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Citation: -- LinkSeeker Document Request -- JL
Journal Title: Radiochimica acta
Volume: 66-7
Start Page: 29
End Page: 35
Year: 1994
Article Title: A comparison between unirradiated UO₂(s) and schoepite solubilities in 1M NaCl medium
Conf. Title: 4th International Conference on Chemistry and Migratory Behaviour of Actinides and Fission Products
Author 1: TORRERO, ME
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Author 4: SANDINO, MCA
Author 5: GRAMBOW, B
Document Type: article
Abbrev. Title: RADIOCHIMICA ACTA
ISSN: 0033-8230
CODEN: RAACAP
Publication Date: R OLDENBOURG VERLAG
Database ID: info:lanl-repo/isi/A1994QE24500007
Month needed: Jul
Day needed: 5
Year needed: 2005
Document availability: Send article only if in the Library collection
Read copy right agreement: Yes
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A Comparison Between Unirradiated $\text{UO}_2(\text{s})$ and Schoepite Solubilities in 1 M NaCl Medium

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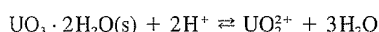
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$\text{UO}_2(\text{s})$ / Synthetic schoepite / Solubility constant / Chloride medium / Interaction coefficients

Abstract

In this study, the dissolution of unirradiated $\text{UO}_2(\text{s})$ under oxidizing conditions (5% O_2/N_2) in 1 M NaCl was investigated at neutral pH. A decrease in pH and subsequent return to neutrality led to the formation of a yellow solid phase precipitated on the $\text{UO}_2(\text{s})$ surface, closely resembling schoepite, $\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}(\text{s})$, (chemically equivalent to $\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{s})$). The uranium concentrations measured in solutions matched schoepite solubility. These solubility data have been compared with the values obtained from parallel experiments on the solubility of synthetic schoepite in the same ionic medium. Both approaches gave similar results. The morphology of the solids has also been compared by means of Scanning Electron Microscopy.

The obtained solubility data have been evaluated using the computer program C-LETAGROP with the thermodynamic constants being calculated by means of the Specific Interaction Theory for the corresponding ionic medium, 1 M NaCl. The solubility constants, $\log K_{\text{so}}$, for the reaction



obtained at 1 M NaCl and $T = 25^\circ\text{C}$ are: 5.92 ± 0.08 (schoepite on $\text{UO}_2(\text{s})$), and 5.57 ± 0.08 (synthetic schoepite). The extrapolated values to the infinite dilution standard state are 5.73 ± 0.28 and 5.38 ± 0.20 , respectively.

Introduction

Many countries consider direct disposal of spent nuclear fuel in deep geological formations as the principal strategy for isolating high level reactor wastes. The chemical durability of spent fuel under disposal conditions has extensively been studied [1]. Nevertheless, the release/retardation processes of the different radionuclides are not yet fully understood.

Under reducing conditions, it seems [2] that the release of radionuclides from spent fuel is controlled by the solubility of $\text{UO}_2(\text{s})$, the main component of the waste matrix. However, under oxidizing conditions, $\text{UO}_2(\text{s})$ is not thermodynamically stable. Therefore, it will go through an oxidative dissolution process. This reaction is complex and it may lead to the formation of secondary phases of uranium which might control the long-term release of radionuclides as well as the aqueous uranium concentration. Depending on the chemistry of the contacting groundwaters, different

solid alteration products such as hydroxides, silicates, phosphates etc., could form [3].

In spent fuel and $\text{UO}_2(\text{s})$ dissolution studies [4, 5, 6], it has been observed that the solution concentration of uranium reaches apparently a constant value after short periods of time. Schoepite $\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}(\text{s})$, (chemically equivalent to $\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{s})$), has been identified as an alteration product in some spent fuel dissolution studies [2, 7]. Initial attempts to identify constraints for uranium release from spent fuel seem to indicate that solution concentrations were in close agreement to schoepite solubility [8, 9]. However, an intrinsic difficulty is that schoepite is not a well defined phase. Several polytypes occur [10, 11], often poorly characterized. Some of them may also coexist. The solubility of this solid is also very much dependent on the degree of crystallinity [12, 13], which may be influenced, e.g., by the formation conditions. All these factors lead to a large uncertainty in predicting its solubility.

