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THE EFFECTS OF DOPING LEVEL, CARBONATE, Fe AND H_2 ON THE CORROSION POTENTIAL AND DISSOLUTION RATE OF ^{238}Pu-DOPED UO_2

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ABSTRACT

The effects of doping level, carbonate, Fe and H_2 on the corrosion potentials (E_{corr}) of ^{238}Pu-doped UO_2 electrodes were examined. Results show that E_{corr} values increase with increasing doping level whereas the presence of 0.1M carbonate, 0.1 g Fe or 3% H_2 reduce E_{corr}. Dissolution rates derived from batch dissolution experiments with the same ^{238}Pu-doped materials increase only slightly with doping level but increase more significantly in the presence of 0.1M carbonate. Fractional dissolution rates derived from these dissolution experiments are several orders of magnitude higher than those quoted in recent literature, as a result of the strong α-fields from these materials and the absence of H_2 and Fe in the dissolution experiments.

I. INTRODUCTION

One approach for the long-term management of used nuclear fuel is to emplace the used fuel deep underground in a stable geological formation. In Canada, a conceptual geologic repository has been designed for a granitic environment, in which the used nuclear fuel (mainly UO_2 fuel from CANDU reactors) would be placed in the repository in corrosion-resistant Cu containers with steel inserts. The containers are designed to retain their integrity for at least 100,000 years [1]. After the containers have been breached, the used fuel itself remains a barrier for release of radionuclides and, therefore, the rate of dissolution of the used fuel is of interest.

Geochemical conditions in a deep geologic repository would be expected to be reducing by the time groundwater has breached the corrosion-resistant containers. Any entrapped oxygen would have reacted relatively quickly after repository closure with container materials and minerals in the buffer and backfill materials and in the rock, while microbial reactions may also play a role.

Uranium dioxide is very insoluble under reducing conditions and the long-term stability of the fuel will, therefore, largely be determined by the oxidants produced by α-radiolysis of water, because the dose-rate from α-radiation will exceed that from γ/β- radiation beyond a fuel age of ~200 years and will persist for more than 10 000 years [2]. However, since 200-year old used fuel is not available at present, it is not possible to exclude γ/β radiolysis effects from any experiments conducted with spent fuel, which makes it difficult to experimentally address the long-term dissolution rate. Therefore, recent work has included studies with α-doped UO_2 and this paper reports on results from electrochemical and dissolution experiments performed with ^{238}Pu-doped UO_2 materials.

The dissolution of UO_2 in the presence of oxidants is an electrochemical process in which insoluble U(IV) is oxidized to soluble U(VI) prior to dissolution[2]. The main oxidants from α-radiolysis of water are H_2O_2 and O_2. The use of external α-sources [3, 4, 5], and chemically added H_2O_2 (as a surrogate for radiolytically produced oxidants [6]) in electrochemical experiments has provided much information on the basic chemistry and electrochemistry of α-radiolysis effects on UO_2 fuel dissolution. These experiments measure the corrosion potential (E_{corr}), which is the electric potential at which the anodic current (from the U(IV) oxidation process) and the cathodic current (from the oxidant reduction process) are equal but of opposite sign such that no net current flows. An E_{corr} value of about –100 mV corresponds to a surface composition of about $UO_{2.33}$, which has been suggested as the threshold composition beyond which oxidative dissolution becomes significant [2, 3]. It also represents the end of the fluorite structure range for UO_{2+x} [7].

Recently, corrosion potentials (E_{corr}) measured with ^{238}Pu-doped UO_2 electrodes [8] in 0.1M $NaClO_4$ and published E_{corr} data obtained with undoped UO_2 electrodes in the presence of external α-sources [3, 9] were compared. Results showed that the E_{corr} values for ^{238}Pu-doped electrodes were in good agreement with the published values obtained with undoped UO_2 electrodes, for the same α-source strengths [10]. Studies elsewhere involved dissolution experiments with α-doped UO_2 in N_2-degassed demineralised water [11, 12]. In these studies uranium release rates were measured from UO_2 pellets that were doped uniformly (using a sol-gel precipitation method) with either 0.1 or 10 wt.% of the α-emitter ^{238}Pu. Results showed that the amount of uranium released by dissolution was only approximately one order of magnitude greater than the amount released from an undoped pellet and the release rate measured was approximately the same as that determined for unirradiated UO_2 in aerated demineralised water [11]. Similar trends were found in subsequent experiments with crushed (higher surface area) samples [12].

II. INFLUENCE OF EXTERNAL PARAMETERS ON E_{corr} VALUES AND DISSOLUTION RATES

Shoesmith[1] has reviewed the effects of numerous parameters (including external α-source strength, pH, temperature, carbonate concentration and other groundwater species such as Ca and Si) on fuel corrosion processes under waste disposal conditions in detail. The effects of H_2 on UO_2 dissolution also have been discussed recently [13, 14, 15, 16].

II.A. Influence of Source Strength

From studies with external α-sources it has been shown that the steady-state E_{corr} becomes independent of source strength above ~250 μCi [3, 9]. The corrosion behaviour of UO_2 exposed to α-radiolytically decomposed water is very similar to that observed in the presence of H_2O_2. Theoretical calculations indicate that the H_2O_2 concentrations generated by α-source strengths above 250 μCi are in the range were E_{corr} is indeed independent of the H_2O_2 concentration.

