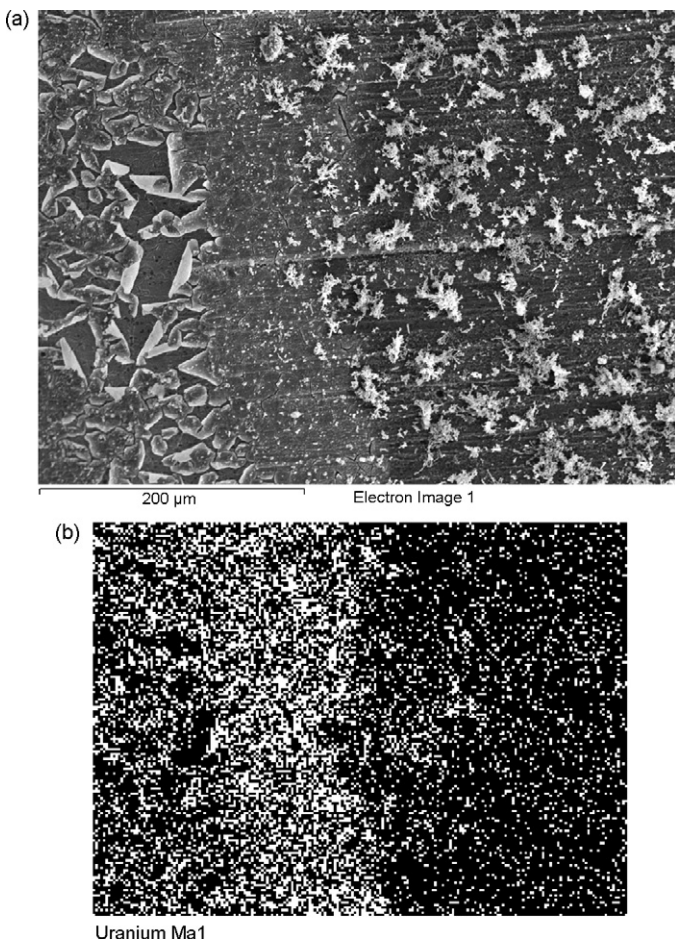


Fig. 6. (a) General view of the carbon steel coupon; (b) Uranium mapping on the surface of the steel coupon.

4. Conclusions

Magnetite formed on carbon steel under anoxic conditions has been observed to remove uranium from solution via surface sorption and reductive precipitation. After experiment,

residual concentrations of aqueous uranium were similar to those previously obtained in amorphous UO_2 precipitation experiments.

Magnetite generated on a steel coupon both removes and chemically reduces uranium from solution. Partial reduction of uranium to form non-stoichiometric UO_2 is strongly indicated by both XPS and XRD data.

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