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# Dissolution of unirradiated $\text{UO}_2$ fuel in synthetic saline groundwater

Experimental methods and preliminary results

Kaija Ollila

VTT Chemical Technology

December 1997

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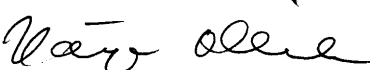
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Tiivistelmä – Abstract <p>This report presents the experimental methods and preliminary results obtained from dissolution experiments of unirradiated UO<sub>2</sub> pellets in synthetic saline reference groundwater (I = 0.5 M). The composition of the synthetic groundwater is based on groundwater studies within the site investigations of spent fuel disposal in the Olkiluoto area. Redox conditions include oxic (air-saturated) and anoxic (anaerobic glove box, N<sub>2</sub>). An attempt is made to adjust the Eh of the aqueous phase under N<sub>2</sub> atmosphere by the addition of natural redox species of groundwater, e.g. S<sup>2-</sup>, Fe<sup>2+</sup>, in order to keep uranium predominantly in the tetravalent state. The earlier stability tests have shown that low Eh values, -300...-200 mV, can be maintained for a time period of several months in Allard groundwater with these redox species. Under these conditions it is expected that dissolved uranium is partially at the tetravalent state. The release of uranium is measured during static batch dissolution experiments at 25°C. The ratio of pellet surface area to water volume is varied.</p> <p>Under oxic (air-saturated) conditions, uranium would seem to attain a steady state in saline groundwater at a lower level (4·10<sup>-6</sup> mol/l) than in Allard groundwater (2·10<sup>-5</sup> mol/l). The modelling calculations (EQ3/6) predict that uranyl silicates and CaUO<sub>4</sub> are potential U-bearing secondary phases in saline groundwater.</p> <p>Under anoxic conditions, the addition of redox species lowers the uranium concentrations in the aqueous phase. The effect is greatest in the amounts of uranium measured in the filtered samples. The uranium concentrations at low Eh in the filtered samples are close to the theoretical solubility of UO<sub>2</sub>.</p>	
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Tiivistelmä – Abstract <p>Tässä raportissa on esitetty kokeelliset menetelmät ja alustavat tulokset säteilyttämättömien UO<sub>2</sub>-pellettien liukenemiskokeista synteettisessä suolaisessa referenssipohjavedessä (I = 0.5 M). Suolaisen referenssiveden koostumus perustuu pohjavesitutkimuksiin Olkiluodossa. Redox-olosuhteet vaihtelevat hapettavista (ilmakyllästetyt) pelkistäviin (anaerobinen kaappi, N<sub>2</sub>). Uraanin suhteen pelkistävät olosuhteet pyritään aikaansaamaan lisäämällä vesifaasiin luonnon pohjaveden redox-spesieksiä, esim. S<sup>2-</sup>, Fe<sup>2+</sup>. Aikaisemmat testit ovat osoittaneet, että tällä tavalla voidaan ylläpitää matala Eh, -300...-200 mV, useita kuukausia Allardin vedessä typpi-atmosfäärissä. Näissä redox-olosuhteissa uraanin odotetaan olevan ainakin osittain U(IV) -hapetustilalla. Uraanin vapautumista UO<sub>2</sub>-pelleteistä mitataan käyttäen staattista batch-liukenemiskoemenetelmää (25°C). Pelletin pinta-alan ja veden tilavuuden suhdetta vaihdellaan.</p> <p>Hapettavissa (ilma-) olosuhteissa uraanin määrä suolaisessa referenssipohjavedessä näyttäisi stabiloituvan matalampaan arvoon (4·10<sup>-6</sup> mol/l) kuin Allardin vedessä (2·10<sup>-5</sup> mol/l). Mallinnuslaskujen (EQ3/6) mukaan uranyylisilikaatit ja CaUO<sub>4</sub> ovat mahdollisia uraanin sekundaarisia faaseja referenssivedessä.</p> <p>Hapettomissa olosuhteissa (N<sub>2</sub>) redox-spesies -lisäykset pienentävät uraanin vapautumista vesifaasiin. Vaikutus on suurin suodatetuista näytteistä mitatuissa uraanipitoisuuksissa. Matalassa Eh:ssa ne ovat lähellä UO<sub>2</sub> :n teoreettista liukoisuutta.</p>	
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## Foreword

Within the European Commission Nuclear Fission Safety Program (1994 - 1998) the research project 'Source term for performance assessment of spent fuel as a waste form' (Contract No. F14W - CT95 - 0004) has jointly been started by Forschungszentrum Karlsruhe, (FZK.INE, Germany), Empresa Nacional de Residuos Radioactivos (ENRESA, Spain), Commissariat a l' Energie Atomique, Direction du Cycle du Combustible, Service de Confinement des Déchets (CEA/Valrho, France), Freie Universität Berlin, FB Chemie (FU, Germany), Institute for Transuranium Elements (JRC-ITU, Germany), Studiezentrum voor Kernenergie, Waste & Disposal (SCK.CEN, Belgium), Studsvik Material AB, (STUDMAT, Sweden) and Technical Research Centre of Finland, Chemical Technology (VTT, Finland). B. Grambow from Forschungszentrum Karlsruhe is the coordinator of the project. The Finnish studies are funded by the European Commission and Posiva Oy. The contact persons for Posiva Oy are Margit Snellman and Jukka-Pekka Salo. The contact person for VTT Chemical Technology is Kaija Ollila.

## 1 Introduction

The spent fuel from Finnish nuclear power plants is planned to be disposed of in a repository to be constructed at a depth of about 500 meters in crystalline granitic bedrock. Under reducing conditions normally prevailing in deep granitic groundwater,  $\text{UO}_2$  (or  $\text{U}_4\text{O}_9$ ), the main component of the spent fuel, is the stable uranium solid and has a very low solubility or dissolution rate. Under disposal conditions the stability of spent fuel depends on the near-field chemical conditions, the effects of radiolysis ( $\alpha$ ), canister materials (steel, copper) and their corrosion products, backfill materials (bentonite) and the composition of groundwater. The dissolution rate of  $\text{UO}_2$  is strongly affected by the redox conditions, especially by the availability and the nature of oxidants from  $\alpha$ -radiolysis. The composition of granitic groundwater, which will come into contact with spent fuel, depends on the geological formation and the interactions with bentonite. The presence of Si and Ca in groundwater has been observed to affect the dissolution rate of unirradiated  $\text{UO}_2$ . Gray and Wilson /1995/ showed that the addition of Si and Ca to a bicarbonate solution could reduce the dissolution rate up to 100 times.

This report presents the experimental methods and preliminary results obtained from dissolution experiments of unirradiated  $\text{UO}_2$  pellets in synthetic saline reference groundwater. Redox conditions include oxalic (air-saturated) and anoxic (anaerobic glove box,  $\text{N}_2$ ) conditions. An attempt is made to control the Eh of the aqueous phase under  $\text{N}_2$  atmosphere by the addition of the natural redox species of groundwater ( $\text{S}^{2-}$ ,  $\text{Fe}^{2+}$ ) in order to keep uranium predominantly in the tetravalent state. Earlier analyses of uranium oxidation state /Ollila et al 1996/ have shown that in synthetic groundwater after contact with unirradiated  $\text{UO}_2$  pellets under similar conditions dissolved uranium was mainly in the hexavalent state in the absence of redox species. Tests to investigate the effect of metallic iron were started. A preliminary comparison of the experimental data is made with the solubilities calculated using the geochemical code EQ3/6 in order to evaluate solubility (steady state) limiting factors. The solubilities are based on the databases of NEA Thermochemical Database Project (TDB) /Grenthe et al 1992/, and of the Lawrence Livermore National Laboratory (composite database) /Wolery 1992/.