II.B. Effects of Carbonate

The effects of carbonate concentration on UO_2 dissolution can be categorized into four concentration ranges [2]: In the absence of carbonate, corrosion deposits consisting of U(VI) products can accumulate on the UO_2 surface and increase E_{corr} values while suppress the dissolution rate. At low carbonate concentrations ($<10^{-3}$ M), the predominant influence of carbonate seems to be its thermodynamic ability to increase the UO_2^{2+} solubility, and hence prevent the deposition of corrosion products on the UO_2 surface. This lowers the value of E_{corr}. For concentrations between 10^{-3} and 10^{-1} M, carbonate is also kinetically involved in the dissolution process, via the formation of surface intermediates which, once dissolved, would lower E_{corr} values and increase dissolution rates. For high carbonate concentrations ($> 10^{-1}$ M), the presence of a precipitated surface phase such as UO_2CO_3 begins to limit the rate of dissolution and E_{corr} and the dissolution reaction become much less dependent on carbonate concentration.

II.C. Effects of Fe

There are three mechanisms by which Fe(II) could lead to a decrease in E_{corr} [8]. First, Fe(II) can react with radiolytically produced H_2O_2. Consumption of H_2O_2 by reaction with Fe(II) would result in a decrease in E_{corr} (provided that the H_2O_2 concentration is sufficiently low that the potential is not controlled by H_2O_2 decomposition). Second, Fe(II) can reduce U(VI). The resulting decrease in the dissolved U(VI) concentration could lead to a decrease in E_{corr}, if the interfacial anodic dissolution process (that produces UO_2^{2+}) is reversible. Third, heterogeneous reduction of U(VI) surface states on the electrode surface by Fe(II) would shift E_{corr} to more negative values. Experimental evidence suggests that redox effects involving Fe may significantly decrease the rate of U transport through a used-fuel repository via simultaneous sorption and reduction/precipitation processes [17]. However, general statements regarding the ability of Fe(II) to reduce U(VI) should be made with caution because the potential of the Fe(II)/Fe(III) and U(IV)/U(VI) redox couples are so similar that even small variations in the concentrations of complexing ligands may be extremely important in predicting the effect of Fe(II). The presence of Fe and Fe(II) in substantial amounts would likely cause U(VI) reduction but the presence of small amounts of dissolved Fe(II) would not be equally effective or at least U(VI) reduction would be orders of magnitude slower [17].

II.D. Effect of H_2

Recent Swedish work [13, 14, 15, 16] has shown that the presence of an overpressure of H_2 can reduce UO_2 dissolution rates by orders of magnitude. A H_2 overpressure could form in a geologic repository as a result of the anoxic corrosion of the inner steel vessel of the container and water radiolysis. The precise mechanism responsible for the effect of H_2 is still somewhat unclear. According to Spahiu and Sellin [14] and Ekeroth [15], the suppressing effect of H_2 appears to be mainly due to its effect on radical combination (i.e., H_2 reaction with $OH^{\cdot}$), rather than to the reduction of U(VI) to U(IV) as initially thought [13]. King and Shoesmith [16] discuss in detail several possible mechanisms that could explain the suppressing effects of H_2 on E_{corr} values. They conclude that the precise mechanism of the effect of H_2 is unclear but that it appears to involve a surface heterogeneous process (i.e., a combination of the oxidation of H_2 and reduction of U(VI), possibly in specific regions of the UO_2 surface) rather than a homogeneous solution process (i.e., consumption of radiolytically produced oxidants by H_2 or reduction of dissolved U(VI) by H_2). Werme et al. [18] state that the presence of reducing agents such as Fe(II) and H_2 in a repository system is very important for limiting the dissolution of used UO_2 fuel and that H_2 is more effective than Fe(II) in lowering uranium concentration in solution.

III. PURPOSE OF THIS STUDY

The large body of work on UO_2 dissolution reviewed by Shoesmith [2] included dissolution and electrochemical studies with undoped UO_2, SIMFUEL (fuel doped with non-radioactive elements) and UO_2 exposed to external α-sources at close distance (30 μm) to the UO_2 surface. This paper describes results from electrochemical and dissolution experiments with ^{238}Pu-doped UO_2, in which the influence of doping level, carbonate, Fe and H_2 on E_{corr} and the UO_2 dissolution rate were examined. The purpose of this work was to confirm the effects of these parameters observed on undoped UO_2 or on UO_2 in the presence of external α-sources.

IV. EXPERIMENTAL APPROACH

IV.A. Fabrication of ^{238}Pu-doped Materials and Electrodes

The ^{238}Pu-doped materials were fabricated by mechanically mixing UO_2 powder with small quantities of PuO_2 powder, followed by pressing and sintering. The procedure has been described elsewhere in detail [19]. The materials prepared contained nominally about 1, 10 and 100 Ci/kg UO_2 (0.006, 0.06 and 0.6 wt% ^{238}Pu). Typical used CANDU fuel contains ~1 Ci/kg UO_2 (α-activity) at a cooling time of 20 to 50 years and a burnup of 685 GJ/kg. Undoped pellets were also prepared specifically for this study from the same UO_2 powder, using the same mixing, pressing and sintering procedures.

