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**Kinetics of  $\text{UO}_2$  (s) dissolution under  
reducing conditions:  
Numerical modelling**

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KINETICS OF  $UO_2(s)$  DISSOLUTION UNDER REDUCING  
CONDITIONS: NUMERICAL MODELLING

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KINETICS OF  $\text{UO}_2(\text{s})$  DISSOLUTION UNDER REDUCING CONDITIONS:  
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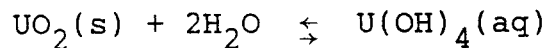
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ABSTRACT

A numerical model is presented that describes the dissolution and precipitation of  $\text{UO}_2(\text{s})$  under reducing conditions. For aqueous solutions with  $\text{pH} > 4$ , the main reaction is:



The rate constant for the precipitation reaction is found to be  $\log(k_p) = -1.2 \pm 0.2 \text{ h}^{-1} \text{ m}^{-2}$ , while the value for the rate constant of the dissolution reaction is  $\log(k_d) = -9.0 \pm 0.2 \text{ mol}/(1 \text{ h m}^2)$ .

Most of the experiments reported in the literature show a fast initial dissolution of a surface film of hexavalent uranium oxide. Making the assumption that the chemical composition of the surface coating is  $\text{U}_3\text{O}_7(\text{s})$ , we have derived a mechanism for this process, and its rate constants have been obtained.

The influence of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  on the mechanism of dissolution and precipitation of  $\text{UO}_2(\text{s})$  is still unclear. From the solubility measurements reported, one may conclude that the identity of the aqueous complexes in solution is not well known. Therefore it is not possible to make a mechanistic interpretation of the kinetic data in carbonate medium.



TABLE OF CONTENTS

	Page
	ii
	1
1	1
2	2
2.1	2
2.2	3
2.3	3
3	4
3.1	5
3.2	7
3.3	7
4	8
4.1	8
4.2	11
4.3	11
4.4	12
4.5	12
5	14
6	16





INTRODUCTION

Reducing conditions are expected to prevail around deep geologic repositories for spent nuclear fuel in crystalline rocks. However, in the near vicinity of the spent fuel elements, a local oxidising environment might be produced due to water radiolysis. The migration of many actinides from such a repository will therefore be affected by an initial dissolution under oxidising conditions, and a later precipitation under reducing conditions when the flowing groundwater reaches the surrounding geologic environment (Garisto and Garisto, 1986).

A precise numerical modelling of such processes requires the rate of spent fuel dissolution under oxidising conditions, as well as the rate of precipitation of stable actinide solid phases under reducing conditions. Modelling efforts reported in the literature are constrained by the lack of relevant rate constants (Light et al., 1988; Garisto and Garisto, 1986; Bruton and Shaw, 1988; Murphy and Smith, 1988; Apted and Engel 1988; etc).

While the dissolution kinetics of  $\text{UO}_2(\text{s})$  (the main component of spent nuclear fuel) under oxidising conditions has been reported in the literature (Johnson and Shoesmith, 1988; Posey-Dowty et al., 1987, and references therein), the precipitation of  $\text{UO}_2(\text{s})$  under reducing conditions has not been studied as extensively.

In this paper we examine the experimental data available in the literature on the dissolution and precipitation kinetics of  $\text{UO}_2(\text{s})$  under reducing conditions. Our purpose is to find rate constants and mechanisms that might be included in geochemical modelling codes to predict the chemical evolution of nuclear waste repositories under



diverse scenarios. This kind of data is also needed to model uranium ore deposition, uranium mill tailings management, in-situ mining (Nguyen et al., 1983; Zheng and Bautista, 1988), etc.

## 2

LITERATURE STUDIES

Recently we have reported the dissolution of un-irradiated  $\text{UO}_2$  nuclear fuel under hydrogen atmosphere (Bruno et al., 1988, and Bruno et al., 1990). In these studies we found that when aqueous solutions are brought in contact with  $\text{UO}_2$ , there is a fast initial increase in the uranium concentration, due to the dissolution of a surface coating of  $\text{U}_3\text{O}_7$ , as discussed below. In a later stage of the experiments, uranium concentrations were found to decrease exponentially as  $\text{UO}_2$  was precipitated. This behaviour is similar to the findings reported by Ogard and Duffy (1981). We will also try to correlate our findings with other experimental data in the literature.

2.1 OXIDATION PROPERTIES OF  $\text{UO}_2$ 

It is well known that  $\text{UO}_2$  adsorbs  $\text{O}_2$  even at low temperature (Belle, 1961), and that adsorbed hydrogen has little influence on later oxygen chemisorption (IAEA, 1965). Sunder et al. (1982, 1983 and 1987) describe the quick formation ( $\sim 1$  min) in neutral aqueous solutions of a surface layer of  $\text{UO}_{2.33}$  ( $\sim \text{U}_3\text{O}_7$ ) at  $\sim 545$  mV followed by its dissolution. This initial surface oxidation is unaffected by the presence of carbonate or phosphate ions in the solutions (Sunder et al., 1983). The  $\text{UO}_2(\text{s})$  affinity for oxygen appears to be rather high indeed, as the potential of  $\text{UO}_2$  pellets in a pH $\sim 9$  solution under  $\text{N}_2$  atmosphere is reported to increase up to  $\sim 330$  mV in  $\sim 140$  hours (Johnson et al., 1982) and to  $\sim 100$  mV in  $\sim 25$  hours (Sunder et al., 1987).



The surface oxidation state of  $\text{UO}_2$  can be studied by X-Ray Photoelectron Spectroscopy, XPS, (Sunder et al., 1987; Parks and Pohl, 1988). With this technique, the surface composition of the oxide is found to be  $\sim\text{UO}_{2.2}$  under reducing conditions. Under oxidising conditions, XPS analysis of the oxide surface gives a composition of  $\text{U}_3\text{O}_7$  (Sunder et al., 1987).