This work is a part of the EU-R&D program 1994-1998: Nuclear Fission Safety, entitled '*Source term for performance assessment of spent fuel as a waste form*'. The contracted combined experimental and modelling work aims at source term quantification for evaluating spent fuel performance within the engineered barriers of the disposal system in granite, clay and salt formation. The program is directed 1) a basic understanding of the mechanism and quantification of rates of fuel matrix dissolution in the three geological environments both under oxidizing and reducing conditions, 2) an understanding and quantification of solubility, sorption and coprecipitation equilibria for individual radionuclides, 3) an understanding of the effect of near field materials on reaction rates and radionuclide release. The objective is to develop models



(thermodynamics on actinides, geochemical reaction path, radiolysis, mechanism of fuel dissolution) for assessing radionuclide release from spent fuel. The experimental studies include four materials (UO<sub>2</sub>, SIMFUEL, spent UO<sub>2</sub>-fuel, burn-up to 50 MWd/kgU and spent MOX-fuel) under a variety of conditions.

The research to be carried out at VTT Chemical Technology is focused on the effects of granitic water composition (saline, fresh) and redox conditions on UO<sub>2</sub> solubility and dissolution mechanisms. The effects of near-field materials, bentonite and metallic iron will be studied. The experiments are performed using unirradiated UO<sub>2</sub> fuel, both in pellet and powdered form. Dissolution rates are studied by tests at low S/V. Maximum solution concentrations of uranium and information on secondary alteration products are provided by the dissolution tests at high S/V. Precipitation tests will be performed to give stable solid phases.

## 2 Methods of experiments

### 2.1 Materials

All the dissolution experiments of this report have included the use of unirradiated sintered polycrystalline UO<sub>2</sub> fuel in pellet form. The pellets had an average mass of 4.8 grams and a geometrical surface of  $3.3 \cdot 10^{-4} \text{ m}^2$ . A predissolution period was carried out for the pellets both under oxic and anoxic conditions, in an attempt to remove a more soluble oxidized layer that might have been present on the surface due to the earlier manipulation of the pellets in air. The composition of water was similar to that used later in the dissolution experiments.

Metallic iron was added as iron chips (Baker Chemicals, reducing power as Fe 100.3 %).

### 2.2 Synthetic saline groundwater

The composition of the synthetic water is based on groundwater studies within the site investigations of spent fuel disposal in the Olkiluoto area, and the synthetic saline water represents the groundwater found at a depth of 600 m. The saline Na-Ca-Cl water has a low alkalinity. The ionic strength is 0.5 M. The composition of the synthetic water was planned separately for air-saturated and anoxic (N<sub>2</sub> atmosphere) conditions with the help of EQ3/6 modelling and stability tests /Vuorinen et al 1997/. Table 2-1 gives the compositions. Redox species (S<sup>2-</sup>, Fe<sup>2+</sup>) were added to the waters under anoxic conditions, see the following paragraph.

normally stays below 1 ppm (0.1...0.5 ppm). The carbon dioxide content is  $\approx 0.1$  ppm /Vuorinen et al 1997/. The experimental vessels were kept tightly closed during the experiments. All the samplings were made inside the glove box.

An important parameter to be considered is the Eh of the aqueous phase. Under anaerobic ( $N_2$ ) conditions it may vary from slightly oxidizing to reducing depending on the composition of the gas phase (trace  $O_2$ ,  $H_2$ ) and the composition of the aqueous phase. The complex formation of uranium with carbonate probably affects the relative stabilities of the oxidation states. This makes U(VI) stable in a more reducing redox regime than in the absence of carbonate, increasing solubility /SKI Project 1991/. Earlier  $UO_2$  dissolution studies in synthetic groundwater (Allard) in  $N_2$  atmosphere have shown that dissolved uranium was mainly ( $> 90\%$ ) at the U(VI) state /Ollila et al 1996/. Obviously, the trace oxygen content in the atmosphere of the box is enough to cause slightly oxidizing conditions for uranium. The steady-state concentrations of uranium were nevertheless low ( $2 \cdot 10^{-8}$  M).

The earlier tests in Allard groundwater /Ollila 1997/ have shown that lower Eh values can be achieved by the addition of redox species of natural groundwater,  $Fe^{2+}$ ,  $S^{2-}$ . The Eh values ranged from -300 ... -200 mV (1 ppm  $Fe^{2+}$ , 1-5 ppm  $S^{2-}$ ). The Eh value for synthetic groundwater (saline) in the absence of redox species fluctuates. Values from -20 ... +130 mV have been measured. Based on the tests in Allard groundwater a series of redox conditions were selected for the dissolution experiments in synthetic saline groundwater, see Table 2-2. The pH and Eh are measured for groundwater samples without  $UO_2$  pellets under similar conditions in order to follow the stability of the synthetic groundwater, parallel with the dissolution experiments of long duration. During the first 3-4 months there are minor changes, see Table 2-2. The concentrations of redox species represent the total amounts of  $S^{2-}$  and  $Fe^{2+}$ , that were added to the solutions. It is probable that they are immediately partially oxidized. The analyses of  $S^{2-}$ ,  $Fe^{2+}$  and  $Fe^{3+}$  contents will give information about this. So far there is no analysed data available.

## 2.4 Dissolution procedure

The method of the dissolution experiments is, both under oxic and anoxic conditions, a static batch dissolution procedure.  $UO_2$  pellets are immersed in equilibrated synthetic groundwater in polyethylene bottles. The ratio of pellet surface area (geometric) to water volume (S/V) varies from 0.66...19.8  $m^{-1}$ , see Table 2-2. Small aliquots are taken (0.5 ... 2 ml) periodically for further analysis for uranium. These aliquots are replaced with fresh water which has similar composition, in order to keep the water volume same. The amounts of uranium in unfiltered, microfiltered (membranes of 0.45  $\mu m$ , selected samplings) and ultrafiltered (nominal cut-off value of 50 000 M, selected samplings) samples are measured as a function of time.

Table 2-2. The experimental conditions.

Test series code	Atmosphere	S/V <sup>1)</sup> [m <sup>-1</sup> ]	Redox species addition	Eh [mV]	pH
OL-SR	N <sub>2</sub>	0.66	no redox species	-20...+130 <sup>2)</sup>	8.3...8.1 <sup>2)</sup>
OL-SR-S-Fe	“	“	1 ppm S <sup>2-</sup> , 0.01 ppm Fe <sup>2+</sup>	-213...-208 <sup>2)</sup>	8.8...8.7 <sup>2)</sup>
OL-SR-Fe	“	“	1 ppm Fe <sup>2+</sup>	-208...-170 <sup>2)</sup>	8.2...8.0 <sup>2)</sup>
OL-SR-S1	“	“	3 ppm S <sup>2-</sup>	-255...-255 <sup>2)</sup>	9.1...9.2 <sup>2)</sup>
OL-SR-S3	“	“	5 ppm S <sup>2-</sup>	-279...-258 <sup>2)</sup>	9.6...9.5 <sup>2)</sup>
OL-SR-H1	“	19.8	no redox species	-20...+130 <sup>2)</sup>	8.3...8.1 <sup>2)</sup>
OL-SR-H3	“	“	1 ppm S <sup>2-</sup> , 0.01 ppm Fe <sup>2+</sup>	-213...-208 <sup>2)</sup>	8.8...8.7 <sup>2)</sup>
OL-SR-H5	“	“	no redox species metallic Fe; (5 grams iron chips/ 50 ml of solution)	-	9.3...8.8 <sup>3)</sup>
OL-SR-H7	“	“	1 ppm S <sup>2-</sup> , 0.01 ppm Fe <sup>2+</sup> metallic Fe; (5 grams iron chips/ 50 ml of solution)	-	9.4...9.2 <sup>3)</sup>
OL-SO-U1	air	0.66	-	-	7.2...7.1 <sup>4)</sup>
OL-SO-U11	“	1.98	-	-	7.2...7.1 <sup>4)</sup>
OL-SO-U111	“	19.8	-	-	7.2...7.1 <sup>4)</sup>

