



PII S0016-7037(97)00337-2

Solid-liquid phase equilibria of U(VI) in NaCl solutions

P. DÍAZ AROCAS^{1,*} and B. GRAMBOW^{2,†}¹CIEMAT, Instituto de Tecnología Nuclear, 22. 28040 Madrid, Spain²Forschungszentrum Karlsruhe (FZK), Institut für Nukleare Entsorgungstechnik, 76021 Karlsruhe, Germany

(Received June 27, 1997; accepted in revised form September 18, 1997)

Abstract—Solid-liquid phase equilibria and equilibrium phase relationships of U(VI) in up to 5 m NaCl solutions were studied by analyzing the precipitation process in initially oversaturated solutions at different pH values. Comparison to corresponding behavior in NaClO₄ media is made. Solid precipitates and solution concentrations of U were characterized as a function of time and pH. In NaClO₄ media schoepite (UO₃·2H₂O) was found to be the stable phase between pH 4 and 6. By contrast, in NaCl media, sodium polyuranates formed. For a given NaCl concentration and pH, differences in the solubility concentration of about 3 orders of magnitude were observed, as attributed to metastability with respect to crystallinity and Na/U ratio of the precipitates. Average solubility constants log K[°]_{so} were calculated for schoepite (log K[°]_{so} = 5.37 ± 0.25) and for Na_{0.33}UO_{3.16}·2H₂O (log K[°]_{so} = 7.13 ± 0.15). Based on these data and together with a critical review of literature data on schoepite and polyuranates a solid solution model is developed, describing composition and phase transformation of Na-polyuranates as a function of the activity ratio Na/H in solution. Solid solution formation is rationalized within the structural context of uranyl mineral sheet structure topologies and interlayer water properties. Copyright © 1998 Elsevier Science Ltd

1. INTRODUCTION

More than 170 uranyl(VI) containing mineral species are known (Burns et al., 1996). These minerals are important indicators for the genesis and alteration of uranium ore deposits, influence spent fuel dissolution under oxidizing conditions, and may control decay series nuclide mobility by sorption or coprecipitation. Upon groundwater contact with primary U(IV) phases under oxidizing conditions, typical secondary phases are initially U(VI) oxide hydrates such as schoepite, dehydrated schoepite, becquerellite, compreignacite, and sodium polyuranates (VI) (Wang, 1981; Wang and Katayama, 1982; Brush, 1980; Wronkiewicz et al., 1992; Torrero et al., 1994). Depending on groundwater composition, uranyl silicates, alkaline uranyl silicates (Wronkiewicz et al., 1996), or uranyl phosphates may follow later in the paragenetic sequence. Schoepite, dehydrated schoepite, compreignacite, and becquerellite were observed both in spent fuel and UO₂ leaching experiments (Wang and Katayama, 1982; Stroes-Gascoyne et al., 1985; Wronkiewicz et al., 1996) and as alteration products of natural uraninite (Pearcy et al., 1994). Sodium polyuranates were encountered in UO₂ leaching experiments performed at 150°C (Wang, 1981). Often, minerals formed are not pure stoichiometric phases but are solid solutions. For example, pure alkali free uranyl oxyhydroxides (schoepite, dehydrated schoepite) are extremely difficult to synthesize. These phases commonly contain trace amounts of alkali, and pure phase synthesis requires application of organic bases for precipitation from aqueous solutions.

The composition of the alteration phase assemblages of uraninite and spent fuels depends on the dissolution characteristics of the primary phases as well as on kinetics of crystalli-

zation and groundwater composition (Wronkiewicz et al., 1996). The purpose of our work is to establish the stability fields and metastability limits of uranyl phases in the Na/Cl/U(VI)/H₂O system. Of primary interest are sodium polyuranates and the phase boundary between schoepite and these uranate phases. The conditions for formation of sodium polyuranates with a large range of Na/U ratios were studied by many researchers (Maly and Vesely, 1958; Tomazic and Branica, 1972; Wamser et al., 1952; Ricci and Loprest, 1955; Sutton, 1955; Brush, 1980; Cordfunke and Loopstra, 1971; Hoekstra, 1965; Pongi et al., 1980). Equilibrium phase relationships are still far from being clear. In addition to Na₂U₂O₇, low temperature phases are probably phases with Na/U ratios of 0.8 and of 0.33 (Gmelin, 1978).

In the U(VI)-Na-Cl-H₂O system, it may be expected that the phase assemblages formed in short term experiments are of metastable nature, rather than representing thermodynamic equilibrium. Depending on phase crystallinity, a variability of up to 3 orders of magnitude in the apparent equilibrium U concentration with synthesized schoepite was observed (Torrero et al., 1994). Even after more than a year of schoepite/water contact, apparent solubilities remained much higher than calculated from calorimetric data (Torrero et al., 1994). Consequently, metastable structures of schoepite may exist for long periods. The suite of uraninite alteration products formed under oxidizing conditions is often difficult to characterize because a multitude of poorly crystalline phases coexist (Finch and Ewing, 1990). Often more than twenty phases are found at a given location. It would probably violate the Gibbs phase rule if all these phases would coexist under equilibrium conditions.

It is a consequence of these observations that an assessment of realistic stability fields of stable and metastable phases requires a study of precipitation kinetics. In solubility or precipitation experiments with synthesized U(VI) oxide hydrates or uranate(VI) phases, it is difficult to distinguish between stable and metastable phases. In certain cases phase transfor-

* Work performed as visiting scientist at Forschungszentrum Karlsruhe.

† Author to whom correspondence should be addressed.

Table 1. Initial experimental conditions (T = 25.0°C).

Experiment	Medium	[U] molal	pH _{corr} ^{a)}	Atmosphere
S-5	3 m NaCl	6.75E-3 ± 3E-4	5.2 ± 0.05	Ar
S-19		1.13E-2 ± 5E-4	5.6 ± 0.05	Ar
S-6		6.65E-3 ± 3E-4	6.1 ± 0.05	Ar
S-18		1.08E-2 ± 4E-4	7.2 ± 0.05	Ar
Ar-1		4.20E-2 ± 2E-3	4.8 ± 0.05	Ar
S-1	5 m NaCl	4.66E-3 ± 2E-4	5.6 ± 0.05	Ar
S-7		2.34E-2 ± 9E-4	5.6 ± 0.05	Ar
S-15		1.40E-2 ± 7E-7	6.1 ± 0.05	Ar
S-2		4.21E-3 ± 2E-4	6.5 ± 0.05	Ar
S-8		9.88E-3 ± 4E-4	6.5 ± 0.05	Ar
C	0.5 m NaClO ₄	2.40E-2 ± 9E-4	6.5 ± 0.05	Ar
B		1.00E-2 ± 4E-4	6.5 ± 0.05	Air
S-16		7.40E-3 ± 4E-4	7.1 ± 0.05	Ar
S-17		1.19E-2 ± 6E-4	7.6 ± 0.05	Ar
S-21		7.07E-3 ± 3E-4	8.9 ± 0.05	Ar
S-9		1.24E-2 ± 5E-4	4.7 ± 0.05	Ar
S-10		8.31E-3 ± 4E-4	6.3 ± 0.05	Ar

^{a)} Corrections for liquid junction potential were performed by calibration with solution of known activity of HCl with reference to the rational pH scale $\text{pH} = \text{pm}_{\text{H}^+}$ (see text).

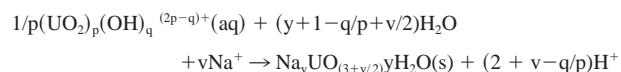
mation does occur, clearly indicating instability of the primary phase (Sandino et al., 1994). However, phase transformation rates will be slow if the transformation affinity is rather small. Synthetic U(VI) oxide hydrate and uranate(VI) phases are often poorly crystalline (Ricci and Loprest, 1955; Sandino, 1991) and the well known dependence of solubility on particle size and crystallinity impedes exact determination of phase boundaries by solubility tests with synthesized phases. The situation is similar when the experiments are conducted by precipitation from initially oversaturated solutions. Initially precipitating phases are often not the most stable phases. According to Ostwald's step rule the system tends to decrease its overall Gibbs free energy on the fastest reaction path, with the fastest-forming phases often being the less stable poorly crystalline phases. A further complication arises from the fact that reported thermodynamic (calorimetric) data on uranate(VI) phases in the Na-U(VI)-Cl-H₂O system (Carnall, 1966; Cordfunke and Loopstra, 1971; Brush, 1980; Cordfunke et al., 1982; Tso et al., 1985) were obtained for phases synthesized at high temperatures T, mainly for Na₂U₂O₇, for α - and β -Na₂UO₄ and for α - and β -Na₄UO₅, which may not form in aqueous media at low temperature. Only a combination of solubility and precipitation techniques along with thermodynamic calculations will allow a satisfactory determination of stability ranges of stable and metastable phases.

This paper reports on the approach of solid-liquid phase equilibria from oversaturated U(VI)-containing carbonate-free NaCl and NaClO₄ solutions at 25°C and pH values between 4 and 8. The precipitation process was studied as a function of time at selected constant pH values. Discussion is focused on the influence of the crystallinity of precipitates, solution pH, and Na-concentration on the equilibrium boundary between schoepite and sodium polyuranates and the Na/U ratio of polyuranates. An ideal solid solution model is suggested describing composition and phase transformation of Na-polyuranates as a function of the activity ratio Na⁺/H⁺ in solution.

2. EXPERIMENTAL DETAILS

2.1. Test Description

A weighted aliquot of a rather concentrated UO₂Cl₂ solution of known molality was added to selected salt solutions (3 and 5 m NaCl and 0.5 m NaClO₄) to achieve initial U(VI)-concentration of about 0.01 m. The resulting solutions were titrated with a NaOH-containing background electrolyte to reach a preselected pH value. The initial experimental conditions are summarized in Table 1. The pH values were kept constant during the experiments by further NaOH addition to compensate the acidification of the solution, either due to adsorption of Na-ions (or Na⁺/H⁺ ion exchange) at the surface of the precipitating solids or by the general precipitation reaction



with $(\text{UO}_2)_p(\text{OH})_q^{(2p-q)+}$ being a positive mono- ($p = 1$) or polynuclear ($p > 1$) hydrolyzed uranyl species. After some weeks the precipitation rate slowed down, and no further addition of NaOH was necessary. The temperature was kept at $25 \pm 0.2^\circ\text{C}$. Experiments were kept free of carbonate by bubbling inert gas (N₂, saturated at the water activity of the experiment) through the solution. Samples of an aqueous suspension of the precipitate were taken periodically. To study colloid formation the samples were filtered by two types of membranes with pore diameters of 0.2 μm and 1.8 nm (ultrafiltration). The experiment was terminated when the solution concentrations of U remained constant for one month.

2.2. Reagents Used

All reagents used were P.A. quality. The uranyl chloride solution was prepared, based on the method proposed by Prins (1973) by precipitation of an uranyl oxide hydrate phase from an uranyl nitrate solution below pH 6, phase separation by centrifugation, washing of the precipitate to remove impurities of NO₃ and Na, determination of the specific U content and dissolution of the precipitate in a stoichiometric amount of HCl. The final UO₂Cl₂ solution was analyzed for U by gravimetry; for Na by ICP/AES, and for Cl and NO₃ by ion chromatography. The analyses showed less than 0.13wt% of Na impurity.

2.3. Analytical Techniques and Samples Preparation

2.3.1. Solid samples

Samples of the precipitated solid phases were prepared from aliquots of an aqueous suspension of the precipitate in its mother liquid. The suspension was filtered by membranes with an average pore size of 0.2 μm . The precipitates were cleaned by rinsing with 60 mL of pure water to remove the adhering NaCl solution. The precipitates were dried in a desiccator over silica gel for one day at room temperature. This procedure did neither dehydrate the solid precipitates nor change Na content significantly.

For analyses by scanning electron microscope and energy dispersive X-ray spectroscopy (SEM-EDS), samples were placed on a carbon-coated holder and were sputtered with gold. The X-ray diffraction analyses were performed with a SIEMENS D-5000 diffractometer using Cu K α radiation using a few milligrams of the wet sample placed directly on a holder. Thermogravimetric and differential scanning calorimetric (TG-DSC) analyses were performed using about 10 mg of solid with a heating rate of 10°C/min.

The solid phases were analyzed for Na to identify potential Na-polyuranate formation and to correct for potential NaCl contamination. Cl was also determined. After dissolving in acid, Na was analyzed by inductively coupled plasma/atomic emission spectrometry (ICP/AES) and Cl by ion chromatography. We have assumed that all Cl found resulted exclusively from the NaCl contamination of the precipitates, and the corresponding Na-content was subtracted from the Na-uranate analyses. In only few samples the Na-content could not be determined because the Cl contents were in excess of Na, probably resulting from uncertainties in the Cl analyses. Uranium as U₃O₈ and H₂O contents were analyzed gravimetrically by heating the solid to 800°C. For Na-rich precipitates the corresponding Na₂O weight was subtracted from the total (Na₂O)_xU₃O₈ weight. Carnall et al. (1966) stated that in contrast to UO₃ the anhydrous polyuranates remain thermally stable until 900°C. Hence, by heating polyuranates to 800°C the water content of the solid may be determined directly.

2.3.2. Solution Analyses

Initial and final concentrations of NaCl and NaClO₄ in solution were determined gravimetrically. Uranium concentrations were analyzed by ICP/AES or by Scintrex. If necessary, U was extracted from the salt solution by means of Chelex 100 prior to the analyses. Methods are described by Strachan et al. (1989) and Diaz Arocas and Grambow (1993). The pH of the solution was measured using a Ross electrode. Corrections for liquid junction potential were performed by calibration with solutions of known activity of HCl with reference to the rational pH scale ($\gamma_{\text{H}^+} = 1$). The corrected pH-value, i.e., the negative logarithm of the molality of H⁺ ions, was calculated from the measured pH values by the relation $\text{pH}_{\text{corr}} = -\log m_{\text{H}^+} = \text{pH}_{\text{meas}} + x$. By the calibration method x values were determined as of -0.05, 0.43, and 0.95 for 0.5m NaClO₄ solution, and 3m and 5m NaCl solutions, respectively. Errors in pH-measurements were within ± 0.05 pH units.