Moreover, the solution chemistry of U(VI) is not completely understood. The stability of certain uranyl hydroxo complexes is just an estimation [14–16]. This lack of thermodynamic knowledge along with the inherent problems due to the corrections for ionic strength [17], are of crucial importance, particularly in chloride media.

As a contribution to the assessment of uranium oxides solubilities in chloride media, the dissolution of unirradiated $\text{UO}_2(\text{s})$ under oxidizing conditions has been studied in conjunction with the formation and solubility of schoepite in carbonate free 1 M NaCl solutions. The results of these investigations may be of relevance both for saline environments and for deep granitic groundwaters.

Experimental

Materials

Chemicals used in this study, $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}(\text{s})$, $\text{NaOH}(\text{s})$, $\text{NaCl}(\text{s})$ and HCl were of analytical grade (Merck). All solutions were prepared with bidistilled water either from a Nanopour system or from a Millipore Corp. Milli-Q system.

1. Unirradiated $UO_2(s)$

Unirradiated crystalline uranium dioxide powder with a particle size between 10–50 μm has been used. The solid was washed several times before starting the dissolution experiments with diluted perchloric acid and degassed distilled water. The solid surface was analyzed by using a VG Scientific Microlab MK II XPS Spectrometer with $Al K_{\alpha}$ exciting radiation. The O/U ratio at the surface was 2.1.

2. Synthesis of schoepite

Schoepite $UO_2(OH)_2 \cdot H_2O(s)$, (chemically equivalent to $UO_3 \cdot 2H_2O(s)$), was precipitated from a solution of uranyl nitrate by adding dropwise a concentrated NaOH solution under constant $N_2(g)$ stream at room temperature. The pH was kept below 7 during the precipitation process. The solid was left to crystallize for 2 weeks at room temperature. The final product was a fine-grained yellow phase. After separation from its mother liquid, the solid was thoroughly washed with bidistilled water. This phase was characterized by XPD and SEM-EDX. The XPD pattern showed the presence of peaks corresponding to a poorly crystalline uranyl hydroxide hydrated phase, (microcrystalline powder), which was also corroborated with SEM micrographs. The obtained XPD pattern resembled the pattern for metaschoepite given in the literature [18]. The EDX analysis did not detect any other element different than uranium as a component of the precipitate.

Procedures

1. Dissolution/precipitation experiments with $UO_2(s)$ under oxidizing conditions

The solid was put in contact with 1 M NaCl solutions. The initial pH of the experiments was 5.0. The pH was measured with a combined glass electrode (Hamilton) which was calibrated in the same ionic medium via a Gran plot [19]. The pH of the test solutions was changed either using HCl or CO_2 -free NaOH solutions. Oxidizing conditions were achieved using a mixture of 5% O_2 in N_2 . The redox potential of the bulk solution was monitored by measuring the potential between a platinum wire and a Ag/AgCl reference electrode. The p_e measured was 7.5. The experiments were performed in Teflon vessels at room temperature.

At pH 5, no alteration product was observed. For improving the conditions for the formation of secondary phases, the pH was, at first, decreased to 3.5 in order to increase the dissolution rate of $UO_2(s)$, [20]. Therefore, the concentration of uranium in solution increases significantly. After one month the pH was increased up to 8.2 and the precipitation of a yellow solid phase was observed.

The response of uranium concentrations on addition of NaOH and/or HCl was studied in the pres-

ence of both, $UO_2(s)$ and the yellow precipitate. After each addition, equilibrium was assumed to be attained when the pH remained constant (± 0.1 pH units) during three days. This took normally three weeks. Once that the equilibrium was reached, aliquots for further analysis of the solution were taken. The equilibrium criterion was confirmed by approaching the same pH from both sides, acid and basic, i.e., from super- or undersaturated conditions, respectively. The corresponding uranium concentrations were the same in both cases. The overall duration of the experiments was longer than 500 days.

