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Validation of an electrochemical model for the oxidative dissolution of used CANDU fuel

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Abstract

Measured dissolution rates of UO_2 and used fuel powders are compared to dissolution rates predicted from electrochemical measurements on fuel pellets. This comparison was made for rates as a function of dissolved oxygen concentration, carbonate/bicarbonate concentration, and gamma irradiation dose rate. Measurements were also made as a function of temperature over the range 25–75°C. Good agreement was obtained between measured and predicted rates in aerated carbonate solutions confirming that the dissolution reaction is electrochemical in mechanism and that its rate can be predicted electrochemically. For non-complexing solutions agreement was not as good since electrochemical measurements on dissolution of fuel pellets appeared to be inhibited by the formation of secondary phases in occluded grain boundaries. Measured dissolution rates on powders do not appear to be affected in this manner since few occluded grain boundaries are present. Predicted and measured rates in gamma irradiated solutions, while measured under different conditions, showed the same general trends, and compare well to published literature values. In aerated non-complexing solutions and in aerated carbonate solutions the effect of gamma irradiation becomes insignificant below $\sim 1 \text{ Gy h}^{-1}$ and $\sim 10 \text{ Gy h}^{-1}$, respectively. Crown copyright © 1998 Published by Elsevier Science B.V. All rights reserved.

1. Introduction

Any environmental assessment of used fuel disposal requires a prediction of the release rate of radionuclides from the fuel, once contact with groundwater is established. Since the great majority of radionuclides are contained within the grains of the fuel pellets they are expected to be released at a rate governed by the dissolution rate of the uranium oxide matrix. Although UO_2 is highly insoluble, the solubility of uranium increases by many orders of magnitude under oxidizing conditions. This makes fuel dissolution rates and, hence, radionuclide release rates potentially very dependent on vault redox conditions.

The redox conditions within a waste vault will evolve with time from initially oxidizing to eventually non-ox-

idizing as oxygen, trapped within the vault on sealing, is consumed and radiation fields, which can produce oxidants by the radiolysis of water, decay. Effective containment of the fuel should prevent its contact with groundwater until this redox evolution is complete. However, if justifiable assurances are to be given that radionuclide releases from a waste vault will be very limited, it is necessary to determine the consequences of varying redox conditions on spent fuel dissolution.

Since the dissolution of UO_2 is a corrosion reaction we have applied a wide variety of electrochemical methods to develop both an understanding of the dissolution process and the framework of a model which can be used to predict fuel dissolution rates as a function of evolving redox conditions. The experimental approaches employed and the results obtained have been discussed in detail elsewhere [1–3]. The model developed has been applied to predict the behaviour of spent fuel in a prematurely failed copper container when exposure of the fuel to oxidizing conditions is unavoidable [4].

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A comparison of these predictions to measured used-fuel dissolution rates yielded reasonable agreement considering the difficulties in measuring surface areas. While such agreement may be gratifying it was acknowledged that it could have been, at least in part, fortuitous [4].

To justify the wide ranging application of this model, a much more extensive process of verification is required. In this report we will briefly review the electrochemical model and compare predictions based on it to dissolution rates measured in our flow-through experiments on UO_2 and used fuel samples. Comparisons of model predictions to rates measured by other experimenters will also be made although no attempt is made to comprehensively review all existing data on UO_2 dissolution rates.

2. The oxidative dissolution model

A large body of evidence exists demonstrating that the dissolution of UO_2 under oxidizing conditions is an electrochemical process [1]. For sufficiently oxidizing conditions, a potential difference exists across the dissolving solid–solution interface and dissolution proceeds at the corrosion potential. This potential is determined by the relative kinetics of the fuel oxidation, causing dissolution, and oxidant reduction half-reactions which comprise the overall process. However, the coupling of these two half-reactions to yield the overall corrosion process is a short circuit reaction and yields no current in an external measuring circuit. The kinetics of either half-reaction can be determined electrochemically by applying potentials positive (fuel dissolution) or negative (oxidant reduction) to the corrosion potential and recording the steady-state electrochemical current as a function of this applied potential. The dissolution rate is then determined by extrapolating these steady-state currents to the corrosion potential; i.e., to the open-circuit condition with zero applied potential. The application of this model to predict UO_2 dissolution rates in aqueous solutions containing either dissolved oxygen or hydrogen peroxide, and in solutions in which radiolytic oxidants are formed by gamma or alpha radiation, has been previously described [2,5,6].

3. Electrochemical data on UO_2 dissolution

Dissolution currents have been measured as a function of applied electrochemical potential in 0.1 mol l^{-1} NaClO_4 (pH=9.5) solutions and in this solution containing various amounts of Na_2CO_3 (0.005–0.1 mol l^{-1}) [7,8] and Sunder (unpublished data). These measurements were made at rotating-disc electrodes rotating at 16.7 Hz in an attempt to avoid the accumulation on the

dissolving surface of precipitated dissolution products. Measurements in neutral to slightly alkaline perchlorate solutions are considered appropriate for predicting the behaviour of fuel in the non-complexing groundwaters anticipated in a waste vault located in the Canadian shield. Measurements in carbonate solutions allow the effects of complexing anions, present in groundwater, to be taken into account.