3. RESULTS

3.1. Experiments in 0.5 m NaClO₄ and in Nitrate Media

Experiments performed in 0.5 m NaClO₄ solution at pH values of 4.7 and 6.3 resulted in the formation of crystalline yellow phases with a morphology (Fig.1) resembling that of schoepite as described by Finch and Ewing (1991). The average diameter of the crystal plates was about 1mm. The x-ray patterns (Fig. 2) match a phase designated synthetic metaschoepite by JCPDS (1992), card No. 18-1436, Debets and Loopstra (1963). No phase change with the time of experiment was observed. Chemical and gravimetric analyses on the solid resulted in the formula Na_{0.01}UO_{3.005}·1.7H₂O. DSC analyses showed an endothermic peak at 130.1 \pm 0.7°C, which appears to be associated with the dehydration process observed thermogravimetrically. The enthalpy of

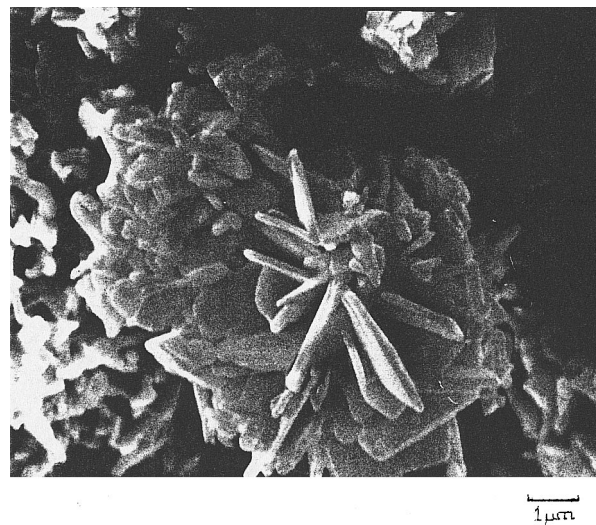


Fig. 1. Morphology of crystalline yellow phase precipitated in experiments performed in 0.5 m NaClO₄. The average diameter of crystal plates is 1 μm .

dehydration ΔH_{dehyd} was 149 \pm 5 J/g. TG-DSC analyses results were compared with those of the uranyl oxide hydrate phase formed in nitrate media for the preparation of UO₂Cl₂ solutions (see above). The latter phase has an X-ray pattern (metaschoepite) similar to the phases formed in perchlorate media. The nominal composition of this phase was Na_{0.13}UO_{3.06}·2H₂O. An endothermic peak of dehydration was observed at 134 \pm 3°C with $\Delta H_{\text{dehyd}} = 175 \pm 3$ J/g.

For the two experiments in perchlorate media, the changes of U concentrations in solution with time are shown in Fig. 3. Initially, the U concentration in solution decreased faster at 6.3 than at pH 4.7, probably resulting from a higher degree of oversaturation. In order to test whether equilibrium was attained, the experiment at pH 4.7 was interrupted after 170 days, and about 98% of the solution was replaced by fresh NaClO₄ solution of the same pH, resulting in a dilution by about a factor of 70. The replacement of the solution was performed by keeping the precipitate wet under Ar-atmosphere and by continuously controlling pH. The solution resaturated relatively fast, with U concentrations about three times lower than before solution replacement. Either the equilibrium U concentration values are between the value obtained from initially oversaturated and from undersaturated conditions, or the equilibrium concentrations did decrease due to an increase in the average particle size of the precipitate due to the dissolution of the finest particles upon solution replenishment. Differences between filtered and ultrafiltered samples were small. Hence, colloid formation did not greatly influence our results. The total U concentrations in solution approaching equilibrium from supersaturation were 5·10⁻⁵ m at pH 4.7 and 10⁻⁷ m at pH 6.3 (Table 2).

3.2. Experiments in 3 m NaCl Solutions

Experiments performed in 3 m NaCl between pH 5.2 and 7.2 resulted in the formation of yellow crystals with plate like habit, an average diameter less than 2 μm , and a thickness of

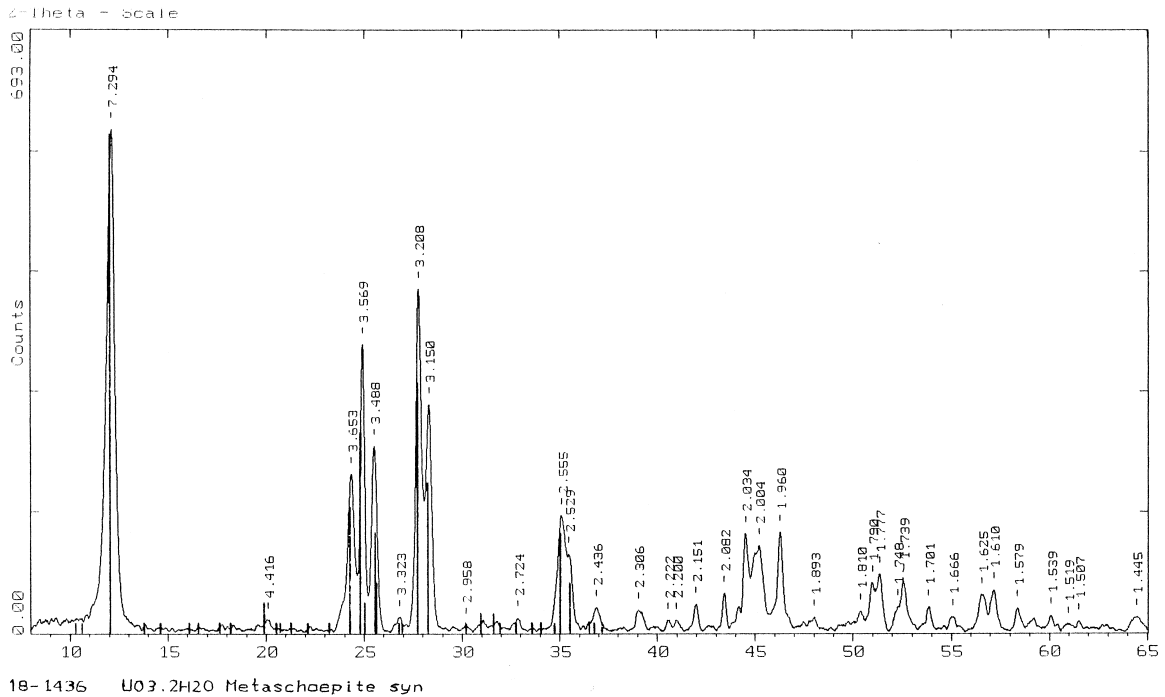


Fig. 2. X-ray patterns of the solid precipitated in 0.5 m NaClO_4 solution. These match a phase designated as synthetic schoepite: JCPDS 1992, card 18-1436 (straight lines).

about 100 nm (SEM analyses). The morphology was similar to schoepite formed in NaClO_4 media (Fig. 4a). The results from chemical analyses of the solid phases formed are given in Table 2. The phases formed had an average nominal polyuranate composition of $\text{Na}_{0.3}\text{UO}_{3.15}\cdot y\text{H}_2\text{O}$. The water contents range from $y = 1.56$ to 5.5. The X-ray powder diffraction data were similar for the phases formed between pH values from 5.2 to 6.1 but were markedly different from those of the phase formed at pH 7.2 (Fig. 5). Based on X-ray data, no phase transformation with time was observed in any experiment. The X-ray

patterns of the phase formed between pH 5.2 and 6.1 closely match the XRD-data reported by Pongi et al. (1980), for the polyuranate $\text{Na}_{0.33}\text{UO}_{3.16}\cdot 2\text{H}_2\text{O}$ and for the sodium polyuranate S.P.II ($\text{Na}:\text{U} = 0.33$) reported by Brush (1980).

TG-DSC analyses of the solid formed at pH 5.2 showed two endothermic peaks, one at 113 ± 3 and another one at $130 \pm 1^\circ\text{C}$. The enthalpy of dehydration ΔH_{dehyd} was calculated for the sum of the two peaks as $146 \pm 5 \text{ J/g}$. The ΔH_{dehyd} value obtained is similar to the value obtained for metaschoepite formed in NaClO_4 media. However, the split into two endo-

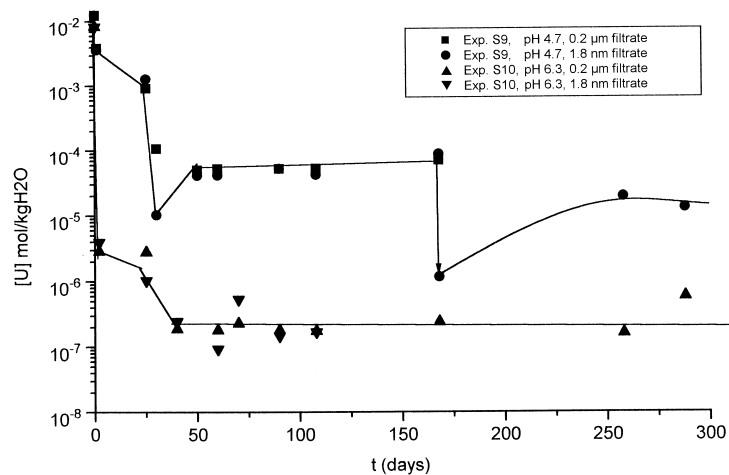


Fig. 3. Uranium concentration in solution vs. time, for the precipitation experiments performed in 0.5 m NaClO_4 solutions. S9):pH = 4.7. From $t = 0$ to $t = 170$ days results correspond to oversaturated conditions. From 170 days results correspond to undersaturated solutions. S10):pH = 6.3. Results correspond to oversaturated solutions.

Table 2. Solid phase stoichiometry.

	Experiment	pH _{corr.}	Stoichiometry	Equilib. U-conc. molal
3 m NaCl	S-5	5.2	Na _{0.25} UO _{3.12} · (1.95 ± 0.2)H ₂ O	1.4E-5 ± 2.4E-6
	S-19	5.6	Na _{0.11} UO _{3.05} · (1.86 ± 0.1)H ₂ O	1.9E-5 ± 6.5E-7
	S-6	6.1	Na _{0.42} UO _{3.21} · (5.85 ± 0.2)H ₂ O	2.0E-6 ± 2.0E-7
	S-18	7.2	Na _{0.36} UO _{3.18} · (3.2 ± 0.1)H ₂ O	3.1E-6 ± 1.1E-6
5 m NaCl	AR-1	4.8	Na _{0.29} UO _{3.15} · (3.0 ± 0.1)H ₂ O	1.2E-2 ± 5E-3
	S-1	5.6	Na _x UO _{3+x/2} · yH ₂ O ^{a)}	4.7E-4 ± 1.5E-4
	S-7	5.6	Na _x UO _{3+x/2} · (2.4 ± 0.2)H ₂ O ^{a)}	3.4E-5 ± 4.8E-5
	S-15	6.1	Na _{0.11} UO _{3.05} · (1.54 ± 0.2)H ₂ O	2.9E-4 ± 8.7E-5
	S-2	6.5	Na _x UO _{3+x/2} · yH ₂ O ^{a)}	9.0E-5 ± 3.5E-6
	S-8	6.5	Na _{0.14} UO _{3.07} · (2.53 ± 0.1)H ₂ O	3.3E-6 ± 1E-6
	C	6.5	Na _{2.1} UO _{4.05} · (6.9 ± 0.2)H ₂ O	1.4E-3 ± 4E-4
	B	6.5	Na _{0.38} UO _{3.19} · (3.1 ± 0.1)H ₂ O	3.4E-4 ± 3.4E-5 ^{b)}
	S-16	7.1	Na _{0.29} UO _{3.15} · (2.85 ± 0.2)H ₂ O	4.6E-4 ± 2E-4
	S-17	7.6	Na _{0.45} UO _{3.23} · (4.5 ± 0.1)H ₂ O	9E-5 ± 5E-5
	S-21	8.9	Na _{0.68} UO _{3.34} · (2.15 ± 0.1)H ₂ O	3.0E-5 ± 2E-5
	0.5 m NaClO ₄	S-9	4.7	Na _{0.01} UO ₃ · (1.7 ± 0.1)H ₂ O
S-10		6.3	Na _x UO _{3+x/2} · (4.7 ± 0.3)H ₂ O ^{a)}	1.0E-7 ± 1.1E-8

^{a)} Data for Na or H₂O content of the phase are unreliable due to NaCl contamination.

^{b)} Average of only two short-term values, not included in Fig. 12.

thermic peaks for phases formed in NaCl media suggests the presence of two different sites of the water molecules in the polyuranate structure. Additionally, a small exothermic effect

of -19 ± 1 J/g was observed at 210°C, also absent in perchlorate media.

The precipitate formed at pH 7.2 showed an X-ray diffrac-

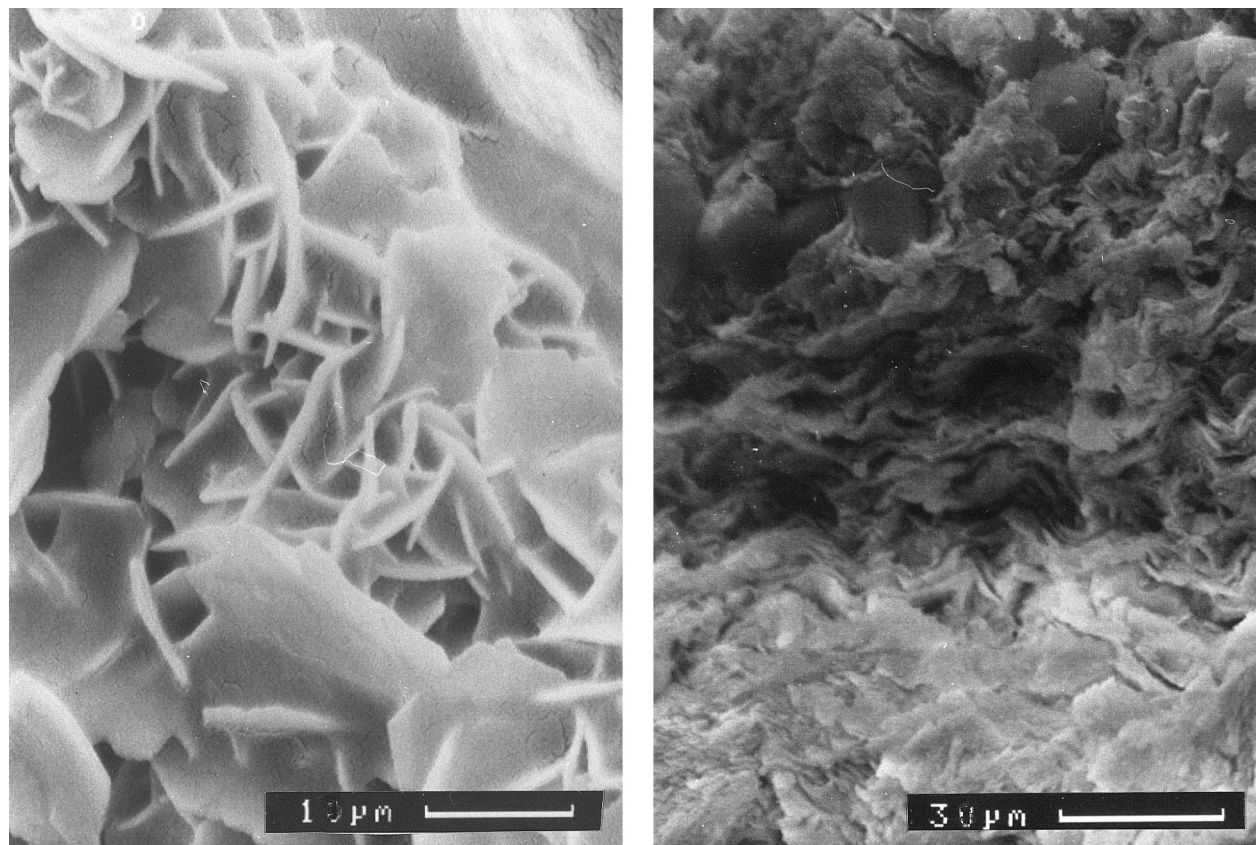


Fig. 4. (left) Morphology of the precipitated solid in 3 m NaCl solutions at 5.2. Similar crystals are observed at pH 5.6 and 6.1. In this pH range the crystal average diameter is between 0.3 and 2 μm and the thickness about 100 nm. (right) SEM micrograph of the solid formed in 3 m NaCl solution at pH=7.2. NaCl crystals were observed between a mass corresponding to the Na-(poly)uranate phase.

