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Electrochemical studies of the effect of H_2 on UO_2 dissolution

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Abstract

This report summarises evidence for the effect of H_2 on the oxidation and dissolution of UO_2 derived from electrochemical studies. In the presence of γ-radiation or with SIMFUEL electrodes containing ε-particles, the corrosion potential (E_{CORR}) of UO_2 is observed to be suppressed in the presence of H_2 by up to several hundred millivolts. This effect has been observed at room temperature with 5 MPa H_2 (in the case of γ-irradiated solutions) and at 60°C with a H_2 partial pressure of only 0.002–0.014 MPa H_2 with the SIMFUEL electrode. The suppression of E_{CORR} in the presence of H_2 indicates that the degree of surface oxidation and the rate of dissolution of UO_2 is lower in the presence of H_2.

The precise mechanism of the effect of H_2 is unclear at this time. The mechanism appears to involve a surface heterogeneous process, rather than a homogeneous solution process. Under some circumstances the value of E_{CORR} approaches the equilibrium potential for the H_2/H^+ couple, suggesting galvanic coupling between sites on which this electrochemical process is catalysed and the rest of the UO_2 surface. It is also possible that $H^\bullet$ radical species, either produced radiolytically from H_2O or by dissociation of H_2 on ε-particles or surface-active UO_{2+x} sites, reduce oxidised U(V)/U(VI) surface states to U(IV). The effect of H_2 on reducing the degree of surface oxidation is only partially reversible, since surfaces reduced in H_2 atmospheres (re-)oxidise more slowly and to a lesser degree than surfaces not previously exposed to H_2. Homogeneous reactions between dissolved H_2 and either oxidants or dissolved U(VI) cannot explain the observed effects.

Regardless of the precise mechanism, the suppression of the degree of surface oxidation results in lower UO_2 dissolution rates in the presence of H_2. Application of an electrochemical dissolution model to the observed E_{CORR} values suggests that the fractional dissolution rate of used fuel in the presence of H_2 is $<10^{-7}$–10^{-8} year^{-1}.

Contents

1 Introduction

A number of electrochemical studies of the effect of H_2 on UO_2 dissolution have been reported /King et al. 1999; Broczkowski et al. 2004; Stroes-Gascoyne et al. 2004/. In each of these studies, the corrosion potential (E_{CORR}) of a UO_2 electrode has been determined in the presence of H_2. The corrosion potential is a measure of the degree of oxidation of the UO_2 surface, and is established by the balance of the rates of the individual anodic (oxidation) and cathodic (reduction) electrochemical reactions. At E_{CORR}, the total rate of oxidation equals the total rate of the various reduction reactions and no net current flows. The resultant E_{CORR} represents the potential of the entire surface (in the absence of iR drops), even though the individual reactions may be restricted to electrochemically active areas of the surface, such as grain boundaries /Shoesmith et al. 1994/. Since the rate of dissolution of UO_2 can be related to the potential of the surface /Shoesmith et al. 1994, 2003/, provided a suitable dissolution current-potential relationship is available, E_{CORR} measurements can be used to estimate corrosion or dissolution rates of used fuel.

The various studies reported in the literature were conducted using different types of UO_2 and under a variety of environmental conditions. /King et al. 1999/ measured the E_{CORR} of unirradiated UO_2 in deaerated 0.1 $mol \cdot dm^{-3}$ NaCl solution (pH 9.5) at room temperature. The effects of γ-irradiation (dose rate 11–16 $Gy \cdot hr^{-1}$) were studied in the presence of either Ar or H_2 at a pressure of 5 MPa (to simulate the maximum H_2 partial pressure in an underground repository at a depth of 500 m). /Broczkowski et al. 2004/ used 1.5 at.% SIMFUEL electrodes in neutral 0.1 $mol \cdot dm^{-3}$ KCl purged with various pressures of 5% H_2/Ar mixtures at a temperature of 60°C. Finally, as part of a larger experimental program to determine the effects of α-radiolysis, /Stroes-Gascoyne et al. 2004/ report the results of a limited study of the effect of purging with 3% H_2/Ar at atmospheric pressure on the E_{CORR} of α-doped UO_2 in 0.1 $mol \cdot dm^{-3}$ $NaClO_4$ (pH 9.5).

The results of these studies provide an indication of the effect of H_2 on the degree of surface oxidation of UO_2 and of the mechanism(s) involved. In addition, a semi-quantitative measure of the dissolution rate of UO_2 in the presence of H_2 can be obtained from the E_{CORR} measurements.

2 Electrochemical studies of the effect of H_2 on UO_2

2.1 The effect of H_2 on the corrosion potential (E_{CORR}) of UO_2

King et al. /1999/ studied the effect of γ-radiation on the E_{CORR} of UO_2 in the presence of a 5 MPa overpressure of either H_2 or Ar. Figure 2-1 shows the time dependence of E_{CORR} in γ-irradiated solution in the presence of either H_2 or Ar. In unirradiated solutions, there was no significant difference between the steady-state E_{CORR} measured in H_2- or Ar atmospheres (shown by the vertical bar in Figure 2-1). However, when irradiated the steady-state potentials in the presence of H_2 were consistently more negative, and those in an Ar atmosphere, consistently more positive than those measured in the absence of radiation. Thus, not only did the presence of H_2 suppress oxidation caused by the production of radiolytic oxidants (which resulted in the more-positive E_{CORR} values in Ar-deaerated solution), but it also drove the UO_2 potential to more-negative values, consistent with the reduction of oxidised surface sites. The absolute values of E_{CORR} in Figure 2-1, even those in irradiated Ar-purged solutions, are several hundred mV more negative than those generally observed /Shoesmith et al. 1994, 2003/, possibly because of the nature of the particular UO_2 electrode used for these studies.