2. Dissolution experiments with $UO_2(s)$

The dissolution of $UO_2(s)$ has also been studied as a function of pH, in this case without the formation of the yellow solid phase. The conditions and methodology of this experiment were similar as in the experiment (1). Solution samples were taken at different times of the experiment although the pH changed slightly, indicating non equilibrium conditions. The formation of the secondary yellow phase was not observed.

3. Solubility experiments with schoepite

Known amounts of the solid were contacted with 1 M NaCl solutions, at two different initial pH values, (3.30 and 8.40). The pH was measured by a Ross electrode (Orion 81-02) which was calibrated using standard buffer solutions. Measured pH values were corrected for liquid junction potentials. The liquid junction potentials were obtained by comparing potentials measured with the H^+ electrode with the potentials measured in the same solution with a cell without liquid junction potentials using a combination of a H^+ and a Cl^- electrode [21].

The experiments were performed in Teflon-PFA vessels (50 ml) which were sealed and placed in a water bath at $25.0 \pm 0.5^\circ\text{C}$. After 3, 5 and 9 months, aliquots were taken for further analysis from both solid and aqueous phases, which were immediately filtered.

After 9 months of contact, the pH was increased stepwise by adding NaOH. Equilibrium was assumed to be attained when the pH remained constant within ± 0.01 units during 24 hours. The results showed that the system reached equilibrium in 2–3 weeks. After equilibrium was attained, a sample was taken following the procedure described above.

Analysis

In order to ascertain the possible influence of colloids, the samples were filtered through 0.05 and/or 0.2 μm membrane, (Millipore). No variations were observed between samples filtered with the two different pore size membranes. The uranium and sodium contents in solutions were analyzed by ion coupled plasma spec-

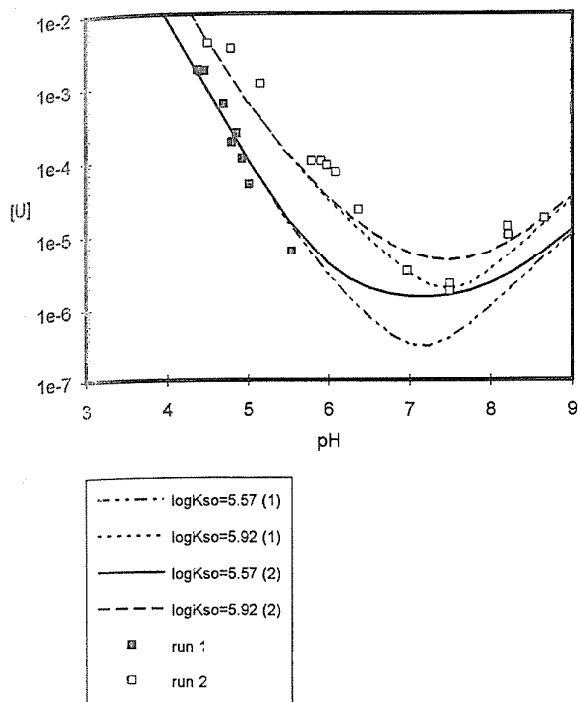


Fig. 1. Uranium concentration as a function of pH. (1) Models not including the complex $\text{UO}_2(\text{OH})_2(\text{aq})$; (2) models including the complex $\text{UO}_2(\text{OH})_2(\text{aq})$.

trophotometry (ICP), using an ARL-3580 spectrophotometer. Some of the uranium samples (lower concentrations) were measured by a Scintrex UA-3 laser fluorescence analyzer [22].

The solid samples were analyzed by X-ray Powder Diffraction, (XPD). The X-ray patterns were recorded on a Siemens-D500 diffractometer using $\text{Cu K}\alpha$ radiation. The solid phases were also examined by Scanning Electron Microscopy and Energy-Dispersive Analysis (SEM-EDX) in a JEOL-35C scanning electron microscope.

Results

1. Dissolution/precipitation experiments with $\text{UO}_2(\text{s})$

It was attempted to characterize the yellow solid precipitate by using XPD, but the phase was amorphous. Micrographs of this solid on the $\text{UO}_2(\text{s})$ surface were obtained by using a JEOL SEM. The largest particle size was only 1 μm . EDX analysis showed only the presence of uranium in the precipitate. The equilibrium concentrations of uranium as a function of pH are shown in Figure 1, (run 2).