Because the ^{238}Pu-doped materials were prepared by mechanically mixing PuO_2 and UO_2 powders, both the bulk and the surface of the doped materials presumably consisted of islands of PuO_2 embedded in a sea of UO_2. Thus, these materials are morphologically similar to MOX fuel but not to CANDU used fuel in which Pu is dissolved in the UO_2 grains. Thus, the behaviour of Pu, observed in these electrochemical and dissolution experiments, is not necessarily the same as would be observed for CANDU used fuel. In particular, Pu and U can dissolve independently from each other whereas, for CANDU fuel, Pu is only released as the UO_2 matrix dissolves. However, the effects of α-radiolysis on uranium behaviour should be similar for the nominal 1 Ci/kg UO_2 material and >200 year old CANDU used fuel (for which α-radiolysis is much more important than γ/β-radiolysis) [20].

The actual composition of the Pu-doped materials was determined by dissolving one quarter of a 3-mm thick disc of each material (including the undoped material) in concentrated HNO_3 containing 0.05M HF. The resulting solutions were analyzed for U and Pu. The actual compositions of the Pu-doped materials are 0.4, 2.2, 12.5 and 80 Ci/kg UO_2 instead of 0, 1, 10 and 100 Ci/kg UO_2. The cause of these differences must be sought in the manner in which these materials were made, as discussed by Stroes-Gascoyne and

Betteridge[20]. All calculations in the present paper have been performed using the actual compositions and activities of the ^{238}Pu-doped materials.

To prepare the electrodes, 3 mm-thick discs were cut from the Pu-doped material pellets, Cu-plated, mounted on stainless steel stubs (using conducting Ag epoxy), encased in an acrylic shell and secured in place with non-conducting epoxy. After curing, the electrodes were polished using 100, 320 and 600 grit wetted silicon carbide paper. Further details on electrode preparation are given by Stroes-Gascoyne et al. [10, 20].

IV.B. Corrosion Potential (E_{corr}) Experiments

Table 1 describes all successful E_{corr} experiments carried out with the Pu-doped electrodes. All experiments were performed in a glass cell in an Ar-flushed plexiglass glovebox specially built for these experiments. The experiments (see Table 1) were carried out in a 540 mL Ar-degassed (30 minutes) 0.1M $NaClO_4$, pH 9.5 solution, or in an Ar-degassed 0.1M $NaClO_4$ solution, containing 0.07M $NaHCO_3$ and 0.03M Na_2CO_3, at pH 9.5. In some experiments 0.1 g of metallic Fe-filings (Fisher^{TM}, degreased iron filings, about 40 mesh) was added. Each experiment was assembled and the solution was degassed for 30 minutes with ultra-pure Ar prior to the start of the experiment. Some experiments were degassed with Ar/3% H_2 instead of Ar. The electrode was polished on 600 grit wetted silicone carbide paper, rinsed with distilled deionized water, dried with Kimwipes and placed immediately in a separate glass cell with degassed solution (same solution composition and gas as for the actual E_{corr} experiment). The Pu-doped electrode was cathodically reduced at –2V for 5 minutes in this separate glass cell, and then transferred immediately to the degassed solution in the experiment glass cell, while keeping the potential at –2V. After the electrode was in place, the potential was removed and E_{corr} was measured over time. A Pt counter electrode and saturated calomel reference electrode (SCE) were used in the experimental set up, with all E_{corr} values quoted with respect to the SCE. During the entire experiment, a stream of Ar (or Ar/3% H_2 in some cases) was flushed over the experiment to maintain deaerated conditions.

The E_{corr} experiments were run for several weeks to several months (approximately 350 to 1650 hours) and Table 1 gives all E_{corr} data obtained for the Pu-doped electrodes at 18 h and 150 h. The specific effects of doping level, 0.1M carbonate, 0.1g Fe and Ar/3% H_2 are explored in Tables 2 to 5 and illustrated in Figures 1 and 2.

Table 1: E_{corr} results at 18 h and 150 h

Expt.	Doping Level Ci/kg UO_2	Carbonate Addition	Fe Addition	Atmosphere	E_{corr} (18 h) (mV)	E_{corr} (150 h) (mV)
1	0.4	0	0	Ar	-270	-128
2	2.2	0	0	Ar	-118	-71
3	2.2	0.1M	0	Ar	-392	-330
4	2.2	0.1M	0	Ar	-132	-143
5	2.2	0	0.1 g	Ar	-375	-246
6	2.2	0	0	Ar/3% H_2	-254	-152
7	2.2	0.1M	0.1 g	Ar	-210	-137
8	12.5	0	0	Ar	-73	+15
9	12.5	0	0	Ar	-256	-148
10	12.5	0.1M	0	Ar	-187	-144
11	12.5	0.1M	0	Ar	-211	-135
12	12.5	0	0.1 g	Ar	-106	-71
13	12.5	0	0.1 g	Ar	-326	-155
14	12.5	0	0	Ar/3% H_2	-243	-146
15	12.5	0.1M	0.1 g	Ar	-28	-15
16	80	0	0	Ar	+25	+126
17	80	0	0	Ar	+56	+80
18	80	0.1M	0	Ar	-84	+10

