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Dissolution of unirradiated UO_2 fuel in synthetic groundwater – Progress report '97

Kaija Ollila

VTT Chemical Technology

June 1998

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Nimeke – Title DISSOLUTION OF UNIRRADIATED UO_2 FUEL IN SYNTHETIC GROUNDWATER – PROGRESS REPORT '97	
Tiivistelmä – Abstract <p>This report presents the results obtained from dissolution experiments with unirradiated UO_2 pellets and UO_2 powder in synthetic groundwaters. The results are partly preliminary, because the dissolution experiments of UO_2 typically need long contact time periods to reach steady state. The purpose is to study the dissolution mechanisms and solubilities of UO_2 in synthetic groundwaters which simulate saline and fresh groundwater environments under the disposal conditions of spent fuel. The redox conditions varied from oxidizing (air-saturated), anaerobic to reducing (N_2, low Eh). The Eh was maintained at a low level (-300 ... -200 mV) by the addition of redox species (S^{2-}, Fe^{2+}) to the aqueous phase. The ratio of UO_2 surface area to water volume was varied. The study is a part of the research project 'Source term for performance assessment of spent fuel as a waste form' within the European Commission Nuclear Fission Safety Program (1994-1998).</p> <p>Under anoxic conditions (N_2), the control of the Eh (-300 ... -200 mV) by the addition of redox species to the aqueous phase seems to lower the solution concentrations of uranium. The solubilities are at the level of the theoretical solubility of the well-crystallized U(IV)oxide, UO_2 (10^{-9} M). In earlier experiments in synthetic groundwater (N_2) without the Eh control, the measured solubilities were one order of magnitude higher. They were close to the solubility of the mixed valence U(IV)(VI)oxide, U_4O_9. The composition of groundwater (saline, fresh) has a minor effect.</p> <p>Under oxidizing (air-saturated) conditions, the experiments with UO_2 powder ($S/V= 1000\ m^{-1}$) and UO_2 pellets ($S/V= 0.66...19.8\ m^{-1}$) have not reached steady state. A preliminary comparison with theoretical solubility data (EQ3/6, NEA and composite databases) was made assuming secondary phases of uranium to limit its solubilities. As the experiments proceed, the solid phases in solution will be analysed after different contact time periods in order to get information on secondary alteration phases that possibly control the uranium solubility.</p>	
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Nimeke – Title UO ₂ POLTTOAINEEN LIUKENEMISMEKANISMIT SYNTEETTISESSÄ POHJAVEDESSÄ – VÄLIRAPORTTI 1997	
Tiivistelmä – Abstract <p>Tässä raportissa esitetään tuloksia UO₂:n liukenemiskokeista, jotka on tehty käyttäen säteilyttämätöntä UO₂ -polttoainetta pelletti- ja jauhemuodossa. Tulokset ovat osittain alustavia, koska liukenemiskokeet vaativat tavallisesti pitkiä aikoja vakiotilan (steady state) saavuttamiseksi. Tavoitteena on tutkia UO₂ :n liukenemismekanismeja ja liukoisuutta vaihtelevan koostumuksen omaavissa synteettisissä pohjavesissä, jotka jäljittelevät suolaista ja makeaa pohjavesiympäristöä loppusijoitusolosuhteissa. Redox-olosuhteet vaihtelivat hapettavista (ilma) pelkistäviin. Syvän pohjaveden pelkistävät redox-olosuhteet pyritään aikaansaamaan anaerobisessa kaapissa (N₂), jossa kaasun happipitoisuus on hyvin pieni (< 1 ppm). Vesifaasiin lisättiin redox-spesieksiä (S²⁻, Fe²⁺) siinä olevan jäännöshapen sitomiseksi. Samalla mitatut redox-potentiaaliarvot (Eh) laskivat vaihdellen tyypillisesti -300 ... -200 mV. Lisäksi vaihdeltiin UO₂:n pinnan ja veden tilavuuden suhdetta. Tutkimus on osa EU-projektia ‘Source term for performance assessment of spent fuel as a waste form’, jota koordinoi Forschungszentrum Karlsruhe (FZK.INE) Saksasta.</p> <p>Hapettomissa olosuhteissa vesifaasin Eh:n säätö näyttää vaikuttavan mitattuihin uraaniliukoisuuksiin. UO₂-pellettien liukenemiskokeissa saavutetaan vakiotila muutamassa päivässä. Mitatut liukoisuudet ovat lähellä kiteisen U(IV)-oksidin, UO₂:n, teoreettista liukoisuutta pelkistävässä olosuhteissa (10⁻⁹M). Aikaisemmissa kokeissa synteettisessä pohjavedessä ilman veden Eh:n säätöä mitatut liukoisuudet olivat kertaluokan korkeampia ollen lähellä U(IV)(VI)-sekaoksidin, U₄O₉:n, teoreettista liukoisuutta. Pohjaveden koostumuksella (suolainen, makea) näyttää olevan vähäinen vaikutus.</p> <p>Hapellisissa olosuhteissa UO₂-jauheen ja UO₂-pellettien liukenemiskokeissa uraanin pitoisuudet vesifaasissa eivät ole vielä saavuttaneet kyllästymistilaa. Uraanin liukenemisnopeus on verrannollinen UO₂ :n pinta-alaan. Kokeiden alkuvaiheessa uraanin pitoisuus kasvaa lineaarisesti ajan funktiona, jonka jälkeen liukenemisnopeus laskee. Raportissa on tehty alustava vertailu teoreettisten liukoisuuksien kanssa (EQ3/6, NEA ja composite lähtötiedostot) olettaen sekundaarisen uranifaasin rajoittavan liukoisuutta. Kokeiden edetessä tutkitaan mahdollisten sekundaaristen faasien koostumusta sopivalla analyysimenetelmällä.</p>	
Avainsanat - Keywords UO ₂ , liukoisuus, liukenemismekanismit, synteettiset pohjavedet, hapettavat, pelkistävät olosuhteet	
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Appendix 1

Foreword

Within the European Commission Nuclear Fission Safety Program (1994 - 1998) the joint research project 'Source term for performance assessment of spent fuel as a waste form' (Contract No. F14W - CT95 - 0004) is in progress 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), the Institute for Transuranium Elements (JRC-ITU, Germany), Studiezentrum voor Kernenergie, Waste & Disposal (SCK.CEN, Belgium), Studsvik Material AB, (STUDMAT, Sweden) and the 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, UO_2 (or U_4O_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 (α), canister materials (steel, copper) and their corrosion products, backfill materials (bentonite) and the composition of the groundwater. The dissolution rate of UO_2 is strongly affected by the redox conditions, especially by the availability and the nature of oxidants from α -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 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 work is a part of the EU-R&D programme 1994-1998: Nuclear Fission Safety, entitled '*Source term for performance assessment of spent fuel as a waste form*'. 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_2 solubility and dissolution mechanisms. The effects of near-field materials, bentonite and metallic iron will also be studied. The experiments are performed using unirradiated UO_2 fuel, both in pellet and powder form.