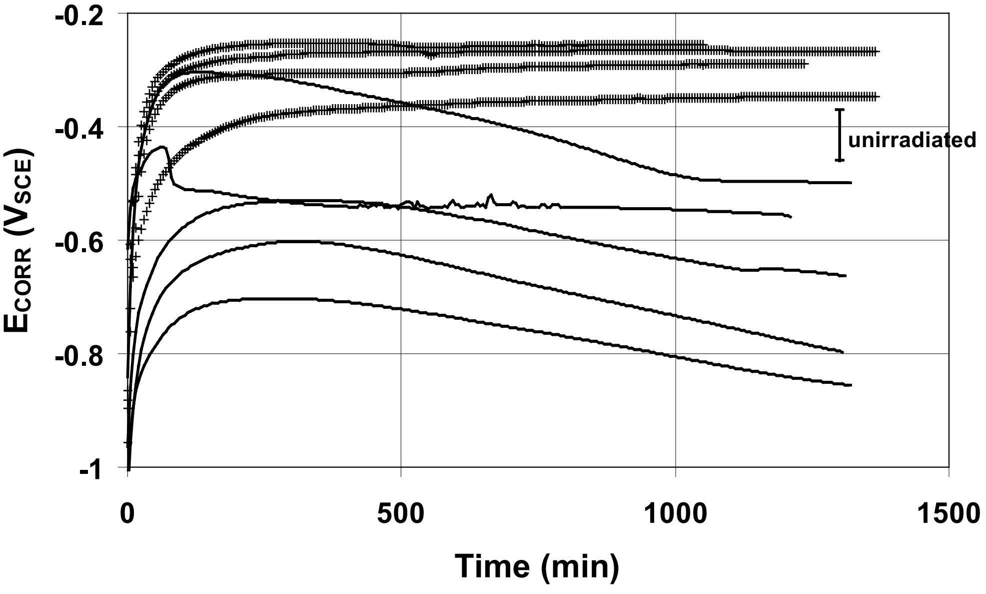

Figure 2-1. *Time dependence of the corrosion potential (E_{CORR}) of UO_2 in γ-irradiated 0.1 mol·dm^{-3} NaCl at room temperature in the presence of 5 MPa H_2 (——) or Ar (++++) /after King et al. 1999/. The results of four or five replicate tests are shown for each set of conditions. The range of E_{CORR} values in unirradiated solutions for both of these gases is also shown as the vertical bar.*

Although the presence of H_2 eventually results in a more-reduced surface state, initially the trend is towards more positive values of E_{CORR} and a more-oxidised surface. In each of the replicate runs, E_{CORR} exhibits a maximum after 100–300 min irradiation, after which the potential steadily decreases. Thus, whatever the effect of H_2, it does not take effect immediately on the pre-reduced electrodes. (The electrodes were cathodically cleaned at a potential of –1.3 V_{SCE} prior to each run). This initial positive shift may indicate that the surface must first oxidise ($UO_2 \rightarrow UO_{2+x}$) prior to "activating" the H_2 effect, suggesting an interfacial surface mechanism rather than a homogeneous radiolysis effect.

Figure 2-1 also shows that, although the results in an Ar atmosphere are reasonably reproducible, those in the presence of H_2 and irradiation exhibit a wide scatter. In addition to being electrochemically cleaned, the electrodes were also mechanically polished between experiments. As described below, it is likely that any electrochemical activity at these potentials occurs at grain boundaries, and the activity of such sites is likely to have been affected by the electrode preparation procedures used between tests. Furthermore, the resistivity of the electrode would increase as surface sites are reduced resulting in poorly poised potentials and greater scatter, especially at the low levels of electrochemical activity indicated by such negative potentials.

However, although the overall level of activity varied between tests (as indicated by the absolute values of E_{CORR}), the time dependence of the H_2 effect was reproducible. Figure 2-2 shows the time dependence of E_{CORR} for four of the H_2 tests from Figure 2-1, corrected for the absolute difference in potential. These runs show a very similar trend and good reproducibility. The final E_{CORR} value (steady-state was not consistently established by the end of the ~22-hr experiments) is between 0.13 V and 0.20 V more negative that the peak value observed after 100–300 mins.

Further evidence for the dual effect of H_2 on UO_2 in the presence of γ-irradiation is evident from Figure 2-3. In these tests, the over-pressurising gas was changed half-way through the experiment, with Ar replacing the initial H_2 purge or vice versa. It is interesting to note that when the electrode is initially oxidised by exposure to an Ar purge during irradiation, subsequent exposure to H_2 results in a reduction in E_{CORR} and a corresponding reduction in the extent of surface oxidation to a level similar to that observed if the electrode is only exposed to a H_2 atmosphere (cf. Figure 2-1). Alternatively, if the electrode is first exposed to H_2, the initial peak in E_{CORR} and subsequent decrease are observed (Figure 2-3), but the subsequent degree of oxidation when the H_2 is replaced by Ar is less than if the electrode is exposed to Ar alone. Thus, the E_{CORR} values following exposure to a H_2/Ar cycle are 80–230 mV more negative than that following initial exposure to Ar alone (Figure 2-3). This observation suggests, therefore, that within the timeframe of the experiment, the initial exposure to H_2 suppresses the subsequent oxidation of the surface.

