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**Validation of the Oxidative Dissolution
Model for Used CANDU Fuel**

**Validation du modèle de dissolution
oxydative pour le combustible CANDU Irradié**

D.W. Shoesmith, S. Sunder, J.C. Tait



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FOR USED CANDU FUEL**

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**Whiteshell Laboratories
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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 to 75°C. Good agreement was obtained 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 so good since electrochemical dissolution on fuel pellets appeared to be inhibited by the formation of secondary phases in occluded grain boundaries. Measurements made on powders appear not 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 $\sim 10^2 \text{ R}\cdot\text{h}^{-1}$ and $\sim 10^3 \text{ R}\cdot\text{h}^{-1}$, respectively.

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VALIDATION DU MODÈLE DE DISSOLUTION OXYDATIVE
POUR LE COMBUSTIBLE CANDU IRRADIÉ

par

D.W. Shoesmith, S. Sunder et J.C. Tait

RÉSUMÉ

On compare les vitesses de dissolution mesurées de l'UO₂ et des poudres de combustible irradié aux vitesses de dissolution prévues à partir des mesures électrochimiques sur des pastilles de combustible. On a effectué cette comparaison pour des vitesses en fonction de la concentration d'oxygène dissous, de la concentration de carbonate et de bicarbonate et du débit de dose de rayonnement gamma. On a également effectué des mesures en fonction de la température entre 25 et 75 °C. On a obtenu une bonne conformité dans les solutions de carbonate aéré, confirmant que la réaction de dissolution est électrochimique de par son mécanisme et que l'on peut prévoir sa vitesse de façon électrochimique. Dans le cas des solutions non chélatantes, la conformité n'a pas été aussi bonne étant donné que la dissolution électrochimique sur les pastilles de combustible semblait être empêchée par la formation de phases secondaires dans les joints de grain occlus. Les mesures effectuées sur les poudres ne semblent pas être influencées de cette manière étant donné que peu de joints de grain occlus sont présents. Les vitesses prévues et mesurées dans les solutions irradiées gamma, tout en étant mesurées dans des conditions différentes, ont présenté les mêmes tendances générales et se comparent bien aux valeurs de la documentation publiée. Dans les solutions non chélatantes aérées et dans les solutions de carbonate aérées, l'effet de l'irradiation gamma est bien au-dessous, respectivement, de $\sim 10^2$ R·h⁻¹ et de $\sim 10^3$ R·h⁻¹.

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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-oxidizing 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 (Sunder and Shoesmith 1991; Shoesmith and Sunder 1991; Shoesmith et al. 1994). 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 (Johnson et al. 1996). 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 (Johnson et al. 1996).

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 to comprehensively review all existing data on UO_2 dissolution rates will be included.

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 (Sunder and Shoesmith 1991). 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 radiolytically decomposed by gamma or alpha radiation, has been described (Shoesmith and Sunder, 1991; Shoesmith and Sunder 1992; Sunder et al. 1997).

3. ELECTROCHEMICAL DATA ON UO_2 DISSOLUTION

Dissolution currents have been measured as a function of applied electrochemical potential in $0.1 \text{ mol}\cdot\text{L}^{-1}$ NaClO_4 (pH = 9.5) solutions and in this solution containing various amounts of Na_2CO_3 ($0.005 \text{ mol}\cdot\text{L}^{-1}$ to $0.1 \text{ mol}\cdot\text{L}^{-1}$) (Shoesmith et al. 1989; Sunder et al. 1996; 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 would then allow the effect of increased complexing ability 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 (Shoesmith et al. 1989) was recorded relatively rapidly (~10 min per 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 (Sunder et al. 1996). Despite this, steady state was not achieved for applied potentials $\leq 350 \text{ mV}$ (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 (Sunder et al. 1996). A variability in the reactivity of different UO_2 specimens may also be a factor as observed by Nicol et al. (1995) and discussed by Shoesmith et al. (1994).

No such problem exists for measurements 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 (Shoesmith et al. 1983; 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 (Sunder et al. 1992).

4. FLOW-THROUGH DISSOLUTION RATE DATA ON UO_2 AND USED FUEL

The dissolution rates of uranium from used fuel and UO_2 were determined using a single-pass, flow-through method described by Gray et al. (1994). The advantage of the single-pass, flow-through technique is that flow rates and specimen size can be controlled so that the UO_2 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 UO_2 dissolution kinetics on pH, temperature, oxygen and carbonate/bicarbonate concentrations can be evaluated.