Two sets of data were measured in non-complexing perchlorate solution. The significant difference between the two sets was the time allowed at each potential for the establishment of steady-state. The first set [7] was recorded relatively rapidly (~ 10 min at each potential) and steady-state was undoubtedly not achieved. A much longer period of time (90 min) was allowed at each potential before recording the current in the more-recent measurements [8]. Despite this, steady state was not achieved for applied potentials ≤ 350 mV (vs. SCE), the current decaying continuously with time. This current decay was attributed to the blockage of the dissolution process by the accumulation at the dissolution sites of oxidized secondary phases (typically $\text{UO}_3 \cdot x\text{H}_2\text{O}$). In support of this claim, electrochemical charge measurements clearly showed that $>90\%$ of the uranium oxidized accumulated on the UO_2 surface. This behaviour suggests that, under neutral, non-complexing, oxidizing conditions, dissolution will eventually be blocked by the formation of such phases. The fact that this can occur on the surface of a rotating disc at 16.7 Hz suggests that dissolution occurs at occluded sites such as in grain boundaries, where local supersaturation with dissolved uranyl species can be rapidly achieved. A more extensive discussion of this effect has been given elsewhere [8]. A variability in the reactivity of different UO_2 specimens may also be a factor as observed by Nicol et al. [9] and discussed by Shoesmith et al. [3].

Blockage of the dissolution process does not occur in experiments made in carbonate solutions, since the accumulation of secondary phases is prevented by the increase in solubility due to complexation of the uranyl ion (UO_2^{2+}) by carbonate. In these experiments, steady state was rapidly established at all potentials and electrochemical charge measurements confirmed that oxidized uranium species were indeed dissolved. Two independent sets of measurements made years apart on different specimens of UO_2 yielded effectively identical dissolution currents as a function of applied potential [10] and Sunder (unpublished data).

Corrosion potential measurements were made in similar solutions (i.e. perchlorate with and without carbonate). Measurements in solutions in the presence of a gamma-radiation field were made in a cell irradiated with a ^{192}Ir gamma source ($t_{1/2} = 73.8$ days). The details of these measurements have been described elsewhere [11].

4. Flow-through dissolution rate data on UO₂ and used fuel

The dissolution rates of uranium from used fuel and UO₂ were determined using a single-pass, flow-through method described by Gray et al. [12]. The advantage of the single-pass flow-through technique is that flow rates and specimen size can be controlled so that the UO₂ dissolves under conditions that are far from solution saturation. This minimizes the effect of the precipitation of dissolved products on uranium dissolution rates and radionuclide release rates. Under such conditions, the steady-state dissolution rates are directly proportional to the effective surface area of the specimen and the dependence of UO₂ dissolution kinetics on pH, temperature, oxygen and carbonate/bicarbonate concentrations can be evaluated.

The preparation of the UO₂ powders used in the dissolution tests and the experimental conditions used have been previously described [12]. With the exception of one experiment in which [HCO₃⁻] was varied from 10⁻⁴ to 0.05 mol l⁻¹, the leachants were either 0.01 mol l⁻¹ NaHCO₃/0.1 mol l⁻¹ NaCl or deionized water (DIW). The solutions were either equilibrated with air at room temperature, or were deaerated by purging the stock solution with 5% H₂/Ar/CO₂ and passing this solution through a flow cell containing a wet-bed catalyst (Pd supported on polymer beads) to remove residual oxygen, just prior to the sample leaching cell. The flow rates of the leachant were about 35 ml h⁻¹, which has been shown to be sufficient to maintain the bulk leachant solution below U saturation conditions [13]. The preparative technique followed for preparation of powdered UO₂ and used fuel samples was similar to that used to produce samples of depleted UO₂ (0.2% ²³⁵U) for interlaboratory testing [12]. The technique involved crushing, washing and screening samples which resulted in powders with a size fraction from 44 to 105 μm and a measured (BET) surface area of 267 cm² g⁻¹. Since the preparative technique used for samples in this report was similar, this surface area is assumed here for the calculation of dissolution rates. The surface area is a significant uncertainty in the calculation of the dissolution rates, particularly with used fuel samples where grain boundaries may contribute additional surface area exposed to the leachant [14]. It is estimated that surface areas for the unirradiated UO₂ samples in this report are within a factor of two of the BET value of 267 cm² g⁻¹ (which may be an overestimate of the actual surface area [14]); for used fuel, however, it is estimated that the surface area may be a factor of 2 to 4 greater, due partly to additional surface area from grain boundaries and to the presence of fines smaller than 44 μm, as the used fuel samples were not washed prior to the dissolution experiments.

The dissolution experiments on UO₂ to determine the effect of dose rate on dissolution rate used a ¹⁹²Ir γ-

source. The initial dose rate to the solution in the flow-through leaching cell was ~300 Gy/h (30,000 R/h), as determined by Fricke dosimetry. The gamma and beta dose rates from 10-a-cooled CANDU fuel are approximately 30 and 300 Gy/h⁻¹, respectively [4]. The initial gamma dose rate from the ¹⁹²Ir source thus approximates the beta dose rate from 10-a-cooled used fuel in contact with water. Since the yield of radiolysis products (i.e. *G*-values; molecules formed or destroyed per 100 eV energy absorbed) is the same for both γ- and β-radiation, the use of a high γ-dose rate to simulate the β-dose rate is justified.