IV.C. UO_2 Dissolution Rate Experiments

A method has been described for predicting the dissolution rate of UO_2 (and used fuel) from measured E_{corr} values [21, 22, 23]. This method uses the relationship between the corrosion current and potential, which is obtained from measurements made under oxidizing conditions, i.e., at high potentials. By extrapolating this relationship to the much lower E_{corr} values, the corresponding corrosion currents and, hence, corrosion rates can be calculated. According to King and Shoesmith [16], caution should be exercised in using dissolution rates derived from extended extrapolations to very low potentials. Furthermore, the relationships between potential and corrosion current (the so-called Tafel slopes) have not yet been established for the Pu-doped electrodes and the corresponding relationship for undoped UO_2 may not be valid for Pu-doped UO_2 materials. Therefore, we will not use the E_{corr} values measured in this study to derive dissolution rates until such relationships are available (experiments are in progress).

Instead, dissolution rates derived from dissolution (or leaching) experiments with the Pu-doped materials [20, 24, 25] are presented and discussed. These experiments investigated the effects of α-dose rate, carbonate and time on the dissolution of UO_2. The effect of precipitation was studied by carrying out the dissolution experiments in perchlorate solution (0.1M $NaClO_4$) and perchlorate/carbonate solution (0.1M $NaClO_4$ + 0.1M carbonate (0.03M Na_2CO_3 and 0.07M $NaHCO_3$)) at pH 9.5. (This carbonate concentration is much higher than would be encountered in a deep geologic repository and is used solely to ensure that the effects of carbonate are measurable). The time dependence of the dissolution rate was investigated by carrying out experiments for different durations.

At the end of the dissolution experiments, the UO_2 discs were removed from solution and the amount of U and Pu dissolved was determined from solution analysis. The amount and composition of any surface precipitate on the UO_2 discs was assessed by exposure to 60 s dips in 0.1M HCl, followed by solution analysis [24, 25]. The specific effects of doping level, carbonate and time on dissolution rates are explored in Tables 6 and 7 and shown in Figure 3.

V. DISCUSSION OF E_{corr} RESULTS

Table 1 shows a summary of all successful E_{corr} experiments carried out with the Pu-doped materials. Any duplicate experiments in Table 1 were averaged for the calculation of specific effects in Tables 2 to 5 and Figures 1 and 2. E_{corr} values at 18 and 150 h are given to show the effects of time on E_{corr}.

V.A. Effect of Doping Level on E_{corr}

Table 2 shows that generally E_{corr} increases as the doping level increases. An exception is the E_{corr} value for the doping level of 12.5 Ci/kg UO_2, which is an average of two duplicate experiments giving very different E_{corr} values (experiments 8 and 9, Table 1). The E_{corr} results of experiment 8 appear to fit the observed trend better, but there is no obvious reason why the results of experiment 9 should be excluded. A doping level increase from 0.4 to 80 Ci/kg UO_2 (factor of 200) resulted in an increase of E_{corr} of about 310 mV after 18 h and about 230 mV after 150 h. These results show clearly that α-radiolysis produces oxidizing conditions, which increase the corrosion potential of the Pu-doped UO_2 electrodes considerably. In terms of dissolution rate effects, the method of Shoesmith and Sunder [21] and Shoesmith et al. [22, 23] predicts an order of magnitude increase in dissolution rate for every 60 mV increase in E_{corr}, using data from experiments with undoped UO_2. If these data were valid for the Pu-doped UO_2 electrodes, this would mean that a doping level increase of a factor of 200 would have resulted in a four to five order magnitude increase in dissolution rate. (It needs to be established yet whether the data for undoped UO_2 are valid for the Pu-doped materials)

Table 2: Effects of doping level on E_{corr} values

Doping Level (Ci/kg UO_2)	E_{corr} (18 h) (mV)	E_{corr} (150 h) (mV)
0.4	-270	-128
2.2	-118	-71
12.5	-164^1	-82^1
80	$+41^2$	$+103^2$

[1] Average of Experiments 8 and 9 (Table 1)
[2] Average of Experiments 16 and 17 (Table 1)

V.B. Effect of Carbonate on E_{corr}

Table 3 quantifies the effects of 0.1M carbonate on E_{corr}, for the doping levels from 2 to 80 Ci/kg UO_2. For four of the six E_{corr} data points, averages of two duplicate experiments were used (Table 1). The data in Table 3 and Figures 1 and 2 show that the presence of 0.1M carbonate lowers E_{corr} values. The amount of reduction is about 100 to 150 mV, except again for the electrodes with a doping level of 12.5 Ci/kg UO_2. For this doping level, one of the measured E_{corr} values, in the absence of carbonate, was very low (experiment 9, see above).

As discussed in the introduction, a carbonate concentration of 0.1M will give rise to some intermediate surface carbonate complexes of U(VI) but these eventually will dissolve, leaving the electrode surface with very little or no U(VI), and thereby reducing the value of E_{corr} as observed However, the carbonate mechanism also involves the catalysis of the anodic reaction which can result in an increase in the dissolution rate even though E_{corr} has decreased.