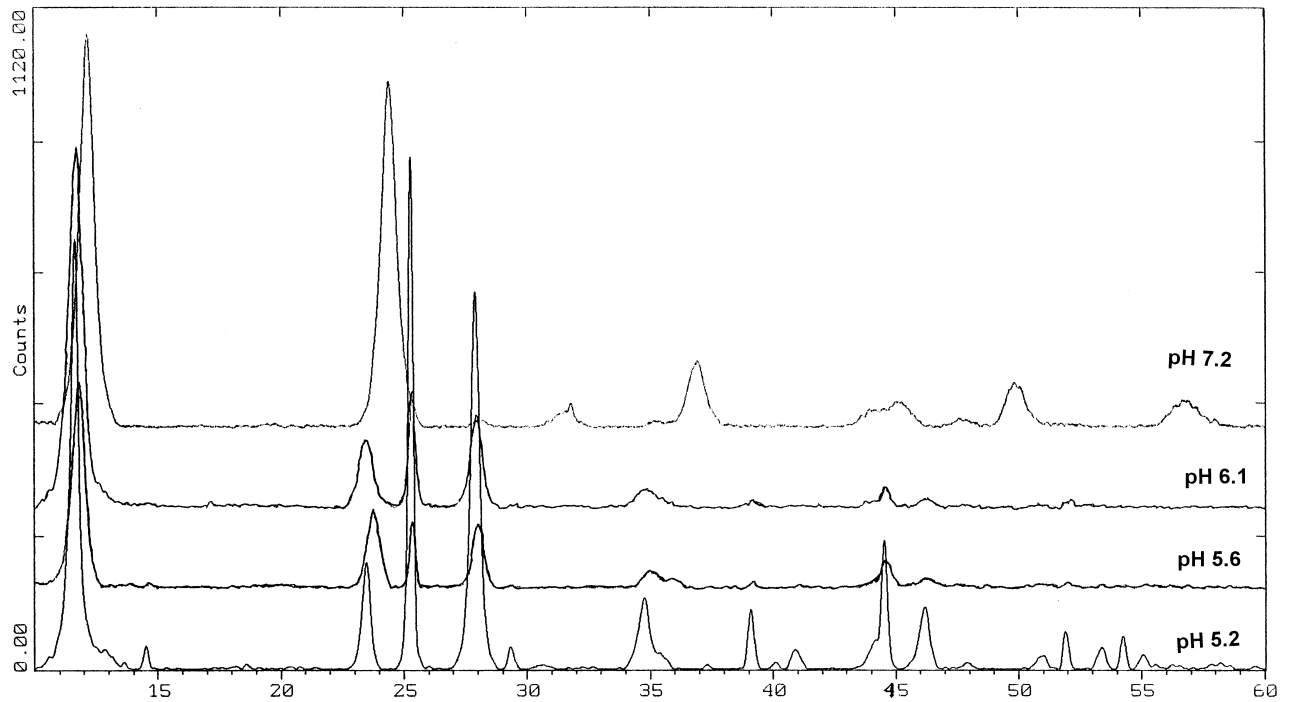


Fig. 5. X-ray patterns vs. pH of the solid formed in 3 m NaCl solutions. X-ray patterns of the solid precipitate at pH values between 5.2 and 6.1 match X-ray data reported by Pongi et al. (1980) and Brush (1980) for solids with Na/U ratio 0.33.

tion pattern with fewer reflections. Only the 004 reflection remained. Nevertheless, the chemical composition of the precipitate was similar to those formed at lower pH values. An SEM micrograph (Fig. 4b) showed a fine grained Na-(poly)uranate with a crystal habit similar to those observed at lower

pH values but with smaller particle size. NaCl crystals formed during drying of the solid sample were also observed.

The resulting total U concentrations in solution vs. time are shown in Fig. 6. Final equilibrium concentrations are included in Table 2. Differences between filtrated and ultrafiltrated sam-

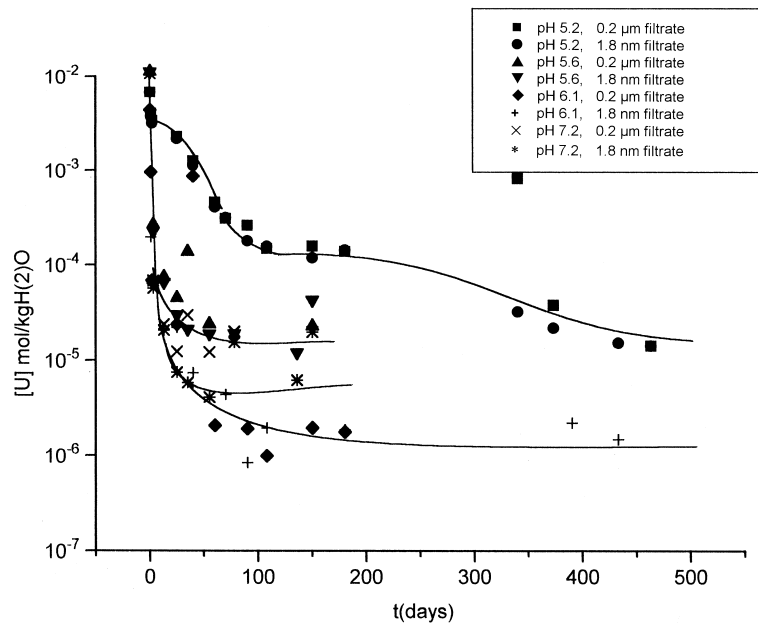


Fig. 6. Uranium concentration in solution vs. time for the experiments performed in 3 m NaCl solutions at several pH values.

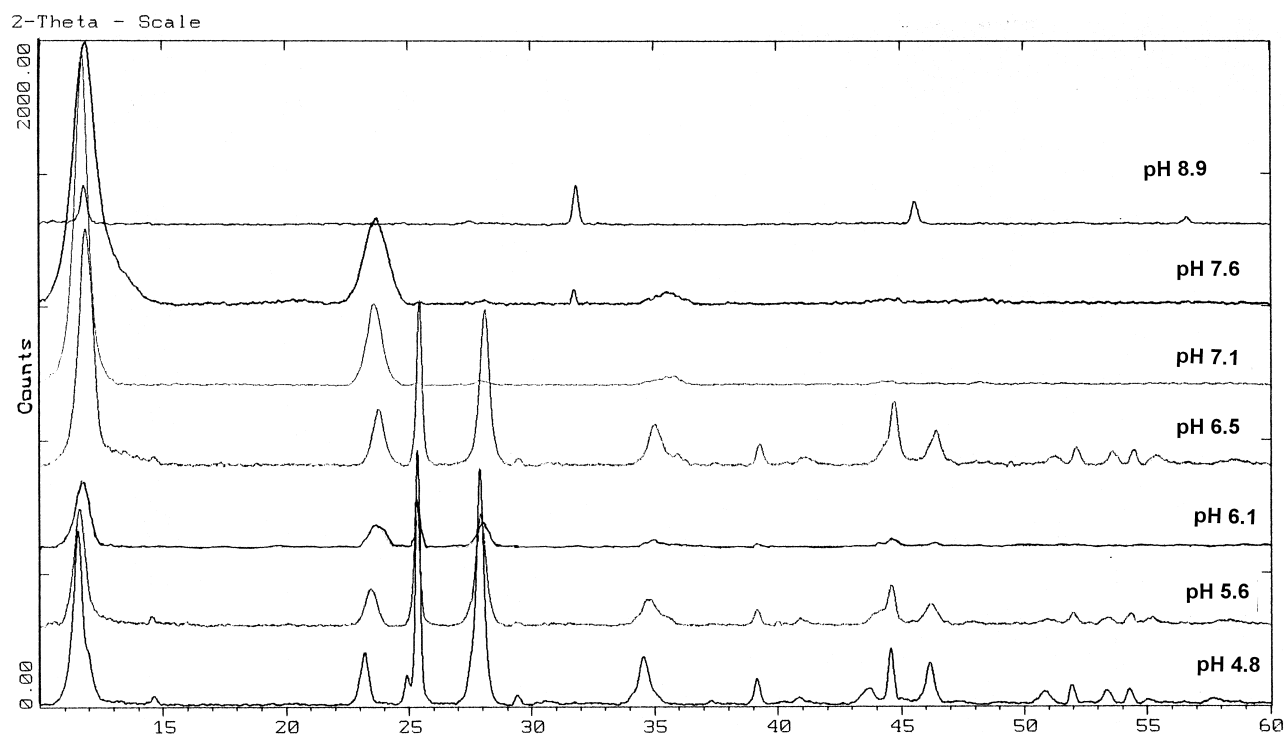


Fig. 7. X-ray patterns vs. pH of the solids precipitated in 5 m NaCl solutions. Phases formed at pH values between 4.8 and 6.5 show X-ray patterns similar to those for the corresponding phases formed in 3 m NaCl solutions in the same pH range. At pH 7.1-8.9 a less crystalline phase is formed (see discussion in text). For pH 7.6 and 8.9 the small peaks observed at $2\theta = 31.8, 45.5,$ and 56.4 correspond to contamination of the samples by halite (NaCl) formed during drying of the precipitate after insufficient washing.

ples were not significant (one exception at pH 5.2, 340 day my result from contamination) indicating that colloid formation did not significantly contribute to the total U concentration in solution. At pH 5.2 the U concentration decreased slowly with time, first reaching a plateau and then decreasing further. Maybe this reflects a slow phase transformation, which was not detectable by the X-ray data. Possibly, due to higher degrees of supersaturation, at higher pH values the U concentration in solution decreased faster, by about 2 orders of magnitude in the first week. No phase transformation was observed.

3.3. Experiments in 5 m NaCl Solutions

Experiments performed in 5 m NaCl solution in the pH range from 4.5 to 8.5 resulted in yellow microcrystalline solids at pH values between 4.5 and 7.1 and orange solids at higher pH values (pH = 7.6 and 8.9). The average particle size was generally smaller (plates of about 0.5 mm in diameter and 50 nm in thickness) than that of the solids formed in 3 m NaCl solutions.

A comparison of X-ray patterns of solids formed at various pH is shown in Fig. 7. The results indicate that the precipitates formed in the pH range between 4.8 and 6.5 had similar crystal structures. The X-ray patterns of these phases were also similar to those of the sodium polyuranates observed in 3 m NaCl solution (according to the designation of Brush, 1980: S.P.II). Similarly, as for experiments performed in 3 m NaCl solution, the average of Na/U ratio is 0.33 for most of these phases (see

Table 2). At pH 7.1 phase transformation with time was observed. The initially formed solids had X-ray patterns similar to those of the polyuranates formed at lower pH values. However, with time this phase was transformed to a phase of smaller particle size and/or poorer crystallinity (Fig. 8). The patterns show only few reflections similar to those of the phase formed at pH 7.5 in 3 m NaCl solution. At pH 7.6 a phase displaying this pattern was formed immediately (compare final X-ray pattern in Fig. 8 with those obtained at pH 7.6, Fig. 7). At pH values of 8.9, the X-ray pattern corresponds to an amorphous phase or to nanocrystals where diffraction cannot be produced due to the small crystallite sizes. SEM analyses showed a similar crystal morphology as observed for the phases formed at lower pH values, but with smaller crystal size. The Na-content of was clearly higher than in phases formed at lower pH (see Table 2).

DSC analyses of a precipitate formed at pH 6.5 showed two endothermic peaks, similar to those observed in the precipitates formed in 3 m NaCl solution, one at $115 \pm 3^\circ\text{C}$ and another $132 \pm 3^\circ\text{C}$, (Fig. 9). The enthalpy ΔH_{dehydr} for the dehydration reaction was calculated as 145 ± 1 J/g considering the total area of the two peaks.

At all pH values the solution concentrations of U initially decreased fast, followed by a slow decrease towards metastability or equilibrium values (Fig. 10). Final solution concentrations are included in Table 2. The titration procedure (degree of supersaturation, speed of addition of NaOH, etc.) strongly influenced the course of decreasing U concentration with time

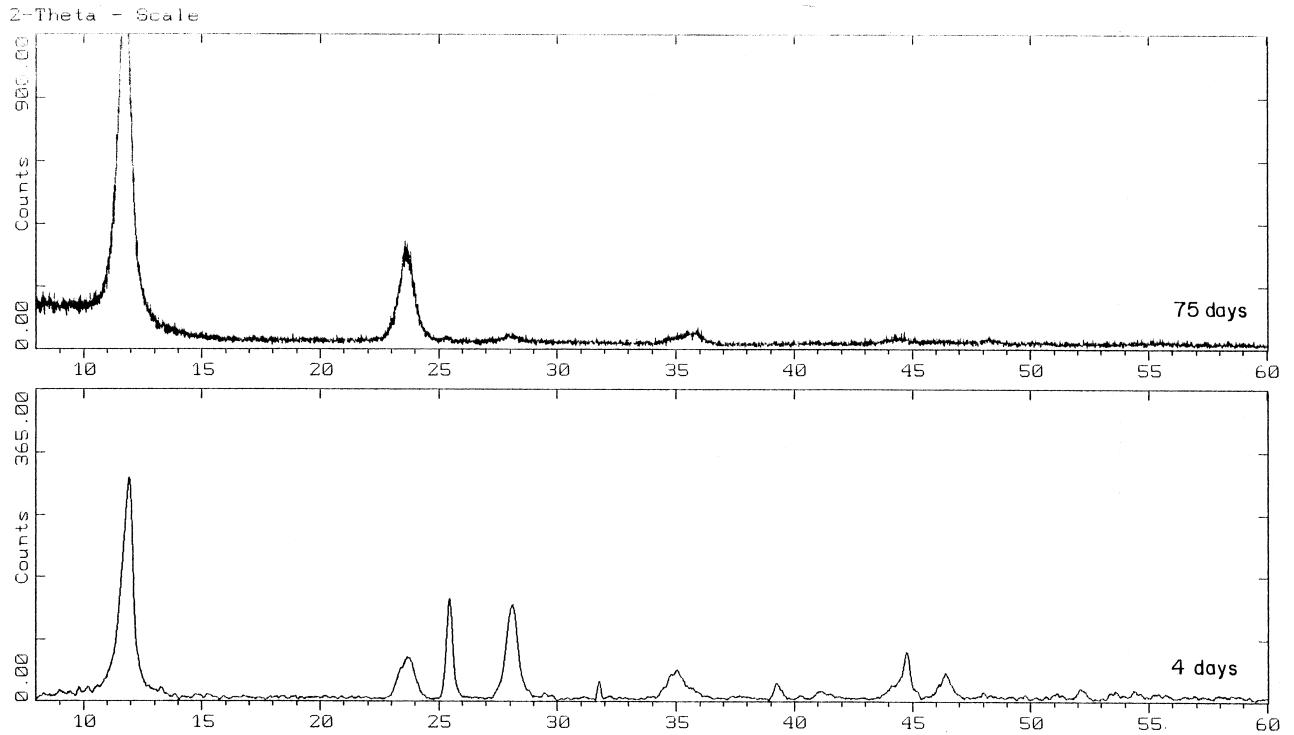


Fig. 8. X-ray pattern after 4 and 75 days for the solid formed at pH = 7.1 in 5 m NaCl solutions. A solid phase transformation is shown (to see description in text).

and the final equilibrium value. Figure 11 compares the evolution of U concentration with time for various experiments performed at pH 6.5. Differences of 3 orders of magnitude in the final U concentration were detected. X-ray powder patterns (not shown here) indicate differences in crystallite sizes among the solids phases. Chemical and DSC analyses show a vague relation between H₂O content and Na/U ratio and solubility values. The results (see Table 2) show both a much higher H₂O content and Na/U ratio of the highly soluble, less crystalline phase (experiment C). The initial U concentration in experi-

ment C was higher than in any other experiment performed at this pH value (see Table 1). The high degree of supersaturation leads to the formation of small crystals.