This report presents the results obtained from dissolution experiments with unirradiated UO_2 pellets and UO_2 powder in synthetic groundwaters. The saline and fresh (Allard) groundwaters are reference groundwaters in the investigations of spent fuel disposal. The granite/bentonite groundwater (by Ciemat, Spain) simulates the effects of bentonite on spanish groundwater. Redox conditions include oxic (air-saturated) and anoxic (anaerobic glove box, N_2) conditions. An attempt is made to maintain the Eh of the aqueous phase under N_2 atmosphere at a low level by the addition of the natural redox species of groundwater (S^{2-} , Fe^{2+}) in order to keep uranium predominantly in the tetravalent state. A 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.

2 Methods of experiments

2.1 Materials

Unirradiated sintered polycrystalline UO_2 pellets and UO_2 powder were used in the experiments. 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 in synthetic groundwater was carried out for the pellets under 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.

UO_2 powder (prepared by ABB Atom, Sweden) has a particle size of $0.7 \mu\text{m}$, which results in a high specific surface area of $5.4 \text{ m}^2/\text{g}$ (BET-method). The composition ratio O/U is 2.10 (gravimetric method). The powder has been treated with a mixture of nitrogen and air in order to stabilize it against spontaneous oxidation.

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

2.2 Synthetic groundwaters

Three types of synthetic groundwaters are used in the experiments. Table 2-1 gives the compositions.

The saline groundwater represents the groundwater found at a depth of 600 m in granitic bedrock. The composition is based on groundwater studies within the site investigations for spent fuel disposal in the Olkiluoto area. 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_2 atmosphere) conditions with the help of EQ3/6 modelling and stability tests /Vuorinen et al. 1997/.

The Allard groundwater is the reference groundwater for fresh groundwater conditions at great depths in granitic bedrock. The composition has been modified due to the stability problems of the original Allard groundwater both under air-saturated conditions and in N_2 atmosphere /Vuorinen and Snellman 1998/. The Ca, Mg, Si and carbonate contents were lowered in order to prevent the precipitation of calcite and silicate phases, and the loss of carbonate from solution.

The granite/bentonite groundwater by Ciemat /Martínez et al 1996/ simulates the effects of bentonite on spanish granitic groundwater. This saline synthetic groundwater has a high NO_3^- content (110 mg/l) compared with all the other groundwaters of Table 2-1.

Table 2-1. The compositions of the synthetic groundwaters.

	Saline granitic groundwater (air) /Vuorinen et al. 1997/		Saline granitic groundwater (N ₂) (log pCO ₂ = -7) /Vuorinen et al. 1997/		Fresh granitic groundwater (air) /Allard et al. 1981/		Modified Allard groundwater (air) /Vuorinen and Snellman 1998/		Modified Allard groundwater (N ₂) (log pCO ₂ = -4) /Vuorinen and Snellman 1997/		Granite/bentonite groundwater (air) /Martínez et al. 1996/	
	mg/l	mmol/l	mg/l	mmol/l	mg/l	mmol/l	mg/l	mmol/l	mg/l	mmol/l	mg/l	mmol/l
Na ⁺	4800	209	4800	209	52	2.3	52	2.3	52	2.3	3750	163
Ca ⁺	4000	100	4000	100	18	0.45	10	0.25	5.1	0.13	135	3.37
Mg ²⁺	56	2.3	55	2.3	4.3	0.18	2.8	0.12	0.7	0.03	600	24.7
Sr ²⁺	35	0.40	35	0.40	-	-	-	-	-	-	-	-
K ⁺	21	0.54	21	0.54	3.9	0.10	3.9	0.10	3.9	0.10	20	0.5
HCO ₃ ⁻	10	0.16	-	-	123	2.01	91	1.5	65	1.07	27	0.44
SiO ₂	2.5	0.04	-	-	8	0.13	2.9	0.05	1.7	0.028	8.3	0.14
Br ⁻	105	1.31	105	1.31	-	-	-	-	-	-	15	0.19
F ⁻	1.2	0.063	1.2	0.063	-	-	-	-	-	-	-	-
Γ	0.9	0.007	0.9	0.007	-	-	-	-	-	-	-	-
SO ₄ ²⁻	4.2	0.044	4.2	0.044	9.6	0.10	9.6	0.10	9.6	0.10	1500	15.6
B ³⁺	0.9	0.08	0.9	0.08	-	-	-	-	-	-	-	-
Cl ⁻	14600	412	14600	412	58	1.6	47	1.3	52	1.5	6550	185
NO ₃ ⁻	-	-	-	-	-	-	-	-	-	-	110	1.77
pH _{measured}	7.0 - 7.1		8.0 - 8.1		8.4		8.3 - 8.4		8.7 - 8.8		7.5	
pH _{theoretical}	7.4		8.3		8.2		8.4		8.8		7.3	

2.3 Redox conditions

The redox conditions include:

- 1) oxidizing, air-saturated conditions (pO₂ = 0.2 atm)
- 2) anaerobic conditions (N₂ atmosphere, O₂ < 1 ppm)
- 3) reducing conditions (N₂ atmosphere, O₂ < 1 ppm, low Eh)

The oxic experiments are carried out in polyethylene bottles. The bottles are kept loosely closed during dissolution periods in order to allow equilibrium with air in the aqueous phase.

The anoxic conditions of deep groundwater are simulated in an anaerobic glove box filled with nitrogen (adsorbers for O₂ and CO₂ : Cu catalyst and molecular sieve, respectively). The pellets were immersed in deaerated (with N₂) synthetic groundwater in polyethylene bottles inside the glove box. The oxygen concentration in the atmosphere of the box 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.

An important parameter to be considered is the Eh of the aqueous phase. Under anaerobic (N₂) conditions, it may vary from slightly oxidizing to reducing depending on the composition of the gas phase (trace O₂ , H₂) 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 UO₂ dissolution studies in synthetic groundwater (Allard) in N₂ 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, Fe²⁺, S²⁻, typically present in natural groundwaters. The Eh values in the presence of these redox species ranged from -300 ... -200 mV (1 ppm Fe²⁺ , 1-5 ppm S²⁻). The Eh value for synthetic groundwater in the absence of redox species fluctuates. Values from -20 ... +130 mV have been measured. The water chemistry (pH and Eh) of different groundwaters (without UO₂ pellets) is followed under similar conditions in order to study the stability during long dissolution periods, parallel with the dissolution experiments. Figure 2-1 gives the measured Eh and pH values as a function of time in saline groundwater with the S²⁻ content of 3 ppm. A platinum electrode (Yokogawa) was used as the redox electrode in combination with a Ag/AgCl reference electrode (Yokogawa). The reference electrode is filled with a gelled electrolyte solution. There is a slight trend towards lower Eh during the follow-up period of 330 days, (Eh: - 250 ... - 300 mV, pH: 9.1...9.3). The sulphide content is decreased after the addition to synthetic groundwater probably by reacting with the trace oxygen in N₂ atmosphere, see Table 2-2. The determination was made using a standard spectrophotometric method (SFS 3038). The determination of the ferrous iron was made by a ferrozine method /Dimmock et al. 1979/.