Table 3: Effects of carbonate on E_{corr} values

Doping Level (Ci/kg UO_2)	Carbonate Addition	E_{corr} (18 h) (mV)	E_{corr} (150 h) (mV)
2.2	0	-118	-71
2.2	0.1M	-262[1]	-236[1]
12.5	0	-164[2]	-82[2]
12.5	0.1M	-199[3]	-139[3]
80	0	+41[4]	+103[4]
80	0.1M	-84	+10

[1] Average of Experiments 3 and 4 (Table 1)
[2] Average of Experiments 8 and 9 (Table 1)
[3] Average of Experiments 10 and 11 (Table 1)
[4] Average of Experiments 16 and 17 (Table 1)

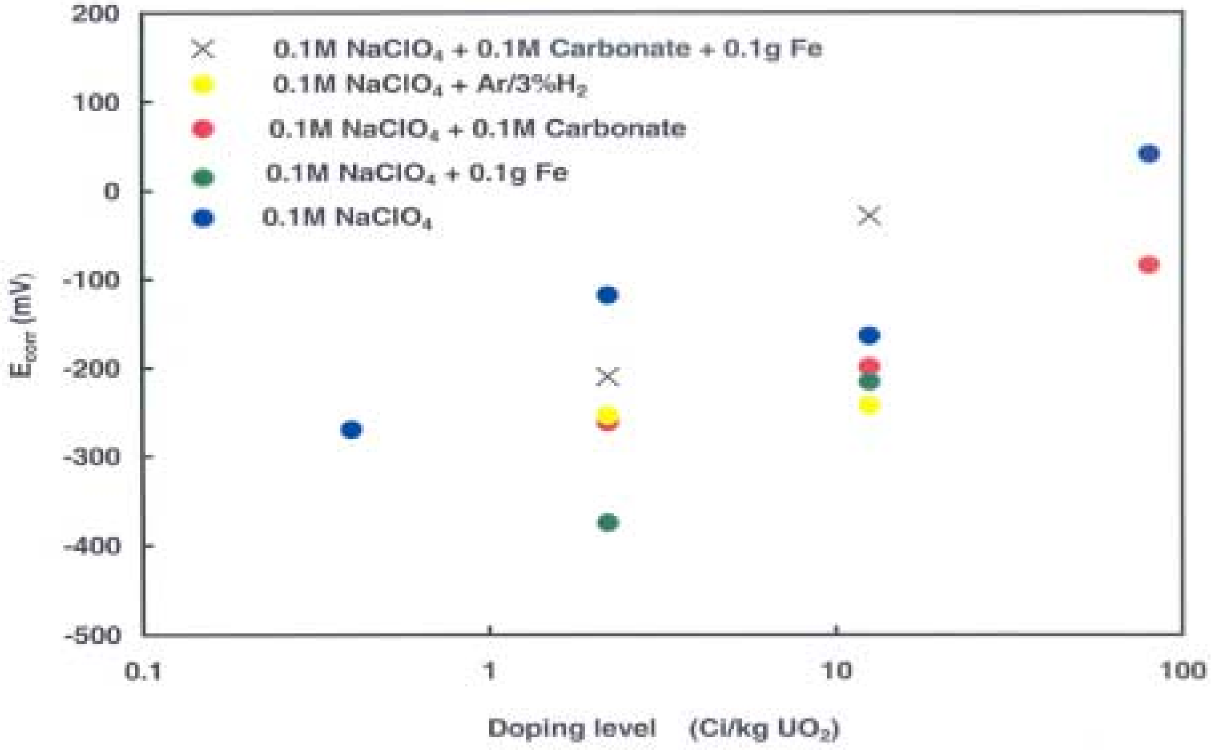

Figure 1: E_{corr} values as a function of doping level at 18 h under different conditions.