4. DISCUSSION

4.1. Solid Phases Compositions

The phases formed are characterized mainly by their water content γ and Na/U ratio. The principal solid phase formed under neutral to slightly acid conditions in NaCl solutions is a Na-

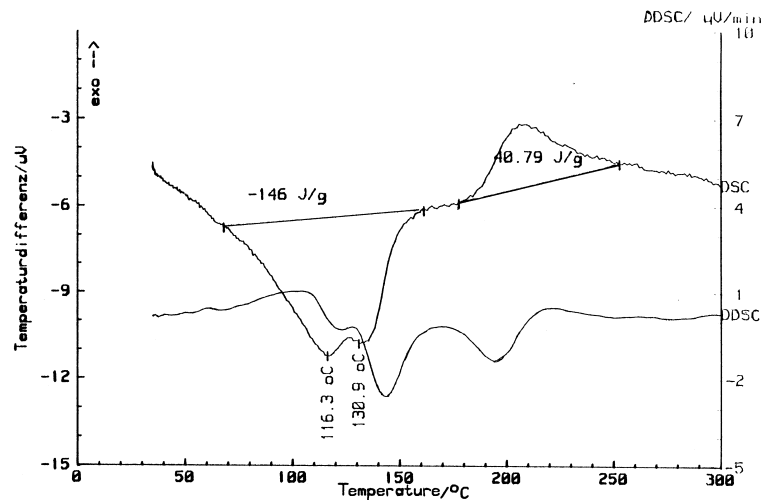


Fig. 9. DSC analyses of the solid precipitated at pH = 6.5 in 5 m NaCl solutions.

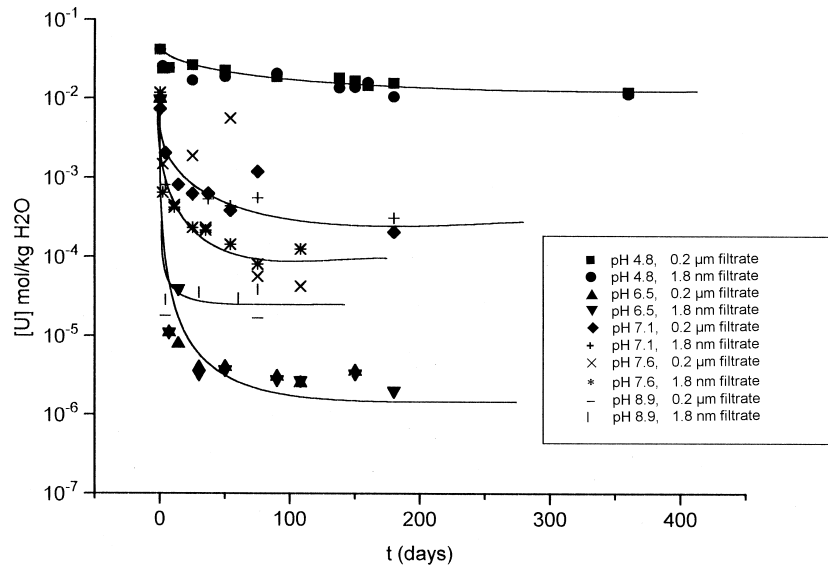


Fig. 10. Uranium concentration in solution vs. time for the experiments performed in 5 m NaCl solutions at several pH values.

polyuranate with an average composition $\text{Na}_{0.33}\text{UO}_{3.16} \cdot y\text{H}_2\text{O}$. Metaschoepite was observed only in 0.5 m NaClO_4 media. This difference may not necessarily result from the different ionic medium but from the different sodium concentration applied or from both. In more alkaline media more Na-rich phases are formed, but the present data do not allow detailed analyses. The X-ray data indicate a clear change when comparing phases formed at pH 5-6 to those formed at pH 8. The precipitates formed in the present work are poorly crystalline, and the X-ray patterns did not permit a detailed structural analyses. A detailed discussion of phase relationships and phase boundaries in the context of structural changes is, therefore, based on literature data discussed below.

4.2. Solubility of the Precipitates

Figure 12 shows a plot of final U concentration vs. pH for all experiments performed. Included are calculated solubility curves discussed further below. Each measurement value in this plot corresponds to the average value of the U concentrations in solution obtained by repeated sampling under apparent equilibrium conditions. Error bars include uncertainties in U-analyses and pH-measurements as well as variations in the equilibrium concentration as a function of time. The equilibrium U concentration obtained in 0.5 m NaClO_4 solution are at least 1 order of magnitude lower than the corresponding values in NaCl media at the same pH. At pH 6.9 in NaClO_4 about 2

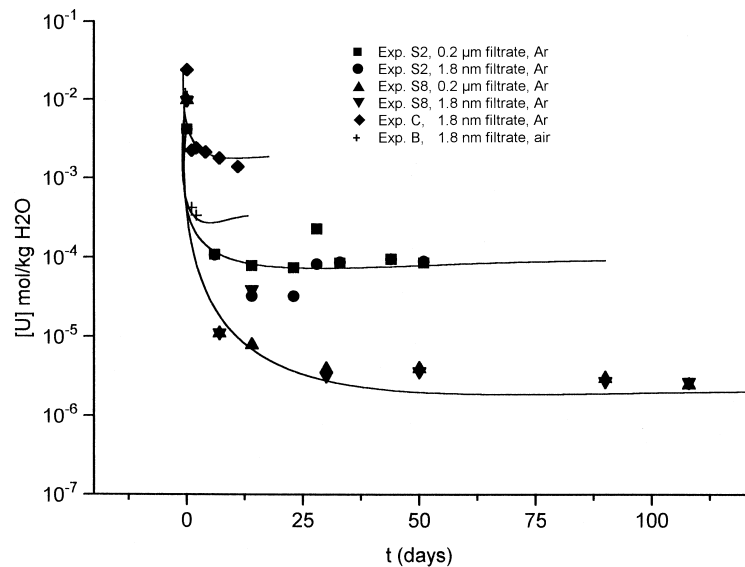


Fig. 11. Uranium concentration in solution vs. time for several experiments performed at pH = 6.5 in 5 m NaCl solutions (to see discussion in text).

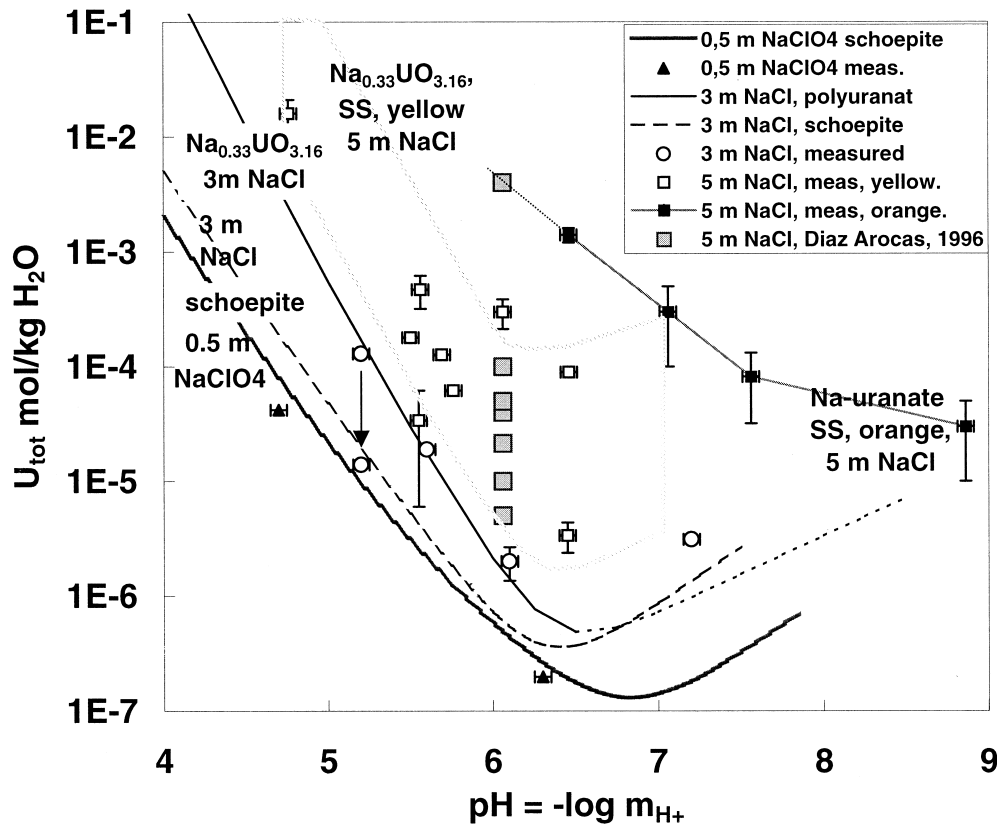


Fig. 12. Apparent equilibrium U concentration with associated uncertainties vs. ($\text{pH} \equiv -\log m_{\text{H}^+}$) for most experiments performed. Data represent average values obtained at various time intervals, once apparently constant U concentrations were reached. At pH 5.2 (3 m NaCl) both the intermediate plateau concentration and the lower long-term equilibrium concentration are given. Comparison with solubility curves of schoepite ($\log K_{\text{so}}^{\circ} = 4.83$, O'Hare, 1988) calculated for 3 m NaCl and 0.5 m NaClO_4 solutions and with a calculated solubility curve for $\text{Na}_{0.33}\text{UO}_{3.16}\cdot 2\text{H}_2\text{O}$ ($\log K_{\text{so}}^{\circ} = 7.13$, determined by fit to the data). Curves or ranges for the two polyuranate solid solutions (SS) formed in 5 m NaCl solution are used as a guide to the eye and do not reflect calculated values.

orders of magnitude lower than the solubility values reported by Sandino (1991), for microcrystalline schoepite for the same ionic medium. The disagreement in the solubility values could be related to differences in the crystallinity of the solid phases.

For the experiment performed at pH 5.2 in 3 m NaCl solution both the intermediate plateau (Fig. 6) and the much lower long-term (>1 year) equilibrium concentration are plotted. Considering only the intermediate plateau together with the equilibrium concentrations of U in 3 m NaCl solution at higher pH values, a smooth curve with a qualitatively expected trend with pH is obtained. On the other hand, with the apparent long-term equilibrium concentration at pH 5.2, no consistent pH-trend, but a maximum at pH of 5.6 is obtained, indicating that the long-term phase at pH 5.2 is not the same anymore as the phases formed at higher pH. Consequently, the phase formed at pH 5.2 may have been transformed with time (schoepite formation from polyuranate?).

For 5 m NaCl solution literature data, obtained under similar conditions (Diaz Arocas, 1996) are included in Fig. 12 for comparison. The reported pH of 5.6 (Pitzer convention) was changed to a 6.1, to allow for consistency with the pH-scale of the present work (pH_{H^+}). The apparent equilibrium data obtained in 5 m NaCl solution for $\text{Na}_{0.33}\text{UO}_{3.16}\cdot y\text{H}_2\text{O}$ vary by about 1.5 orders of magnitude, much more than in 3 m NaCl

solution. As has been demonstrated by Diaz Arocas (1996), this is an effect of variations in crystallite sizes and, therefore, of the precipitation method used. Lowest concentrations of U are achieved when the pH is adjusted discontinuously with NaOH, allowing the pH to drift due to the precipitation reaction to more acid values during the drift intervals of 12–24 hr (see discussion in Diaz Arocas, 1996). The periodic slight reacidification may have resulted in the redissolution of initially formed smallest crystals. The resulting larger average particle size decreased the solubility of the precipitate. Higher concentrations of U are achieved when the pH is controlled permanently, avoiding the acid drift.

In contrast to the apparent equilibrium data for the yellow polyuranate(VI) $\text{Na}_{0.33}\text{UO}_{3.16}\cdot y\text{H}_2\text{O}$, the solubility data for the orange Na-uranate(VI) solid solution seem to follow a smoothly decreasing trend with pH. The phase boundary between the two uranates is probably close to pH 7.5. At this pH, phase transformation of the initially formed $\text{Na}_{0.33}\text{UO}_{3.16}\cdot y\text{H}_2\text{O}$ has been observed with time. The exact position of the phase boundary may strongly depend on the crystallinity of the phases formed. For example, at initially high oversaturation (experiment C, Table 1) formation of the orange phase is observed even at pH of 6.9, as a rather soluble metastable phase, despite the much higher stability

of $\text{Na}_{0.33}\text{UO}_{3.16}\cdot 2\text{H}_2\text{O}$. Large variability in U concentrations (up to 3 orders of magnitude) at this pH value are the consequence.