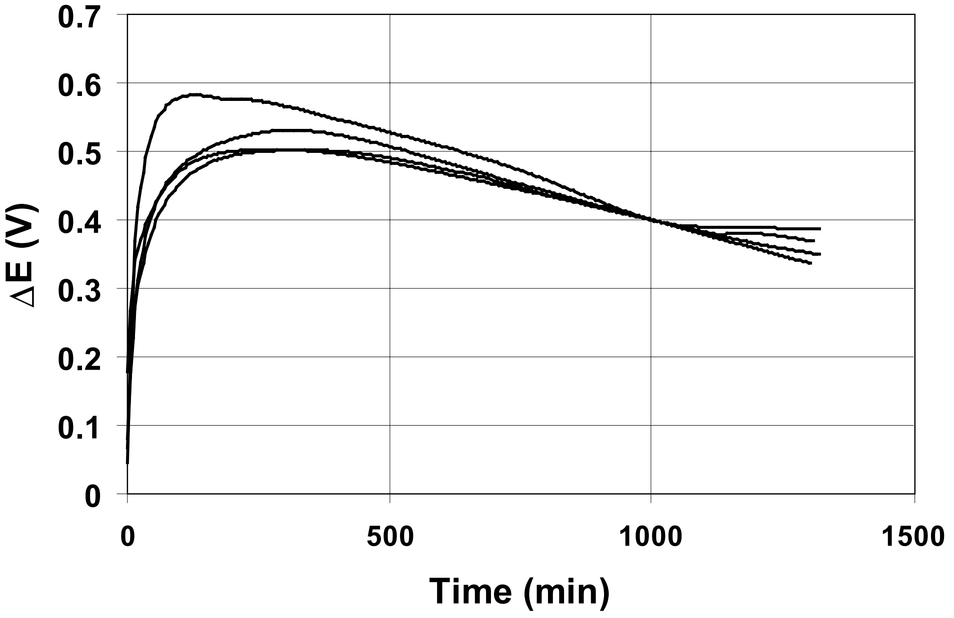

Figure 2-2. *Relative change in the corrosion potential of* UO_2 *during γ-irradiation in the presence of 5 MPa* H_2 *for four replicate runs from Figure 2-1 /after King et al. 1999/. The* E_{CORR} *values from Figure 2-1 have been corrected by subtracting a constant value in order to give a value of 0.4 V after a time of 1,000 min for each run.*

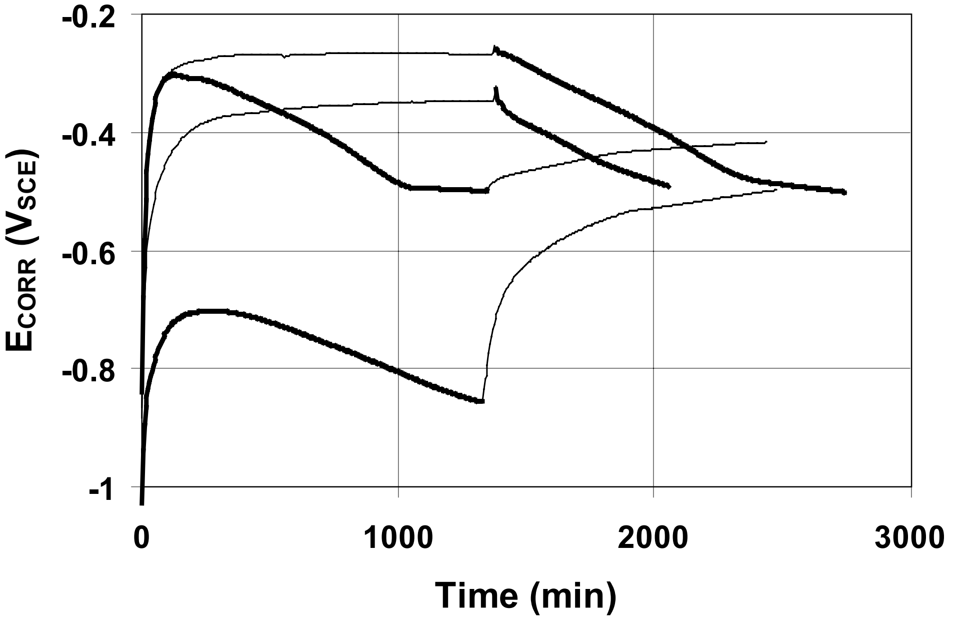

Figure 2-3. *Effect of changing from* H_2 *(heavy line) to Ar (light line) overpressure on the* E_{CORR} *of* UO_2 *in γ-irradiated 0.1 mol·dm*$^{-3}$ *NaCl solution (pH 9.5) at room temperature after /King et al. 1999/.*

In summary, the results of /King et al. 1999/ indicate that the presence of H_2 inhibits the surface oxidation of UO_2 in irradiated solutions. Significantly, there was no difference in E_{CORR} between H_2 and Ar atmospheres in the absence of irradiation. Values of E_{CORR} determined in irradiated H_2-containing solutions were 40–400 mV more negative than those in unirradiated solutions purged using either H_2 or Ar. The steady-state E_{CORR} values measured in the presence of 5 MPa H_2 are shown in Figure 2-4.

A similar suppression of E_{CORR} by H_2 was reported by /Broczkowski et al. 2004/, in this case in the absence of irradiation. These tests were performed using a SIMFUEL electrode, which contains inert species to simulate various radioactive constituents of used fuel. In this case, the important additives appear to be noble metals present as ε-particles, since the effect of H_2 was not observed in so-called “split SIMFUEL” not containing these particles. Figure 2-5 shows the effect of increasing H_2 partial pressure (p_{H2}) on the E_{CORR} of a SIMFUEL electrode in neutral 0.1 mol·dm^{-3} KCl at 60°C. The value of E_{CORR} decreases with increasing p_{H2}, eventually attaining values almost as negative as those observed by /King et al. 1999/ at much higher p_{H2} on UO_2 in the presence of γ-radiation (cf. Figure 2-1). The near-steady-state E_{CORR} values from Figure 2-5 are plotted as a function of p_{H2} in Figure 2-4. The dependence of E_{CORR} on p_{H2} from Figure 2-5 is