## 2.2 LEACHING OF $\text{UO}_2$ SPENT FUEL

Several studies on the dissolution of nuclear fuel under reducing conditions have been published. In many instances the uranium concentrations are high under an initial period of time due to the dissolution of the  $\text{UO}_{2+x}$  surface layer, and they later decrease with time as either  $\text{UO}_2$  or secondary solid phases are precipitated. Examples of such behaviour are found in Wilson (1988), Johnson and Joling (1982) and Johnson et al. (1982).

## 2.3 U(VI) REDUCTION WITH HYDROGEN

The hydrogen reduction of U(VI)-solutions has been reported as a concentration step in the extractive metallurgy of low level uranium ores. (Forward and Halpern, 1953 and 1954; Bunji and Zogovic, 1958; Balaceanu et al., 1958). In order to achieve fast and complete U(VI) reduction and  $\text{UO}_2$  precipitation, these authors studied the effect of several catalysts (Ni, Ni-Raney and  $\text{UO}_2$ ), hydrogen pressure, temperature and  $\text{HCO}_3^-/\text{CO}_3^{2-}$  concentrations.

The work by Bunji and Zogovic (1958) is interesting because it shows that  $\text{UO}_2(\text{s})$  is in fact capable to accomplish complete reduction of an U(VI) solution. Their results also imply that the active surface area was also



changing during the experiments of Forward and Halpern (1953) and Balaceanu et al. (1958).

Balaceanu et al. (1958) observed that sodium bicarbonate decreases the rate of U(VI) reduction, while the effect of  $\text{Na}_2\text{CO}_3$  in their experiments was negligible. Balaceanu et al. (1958) concluded that  $\text{HCO}_3^-$  prevents the formation of an initial carbonate precipitate of intermediate oxidation degree by keeping U(IV) in solution. An inspection of the data in Figure 14 at 70°C of Balaceanu et al. (1958) gives a dependence of the precipitation rate as a power of  $\sim -1.5$  on the activity of the bicarbonate ion.

In order to obtain the temperature dependence of the precipitation rate, we have fitted a first degree kinetic expression and Arrhenius equation to the data of Forward and Halpern (1953) and Bunji and Zogovic (1958). The calculated activation energy is  $E_a = 23.6$  kcal/mol from the data of Bunji and Zogovic (1958) using  $\text{UO}_2$ -catalyst on solutions probably containing 20 g/l  $\text{Na}_2\text{CO}_3$  and 32 g/l  $\text{NaHCO}_3$ , and  $E_a = 10.9$  kcal/mol from the data of Forward and Halpern (1953) using Ni-catalyst on solutions probably containing 50 g/l  $\text{Na}_2\text{CO}_3$ . This can be compared with values between 12 and 15 kcal/mol obtained by Balaceanu et al. (1958) using Ni-Raney catalyst.

### REACTION MECHANISMS

The data by Bruno et al. (1988), Bruno et al. (1990), Johnson and Joling (1982), Ogard and Duffy (1981), etc, may be divided in two time periods: a fast increase in uranium concentration (up to 1-5 hours), and a slower decrease in uranium levels due to  $\text{UO}_2$  crystal growth.

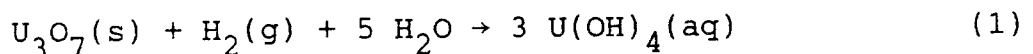




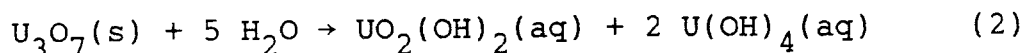
## 3.1 DISSOLUTION PERIOD

The fast initial dissolution of uranium is due to the dissolution of hexavalent uranium oxides from the  $\text{UO}_2$ -surface. This fast dissolution has also been observed by Posey-Dowty et al. (1987). We will assume that a coating of  $\text{U}_3\text{O}_7$  on the  $\text{UO}_2(\text{s})$  surface is responsible for the initial increase of U-concentration, and therefore, that the surface area of the dissolving solid is constant and equal to the surface area of the substrate ( $\text{UO}_2(\text{s})$ ). If the dissolving solid was made up of fine particles, the surface area would decrease with time, as the fine particles decrease in size, and eventually disappear completely, leaving zero surface area. In that case the equations derived below would be different. However, fine particles can not be the reason for the initial high uranium concentrations in our experiments because of two facts: firstly, the solid phase was pretreated with dilute acid, and secondly, the same solid sample was used for consecutive experiments in which the aqueous solution was replaced for a fresh one, and the result in all cases was an initial increase of uranium concentration followed by an exponential decrease.

The reactions taking place under the initial time period are either



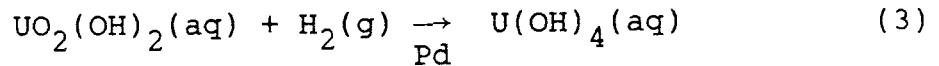
or



for this later reaction, the stoichiometry of the U(VI) hydroxo complex will depend on the pH of the experiments, and might as well be  $\text{UO}_2\text{OH}^+$  or  $\text{UO}_2(\text{OH})_4^{2-}$ . However, according to the thermodynamic data available, the dominating U(IV) hydroxo complex is  $\text{U}(\text{OH})_4(\text{aq})$  for pH values above four.



From experiments performed at Stockholm (Ciavatta et al., 1983; Bruno et al., 1989) we believe that due to the low uranium concentrations involved ( $\ll 10^{-5}$  M) and in the presence of a Pd-black catalyst, the reduction of the uranyl complex with hydrogen,



takes place within some minutes. If reaction (3) is fast enough, we can well assume that all uranium is present in the solutions as  $\text{U}(\text{OH})_4(\text{aq})$ , and that eqn. (2) can be neglected in our data analysis.

