

INFO #: 18392171

LOS ALAMOS NATIONAL LABORATORY
Jean-Francois Lucchini

Entered: 4/2/2008 10:31:00AM

NB 04/09/2008
12:00 AM PT
A

SHIP VIA: **Ariel**

Ariel

FILLED ON: 04/02/2008

Infotrieve, Inc.

1888 Century Park East, Ste 600

Los Angeles, CA 90067

Phone 800-422-4633 or 203-423-2175

Fax



Holdings

Send article only if in the Library collection

NB 04/09/2008
12:00 AM PT
A

SHIP TO: 14288 / 1351613

LOS ALAMOS NATIONAL LABORATORY
Jean-Francois Lucchini
A141

Please contact us if you have questions or comments regarding this article.

Email: service@infotrieve.com

Phone: (800) 422-4633

CUSTOMER INFO
PHONE: +1.505.234.5556
FAX: +1.505.887.3051
TEAM: T8-14288
COURIER:

ARTICLE INFORMATION

ARIEL:

0033-8230

NOTES:

Radiochimica Acta

66-67():37 43 1994

MAIN 1962-1993

Publisher 2000-2002 Online

Publisher 2002-9999 Online

SANDINO, MCA GRAMBOW, B

international conference on chemistry and migration behavior of actinides

Send article only if in the Library collection

CCD	0
SHIP VIA	Ariel
ORDER #	
BILLING REF	
ORDERED ON	04/02/2008
FILLED ON	04/02/2008
NEED BY	04/09/2008
ATTENTION	Jean-Francois Lucchini
INFO #	18392171

This document is protected by U.S. and International copyright laws. No additional reproduction is authorized. Complete credit should be given to the original source.

Solubility Equilibria in the U(VI)-Ca-K-Cl-H₂O System: Transformation of Schoepite into Becquerelite and Comptjeignacite

By M. C. Amaia Sandino and Bernd Grambow

Kernforschungszentrum Karlsruhe GmbH, Institut für Nukleare Entsorgungstechnik, 76021 Karlsruhe, Germany

Schoepite / Becquerelite / Comptjeignacite / Solubility / Crystallinity

Abstract

Schoepite type phases, (UO₂ · xH₂O(s)), have been reported as corrosion products of spent fuel in long-term leaching experiments under oxidizing conditions. This paper describes the transformation of such a phase into two different phases: (a) becquerelite, CaU₆O₁₉ · 11H₂O(s), and (b) comptjeignacite, K₂U₆O₁₉ · 11H₂O(s).

It has been proven that the uranyl hydroxide solid transforms spontaneously into these two phases (a) and (b), at room temperature after a short contact time in the presence of Ca²⁺ and/or K⁺ ions, respectively. Analysis of the solution data indicates that equilibrium was reached and also, the predominance of the hydrolysis reaction vs. the chloride complexation of the uranyl ion at pH values higher than 4.5, even at the high chloride concentration. The solubility products of the two phases were determined in 1 m CaCl₂ and 1 m KCl solutions, respectively. The values were extrapolated to the reference state $I = 0$.

The effect of calcium and potassium concentrations in natural waters on the formation of possible secondary phases of uranium(VI) is assessed in the light of these new data.

Introduction

During the last years, a vast amount of work has been performed on the fate of the spent fuel in deep geological repositories, [1 and the references therein]. In order to predict the long-term behaviour of the nuclear waste, a substantial number of thermodynamic data on solution species and solid phases must be determined. Under oxidizing conditions schoepite type phases (UO₂ · xH₂O(s)), have been identified as corrosion products of spent fuel [2, 3]. Secondary phases, i.e., the alteration phases of UO₂(s) (the main component of the waste), could determine the overall behaviour of the waste matrix since precipitation processes could either limit or drive the dissolution of the waste as well as control the maximum solution concentrations of radionuclides.