- 1) *S/V is based on the geometric surface area of the pellet*
- 2) *Eh<sub>1</sub>...Eh<sub>2</sub>, pH<sub>1</sub>...pH<sub>2</sub>, Eh and pH measured for parallel groundwater samples (without UO<sub>2</sub> pellets) after two weeks' and four months' period from the beginning of the dissolution tests under anaerobic conditions, respectively.*
- 3) *pH<sub>1</sub>...pH<sub>2</sub>, pH measured in the experimental vessel (with UO<sub>2</sub> pellets) after two weeks' and three months period from the beginning of the dissolution tests under anaerobic conditions.*
- 4) *pH<sub>1</sub>...pH<sub>2</sub>, pH measured for parallel groundwater samples (without UO<sub>2</sub> pellets) at the beginning of the dissolution tests and after three months period.*

For the experiments under anoxic conditions, the synthetic groundwater was prepared as follows: Na- and Ca-chlorides were dissolved in deionized water under atmospheric conditions. The solution was deaerated with  $N_2$ , and transferred into the glove box. The rest of the components were pipetted from the pre-prepared deaerated stock solutions to the Na-Ca-Cl solution in the glove box. The pH of the final solution was adjusted with 0.01 N NaOH to 8.3. The solution was allowed to equilibrate in the glove box for at least one week. The pH was readjusted if necessary. The additions of the redox species were made ten days before the initiation of the tests. The stock solutions for the  $S^{2-}$  and the  $Fe^{2+}$  were prepared by dissolving  $Na_2S \cdot 9H_2O$  and  $FeCl_2 \cdot 4H_2O$  in deaerated deionized water in the glove box, respectively. A suitable volume of these solutions was added to synthetic groundwater. Only fresh stock solutions were used.

Prior to the start of the dissolution experiments, a predissolution was carried out for the pellets both under oxic and anoxic conditions. One pellet (alternatively 3 or 6 pellets) was immersed in 50 ml of aerated and deaerated synthetic saline groundwater in bottles made of polypropylene, respectively. The duration of this predissolution period, with changing of water every two days, was 15...17 days. The amount of uranium released into the water phase per day was followed. As the dissolution rate stabilized the predissolution was finished.

## 2.5 Analytical methods

The uranium contents in the aqueous phase were analysed by ICP-MS. The detection limit of uranium with this method is lowered by the salinity of synthetic groundwater, because the samples must be diluted by a factor 30. The detection limit of uranium is  $1...2 \cdot 10^{-9}$  M (conventional sample nebulization). The uranium contents of the latest sampling in the anoxic series with the redox control (Figure 3-5, p. 13) were analysed by ICP-MS with a high-efficiency sample nebulization device (Mistral), which improves the detection limit for uranium by one order of magnitude. The microfiltration of the samples was carried out using the Millex-HV 0.45  $\mu m$  filter units of Millipore.

The pH and Eh were measured with an Orion Research expandable ion analyser. A platinum electrode (Yokogawa) was used as redox electrode in combination with a Ag/AgCl reference electrode (Yokogawa). The reference electrode is filled with a gelled electrolyte solution. This type of electrode proved to be practical under dry anaerobic conditions, because refilling is not necessary.

### 3 Preliminary results

#### 3.1 Oxidic conditions

A general result from the dissolution experiments of spent fuel and unirradiated  $\text{UO}_2$  pellets performed in the presence of atmospheric oxygen is that the solution concentration of uranium attains a steady state after some time period /Forsyth and Werme 1992, Grambow 1989/. In dissolution experiments of unirradiated  $\text{UO}_2$  pellets in synthetic Allard groundwater (granitic) under air-saturated conditions /Ollila 1995/, a constant value for the solution concentration of uranium was reached after 500 days' period at a concentration of  $1 - 2 \cdot 10^{-5}$  mol/l, which is in good agreement with the results of spent fuel dissolution experiments by Forsyth and Werme /1992/. A low S/V ratio ( $1.8 \text{ m}^{-1}$ , geometric) was used in this test series. In the synthetic bentonite groundwater, which simulates the effects of bentonite in granitic groundwater, a steady state was attained at a concentration of one order of magnitude lower,  $1 \cdot 10^{-6}$  mol/l. The main differences between the synthetic groundwaters were the higher contents of  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$  and  $\text{Si}^{4+}$  in bentonite groundwater. In deionized water, the corresponding steady-state value was  $3 - 5 \cdot 10^{-6}$  mol/l.

The results of the predissolution period are given in Figure 3-1, expressed as uranium dissolution rates. The dissolution rate decreased during this period (17 days) by one order of magnitude, which shows the presence of a more soluble oxidized surface layer. The rate levels out after ten days at about  $1.0 \cdot 10^{-5}$  mol  $\text{m}^{-2} \text{ d}^{-1}$ .

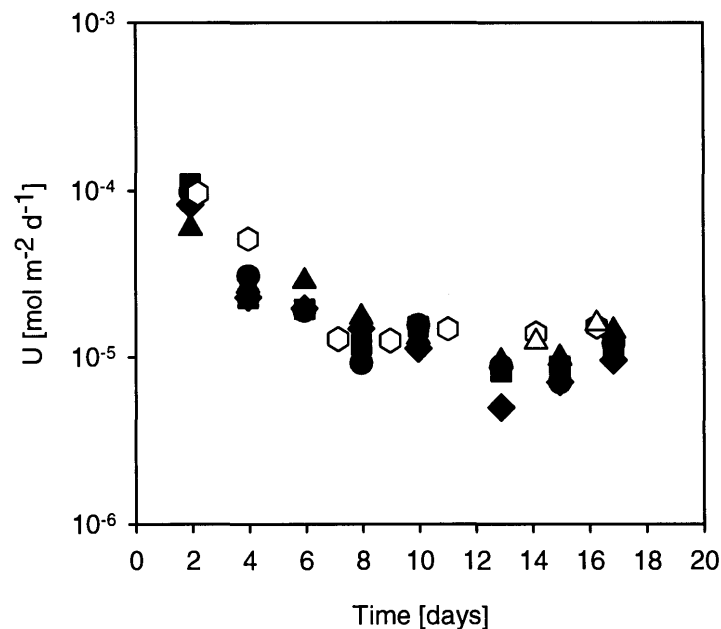


Figure 3-1. Dissolution rates of uranium from  $\text{UO}_2$  pellets during the predissolution period under air-saturated conditions. The rates were calculated per the geometric surface area of the pellet (filled symbols:  $S/V = 6.6 \text{ m}^{-1}$ , open symbols:  $S/V = 39.6 \text{ m}^{-1}$ ).