The preparation of the UO_2 powders used in the dissolution tests and the experimental conditions used have been described by Gray et al. (1994). The leachants were either $0.01 \text{ mol}\cdot\text{L}^{-1} \text{NaHCO}_3/0.1 \text{ mol}\cdot\text{L}^{-1} \text{NaCl}$ or deionized water (DIW). The solutions were either equilibrated with air at room temperature, or were deaerated by purging the stock solution with 5% $\text{H}_2/\text{Ar}/\text{CO}_2$ 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. In one experiment the HCO_3^- concentration was varied from 10^{-4} to $0.05 \text{ mol}\cdot\text{L}^{-1}$. The flow rates of the leachant were about $35 \text{ mL}\cdot\text{h}^{-1}$, which has been shown to be sufficient to maintain the bulk leachant solution below U saturation conditions (Wilson and Gray 1990). The preparative technique followed for preparation of powdered UO_2 and used fuel samples was similar to that used to produce samples of depleted UO_2 (0.2% ^{235}U) for interlaboratory testing (Gray et al. 1994). The technique involved crushing, washing and screening samples which resulted in powders with a size fraction from 44 to $105 \mu\text{m}$ and a measured (BET) surface area of $267 \text{ cm}^2\cdot\text{g}^{-1}$. 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 (Shoesmith et al. 1996). It is estimated that surface areas for the unirradiated UO_2 samples in this report are within a factor of two of the assumed value of $267 \text{ cm}^2\cdot\text{g}^{-1}$; however, surface areas for used fuel may be a factor of 4 to 6 greater, due partly to additional surface area from grain boundaries and to the presence of fines smaller than $44 \mu\text{m}$, as the used fuel samples were not washed prior to leaching.

The dissolution experiments on UO_2 to determine the effect of dose rate on dissolution rate used a ^{192}Ir γ -source. The initial dose rate to the solution in the flow-through leaching cell was $\sim 30,000 \text{ R}\cdot\text{h}^{-1}$ ($\sim 300 \text{ Gy}\cdot\text{h}^{-1}$), as determined by Fricke dosimetry. The gamma and beta dose rates from 10-a-cooled fuel are approximately 3000 and $30,000 \text{ R}\cdot\text{h}^{-1}$ (30 and $300 \text{ Gy}\cdot\text{h}^{-1}$) respectively (Johnson et al. 1996). The initial gamma dose rate from the ^{192}Ir source thus approximates the beta dose rate from used fuel in contact with water. Since the yield of radiolysis products (i.e., G-values, or 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 UO_2 AND USED FUEL

Measured and predicted dissolution rates of uranium from UO_2 and used fuel as a function of oxygen concentration are shown in Figure 1. The predicted dissolution rates from Shoesmith and Sunder (1991) are based on electrochemical measurements on UO_2 in $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ NaClO}_4$ solution. The data points at an oxygen concentration of $10^{-8} \text{ mol}\cdot\text{L}^{-1}$ are estimates based on the partial pressure of oxygen in the anaerobic chamber in which the experiments were performed and were not used to derive the best fit to the data. The oxygen dependence appears to be first order. The remaining data are measured dissolution rates of UO_2 derived from uranium concentrations in solution. The reaction orders are about 0.7. Grambow et al. (1996) have also presented data on UO_2 dissolution in the presence of various oxidants (H_2O_2 , ClO^- , O_2) and have shown that the dissolution rate is about first-order with respect to oxidant concentration. The dissolution rate of used fuel (Figure 1) appears to be less dependent upon oxygen concentration than that of UO_2 . The lower reaction order (0.39) may be an artifact since radiolytic oxidants will be produced near the surface of the fuel which 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 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

The dissolution rates of uranium from unirradiated UO_2 in the presence of carbonate ion in aerated solution are shown in Figure 2 for both flow-through dissolution tests (Tait, unpublished data; de Pablo et al. 1997) and for electrochemical data (Sunder, unpublished data; Shoesmith et al. 1989) measured in $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ NaClO}_4$ ($\text{pH} \sim 9.5$). The uranium dissolution rate increases with increasing bicarbonate concentration, up to $[\text{HCO}_3^-] \sim 0.5 \text{ mol}\cdot\text{L}^{-1}$, as expected from the ability of bicarbonate to complex U(VI) species and remove them from the oxidized surface of the UO_2 . Except for the early electrochemical data (Shoesmith et al. 1989), the reaction order appears to be about 0.4 to 0.6 with respect to bicarbonate concentration.