2. Dissolution experiments with $\text{UO}_2(\text{s})$

The concentrations of uranium vs. pH obtained during the dissolution of $\text{UO}_2(\text{s})$ without the presence of

the yellow solid precipitate, run 3, are included in Figure 4.

3. Solubility tests for schoepite

The measured solubility data (run 1) are given in Figure 1 as a function of pH. Independent on the initial pH, all the values obtained during the first 9 months of the experiment fall in a narrow range, i.e., $\text{pH} \approx 4$, and $[\text{U}] \approx 10^{-3} \text{ mol dm}^{-3}$. Equilibrium was reached in less than 3 months. The pH changes during the experiment may be explained in terms of an adsorption/ion exchange process on the solid surface. However, this phenomenon needs further investigations.

The composition and morphology of the solid phases were analyzed at different stages of each experiment. The XPD results showed a significant increase in crystallinity, after the first 3 months, but the crystallinity remained constant during the further course of the experiment (15 months). The X-ray patterns were not influenced by the experimental conditions (initial pH and pH changes). The interpretation of the XPD patterns is not straightforward, since in the system $\text{UO}_3\text{-H}_2\text{O}(\text{s})$ several phases (schoepite I, II and III, meta and para etc.) can form and under certain conditions can coexist [10, 11]. Nevertheless, the patterns obtained pointed out the existence of the same phase in all the experiments. The peak positions and intensities were in excellent agreement with the values reported in the literature for metaschoepite, $\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{s})$, [18]. This is illustrated in Figure 2, where the XPD patterns recorded for two samples at two different times, 6 and 13 months of the experiment, are compared with the metaschoepite pattern.

The SEM micrographs obtained (see Figure 3) showed the tabular morphology characteristic of this phase [23]. Sodium was not found by EDX in any of the solid samples. This information together with the corresponding XPD patterns lead to the conclusion that the nature of the solid phase did not change under the conditions of this study.

Evaluation of the data

Taking into account that the schoepite phase did not change in the course of the solubility tests in 1 M NaCl, the uranium concentrations obtained can be considered representative for the solubility of this solid, (run 1). Furthermore, the dissolution/precipitation studies of $\text{UO}_2(\text{s})$ under oxidizing conditions resulted in the formation of a similar type of solid phase, (run 2).

In order to obtain the corresponding solubility products, the solubility data, run 1 and run 2, have been evaluated using the computer program C-Letagrop, [24]. The experimental data ($-\log[\text{H}^+]$, $[\text{U}]_e$) for each run were treated separately, based on the existence of two solids with different degrees of crystal-