$$\frac{dE_{CORR}}{dp_{H_2}} = -0.46 \text{ V} \qquad (1)$$

The final set of E_{CORR} measurements shown in Figure 2-4 are those of /Stroes-Gascoyne et al. 2004/ measured in non-complexing 0.1 mol·dm^{-3} $NaClO_4$ solution (pH 9.5) at room temperature using an α-doped electrode. The solution was purged with 3% H_2/Ar at atmospheric pressure. Two E_{CORR} values are shown corresponding to electrodes containing sufficient ^{238}Pu to produce α-activities equal to, and ten times higher than, that for 40-year-old CANDU fuel (α-activity of 1 and 10 Ci·kg^{-1}, respectively). These potentials are the highest of any of those reported, but are not inconsistent with those reported by /Broczkowski et al. 2004/.

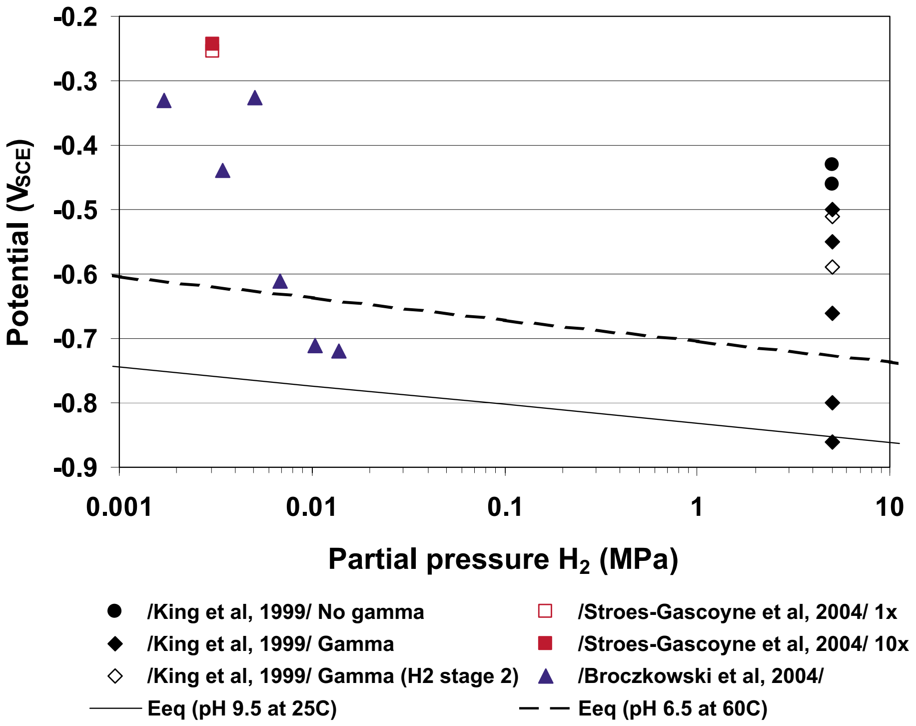

Figure 2-4. *Comparison of E_{CORR} values measured in the presence of H_2 by various workers and the equilibrium potential for the H_2/H^+ redox couple.*

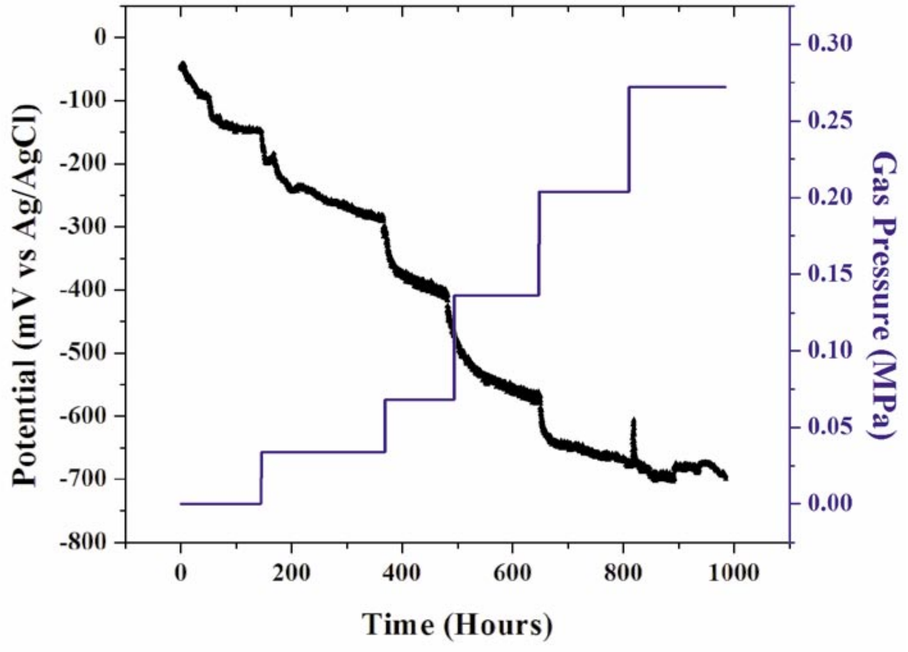

Figure 2-5. *Effect of H_2 partial pressure on the E_{CORR} of a 1.5 at.% SIMFUEL electrode in 0.1 mol·dm^{-3} KCl solution purged with 5% H_2/Ar at 60°C /Broczkowski et al. 2004/.*

2.2 Interpretation of E_{CORR} values

From an electrochemical perspective, the oxidation behaviour of UO_2 can be divided into various potential ranges /Shoesmith et al. 1994/. Three potentials have been identified:

$E < –0.4\ V_{SCE}$ the surface undergoes reversible oxidation.

