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Sorption and Reduction of Uranium(VI) on Iron Corrosion Products under Reducing Saline Conditions

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Abstract

Pertinent to the behaviour of carbon steel based nuclear waste packages in saline geological environments, sorption and reduction of U(VI) on real container corrosion products has been studied in an Ar/8% H_2 flushed glove box. A carbon steel was corroded in $MgCl_2$ -brine at elevated temperatures. U(VI) was added and the redox states both of uranium and iron and their distribution among solid and liquid phases were investigated. The corrosion products initially consisted to more than 97% of hydrous Fe(II) oxides containing Cl^- and Mg^{2+} , but always some magnetite was present. In the course of the sorption step, the amount of magnetite increased. Reaction products buffer pH values of the system in a very narrow neutral range. Less than 1% of iron or uranium were found in colloidal state and already after one day, more than 98% of initially dissolved uranium was found associated with the immobile phases. A reciprocal relationship of solution concentrations of uranium with the nominal mass of magnetite was found. Behaviour of uranium species was rationalized in terms of Eh/pH diagrams. Reduction of hexavalent to tetravalent uranium was observed but to a much less pronounced extent than expected from thermodynamical considerations.

Introduction

Quantification of source terms for radionuclide release from high-level nuclear waste packages in a future underground repository requires thorough understanding of the effect of the container material. The container may act both as a physical and as a chemical barrier against radionuclide mobilization. As a physical barrier the container can prevent water access to the waste form for a period of a few hundred years, thus delaying waste form corrosion during the initial disposal phase, where elevated temperatures are prevailing due to radioactive decay. Important aspects are the time dependency of container corrosion, corrosion mechanisms, localized corrosion phenomena, resulting in estimated container life times and failure probability distributions. These effects have been extensively studied by various research groups [1, 2]. Based on these studies, carbon steels were identified as promising materials for manufacturing long-term corrosion resistant disposal containers in rock salt. Corrosion rates in disposal relevant $MgCl_2$ -rich brines were about 70 $\mu m/a$ at 90°C and 200 $\mu m/a$ at 150°C.

In the case of container failure the partly corroded carbon steel container can act as a chemical barrier for radionuclide species eventually released from the waste form (HLW glass, spent fuel etc.). Container corrosion generates a reducing geochemical environment in the near field of the disposed waste packages, favorable for limiting potential radionuclide migration. The reducing effect of iron corrosion has been observed to dominate over the oxidizing effect of gamma-radiolysis [4] and, thus, might stabilize the sparingly soluble tri- and tetravalent oxidation states of the actinide elements and of Tc. Moreover, container corrosion products are very efficient scavengers, decreasing the mobility of radionuclides both by sorption and coprecipitation phenomena. Qualitatively, these effects are quite well known. Many so called multiple materials interaction tests were performed. For example, in contact with dissolving spent fuel and HLW glass [3, 4], solution concentrations of Sr90, Sb125, Eu154/155, Tc99, Am241, Cm242/244, Np237, Pu238/239/240 and U were significantly reduced if iron was present.

This paper focuses on the behaviour of dissolved uranium in the presence of corroded carbon steel. Uranium is an important element in the context of radioactive waste disposal. In the case of direct disposal of spent fuel uranium is the main component and represents the waste matrix. Together with its daughter nuclides, uranium has been shown to contribute significantly to the overall radiological impact of the repository after 10^5 years of disposal [5]. Uranium mobility in natural water systems is often strongly reduced in the presence of Fe(III)hydroxides. Sorption isotherms as well as surface complexation models were employed to explain uranyl sorption data [6, 7]. It has been shown for carbonate free solutions that trace U(VI) concentrations are reduced by as much as a factor of 1000 in the presence of iron(III) oxyhydroxides [7]. The information on sorption behaviour of ferric oxyhydroxides cannot yet be used in performance assessments of the waste container as a chemical barrier, because (1) the real corrosion products formed on iron surfaces under anaerobic conditions may be in the oxidation state Fe(II), and, in contrast to large emphasis in the literature on iron(III) oxyhydroxides, very little is known on sorption effects of uranium on iron(II) (hydr)oxides, (2) it is not yet possible to distinguish between sorption, coprecipitation

and redox processes and (3) for many radionuclides of nuclear wastes, the pertinent data are not yet available.