Table 2-2. *The S(-II) and Fe (+II) contents (mg/l) in saline groundwater. The determinations were made after one year in an anaerobic glove box.*

Redox species addition	S(-II), Fe(+II) contents [ppm]	Eh [mV]
1 ppm S(-II)	0.52	-230
3 ppm S(-II)	2.16	-285
5 ppm S(-II)	3.84	-295
1 ppm Fe(+II)	0.87	-105

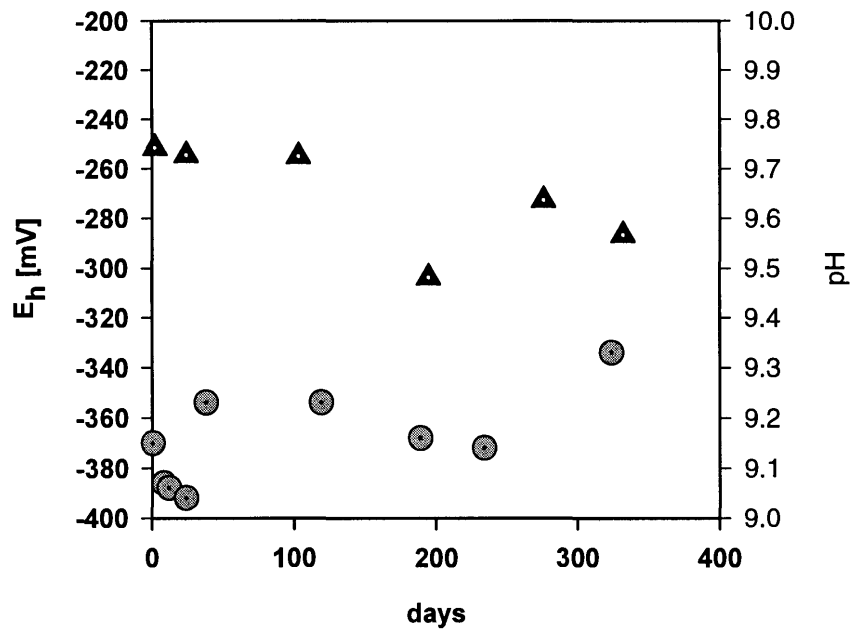


Figure 2-1. The measured Eh (black symbols) and pH (light-coloured) values in saline groundwater under anaerobic conditions.

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 or a UO_2 powder is immersed in equilibrated synthetic groundwater in polyethylene bottles. The ratio of UO_2 surface area to water volume (S/V) is $0.66\text{--}19.8\text{ m}^{-1}$ (geometric surface area) in the experiments with pellets, and 1000 m^{-1} (specific surface area) in the experiments with powder. Small aliquots (0.5...2 ml) are periodically taken for further analysis for uranium. These aliquots are replaced with fresh water which has a similar composition, in order to keep the water volume the same. The amounts of uranium in unfiltered, microfiltered (membranes of $0.45\text{ }\mu\text{m}$, selected samplings) and ultrafiltered (nominal cut-off value of $50\text{ }000\text{ M}$, selected samplings) samples are measured as a function of time. The detailed experimental methods were given in the previous progress report /Ollila 1997/.

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 water-changing every two days, was 15...17 days. The dissolution rate decreased during this period by one order of magnitude, which showed the presence of a more soluble oxidized surface layer. The surface of UO_2 powder was not pretreated by predissolution prior to the start of the experiments.

2.5 Analytical methods

The uranium contents in the aqueous phase were analysed by ICP-MS. The sensitivity of 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 $1.3 \cdot 10^{-10}$ M with a high efficiency sample nebulization device (Mistral). In Allard groundwater, the detection limit with the conventional nebulization method is low, $8.4 \cdot 10^{-11}$ M.

3 Results

3.1 Oxidic conditions

A general result from the dissolution experiments with spent fuel and unirradiated UO_2 pellets performed in the presence of atmospheric oxygen is that the solution concentration of uranium attains a steady state after a certain time period /Forsyth and Werme 1992, Grambow 1989/. In previous dissolution experiments with unirradiated UO_2 pellets in synthetic granitic groundwater by Allard /1981/ under air-saturated conditions, a constant value for the solution concentration of uranium was reached after a 500-days'-period at a concentration of $1 - 2 \cdot 10^{-5}$ mol/l /Ollila 1995/, which is in good agreement with the results of the spent fuel dissolution experiments by Forsyth and Werme /1992/. A low S/V ratio (1.8 m^{-1} , geometric) was used in those experiments. In the parallel experiments in synthetic bentonite groundwater by Snellman /1986/, which simulates the effects of bentonite on fresh granitic groundwater, a steady state was attained at a concentration of one order of magnitude lower, $1 \cdot 10^{-6}$ mol/l. The main effects of bentonite were the higher pH and the higher contents of HCO_3^- , SO_4^{2-} , Na^+ and Si^{4+} . In deionized water, the corresponding steady-state value was $3 - 5 \cdot 10^{-6}$ mol/l.

Table 3-1 lists the UO_2 dissolution experiments in progress under air-saturated conditions. The experimental time hitherto is 84 days in the tests with UO_2 powder and 400 days in the tests with UO_2 pellets. The concentrations of uranium measured in the aqueous phase during the dissolution of UO_2 powder in different groundwaters are given in Figures 3-1...3.3.

Table 3-1. *The experimental conditions of the oxidic (air-saturated) dissolution tests.*

Solid	Synthetic groundwater	pH _{measured}	S/V [m^{-1}]	Duration [days]
UO_2 powder	Allard	8.4	1000	84
"	modified Allard	8.3 - 8.4	"	"
"	saline	7.0 - 7.1	"	"
"	granite/bentonite	7.5	"	"
UO_2 pellets	saline	7.0 - 7.1	0.66	350
"	"	"	1.98	"
"	"	"	19.8	"