$E > –0.4\ V_{SCE}$ the surface undergoes irreversible oxidation.

$E = –0.1\ V_{SCE}$ the surface composition corresponds to $UO_{2.33}$.

As shown in Figure 2-4, the majority of E_{CORR} measurements in the presence of H_2 fall into the range corresponding to reversible oxidation, and the discussion here is limited to that range. Reversible oxidation refers to the electrochemical observation that the oxidation and reduction of UO_2 electrodes at potentials less than $–0.4\ V_{SCE}$ occurs “reversibly.” Thus, in a potentiodynamic scan, the total extent of reduction is equal to the total amount of oxidation that occurred during the prior oxidation scan. Within this potential region, electrochemical activity is believed to be restricted to non-stoichiometric regions assumed to be located at grain boundaries as a consequence of the original reductive sintering process /Shoesmith et al. 1994/.

There are a number of possible electrochemical reactions that could occur at grain boundaries and other surface-active sites. Dissolution and oxidation reactions, such as

$$UO_2 \rightarrow UO_2^{2+} + 2e^- \tag{2a}$$

$$UO_2 + 2CO_3^{2-} \rightarrow UO_2(CO_3)_2^{2-} + 2e^- \tag{2b}$$

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^- \tag{2c}$$

$$H_2 \rightarrow 2H^+ + 2e^- \tag{2d}$$

can couple to reduction reactions, such as

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{3a}$$

$$H_2O_2 + 2e^- \rightarrow 2OH^- \tag{3b}$$

$$2H^+ + 2e^- \rightarrow H_2 \tag{3c}$$

Although thermodynamically possible /Pourbaix, 1974; Grenthe et al. 1992/, the kinetics of H_2 oxidation (Reaction (2d)) and of H^+ reduction (Reaction (3c)) are typically slow and these reactions are generally of minor importance in neutral-alkaline solutions.

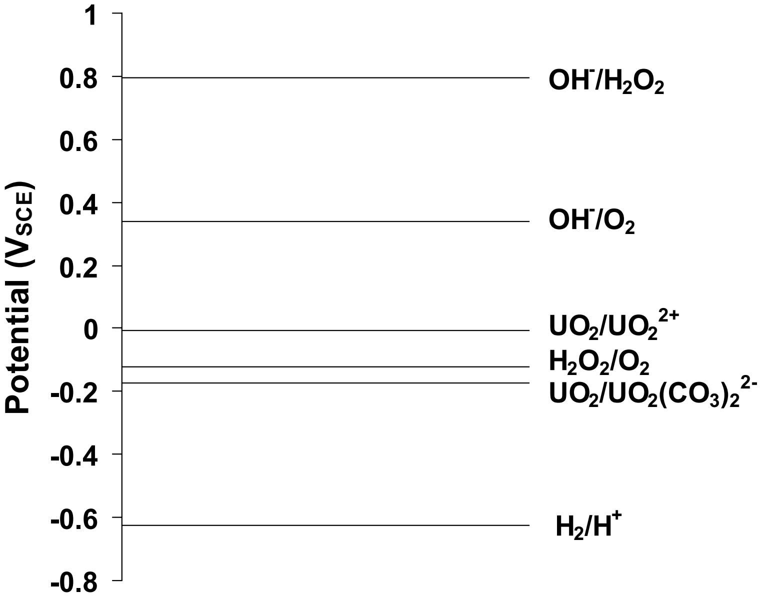

Figure 2-6. *Reversible potentials for a number of electrochemical couples of relevance for the dissolution of* UO_2 *in oxidising and reducing environments. The potentials were calculated for pH 9.5 at 25°C assuming fugacities and activities of* 10^{-6} *for gaseous and dissolved species, respectively, except for* CO_3^{2-}*, for which an activity of* 10^{-3} *was assumed.*

The potential of a surface on which electrochemical reactions are occurring can be established by a number of different processes. A "mixed-potential" results from the coupling of oxidation and reduction processes from different electrochemical couples, for example, the coupling of the oxidation of UO_2 as UO_2^{2+} (Reaction (2a)) and the reduction of H_2O_2 (Reaction (3b)). By definition, the mixed-potential must lie between the reversible (or equilibrium) potentials for the two half-reactions. Figure 2-6 shows the reversible potentials for a number of pertinent electrochemical couples. Alternatively, the surface potential may be determined by the oxidation and reduction processes of the same electrochemical couple. In such cases, the potential may be termed a "redox" potential. Here the term "corrosion potential" is used to refer to the electrochemical potential of the surface under open-circuit conditions (i.e. no net current flow), regardless of the nature of the potential-determining processes.

Figure 2-4 compares the observed E_{CORR} values and the reversible potential for the H_2/H^+ couple, i.e.

$$H_2 = 2H^+ + 2e^- \qquad (4)$$

for the experimental conditions used by /King et al. 1999/ and /Broczkowski et al. 2004/. It is apparent that some of the observed potentials are close to the reversible H_2/H^+ potential, suggesting that the observed corrosion potential could reflect the redox potential for Reaction (4). Other measured potentials are more positive than the H_2/H^+ reversible potential, perhaps resulting from a mixed-potential between UO_2 oxidation as UO_2^{2+} (all data presented here were obtained in the absence of CO_3^{2-}) and the cathodic reduction of trace oxidants (residual O_2 or the products of α- or γ-radiolysis). For that to be the case, however, the interfacial concentration of dissolved U(VI) would have to be much lower than the activity of 10^{-6} assumed for the calculation of the reversible potential for Figure 2-6.