5. Comparison of uranium dissolution rates from flow-through data and derived rates from electrochemical data

5.1. Effect of oxygen on uranium dissolution rates from UO₂ and used fuel

Measured and predicted dissolution rates of uranium from UO₂ and used fuel as a function of dissolved oxygen concentration are shown in Fig. 1. The predicted dissolution rates [2] are based on electrochemical measurements on UO₂ in 0.1 mol l⁻¹ NaClO₄ solution. The reaction order with respect to O₂ obtained from the electrochemical model is ~1.0–~1.1 depending on whether only the more reliable rates at higher [O₂] (●) or the whole data set (●,◇), Fig. 1, were included in the data fit. The points at an [O₂] of 10⁻⁸ mol l⁻¹ are only estimates based on the concentration of oxygen in the anaerobic chamber in which the experiments were performed and are not included in either fit.

The uranium dissolution rates measured by Tait and Luht [15] and data selected from Steward and Weed [16], which were measured at comparable temperatures and carbonate concentrations on similarly treated UO₂ powders, were used to derive the reaction order with respect to oxygen. Both the rate values and their reaction order with respect to oxygen (0.7) for these two sets of data are in close agreement. The rates measured on 1 mm particles by Casas et al. [17] are closer to the rates predicted from electrochemical measurements of Shoesmith and Sunder [2] on unirradiated pellets (Section 3), but have a dependence on [O₂] similar to other measured values.

The measured dissolution rate for used fuel appears to be less dependent upon [O₂] than that of unirradiated UO₂ (Fig. 1). This lower reaction order (0.39) may be an artefact since radiolytic oxidants will be produced near the surface of the fuel and could increase the dissolution rate at low dissolved oxygen concentrations. The water layer near the surface of used fuel also contains oxidants formed by the radiolysis of water in addition to the dissolved oxygen. This will lead to an increase in the

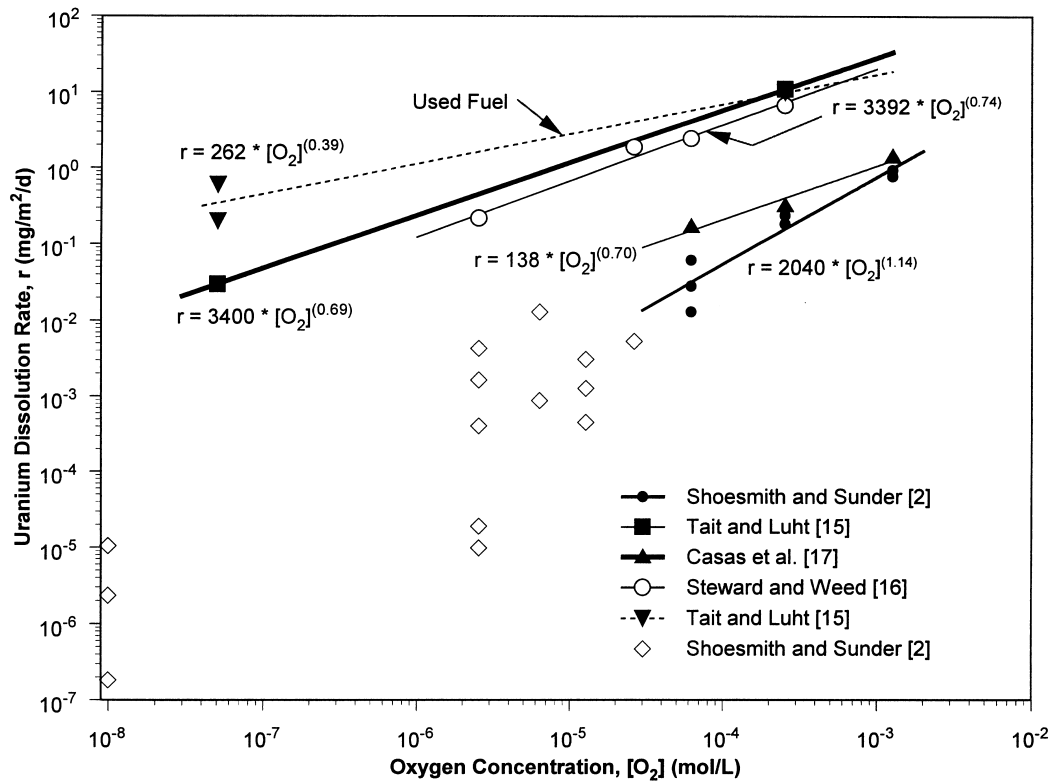


Fig. 1. Dissolution rates (r) of uranium from UO_2 and used fuel, as a function of oxygen concentration $[\text{O}_2]$ at 25°C: (a) predicted using the electrochemical model for oxygenated $0.1 \text{ mol l}^{-1} \text{ NaClO}_4$ (pH = 9.5) [2]; (b) measured in $0.01 \text{ mol l}^{-1} \text{ NaHCO}_3/0.1 \text{ mol l}^{-1} \text{ NaCl}$ (pH ~9) on UO_2 and used CANDU fuel [15]; (c) measured in oxygenated MgCl_2 brine (pH = 4.5) [17]; (d) measured in oxygenated $0.02 \text{ mol l}^{-1} \text{ NaHCO}_3$ (pH ~9) [16].

dissolution rate and an apparent decrease in the reaction order with respect to $[\text{O}_2]$.