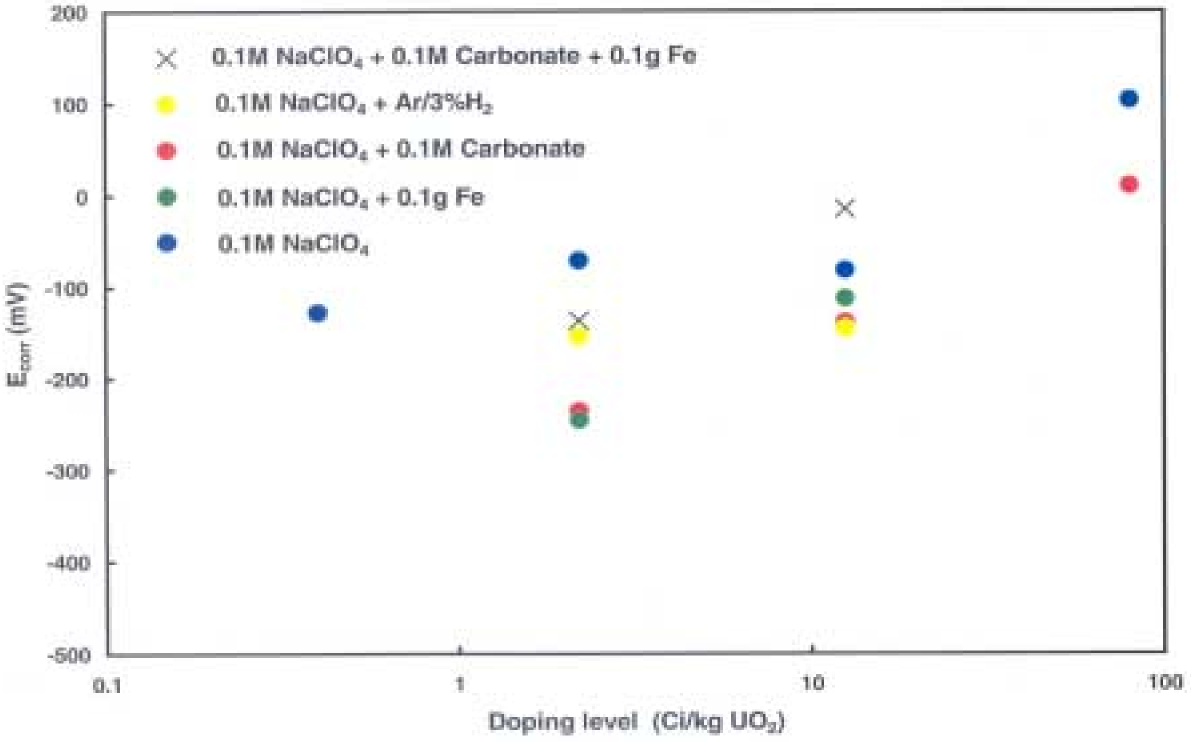

Figure 2: E_{corr} values as a function of doping level at 150 h under different conditions.

V.C. Effect of Fe on E_{corr}

Table 4 examines the effects of the presence of 0.1 g Fe filings on E_{corr} values. The effects are again illustrated in Figures 1 and 2. Although only two data points are available it appears that for the 2.2 Ci/kg UO_2 doping level the presence of Fe lowers E_{corr} values considerably (up to ~ 250 mV) below the values in 0.1M $NaClO_4$ solutions. The differences for the 12.5 Ci/kg UO_2 doping level are less pronounced, but nevertheless still observable. The smaller difference for this doping level may again arise because the E_{corr} value measured in 0.1M $NaClO_4$ solution in experiment 9 was so low. As discussed, the presence of Fe may reduce some U(VI) formed in solution or on the electrode surface or Fe may react with H_2O_2. In either case, less U(VI) would be formed and E_{corr} will be reduced. Based on the reduction in E_{corr}, the presence of 0.1 g Fe would reduce the dissolution rate by up to four orders of magnitude, if the model and data of Shoesmith and Sunder [21] were applicable to these Pu-doped electrodes.

Table 4: Effects of Fe on E_{corr} values

Doping Level (Ci/kg UO_2)	Fe Addition	E_{corr} (18 h) (mV)	E_{corr} (150 h) (mV)
2.2	0	-118	-71
2.2	0.1 g	-375	-246
12.5	0	-164[1]	-82[1]
12.5	0.1 g	-216[2]	-113[2]

[1] Average of Experiments 8 and 9 (Table 1)

[2] Average of Experiments 12 and 13 (Table 1)

V.D. Effect of H_2 on E_{corr}

Table 5 shows the effects of the presence of 3% H_2 in the Ar cover gas on E_{corr} values. Although again only two data points are available, the results in Table 5 and Figures 1 and 2 show that the presence of Ar/3% H_2 lowers E_{corr} values (by about 80 to 140 mV), compared to the values obtained in 0.1M $NaClO_4$ solutions under Ar. It appears that for both doping levels tested (2.2 and 12.5 Ci/kg UO_2), the E_{corr} values are very similar (both at 18 h and 150 h) in the presence of 3% H_2. This similarity suggests that there is sufficient H_2 to react with all oxidants produced at either doping level. However, this does not explain the observed increase in E_{corr} values over time at both doping levels, which suggests a continuous slow oxidation of the electrodes, presumably by radiolysis products.

Suppression of E_{corr} by hundreds of mV (to close to the reversible potential for the H_2/H^+ couple) has been observed in other experiments (with and without a γ-radiation field) [16]. This has been interpreted to mean that surface reactions with H_2 were involved or that (in a radiation field) radiolytical yields of reductants (H_2 and $H^\cdot$ radicals) were increased which suppressed the potential. As discussed in the introduction, the precise mechanism of the H_2 effect is not clear and may be different depending on the type of UO_2 used [16].

In this study, the decrease in E_{corr} in the presence of Ar/3% H_2, is much less (~80–140 mV) than found by others and E_{corr} values increase over time for both doping levels. This suggests that there is an effect of H_2 on E_{corr} but that the effect is not strong enough, at either doping level, to counteract the continuous oxidation over time resulting from the production of oxidants by α-radiolysis. More data are needed before any firmer conclusions can be formulated. Based on the reduction in E_{corr}, the presence of 3% H_2 would reduce the dissolution rate of the Pu-doped material by up to two orders of magnitude, if the model and data of Shoesmith and Sunder [21] were applicable to these electrodes.