A further possibility is that the measured E_{CORR} reflects the redox potential for the couple

$$UO_2 = UO_2^{2+} + 2e^- \qquad (5)$$

For the potential to respond to this equilibrium, the oxidation and reduction reactions need to be reversible. Potentials of –0.5 V_{SCE} and –0.8 V_{SCE} would correspond to dissolved U(VI) activities of 10^{-23} and 10^{-33}, respectively. Given the presence of electroactive impurities in the solution and other electrochemical reactions on the surface, it is unlikely that such low concentrations would “poise” the potential of the electrode.

3 The mechanism of the effect of H_2 on the dissolution of UO_2

There are a number of mechanisms that could explain the effect of H_2 on the E_{CORR} of UO_2 electrodes. These mechanisms can be broadly classified as being either homogeneous reactions in solution or heterogeneous reactions on the UO_2 surface. Homogeneous reactions involve the reaction of H_2 with species in solution, with the reactants subsequently interacting with the UO_2 surface. Heterogeneous reactions involve the direct interaction of H_2 on the UO_2 surface itself.

Homogeneous mechanisms

One mechanism by which H_2 could suppress oxidation of the UO_2 surface in the presence of irradiation is through consumption of radiolytically produced oxidants. The results of homogeneous reaction modelling suggest that the observed effect of H_2 on the dissolution of used fuel can be explained by the consumption of $OH^\bullet$ radicals and the consequent reduction in the yield of radiolytic oxidants /Jonsson et al. 2004, Lundstrom 2002/.

However, such a mechanism alone cannot explain the observed effects of H_2 on E_{CORR} of UO_2 electrodes. The results of /King et al. 1999/ clearly demonstrate that the presence of H_2 and γ-radiation results in more-reducing conditions (as indicated by the more-negative E_{CORR} values) than in the absence of irradiation (Figure 2-1). If the only effect of H_2 was to consume radiolytic oxidants, the value of E_{CORR} in the presence of H_2 and γ-radiation would be expected to be the same as that in the absence of radiation, rather than 40–400 mV more negative. In addition, reaction between dissolved H_2 and $OH^\bullet$ radicals would be expected to be fast, but the evidence in Figures 1–3 shows that for the initial 100–300 mins E_{CORR} shifts to more-positive potentials, indicative of a surface becoming slowly oxidised. Reactions of radical species tend to operate over timescales of fractions of a second, rather than hundreds of minutes. Perhaps the most convincing evidence to discount an over-riding effect of $H_2/OH^\bullet$ interactions are the data of /Broczkowski et al. 2004/, in which there was no radiolysis, although E_{CORR} was suppressed by several hundred mV in the presence of H_2.

A second possible homogeneous mechanism involves the reduction of dissolved U(VI) by H_2. This mechanism is most often invoked to explain the results of non-electrochemical leaching tests, in which the principle measurement is that of the concentration of dissolved U. /Jonsson et al. 2004/ specifically discount this process as being responsible for the low [U] observed in leaching studies. As noted above, in order to explain the low E_{CORR} values reported here, such a mechanism would require the UO_2 dissolution reaction to be reversible and the interfacial $[UO_2^{2+}]$ to be incredibly small.

A homogenous reaction mechanism not generally explored in the literature is the effect of H_2 on the yield of radiolytic reductants. Such species are generally considered less reactive than the corresponding oxidants. Nevertheless, an increased concentration of $H^\bullet$ radicals could reduce oxidised surface species, as suggested by the results of /King et al. 1999/. However, the inability to properly account for heterogeneous surface reactions in existing homogeneous radiolysis models makes detailed analysis of this mechanism difficult. Although such a mechanism might explain the results of /King et al. 1999/, it would not of course explain the non-irradiated observations of /Broczkowski et al. 2004/.

Heterogeneous mechanisms

The similarity between some of the observed E_{CORR} values and the reversible potential for the H_2/H^+ couple (Figure 2-4) suggests that surface reactions involving H_2 may be responsible for the suppression of E_{CORR} in H_2 environments. For the SIMFUEL electrodes used by /Broczkowski et al. 2004/, Reaction (4) is likely to be catalysed on the noble metal ε-particles, a conclusion supported by the absence of an effect of H_2 for the split SIMFUEL electrodes /Broczkowski et al. 2004/. Noble metals are known to catalyse the H_2/H^+ couple, with exchange current densities for metals such as Pd, Pt and Rh up to nine orders of magnitude higher than for less-catalytic metals such as Pb and Hg /Bockris and Reddy 1970/. Galvanic coupling between the ε-particles and the rest of the UO_2 surface would then suppress the potential of the entire electrode /Broczkowski et al. 2004/. The extent of galvanic coupling would be determined by the size and distribution of ε-particles within the UO_2 matrix, as well as by the electrical conductivity of both the solution and the electrode. A similar mechanism would also be expected for used fuel.

Catalysis of the H_2/H^+ couple on ε-particles, however, cannot explain the E_{CORR} values close to the reversible potential observed by /King et al. 1999/ on UO_2 electrodes. Alternatively, the combination of high H_2 partial pressure and radiolytically produced $H^\bullet$ radicals might be sufficient to catalyse this reaction to a similar degree as on noble metal surfaces. There is evidence for enhanced radiolysis effects at oxide surfaces /Petrik et al. 1999/, with enhanced H_2 yields, and possibly also of $H^\bullet$ radicals, for oxides with band gaps of ~5 eV. In general, there is a poor understanding of radiolysis effects at interfaces, but it is possible that increased yields of reducing species could explain the results of /King et al. 1999/. Although the precise mechanism for the catalysis of the H_2/H^+ reaction remains unclear in the case of UO_2 irradiated in a H_2 atmosphere, the similarity of the observed E_{CORR} and the reversible potential suggests that the measured potential reflects the reversible potential for this couple.