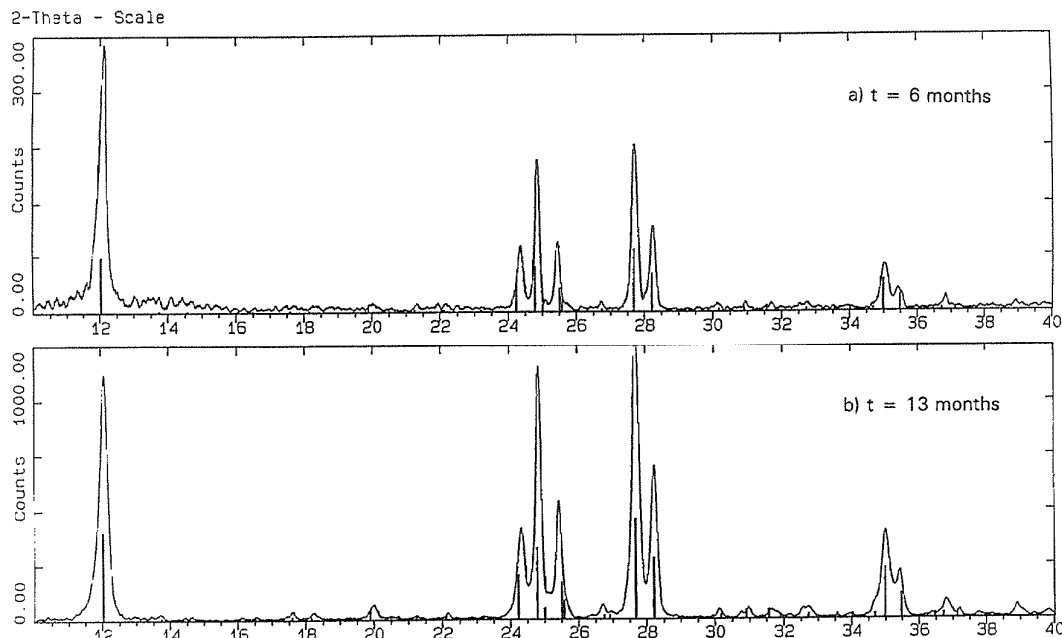


Fig. 2. X-ray diffractograms of synthetic schoepite at two times of the experiments compared with the patterns of metaschoepite (JCPDS no. 18-1436).

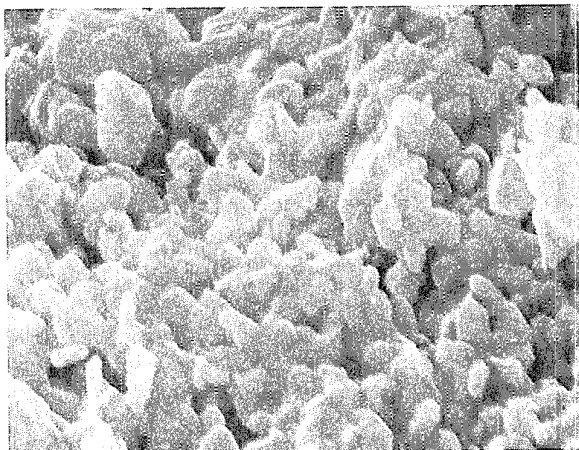
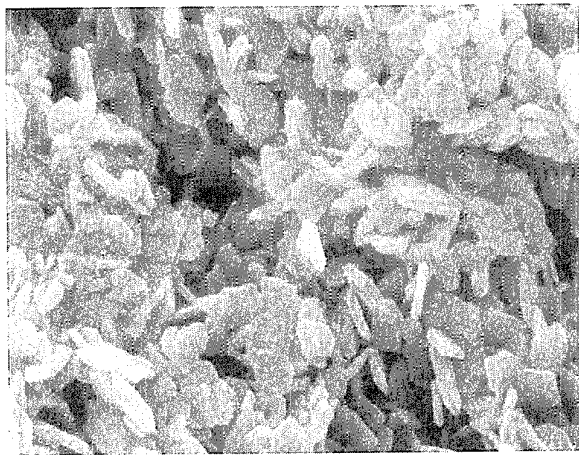


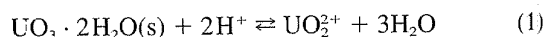
Fig. 3. SEM micrographs of synthetic schoepite (magnification $\times 20000$).

Table 1. Equilibrium constants at $I = 0$ and at 1 M NaCl

Species	$\log \beta_{p,0}^0$	$\log \beta_{p,1}$
UO_2OH^+	-5.2 ^a	-5.21
$(\text{UO}_2)_2(\text{OH})_2^{2+}$	-5.62 ^a	-6.04
$(\text{UO}_2)_3(\text{OH})_2^{2+}$	-11.9 ^a	-12.32
$(\text{UO}_2)_4(\text{OH})_7^+$	-21.9 ^a	-23.35
$(\text{UO}_2)_3(\text{OH})_5^+$	-15.55 ^a	-16.81
$\text{UO}_2(\text{OH})_2(\text{aq})$	< -10.3 ^a	-11.5 ^c
$(\text{UO}_2)_3(\text{OH})_7^-$	-32.2 ^b	-32.39
$\text{UO}_2(\text{OH})_3^-$	-19.74 ^b	-19.55
UO_2Cl^+	0.17 ^c	-0.40
$\text{UO}_2\text{Cl}_2(\text{aq})$	-1.1 ^a	-1.62
OH^-	-14.0 ^a	-13.77

^a [14], ^b [13], ^c [15].

linity, corresponding to the run 1 and run 2, respectively. The solubility constants, K_{so} , for the reaction:



were calculated for 1 M NaCl solution using the thermodynamic data base listed in Table 1. Most of the stability constants for the different uranyl complexes at zero ionic strength correspond to the values recommended by the NEA [14]. As mentioned before, the hydrolysis of uranium is not yet fully understood. This specially applies to the neutral complex, $\text{UO}_2(\text{OH})_2(\text{aq})$, and the polynuclear species, $(\text{UO}_2)_4(\text{OH})_7^+$.