Schoepite has been found as a weathering product of uraninite in natural uranium deposits. In the presence of various elements, uranyl hydroxides are not the long-term stable phases, [4, 5]. They undergo a transformation into different phases, e.g., M_n[(UO₂)₂O₃(OH)₂] · qH₂O(s), where M represents divalent cations, commonly Ca²⁺, Pb²⁺, Ba²⁺, and also monovalent cations such as K⁺. The transformation reaction is generally dependent on external parameters

like pH and groundwater composition. Even though some of the possible secondary phases have previously been studied, the thermodynamic data for most of these compounds are scarce.

Important minerals in this family of uraninite alteration products, the becquerelite structural group [6], are comptjeignacite, K₂U₆O₁₉ · 11H₂O(s) and becquerelite, CaU₆O₁₉ · 11H₂O(s). They have also been identified as products in the oxidative corrosion of synthetic UO₂(s) [7, 8]. The transformation from schoepite to becquerelite has recently been demonstrated under laboratory conditions at 60 °C, [9]. However, there is still a lack of thermodynamic data for both of these solid phases.

The work presented here is part of a larger research project dealing with the identification and characterization of the different solid phases that could form under the conditions prevalent in a salt repository. This report deals with the experimental results obtained so far on the transformation reaction of schoepite type phases (hydrated uranyl hydroxide) into calcium and potassium phases, as well as the determination of their solubilities.

Experimental

Materials

The chemicals used in this study, UO₂(NO₃)₂ · 6H₂O(s), NaOH(s), CaCl₂(s), KCl(s), KOH(s), Ca(NO₃)₂(s) and (CH₃)₂NOH · 5 H₂O(s) (TMAHP), were of analytical grade (Merck, Aldrich). All solutions were prepared with bidistilled water from a Millipore Copr. Milli-Q system. The leachant solutions were deaerated with N₂ or Ar prior to the initiation of the experiments.

Synthesis of the solid phases

The uranyl hydroxide used in these experiments was precipitated as described elsewhere [10]. After separation from its mother liquid, the solid was thoroughly washed with bidistilled water. The phase was characterized by X-ray Powder Diffraction, XPD, and Scanning Electron Microscopy and Energy-Dispersive Analysis, SEM-EDX. The XPD pattern (see Figure 1a) showed the presence of peaks corresponding to a microcrystalline hydrated uranyl hydroxide phase cor-