Although some of the measured E_{CORR} values are close to the reversible H_2/H^+ potential, others are significantly more positive (Figure 2-4). Furthermore, the dependence of E_{CORR} on the partial pressure of H_2 from Figure 2-5 (–0.46 V/dec) is much greater than the theoretical value of –0.03 V/dec for Reaction (4). Thus, the reversible H_2/H^+ potential does not dominate the observed potential for the majority of measurements in Figure 2-4. Undoubtedly, the electrochemical activity is restricted to specific areas on the surface (either ε-particles in the case of SIMFUEL or non-stoichiometric grain boundaries for UO_2), and it is possible that these areas cannot efficiently galvanically couple to the remainder of the surface. In the case of the UO_2 studies of /King et al. 1999/, mechanically polishing the surface between experiments would present a different surface in each test, with possible significant differences in grain boundary activity. In addition, for the SIMFUEL experiments of /Broczkowski et al. 2004/, the H_2/H^+ equilibrium may only be established on the ε-particles at higher p_{H2}.

The more-positive potentials observed by both /King et al. 1999/ and /Broczkowski et al. 2004/ may represent potential control by a combination of the H_2/H^+ redox couple and a mixed-potential involving U(IV)/U(VI). The initial increase in E_{CORR} observed by /King et al. 1999/ in irradiated H_2 environments suggests that the electrode undergoes some oxidation initially, possibly restricted to reactive grain boundaries. The subsequent decrease in E_{CORR} indicates a slower reduction process, possibly coupling the reduction of U(VI) to the oxidation of H_2

$$\mathrm{U(VI)} + 2e^- \rightarrow \mathrm{U(IV)} \tag{6a}$$

and

$$H_2 \rightarrow 2H^+ + 2e^- \tag{6b}$$

The mixed-potential for this coupled process would lie somewhere between –0.01 V_{SCE} and –0.63 V_{SCE}, for the conditions assumed for Figure 2-6. Progressive reduction of U(VI) would shift the potential to more negative values, as observed at longer times in Figure 2-1 and for increasing p_{H2} in Figure 2-5.

Alternatively, there could be direct reduction of oxidised U surface states (U(V) or U(VI)) by $H^•$ radicals, generated either radiolytically

$$H_2O \xrightarrow{\gamma} OH^• + H^• \tag{7a}$$

or dissociatively on ε particles or surface-active sites

$$H_2 \xrightarrow{\varepsilon\text{–particle or U(V) surface site}} 2H^• \tag{7b}$$

The dissociation of H_2 on U(V) surface-active sites is consistent with the apparent requirement for initial oxidation of the surface prior to the suppression of E_{CORR} by H_2 in γ-irradiated solutions (Figure 2-1). The $H^•$ radicals may then reduce oxidised surface sites, suppressing E_{CORR}, the degree of surface oxidation and the rate of dissolution

$$\mathrm{U(V)} + H^• \rightarrow \mathrm{U(IV)} + H^+ \tag{8}$$

The involvement of surface U(V) sites remains to be proven.

4 Consequences of the suppression of E_{CORR} on the dissolution rate

Regardless of the precise mechanism, the general suppression of E_{CORR} in the presence of H_2 will suppress the dissolution rate of UO_2. A general framework has been developed for predicting the dissolution rate of UO_2 and used fuel using electrochemical principles /Shoesmith and Sunder 1991, Shoesmith et al. 1998/, and implemented in detail in the Mixed-Potential Model /Shoesmith et al. 2003/. This model is most reliable under oxidising conditions, similar to those under which the electrochemical input parameters were determined. However, the same model can be used to semi-quantitatively predict the dissolution rate under more reducing conditions, since in principle the dissolution rate should be related to the potential regardless of its value.

The electrochemical dissolution model relates the rate of matrix dissolution to the potential of the UO_2 (used fuel) surface. At room temperature, the rate of dissolution is predicted to decrease by a factor of 10 for every ~60 mV decrease in potential. As an illustration of the suppression of the potential caused by H_2, Figure 4-1 compares the E_{CORR} values from Figure 2-4 with the ranges of values measured under different oxidising conditions /taken from King and Kolar, 2002/. Although there is some overlap between the E_{CORR} values measured in the presence of H_2 and those measured in deaerated solutions and at low O_2 partial pressures, the potentials measured under oxidising conditions are up to 1 V more positive than those with H_2. This potential difference would correspond to a difference in dissolution rates of up to sixteen orders of magnitude.

Figure 4-2 shows the range of predicted matrix dissolution rates based on the E_{CORR} values from Figure 2-4 and the electrochemical model of /Shoesmith and Sunder, 1991/. A specific surface area for used fuel of 2 $cm^2 g_U^{-1}$ was assumed in order to convert the mass rate to a fractional dissolution rate /Sunder et al. 1997/. Caution should be exercised in using the absolute dissolution rates shown in Figure 4-2 because of the extended extrapolation required for the prediction to such low potentials. However, the data suggest that the dissolution rate decreases with increasing H_2 partial pressure. Furthermore, even at relatively low p_{H2}, the fractional dissolution rate is of the order of 10^{-7}–10^{-8} $year^{-1}$, in good agreement with the best-estimate rate derived from leaching studies /Werme et al. 2004/. Based on the electrochemical measurements alone, the dissolution rate is likely to be significantly lower, especially at higher H_2 partial pressures. At a H_2 partial pressure of 5 MPa, corresponding to a repository depth of 500 m, the predicted dissolution rate is in the range 10^{-11}–10^{-18} $year^{-1.}$