In the case of the neutral species, the value given by the NEA, $\log \beta_{1,2} < -10.3$, [14], is only an upper limit, very likely being overestimated. This has been recently confirmed by Silva [15]. He pointed out that a much better agreement between his experimental and calculated data was achieved using a lower value for

Table 2. Ion interaction coefficients $\epsilon_{i,k}$ with $k = \text{Cl}^-$, Na^+ , ClO_4^- [14]

$j \quad k \rightarrow$	ClO_4^-	Cl^-	Na^+
H^+		0.12 ± 0.01	
OH^-			0.04 ± 0.01
UO_2^{2+}	0.46 ± 0.03		
$(\text{UO}_2)_2(\text{OH})_2^{2+}$	0.57 ± 0.07	0.69 ± 0.07	
$(\text{UO}_2)_3(\text{OH})_4^{2+}$	0.89 ± 0.23	0.50 ± 0.18	
$(\text{UO}_2)_3(\text{OH})_5^+$	0.45 ± 0.15	0.81 ± 0.17	
$(\text{UO}_2)_4(\text{OH})_7^+$	0.45 ± 0.15	0.81 ± 0.17	
$\text{UO}_2(\text{OH})_5^+$			-0.09 ± 0.05
$(\text{UO}_2)_4(\text{OH})_7^+$			-0.09 ± 0.05
UO_2Cl^+	0.33 ± 0.04		

its equilibrium constant, $\log \beta_{1,2} = -11.5$. Choppin [16] has also reported a lower value for the stability constant of this monomeric complex, $\log \beta_{1,2} = -12$. Both values are consistent with the upper stability limit proposed by the NEA, [14].

The polynuclear complex $(\text{UO}_2)_4(\text{OH})_7^+$ is not very well established. The literature values of the equilibrium constant are not well defined by the scarce experimental data, [25–27]. Based on this, the NEA review, [14], gives only an estimation for the formation constant. The addition or omission of this particular species to our chemical model will not influence the results, since this complex is only predominant at very high uranium concentrations which are out of the range of the experimental work presented here.

The extrapolation of the equilibrium constants from zero ionic strength to a 1 M NaCl solution was done using the specific interaction theory, SIT [17]. The interaction coefficients used in this study are listed in Table 2. They correspond to the values recommended by the NEA review [14].

The chemistry of the uranyl ion in chloride medium has recently been evaluated by the NEA [14], using the SIT theory. In order to explicitly account for chloride complexation, the authors did not use the binary interaction coefficient, $\epsilon(\text{UO}_2^{2+}, \text{Cl}^-) = 0.21$, reported by Ciavatta [28], since this value is obtained from binary UO_2Cl_2 solutions without considering chloride complexation. Instead, uranium chemistry in chloride media is treated similarly as in perchlorate media, with $\epsilon(\text{UO}_2^{2+}, \text{Cl}^-) \approx \epsilon(\text{UO}_2^{2+}, \text{ClO}_4^-) = 0.46$. Differences between the two media are considered as resulting exclusively from the formation of chloro complexes.

The uranyl ion forms rather weak chloro complexes [29]. The ionic strength dependence of their stability constants has also been evaluated by Grenthe *et al.*, [14], using the SIT theory with perchlorate as non complexing background electrolyte. To be consistent with the interaction model for the free uranyl ion, the interaction coefficients for the mono chloro complex in perchlorate and chloride media are considered equal, i.e., $\epsilon(\text{UO}_2\text{Cl}^+, \text{Cl}^-) = \epsilon(\text{UO}_2\text{Cl}^+, \text{ClO}_4^-)$. Whether or not these data are applicable to pure chloride media remains to be demonstrated.