The present work attempts to address the first two questions related to salt as disposal medium, $MgCl_2$ dominated aqueous solutions, carbon steel as container material and uranium as potential sorbate. Previous work on the brine/steel system showed magnetite and $(Fe,Mg)(OH)_2$ [8] as main corrosion products under closed system conditions. However, due to the initial presence of oxidants or due to radiolysis effects, formation of β - $FeOOH$, α - Fe_2O_3 etc., may not be excluded.

Experimental

Three corrosion experiments (No. 1, 2 and 3) were performed in two steps. At first, a preselected carbon steel (fine grained steel TStE355; composition in wt%: C = 0.17, Si = 0.4, Mn = 1.49, P-S < 0.1, bal. Fe) has been corroded for a lengthy time period in a $MgCl_2$ rich brine at elevated temperatures. Then U(VI) was added to the experiment and the chemical evolution of the system was studied. For comparison, a fourth experiment (No. 4) was performed with U(VI) added already prior to the Fe-corrosion step. The initial corrosion conditions were selected as to represent a potential accidental situation which may occur at worst in a repository in rock salt. The solution was composed of $MgCl_2 = 26.8$ wt%, $KCl = 4.7$ wt%, $NaCl = 1.4$ wt%, $MgSO_4 = 1.4$ wt%, $H_2O = 65.7$ wt%, which corresponds to a saturated brine of kainite, halite, sylvine, carnallite and kieserite at $55^\circ C$ (point Q of the quinary Na/K/Mg/Cl/ SO_4 system of the oceanic salts; composition in wt%:). For the experiments at higher temperatures solid NaCl was added for re-saturation. The test conditions after addition of U(VI) are summarized in Table 1.

Step A: Finely grained steel platelets were immersed in 200 ml of air saturated brine in PTFE lined autoclaves at 90° and $150^\circ C$. The experiments were performed under closed system conditions for 3 to 6 months. No attempt was made to exclude initial air from the system leading to about 15 mg of oxygen in the system. By consumption of oxygen upon steel corrosion, anoxic conditions are expected to be achieved in a few days. The carbonate content is confined to the initial content of CO_2 in air and the dissolved carbonate in the slightly acidic solution (C_{tot} ca. $10^{-5} m$). It is expected that under these conditions U-carbonate complexes are of minor significance. After terminating the corrosion experiment, the autoclaves were opened either in an Ar-stream (experiment 1) in an inflatable Ar filled bag (experiment 2) or in a Ar/8% H_2 flused glove box (experiments 3 and 4). Samples were taken from the solution and from the corrosion products.

Step B: U(VI) chloride solution was added to the system and an initial U concentration of $10^{-4} m$ was established. The experiments 1 to 3 were continued for more than one month at room temperature, either in

Table 1. Experimental conditions after addition of uranium and distribution of uranium among solid and liquid phases U contents in colloids and particulate matter calculated from the concentration difference of various filtrates