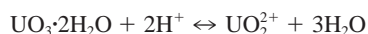
4.3. Determination of Solubility Constants

The experimental solubility data were used to calculate solubility constants $\log K_{\text{so}}$ as far as the mono- and polynuclear hydrolysis behavior of the uranyl ion in the aqueous phase is known for the respective ionic medium. Very little is known on the solution chemistry of U(VI) in chloride media (Dunsmore and Sillén, 1963, Grenthe et al., 1992), in contrast to the perchlorate media, allowing prediction of stability constant of important solution complexes (hydrolysis, carbonates) only for ionic strength lower than 3.

A solubility constant for schoepite formed in 0.5 m NaClO_4 can be calculated using the hydrolysis constants $\log \beta_{11} = -6.10$, $\log \beta_{13} = -19.15$, $\log \beta_{22} = -6.03$, $\log \beta_{34} = -12.61$, $\log \beta_{21} = -2.25$, $\log \beta_{47} = -23.09$, and $\log \beta_{35} = -16.45$ calculated for 0.5 M NaClO_4 solution by using the Specific Interaction Theory (SIT) with procedures, standard state hydrolysis constants, and interaction coefficients given by Grenthe et al. (1992). The value obtained by a fit to the data reported in this paper (Table 2) is $\log K_{\text{so}} = 5.14$. This solubility constant was extrapolated to infinite dilution using the relation (1)

$$\log K_{\text{so}}^{\circ} = \log K_{\text{so}}^{\circ} + 3\log \gamma_{\pm}(\text{UO}_2(\text{ClO}_4)_2) - 4\log \gamma_{\pm}(\text{HClO}_4) + 3\log a_w \quad (1)$$

for the reaction

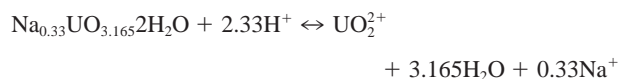


Activity coefficients and water activities were calculated as $\gamma_{\pm}(\text{UO}_2(\text{ClO}_4)_2) = 0.522$, $\log \gamma_{\pm}(\text{HClO}_4) = 0.726$ and $a_w = 0.996$ from interaction coefficients and equations given by Pitzer (1979) and mixing data of Kim and Frederick (1988). The resulting value for the standard state solubility constant is $\log K_{\text{so}}^{\circ} = 4.7$.

For calculating solubility constants from our equilibrium data for $\text{Na}_{0.33}\text{UO}_{3.16}\cdot 2\text{H}_2\text{O}$ in 3m NaCl solution we used the experimentally determined hydrolysis constants for the uranyl ion measured in the same ionic medium as reported by Dunsmore and Sillén (1963). We only used experimental data between pH 5.2 and 6.1 because at higher pH, the hydrolysis model is not sufficient clear. For the experiment performed at pH 5.2, we only used the equilibrium concentration of the first plateau (Fig. 6). In the long-term, the concentration decreased by more than an order of magnitude, may be due to phase transformation of polyuranate to schoepite. In the pH range between 5.2 and 6.1 the significant solution species are the free uranyl ion and the polynuclear complexes $(\text{UO}_2)_2(\text{OH})_2^{2+}$, $(\text{UO}_2)_3(\text{OH})_4^{2+}$, and $(\text{UO}_2)_3(\text{OH})_5^+$. Chloride complexation of the uranyl ion is implicitly accounted for in the reported values of the hydrolysis constants. By fitting the experimental data to a calculated solubility curve a $\log K_{\text{so}} = 7.95 \pm 0.15$ was obtained. The conditional solubility constant is extrapolated to zero ionic strength as $\log K_{\text{so}}^{\circ} = 13 \pm 0.15$ using the Eqn. 2

$$\log K_{\text{so}}^{\circ} = \log K_{\text{so}}^{\circ} + 3\log \gamma_{\pm}(\text{UO}_2\text{Cl}_2) + 0.66\log \gamma_{\pm}(\text{NaCl}) - 4.66\log \gamma_{\pm}(\text{HCl}) + 3.165 \log a_w \quad (2)$$

for the reaction



with mean activity coefficients $\gamma_{\pm}(\text{UO}_2\text{Cl}_2) = 0.619$ and $\gamma_{\pm}(\text{HCl}) = 0.974$, $\gamma_{\pm}(\text{NaCl}) = 0.714$ and water activity $a_w = 0.893$ calculated for 3m NaCl solutions from interaction coefficients and equations given by Pitzer (1991) and binary and ternary mixing parameter of Kim and Frederick (1988). The error in the $\log K_{\text{so}}^{\circ}$ value of 0.15 (i.e., ca 40%) is calculated, considering the error in the measured equilibrium concentration values (included in Table 2) which is given by the variation of analyses results as a function of experimental time and the analytical error (the latter is smaller than 10%), the error in the value of the hydrolysis constants (given by Dunsmore and Sillén, 1963, as <3%) and the error obtained from an overall fit of the average data as a function of pH to the solubility/pH curve (Fig. 12). The latter error was calculated as the quadratic mean for the deviation (in terms of $\log K_{\text{so}}$ units) of the average data from the calculated curve.

If one assumes that the initially formed polyuranate is slowly transformed to schoepite, the measured long-term equilibrium concentration of U would correspond to a solubility constant at infinite dilution of $\log K_{\text{so}}^{\circ} = 4.7$, using the above described hydrolysis model and mean activity coefficients. This value is rather similar to that in perchlorate media.

The U concentration values at equilibrium in 5 m NaCl solution were not used for calculating $\log K_{\text{so}}$ values because stability constants for this ionic medium are not known and can not yet be estimated reliably from thermodynamic models. The available data for 3m NaCl solution (Dunsmore and Sillén, 1963) seem to indicate that trinuclear complexes are the dominant solution complexes between pH 5 and 6. With this assumption, the measured variance in the solubility concentration at a given pH of about 1.5 orders of magnitude corresponds to a variance in $\log K_{\text{so}}^{\circ}$ values of about 0.5 for the polyuranate, probably due to the well known relation between particle size and solubility.

4.4. Comparison of Solubility Constants with Literature Data

Our results may be compared with literature data. Theoretical solubility values may be derived from calorimetric data of O'Hare et al. (1988) and Grenthe et al. (1992). Using these data, the calculated standard state equilibrium constant for schoepite is $\log K_{\text{so}}^{\circ} = 4.83$. For comparison, theoretical solubility curves of schoepite were calculated with this constant both for 3 m NaCl and for 0.5 m NaClO_4 solutions, using the appropriate hydrolysis models and sets of mean activity coefficients described above. Experimental data in 0.5 m NaClO_4 and the one low long-term value in 3 m NaCl solution closely match the calorimetrically bases curves.

The solubility of uranyl oxide hydrates (in particular schoepite) has been experimentally measured by numerous authors (Kraus and Nelson, 1948; Gayer and Leider, 1955; Babko and Kodenskaya, 1960; Sandino, 1991; Kramer-Schnabel et al., 1992; Meinrath and Kimura, 1993; and Torrero et al., 1994). For comparison with our data, a summary of experimental

Table 3. Comparison of conditional solubility constants and corresponding values for the infinite dilution standard for schoepite and alkali/alkali earth polyuranates.

Solid	Conditions	Log K_{so}	Log K_{so}^0	Reference
UO ₃ *2H ₂ O	Calorimetry	—	4.83	O'Hare et al., 1988, Grenthe et al. 1992
UO ₂ (OH) ₂ probably UO ₃ *2H ₂ O	0.1 m NaNO ₃	4.0	3.84	Kraus and Nelson, 1948
UO ₃ *H ₂ O probably ** UO ₃ *2H ₂ O	<0.01 m HClO ₄ pH 3.9-5	5.6	5.6*	Gayer and Leider, 1955
UO ₂ (OH) ₂ probably UO ₃ *2H ₂ O	0.2 m NH ₄ NO ₃ pH 3.6-4.6	5.40 (5.74)	5.24 (5.58)	*Baes and Mesmer, 1976 Babko and Kodenskaya, 1960
Amorphous UO ₃ *2H ₂ O	0.5 m NaClO ₄ pH 6.7-9	6.59	6.35	Sandino, 1991
Micro-crystalline UO ₃ *2H ₂ O	0.5 m NaClO ₄ pH 6.7-9	6.22	5.97	Sandino, 1991
UO ₃ *2H ₂ O	0.1 m NaClO ₄	5.28	5.06	Meinrath and Kimura, 1993
UO ₃ *2H ₂ O	0.1 m NaClO ₄ pH 4.5-5.5	5.35	5.13	Kramer-Schnabel, 1993
UO ₃ *2H ₂ O	0.5 m NaClO ₄	5.14	4.70	This work, two tests
UO ₃ *2H ₂ O	1 m NaCl	5.57	5.48	Torrero et al., 1994
UO ₃ *2H ₂ O	1 m NaCl/UO ₂	5.92	5.73	Torrero et al., 1994
“UO ₃ *2H ₂ O”	3 m NaCl	5.43	4.7	This work, one test at pH5.2
Weighted average Na _{0.33} UO _{3.16} 2H ₂ O	3 m NaCl	7.95 ± 0.15	7.13 ± 0.15	This work
Becquerellite Ca _{0.16} UO _{3.16} 1.8H ₂ O	1 m CaCl ₂	7.29	7.13	Sandino et al., 1994
Compreignacite K _{0.33} UO _{3.16} 1.8H ₂ O	1 m KCl	6.56	6.33	Sandino et al., 1994
Na ₂ U ₂ O ₇			26	This work, estimated

results is given in Table 3. To facilitate comparison, literature results obtained at various ionic strength in various ionic media were corrected to zero ionic strength. Kraus and Nelson (1948) determined a solubility product $\log K_{sp}$ of -23.5 for the reaction $UO_2(OH)_2(s) = UO_2^{2+} + 2OH^-$, by titration of U(VI) containing 0.1 m NaNO₃ solution with NaOH. The solid phase was not characterized but, comparing to our results in low ionic strength media (NaClO₄, NaNO₃) it was probably not dehydrated but hydrated schoepite (metaschoepite?). Without considering polynuclear complex formation, a solubility constant, $\log K_{so}^0$ of 6.04 was determined by Gayer and Leider (1955) using the Debye Hückel limiting law for activity coefficient correction for the reaction $UO_3 \cdot H_2O + 2H^+ \rightarrow UO_2^{2+} + 2H_2O$ in HClO₄ solutions. Detailed ionic strength data are not reported, but the activity coefficient used for data, $\Delta_{H^+} \approx 0.95$, indicate that rather low ionic strength <0.01m were used. Reanalysis of these data by Baes and Mesmer (1976), considering polynuclear complex formation, yield a value of $\log K_{so}^0 = 5.6$. Solubility products determined by Babko and Kodenskaya (1960) in 0.2 M NH₄NO₃ solutions cannot be used directly in the present context, as contribution of hydrolysis and polynuclear complex formation was not considered. For the determination of meaningful solubility constants the reported raw data were, therefore, reanalyzed using hydrolysis stability constants $\log \beta_{11} = -5.49$, $\log \beta_{22} = -5.83$, $\log \beta_{34} = -12.36$, and $\log \beta_{35} = -16.25$ calculated for 0.2 M NH₄NO₃ solution from the data and SIT procedures given by Grenthe et al. (1992). Reported pH values were interpreted as operational values using the Bates-Guggenheim Convention. For comparison, solubility constants were also calculated by interpreting reported pH values as $-\log m_{H^+}$ (values in brackets in Table 3). Results show that, in the pH range of the

experiments, as much as 50% of dissolved U(VI) should be present as $(UO_2)_2(OH)_2^{2+}$ whereas UO_2OH^+ is insignificant. Solubility constants were extrapolated to zero ionic strength using the relation 3

$$\log K_{so}^0 = \log K_{so} + 3 \log \gamma_{\pm}(UO_2(NO_3)_2) - 4 \log \gamma_{\pm}(HNO_3) + 3 \log a_w \quad (3)$$

Respective trace mean activity coefficients for the ionic medium were calculated using interaction coefficients and equations given by Pitzer (1979). From the reported solubility product, $\log K_{sp} = -23.5$, for the results of Kraus and Nelson (1948) for 0.1 m NaNO₃ solution, a solubility constant K_{so} was calculated using a $\log K_w$ value of -13.76 . The same procedure for extrapolation to zero ionic strength was used as for the data of Babko and Kodenskaya (1960). Sandino (1991) showed that experimental $\log K_{so}$ values of schoepite vary with crystallinity. Experiments were performed in 0.5 m NaClO₄ the pH range 6.7-9.0 using amorphous and microcrystalline schoepite. Kramer-Schnabel et al. (1992) proposed a $\log K_{so} = -22.21$ for UO₃2H₂O, measured in the pH range of 4.5-5.5. Meinrath and Kimura (1993) determined a value $\log K_{so} = 5.28$ for schoepite (recalculated from original data using $\log K_w = 13.78$ given by Meinrath and Kimura, 1993). Experiments were performed in a pH range between 2.8 and 4.6, using schoepite with an X-ray pattern that resembled JCPDS-29-1376. Solubility constants of Kramer-Schnabel et al. (1992) and Meinrath and Kimura (1992) were extrapolated to infinite dilution using the same procedure as described above for our solids formed in 0.5 m NaClO₄ solution. Torrero et al. (1994) determined the solubility of poorly crystalline synthetic schoepite in 1 mol dm⁻³ NaCl solutions and of schoepite precipi-

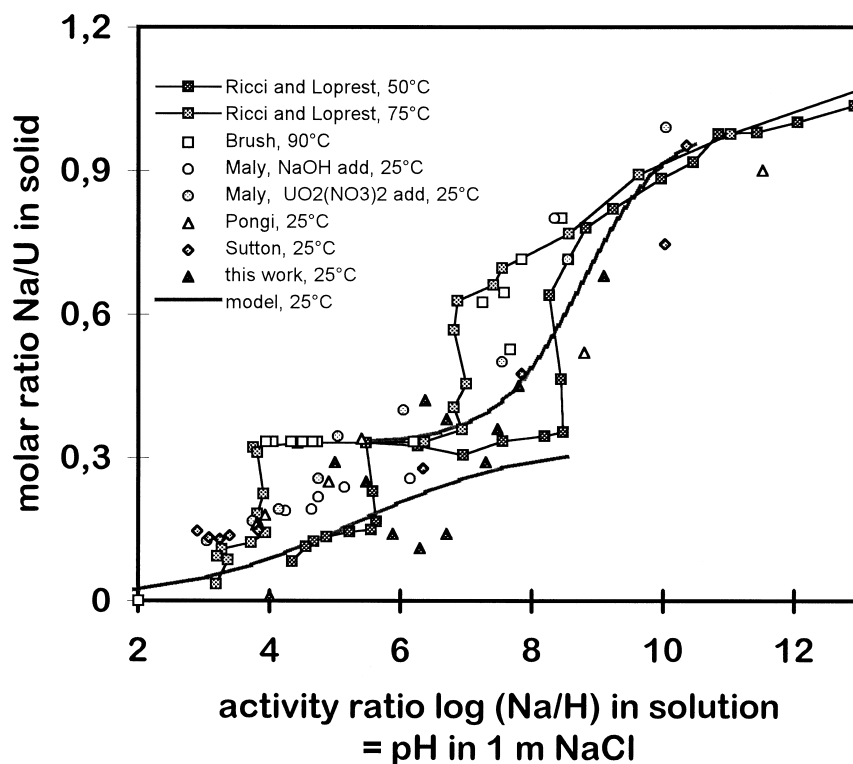


Fig. 13. Composition of the reported phases in terms of the Na/U ratio as a function of the Na/H ratio in solution. Comparison of experimental and literature data with curves calculated based on two solid solution (SS) models: a yellow SS: schoepite/ $\text{Na}_{0.33}\text{UO}_{3.16}\cdot 2\text{H}_2\text{O}$ and an orange SS $\text{Na}_{0.33}\text{UO}_{3.16}\cdot 2\text{H}_2\text{O}/\text{Na}_2\text{U}_2\text{O}_7$.

tated from supersaturated solutions on UO_2 (X-ray data of synthesized schoepite corresponding to the pattern given in JCPDS-18-1436 metaschoepite). The authors reported similarities between U solution concentrations from UO_2 dissolution tests and schoepite solubility.