We will use an exponential equation to describe our experimental data in Bruno et al. (1990), i.e.,

$$\frac{d([\text{U}]_{\text{eq}} - [\text{U}])}{dt} = -k_d [\text{H}^+]^{-0.3} S ([\text{U}]_{\text{eq}} - [\text{U}])$$

or

$$[\text{U}] = [\text{U}]_{\text{eq}} (1 - e^{-(k_d [\text{H}^+]^{-0.3} S t)}) \quad (4)$$

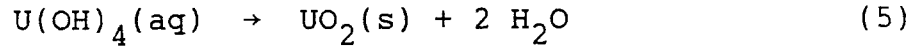
where  $k_d$  is the dissolution rate constant ( $\text{h}^{-1} \text{m}^{-2} \text{M}^{0.3}$ ),  $S$  is the surface area ( $\text{m}^2$ ),  $[\text{U}]_{\text{eq}}$  is the equilibrium solubility of the  $\text{U}_3\text{O}_7(\text{s})$  coating film,  $[\text{U}]$  is the uranium concentration ( $\text{mol/l}$ ) and  $t$  is the time in hours. The solubility of  $\text{U}_3\text{O}_7$  has been calculated as a function of pH for 0.008 M  $\text{NaClO}_4$  solutions ( $25^\circ$ , 1 atm  $\text{H}_2(\text{g})$ ) with the EQ3NR computer program (Wolery, 1983) and the SKBU1 data base (Bruno and Puigdomenech 1989) and found to be:  $[\text{U}]_{\text{eq}} = 3.067 \text{ mg/l}$  in the range pH 6-12 (and increasing slightly to 3.198 at pH=3). In the bicarbonate solutions studied by us in Bruno et al. (1990), the calculated values of  $[\text{U}]_{\text{eq}}$  are higher (up to 4.52 mg/l in 0.1 M  $\text{NaHCO}_3$ ,  $p\text{CO}_2=0.05 \text{ atm}$ ) due to the presence of the  $\text{U}(\text{CO}_3)_5^{6-}$  complex in the thermodynamic model.

Nevertheless, we expect that other carbonate or hydrogen carbonate complexes exist in these solutions, as found by Bruno et al. (1989) and by analogy with the Th(IV) solutions studied by Östhol (1988).



### 3.2 PRECIPITATION PERIOD

The reaction taking place is assumed to be



The experimental data can also be described with an exponential equation:

$$\frac{d([U] - [U]_{\infty})}{dt} = -k_p S ([U] - [U]_{\infty})$$

or

$$[U] = [U]_{\infty} + \{([U]_0 - [U]_{\infty}) e^{-(k_p St)}\} \quad (6)$$

where  $k_p$  ( $h^{-1} m^{-2}$ ) is the rate constant for precipitation,  $[U]_{\infty}$  (mol/l) is the equilibrium solubility of the  $UO_2(s)$  solid phase, and  $[U]_0$  (mol/l) is the initial amount of uranium in the solution (which for our data presented in Bruno et al., 1990 and Bruno et al., 1988, it is equal to the initial amount of uranium in the  $U_3O_7$  coating that dissolves quickly at the beginning of the experiments).

### 3.3 DISSOLUTION OF $U_3O_7$ AND SIMULTANEOUS $UO_2$ CRYSTAL GROWTH

Equations (4) and (6) may be combined as follows:

$$[U] = ([U]_{\infty} - [U]_0) + \{[U]_{eq} (1 - e^{-(k_d [H^+]^{-0.3} St)})\} + \{([U]_0 - [U]_{\infty}) e^{-(k_p St)}\} \quad (7)$$

This equation is adequate to describe uranium concentrations as a function of time in the experiments where a fast initial dissolution of  $U_3O_7$  is followed by the precipitation of  $UO_2(cr)$  under hydrogen atmosphere.



4 RESULTS AND DISCUSSION

Equation (7) was fitted by a least squares procedure to the data published in Bruno et al. (1988) and Bruno et al. (1990) for the unknowns  $[U]_0$ ,  $[U]_\infty$ ,  $k_d$  and  $k_p$ . The fitting to the experimental data is shown in Figure 1.

## 4.1 URANIUM DISSOLVED INITIALLY

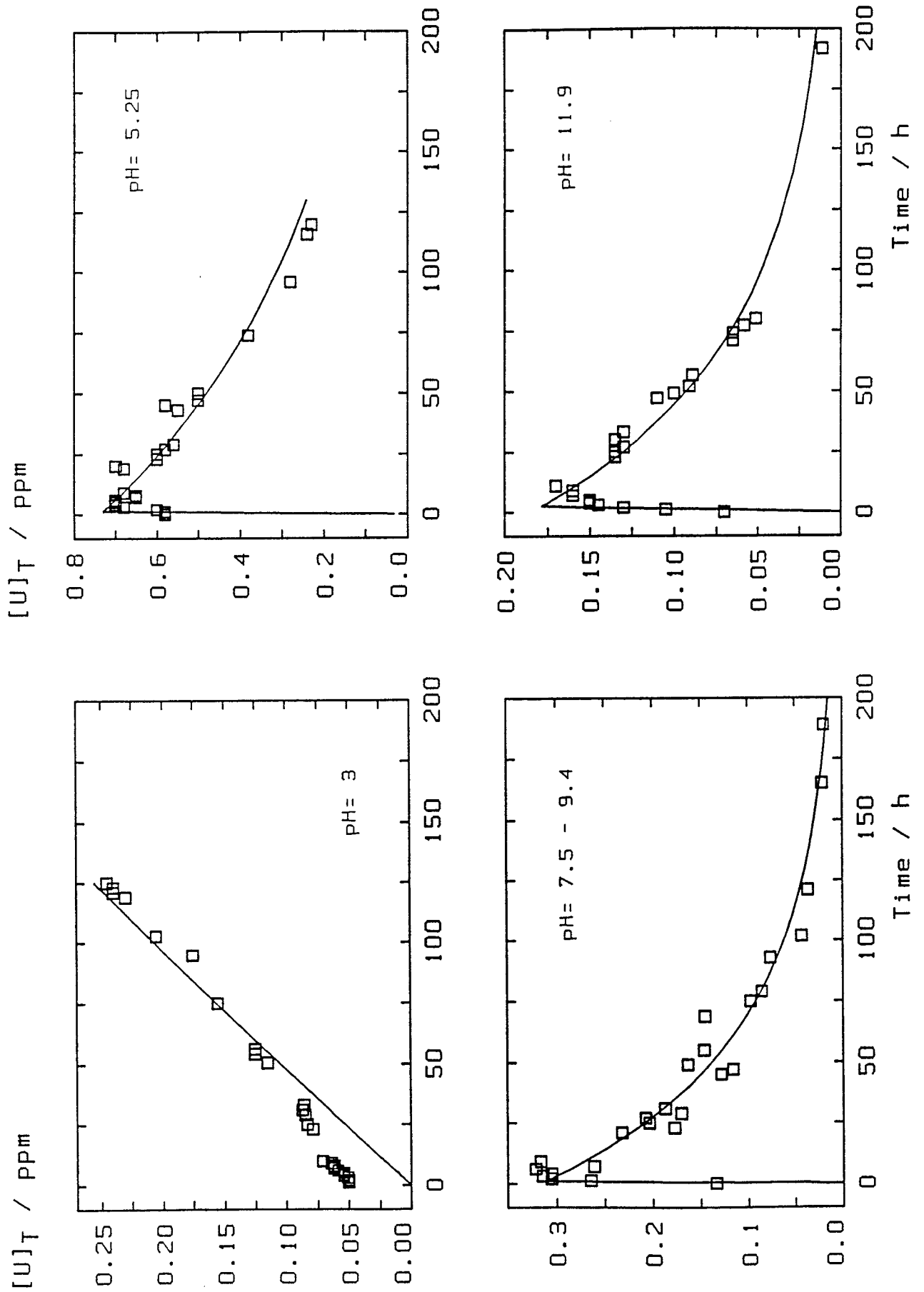
Even if care is taken during experimental procedures to keep an oxygen free atmosphere around  $UO_2(s)$ , an oxygen richer coating ( $U_3O_7$ ) is always formed on the surface of  $UO_2(s)$ . Posey-Dowty et al. (1987) for example, had to use a preleaching treatment to reduce initial uranium dissolution (in absence of oxygen) to less than 0.01 mg/l. In our experiments (Bruno et al., 1988 and Bruno et al., 1990) the total amount of uranium dissolved (equivalent to  $[U]_0$  in eqn. (7)) varied between 0.1 and 1.4 mg/l. Taking into consideration the actual surface area in our experiments (which varied between 0.24 and 2.06 m<sup>2</sup>/l) and the cubic crystal lattice parameter ( $a_0=5.470 \text{ \AA}$ , four  $UO_2$  units in the unit cell, IAEA 1965), we calculate that the depth of  $UO_2$  dissolved, i.e., the  $UO_2$ -thickness equivalent to the  $U_3O_7$ -coating initially present in the experiments, was always less than 4  $\text{\AA}$  (i.e., less than one unit cell deep).