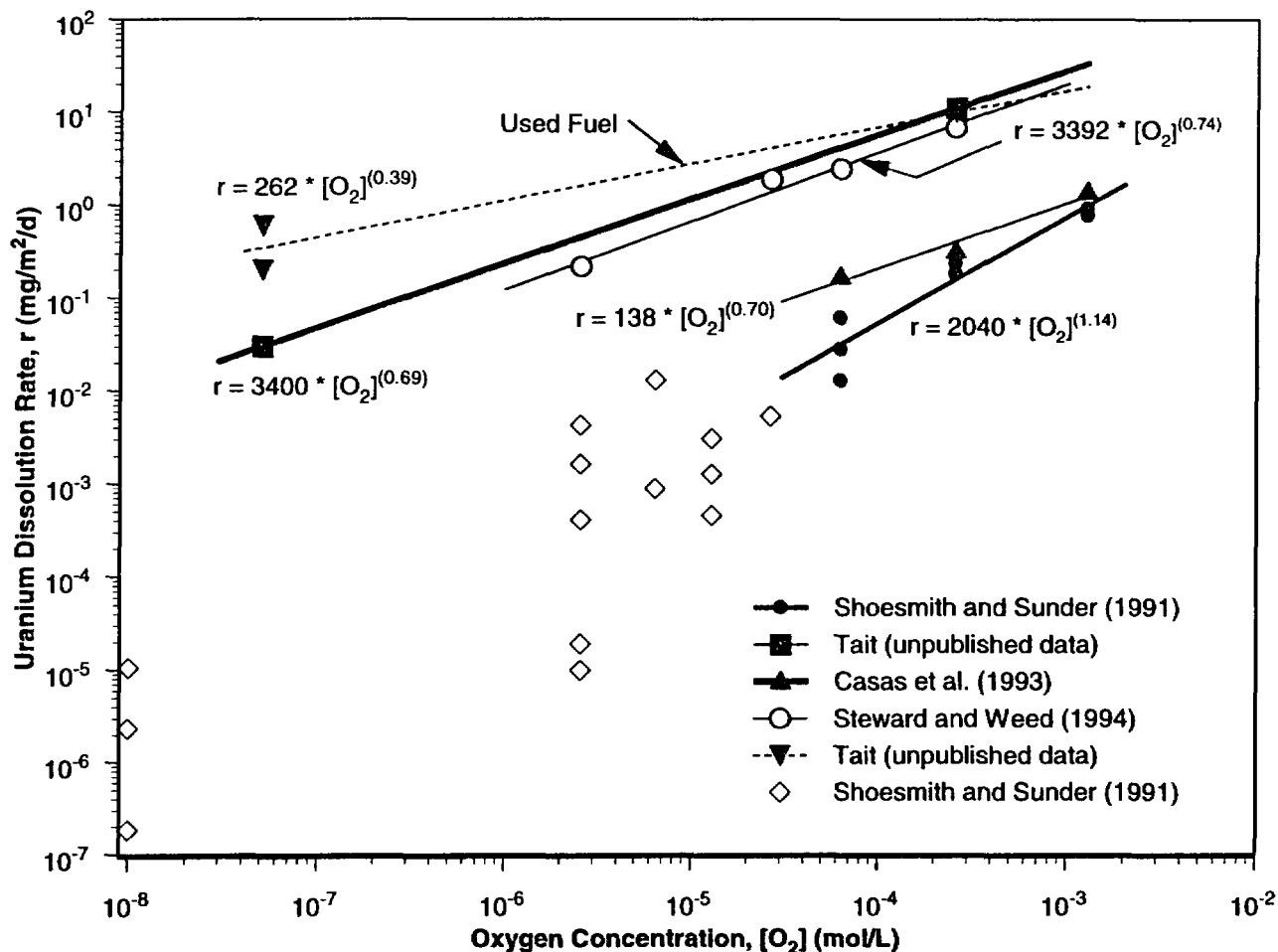


FIGURE 1: Dissolution Rates of Uranium from UO_2 and Used Fuel as a Function of Oxygen Concentration at 25°C:

- (a) (●,◇) predicted using the electrochemical model for oxygenated $0.1 \text{ mol}\cdot\text{L}^{-1}$ NaClO_4 (pH = 9.5) (Shoesmith and Sunder 1991);
- (b) measured in $0.01 \text{ mol}\cdot\text{L}^{-1}$ $\text{NaHCO}_3/0.1 \text{ mol}\cdot\text{L}^{-1}$ NaCl (pH ~ 9) on UO_2 (■) and used CANDU fuel (▼) (Tait, unpublished results);
- (c) (▲) measured in oxygenated MgCl_2 brine (pH = 4.5) (Casas et al. 1993);
- (d) (○) measured in oxygenated $0.02 \text{ mol}\cdot\text{L}^{-1}$ NaHCO_3 (pH ~9) (Steward and Weed 1994).

Equations represent the best fit to the data.