From the comparison of solubility constants extrapolated to $I = 0$ for schoepite, an average value of $\log K_{\text{so}}^\circ = 5.37 \pm 0.25$ may be obtained, attributing zero weight to our data in perchlorate medium (only two experiments) and 3 m NaCl media (only 1 value) and to the data of Sandino (1991) as the reported solubility values are much higher than typically encountered values. Obviously, schoepite with an average solubility constant of $\log K_{\text{so}}^\circ = 5.37$ forms rather easy. Nevertheless, with amorphous or microcrystalline material much higher solubilities can be achieved (Sandino, 1991). Also, if the precipitation process is well controlled, our data in 0.5 m NaClO_4 and at pH 5.2 in 3 m NaCl solution show, that much lower equilibrium concentrations of U may be encountered, approaching the solubility constant of $\log K_{\text{so}}^\circ = 4.83$, obtained from calorimetric measurements.

4.5. Stability Fields in the Na/U(VI)/ H_2O System

The purpose of the present evaluation is to obtain phase boundaries between the various Na-polyuranate, Na-diuranate, and schoepite phases. Our data alone are not sufficient to assess stability fields and formation conditions of U(VI) solid phases, in particular due to the establishment of metastable solid/liquid phase equilibria, so typical for experiments performed at room

temperature. Therefore, we attempt describe our results in the larger context of literature data for schoepite (see above) and the sodium (poly)uranates compositions, both for 25°C and for higher temperatures (<90°C). It is useful to describe the composition of the reported phases in terms of the Na/U ratio as a function of the solution phases in terms of the Na^+/H^+ activity ratio). As some of the required information is not reported in the original literature, missing data were computed from reported experimental conditions. Results are given in Fig. 13.

4.5.1. Evaluation of literature data on Na-polyuranate compositions

Ricci and Loprest (1955) found various solid phases of the general composition $\text{Na}_x\text{UO}_{(3+x/2)}$ at temperatures of 50 and 75°C in carbonate free solutions: a solid solution with x values between 0.11 and 0.16, a stoichiometric compound with $x = 0.33$ (the phase found in our study), a solid solution with x values between 0.66 and 1.45 of which the well known diuranate ($\text{Na}_2\text{U}_2\text{O}_7$) is just a point in the continuous range of this solid solution, and, in the highly alkaline range, a stoichiometric compound with $x = 10$. The authors did not report pH values but the missing information was calculated with the help of the equation

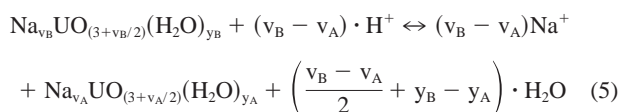
$$\text{pH} = \log a_{\text{OH}} - \log K_{\text{W}} = \log a_{\text{Na}} - \log K_{\text{W}} \quad (4)$$

from the reported solution composition (wt% Na_2O in solution), obtained after equilibration (Na-concentrations) using log

$K_w^\circ(50^\circ\text{C}) = -13.25$, $\log K_w^\circ(75^\circ\text{C}) = -12.69$. For highly alkaline solutions, activity corrections were made (Pitzer equations for the system NaOH/H₂O), but below pH 10, there was only a small error when using concentration ratios instead of activity ratios. The method for calculation of pH is only valid, if dissolved U concentrations are much lower than Na concentrations. Respective U data are not reported, but it was stated that U concentrations were extremely low. We consider the calculation method unreliable for Na-concentrations lower than about 10^{-4} m (pH < 9.5, $\log \text{Na}/\text{H} < 5$) and use data at lower Na/H ratio only in a qualitative manner. Sutton (1955) studied phase formation after four months of equilibration at 25°C by mixing about 0.9 M solutions of UO₂Cl₂ and NaOH in various ratios. For our evaluation, solution concentrations of Na were computed from the ratio of the two mixing solutions, and pH values were determined from the equilibrium data in the Fig. 1 of the authors. By using fast titration experiments, Maly and Vesely (1958) described Na-(poly)uranate formation as a function of pH. Na-polyuranates of similar structure (A) with Na contents between $x = 0.12$ and $x = 0.4$ were observed and between $x = 0.4$ and $x = 1$ a new structure (B) was found. Data for titration both in acid (addition of UO₂(NO₃)₂ and alkaline direction (addition of NaOH) were used in the present evaluation. Sodium activities in solution were considered identical to a hypothetical neutralized solution (0.07 m Na). Solid phase compositions were obtained from the graphical data representation (the authors' Fig. 4). Useful for comparison are also phase formation data from Pongi et al. (1980) obtained by slow stepwise potentiometric titration (programmes lentes). Solid composition and pH are reported. Solution concentrations of Na were computed for the determination of experimental Na⁺/H⁺ ratios from the reported initial Na concentrations and the reported additions of NaOH. Brush (1980) studied polyuranate formation by phase transformations in 0-4 m NaCl solutions at temperatures of 60 and 90°C. Besides dehydrated schoepite, two polyuranate structures with a fixed Na content of $x = 0.33$ were formed (designated S.P.I and S.P.II). Also a solid solution with higher Na contents was observed (S.P.III). Data for the solid solution were only used if phase composition is given (Table 2.5 of the author).

4.5.2. Evaluation of phase relationships

Despite considerable uncertainties, Fig. 13 shows that all data lay in a narrow range at a given pH. Close agreement exists between the data of Ricci and Loprest (1955) for 75°C and of Brush (1980) for 90°C. We can distinguish both stoichiometric phases and solid solutions. Stoichiometric phases are indicated by certain ranges of constant Na/U ratios with changing Na/H ratio. In contrast, solid solution phases continuously change their composition with the change in solution composition. According to the general Eqn. 5 for transformations among phases of the type Na_vUO_(3+v/2)·yH₂O in the Na-U(VI)-H₂O system

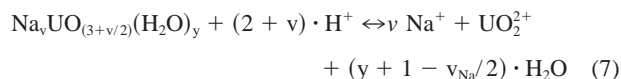


phase transformations of stoichiometric phases at a given water

activity should occur at a fixed Na⁺/H⁺ activity ratio given by the equilibrium constant for the above reaction as

$$\log K_{\text{transform}} = (v_{\text{Na},B} - v_{\text{Na},A})\log(a_{\text{Na}}/a_{\text{H}}) + ((v_{\text{Na},B} - v_{\text{Na},A})/2 + y_B - y_A)\log a_{\text{W}} = \log(K_{\text{so},B}/K_{\text{so},A}) \quad (6)$$

with $K_{\text{so},A}$ and $K_{\text{so},B}$ being the solubility constants for two reactions of generalized form



In case of solid solution formation the Na/U ratio of the solid will vary in a continuous manner with the Na⁺/H⁺-ratio of the solution. For ideal binary solid solutions the composition dependent solubility constant K_{SS} may be expressed by the solubility constants K_A and K_B of the endmembers A and B with the mol fractions X_A and $X_B (= 1 - X_A)$ as (Lippmann, 1977 and Gresen, 1981)

$$K_{\text{SS}} = X_A K_A + (1 - X_A) K_B \quad (8)$$

The two terms in this equation are the partial solubility constants of A and B defined by

$$X_A K_A = \frac{a_{\text{Na}^+}^{v_{\text{Na},A}} \cdot a_{\text{UO}_2^{2+}} \cdot a_{\text{H}_2\text{O}}^{(y_A+1+v_{\text{Na},A}/2)}}{a_{\text{H}^+}^{(v_{\text{Na},A}+2)}}; \quad X_B K_B = \frac{a_{\text{Na}^+}^{v_{\text{Na},B}} \cdot a_{\text{UO}_2^{2+}} \cdot a_{\text{H}_2\text{O}}^{(y_B+1+v_{\text{Na},B}/2)}}{a_{\text{H}^+}^{(v_{\text{Na},B}+2)}} \quad (9)$$

Division of the two Eqns. 9 for the endmembers A and B and transformation yields

$$\log \frac{a_{\text{Na}^+}}{a_{\text{H}^+}} = \frac{\log\left(\frac{X_A}{1 - X_A} \cdot \frac{K_A}{K_B}\right) - \left(y_A - y_B + \frac{v_{\text{Na},A} - v_{\text{Na},B}}{2}\right) \cdot \log a_{\text{H}_2\text{O}}}{v_{\text{Na},A} - v_{\text{Na},B}} \quad (10)$$

and for any Na/U ratio in the solid phase we obtain at a water activity close to unity X_A as

$$X_A = \frac{\text{Na}/\text{U} - v_{\text{Na},B}}{v_{\text{Na},A} - v_{\text{Na},B}} \quad (11)$$

The above equations show that the absolute determination of a single solubility constant, for example of our polyuranate, would constrain the solubility constants of all other phases if only the pH values or Na/H ratios of phase transition are known. Thus, using the data of Fig. 13 we may attempt to model phase formation in the Na/U(VI)/H₂O system. The data of Ricci and Loprest (1955) and Brush (1980) seem to indicate that the stability range of the polyuranate with $v_{\text{Na}} = 0.33$ is strongly temperature dependent. The stability limit in the alkaline range is given at 75 and 90°C by $\log \text{Na}/\text{H}$ of about 7 whereas at 50°C the phase is stable up to $\log \text{Na}/\text{H} = 8.5$. For lower temperatures, long equilibration times and metastable phase formation obviously impede an exact determination of stability limits in the alkaline range.

From the two solubility constants (average value of $\log K_{\text{so}}$

= 37 ± 0.25 for easily formed schoepite and $\log K^\circ_{so} = 13 \pm 0.15$ for $\text{Na}_{0.33}\text{UO}_{3.16}\cdot 2\text{H}_2\text{O}$) determined in our study, together with the above equations, we can calculate a hypothetical phase boundary between this schoepite phase and $\text{Na}_{0.33}\text{UO}_{3.16}\cdot 2\text{H}_2\text{O}$ resulting in an activity ratio $\log \text{Na}/\text{H} = 5.3$. Consequently, in a 1 molal NaCl solution schoepite should form below about pH 5.3, the polyuranate at higher pH values. However, solid solution formation as well as uncertainties in the solubility product of schoepite smears out such a clear phase boundary (Fig. 13), even at temperatures as high as 90°C. This is consistent with the ion exchange behavior observed for Na-polyuranates (Biglin, 1989a,b). Obviously schoepite can be transformed to Na-polyuranates by means of an ion exchange mechanism. As will be discussed further below, the ease of such phase transformation may be attributed to the high mobility of Na-ions and water molecules in the interlayers.

Though Fig. 13 indicates solid-solution formation in the range between $0 < \nu_{\text{Na}} < 0.33$, the composition of the acidic endmember remains uncertain. The literature data from tests at higher temperatures indicate that more than one solid solution may occur in this composition range (Fig. 13). In the absence of more accurate experimental data, we may describe the compositional behavior by a solid solution between schoepite and a polyuranate with the composition of $\text{Na}_{0.33}\text{UO}_{3.16}\cdot 2\text{H}_2\text{O}$. Using Eqn. 10 the composition of this solid solution is calculated as the function of the Na/H activity ratio in solution. Results are included in Fig. 13. At the alkaline side of the stability range this yellow solid solution has the composition $\text{Na}_{0.33}\text{UO}_{3.16}\cdot 2\text{H}_2\text{O}$. At higher pH values (or Na/H ratios), this solid solution becomes unstable and is transformed to another solid solution of orange color with an acid endmember having an ν_{Na} range of about 0.33-0.8 and an alkaline endmember with $\nu_{\text{Na}} \geq 1$. The solubility constant of the acid endmember $\text{Na}_x\text{UO}_{3+0.2}\cdot 2\text{H}_2\text{O}$ can be estimated from Eqn. 6 and the $\log K^\circ_{so}$ value for $\text{Na}_{0.33}\text{UO}_{3.16}\cdot 2\text{H}_2\text{O}$, a water activity of unity and the activity ratio $\log \text{Na}/\text{H} = 7.5$ as the location of the phase boundary is estimated from the data in Fig. 13. Using additionally Eqn. 10, best fit to the experimental data in Fig. 13 can be obtained with $\nu_{\text{Na}}=0.33$ for the acid and $\nu_{\text{Na}}=1$ and $\log K^\circ_{so} = 13$ for the alkaline endmember indicating solid solution formation between $\text{Na}_{0.33}\text{UO}_{3.16}\cdot y\text{H}_2\text{O}$ and $\text{NaUO}_{3.5}\cdot y\text{H}_2\text{O}$ ($\text{Na}_2\text{U}_2\text{O}_7$). The $\log K^\circ_{so}$ value of 26 for $\text{Na}_2\text{U}_2\text{O}_7$ is much higher than the value of 22.6 calculated from the thermodynamic data for this phase (calorimetric data for high temperature phase) given by Grethe et al. (1992). Using data of the high temperature phase would significantly overestimate the stability range of this orange solid solution. Results of model calculations are included in Fig. 13.

The transformation conditions between orange and yellow solid solutions are given by the requirement of equal equilibrium activities of the uranyl ion at the transition point. Calculations of U concentrations in equilibrium with the two solid solutions were performed by help of Eqn. 8, resulting in a $\log a_{\text{Na}}/a_{\text{H}}$ of transformation of about 10. This would agree with an extrapolation of the transformation boundaries observed in the high temperature data to 25°C, and it would indicate that all solids with Na/U molar ratios higher than 0.33 are metastable below $\log a_{\text{Na}}/a_{\text{H}} = 10$.