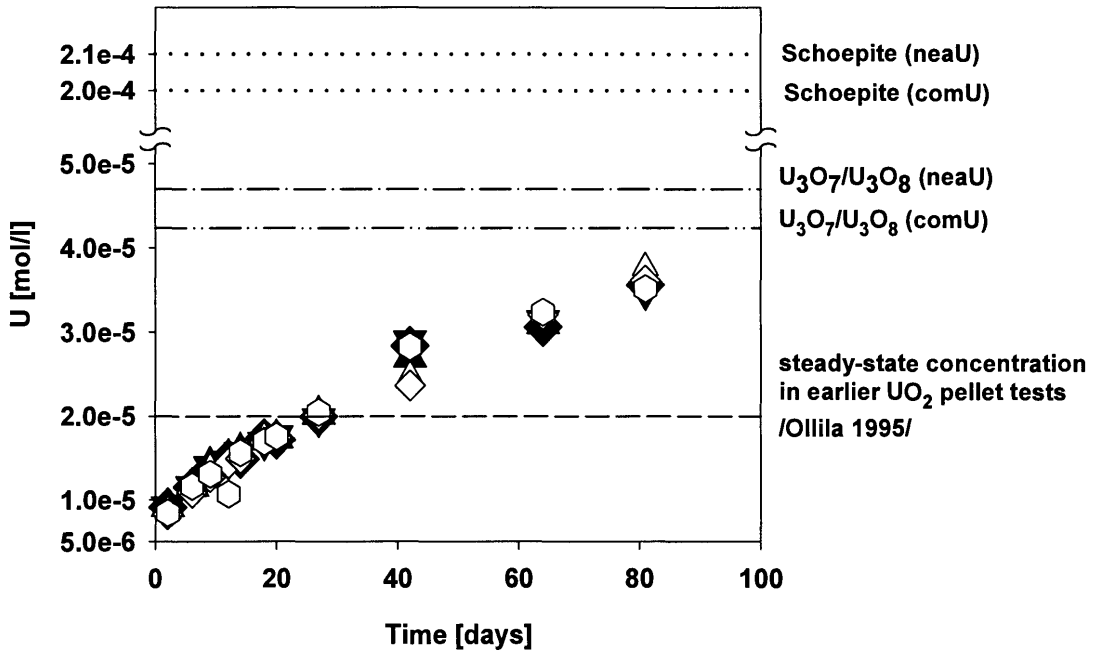


Figure 3-1. Uranium concentration vs. contact time in air-saturated Allard groundwaters during dissolution of UO_2 powder ($S/V = 1000 \text{ m}^{-1}$, filled symbols: Allard groundwater /Allard et al 1981/, open symbols: modified Allard groundwater /Vuorinen and Snellman 1998/). The measured data is for two parallel experiments in both groundwaters. The dashed lines show theoretical uranium solubilities (EQ3/6) in equilibrium.

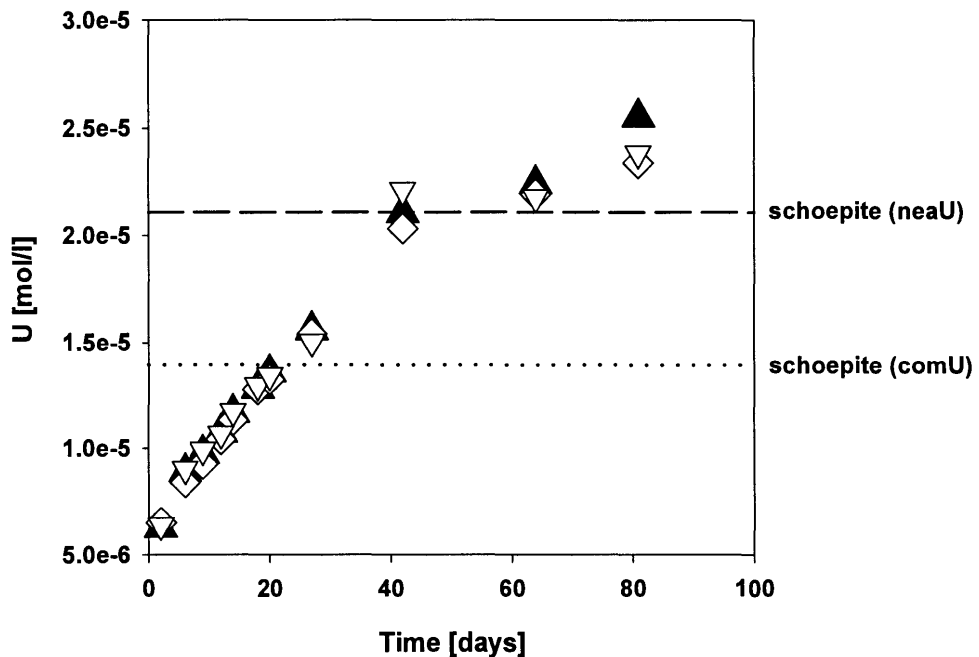


Figure 3-2. Uranium concentration vs. contact time in air-saturated saline groundwater during dissolution of UO_2 powder ($S/V = 1000 \text{ m}^{-1}$, filled symbols: unfiltered samples, open symbols: microfiltered samples, $0.45 \mu\text{m}$). The measured data is for two parallel experiments. The dashed lines show theoretical uranium solubilities (EQ3/6) in equilibrium.

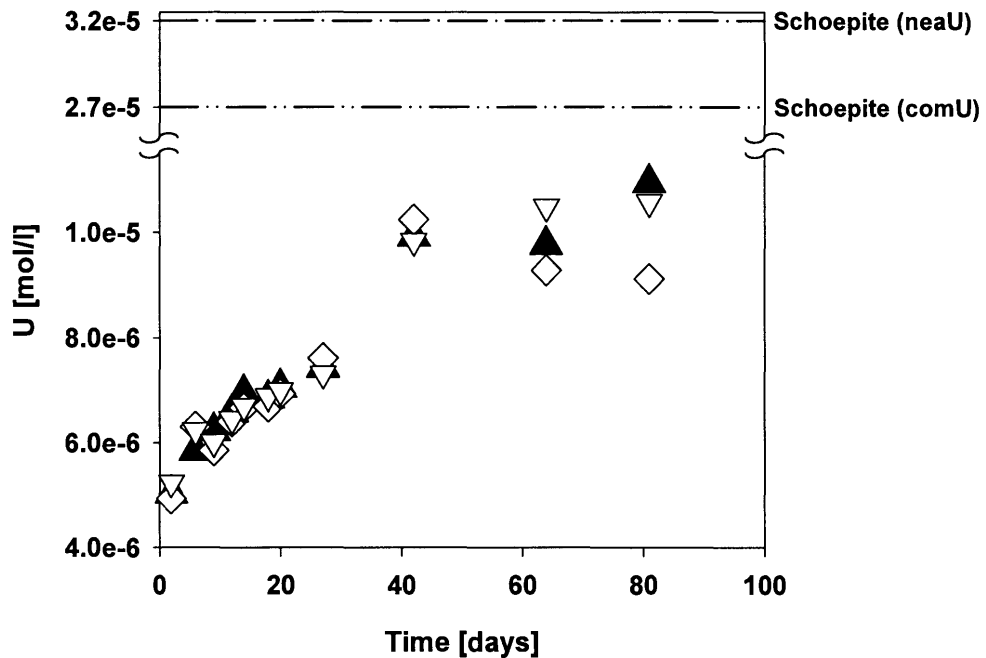


Figure 3-3. Uranium concentration vs. contact time in air-saturated Spanish granite/bentonite groundwater during dissolution of UO_2 powder ($S/V = 1000 \text{ m}^{-1}$, filled symbols: unfiltered samples, open symbols: microfiltered samples, $0.45 \mu\text{m}$). The measured data is for two parallel experiments. The dashed lines show theoretical uranium solubilities (EQ3/6) in equilibrium.