Table 5: Effects of H_2 on E_{corr} values

Doping Level ($Ci/kg\ UO_2$)	Atmosphere	E_{corr} (18 h) (mV)	E_{corr} (150 h) (mV)
2.2	Ar	-118	-71
2.2	Ar/3% H_2	-254	-152
12.5	Ar	-164[1]	-82[1]
12.5	Ar/3% H_2	-243	-146

[1] Average of Experiments 8 and 9 (Table 1)

V.E. Combined Effect of 0.1M Carbonate and 0.1 g Fe

Two E_{corr} experiments were carried out in which both 0.1M carbonate and 0.1 g Fe filings were present (Table 1, experiments 7 and 15). Figures 1 and 2 show that the E_{corr} values from these experiments are higher than from the experiments with only one additive (either 0.1M carbonate, 0.1 g Fe or 3% H_2). Although carbonate may have complexed with Fe(II), possibly negating the effect of Fe(II) or Fe, there should have been ample carbonate left to have a measurable effect on E_{corr}. In fact, the E_{corr} values obtained in experiment 15 (12.5 $Ci/kg\ UO_2$) are actually higher than the average E_{corr} value in solutions with no additives (experiments 8 and 9); but, as discussed before, the latter value may be artificially low, because the E_{corr} value for experiment 9 appears to be too low. Both experiments 7 and 15 seem to suggest that the effects of 0.1M carbonate and 0.1 g Fe at least partially cancel each other out, but an explanation for such an effect is not obvious.

VI. DISCUSSION OF RESULTS FROM DISSOLUTION STUDIES

VI.A. Influence of Doping Level on Dissolution Rates

Because we have not established a current-potential relationship for the Pu-doped electrodes, the E_{corr} values were not used to calculate corrosion rates. We attempted to measure the amount of U in solution and precipitated on the electrodes (via dissolution in acid) after termination of each E_{corr} experiment in order to calculate a dissolution rate. However, in earlier E_{corr} experiments, the electro-reduction step appeared to allow excess U in solution [8] while in later experiments, in which the electro-reduction step was done in a separate solution, large quantities of U appeared in solution in some cases, presumably from small particles dislodging from the electrodes, (Stroes-Gascoyne et al., unpublished results, 2004). Therefore, these measured U concentrations and resulting UO_2 dissolution rates are likely not representative of the dissolution process and the results are not shown here.

The results of the static dissolution experiments [20, 24, 25] are shown in Tables 6 and 7 and in Figure 3. Table 6 and Figure 3 show an increase in dissolution rate of about a factor of 5 to 7 over the doping level range of 0.4 to 80 $Ci/kg\ UO_2$ (factor of 200). Therefore, doping level does not appear to have a large influence on the dissolution rate, based on the results of the batch dissolution experiments. (Note that these results do not agree with changes in dissolution rates implied by changes in E_{corr} based on the model and data of Shoesmith and Sunder [21] (Section V.A)).

The dissolution rates given in Table 6 can be converted to fractional dissolution rates by using a specific surface area of 2 cm^2/g U [16]. Fractional release rates range from about 2 x 10^{-6} to 3 x 10^{-5} per year, one to three orders of magnitude higher than the values quoted by King and Shoesmith [16] for fractional dissolution rates in the presence of H_2 (i.e., 10^{-7} to 10^{-8} per year) and two orders of magnitude higher than the peak fractional dissolution rate of 10^{-7} per year (range of 10^{-6} to 10^{-8} per year) quoted by Werme et al. [18]. The higher fractional dissolution rates in our study were obtained in the presence of mostly strong radiation fields and in the absence of H_2 or Fe, whereas much lower radiation levels were used in some of the studies used by Werme et al. [18] to calculate fractional dissolution rates and H_2 was present in the studies quoted by King and Shoesmith [16].

Table 6: Effects of doping level on dissolution rates

Doping Level ($Ci/kg\ UO_2$)	Dissolution Rate ($mg/m^2.d$) (167 d)	(270 d)
0.4	3.5 x 10^{-1}	1.3 x 10^{-1}
2.2	4.2 x 10^{-1}	3.6 x 10^{-1}
12.5	8.4 x 10^{-1}	5.7 x 10^{-1}
80	18.1 x 10^{-1}	8.6 x10^{-1}