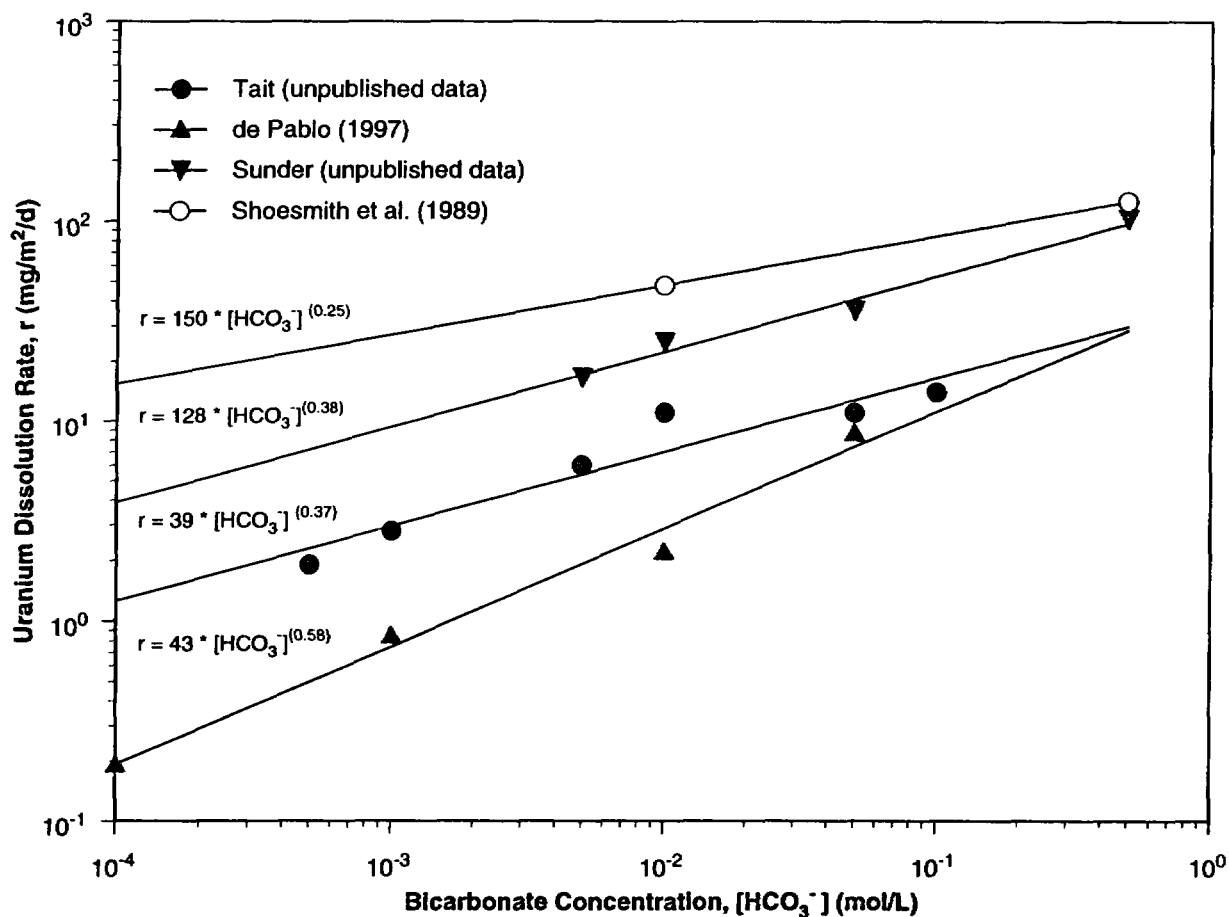


FIGURE 2: Dissolution Rates of Uranium from UO_2 as a Function of Bicarbonate Ion Concentration in Aerated Solution at 25°C :
 (a) measured in aerated NaHCO_3 solution with $\sim 0.1 \text{ mol}\cdot\text{L}^{-1}$ NaCl ($\text{pH} \sim 9$) (Tait, unpublished results (\bullet); de Pablo et al. (1997) (\blacktriangle);
 (b) predicted using the electrochemical model for aerated NaHCO_3 solution with $0.1 \text{ mol}\cdot\text{L}^{-1}$ NaClO_4 ($\text{pH} = 9.5$) (Sunder, unpublished results (\blacktriangledown); Shoesmith et al. (1989) (\circ)).
 Equations represent the best fit to the data.

5.3 EFFECT OF GAMMA DOSE RATE ON URANIUM DISSOLUTION RATES FROM UO₂

Figure 3 compares dissolution rates of unirradiated UO₂ as a function of γ -dose rate in aerated/oxygenated solutions and as a function of square root of the dose rate in Figure 4. The dissolution rates are those predicted from our electrochemical model (Shoesmith and Sunder, 1991) and those measured from uranium concentrations in solution by Christensen et al. (1990), Gromov (1981) and Tait (unpublished data). The dissolution rates calculated using the electrochemical model are for experiments in aerated, non-complexing solutions at slightly alkaline pH (0.1 mol·L⁻¹ NaClO₄, pH ~ 9.5). The rates measured by Gromov are for aerated solutions which are either strongly acidic (0.05 mol·L⁻¹ H₂SO₄, i.e., pH ~ 1) or contain strongly complexing anions, i.e., alkaline carbonate solutions (0.38 mol·L⁻¹ Na₂CO₃ + 0.36 mol·L⁻¹ NaHCO₃, pH ~ 10). The rate measured by Christensen et al. (1990) is for an O₂-saturated solution containing a borate buffer, pH 8.2. Tait measured rates in a solution containing 0.1 mol·L⁻¹ NaCl and 0.01 mol·L⁻¹ NaHCO₃, pH ~ 8.5. (Note: while the results of Gromov and Christensen et al. are for "batch" type experiments, the results of Tait (unpublished data) are for "continuous-flow" experiments", i.e., the solution was flowing over powder-UO₂ samples. Also, the measurements by Gromov are at much higher dose rates than those used in the electrochemical experiments.)