Figure 1 Comparison of results from eqn. (7) (shown as continuous lines) with our experimental data (squares) from Bruno et al. (1988, 1990). All experiments were performed at 25°C,  $p(H_2) = (0.97 - p(CO_2)) \text{ atm}$ ,  $I=0.008 \text{ mol/l Na(ClO}_4, HCO_3)$ , except for the last<sup>2</sup> graph, where  $NaClO_4$  was not added. The same time scale has been used in all graphs in order to facilitate intercomparison between experiments, except for the last graph, where the time dependence of the data was much slower.



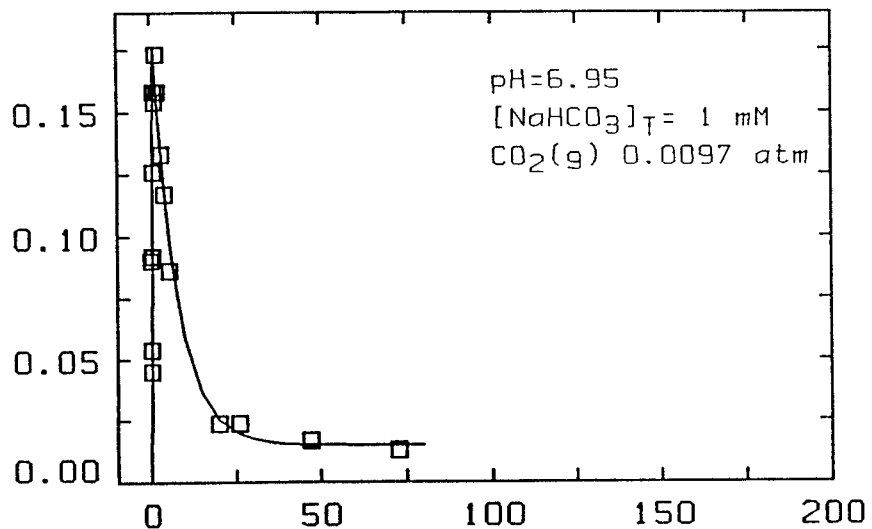


Figure 1 (continued).