| Test | Duration [d] | T [$^\circ C$] | pH | Eh [mV] | U conc. [$\mu mol/l$] | | U distribution [%] | | | U(IV)/U(tot) ratio [%] in | | | Fe_3O_4 [g] | |
|------|--------------|------------------|------|---------|-------------------------|-------|--------------------|---------|---------|---------------------------|--------|---------|---------------|---------|
| | | | | | nonfilt. | 18 A | solut. | colloid | partic. | solid | solut. | colloid | | partic. |
| 1B | 0 | 25 | 7.5 | -415 | | | | | | | | | 0.78 | |
| | 5 min | 25 | 7.29 | -388 | | | | | | | | | 0.78 | |
| | 1 | 25 | 7.26 | -309 | 2.62 | 0.93 | 0.84 | 1.54 | 97.62 | | | | | |
| 2B | 22 | 25 | 7.38 | -88 | 67.91 | 0.06 | 0.06 | 61.68 | 38.26 | | | | | |
| | 27 | 25 | 7.24 | -69 | 0.00 | 0.60 | 0.54 | | 99.46 | | | | | |
| | 5 min | 25 | 6.86 | -380 | 127.10 | 23.11 | 18.18 | 81.82 | 0.00 | | | | 0.80 | |
| 3B | 1 | 25 | 6.79 | -244 | 54.12 | 1.72 | 1.36 | 41.22 | 57.42 | | | | 0.80 | |
| | 0 | 25 | 6.54 | -341 | | | | | | | | | 0.46 | |
| | 5 min | 25 | 6.52 | -316 | 109.20 | 2.35 | 2.15 | 0.73 | 97.12 | 0.00 | | | 0.46 | |
| 4B | 1 | 25 | 6.55 | -317 | 48.74 | 0.24 | 0.10 | 0.11 | 44.42 | 55.37 | 15 | 42 | 51 | 0.2 |
| | 7 | 25 | 6.62 | -291 | 48.32 | 0.05 | 0.04 | 0.04 | 44.17 | 55.75 | 13 | 81 | 65 | 0.5 |
| | 33 | 25 | 6.58 | -204 | 0.50 | 0.07 | 0.06 | 0.40 | 99.55 | | 13 | 31 | 55 | 0.2 |
| 105 | 150 | 6.67 | -280 | 0.34 | 1.97 | 1.81 | | 98.19 | | 50 | | | 1.3 | |

inert atmosphere (experiments (1) and (2)) or in the Ar/8% H_2 flushed glove box (experiment (3)). In test 1 all corroded iron coupons were removed from the reaction vessel, before adding uranium(VI), whereas in the other experiments some metallic Fe was left in the system. After certain time steps samples were taken from solution and solid as described above both for Fe and U analyses. Analyses of the Fe contents and of the nature of solid phases should detect potential air oxidation of the corrosion solution.

In order to avoid air contamination (oxidation, CO_2 -uptake) $Eh_{25^\circ C}$ and $pH_{25^\circ C}$ values were determined only a few minutes after solution sampling. Measurements were performed in Ar-atmosphere and in case of Eh values also in the Ar/8% H_2 -atmosphere in the glove box. Measured pH and Eh data were corrected for liquid junction potential according to Ref. [9]). The liquid junction potential of the Eh-electrode (Pt) was determined by measuring the potential of the electrode in H_2 -saturated (1 atm) brine ($Eh = (-59 \cdot pH)$ mV) at a known activity a_{H^+} . Reported pH and Eh values are consistent with Pitzer's ionic splitting convention.

Solution samples (acidified) were analyzed for Fe(tot) by ICP-AES, Fe(II) and Fe(III) by ion chromatography [10]. Fe(tot) values calculated from the sum of Fe(II) and Fe(III) and measured by ICP-AES agree in most cases within 5%. Filtered (0.45 μm membranes), ultrafiltered 18 \AA and nonfiltered solutions were analyzed. The samples were acidified with HCl after filtration in order to decrease the rate of oxidation of Fe(II). Solid samples (sediments and corrosion products remaining on the iron coupons) were characterized by XRD, SEM-EDX, and BET and by chemical dissolution in HCl to determine Fe(II)/Fe(III) ratios and also uranium concentrations. In some solids Cl^- was determined by ion chromatography and Mg^{2+} by ICP-AES. Care was taken to avoid air oxidation prior to analyses by BET and XRD. For BET surface area determination, the samples were dried 8 h or 3 d at 100°C (experiment 2 or 3 respectively) or at 25°C over $CaCl_2$ in an inert or Ar/ H_2 atmosphere (experiment 3, 5 weeks after U-addition). X-ray data were obtained from dried (100°C, experiment 1) and wet samples (experiments 2 to 4) about 1 h after test termination.