Table 3. Set of the solubility constants for reaction 1 obtained at 1 M NaCl and $T = 25^\circ\text{C}$ and the corresponding extrapolated values to the infinite dilution standard state

Run	$\log K_{so} \pm 2\sigma$	$\log K_{so}^0 \pm 2\sigma^*$
1	5.57 ± 0.08	5.38 ± 0.20
2	5.92 ± 0.08	5.73 ± 0.28

* The uncertainty assigned to the extrapolated values was calculated using the following equation, $\sigma_{\log K_{so}^0} = ((\sigma_{\log K_{so}})^2 + (m_{\text{Cl}^-} \cdot \sigma_{\text{De}})^2)^{1/2}$ where De is the result of the values listed in Table 2.

In contrast to the interaction coefficients for the mono chloro complex and the free uranyl ion, interaction coefficients for some of the hydroxo complexes are different for the chloride and perchlorate media, (see Table 2). The equilibrium constants obtained using these parameters for the species, $(\text{UO}_2)_2(\text{OH})_2^{2+}$, $(\text{UO}_2)_3(\text{OH})_4^{2+}$ and $(\text{UO}_2)_3(\text{OH})_5^+$ could be compared with the values, reported by Rush *et al.* [30], from potentiometric experiments.

In the case of the complexes UO_2OH^+ and $(\text{UO}_2)_4(\text{OH})_7^+$, no data exist for the interaction coefficients of these species in chloride media. As mentioned before, the polynuclear species is not predominant under the conditions of our experiments. We assumed that its interaction coefficient is of the same order as the interaction coefficient corresponding to the complex $(\text{UO}_2)_3(\text{OH})_5^+$ with Cl^- ions. The interaction coefficient for the monomeric complex, UO_2OH^+ , in chloride medium is unknown and in perchlorate medium, it is badly defined (-0.06 ± 3.7). In order to test whether these species are of importance in our calculations, computer runs were performed with and without considering the existence of these complexes. No differences were observed.

The results of the calculations, $\log K_{so}$, with Silva's value for $\log \beta_{1,2}$, are given in Table 3 together with the corresponding values at zero ionic strength, $\log K_{so}^0$. A comparison between the experimental and theoretical data calculated with the model is given in Figure 1 showing a good agreement. The same calculations were carried out without including chloride complexes (UO_2Cl^+ and $\text{UO}_2\text{Cl}_2(\text{aq})$). The values of $\log K_{so}$ (run 1, 5.64 ± 0.08 and run 2, 5.89 ± 0.05) were, within the uncertainty limit, the same as the values given in Table 3. This fact indicates that chloride complexation is irrelevant at 1 M NaCl medium.

Discussion

The data from our study do not allow us to derive stability constants for the aqueous complexes of the uranyl ion. However, when comparing our experimental results with calculations using the uranium(VI) solution chemistry model of the OECD/NEA [14], with only the solubility constants being fitted, we find out that this model describes our data quite well. Similarly as Silva [15] and Choppin [16], we find further

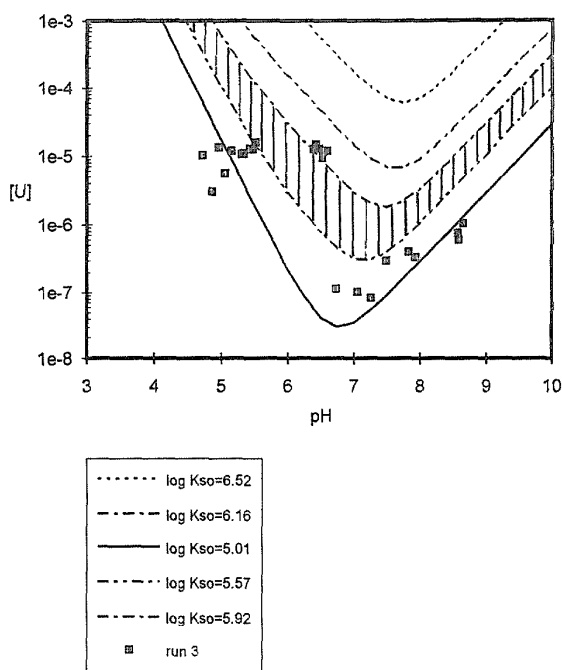


Fig. 4. Solubility models for different kinds of schoepite.

evidence that the upper limit for the stability constant of the $\text{UO}_2(\text{OH})_2(\text{aq})$ complex given by the NEA [14] is overestimated. As can be seen from Figure 1, its stability is definitively not higher than the refined upper limit given by Silva [15]. The calculated solubility constants are similar even if the complex is omitted in the chemical model (lower curves in Figure 1).