$[U]_T$  / ppm



$[U]_T$  / ppm

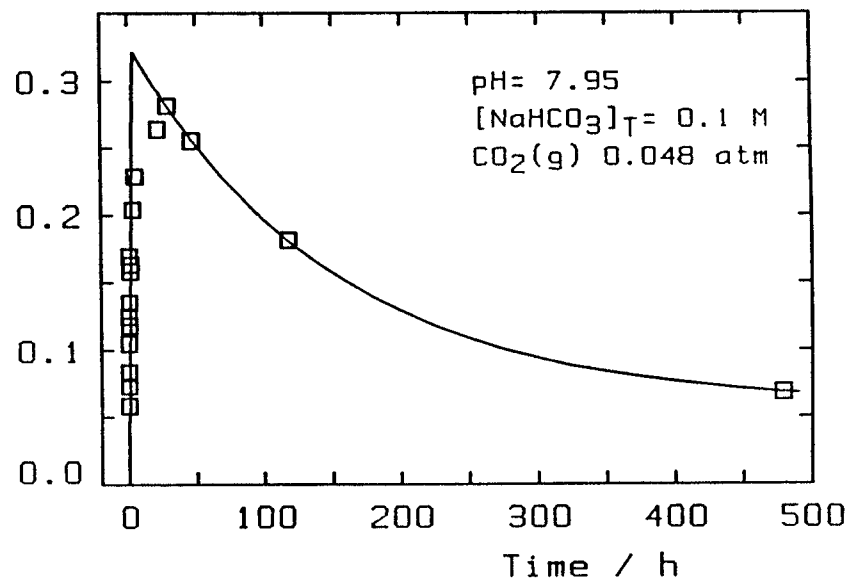
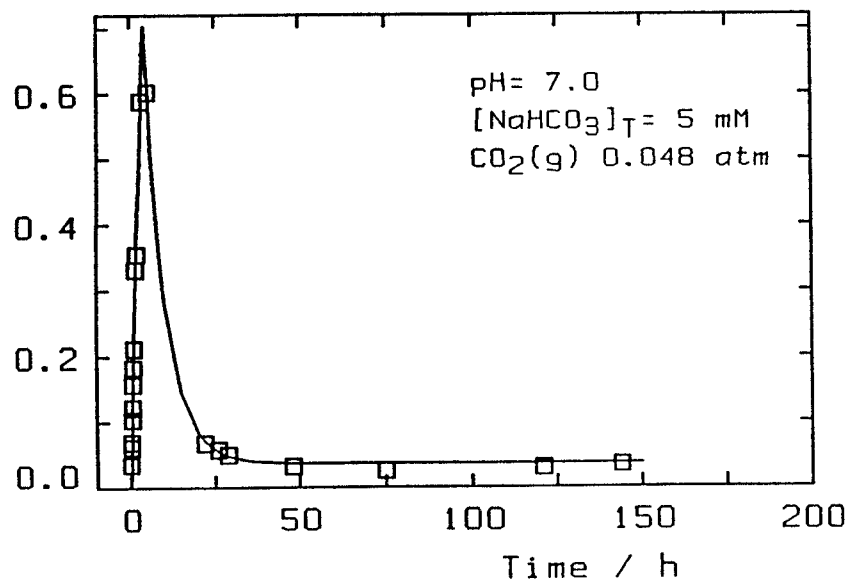
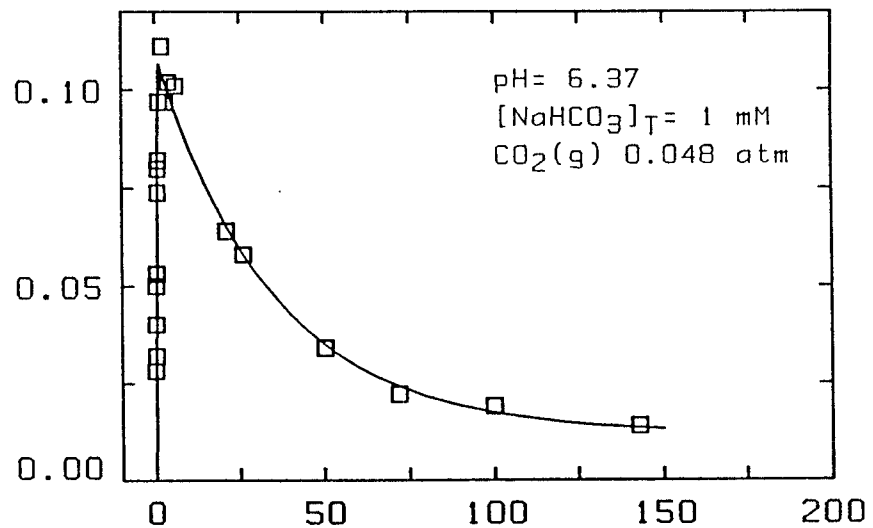
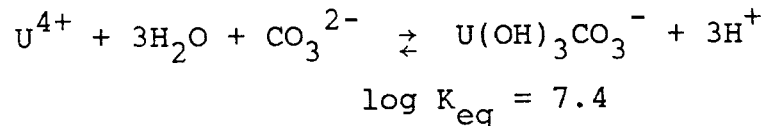


Figure 1 (continued).



#### 4.2 URANIUM SOLUBILITY

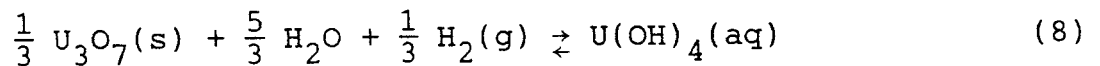
The  $\text{UO}_2$ -solubility (parameter  $[\text{U}]_\infty$  in eqn. (7)) was found to be 0.0043 mg/l for the carbonate free solutions of Bruno et al. (1988), and slightly higher (up to 0.057 mg/l in 0.1 m  $\text{NaHCO}_3$ , pH=7.95) for our experiments published in Bruno et al. (1990). This solubility level is similar to the data reported by Rai et al (1990) for amorphous U(IV) oxide. As an explanation for the increase of  $\text{UO}_2(\text{s})$  solubility in carbonate solutions, we propose (in analogy with the Th(IV)- carbonate system studied by Östhol, 1988) the following reaction,



It is quite clear from the scarcity of the data, that more experimental work is needed to elucidate both the stoichiometry and thermodynamic properties of the complex formation between U(IV) and  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  ligands.

#### 4.3 RATES OF $\text{U}_3\text{O}_7$ DISSOLUTION

The overall dissolution reaction is (c.f. eqn. (1))



$$K_{\text{eq}}^{\text{U}_3\text{O}_7} = 10^{-4.89} = \frac{[\text{U}(\text{OH})_4]_{\text{eq}}}{p(\text{H}_2)_{\text{eq}}^{1/3}} = \frac{k_{\text{d}}^{\text{U}_3\text{O}_7}}{k_{\text{p}}^{\text{U}_3\text{O}_7}} \quad (9)$$

where  $p(\text{H}_2)$  is the hydrogen partial pressure, which was kept constant within each of our experiments in Bruno et al. (1988) and Bruno et al. (1990). We will assume that the net reaction rate (dissolution minus precipitation) for reaction (8) may be written as:



$$\frac{d[U]}{dt} = S k_d^{U_3O_7} [H^+]^{-0.3} p(H_2)^{1/3} - S k_p^{U_3O_7} [H^+]^{-0.3} [U(OH)_4]$$

and using equation (9),

$$\frac{d[U]}{dt} = S k_d^{U_3O_7} [H^+]^{-0.3} p(H_2)^{1/3} \left(1 - \frac{[U(OH)_4]}{[U(OH)_4]_{eq}}\right) \quad (10)$$