Uranium concentrations were determined by Isotope Dilution ICP-mass spectrometry after selective uranium separation by extraction chromatography using a resin containing diamyl amyl phosphonate (U/TEVA, Eichrom Co., USA) [11]. Oxidation states of uranium were determined separately by prior anion exchange separation (Dowex 1) of uranyl chlorocomplexes from 4.5 M HCl solution. Cationic U(IV) species are not retained under these conditions. Additionally, total uranium concentrations were measured in a separate sample. The procedure is described in detail by Fattahi and Guillaumont [12]. All reagents used throughout the oxidation state analysis were bubbled with argon to minimize oxygen contamination. The

separation itself was carried out in the glove box flushed with Ar/ H_2 .

Thermodynamic constraints

In order to estimate the stability ranges of dominant uranium species and valence states, geochemical calculations were performed, using the code EQ3/6. The electrolyte theory of Pitzer was used to calculate activity coefficients for the free uranyl ion and for U^{4+} in chloride media. Both, for U(VI) and for U(IV), chloride complexation is considered implicitly within the numerical values of the mean activity coefficients. For the UO_2^{2+}/Cl^- system binary interaction coefficients are reported [13], and together with a θ value of 0.0231 for Na^+/UO_2^{2+} interaction [14] mean trace activity coefficients of uranyl chloride in NaCl solutions were calculated. Mean activity coefficients for the binary U^{4+}/Cl^- system are not known but may be considered identical to respective values of the chemically homologue Th^{4+}/Cl^- system reported by [15]. Using these data and an E_0 value of 269 mV [16] for the U(IV)/U(VI) redox equilibrium at infinite dilution, the ionic strength dependency of the redox reaction under acid conditions is calculated.

To calculate redox equilibria at neutral to alkaline pH values, hydrolysis reactions, both of U(VI) and of U(IV) needs to be considered. The calculation of the predominance fields of the various hydrolysis species is made for 3 m NaCl solution and a typical total uranium concentration of 10^{-5} m. Under these conditions, polynuclear U(VI) complexes dominate the hydrolysis behavior of the uranyl ion and respective conditional stability constants are given by [17]. For $(UO_2)_3(OH)_7^-$ and $UO_2(OH)_3^-$, stability constants are only available up to Na concentrations of 0.5 m ($NaClO_4$) and since at this ionic strength stability constants are within the error range of the standard state values [18], the latter were used in the calculations. Data for the ionic strength dependency of the hydrolysis reactions in the Na/U(IV)/Cl-system are not known but may be estimated by analogy to the Na/Th/Cl system reported by Felmy *et al.* [19]. These authors describe the solubility of $Th(OH)_4(am)$ in 0–3 m NaCl solutions with only two solution species: Th^{4+} and $Th(OH)_4(aq)$. They did not find any ionic strength dependence of solubility in the dominance range of $Th(OH)_4(aq)$. A similar behaviour for $U(OH)_4(aq)$ is assumed and a β_{14}° value of -9.0 [20] has been used.

Results and discussion

After opening the reaction vessels prior to the addition of U(VI), Eh-values were always only a few 10 mV more oxidizing than the lower water stability limit (see Fig. 1, Table 1). During the sorption reaction the solution became slightly more oxidizing. The final pH in experiments performed at 150°C was about 0.8 units lower than that from the experiment performed at

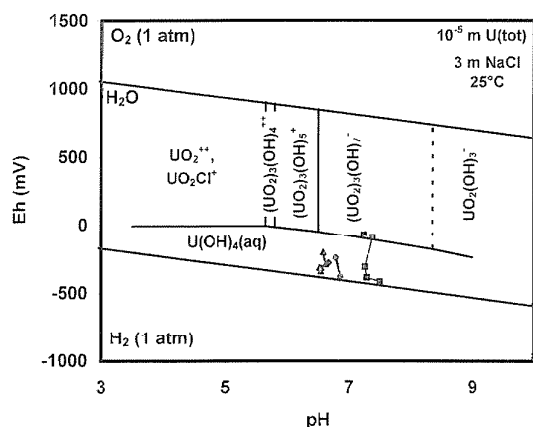


Fig. 1. Stability fields of various solution species of uranium at 25°C in 3 m NaCl solutions and experimentally measured Eh and pH values: ■ test 1, ● test 2, ▲ test 3, ◆ test 4.