After the predissolution period the pellets were immersed in pre-equilibrated synthetic saline groundwater and the dissolution experiments were initiated. Three different S/V ratios, 0.66, 1.98, 19.8 m<sup>-1</sup>, were used. The purpose of the lowest ratio is to prevent the saturation of possible secondary uranium phases in order to measure dissolution rates. The middle value is similar to the one used earlier in the experiments in the other synthetic granitic groundwaters with lower salinity (Allard groundwater, bentonite groundwater) /Ollila 1995/. The higher S/V ratios aim at studying solubility and the formation of the secondary alteration phases of uranium. An additional experiment with a high S/V ratio (1000 m<sup>-1</sup>) will be initiated later.

The concentrations of uranium measured in the aqueous phase during the initial stage of dissolution (80 days) are shown in Figure 3-2, presented per water volume unit in the upper Figure and per surface area unit in the lower Figure. The solution concentration of uranium increases linearly at lower S/V values (0.66, 1.98 m<sup>-1</sup>). The rate of dissolution of uranium is constant,  $3.2 \cdot 10^{-6}$  mol m<sup>-2</sup> d<sup>-1</sup>, and proportional to surface area. At the highest S/V value (19.8 m<sup>-1</sup>), the solution concentration increases in the same way up to 30 days' contact time, but the dissolution rate seems to slow down after that. There is only a small increase in the solution concentration between the last two samplings. It probably begins to level out. The concentrations in Figure 3-2 represent unfiltered samples. Parallel samples with microfiltration were taken in the last sampling (80 days). There were no clear differences.

Figure 3-3 gives a preliminary comparison with the theoretical solubilities of uranium in equilibrium. The details of the modelling (EQ3/6) are presented in App. 1. In the solution concentration of uranium,  $3.6 \cdot 10^{-6}$  mol/l, there are three supersaturated phases of uranium: CaUO<sub>4</sub> (NEAU, COMU), soddyite (COMU) and haiweeite (COMU) in synthetic saline groundwater. The solubilities of these phases are 1-2 orders of magnitude lower, see App. 1. Schoepite is not saturated. Additionally, the solubility of uranium was calculated at the U<sub>3</sub>O<sub>7</sub>/U<sub>3</sub>O<sub>8</sub> redox potential, see Figure 3-3. This simulates the situation, in which the controlling factor is the redox potential at the UO<sub>2</sub> surface rather than the redox potential of the bulk solution (Eh) /Grambow 1989/. In the EQ3/6 simulation the mineral equilibrium between different uranium oxides fixes the oxygen partial pressure. The redox potential in this case is considerably lower than the redox potential given by the oxygen partial pressure (App. 1). In Allard groundwater, the steady-state solution concentration of uranium,  $1 - 2 \cdot 10^{-5}$  mol/l, under air-saturated conditions was close to the calculated solubility of uranium at the U<sub>3</sub>O<sub>7</sub>/U<sub>3</sub>O<sub>8</sub> redox potential /Ollila 1995/. In saline groundwater, the uranium would seem to stabilize at a lower concentration, which is also close to the solubility at this redox potential. More experimental data are needed to confirm this.

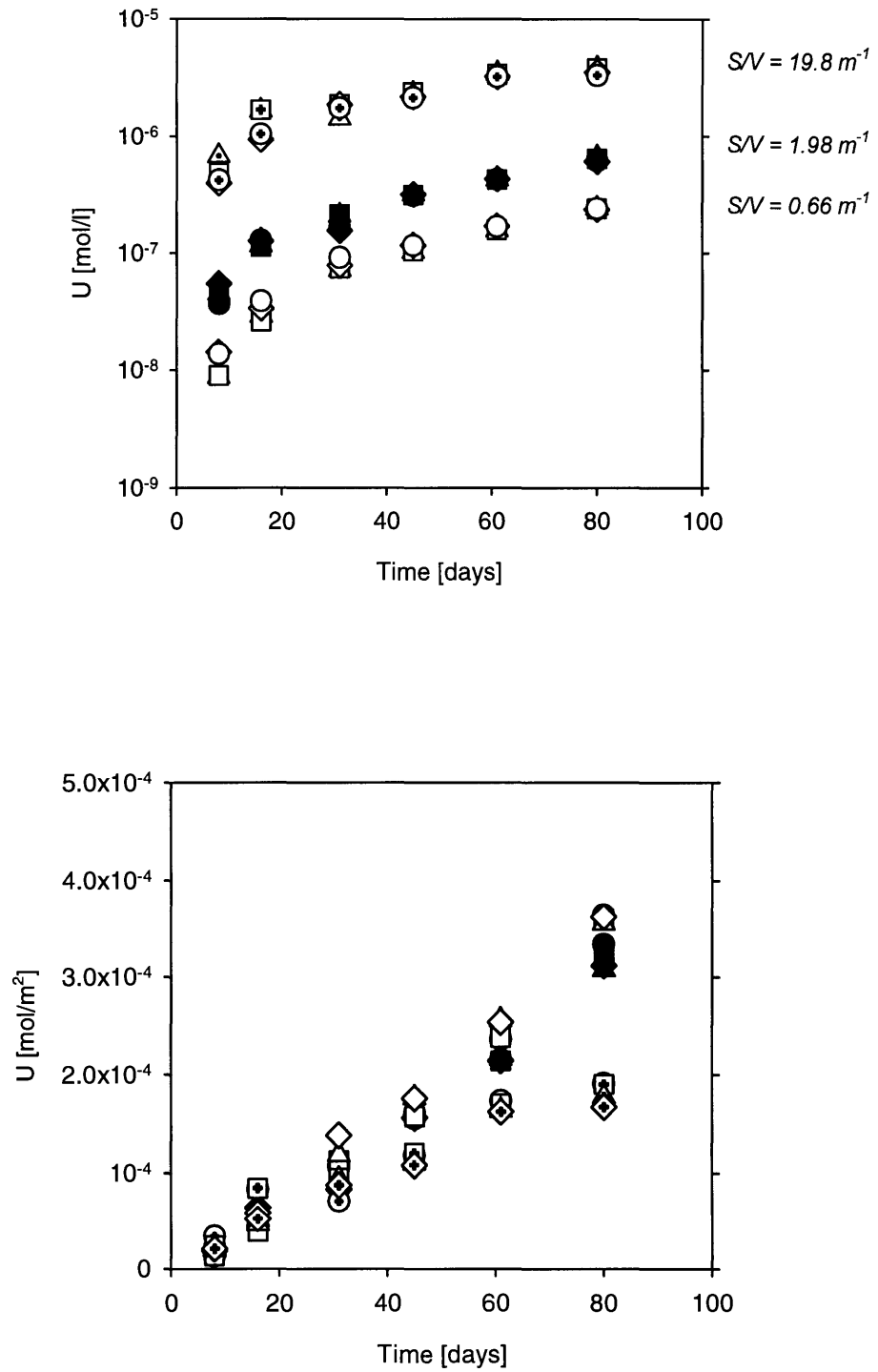


Figure 3-2. Uranium concentration (mol/l, mol/m<sup>2</sup>) versus contact time in air-saturated synthetic saline groundwater (two parallel experiments per each  $S/V$ , two parallel samplings) - the identical symbols in the upper and lower figures.