A comparison between equations (10) and (4) gives:

$$k_d [U(OH)_4]_{eq} = k_d^{U_3O_7} p(H_2)^{1/3}$$

Least-squares fitting to eqn. (7) of the data by Bruno et al. (1988) in carbonate-free solutions at  $pH \geq 3$  gives  $\log(k_d/(h^{-1} m^{-2} M^{0.3})) = -2.5 \pm 0.5$ . Using the calculated value for the equilibrium  $U_3O_7$ -solubility (3.067 mg/l) and the equilibrium constant given in eqn. (9) we obtain:

$$k_d^{U_3O_7} \simeq 10^{-7.4 \pm 0.5} h^{-1} m^{-2} atm^{-1/3} M^{0.3} \quad (11)$$

and

$$k_p^{U_3O_7} = 10^{-2.5 \pm 0.5} h^{-1} m^{-2} M^{0.3}$$

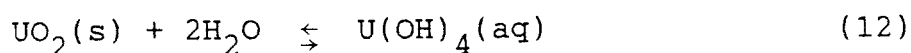
The corresponding values obtained from the experiments in bicarbonate solutions studied in Bruno et al. (1990) are  $\log(k_d/(h^{-1} m^{-2} M^{0.3})) = -3.0 \pm 0.5$ , which now gives:

$$k_d^{U_3O_7} = 10^{-7.9 \pm 0.5} ; \quad k_p^{U_3O_7} = 10^{-3.0 \pm 0.5}$$

The difference seems to be within the experimental error estimates, and based on this evidence we must conclude that the bicarbonate media used by us in Bruno et al. (1990) does not influence the  $U_3O_7$  dissolution and precipitation reactions under hydrogen atmosphere.

#### 4.4 RATES OF $UO_2$ PRECIPITATION

For the precipitation process, we consider the following reaction (c.f. eqn. (5)),







$$K_{eq}^{UO_2} = [U(OH)_4]_{eq} = \frac{k_d^{UO_2}}{k_p^{UO_2}} \quad (13)$$

The value for the equilibrium constant ( $K_{eq}^{UO_2}$ ) will depend on the crystallinity of the solid phase used in the experiments (Bruno, 1989). For our experiments in Bruno et al. (1988) and Bruno et al. (1990) we use the value of  $10^{-7.743}$  mol/l (equivalent to an uranium concentration at equilibrium of 0.0043 mg/l). The net precipitation rate for reaction (12), i.e., precipitation minus dissolution, may be written as

$$\frac{d[U]}{dt} = -k_p^{UO_2} S [U(OH)_4] \left(1 - \frac{[U(OH)_4]_{eq}}{[U(OH)_4]}\right) \quad (14)$$

which can be compared with equation (6) to give  $k_p^{UO_2} = k_p$ . The values obtained from least squares fitting of the data from Bruno et al. (1988) to equation (7) are:

$$k_p = 10^{-1.24 \pm 0.2} \text{ h}^{-1} \text{ m}^{-2} \quad (15)$$

which together with equation (13) gives,

$$k_d^{UO_2} = 10^{-8.99 \pm 0.2} \text{ mol}/(1 \text{ h m}^2)$$

which agrees fairly well with the values obtained by us using the thin-film flow reactor (Bruno et al., 1990). For the four batch experiments in carbonate solutions of Bruno et al. (1990), the values obtained of  $k_p$  varied between 0.0032 and 0.097  $\text{h}^{-1} \text{ m}^{-2}$ . The slower kinetics are found in the most concentrated bicarbonate solutions, in agreement with the data of Balaceanu et al. (1958). This might be due to the formation of a carbonate containing film which appears to be an electrical insulator (Nedes et al., 1975). However, we do not find a clear correlation between the composition of the solutions studied by us in Bruno et al. (1990), and the rate constants for  $UO_2$  precipitation, and it seems that the reaction mechanisms may be as complex as that of the oxidative dissolution of  $UO_2$  in carbonate solutions



(Johnson and Shoesmith, 1988; Sunder et al., 1982). As stated previously, the uranium(IV) speciation of these solutions is uncertain, and therefore more equilibrium and kinetic data is needed before any further conclusions can be reached about the mechanisms taking place under hydrogen atmosphere in bicarbonate solutions.

Using Arrhenius equation and the activation energy of  $E_a = 23.6$  kcal/mol for the data of Bunji and Zogovic (1958), we obtain a rate constant for the reduction of U(VI) and  $UO_2$  precipitation at 25°C of  $3.2 \cdot 10^{-8} / (h \text{ g}_{UO_2} \text{ atm})$ . The surface area was increasing during the experiments of Bunji and Zogovic (1958). Furthermore, specific surface areas for  $UO_2$  vary with the degree of crystallinity from 80 to  $0.2 \text{ m}^2/\text{g}$  (Greiling and Lieser, 1984; Bruno, 1989). If a value of  $80 \text{ m}^2/\text{g-}UO_2$  is used, a rate constant of  $k_p = 2.6 \cdot 10^{-6} (\text{h m}^2 \text{ atm})^{-1}$  is obtained for solutions containing about 0.2 mol/l  $Na_2CO_3$  and 0.4 mol/l  $NaHCO_3$ . Taking into account that the presence of bicarbonate slows down the reaction (Balaceanu et al., 1958), this rate constant agrees qualitatively well with the values of  $5.8 \cdot 10^{-2}$  (eqn. 15, without bicarbonate) and  $(3.24 \pm 0.05) \cdot 10^{-3}$  for our 0.1 mol/l  $NaHCO_3$  experiment in Bruno et al. (1990).