5.2. Effect of carbonate on uranium dissolution rates from UO_2

Dissolution rates of unirradiated UO_2 in aerated solutions containing various amounts of carbonate are shown in Fig. 2 for both flow-through experiments [15,18] and for electrochemical predictions [7] and Sunder (unpublished data). As expected the measured and predicted rates are higher than in non-complexing solutions (Fig. 1) and increase with increases in $[\text{HCO}_3^-]$ due to the complexing ability of the carbonate ion for U(VI) species. Considering the differences in the nature of the UO_2 specimens used and the uncertainties in estimating the surface areas of UO_2 powders, the agreement between measured and predicted dissolution rates is good and suggests that dissolution rates can be predicted using the electrochemical model. With the exception of the early electrochemically predicted rates [7], both measured and predicted rates have a reaction order with respect to $[\text{HCO}_3^-]$ of ~0.4–0.6.

5.3. Effect of gamma dose rate on uranium dissolution rates from UO_2

Fig. 3 compares dissolution rates of unirradiated UO_2 as a function of gamma dose rate in aerated/oxygenated solutions. The rates are those predicted from electrochemical measurements [2] and from measured uranium concentrations in batch type experiments [19,20] and from flow-through experiments [15]. Rates from electrochemical measurements are for $0.1 \text{ mol l}^{-1} \text{ NaClO}_4$ (pH ~9.5). Those measured by Gromov [20] are for either strongly acidic conditions ($0.05 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$; pH ~1) or alkaline carbonate solutions ($40 \text{ g l}^{-1} \text{ Na}_2\text{CO}_3 + 30 \text{ g l}^{-1} \text{ NaHCO}_3$, (~1.0 mol l^{-1} in total carbonate), pH ~10); those by Christensen [19] in O_2 saturated borax buffer (pH ~8.2); and those by Tait and Luht [15] in $0.1 \text{ mol l}^{-1} \text{ NaCl} + 0.01 \text{ mol l}^{-1} \text{ NaHCO}_3$ (pH ~8.5). The rates in Fig. 3 are plotted logarithmically to facilitate their inter-comparison. The dependence on dose rate can be expressed empirically by the slope of these plots. The data from Gromov [20] for acidic solutions have approximately the same dependence on dose rate (0.32) as the values predicted elec-

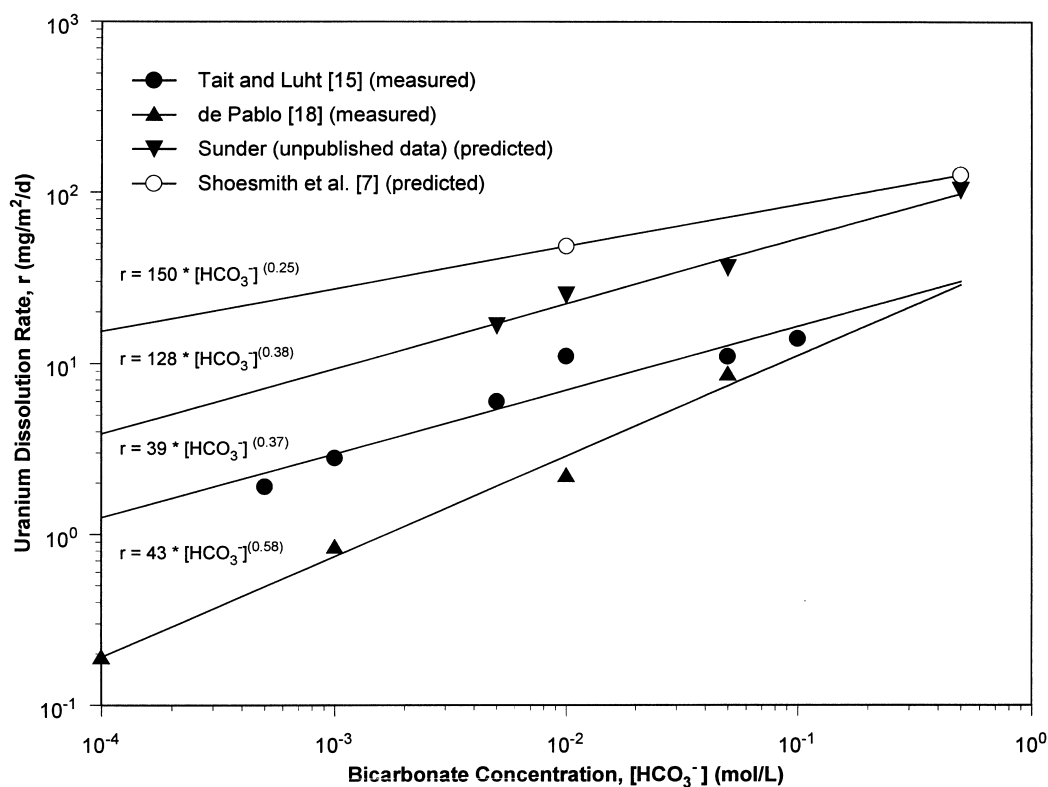


Fig. 2. Dissolution rates (r) of uranium from UO_2 as a function of bicarbonate ion concentration $[\text{HCO}_3^-]$ in aerated solution at 25°C : (a) measured in aerated NaHCO_3 solution with $\sim 0.1 \text{ mol l}^{-1}$ NaCl ($\text{pH} \sim 9$) [15,18] (\bullet); (b) predicted using the electrochemical model for aerated NaHCO_3 solution with 0.1 mol l^{-1} NaClO_4 ($\text{pH} = 9.5$) (Sunder, unpublished results), [7]).

trochemically (0.33–0.43) depending on which set of data is fitted), whereas those from Tait and Luht [15] have a slightly higher dependence (0.62). The single value from Christensen [19] would be comparable to the electrochemical data, but is measured in oxygenated, as opposed to aerated, solution. The rates from Gromov in alkaline carbonate are unrealistically low and not considered further.