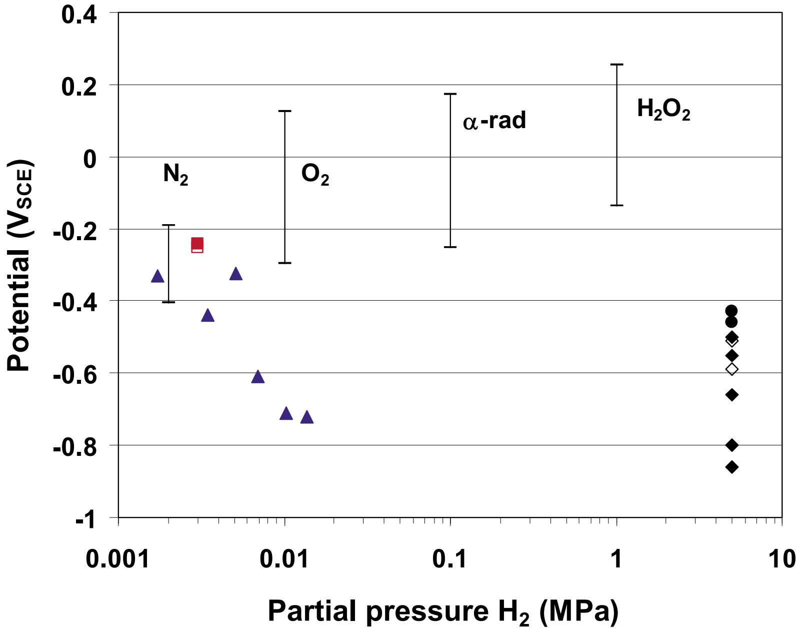

Figure 4-1. *Comparison of* E_{CORR} *values measured in the presence of* H_2 *(individual data points from Figure 2-4) with ranges of values measured under various oxidising conditions. The ranges of* E_{CORR} *for deaerated (*N_2*),* O_2 *(*10^{-8}*–0.0014 mol·dm*$^{-3}$ O_2*), α-radiolysis (electrode activity 4–800 µCi), and* H_2O_2 *(*10^{-6}*–0.1 mol·dm*$^{-3}$ H_2O_2*) conditions are taken from the compilation of /King and Kolar, 2002/ and are shown at arbitrary* H_2 *partial pressures for clarity.*

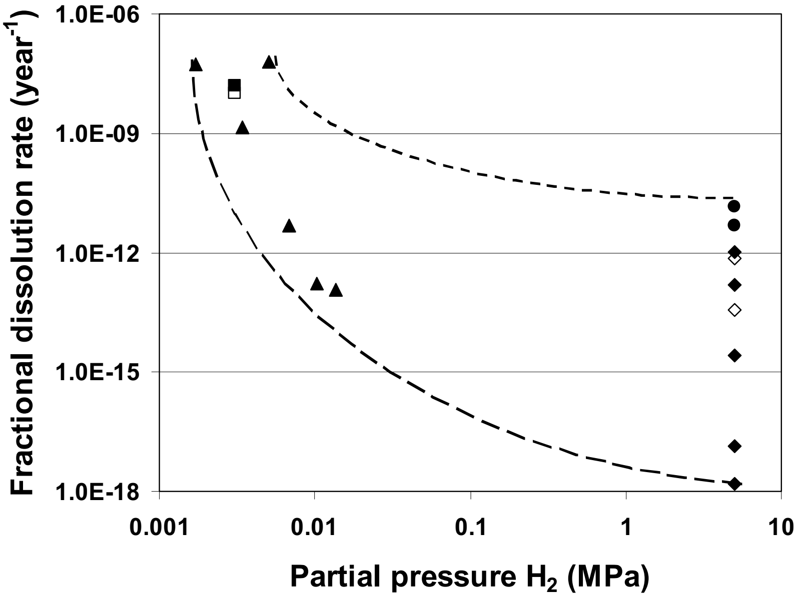

Figure 4-2. *Range of predicted fractional dissolution rates for* UO_2 *based on the measured* E_{CORR} *values in* H_2*-containing solution from Figure 2-4 and the electrochemical model of /Shoesmith and Sunder, 1991/.*

5 Summary

Various electrochemical studies of the behaviour of UO_2 in the presence of H_2 suggest a significant suppression of the degree of oxidation and dissolution of the surface. Suppression of the corrosion potential by H_2 has been observed for UO_2 at high partial pressures (5 MPa H_2) in γ-irradiated solutions at room temperature and at lower partial pressures (0.002–0.014 MPa H_2) on SIMFUEL electrodes containing noble metal ε-particles at 60°C.

The mechanism of the H_2 effect is not certain, but appears to involve the catalysis of the H_2/H^+ redox couple on the UO_2 surface. This reaction occurs on the ε-particles in the case of SIMFUEL electrodes and, likely, at non-stoichiometric grain boundaries on UO_2 electrodes. These sites can galvanically couple to the remainder of the UO_2 surface and, in some cases, polarise the potential of the entire surface close to the equilibrium potential of the H_2/H^+ couple. The reduction of oxidised U(V)/U(VI) surface sites coupled with the oxidation of $H^•$ radicals to H^+ may also play a role in the mechanism. The homogeneous consumption of radiolytic or trace oxidants by H_2 in solution cannot explain the observed effects, since a combination of γ-radiation and H_2 results in significantly more-reducing conditions than H_2 alone.

An electrochemical model has been used to predict dissolution rates based on the measured E_{CORR} values. Caution should be exercised in using the absolute dissolution rates, since the predictions require extrapolation to potentials hundreds of millivolts more negative than those at which the input data were determined. Nevertheless, the electrochemical model predicts maximum fractional dissolution rates in the presence of H_2 of 10^{-7}–10^{-8} $year^{-1}$. The rate decreases with increasing H_2 partial pressure, with rates of $<10^{-11}$ $year^{-1}$ possible at repository depth, corresponding to a H_2 partial pressure of 5 MPa.

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