The main objective of the high S/V tests (1000 m^{-1}) is to obtain information on maximum solution concentrations of uranium and on secondary alteration products that possibly control the uranium concentration in solution. Several parallel tests have been initiated in order to study the solid phase at the different stages of dissolution. UO_2 powder is allowed to react with synthetic groundwater for different time periods. The aqueous phase and solid phases will be analysed at the end of these periods.

Figures 3-1...3-3 show the evolution of the uranium concentration vs. time in the test series in different groundwaters. At the early stages of dissolution, the uranium concentration increases linearly in all groundwaters. It starts to level out after 40 days in saline and granite/bentonite groundwaters, while in Allard groundwater it continues to increase. The modification of the composition of Allard groundwater (Table 2-1, p. 3) does not seem to have an effect. Preliminarily, the theoretical (EQ3/6) solubilities of uranium in equilibrium with some solid phases have been presented for comparison. The solubilities have been calculated using the uranium databases of NEA (data0.nea.R2) /Grenthe et al. 1992/ and of the Lawrence Livermore National Laboratory (composite database, data0.com.R2) /Wolery 1992/. Earlier comparisons between the calculations and the data from the experiments with spent fuel and unirradiated UO_2 pellets seemed to indicate that the solution concentration of uranium is controlled by some kind of oxidized phase /Forsyth and Werme 1992, Ollila 1995/. Two different solubility constraints have been assumed in Figures 3-1...3-3. Schoepite was assumed to be the solubility-limiting phase. In earlier dissolution experiments with UO_2 pellets, the uranium (low S/V) seemed to attain a steady state in deionized water at the concentration which was close to the schoepite solubility. In Allard groundwater, the steady state was at a lower level than the schoepite solubility. It was close to the

calculated solubility at the U_3O_7/U_3O_8 redox potential /Grambow 1989, Ollila 1995/. Preliminary comparison shows that the solution concentration of uranium is approaching this solubility in Allard groundwater also in the experiment with the high S/V, Figure 3-1. In saline and granite/bentonite groundwaters, the solution concentration would seem to reach the level of the schoepite solubility, Figures 3-2 and 3-3. More experimental data and the analyses of solid phases are needed to give information on steady-state controlling factors.

Figure 3-4 gives the solution concentrations of uranium in air-saturated saline groundwater in the experiments with UO_2 powder ($S/V = 1000 \text{ m}^{-1}$), and in the experiments with UO_2 pellets ($S/V = 0.66 \dots 19.8 \text{ m}^{-1}$). In the latter experiments, long experimental times are needed to reach steady states. The uranium concentration increases rapidly in the beginning and is followed by a slower increase. The experiments are continued until the uranium attains steady state. The dissolution rate is proportional to surface area, when the experiments with UO_2 powder and UO_2 pellets are compared.

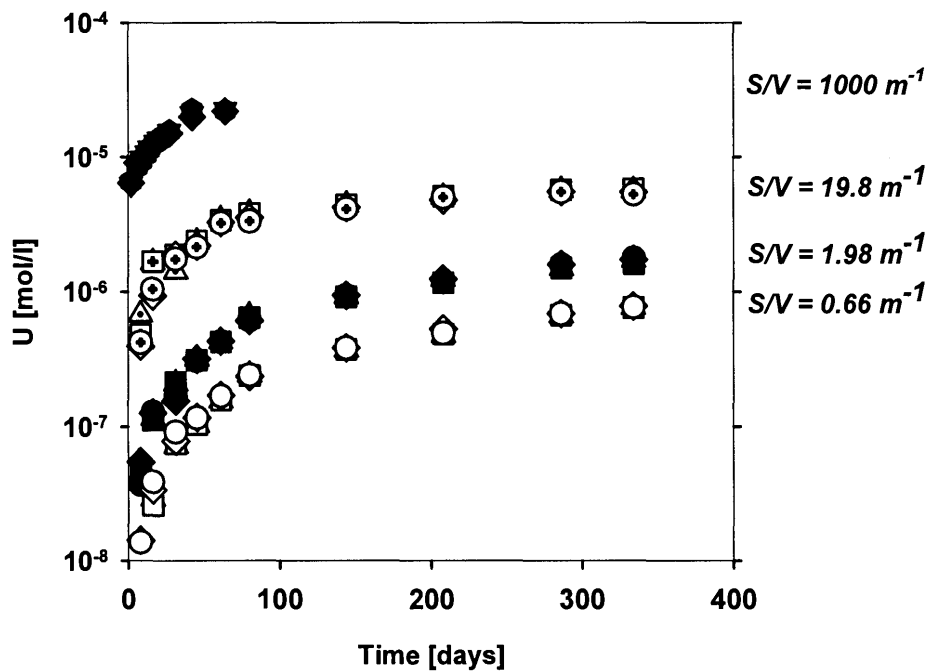


Figure 3-4. Uranium concentration vs. contact time in air-saturated saline groundwater in the experiments with different S/V. The measured data at each S/V is for two parallel experiments.

3.2 Anoxic conditions

In earlier dissolution experiments with UO_2 pellets in synthetic groundwaters (Allard groundwater /1981/, bentonite groundwater /Snellman 1986/) under anoxic (N_2) atmosphere /Ollila 1995/, the measured concentrations of uranium at steady state were at the level of calculated U_4O_9 ($\text{UO}_{2.25}$) solubilities, which are clearly higher than the solubilities of well-crystallized UO_2 . No reducing species were added to the solutions in those 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. 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 $\text{UO}_{2.25}$ (U_4O_9) solubilities, which is a surface oxidation product of UO_2 .

Table 3-2 and 3-3 list the UO_2 dissolution experiments under anoxic conditions in the glove box. All the experiments are carried out with UO_2 pellets.

Table 3-2. *The experimental conditions of the anoxic (N_2) dissolution experiments with UO_2 pellets in synthetic saline groundwater.*

Redox species addition	Eh [mV]*	pH*	S/V [m^{-1}]	Duration [days]
none	-20...+175	8.3...8.0	0.66	300
1 ppm S(-II) 0.01 ppm Fe(+II)	-215...-230	8.8...8.8	“	“
1 ppm Fe (+II)	-208...-105	8.2...7.8	“	“
3 ppm S (-II)	-255...-285	9.1...9.3	“	“
5 ppm S (-II)	-280...-295	9.6...9.6	“	“
none	-20...+175	8.3...8.0	19.8 m^{-1}	“
1 ppm S(-II) 0.01 ppm Fe(+II)	“	“	“	“
metallic Fe	-	9.3...8.8	“	“
1 ppm S(-II) 0.01 ppm Fe(+II) metallic Fe	-	9.4...9.0	“	“

* $E_{h1}...E_{h2}$, $pH_1...pH_2$, Eh and pH measured for parallel groundwater samples (without UO_2 pellets) after two weeks' and ten months' period under anaerobic conditions, respectively.