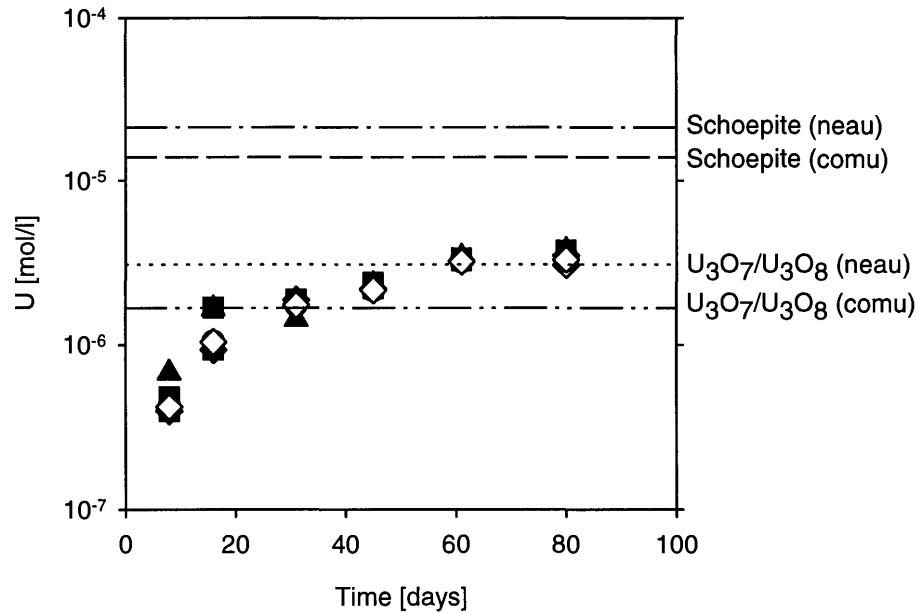


Figure 3-3. Preliminary comparison of measured uranium concentrations in synthetic saline groundwater ( $S/V = 19.8 \text{ m}^{-1}$ ) with theoretical uranium solubilities (EQ3/6) in equilibrium (neau: the NEA database, Grenthe et al 1992, comu: the composite database, Wolery 1992). Details of the solubility calculations are given in App. 1.

### 3.2 Anoxic conditions

In earlier dissolution experiments of  $\text{UO}_2$  pellets in synthetic groundwaters (Allard groundwater, bentonite groundwater) under similar conditions /Ollila 1995/, the measured concentrations of uranium at steady state were at the level of calculated  $\text{U}_4\text{O}_9$  ( $\text{UO}_{2.25}$ ) solubilities, which is clearly higher than the solubilities of well-crystallized  $\text{UO}_2$ . No redox species were added to the solutions in these experiments. The oxidation state of uranium in the aqueous phase was determined after the contact time of 500 days. According to the analyses, uranium was mainly at the U(VI) state and only a small fraction (1 - 9 %) at the U(IV) state. Obviously, the trace oxygen content in the atmosphere of the box is enough to cause slightly oxidizing conditions for uranium in the absence of reducing agents. This is in agreement with the solution concentrations being at the level of  $\text{UO}_{2.25}$  solubilities, which is a surface oxidation product of  $\text{UO}_2$ .

The dissolution rates measured in synthetic saline groundwater during the predissolution period, which was carried out prior to the initiation of the dissolution experiments, are shown in Figure 3-4. No redox species were added to solution at this stage. The dissolution rate decreased by 1-2 orders of magnitude. The dissolution rates were higher for  $S/V = 19.8 \text{ m}^{-1}$  at the end of the predissolution. It is possible that the pre-oxidized surface layer has not entirely dissolved.



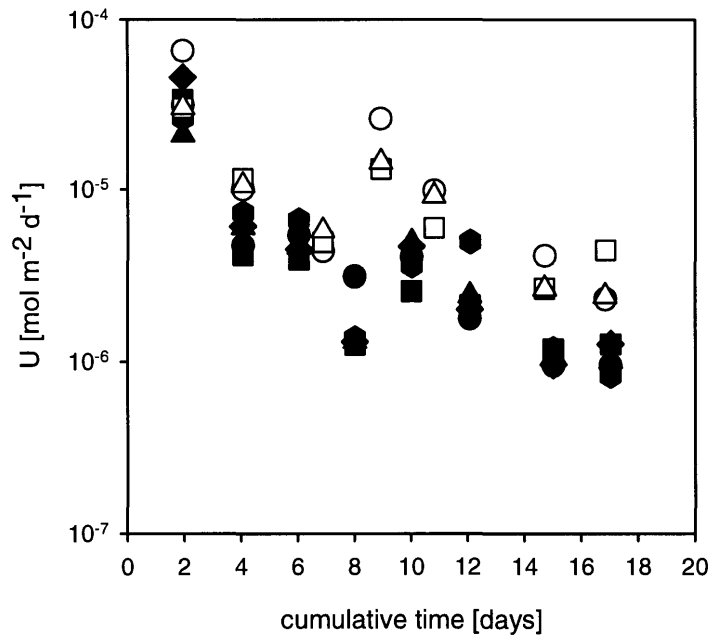


Figure 3-3. Dissolution rates of uranium from  $UO_2$  pellets during the predissolution period under anoxic conditions ( $N_2$ ). The rates were calculated per the geometric surface area of the pellet (filled symbols:  $S/V = 6.6 \text{ m}^{-1}$ , open symbols:  $S/V = 19.8 \text{ m}^{-1}$ ).

The solution concentrations of uranium as a function of time in the dissolution experiments with the higher  $S/V$ ,  $19.8 \text{ m}^{-1}$  (see Table 2-2, p. 13), are shown in Figure 3-4, both in the absence (upper figure) and in the presence of redox species (lower figure). The results of two parallel experiments are included. Uranium reached a constant level after a few days. The addition of redox species lowers the uranium concentrations in the aqueous phase. The effect is greatest in the amounts of uranium measured in the filtered samples. The concentrations in the filtered samples at lower Eh ( $-0.21 \text{ V}$ , measured value) are at the detection limit of the analytical method or smaller (ICP-MS), which is at the level of the theoretical solubility of  $UO_2$  (EQ3/6). The details of the solubility calculations are given in Apps. 2 and 3. There are four supersaturated uranium phases (listed in App. 2) at the solution concentration level (unfiltered) measured in the absence of redox species, while at the solution concentration level measured in the presence of  $1 \text{ ppm } S^{2-}$  and  $0.01 \text{ ppm } Fe^{2+}$  only  $UO_2$  and  $U_4O_9$  are supersaturated.

There is a clear difference between the unfiltered and filtered samples at lower Eh. One reason for this may be the dissolution and precipitation of aforementioned pre-oxidized surface layer, which possibly has not entirely dissolved during the predissolution period. The predissolution period for the both test series of Figure 3-4 was carried out in synthetic saline groundwater without redox species ( $S/V = 19.8 \text{ m}^{-1}$ ). In order to study this possibility, the re-initiation of the dissolution experiment is planned.