5.4. Effect of temperature on uranium dissolution rates from UO_2

The flow-through experiment has been used to measure the temperature dependence of the dissolution rate from unirradiated UO_2 over the temperature range 25 – 75°C [15]. There have been no comparable electrochemical measurements. An Arrhenius plot, (Fig. 4) yielded an activation energy of 47 kJ mol^{-1} in an aerated solution. This compares well with another measurement of activation energy of 41 kJ mol^{-1} , which took into account the combined effect of temperature and bicarbonate concentration [18].

6. Discussion

In Section 3, two sets of electrochemical dissolution currents as a function of applied potential measured in non-complexing solutions were discussed. The question remains as to which is the most appropriate set to use in predicting rates which can be legitimately compared to those measured in the flow-through experiments. The use of crushed powders in flow-through experiments means the influence of occluded grain boundaries is minimal. In the most recently recorded set of electrochemical data [8], extensive blockage of dissolution sites, thought to be predominantly at grain boundaries, occurred due to the length of time allowed in an unsuccessful attempt to establish steady-state. In the earlier measurements, currents were recorded before such extensive blockage occurred. Consequently, the earlier set is more likely to duplicate the conditions prevailing in the flow-through experiments and has been used in the comparisons presented. No such dilemma exists for electrochemical data recorded in carbonate solutions in which steady-state dissolution currents were easily measurable.

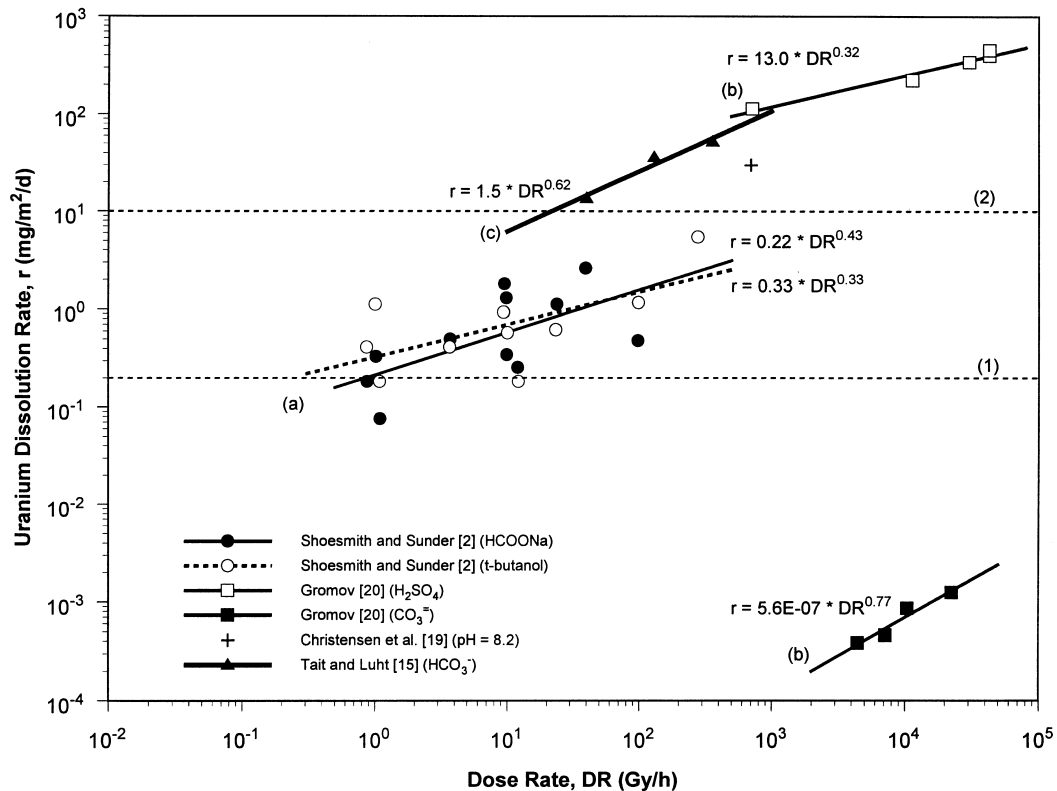


Fig. 3. Dissolution rates (r) of uranium from UO_2 in irradiated, aerated/oxygenated solutions as a function of the gamma dose rate (DR): (a) predicted using the electrochemical model of Shoesmith and Sunder [2], in aerated $0.1 \text{ mol l}^{-1} \text{ NaClO}_4$ ($\text{pH} = 9.5$) solutions with $0.01 \text{ mol l}^{-1} \text{ HCOONa}$ (\bullet) or with $0.01 \text{ mol l}^{-1} t\text{-butanol}$ (\circ); (b) measured by Gromov [20] in acidic sulphate solution ($\text{pH} \sim 1$), and alkaline carbonate solution ($\text{pH} \sim 10$); (c) measured by Tait and Luht [15] in $0.1 \text{ mol l}^{-1} \text{ NaCl}$ and 0.01 M NaHCO_3 ($\text{pH} = \sim 8.5$) solution; (d) measured by Christensen et al. [19] in oxygenated solution ($\text{pH} = \sim 8.2$)(+). (Note: $1 \text{ Gy/h}^{-1} = 100 \text{ R/h}^{-1}$). The horizontal dashed lines show the rate predicted for unirradiated aerated solution (1) (from Fig. 1) and the rate measured in flow-through experiments in bicarbonate solution (2) (from Fig. 2).