Table 3-3. *The experimental conditions of the anoxic (N₂) dissolution experiments with UO₂ pellets in modified Allard groundwater (log pCO₂= -4, see p. 3).*

Redox species addition	Eh [mV]*	pH*	S/V [m ⁻¹]	Duration [days]
none	-	8.8	0.66	70
1 ppm S(-II)	-250	9.0	“	“
3 ppm S (-II)	-290	9.2	“	“
5 ppm S (-II)	-310	9.4	“	“
1 ppm Fe(+II)	-430	8.7	“	“
none	-	8.8	19.8 m ⁻¹	15
3 ppm S(-II)	-230	9.2	“	“
metallic Fe	-	8.8	“	15

* *Eh and pH measured for parallel groundwater samples (without UO₂ pellets) after two weeks' period under anaerobic conditions.*

The solution concentrations of uranium as a function of time in saline and Allard groundwater in the experiments with the low S/V 0.66 m⁻¹, are given in Figures 3-5...3-8. Figures 3-6 and 3-8 include the measured data for four experiments with different contents of sulphide and ferrous iron. Each experiment has a parallel experiment. The Eh in synthetic groundwater containing sulphide has remained relatively stable (see Table 3-2) during a ten-months'-period under anaerobic conditions, while in synthetic groundwater containing ferrous iron it has changed.

The control of the Eh by the addition of redox species to synthetic groundwater seems to lower the uranium concentrations in solution. In the experiments without redox species (Figures 3-5 and 3-7) the concentration increases slowly during the experimental time of 300 days. The measured Eh values in the absence of redox species typically vary (-20 ... +175 mV). In the experiments with redox species and therefore low Eh, the solution concentration of uranium attains a constant level after a few days. It is close to the detection limit of the analytical method in saline groundwater. In Allard groundwater the sensitivity is clearly better. No differences were observed between the filtered (0.45 µm) and unfiltered samples.

Comparison of the measured data at low Eh with the calculated solubilities (EQ3/6) of uranium oxides shows that the solution concentration is at the level of the theoretical solubility of the well-crystallized solid, UO₂, in both groundwaters.

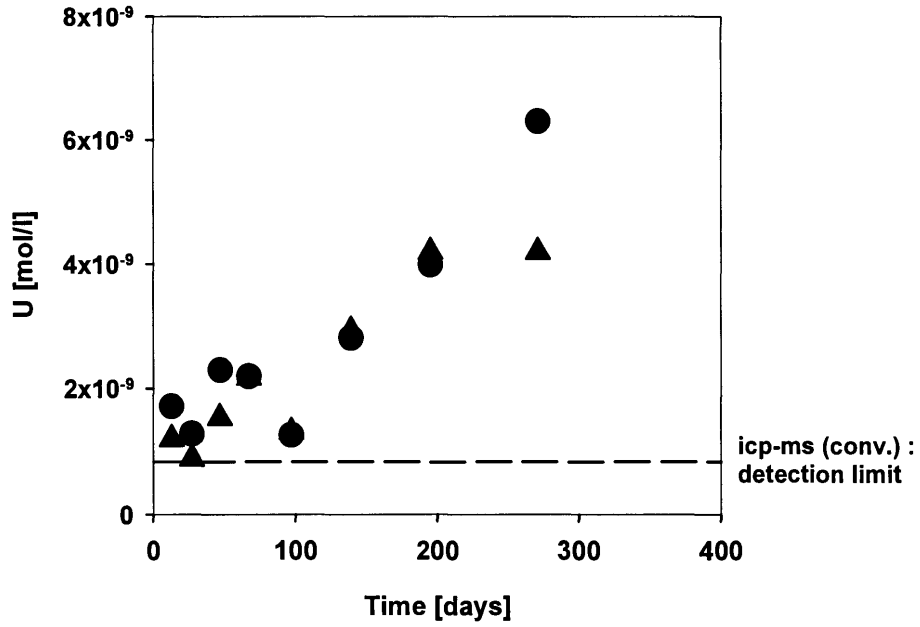


Figure 3-5. Uranium concentration vs. contact time in anoxic (N_2) saline groundwater during dissolution of UO_2 pellets ($S/V = 0.66 \text{ m}^{-1}$). The measured data is for two parallel experiments.

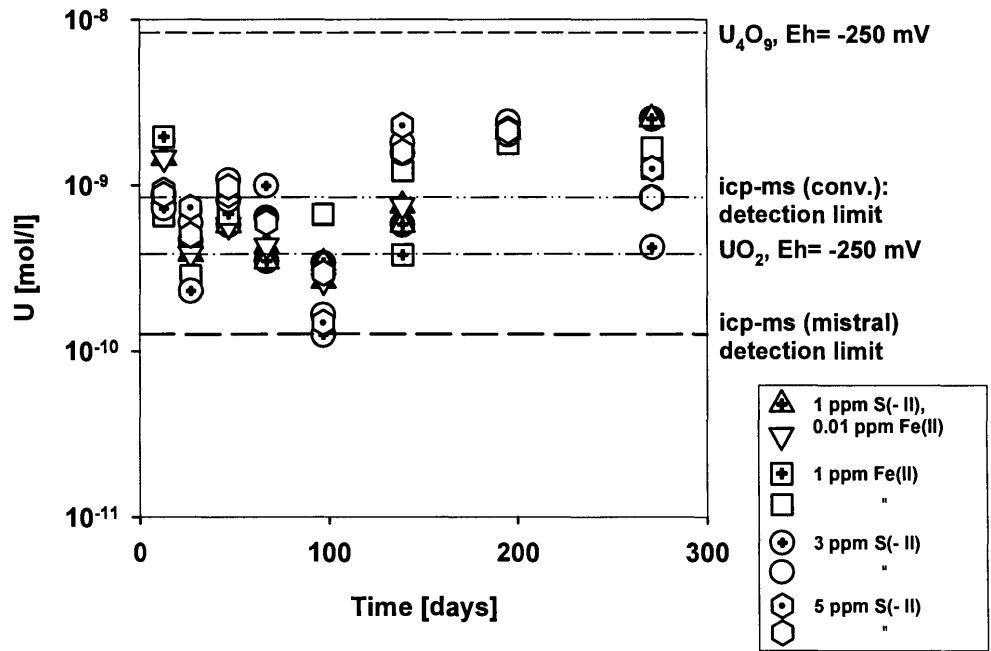


Figure 3-6. Uranium concentration vs. contact time in anoxic (N_2) saline groundwater during dissolution of UO_2 pellets ($S/V = 0.66 \text{ m}^{-1}$) at low Eh (-200...-300 mV). The reference lines show the theoretical solubilities of U solid phases (EQ3/6, composite database) possibly controlling the solubility.