The measured dissolution rates in acidic, alkaline carbonate, and near neutral solutions, show a dose rate dependence close to that predicted by our electrochemical model, Figure 3. Not surprisingly, Gromov's values in acidic solutions are significantly higher than our predictions. (Uranium oxides have much higher solubility in acidic solutions (Sunder and Shoesmith 1991)). Gromov's rates in carbonate solutions are surprisingly low and inconsistent with our predictions and the measurements of other workers. The dissolution rates from Christensen et al. (1990) and Tait (unpublished data) are slightly larger than those predicted by the electrochemical model. The solution used by Tait contained carbonate anion which is known to increase the UO₂ dissolution rates (Sunder and Shoesmith, 1991). The dissolution rate from Christensen et al. may be higher because it was measured in oxygenated, as opposed to aerated solutions used in the electrochemical experiments. Considering the uncertainty in the surface area of the samples (Shoesmith et al. 1996), the agreement between the measured dissolution rates and those calculated using our electrochemical model is very gratifying.

5.4 EFFECT OF TEMPERATURE ON URANIUM DISSOLUTION RATES FROM UO₂

The flow-through dissolution experiment was used to measure the temperature dependence of the uranium dissolution rate from unirradiated UO₂ in aerated solution over the temperature range from 25 to 75°C and the results are shown in Figure 5 (Tait, unpublished data). There have been no comparable electrochemical measurements to determine the temperature dependence. An Arrhenius plot of the dissolution rate gave an activation energy of 47.4 kJ·mol⁻¹ for UO₂ under aerated/bicarbonate solution conditions which is significantly higher than the activation energy of 33.45 kJ·mol⁻¹ used a recent safety assessment study (Johnson et al. 1996). Under deaerated conditions the activation energy decreases to about 18.4 kJ·mol⁻¹. The latter activation energy is somewhat difficult to determine, given the small differences in uranium dissolution rates at the low uranium concentrations involved.

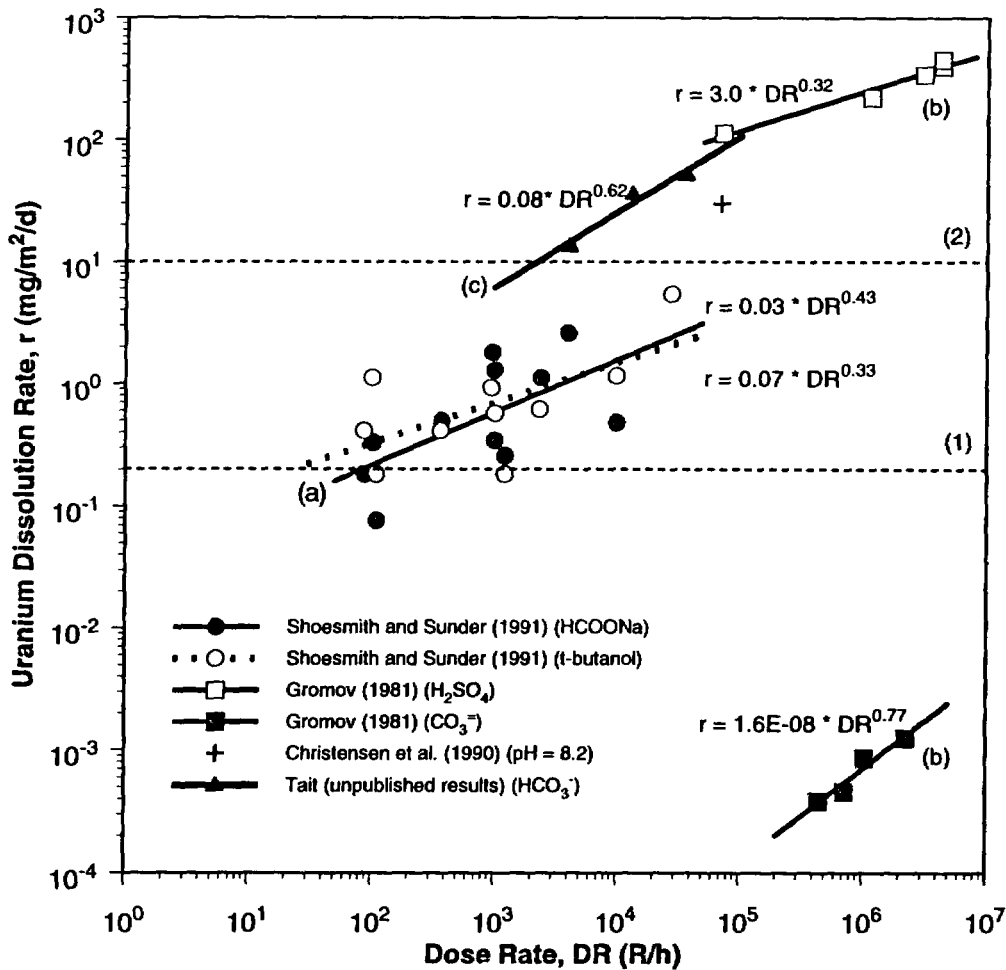


FIGURE 3: Dissolution Rates of Uranium from UO_2 in Irradiated, Aerated/Oxygenated Solutions as a Function of the Gamma Dose Rate:

- (a) predicted using the electrochemical model (Shoosmith and Sunder 1991) in aerated $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ NaClO}_4$ ($\text{pH} = 9.5$) solutions with $0.01 \text{ mol}\cdot\text{L}^{-1} \text{ HCOONa}$ (●) or with $0.01 \text{ mol}\cdot\text{L}^{-1} t\text{-butanol}$ (○);
- (b) measured by Gromov (1981) in acidic sulphate solution ($\text{pH} \sim 1$) (□), and alkaline carbonate solution ($\text{pH} \sim 10$) (■);
- (c) measured by Tait et al. (unpublished results) in $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ NaCl}$ and 0.01 M NaHCO_3 ($\text{pH} = \sim 8.5$) solution using a flow-through cell (▲);
- (d) measured by Christensen et al. (1990) in oxygenated solution ($\text{pH} = \sim 8.2$) (+).

(Note: 1 Rad = 10 mGy).

The horizontal dashed lines show the rate predicted for unirradiated aerated solution (1) (from Figure 1) and the rate measured in flow-through experiments in bicarbonate solution (2) (from Figure 2). Equations represent the best fit to the data.

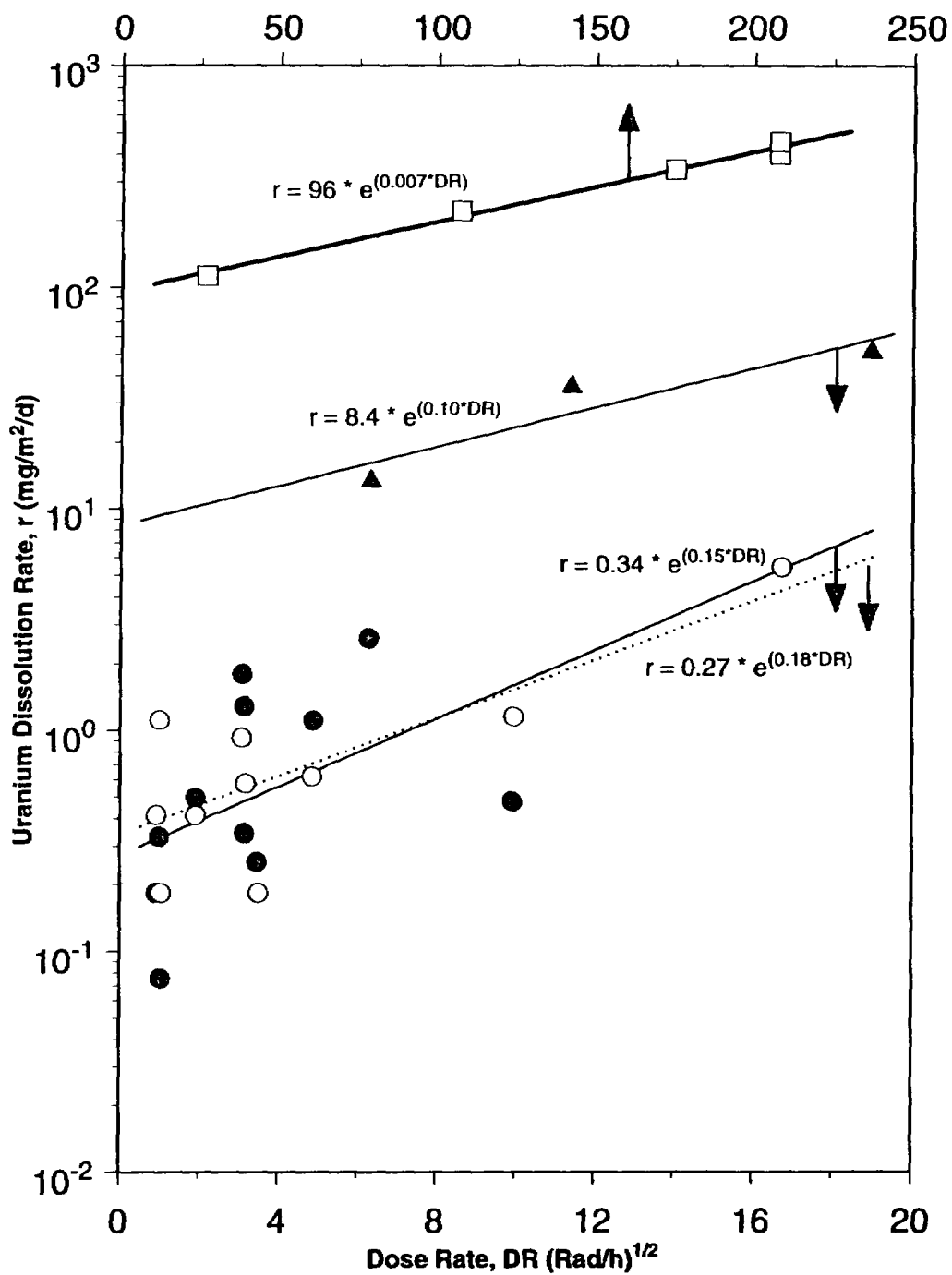


FIGURE 4: Predicted (Shoesmith and Sunder, 1991) and Measured (Gromov, 1981; Tait (unpublished data)) Dissolution Rates of Uranium from UO_2 . Data taken from Figure 3, and replotted against the square root of the gamma dose rate. Equations represent the best fit to the data.

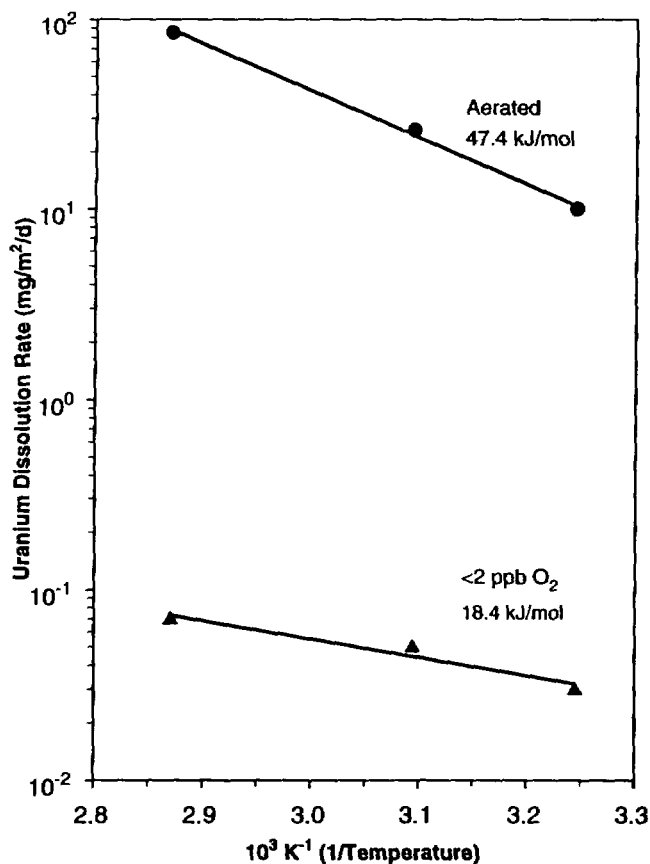


FIGURE 5: Dissolution Rates of Uranium from UO_2 in Flow-through Experiment as a Function of Temperature in $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ NaCl}/0.01 \text{ mol}\cdot\text{L}^{-1} \text{ NaHCO}_3$. Upper curve is under air saturated conditions; lower curve is for oxygen depleted conditions ($\sim 2 \text{ ppb O}_2$ in solution). The values are the calculated activation energies.

6. DISCUSSION

6.1 APPROPRIATE ELECTROCHEMICAL DATA