Despite the uncertainties in the measurements, the reliability in the flow-through method in producing reproducible values of dissolution rate was demonstrated by the results of a series of tests conducted on identical samples of unirradiated UO_2 under identical conditions in three laboratories. In these tests, steady-state dissolution rates averaged 2.2 ± 0.5 , 1.5 ± 0.9 and $5.5 \pm 2.7 \text{ mg m}^{-2} \text{ d}^{-1}$ ($\pm\sigma$) at PNL, WL and LLNL, respectively [12]. It is instructive that the rates measured on 1 mm UO_2 fragments [17] are closer in value to those predicted from electrochemical measurements on pellets than to measurements on powders (Fig. 1). These differences may reflect both the uncertainties in determining surface areas and the importance of exposed, as opposed to occluded, grain boundaries. Powders would have more exposed and unoccluded grain boundaries than fuel fragments and pellets. Enhanced grain boundary reactivity and the absence of blockage due to the accumulation of oxidized secondary phases would then lead to

higher dissolution rates for powder than expected on fragments and pellets.

Giménez et al. [21] investigated the dissolution of powders ($10\text{--}50 \text{ }\mu\text{m}$), fragments ($900\text{--}1100 \text{ }\mu\text{m}$) and pellets in solutions containing various oxidants (H_2O_2 , ClO^-) but saw no difference in rates. These measurements were made over the first few days of exposure and hence are a measure of the reactivity of the original surface. In this regard they are comparable to the electrochemical measurements also made over a limited exposure period [2,7]. The rates, normalized for exposed surface areas, were very similar to those predicted from our electrochemical measurements. Loida et al. [22] did observe differences in dissolution rates for used fuel, measured in batch experiments, depending on the physical nature of the specimen. In this case the rates measured on powders were less than those measured on pellets/fragments, an observation attributed to the rapid depletion of radiolytic oxidants at the surface of the

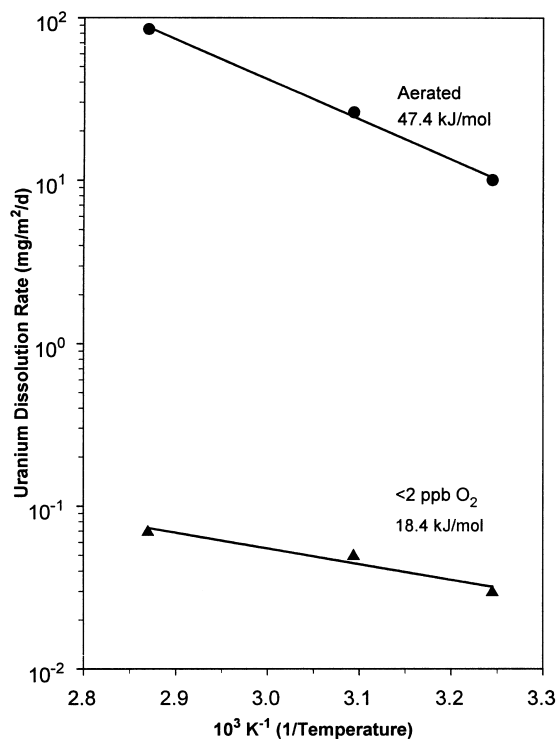


Fig. 4. Dissolution rates of uranium from UO_2 in flow-through experiment as a function of temperature in $0.1 \text{ mol l}^{-1} \text{ NaCl}/0.01 \text{ mol l}^{-1} \text{ NaHCO}_3$ (Tait and Luht [15]). Upper curve is under air-saturated conditions; lower curve is for oxygen depleted conditions ($\sim 2 \text{ ppb O}_2$ in solution). The values given are activation energies.

powder. While this may be a possible explanation for used fuel it cannot explain the differences observed between our predicted rates from measurements on pellets and those from measurements in flow-through experiments, which show the opposite trend with particle size.

The absence of occluded grain boundaries rather than their enhanced reactivity would appear the most likely explanation for the higher dissolution rates on powders compared to pellets and fragments. This is supported by the similarity in rates measured on these various specimens when HCO_3^- is present (Fig. 2). In this case the increased solubility would prevent formation of the secondary phases which block dissolution at occluded grain boundaries. This similarity between rates measured on powders and those predicted from measurements made on pellets also suggests that the uncertainties in surface areas may not be as large as originally suspected.