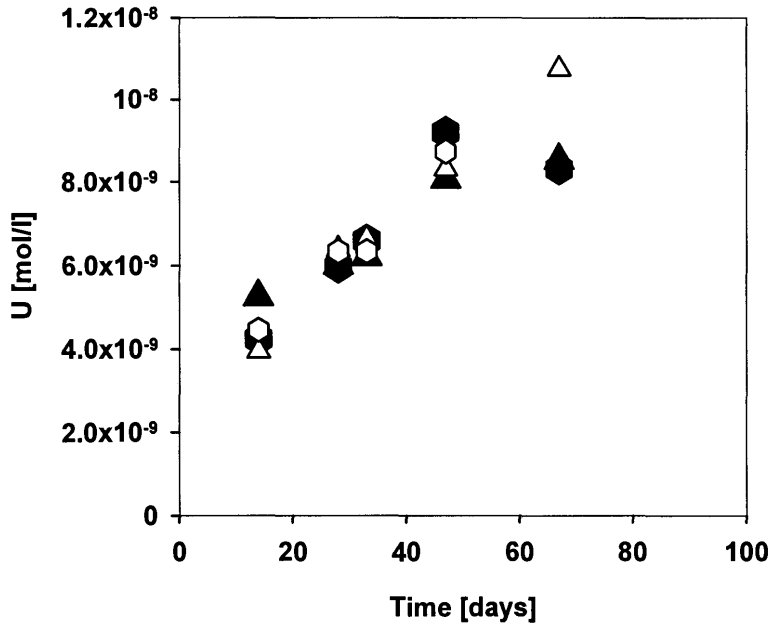


Figure 3-7. Uranium concentration vs. contact time in anoxic (N_2) Allard groundwater during dissolution of UO_2 pellets ($S/V= 0.66 m^{-1}$). The measured data is for two parallel experiments.

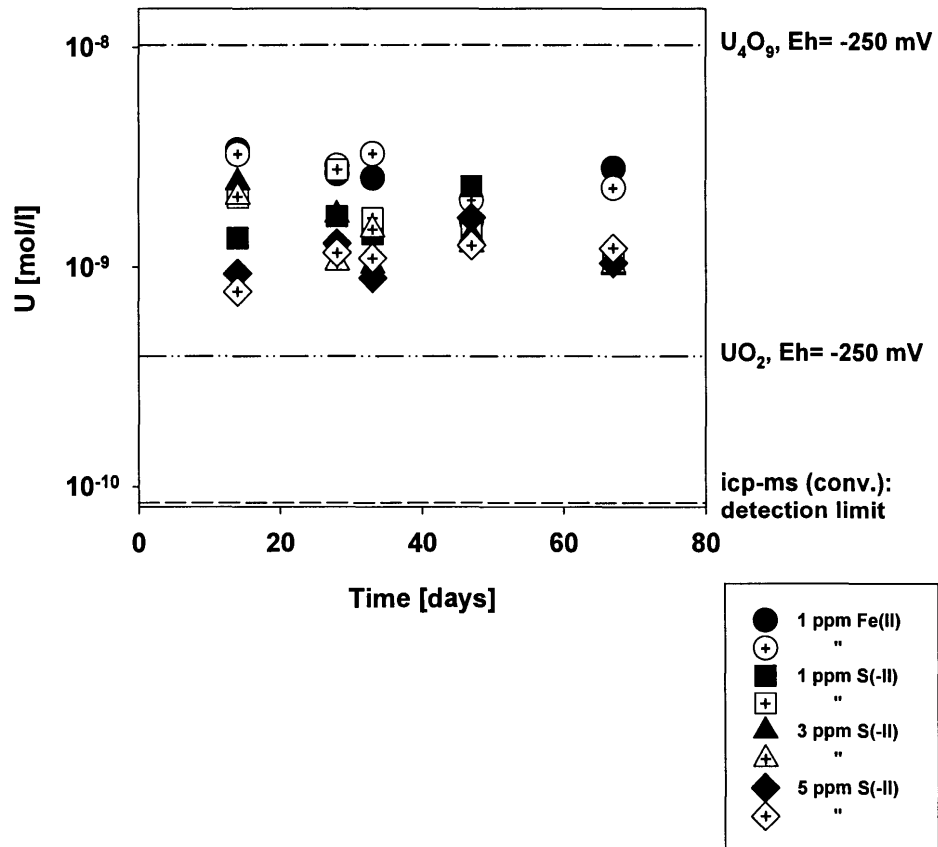


Figure 3-8. Uranium concentration vs. contact time in anoxic (N_2) Allard groundwater during dissolution of UO_2 pellets ($S/V= 0.66 m^{-1}$) at low Eh (-200...-300 mV). The reference lines show the theoretical solubilities of U solid phases (EQ3/6, composite database) possibly controlling the solubility.

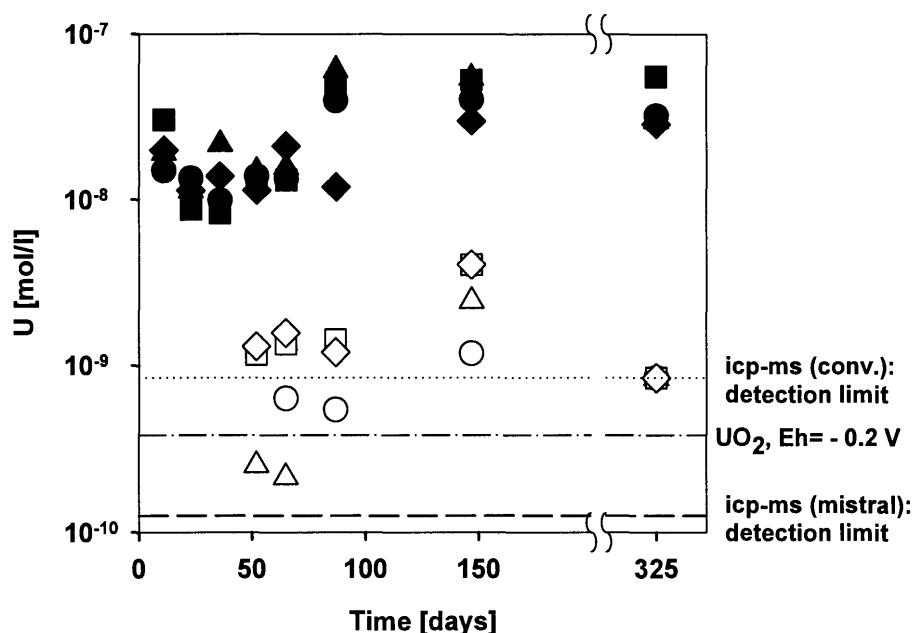


Figure 3-9. Uranium concentration vs. contact time in anoxic (N_2) synthetic saline groundwater during dissolution of UO_2 pellets at low Eh (-200 mV), $S/V = 19.8$ m^{-1} .

In the experiment with the higher S/V at low Eh, Figure 3-9, the measured concentrations of uranium in the unfiltered samples are higher, while in the filtered samples (0.45 μm) they are at the same level as in the experiments with the lower S/V (Figure 3-6).