90°C. For a given temperature the pH was independent on reaction progress. Additional experiments, performed in our laboratory at various initial pH value showed always about the same final pH value indicating that the system is buffered. After addition of U(VI) (experiments 1–3) less than 1% of dissolved Fe was found in colloidal state. SEM analyses showed two types of corrosion products: one with typical grain sizes of about 100 nm with the constituting elements Fe, O, Mg, and Cl, being analyzed by EDX. By analysis of the steel corrosion products using XRD mainly $(\text{Fe}, \text{Mg})(\text{OH})_2/\text{Fe}(\text{OH})_3\text{Cl}$ and magnetite (Fe_3O_4) phases were identified. Specific surface areas of corrosion products were found to be about 10 m²/g.

Sorption behaviour of uranium

As can be seen from Table 1, our experimental results show a strong reduction of initial uranium concentrations in solution already 5 minutes after adding U(VI) to the system. Less than 0.7% of dissolved uranium is bound to colloids. After 1 day in all cases more than 98% of the initial uranium is found associated with suspended particulate material and, to a larger extent, with the sediments. This may be an effect either of sorption, or of precipitation. Ultrafiltered solution concentrations of uranium in some of the experiments were as low as expected (10^{-7} – 10^{-8} m) [20], if an equilibrium with $\text{U}(\text{OH})_4$ (am) is assumed. However, only about 15% of the uranium content of ultrafiltered samples of experiment 3 was indeed identified as tetravalent uranium (see discussion below). Alternatively, U(VI) solid phases such as uranyl oxide hydrates may have been precipitated. However, previous laboratory experiments have shown that in the absence of elemental iron initial U(VI) concentrations of 10^{-4} m should remain metastable in solution at all pH values. This reasoning is not yet conclusive but it indicates a high probability that sorption and not precipitation is controlling the decrease of uranium

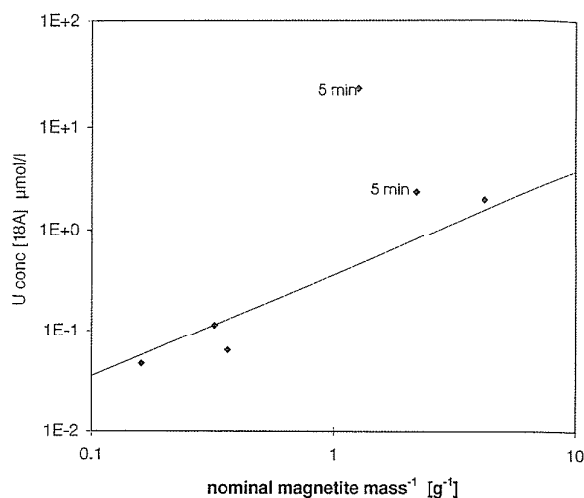


Fig. 2. Relation between the experimentally measured concentration of uranium in ultrafiltered solution samples and the inverse nominal mass of magnetite, as calculated from the Fe(III)/Fe(tot) ratio in the sedimented corrosion products. "5 min" indicates solution samples taken 5 minutes after addition of uranium to the brine.

concentrations in solution. More definite answers will be obtained later in this research project by performing similar experiments with different initial concentrations of uranium. If sorption occurs one has to distinguish four cases: sorption either of tetravalent or hexavalent uranium on either hydrous Mg^{2+} and Cl^- rich ferrous oxides or on magnetite. The uranium content of sediments and suspended particulate matter was essentially U(VI). Consequently we will refrain from discussion of sorption of tetravalent uranium.