The value of 0.7 obtained for the reaction order with respect to O_2 is consistent with previously published values. Both Needes et al. [23] and Hiskey [24] obtained a reaction order of ~ 0.6 for experiments in carbonate solutions, when the accumulation of precipitated sec-

ondary phases would definitely be absent. This consistency suggests that problems with precipitates were minimal in the flow-through experiments, and that the rates are for unimpeded dissolution from the fuel surface. A fractional reaction order with respect to O_2 is consistent with the coupling together of two electrochemical half reactions, the anodic dissolution of UO_2



and the oxidant reduction reaction



to yield the overall oxidative dissolution reaction. The reaction order depends on the kinetics of these half reactions as expressed by their Tafel slopes; i.e. the slope of a plot of the logarithm of current against applied potential [3]. For oxidative dissolution driven by O_2 reduction, values of Tafel slope have been measured for both reactions. For the anodic fuel dissolution reaction (1) a slope of $\sim 60 \text{ mV}^{-1}$ was obtained in non-complexing solutions [8]. For the reduction of O_2 the Tafel slope can vary between 120 and $\geq 200 \text{ mV}^{-1}$ [25,26]. Although a full mixed-potential model remains to be developed, these values suggesting the reaction order for O_2 reduction should be in the range $0.66\text{--}0.8$, which is in good agreement with the measured value of between 0.69 and 0.74 (Fig. 1).

Two limiting cases of reaction order with respect to $[\text{O}_2]$ can be envisaged [7]. A value of 1 suggests that the oxygen reduction reaction is rate controlling, since the order with respect to O_2 for cathodic reduction is 1 [25–27]. (It should be noted here that reaction orders < 1 can be obtained for the cathodic reduction of O_2 on specimens of UO_2 which appear to be highly non-stoichiometric, and hence reactive, in the grain boundaries [28].) This would be the case if the anodic fuel dissolution reaction (1) were fast, a situation which could prevail in carbonate containing solutions. The reported observations of Gray and Wilson [29] that for spent fuel, the dissolution rate is 0 at 25°C but 0.8 at 75°C , appears to encompass both these possibilities.

However, these expectations are at odds with electrochemical measurements, which yield a reaction order of ~ 1 even though secondary phases are expected to be blocking the anodic dissolution reaction, Fig. 1. Closer scrutiny of the electrochemical data points in this figure suggest that a plot through the four points at high O_2 concentrations would yield a slope of close to 0.7. This would suggest that the electrochemical data points for lower O_2 concentrations are unreliable, but without further experiments, this remains speculative. Grambow et al. [30] also found an approximately first-order dependence on oxidant concentration, and concluded the oxidation of the UO_2 was the slow step, consistent with the overall rate control by reaction (2). These rates were

measured on pellets or 1 mm fragments over short times (up to 5–10 days), as were the measurements on which electrochemical predictions are based. Whether or not the form of the fuel specimens is important remains to be demonstrated.

Doubt has been expressed that our electrochemical model can be applied at lower oxidant concentrations since there appears to be a change in mechanism of the oxidation/dissolution of UO_2 as redox conditions become anoxic [1,2]. For potentials ≤ -100 mV (vs. SCE) the composition of the surface is thought to change rapidly with potential as oxidation from UO_2 to $\text{UO}_{2.33}$ occurs, although dissolution has been detected at potentials as low as -300 mV (vs. SCE) [31]. When the surface composition is changing in this manner, the steady-state conditions required for the application of our electrochemical model do not exist. For this reason we have generally ignored rates determined for corrosion potentials below -100 mV (vs. SCE) in determining the fit to our data which can then be extrapolated to lower potentials to predict dissolution rates. This is equivalent to using only the data points at higher $[\text{O}_2]$ (● in Fig. 1) to determine the relationship between rate and $[\text{O}_2]$, a procedure used recently to predict rates as a function of gamma and alpha radiation dose rates [4]. Implicit in this procedure is the assumption that our model does apply at lower potentials (less oxidizing redox conditions), an assumption which appears to be borne out by the measured rates plotted in Fig. 1.

With the exception of the early electrochemical rates [7], both measured and predicted rates have a reaction order with respect to $[\text{HCO}_3^-]$ of ~ 0.4 – 0.6 . These values are consistent with published values of 0.46 for dissolution in carbonate solutions [24] and 0.53 for dissolution in oxygenated carbonate solutions [32]. As for O_2 , the dependence on HCO_3^- can be determined from electrochemical measurements of Tafel slopes for reactions (1) and (2). From our measured slopes [10,25] we would predict a value between 0.34 and 0.4 in good agreement with both electrochemical and measured values (Fig. 2). Using mixed-potential theory to evaluate the Tafel slope, Hiskey [32] predicted a value of 0.5. The value of 0.58 obtained by de Pablo et al. [18] is higher than predicted electrochemically and suggests a different kinetic balance between the two half reactions, (1) and (2), involved in the overall corrosion reaction. The highest value would be consistent with either a more rapid rate of O_2 reduction or a slowed rate of anodic dissolution of UO_2 . Since their rates are the lowest (Fig. 2) the second explanation appears most likely.

While this agreement between measured and predicted rates is gratifying it should be recognized that the influence of $\text{HCO}_3^-/\text{CO}_3^{2-}$ on UO_2 dissolution could be quite complex, and very dependent on concentration.

(i) At low concentrations the predominant influence may simply be the thermodynamic ability to increase

UO_2^{2+} solubility and, hence, to prevent the deposition of the secondary phases which block dissolution.

(ii) At intermediate concentrations ($\geq 10^{-3}$ mol l^{-1}), $\text{HCO}_3^-/\text{CO}_3^{2-}$ is kinetically involved in the dissolution reaction [3].

(iii) For high concentrations, the presence on the surface of a phase such as UO_2CO_3 begins to impede the dissolution reaction which then becomes less dependent on $[\text{HCO}_3^-]$.