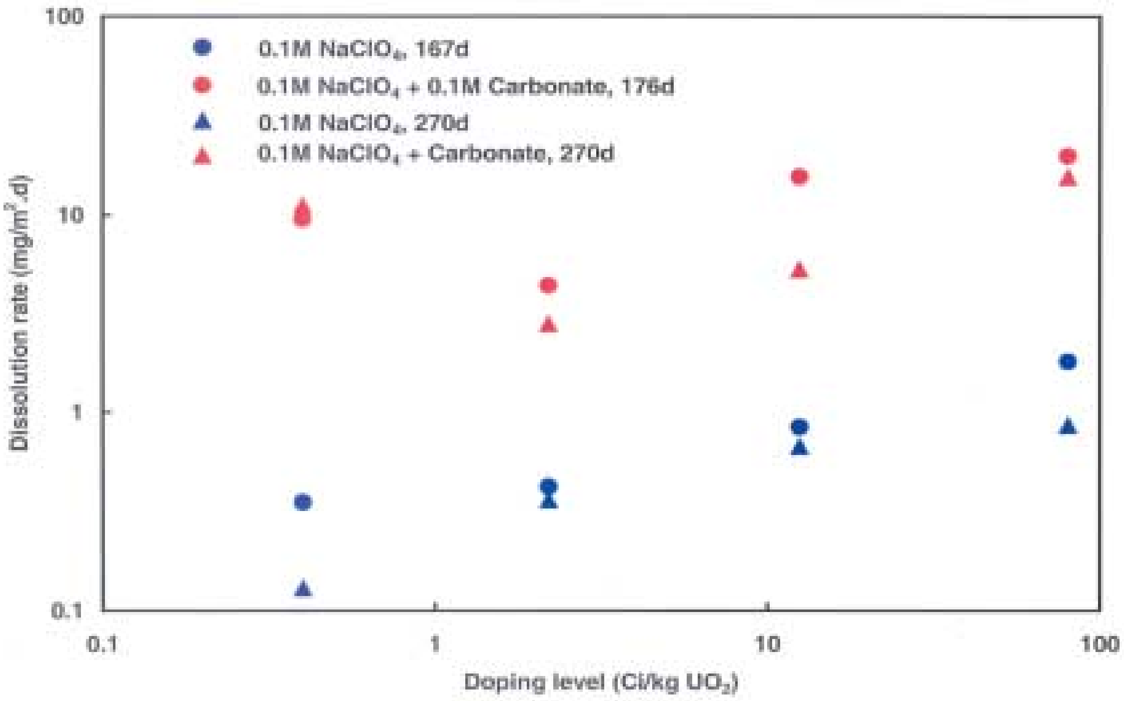

Figure 3: Dissolution rates as a function of doping level, carbonate concentration and time.

VI.B. Influence of Carbonate on Dissolution Rates

Table 7 and Figure 3 illustrate the influence of 0.1M carbonate on the dissolution rate. An increase in dissolution rate of about a factor of 10 to 20 was observed for doping levels of 2.2, 12.5 and 80 Ci/kg UO_2. As discussed in the introduction, at the 0.1M carbonate level used here, the effect of carbonate is expected to be both of a thermodynamic and kinetic nature. Tables 6 and 7 and Figure 3 also show that the dissolution rate appeared to decrease somewhat over time, both in the absence and presence of 0.1M carbonate, presumably because initial dissolution takes place at preferred (or high-energy) surface sites that disappear over time [18, 20].

Table 7: Effects of carbonate on dissolution rates

Doping Level (Ci/kg UO_2)	Carbonate (M)	Dissolution Rate ($mg/m^2.d$) (167 d)	(270 d)
0.4	0	3.5×10^{-1}	1.3×10^{-1}
0.4	0.1	9.5	11.2
2.2	0	4.2×10^{-1}	3.6×10^{-1}
2.2	0.1	4.4	2.8
12.5	0	8.4×10^{-1}	5.7×10^{-1}
12.5	0.1	15.6	5.3
80	0	18.1×10^{-1}	8.6×10^{-1}
80	0.1	19.9	15.6

Figure 3 shows that, for the 0.4 Ci/kg UO_2 doping level, the influence of 0.1M carbonate on dissolution rate appears to be almost two orders of magnitude – much higher than for the other doped materials. Since the data at 167 d and 270 d came from two separate experiments, it is unlikely that these data are spurious. This nominally undoped material contains mostly $^{239+240}Pu$, with a very small quantity of ^{238}Pu, giving an overall α-doping level of only 0.4 Ci/kg UO_2 but a somewhat larger Pu mass fraction than for the material with the highest doping level of 80 Ci/kg UO_2, (Stroes-Gascoyne et al., unpublished results, 2004). Shoesmith [2] has noted that the oxidant reduction rate on SIMFUEL (or used fuel) is higher than on UO_2 under conditions where no surface films block the dissolution process. The suggested explanation for this effect is that rare earth doping changes the stoichiometry of the UO_2 in the SIMFUEL and used fuel and hence the rate of oxidant reduction on that material. Our "undoped" sample was lowest in α-activity but highest in Pu mass, compared to the other doped materials. Since Pu is redox sensitive, somewhat similar to rare earths, it is possible that the oxidant reduction process is faster on this material when there is no blockage of the surface by precipitate films (i.e., in 0.1M carbonate), possibly resulting in the higher dissolution rates. (Although we have no knowledge of the actual oxidation state of Pu in our Pu-doped materials, it was noted that the presence of Pu apparently led to hypo-stoichiometry and high resistivity upon annealing of these materials [19], suggesting an influence of the presence of Pu on the stoichiometry of the materials).

VII. CONCLUSIONS

The electrochemical experiments with the Pu-doped electrodes have shown that the presence of 0.1M carbonate, 0.1 g Fe or 3% H_2 all reduce E_{corr}, as expected. It is however, not yet possible to quantify these effects in terms of a reduction in dissolution rate because the relationship between the corrosion current and potential for these materials needs to be established in order to derive appropriate dissolution rates from the E_{corr} measurements. Dissolution rates derived from batch dissolution experiments do not appear to depend very strongly on doping level over the range of 2 to 80 Ci/kg UO_2, but are affected by the presence of carbonate. Fractional dissolution rates from this study are one to three orders of magnitude higher than those quoted in recent reports as a result of the strong alpha fields and the absence of H_2 and Fe in our dissolution experiments. Overall, the trends observed confirm the expectations from previous observations with undoped UO_2. In a geologic repository, the effects of carbonate (from groundwater and minerals in buffer materials) would enhance dissolution rates, whereas the effects of Fe (from container materials) and H_2 (also largely from corrosion of container materials and some from radiolysis) would counteract the effects of oxidants (produced by α-radiolysis of water) on used fuel corrosion rates.

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