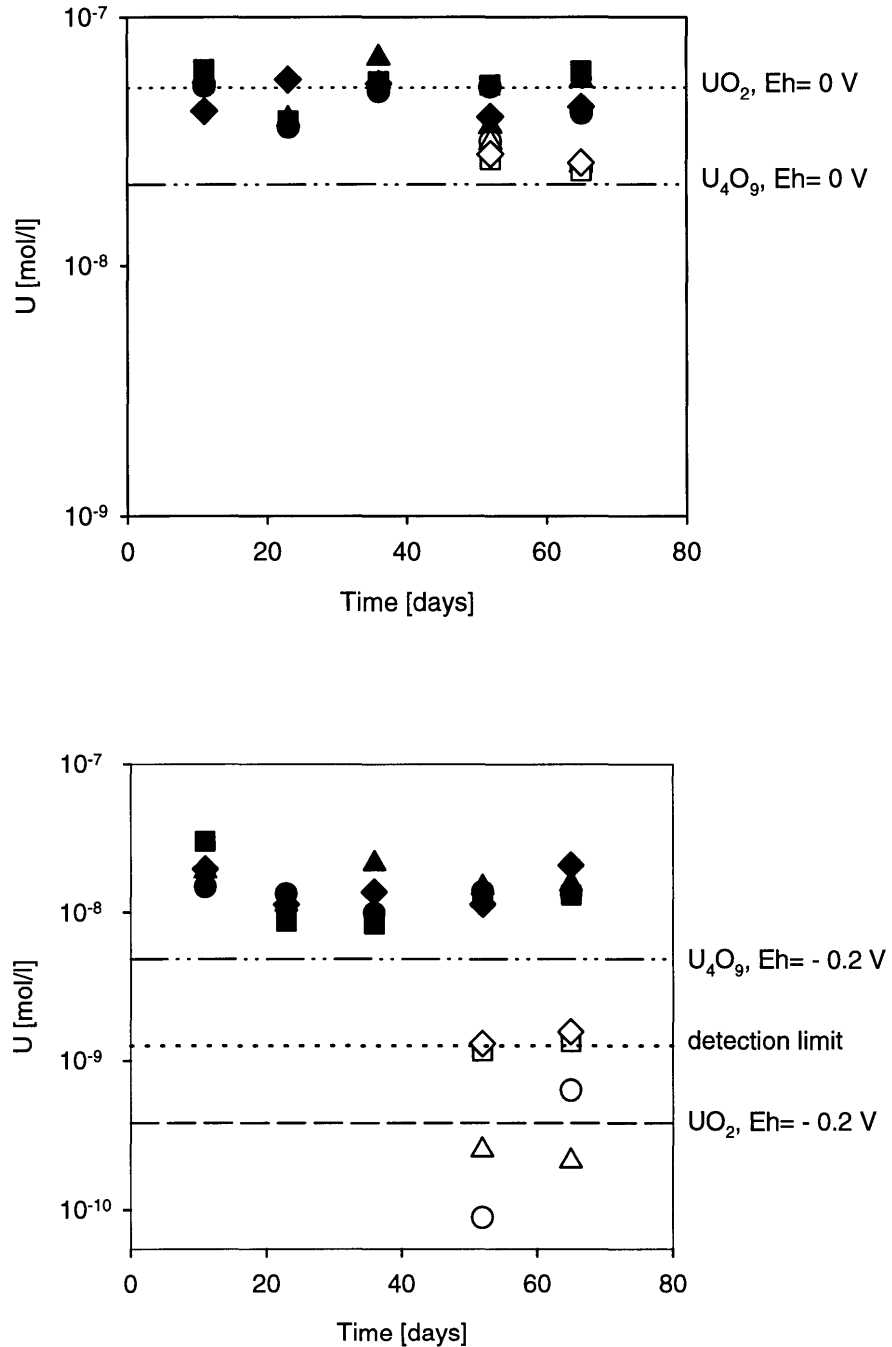


Figure 3-4. Uranium concentration (mol/l) versus contact time in anoxic ( $N_2$ ) synthetic saline groundwater,  $S/V=19.8\text{ m}^{-1}$ , in the absence of redox species ( $Eh=-0.02\dots+0.13\text{ V}$ ): upper figure, and in the presence of 1 ppm  $S^{2-}$ , 0.01 ppm  $Fe^{2+}$  ( $Eh=-0.21\text{ V}$ ): lower figure. The filled and open symbols give the contents in the unfiltered and microfiltered ( $0.45\text{ }\mu\text{m}$ ) samples, respectively. The dashed lines give the theoretical solubilities of  $UO_2$  and  $U_4O_9$  (EQ3/6).

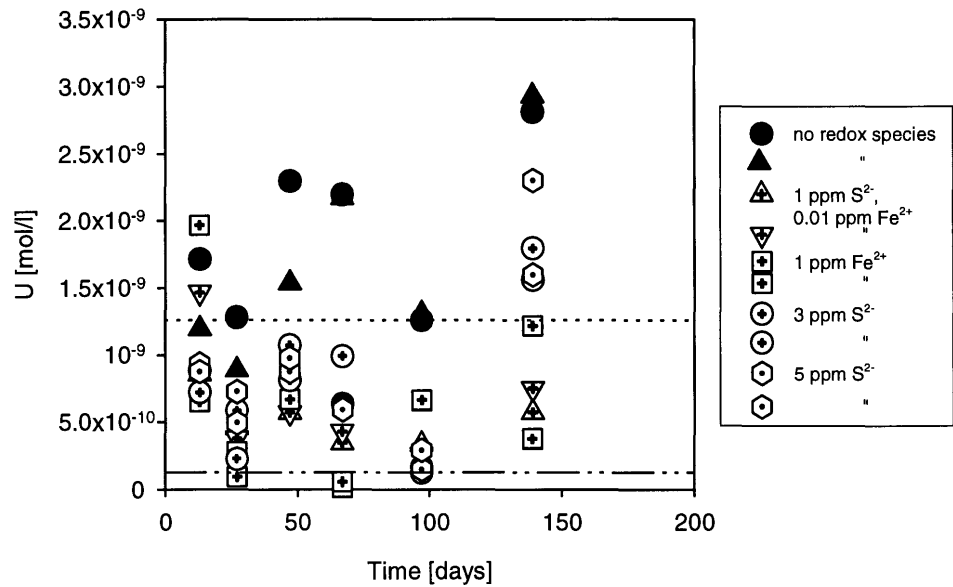


Figure 3-5. Uranium concentration (mol/l) versus contact time in anoxic ( $N_2$ ) synthetic saline groundwater,  $S/V = 0.66 \text{ m}^{-1}$ , in the absence of redox species (black symbols) and in the presence of redox species (white symbols). The dotted and dash-dot-dot lines show the detection limits of ICP-MS with conventional and high efficiency (Mistral) nebulization, respectively.

In the dissolution experiments with the lower  $S/V$ ,  $0.66 \text{ m}^{-1}$  (see Table 2-2, p. 13), the solution concentrations are close to the detection limit of the analytical method after the experimental time of 140 days, especially in the experiments with redox species and therefore lower Eh. The samples of the latest samplings (140 days) were analysed with ICP-MS using the high efficiency nebulization device. The detection limit for U in synthetic saline groundwater is with this method 0.03 ppb. More samplings are needed as a function of time in order to see the steady-state concentrations. The calculated solubilities (EQ3/6) for each redox conditions (measured Eh values) are presented in Apps. 2-4.

The addition of metallic Fe seems to have an effect on uranium concentrations in the aqueous phase in preliminary static experiment experiments, Figures 3-6 and 3-7. Scatter in the data is large. The concentrations represent unfiltered samples. The concentrations in the microfiltered samples were all clearly lower, below the detection limit of the analytical method. This suggests precipitation of uranium to occur. New experiments are planned with separate experimental flasks for each dissolution period in order to analyse total release of uranium, including possible sorption onto metallic Fe.