When comparing the results from the $\text{UO}_2(\text{s})$ dissolution/precipitation tests with the data from schoepite solubility in the same ionic medium (Figure 1), it becomes obvious that the solubility differs by about a factor of 10. The higher concentrations of uranium obtained in the dissolution tests can be rationalized by the amorphous nature of the precipitate formed from supersaturated solutions in the presence of dissolving $\text{UO}_2(\text{s})$, as opposed to the microcrystalline nature of the schoepite used in the solubility tests. With respect to the microcrystalline schoepite, the precipitate formed in the presence of $\text{UO}_2(\text{s})$ is metastable. However, from a kinetic point of view it must be considered rather stable, as the solution concentrations of uranium appear to be in equilibrium with this phase (similar concentrations reached from super- and undersaturation in the dissolution/precipitation tests). Even after 500 days no phase transformation to a more stable phase was observed.

Figure 4 shows a comparison of our results with data calculated from the solubility constants of schoepite reported in the literature [13]. Ionic strength corrections to 1 M NaCl medium were made in the same way as described above. The same model for the solution chemistry of uranium was used. The upper two curves represent schoepite type phases which are

kinetically sufficient stable to perform long-term solubility tests. No phase transformation was reported in the original literature [12, 13]. Hence, even these types of solid phases might form under certain conditions in chloride media. The lower curve is calculated from the NEA recommended [14] solubility constant of well crystalline schoepite obtained through thermodynamic cycles based on calorimetric data. A comparison of all curves in Figure 4, shows that the solubility of schoepite type phases varies by almost three orders of magnitude.

Included in Figure 4 are data from $\text{UO}_2(\text{s})$ dissolution tests in 1 M NaCl solutions, (run 3). As can be seen, the data are slightly lower than the schoepite solubility measured in the dissolution/precipitation tests and in the solubility experiments (shadowed range) in the same ionic medium. The solution concentrations achieved in this test show some similarities with equilibrium concentrations of uranium with respect to well crystalline schoepite. However, no yellow alteration phase was observed in the dissolution tests. There are two possible explanations for this discrepancy: (1) schoepite is not formed and solution concentrations are kinetically controlled, being by pure chance similar to schoepite solubility or (2) small amounts of non-detectable schoepite have formed, just sufficient to control the aqueous concentrations in the experiment.

Conclusions

The dissolution of $\text{UO}_2(\text{s})$ in 1 M NaCl under oxidizing conditions has been investigated. A decrease in pH and subsequent return to neutrality led to the formation of a yellow solid phase precipitated on the $\text{UO}_2(\text{s})$ surface, closely resembling schoepite. The uranium concentrations measured in solutions matched schoepite solubility. The solubility of well characterized schoepite has also been measured in 1 M NaCl solutions.

Our data indicate that the model for the solution composition of uranium(VI) given by the NEA is in principle applicable to 1 M NaCl solutions. However, as also found by Silva [15] and Choppin [16], the upper limit for the stability constant for the formation of $\text{UO}_2(\text{OH})_2(\text{aq})$ appears to be overestimated.

Experimental conditions strongly influence the outcome of solubility studies in the U(VI)- H_2O system. Metastable solid phases may persist for long periods of time and depending on the solid phase present, associated equilibrium solution concentrations of uranium may vary by orders of magnitude. Further thermodynamic and kinetic studies on the dependence of solubility on crystallinity, specific surface area and on the long-term phase transformations of metastable phases are needed.

Acknowledgements

This work has been financially supported by KFK-INE (Germany) and ENRESA (Spain). We thank the assis-

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ance of Mrs. Dietl for ICP measurements, Mrs. Schlieker for XPD analysis and Dr. Bernotat for SEM-EDX analysis.

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