Considering the large stability range for Na-polyuranates and the ease of their formation in laboratory systems, it is surprising

that these solids are rare or absent as minerals in natural aquatic systems. Polyuranate phases with Na/U ratios > 0.3 should form in more alkaline groundwaters with $\log \text{Na}/\text{H} > 5$. In order to explain this discrepancy, systematic calculations were performed (Blanc and Grambow, in prep.) in the whole halite and calcite of magnesite saturated nie component (U(VI), Na, K, Mg, Ca, SO_4 , Cl, CO_3 , OH)/ H_2O system of oceanic salts. The results show that $\text{Na}_{0.33}\text{UO}_{3.16}\cdot 2\text{H}_2\text{O}$ is unstable in large ranges of composition with respect to either compreignacite or CaUO_4 and becquerellite and should form only in rather pure NaCl solutions.

4.6. Structural Context

Solid solution formation is generally limited by crystallographic constraints. As noted by Pongi et al. (1980) polyuranates show a significant displacement of the principal peaks of schoepite. Nevertheless, structurally, and by crystal habits, this phase appears to be closely related to schoepite. Similar to about 80% of uranyl minerals with refined structures, schoepite contains layers of polymerized uranyl coordination polyhedra (Finch et al., 1996a; Burns et al., 1996). The same is true for many polyuranates. The structure of schoepite is related to that of dehydrated schoepite, $\alpha\text{-UO}_2(\text{OH})_2$ with molecular water bonding uranyl oxy-hydroxide layers parallel to (001) (Christ and Clark, 1960). Hydrogen bridges are bonding the sheets together.

In the polyuranate structure, sodium ions occupy interlayer sites (Brush, 1980). Brush (1980) has also shown that the Na-ions stabilize the hydrated structure to dehydration in aqueous solutions, even at temperatures as high as 110°C, as opposed to schoepite, which loses interlayer H_2O in aqueous solutions at such temperatures.

The uranyl hydroxide sheets in schoepite and polyuranates may be written with the general formula $[\text{UO}_2\text{O}_x(\text{OH})_{2-x}]^{-x}$, with the layer charge depending on the cation content of the interlayers. The formula of the observed sodium-polyuranate $\text{Na}_{0.33}\text{UO}_{3.16}\cdot y\text{H}_2\text{O}$ may be written with becquerellite-type sheets $\text{Na}_2[(\text{UO}_2)_3\text{O}_2(\text{OH})_3]_2(\text{H}_2\text{O})_{6-8}$, or with schoepite-type sheets $\text{Na}_4[(\text{UO}_2)_4\text{O}_3(\text{OH})_4]_2(\text{H}_2\text{O})_{14}$. Similar structural formula are reported for other interlayer cations

becquerellite	$\text{Ca}[(\text{UO}_2)_3\text{O}_2(\text{OH})_3]_2(\text{H}_2\text{O})_8$
fourmarierite	$\text{Pb}[(\text{UO}_2)_4\text{O}_3(\text{OH})_4]_2(\text{H}_2\text{O})_4$
billietite	$\text{Ba}[(\text{UO}_2)_3\text{O}_2(\text{OH})_3]_2(\text{H}_2\text{O})_4$
compreignacite	$\text{K}_2[(\text{UO}_2)_3\text{O}_2(\text{OH})_3]_2(\text{H}_2\text{O})_8$
schoepite	$[(\text{UO}_2)_8\text{O}_2(\text{OH})_{12}]_2(\text{H}_2\text{O})_{12}$

For schoepite and the above phases (with the possible exception of compreignacite, where the structure has never been refined) the sheets are similarly structured. Each is based on oxygen anion-topologies that contain triangles and pentagons that are populated with uranyl ions (Burns et al., 1996). We predict that the same is true for Na-polyuranate $\text{Na}_{0.33}\text{UO}_{3.16}\cdot y\text{H}_2\text{O}$, but this has to be confirmed by respective X-ray analysis. There are indications that the Na/U ratio of 0.33 in the polyuranate is not variable, i.e., it is a stoichiometric phase (Brush, 1980; Pongi et al., 1980; Ricci and Loprest,

Table 4. Enthalpy of dehydration in air.

Medium	Weight loss 40–80°C (“sorbed water”)		Weight loss 80–135°C (“structural water”)		Phase stoichiometry	Enthalpie of dehydration $\Delta_f H$ (kJ/mol) per	
	wt%	mol fraction	wt%	mol fraction		mol “schoepite”	mol structural H ₂ O
3 m NaCl	1.45	0.26	5.96	1.06	Na _{0.21} UO _{3.105} ·1.65H ₂ O	46.8	44.1
5 m NaCl	3.45	0.61	6.62	1.18	Na _{0.14} UO _{3.07} ·2.23H ₂ O	48.1	40.7
0.5 m NaClO ₄	3.4	0.61	6.09	1.09	Na _{0.01} UO _{3.005} ·1.7H ₂ O	47.2	43.3
UO ₂ (NO ₃) ₂ + NaOH	3.4	0.61	7.35	1.31	Na _{0.13} UO _{3.06} ·2H ₂ O	56.3	42.9
Calorimetry ^{a)}				1.10 ^{c)}	UO ₃ ·2H ₂ O	53.8	48.9
H ₂ O(l) → H ₂ O(g) ^{b)}					H ₂ O(l)		39.2 (44.0)

^{a)} Calculated from data in Grenthe et al. (1992): $\Delta_f H_{m,UO_3 \cdot 2H_2O}^0 = -1826.1 \text{ kJmol}^{-1}$; $\Delta_f H_{m,UO_3 \cdot 0.9H_2O}^0 = -1506.3 \text{ kJmol}^{-1}$; $\Delta_f H_{m,H_2O,gas} = -241.83 \text{ kJmol}^{-1}$, using Cp values given in Grenthe et al. (1992) it can be shown that $\Delta_f H$ values are similar for 25 and 130°C

^{b)} calculated with $\Delta_f H_{m,H_2O(l)}^0 = -285.83 \text{ kJmol}^{-1}$ and steam tables of Haar et al. (1984) both for 25°C and for 130°C (25°C value in brackets)

^{c)} nominal value for the formation of dehydrated schoepite UO₃ · 0.9H₂O.

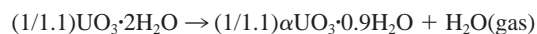
1955). On the other hand it has been shown that Na-ions of this phase are readily exchangeable with Na-22 ions in solution (Baran, 1988; Bilgin, 1989a,b). These two observations are not at conflict with each other if one describes the polyuranate as an ion exchanger with a cation exchange capacity given by the cation/U ratio of 0.33. If this phase has a fixed Na/U ratio, this means that higher quantities of Na-ions cannot be inserted into the interlayers without changing the sheet structure. Indeed, the sheets of the Na-diuranate (Na₂U₂O₇) structure are composed of hexagonal rather than pentagonal-coordinated uranyl polyhedra (Burns et al., 1996). This change in layer structure may be a response to the increased layer charge. Also the coulombic repulsion of Na-ions in the interlayers may prevent insertion of additional Na-ions into the interlayers. In the polyuranate structure the Na-ions are rather loosely bound, as is indicated by the fact that the interlayer cations are readily exchangeable with other alkali or with alkali earth elements (Biglin, 1989b). The data of Biglin (1989b) show that almost the total alkali ion content of the interlayer participates in the exchange reaction. We may conclude that the cations in the interlayer are quite mobile. This may explain the ease of phase transformation as observed by Sandino et al. (1994) for the systems schoepite/compreignacite/ KCl-solution and schoepite/ becquerellite/ CaCl₂-solution.

4.7. Properties of Interlayer Water in Schoepite and Polyuranates

A comparison of TG-DSC analyses results with values calculated from literature data (O’Hare et al., 1988; Grenthe et al., 1992) is shown in Table 4. TG-DSC analyses of polyuranate and schoepite phases have shown that about 30 wt% of the water content released until 200°C is lost in the temperature range of 40–80°C, maybe at least in part as surface adsorbed water. The further water loss up to 200°C is associated with an endothermic reaction in the temperature range of about 80–135°C, indicating loss of structural (interlayer) water. An average loss of 1.16 formula units of water between 80 and 135°C is observed, closely resembling the release of interlayer water during the dehydration of schoepite (metaschoepite UO₃·2.0H₂O instead of the ideal schoepite (UO₂)₈O₂(OH)₁₂(H₂O)₁₂, = UO₃·2.25H₂O, Finch

et al., 1996a) to the structurally similar α -dehydrated schoepite (UO₃·0.9H₂O). Hence, the release of interlayer water in the TG-DSC analyses is obviously close to completion at 135°C and is rather similar for schoepite and for the sodium polyuranates. The differences in the measured enthalpies of dehydration $\Delta_f H$ values can at large be explained by the differences in the water content of the solid phases. The specific enthalpy of dehydration per mole of interlayer water is similar for the polyuranates and for schoepite. However, the polyuranate structure appears to contain two energetically different sites of interlayer water, since in the temperature range of 80–135°C two endothermic peaks were observed in comparison to only one peak for schoepite.

The average specific enthalpy of hydration of 43.3 kJ/mol(H₂O) obtained from our schoepite and polyuranate data is slightly lower than the value of 48.9 kJ/mol(H₂O) calculated for isothermal dehydration at 135°C (408K) of schoepite according to



using the equation

$$\Delta_{dehyd} H_{m(H_2O)}^{408} = \frac{1}{1.1} \cdot \Delta_f H_{UO_3 \cdot 0.9H_2O}^{408} + \Delta_f H_{H_2O,gas}^{408} - \frac{1}{1.1} \cdot \Delta_f H_{UO_3 \cdot 2H_2O}^{408} \quad (12)$$

with the enthalpies of formation of O’Hare et al. (1988); evaluated by Grenthe et al. (1992) for schoepite ($\Delta_f H^0 = -1826.1 \text{ kJ/mol}$) and dehydrated schoepite ($\Delta_f H^0 = -1506.3 \text{ kJ/mol}$) and $\Delta_f H^0 = -241.83 \text{ kJ/mol}$ for water vapor. Corrections for temperature were made by the heat capacity integration using C_p data given by Grenthe et al. (1992) for schoepite (C_p(T) = 84.238 + 0.294592T), Cp° = 140 J/(K.mol) for $\alpha UO_3 \cdot 0.9H_2O$ and $\Delta_f H^{408}$ of H₂O was calculated from the standard state value and the steam tables of Haar et al. (1984). Within the accuracy of the data the calculated specific dehydration enthalpy is the same for 25 and 135°C.

A comparison of the specific enthalpy of dehydration of our precipitates to the enthalpy of evaporation of liquid water (135°C) shows close similarities (Table 3), indicating that the

Table 5. Comparison of the calculated thermodynamic properties at 298.15 K and 1 bar of interlayer and hydroxide water of schoepite to those of free water and metastable ice and to the data for structural water for sheet silicates and for zeolitic water reported by Helgeson (1978).

	$\Delta_f G^\circ$ [kJ/mol]	$\Delta_f H^\circ$ [kJ/mol]	S° [J/(mol.grd)]	V_m [cm ³ /mol]
H ₂ O _(interlayer)	-238.1	-290.7	56.8	19.1
H ₂ O _(hydroxid)	-254.2	-313.9	33.2	9.6
H ₂ O(liq)	-237.1	-285.8	69.95	18.02
H ₂ O(ice)			44.7	
Zeolitic H ₂ O			58.99	8
H ₂ O(sheet silicates)			40.17	13.7

thermodynamic properties of the interlayer water are close to that of free water. This interpretation is further confirmed by calculating the standard enthalpy, Gibbs free energy, entropy, and the volumetric properties of the interlayer water of the schoepite phase (stoichiometry UO₃·2H₂O not UO₃·2.25 H₂O) studied by O'Hare et al. (1988), according to the equations

$$\Delta_f H_{\text{H}_2\text{O},\text{interlayer}}^\circ = \frac{1}{1.1} \cdot (\Delta_f H_{\text{UO}_3\cdot 2\text{H}_2\text{O}}^\circ - \cdot \Delta_f H_{\text{UO}_3\cdot 0.9\text{H}_2\text{O}}^\circ) \quad (13)$$

$$\Delta_f G_{\text{H}_2\text{O},\text{interlayer}}^\circ = \frac{1}{1.1} \cdot (\Delta_f G_{\text{UO}_3\cdot 2\text{H}_2\text{O}}^\circ - \cdot \Delta_f G_{\text{UO}_3\cdot 0.9\text{H}_2\text{O}}^\circ) \quad (14)$$

$$S_{\text{H}_2\text{O},\text{interlayer}}^\circ = S_{\text{H}_2(\text{gas})}^\circ + \frac{1}{2} S_{\text{O}_2(\text{gas})}^\circ - \left(\frac{\Delta_f G_{\text{H}_2\text{O},\text{interlayer}}^\circ - \Delta_f H_{\text{H}_2\text{O},\text{interlayer}}^\circ}{T} \right) \quad (15)$$

and

$$V_{\text{m},\text{H}_2\text{O},\text{interlayer}} = \frac{1}{1.1} \cdot (V_{\text{m},\text{UO}_3\cdot 2\text{H}_2\text{O}} - \cdot V_{\text{m},\text{UO}_3\cdot 0.9\text{H}_2\text{O}}) \quad (16)$$

Molecular volumes were obtained from the crystallographic densities calculated from the dimensions of the orthorhombic unit cell as 64.43 cm³/mol of schoepite and 45.33 cm³/mol of α -dehydrated schoepite. Similar calculations were performed for the dehydration of dehydrated schoepite to γ -UO₃ to obtain the corresponding thermodynamic properties of water bound as hydroxide in the structure. Results of calculations for interlayer water are compared with the respective data for liquid water in Table 5. The calculated apparent thermodynamic properties of interlayer water include also potential thermodynamic contributions resulting from reported structural differences Finch et al. (1996b) between sheet structures of schoepite and dehydrated schoepite. Assuming that these energetic differences are small, the data in Table 5 show a close similarity in the calculated properties of interlayer water with those of free water. The slight decrease in the entropy of only about 13 J/(mol.grd) of interlayer water when compared to free water is similar to that of water loosely held in the channels of zeolites (Helgeson et al., 1978). This indicates that interlayer water is also rather loosely bound, like in zeolites, and much more mobile than the water in the interlayers of sheet silicates. The observation that $S_{\text{H}_2\text{O}(\text{liq})}^\circ > S_{\text{H}_2\text{O}(\text{interlayer})}^\circ > S_{\text{H}_2\text{O}(\text{ice})}^\circ > S_{\text{H}_2\text{O}(\text{hydroxide})}^\circ$ is consistent with the relative magnitude of the

translational, vibrational, and rotational degrees of freedom that one would postulate for these types of water. In contrast to the interlayer water, as expected, there are quite different properties for the water originating from further dehydration of α -UO₃·0.9H₂O to γ -UO₃. The small energetic differences between interlayer and free water create only small stability differences between schoepite and dehydrated schoepite. This may on the one hand explain the large scatter in experimentally measured water contents of solid precipitates and may explain on the other hand that under natural conditions schoepite and dehydrated schoepite may coexist with volumetric constraints playing an important role in deciding whether schoepite or dehydrated schoepite is formed (Finch et al., 1992).