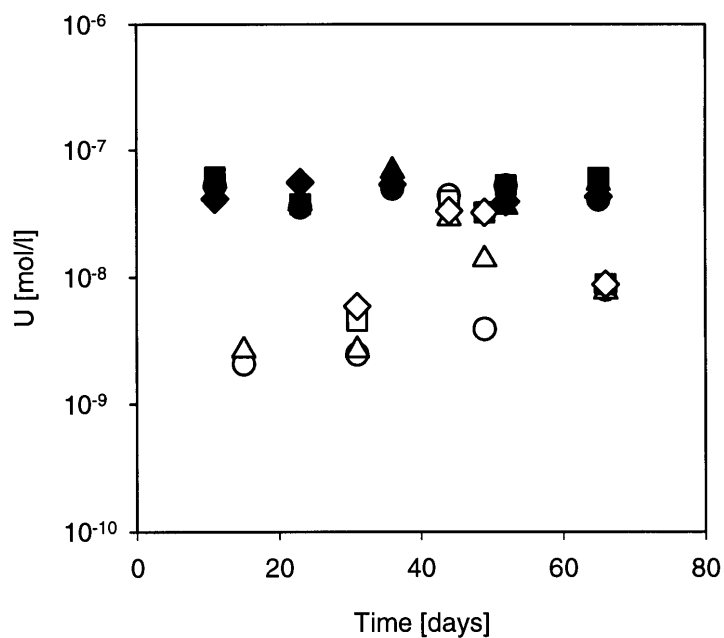


Figure 3-6. Uranium concentration (mol/l) versus time in anoxic ( $N_2$ ) synthetic saline groundwater (no redox species),  $S/V = 19.8 \text{ m}^{-1}$ , in the absence of metallic Fe (filled symbols), and in the presence of metallic Fe (open symbols).

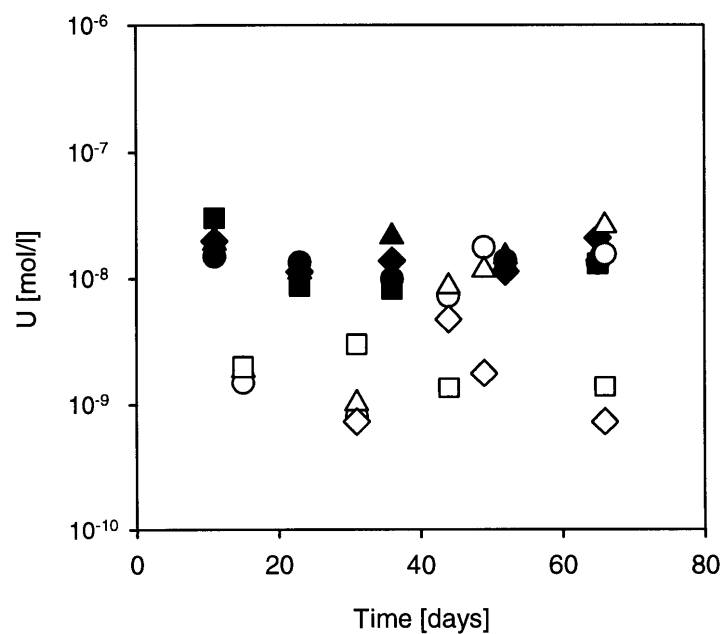


Figure 3-7. Uranium concentration (mol/l) versus time in anoxic ( $N_2$ ) synthetic saline groundwater (1 ppm  $S^{2-}$ , 0.01 ppm  $Fe^{2+}$ ),  $S/V = 19.8 \text{ m}^{-1}$ , in the absence of metallic Fe (filled symbols), and in the presence of metallic Fe (open symbols).

## 4 Preliminary conclusions

Dissolution experiments with unirradiated UO<sub>2</sub> pellets were initiated in synthetic saline groundwater. The experimental method is a static batch dissolution procedure. The redox conditions include oxic (air-saturated) and anoxic (N<sub>2</sub>) conditions. Under anoxic conditions, an attempt is made to control the redox state of the aqueous phase by the addition of natural redox species of groundwater, (1-5 ppm S<sup>2-</sup>, 0.01-1 ppm Fe<sup>2+</sup>). Stability tests have shown that it is possible to adjust the Eh in this way to a lower level (-0.25...-0.20 V) for a time period of several months. Under these conditions it is expected that dissolved uranium is partially at the tetravalent state.

Under air-saturated conditions, uranium would seem to attain a steady state in saline groundwater at a lower level ( $\approx 4 \cdot 10^{-6}$  mol/l) than in Allard groundwater ( $2 \cdot 10^{-5}$  mol/l). The modelling calculations (EQ3/6) show that uranyl silicates and CaUO<sub>4</sub> are potential U-bearing secondary phases in saline groundwater. The dissolution rate of uranium ( $3.2 \cdot 10^{-6}$  mol m<sup>-2</sup> d<sup>-1</sup>) is proportional to surface area.

Under anoxic conditions, the addition of redox species lowers the uranium concentrations in saline groundwater. The effect is greatest in the contents of uranium measured in the filtered samples. The uranium concentrations at low Eh in the filtered samples are at the level of the theoretical solubility of UO<sub>2</sub>.

More experimental data is needed to confirm the steady-state concentrations.

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## 6 Acknowledgements

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## Appendices:

EQ3/6 calculations, uranium - saline reference groundwater:

- App. 1    oxic conditions,  $pH_0 = 7.37$
- App. 2    anoxic conditions, no redox species,  $pH_0 = 8.38$
- App. 3    1) anoxic conditions, addition of 1 ppm S<sup>2-</sup>, 0.01 ppm Fe<sup>2+</sup>,  
           $pH_0 = 8.78$   
          2) anoxic conditions, addition of 1 ppm Fe<sup>2+</sup>,  $pH_0 = 8.36$
- App. 4    1) anoxic conditions, addition of 3 ppm S<sup>2-</sup>,  $pH_0 = 9.24$   
          2) anoxic conditions, addition of 5 ppm S<sup>2-</sup>,  $pH_0 = 9.44$

EQ3/6 calculationsoxic conditionsuranium - saline reference groundwater,  $pH_0 = 7.37^*$ 

Thermo-dynamic database	Solubility control	U solubility $\log CO_2$ fugacity = -3.5			Dominant species ( > 5%)
		redox	U (mol/l)	$pH_1$ **	
COMU ***	Schoepite	$\log O_2$ fugacity= -0.7	$1.39 \cdot 10^{-5}$	7.36	$(UO_2)_2CO_3(OH)_3^-$ (64 %) $UO_2(OH)_2(aq)$ (24 %) $UO_2(CO_3)_2^{2-}$ (5 %) $UO_2(CO_3)_3^{4-}$ (5 %)
NEAU ****	Schoepite	“	$2.11 \cdot 10^{-5}$	7.53	“
COMU	Soddyite $(UO_2)_2(SiO_4) \cdot 2H_2O$	“	$1.85 \cdot 10^{-8}$	7.37	$UO_2(OH)_2(aq)$ (64 %) $UO_2(CO_3)_2^{2-}$ (16 %) $(UO_2(CO_3)_3)^{4-}$ (15 %)
COMU	$CaUO_4$	“	$5.06 \cdot 10^{-8}$	7.37	$UO_2(OH)_2(aq)$ (64 %) $UO_2(CO_3)_2^{2-}$ (16 %) $UO_2(CO_3)_3^{4-}$ (14 %)
NEAU	$CaUO_4$	“	$4.05 \cdot 10^{-8}$	7.57	$UO_2(CO_3)_3^{4-}$ (45 %) $UO_2(OH)_2(aq)$ (32 %) $UO_2(CO_3)_2^{2-}$ (19 %)
COMU	Haiweeite $Ca(UO_2)_2(Si_2O_5)_3 \cdot 5H_2O$	“	$9.65 \cdot 10^{-8}$	7.37	$UO_2(OH)_2(aq)$ (63 %) $UO_2(CO_3)_2^{2-}$ (15 %) $UO_2(CO_3)_3^{4-}$ (14 %)
COMU	$U_3O_7/U_3O_8$ redox potential	Eh= 0.130 V	$1.67 \cdot 10^{-6}$	7.37	$UO_2(OH)_2(aq)$ (46 %) $(UO_2)_2CO_3(OH)_3^-$ (29 %) $UO_2(CO_3)_2^{2-}$ (11 %) $UO_2(CO_3)_3^{4-}$ (10 %)
NEAU	$U_3O_7/U_3O_8$ redox potential	Eh= 0.120 V	$3.08 \cdot 10^{-6}$	7.56	$UO_2(CO_3)_3^{4-}$ (33 %) $UO_2(OH)_2(aq)$ (25 %) $(UO_2)_2CO_3(OH)_3^-$ (25 %) $UO_2(CO_3)_2^{2-}$ (14 %)