#### 4.5 GEOCHEMICAL MODELLING

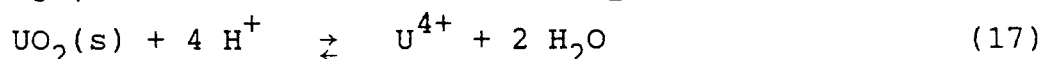
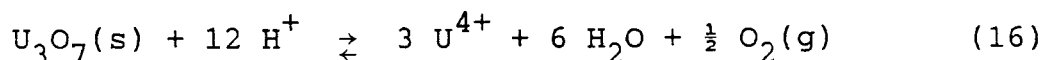
The EQ3/6 geochemical reaction path code package is a convenient tool that may be used to calculate the evolution of geochemical systems that might be actual for a spent nuclear fuel repository (Wolery, 1980 and 1983). The EQ6 code is able to solve kinetic rate laws for reactions included in its data base (Delany et al., 1986).

In the aqueous model of the EQ3/6 package, each chemical reaction includes a product (mineral or aqueous complex) and any number of defined basis species. For the



reactions considered in this work, the basis species are  $\text{H}_2\text{O}$ ,  $\text{H}^+$ ,  $\text{O}_2(\text{g})$ ,  $\text{U}^{4+}$  and  $\text{HCO}_3^-$ .

In order to simulate the dissolution of  $\text{U}_3\text{O}_7$  and the precipitation of  $\text{UO}_2$ , instead of reactions (8) and (12), we have to use the following reactions,



And therefore, new expressions for the net dissolution and precipitation reactions must be written for the EQ3/6 codes. For this purpose we have used the transition state expression (Lasaga, 1981; Delany et al., 1986). Thus for precipitation:

$$\frac{d[\text{U}]}{dt} = -k_p [\text{H}^+]^n S q_- [(1 - (Q_-/K_-)^m)] \quad (18)$$

where  $q_-$  is the kinetic activity product for the reaction products,  $Q_-$  is the ion activity product of the mineral precipitation reaction, and  $K_-$  is the equilibrium constant for the precipitation reaction (c.f. Delany et al., 1986). Equation (18) in its form is essentially equivalent to equations (10) and (14).

We have simulated some of the experimental data reported by us in Bruno et al. (1988) with the EQ3/6 codes and eqn. (18) (and its complementary for dissolution reactions). The input parameters are as follows: for reaction (17) we need the values of  $\log(K_{sp}) = -2.4433$  (equivalent to a  $\text{UO}_2$ -solubility of 0.0043 mg/l) and  $k_p = 1.95 \cdot 10^{-9} / (\text{s cm}^2)$  (c.f. eqn. 15). For reaction (16) we used the value of  $(k_d \cdot [\text{H}^+]^{-0.3}) = 1.93 \cdot 10^{-13}$  (c.f. eqn. 11,  $\text{pH}_{\text{diss}} = 7.5$ ) and an initial amount of  $\text{U}_3\text{O}_7(\text{c})$  ( $[\text{U}]_0$  in eqn. 7) equal to 0.4414  $\mu\text{mol/l}$  (as found by least-squares fitting of the experimental data of Figure 2 to eqn. 7).



The results are presented in Figure 2, which illustrates the potential of the EQ3/6 codes to simulate problems related with uranium geochemistry.

Unfortunately, the EQ6-code incorporates a somewhat primitive integration procedure which performs poorly on stiff kinetic systems, and computer execution times for this kind of problems tend to be very large on slow computers. For example, an EQ6-run from reaction time  $t=159.7$  h, to  $t=200$  h, requires a computer execution time of 9 h 16 min on a VAX-750. The same run, however, requires only an execution time of 0.3 secs on a CONVEX C210. Therefore, without access to a fast mainframe computer, the EQ6 program is almost useless for kinetic calculations.

5

#### ACKNOWLEDGMENT

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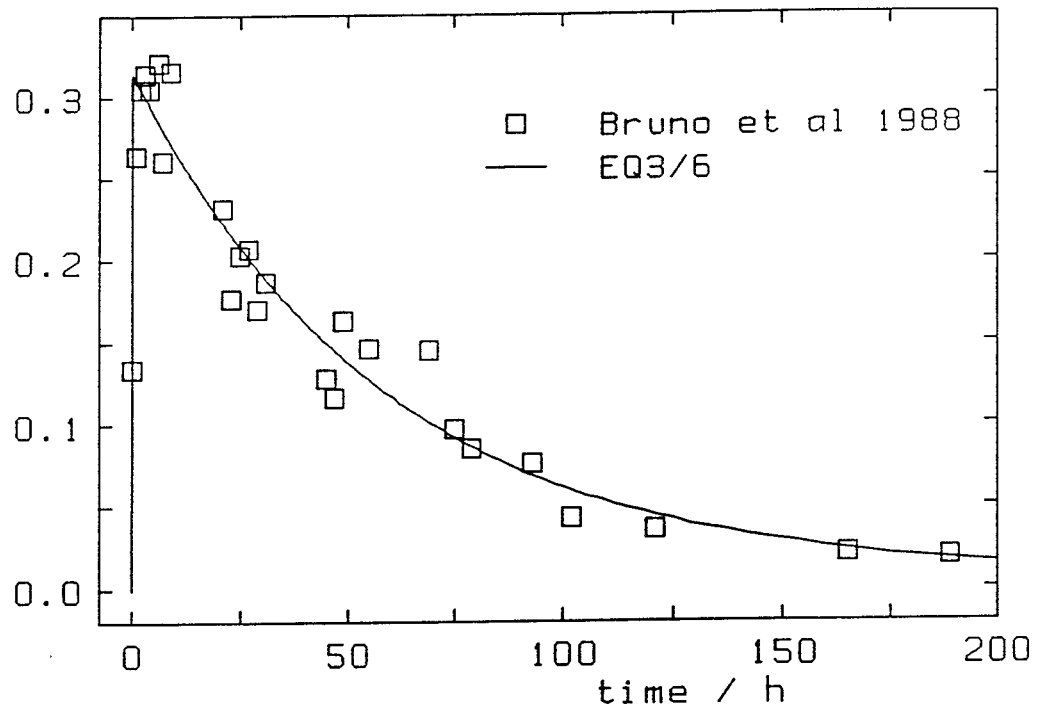
$[U]_{\text{tot}} / (\text{mg/l})$ 

Figure 2 Results from EQ3/6 calculations (continuous line) simulating the displayed data (squares) from Bruno et al. (1988). Experimental data for pH=8.5, 8 mM  $\text{NaClO}_4$ ,  $p(\text{H}_2)=0.97$  atm, amount of  $\text{UO}_2$ : 1.2 g/l (surface area:  $0.2412 \text{ m}^2$ ).