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 that the influence of grain boundaries is minimal. In the most recently recorded set of electrochemical data, 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 conditions. 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 below. No such dilemma exists for electrochemical data recorded in carbonate solutions in which steady-state dissolution currents are easily measurable (Section 3).

6.2 EFFECT OF OXYGEN ON URANIUM DISSOLUTION RATES FROM UO₂ AND USED FUEL

The dissolution rates of uranium from UO₂ and used fuel as a function of dissolved oxygen concentration are shown in Figure 1. The rates of Tait, and Steward and Weed (1994) were measured under comparable conditions on similarly treated UO₂ powders. Both the rate values, and their dependence on [O₂], are in close agreement. The rates measured on 1-mm particles by Casas et al. (1993) are closer to the rates predicted electrochemically from measurements made on unirradiated pellets. These differences in rate values probably reflect the uncertainties in determining the surface areas of UO₂ (Section 4) as well as the difference in importance of grain boundaries. Powdered samples 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 than expected on fragments or pellets.

The reaction order with respect to [O₂] is approximately 0.7 for all measurements. This dependence is consistent with values previously published. Both Needes et al. (1975) and Hiskey (1980) obtained a reaction order of ~ 0.6 for experiments in carbonate solutions, when the accumulation of precipitated secondary phases would definitely be absent. This consistency suggests problems with secondary phases were minimal in measurements made using a flow-through system.

The reaction order obtained from the electrochemical model is 1.0 to 1.1 depending on whether only the more reliable rates at higher [O₂] (●) or the whole data set (●,◇) were included in the data fit, respectively. Whether or not this difference between predicted and measured reaction orders is related to the influence of blocked grain boundaries on predicted rates (Section 3) is difficult to decide.