\* the theoretical pH of the aqueous solution in equilibrium with air

\*\* the theoretical pH of the aqueous solution in equilibrium with the solid phase

\*\*\* COMU: the composite database, Data0.com.R16 /Wolery 1992/

\*\*\*\* NEAU: the NEA database, Data0.NEA.R16 /Grenthe et al 1992/

**EQ3/6 calculations****anoxic conditions**

uranium - saline reference groundwater, no redox species,  $pH_0 = 8.38$  \*

(test series code: OL-SR, OL-SR-H1, table 2-2, p. 5)

<i>Thermo-dynamic database</i>	<i>Solubility limiting solid phase</i>	<i>U solubility</i>			<i>Dominant species (&gt; 5%)</i>
		<i>log CO<sub>2</sub> fugacity = -7.0</i>			
		<i>Eh (V)</i>	<i>U (mol/l)</i>	<i>pH<sub>1</sub> **</i>	
COMU ***	Uraninite UO <sub>2</sub>	-0.1	$4.04 \cdot 10^{-10}$	8.38	U(OH) <sub>4</sub> (aq)
“	U <sub>4</sub> O <sub>9</sub> (UO <sub>2.25</sub> )	“	$1.15 \cdot 10^{-9}$	“	“
“	CaUO <sub>4</sub>	“	$8.67 \cdot 10^{-9}$	“	“
“	U <sub>3</sub> O <sub>7</sub> (UO <sub>2.3333</sub> beta )	“	$2.85 \cdot 10^{-9}$	“	“
“	Uraninite UO <sub>2</sub>	0.0	$5.18 \cdot 10^{-8}$	“	UO <sub>2</sub> (OH) <sub>2</sub> (aq) (70 %) UO <sub>2</sub> (OH) <sub>3</sub> <sup>-</sup> (30 %)
“	U <sub>4</sub> O <sub>9</sub> (UO <sub>2.25</sub> )	“	$2.11 \cdot 10^{-8}$	“	“
“	CaUO <sub>4</sub>	“	$4.37 \cdot 10^{-10}$	“	“
“	U <sub>3</sub> O <sub>7</sub> (UO <sub>2.3333</sub> beta )	“	$2.73 \cdot 10^{-8}$	“	“

\* the theoretical pH of the aqueous solution in equilibrium gas phase

\*\* the theoretical pH of the aqueous solution in equilibrium with the solid phase

\*\*\* COMU: the composite database, Data0.com.R16 /Wolery 1992/



**EO3/6 calculations****anoxic conditions**

uranium - saline reference groundwater

addition of 1 ppm S<sup>2-</sup>, 0.01 ppm Fe<sup>2+</sup>, pH<sub>0</sub> = 8.78 \*

(test series code: OL-SR-S-Fe, OL-SR-H3, table 2-2, p. 5)

<b>Thermo-dynamic database</b>	<b>Solubility limiting solid phase</b>	<b>U solubility</b>			<b>Dominant species (&gt; 5%)</b>
		<i>log CO<sub>2</sub> fugacity = -7.0</i>			
		<b>Eh (V)</b>	<b>U (mol/l)</b>	<b>pH<sub>1</sub> **</b>	
COMU ***	Uraninite UO <sub>2</sub>	-0.20	3.83 · 10 <sup>-10</sup>	8.78	U(OH) <sub>4</sub> (aq)
“	U <sub>4</sub> O <sub>9</sub> (UO <sub>2.25</sub> )	“	4.85 · 10 <sup>-9</sup>	“	“

uranium - saline reference groundwater

addition of 1 ppm Fe<sup>2+</sup>, pH<sub>0</sub> = 8.36 \*

(test series code: OL-SR-Fe, table 2-2, p. 5)

<b>Thermo-dynamic database</b>	<b>Solubility limiting solid phase</b>	<b>U solubility</b>			<b>Dominant species (&gt; 5%)</b>
		<i>log CO<sub>2</sub> fugacity = -7.0</i>			
		<b>Eh (V)</b>	<b>U (mol/l)</b>	<b>pH<sub>1</sub> **</b>	
COMU ***	Uraninite UO <sub>2</sub>	-0.17	3.83 · 10 <sup>-10</sup>	8.36	U(OH) <sub>4</sub> (aq)
“	U <sub>4</sub> O <sub>9</sub> (UO <sub>2.25</sub> )	“	4.37 · 10 <sup>-9</sup>	“	“

\* the theoretical pH of the aqueous solution in equilibrium gas phase

\*\* the theoretical pH of the aqueous solution in equilibrium with the solid phase

\*\*\* COMU: the composite database, Data0.com.R16 /Wolery 1992/

**EO3/6 calculations****anoxic conditions**

uranium - saline reference groundwater

addition of 3 ppm S<sup>2-</sup>, pH<sub>0</sub> = 9.24 \*

(test series code: OL-SR-S1, table 2-2, p. 5)

<i>Thermo-dynamic database</i>	<i>Solubility limiting solid phase</i>	<i>U solubility</i>			<i>Dominant species (&gt; 5%)</i>
		<i>log CO<sub>2</sub> fugacity = -7.0</i>			
		<i>Eh (V)</i>	<i>U (mol/l)</i>	<i>pH<sub>1</sub> **</i>	
COMU ***	Uraninite UO <sub>2</sub>	-0.255	3.83 · 10 <sup>-10</sup>	9.24	U(OH) <sub>4</sub> (aq)
“	U <sub>4</sub> O <sub>9</sub> (UO <sub>2.25</sub> )	“	8.34 · 10 <sup>-9</sup>	“	“

uranium - saline reference groundwater

addition of 5 ppm S<sup>2-</sup>, pH<sub>0</sub> = 9.44 \*

(test series code: OL-SR-H3, table 2-2, p. 5)

<i>Thermo-dynamic database</i>	<i>Solubility limiting solid phase</i>	<i>U solubility</i>			<i>Dominant species (&gt; 5%)</i>
		<i>log CO<sub>2</sub> fugacity = -7.0</i>			
		<i>Eh (V)</i>	<i>U (mol/l)</i>	<i>pH<sub>1</sub> **</i>	
COMU ***	Uraninite UO <sub>2</sub>	-0.26	3.83 · 10 <sup>-10</sup>	9.44	U(OH) <sub>4</sub> (aq)
“	U <sub>4</sub> O <sub>9</sub> (UO <sub>2.25</sub> )	“	7.28 · 10 <sup>-9</sup>	“	“

\* the theoretical pH of the aqueous solution in equilibrium gas phase

\*\* the theoretical pH of the aqueous solution in equilibrium with the solid phase

\*\*\* COMU: the composite database, Data0.com.R16 /Wolery 1992/

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