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## Annual Reports

1977-78

TR 121

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Summaries. Stockholm, May 1979.

1979

TR 79-28

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Summaries. Stockholm, March 1980.

1980

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1981

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1982

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1984

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TR 87-33

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1988

TR 88-32

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### List of SKB Technical Reports 1990

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<sup>2</sup> SKB AB

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#### **Statistical estimation and stochastic simulation using PROPER**

Lars Lovius<sup>1</sup>, Sven Norman<sup>1</sup>, Nils Kjellbert<sup>2</sup>

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<sup>2</sup> SKB AB

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University of Gothenburg, Department of General and Marine Microbiology, Gothenburg  
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Yngve Albinsson, Birgit Sätmark, Ingemar Engkvist, W. Johansson  
Department of Nuclear Chemistry, Chalmers University of Technology, Gothenburg  
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R S Forsyth, T J Jonsson, O Mattsson  
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**Radiolytically induced oxidative dissolution of spent nuclear fuel**

Lars Werme<sup>1</sup>, Patrik Sellin<sup>1</sup>, Roy Forsyth<sup>2</sup>  
<sup>1</sup> Swedish Nuclear Fuel and waste Management Co (SKB)  
<sup>2</sup> Studsvik Nuclear  
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Ulla Bergström, Sture Nordlinder  
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H D Schorscher<sup>1</sup>, M E Shea<sup>2</sup>  
<sup>1</sup> University of Sao Paulo  
<sup>2</sup> Battelle, Chicago  
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**I: Osamu Utsumi uranium mine**

N Waber<sup>1</sup>, H D Schorscher<sup>2</sup>, A B MacKenzie<sup>3</sup>, T Peters<sup>1</sup>  
<sup>1</sup> University of Bern  
<sup>2</sup> University of Sao Paulo  
<sup>3</sup> Scottish Universities Research & Reactor Centre (SURRC), Glasgow  
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M E Shea  
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D C Holmes<sup>1</sup>, A E Pitty<sup>2</sup>, R Noy<sup>1</sup>  
<sup>1</sup> British Geological Survey, Keyworth  
<sup>2</sup> INTERRA/ECL, Leicestershire, UK  
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**Chemical and isotopic composition of groundwaters and their seasonal variability at the Osamu Utsumi and Morro do Ferro analogue study sites, Poços de Caldas, Brazil**

D K Nordstrom<sup>1</sup>, J A T Smellie<sup>2</sup>, M Wolf<sup>3</sup>  
<sup>1</sup> US Geological Survey, Menlo Park  
<sup>2</sup> Conterra AB, Uppsala  
<sup>3</sup> Gesellschaft für Strahlen- und Umweltforschung (GSF), Munich  
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**Natural radionuclide and stable element studies of rock samples from the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil**

A B MacKenzie<sup>1</sup>, P Linsalata<sup>2</sup>, N Miekeley<sup>3</sup>,  
J K Osmond<sup>4</sup>, D B Curtis<sup>5</sup>

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<sup>2</sup> New York Medical Centre

<sup>3</sup> Catholic University of Rio de Janeiro (PUC)

<sup>4</sup> Florida State University

<sup>5</sup> Los Alamos National Laboratory

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**Natural series nuclide and rare earth element geochemistry of waters from the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil**

N Miekeley<sup>1</sup>, O Coutinho de Jesus<sup>1</sup>,  
C-L Porto da Silveira<sup>1</sup>, P Linsalata<sup>2</sup>, J N Andrews<sup>3</sup>,  
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<sup>3</sup> University of Bath

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**Chemical and physical characterisation of suspended particles and colloids in waters from the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil**

N Miekeley<sup>1</sup>, O Coutinho de Jesus<sup>1</sup>,  
C-L Porto da Silveira<sup>1</sup>, C Degueldre<sup>2</sup>

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**Microbiological analysis at the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil**

J West<sup>1</sup>, A Vialta<sup>2</sup>, I G McKinley<sup>3</sup>

<sup>1</sup> British Geological Survey, Keyworth

<sup>2</sup> Uranio do Brasil, Poços de Caldas

<sup>3</sup> NAGRA, Baden, Switzerland

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**Testing of geochemical models in the Poços de Caldas analogue study**

J Bruno<sup>1</sup>, J E Cross<sup>2</sup>, J Eikenberg<sup>3</sup>, I G McKinley<sup>4</sup>,  
D Read<sup>5</sup>, A Sandino<sup>1</sup>, P Sellin<sup>6</sup>

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<sup>5</sup> Atkins ES, Epsom, UK

<sup>6</sup> Swedish Nuclear and Waste Management Co (SKB), Stockholm

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TR 90-21

**Testing models of redox front migration and geochemistry at the Osamu Utsumi mine and Morro do Ferro analogue sites, Poços de Caldas, Brazil**

J Cross<sup>1</sup>, A Haworth<sup>1</sup>, P C Lichtner<sup>2</sup>,  
A B MacKenzie<sup>3</sup>, L Moreno<sup>4</sup>, I Neretnieks<sup>4</sup>,  
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<sup>6</sup> Atkins ES, Epsom, UK

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**Near-field high temperature transport: Evidence from the genesis of the Osamu Utsumi uranium mine analogue site, Poços de Caldas, Brazil**

L M Cathles<sup>1</sup>, M E Shea<sup>2</sup>

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<sup>2</sup> Battelle, Chicago

December 1990

TR 90-23

**Geochemical modelling of water-rock interactions at the Osamu Utsumi mine and Morro do Ferro analogue sites, Poços de Caldas, Brazil**

D K Nordstrom<sup>1</sup>, I Puigdomenech<sup>2</sup>, R H McNutt<sup>3</sup>

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<sup>2</sup> Studsvik Nuclear, Sweden

<sup>3</sup> McMaster University, Ontario, Canada

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**The Poços de Caldas Project: Summary  
and implications for radioactive waste  
management**

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