For the rates plotted in Fig. 2, conditions appear to be as described in (ii). A decrease in the dependence of rate on $[\text{HCO}_3^-]$, such as that described in (iii), does not appear to occur until $[\text{HCO}_3^-] \geq 0.3$ mol l^{-1} [23,32]. Carbonate has also been shown to affect the rate and mechanism of O_2 reduction on UO_2 , although this influence may be confined to concentrations greater than 10^{-1} mol l^{-1} [25,26]. At these high concentrations CO_3^{2-} adsorbs at the U(VI) sites on the UO_2 surface required to co-ordinate and catalyze electron transfer to O_2 . This leads to an inhibition of electron transfer to O_2 .

The dissolution rates as a function of gamma dose rate cannot be straightforwardly compared since they were all recorded under different chemical conditions. The rates measured by Tait and Luht in carbonate solutions [15] are $\sim 10^2$ times higher than those predicted from electrochemical measurements in non-complexing solutions. This is approximately the same difference as that between rates in aerated carbonate-containing and non-complexing solutions (Figs. 1 and 2). The horizontal lines labelled 1 and 2 in Fig. 3 show the rate predicted for unirradiated aerated solution (from Fig. 1), and the rate measured in flow-through experiments in carbonate solution (from Fig. 2). The intersection of these lines with the fitted lines for the plotted rates, suggests that the effect of gamma radiation on the dissolution rate of UO_2 becomes negligible for dose rates less than ~ 1 Gy h^{-1} in aerated non-complexing solutions and less than ~ 10 Gy h^{-1} in aerated carbonate solutions. The dependence of dissolution rate on dose rate is purely empirical since the concentration of radiolytic oxidants is proportional to the square root of dose rate [33].

For deaerated solutions (not shown in Fig. 3) the dissolution rate predicted electrochemically is approximately first order with respect to radiolytic oxidants for high dose rates (≥ 25 Gy h^{-1}) [2,5] and it is possible that this represents transport control of the dissolution process by radiolytically-produced oxidants. In aerated solution, however, the dependence on concentration of radiolytic oxidants is much lower (Fig. 3) and almost certainly affected by the formation of secondary phases. In fact, electrochemical experiments on used fuel specimens have yielded very positive values of corrosion potential [34], which should lead to large dissolution rates. Such large rates were not observed and the evidence for the blockage of dissolution by secondary

precipitates was incontestable. Clearly high gamma/beta radiation dose rates have the potential to cause rapid dissolution under conditions where secondary precipitates are avoided, i.e. in the presence of carbonate. In the absence of carbonate the high corrosion potentials observed reflect the degree of oxidation of the UO_2 and are not directly related to the dissolution rate as predicted by the electrochemical model.

The activation energy value of 47 kJ mol^{-1} measured in flow-through experiments is within the range of published values ($42\text{--}63 \text{ kJ mol}^{-1}$) measured in carbonate solutions [2,18] and consistent with dissolution free of inhibition by precipitated secondary phases. In the absence of carbonate, when such phases are likely to be present on the dissolving surface, lower activation energies ($29\text{--}34 \text{ kJ mol}^{-1}$) are obtained [2]. Under deaerated conditions the activation energy is difficult to determine given the small differences in uranium dissolution rates, but decreases to 18.4 kJ mol^{-1} . For such low $[\text{O}_2]$ it is possible that, for a large surface area of fuel, the dissolution rate is, at least partially, controlled by transport of O_2 to the dissolving surface.

7. Summary and conclusions

A comparison has been made between dissolution rates of UO_2 and used fuel powders measured in flow-through experiments and those predicted on the basis of electrochemical measurements on fuel pellets. Where feasible, comparisons to rates published in the literature have also been made.

In aerated carbonate solutions the measured and predicted rates are close, and the dependence on $[\text{HCO}_3^-]$ are the same. This agreement confirms that UO_2 dissolution rates can be predicted from appropriate electrochemical measurements. The measured activation energy in HCO_3^- solutions is consistent with published values for aerated carbonate solutions when dissolution is unaffected by the presence of secondary phases.

In neutral, non-complexing solutions the agreement is not so good. Predicted values are up to two orders of magnitude lower than measured values obtained using powdered samples but very similar to published rates measured on fuel fragments. This discrepancy appears to be due to the presence of secondary precipitates which block the dissolution process at occluded sites, most likely grain boundaries, present on pellets and fragments but not on powders.

The dependence on $[\text{O}_2]$ and $[\text{HCO}_3^-]$ for measured rates are consistent with published values. For rates predicted electrochemically, the dependence on $[\text{HCO}_3^-]$ is the same as that for measured values. The dependence on $[\text{O}_2]$ is larger than that for measured values despite the fact the influence of secondary phases, thought to be inhibiting dissolution on pellets, is expected to suppress

this dependence. For used fuel, the dissolution rate in aerated non-complexing solutions is marginally higher than that for unirradiated UO_2 . For deaerated solutions, however, it is significantly greater than the rate for UO_2 , presumably as a consequence of enhanced dissolution due to the production of radiolytic oxidants.

Both measured and predicted rates of UO_2 dissolution in gamma-irradiated aerated solutions show a dependence on gamma dose rate. However, irradiation has an insignificant effect on dissolution in aerated, non-complexing solutions for dose rates $< \sim 1 \text{ Gy h}^{-1}$ and on dissolution in aerated $10^{-2} \text{ mol l}^{-1}$ carbonate solutions for dose rates $< \sim 10 \text{ Gy h}^{-1}$.

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