Doubt has been expressed that the electrochemical model can be applied at lower oxidant concentrations since there appears to be a change in mechanism of the oxidation/dissolution of UO₂ as redox conditions become anoxic (Shoesmith and Sunder 1991; Johnson et al. 1996). This change is expected to lead to a more dramatic decrease in dissolution rates as anoxic conditions are approached than shown by the fitted lines in Figure 1. This would suggest that the reaction order with respect to [O₂] determined from the fit to the limited data set in Figure 1 (●) is the most appropriate. This would be consistent with the fitting procedure adopted to predict rates as a function of gamma- and alpha-radiation dose rates (Johnson et al. 1996). However, depending on the reliability of measured dissolution rates at low [O₂] (■, ▼), the rates measured in flow-through experiments indicate no change in mechanism as anoxic conditions are approached.

Grambow et al. (1996) have measured dissolution rates in the presence of various oxidants (H_2O_2 , O_2 , ClO^-) and compared their results to rates predicted electrochemically for solutions containing dissolved O_2 or H_2O_2 (Shoesmith and Sunder 1991). The dissolution rates were independent of the nature of the oxidant and a universal first order dependence on oxidant concentration seemed to hold. They claimed this indicated that the oxidation of UO_2 was the slowest step in the overall dissolution reaction. Some discussion of this possibility has been published elsewhere (Shoesmith et al. 1996). These rates were measured on pellets or 1 mm fragments over short times (up to ~5 to 10 days), as were the measurements on which the electrochemical predictions were based.

6.3 EFFECT OF CARBONATE ON URANIUM DISSOLUTION RATES FROM UO_2

As expected, in carbonate solutions, the measured and predicted rates are higher than in non-complexing solutions and increase with increases in $[\text{HCO}_3^-]$ due to the complexing ability of the carbonate ion for U(VI) species (Figure 2). 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 the dissolution rate can be predicted from the electrochemical model.

With the exception of the early electrochemical rates (Shoesmith et al. 1989) both measured and predicted rates have a reaction order with respect to $[\text{HCO}_3^-]$ of ~ 0.4 to 0.6. These values are consistent with published values of 0.46 for dissolution in carbonate solutions containing H_2O_2 (Hiskey 1980) and 0.53 for dissolution in oxygenated carbonate solutions (Hiskey 1979). The problem with the earlier rates predicted electrochemically seems to be with the value at a $[\text{HCO}_3^-]$ of $10^{-2} \text{ mol}\cdot\text{L}^{-1}$, the value at $0.5 \text{ mol}\cdot\text{L}^{-1}$ showing good agreement with the latter rate at this concentration. One possibility is that this value was measured on poorly sintered UO_2 which appears to support enhanced oxidation at the expense of retarded dissolution (Betteridge et al. 1996). Unfortunately, it is now too late to determine whether this was indeed the case.

6.4 EFFECT OF TEMPERATURE ON URANIUM DISSOLUTION RATES FROM UO_2

The activation energy of $47 \text{ kJ}\cdot\text{mol}^{-1}$ for rates measured in aerated carbonate-containing solutions is within the range of values (42 to $63 \text{ kJ}\cdot\text{mol}^{-1}$) measured in carbonate solutions (Sunder and Shoesmith 1991) 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 to $34 \text{ kJ}\cdot\text{mol}^{-1}$) are obtained (Sunder and Shoesmith 1991). Under deaerated conditions the activation energy is difficult to determine, given the small differences in uranium dissolution rates, but decreases to $18 \text{ kJ}\cdot\text{mol}^{-1}$. 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

In an attempt to justify the application of a model based on electrochemical principles and measurements in waste disposal assessment calculations, the predictions of this model have been compared to actual dissolution rate measurements. The measurements were made in a flow-through experimental system designed to avoid the inhibition of the dissolution process which could be caused by the precipitation of secondary phases on the fuel surface. Rates for both unirradiated UO_2 and used-fuel specimens were measured. A comparison to model predictions was made for rates as a function of oxygen concentration $[\text{O}_2]$, bicarbonate concentration $[\text{HCO}_3^-]$ and gamma radiation dose rates. An activation energy was measured in aerated carbonate solutions and a value consistent with previously published values was obtained. The comparison between predicted and measured rates in carbonate solutions showed very good agreement and confirmed that an electrochemical approach to predicting rates is valid. For non-complexing solutions the agreement with measured rates was not so good, and this was attributed to uncertainties in measured rates due to difficulties in estimating the surface areas of powdered samples used in flow-through measurements, as well as possible differences in the nature of the fuel specimens used. Despite these differences in actual rates, the dependence on $[\text{O}_2]$ was the same for rates from three different sources but somewhat different for model predictions. The comparison for gamma-radiolytically decomposed solutions also yielded quite close agreement considering the differences in experimental conditions used in obtaining the rates compared.

It is clear from these comparisons that an electrochemical modelling approach is justified and that, with the reservations discussed above, the rates predicted can be justifiably used in fuel performance assessment calculations.

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