There is a clear difference between the unfiltered and filtered samples. It was not observed in the parallel experiment without redox species /Ollila 1997/. One reason for this may be the dissolution and subsequent precipitation of the pre-oxidized surface layer, which possibly has not been wholly removed during the predissolution period, or a different dissolution mechanism. The results at high S/V are available for saline groundwater. The similar experiments in Allard groundwater have been started.

The oxidation state of uranium in the aqueous phase was analysed after periods of two months and one year from the beginning in the higher- S/V experiments in saline groundwater, see Table 3-4. The method is based on the separation of the tetravalent and hexavalent states by ion-exchange chromatography in HCl medium, followed by the uranium analyses of each of the fractions by ICP-MS /Ollila et al. 1996/.

Table 3-4. Oxidation state of uranium in the UO_2 dissolution experiment in saline groundwater ($S/V = 19.8$ m^{-1}).

Redox species addition	Eh [mV]	Time	U(IV) [%]	U(VI) [%]
none	-20...+175	2 months	13	87
1 ppm S(-II), 0.01 ppm Fe(+II)	-215...-230	"	63	37
none	-20...+175	one year	-	100
1 ppm S(-II), 0.01 ppm Fe(+II)	-215...-230	"	80	20

4 Summary

This report presents the results obtained from dissolution experiments with unirradiated UO_2 pellets and UO_2 powder in synthetic groundwaters. Redox conditions vary from oxidizing (air-saturated), anaerobic (N_2) to reducing (N_2 , low Eh). The Eh is maintained at a low level by the addition of redox species (S^{2-} , Fe^{2+}) to the aqueous phase. The granitic groundwaters include saline and fresh (Allard) compositions. The granite/bentonite groundwater (by Ciemat, Spain) simulates the effects of bentonite in granitic groundwater. The ratio of UO_2 surface area to water volume (S/V) is varied. The experimental method is a static batch dissolution procedure.

Under air-saturated conditions, the experiments with UO_2 powder at high S/V (1000 m^{-1}) are approaching saturation after an experimental time of 80 days. The experiments with UO_2 pellets at low S/V ($0.66 \dots 19.8 \text{ m}^{-1}$) need long dissolution periods to reach steady state. The uranium concentration increases linearly in the beginning and is followed by a slower increase. After one year's experimental time, the solution concentration of uranium is still increasing. A preliminary comparison with theoretical solubility data (EQ3/6, NEA and composite databases) was made assuming secondary phases of uranium to limit its solubilities. In the high S/V experiments, the solution concentration would seem to reach the level of the schoepite solubility in saline and granite/bentonite groundwaters. As the experiments proceed, the solid phases in solution will be analysed after different contact time periods in order to get information on secondary alteration products that possibly control the uranium concentration in solution.

Under anoxic conditions (N_2) the control of the Eh ($-300 \dots -200 \text{ mV}$) by the addition of redox species to synthetic groundwater seems to lower the solution concentrations of uranium. A steady state is attained after a few days in both groundwaters. It is at the level of the theoretical solubility of the well-crystallized U(IV)oxide, UO_2 (10^{-9} M). In earlier experiments in synthetic groundwater without the Eh control, the measured solubilities were one order of magnitude higher. They were close to the theoretical solubility of the mixed U(IV)(VI)oxide, U_4O_9 .

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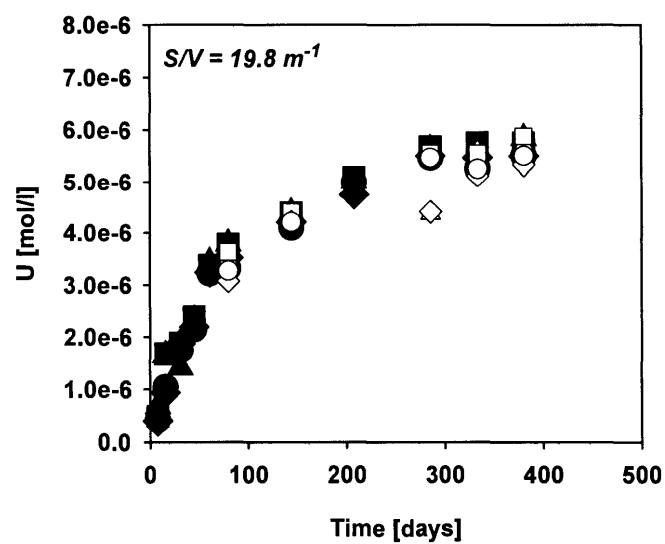
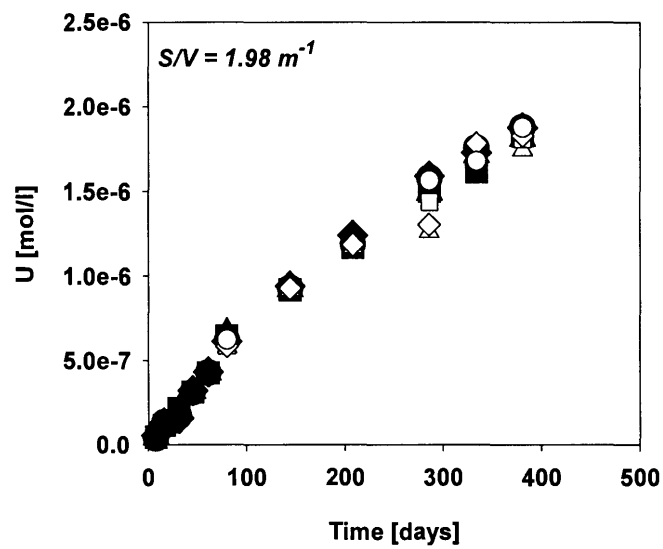
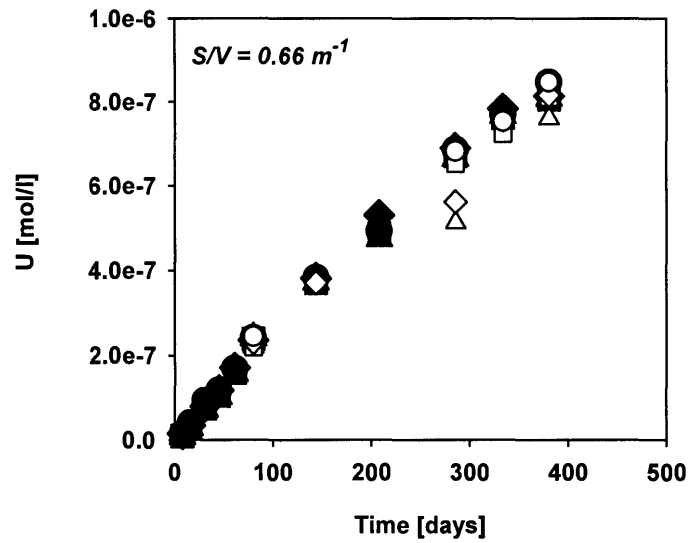
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Uranium concentration vs. contact time in air-saturated saline groundwater in the experiments with UO_2 pellets at different S/V . The measured data at each S/V is for two parallel experiments. The filled and open symbols represent unfiltered and filtered symbols, respectively.

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