In the literature (Christ and Clark, 1960; Finch et al., 1992; Brush, 1980), quite different X-ray patterns of UO₃·yH₂O phases are described varying with the water content in the solid. However, while Christ and Clark (1960) reported an increase in the interlayer distance with decreasing water content, the inverse behavior was observed by Finch et al. (1992). Our data show no clear relation between water content and X-ray data.

5. CONCLUSIONS

Our results show that sheet structures of sodium-containing uranyl oxide hydrates (polyuranates) of various Na/U ratios are the principal solid phases formed at 25°C in NaCl solutions. At least two types of solid solution series were identified: a yellow solid solution series with a maximum Na/U ratio of 0.33 for simplicity assumed to be bound by the endmembers schoepite (metaschoepite) and Na_{0.33}UO_{3.16}·2H₂O and another, orange, solid solution with higher alkali contents. Na-ions and water molecules are very mobile in the interlayers of the yellow solid solution, thus explaining the ease of ion exchange and phase transformation processes.

Phase transformation between these two types of phases may occur at activity ratios log Na/H in solution of about 10. However, alkali rich metastable phases may also occur at lower log Na/H ratios. Pure, alkali free schoepite forms only at very low Na/H activity ratios in solution (log Na/H < 3 at 25°C). Consequently, since many low temperature groundwaters have higher Na/H ratios, natural schoepite phases are expected to contain certain impurities of alkali ions. Polyuranate phases with Na/U ratios > 0.3 should form in more alkaline groundwaters with log Na/H > 5. However, in natural water systems, as opposed to many experimental set-ups, pure NaCl-solutions are absent and competition with other alkali (e.g., K) or alkali earth (e.g., Ca) elements will lead to the formation of thermodynamically more stable phases of a similar structure type (e. becquerellite, compregnacite).

Observed differences of about 3 orders of magnitude in the apparent U equilibrium solution concentration, for a given NaCl solution concentrations can be attributed to two types of metastability: metastability of poorly crystalline phases and metastability of a given Na/U ratio of a solid phase. An average value for the standard state solubility constant at 25°C of easily precipitated (poorly crystalline) schoepite was determined from literature data as log K[°]_{so} 5.37 ± 0.25. However, our experiments also show, that it in carefully controlled precipitation tests, or after rather long precipitation times (ca. 1 yr) much

lower solubility values can be reached, closely matching the solubility constant $\log K^{\circ}_{so} = 4.83$ obtained from calorimetric data (O'Hare et al, 1988).

For the polyuranate $\text{Na}_{0.33}\text{UO}_{3.16}\cdot 2\text{H}_2\text{O}$ a solubility constant of $\log K^{\circ}_{so} = 7.13 \pm 0.15$ was determined from the given experimental data. For $\text{Na}_2\text{U}_2\text{O}_7$ based on reported solubility data a value of $\log K^{\circ}_{so} = 26$ is estimated. A thermodynamic model is proposed, estimating the phase boundary between the two solid solutions as well as the composition of solid phases as a function of solution pH and Na-concentration.

Acknowledgments—This work has been performed under the agreement ENRESA-CIEMAT in the area of Direct Disposal of Spent Fuel and under the agreement for Cooperation in the Area of Direct Disposal of Spent Fuel between ENRESA and FZK. We are grateful to acknowledge the help of Mrs. Dietl (ICP/AES), Dr. Bernotat, and Mr. Spieler (SEM-EDS), Mr. Donath and Mrs. Schlieker (XRD), Mrs. Nesovic (TG-DSC), and Mrs Müller. We are also grateful to acknowledge the instructive and careful reviews by Dr. R. J. Finch, Dr. D. Wronkiewicz, Dr. J. Bruno, and Dr. W. Murphy and the very helpful comments by Prof. I. Grenthe, Dr. Gomez de Salazar, and the comments on parts of the paper by Dr. P. C. Burns.

Editorial handling: E. J. Reardon

REFERENCES

- Babko A. K. and Kodenskaya V. S. (1960) Equilibria in solutions of uranyl carbonate complexes. *Russ. J. Inorg. Chem.* **5**, 1241–1244
- Baes C. F., Jr. and Mesmer R. F. (1976) *The Hydrolysis of Cations*. Wiley.
- Baran V. (1988) Relation between precipitated and high temperature sodium uranates. *J. Radioanal. Nucl. Chem. Lett.* **128**, 155–163.
- Bilgin B. G. (1989a) Isotope and ion exchange of sodium ions in sodium polyuranates. *Chim. Acta Turcica* **17**, 109–116.
- Bilgin B. G. (1989b) Isotopic exchange between precipitated sodium polyuranates and sodium ions in aqueous solution. *Chim. Acta Turcica* **17**, 205–210.
- Brush H. (1980) The solubility of some phases in the System $\text{UO}_3\text{-Na}_2\text{O-H}_2\text{O}$ in aqueous solutions at 60 and 90°C. Ph.D. Dissertation Harvard Univ.
- Burns P. C., Miller M. L., and Ewing R. C. (1996) Uranyl Minerals and Inorganic Phases: A Comparison and Hierarchy of Crystal Structures. *Canadian Mineral.* **34**, 845–888
- Carnall W. T., Walker A., and Neufeldt S. J. (1966) Anhydrous Sodium Polyuranates. *Inorg. Chem.* **5**, 2135–2140.
- Cordfunke E. H. P. and Loopstra B. O. (1971) Sodium Uranates: Preparation and Thermochemical Properties. *J. Inorg. Nucl. Chem.* **33**, 2427–2436.
- Cordfunke E. H. P., Muis R. P., Ouweltjes W., Flotow H. E., and O'Hare P. A. (1982) The thermodynamic properties of Na_2UO_4 , $\text{Na}_2\text{U}_2\text{O}_7$, and NaUO_3 . *J. Chem. Thermodyn.* **14**, 313–322.
- Christ C. L. and Clark J. R. (1960) Crystal chemical studies of some uranyl oxide hydrates. *Amer. Mineral.* **45**, 1026–1061.
- Dawson J. K., Wait E., Alcock K., and Chilton D. R. (1956) Some aspects of the system uranium trioxide-water. *J. Chem. Soc.*, 3531–3540.
- Debets P. G. and Loopstra B. O. (1963) Uranates of ammonium. II. X-ray investigations of the compounds in the system $\text{NH}_3\text{-UO}_3\text{-H}_2\text{O}$. *J. Inorg. Nucl. Chem.* **25**, 945
- Diaz Arocas P. and Grambow B (1993) Chemistry of uranium in brines related to the spent fuel disposal in a salt repository. ENRESA Tech. Rept. No. 06/93.
- Diaz Arocas P. (1996) Precipitation kinetics of U(VI) phases formed in high concentrated saline solutions *J. Nucl. Mater.* **238**, 96–103
- Dunsmore H. S. and Sillén L. G. (1963) Studies on the hydrolysis of metal ions - 47. The uranyl ion in 3 M (Na)Cl medium. *Acta Chem. Scand.* **17**, 2657–2663
- Finch R. and Ewing R. (1991) Uraninite alteration in an oxidizing environment and its relevance to the disposal of spent nuclear fuel. SKB Tech. Rept. 91/15.
- Finch R. J., Miller M. L., and Ewing R. C. (1992) Cyclic weathering of natural uranyl oxide hydrates: Schoepite polytypes and dehydration effects. *Radiochim. Acta* **58/59**, 433.
- Finch R. J., Cooper M. A. and Hawthorne F. C. (1996a) The Crystal Structure of Schoepite $((\text{UO}_2)_8\text{O}_2(\text{OH})_{12})(\text{H}_2\text{O})_{12}$. *Canadian Mineral.* **34**, 1071–1088.
- Finch R. J., Hawthorne F. C., and Ewing R. C. (1996b) Schoepite and dehydrated schoepite. *Mater. Res. Soc. Symp. Proc.* **412**, 361–368.
- Gayer K. H. and Leider H. (1955) The solubility of uranium trioxide, $\text{UO}_3 \cdot \text{H}_2\text{O}$, in solutions of sodium hydroxide and perchloric acid at 25°C. *J. Amer. Chem. Soc.* **77**, 1448–1450.
- Gmelin Handbook of Inorganic Chemistry (1978) *Uranium Supplement Volume C-2: Oxides U_3O_8 and UO_3 , Hydroxides, oxide hydrates, and peroxides*. Springer-Verlag.
- Gresen R. L. (1981) The aqueous solubility product of solid solutions - 1. Stoichiometric saturation, partial, and total solubility product. *Chem. Geol.* **32**, 59–72
- Grenthe I. et al. (1992) *Chemical Thermodynamics of Uranium*. Vol. 1 NEA-TDB/OECD.
- Haar L., Gallagher J. S., and Kell G. S. (1984) *NBS/NRC Steam Tables: Thermodynamic and Transport Properties and Computer Programs for Vapor and Liquid States of Water in SI Units*. Hemisphere Publ.
- Helgeson H. C., Delany J. M., Nesbit H. W., and Bird D. K. (1978) Summary and critique of the thermodynamic properties of rock-forming minerals. *Amer. J. Sci.* **278-A**, 1–229.
- JCPDS (1992) Powder diffraction file.
- Hoekstra H. R. (1965) Infrared spectra of some alkali metal uranates. *J. Inorg. Nucl. Chem.* **27**, 801–808.
- Kim H. T. and Frederick W. J. (1988) Evaluation of Pitzer ion interaction parameters of aqueous mixed electrolytes solutions at 25°C. *J. Chem. Eng. Data* **33**, 278–283.
- Kramer-Schnabel U., Bischoff H., Xi R. H., and Marx G. (1992) Solubility products and complex formation equilibria in the systems uranyl hydroxide and uranyl carbonate at 25°C and I=0.1 M. *Radiochim. Acta* **56**, 183–188.
- Kraus K. A. and Nelson F. (1948) The hydrolytic behavior of uranium and the transuranic elements I. The +5 and +6 oxidation states. AECD-1864.
- Lippmann F. (1977) The solubility products of complex minerals, mixed crystals, and three layer clay minerals. *N. Jb. Miner. Abh.* **130**, 243–263.
- Maly J. and Vesely V. (1958) A contribution to sodium polyuranate chemistry. *J. Inorg. Nucl. Chem.* **7**, 119–128.
- Meinrath G. and Kimura T. (1992) Carbonate Complexation of the uranyl(VI) ion. *J. Alloys Compounds* **202**, 89–93
- Meinrath G. and Kimura T. (1993) Behaviour of U(VI) solids under conditions of natural aquatic systems. *Inorg. Chim. Acta* **204**, 79–85.
- O'Hare P. A. G., Lewis B. M., and Nguyen S. N. (1988) Thermochemistry of uranium compounds: XVII. *J. Chem. Thermodyn.* **20**, 1287–1296.
- Pitzer K. S. (1991) Ion fractionation approach: Theory and data correlation. In *Activity Coefficients in electrolyte solutions* (ed. K. S. Pitzer), pp. 75–153. CRC Press.
- Pongi N. K., Double G., and Hurwic J. (1980) Hydrolyse de U(VI) et uranates de sodium. *Bull. Soc. Chim. France* **9–10**, 347–353.
- Pearcy E. C., Prikryl J. D., Murphy W. M., and Leslie B. W. (1994) Alteration of uraninite from the Nopal I deposit, Peña Blanca District, Chihuahua, Mexico, compared to degradation of spent nuclear fuel in the proposed U.S. high level nuclear waste repository at Yucca Mountain, Nevada. *Appl. Geochem.* **9**, 713–732.
- Prins G. (1973) Uranyl chloride, its hydrates, and basic salts. React. Centrum Nederland Rept. 186.
- Ricci J. E. and Loprest F. J. (1955) Phase relations in the system sodium oxide-uranium trioxide-water at 50 and 75°C. *J. Amer. Chem. Soc.* **77**, 2119–2129.
- Sandino A. (1991) Processes affecting the mobility of uranium in natural waters. Ph.D. Dissertation, KTH.
- Sandino M. C. A. and Grambow B. (1994) Solubility equilibria in the U(VI)-Ca-K-Cl-H₂O system: Transformation of schoepite into bequerelite and comprégnacite. *Radiochim. Acta* **66/67**, 37–43.

- Strachan D. M., Tymochowicz S., Schubert P., and Kingston H. M. (1989) Preconcentration of trace transition metal and rare earth elements from highly saline solutions. *Anal. Chem. Acta* **220**, 243–249.
- Stroes-Gascoyne S. et al. (1985) Dissolution of used CANDU fuel at various temperatures and redox conditions. *Mater. Res. Soc. Symp. Proc.* **50**, 317–326.
- Sutton J. (1955) Hydrolyse de l'ion uranyle et formation d'uranates de sodium. *J. Inorg. Nucl. Chem.* **1**, 68.
- Tomazic B. and Branica M. (1972) Precipitation and hydrolysis of uranium (VI) in aqueous solutions-VII. Boundary conditions for precipitation from solutions of $\text{UO}_2(\text{NO}_3)_2\text{-KOH-K}$. ba. Lanthanum and europium nitrate. *J. Inorg. Nucl. Chem.* **14**, 1319–1332.
- Torrero M. E., Casas I., De Pablo J., Sandino M. C. A., and Grambow B. (1994) A comparison between unirradiated $\text{UO}_2(\text{s})$ and schoepite solubilities in 1 m NaCl medium. *Radiochim. Acta* **66/67**, 29–35.
- Tso T. C., Brown D., Judge A. I., Holloway J. H., and Fuger J. (1985) Thermodynamics of the actinoid elements. Part 6. The preparation and heat capacities of formation of some sodium uranates. *J. Chem. Soc. Dalton Trans.* **4**, 1853–1858.
- Wamser C. A., Belle J., Bersohn E., and Williamsom B. (1952) The constitution of the uranates of sodium. *J. Amer. Chem. Soc.* **4**, 1020–1022.
- Wang R. (1981) Spent fuel special studies progress report: Probable mechanisms for oxidation and dissolution of a single crystal UO_2 surfaces. Battelle Pacific Northwest Lab. Rept. PNL-3566/ UC-70.
- Wang R. and Katayama Y. B. (1982) Dissolution mechanisms for UO_2 and spent fuel. *Nucl. Chem. Waste Management* **3**, 83–90.
- Wronkiewicz D. J. et al. (1992) Uranium release and secondary phases formation during unsaturated testing of UO_2 at 90°C. *J. Nucl. Mater.* **90**, 107–127.
- Wronkiewicz D. J., Bates J. K., Wolf S. F., and Buck E. C. (1996) Ten year results from unsaturated drip tests with UO_2 at 90°C: Implications for the geological disposal of spent nuclear fuel. *J. Nucl. Mater.* **38**, 78–95.