As in low ionic strength solutions sorption of U(VI) on magnetite is reported to be quite strong [21, 22], the total concentrations of uranium in ultrafiltered solution samples have been plotted against the reciprocal nominal mass of magnetite of the corrosion products (Fig. 2). A trend of decreasing U solution concentration with increasing magnetite mass is observed. With high contents of magnetite, the uranium concentrations in solution have decreased by about a factor of 1000. The rather high uranium(VI) concentrations observed at the end of experiment 4 (uranium added already prior to iron corrosion) may thus be explained by the low magnetite contents of the corrosion products immediately after opening the reaction vessel.

A distribution ratio for uranium between solid and liquid phase of 15 (mg_U/g_{magnetite})/(μmol/l) is observed, which is about a factor of 3 higher than reported [22] as initial slope of the adsorption isotherm for CO₂ free 0.5 mmol/l NaCl solutions at pH 5.7. The rather high sorption observed in our tests is surprising considering the high ionic strength and may be explained with the higher specific surface area and higher pH in our test (10 m²/g and pH 6.5 as opposed to 3 m²/g and pH 5.7 in the literature).

Redox state of uranium

According to the low E_h -values measured in the solutions and based on the E_h /pH diagram (Fig. 1) one might expect uranium to exist dominantly in the tetravalent state and iron in the divalent state, respectively. More than 92% of dissolved iron species indeed were Fe(II). Significant reduction of U(VI) to U(IV) was observed, mainly in solution phase. But the highest fractions of U(IV) analyzed in solutions were only about 50% of total uranium (Table 1), even if uranium was already added to the high temperature corrosion experiment (test 4) for few months. Fattahi and Guillaumont [12] discussed the possible oxidation of U(IV) by trace amounts of Fe³⁺ ions under conditions where no Fe²⁺ ions were present initially (pH = 5.5, non complexing anions, $I = 0, 1-1$). They concluded that the oxidation reaction will be thermodynamically favored in the case of $c_{(Fe(III))}/c_{(U)}$ ratios > 0.5 . Additionally at low uranium concentrations kinetic factors can slow down their reduction reaction. Hexavalent uranium may also be stabilized by surface reactions on magnetite. These possible explanations for the disagreement between experimental results and thermodynamic considerations, however, are only plausible in case of overall disequilibrium, either caused by the observed presence of excessive quantities of metastable Fe(III) or in case of Fe²⁺ concentrations at the surface of magnetite lower than bulk values (surface $E_h > \text{bulk } E_h$). In case of global equilibrium, the distribution of uranium species should be given by the distribution estimated in the E_h /pH diagram, Fe(III)/Fe(II) concentration ratios would be lower than 10^{-8} and surface concentrations of Fe²⁺ would equal bulk values.

The measured low fractions of U(IV) in the solid phases could be an artifact caused by the procedure for the U(IV)/U(VI) separation. Oxidation of U(IV) during the separation step in 4.5 M HCl can not be excluded in presence of Fe(III) [23] and the fraction of Fe(III) was higher in the solid than in the liquid. Measured concentrations of U(IV), therefore, should be considered as lower limits.

Conclusions

Experimental data show that the dominant iron corrosion products in MgCl₂-rich salt brines are Cl and Mg containing hydrous ferrous oxides, with traces of magnetite present. Within one day more than 98% of initially dissolved uranium is immobilized on corrosion products. The observed reciprocal relationship of solution concentrations of uranium with the nominal mass of magnetite indicates that magnetite plays a key role in sorption of uranium from solution. Consequently, sorption on the always dominant Fe(II) hydroxides is subordinate to sorption on trace quantities of magnetite and more work is necessary to quantify magnetite formation in the course of iron corrosion in MgCl₂-rich brines. At the observed Eh/pH values, initial solutions are expected to be well oversaturated

with respect to tetravalent uranium hydroxide phases, but very little U(IV) was found in the solid phases. Reduction of hexavalent to tetravalent uranium was observed in the solution phase but to a much less pronounced extent as expected from thermodynamical considerations. Confirmation of procedures to analyse U(IV) and U(VI) will allow evaluation whether these observations are artefacts or caused by excessive presence of ferric iron.

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