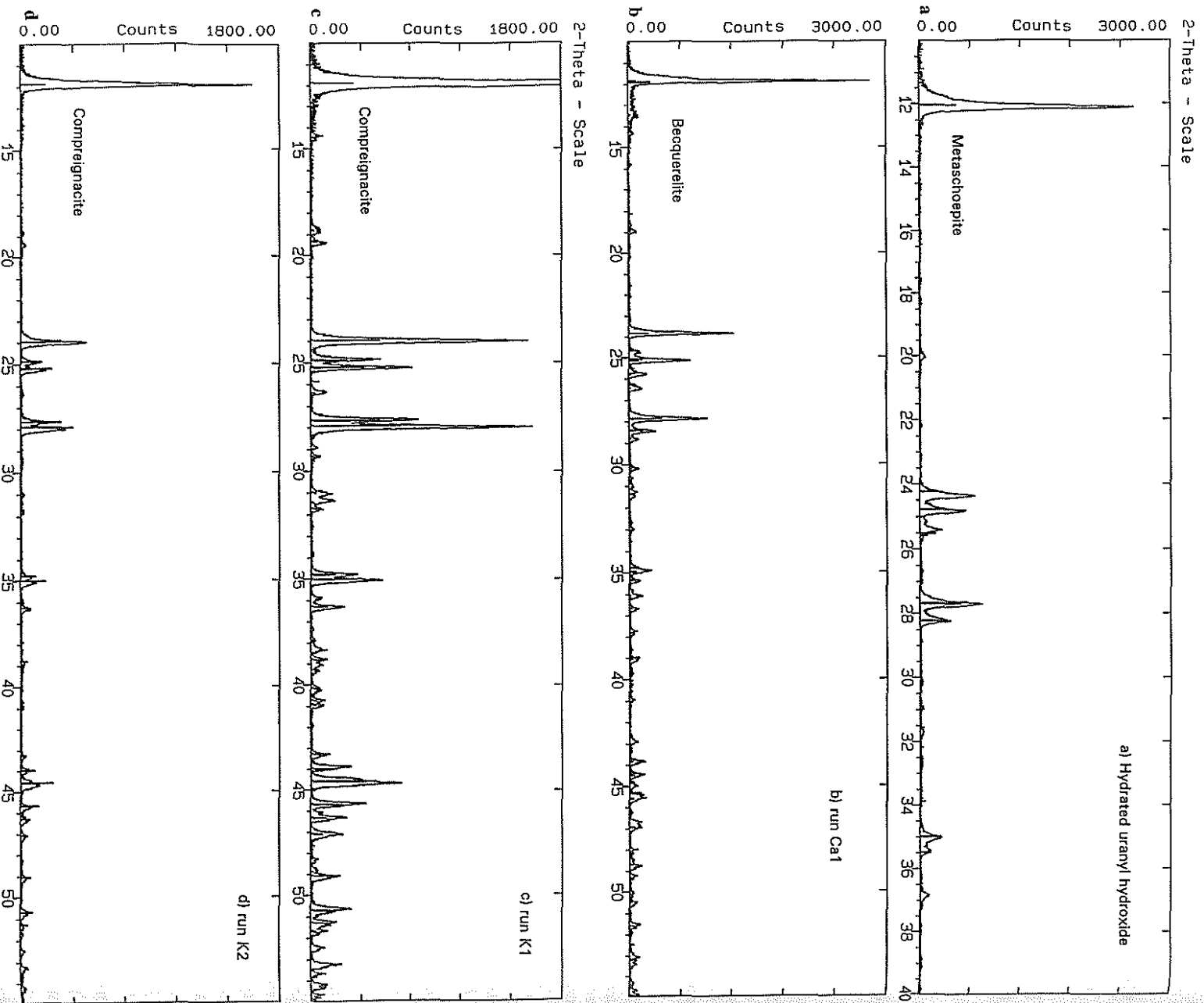


Fig. 1. X-ray diffractograms obtained for the following solids: (a) Hydrated uranyl hydroxide. (b) Calcium phase, run Ca1. (c) Potassium phase, run K1. (d) Potassium phase, run K2. The X-ray are compared with the following data from JCPDS: (a) Metaschoepite n° 18-1436. (b) Bequerelite n° 29-0389. (c) and (d) Compreignacite n° 33-1049.

responding to the JCPDS card n° 18-1436. This set of powder data is just pure schoepite, $\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{s})$ [11]. Since the name metaschoepite refers only to the JCPDS data card number, not to any dehydrated phase, in the following discussion the obtained solid will be called schoepite. The SEM micrographs obtained also

showed the tabular morphology characteristic of this phase [6]. EDX analysis did not detect any other element apart from uranium in the precipitate.

The synthesis of bequerelite, $\text{CaU}_6\text{O}_{19} \cdot 11\text{H}_2\text{O}(\text{s})$ [12], was performed by mixing uranyl and calcium nitrate solutions in the corresponding proportions at

room temperature. The precipitation vessel was sealed and placed in a low temperature incubator at 25 °C. In order to facilitate the precipitation of the solid, the pH was increased by adding tetramethylammonium hydroxide pentahydrate, TMAHP (an organic alkali, which avoids the introduction of other complexing cations), to the solution and the reactor was placed in an oven at 60 °C. After a month, the precipitation of a solid was observed when the pH was ca. 4. After 6 weeks, a sample was taken for analysis and the solid was left in contact with its mother liquid for ageing at 25 °C. After 3 months, the precipitate was filtered, washed several times with bidistilled water and dried at room temperature. The solid was characterized by XPD, chemical analysis and SEM-EDX.

The synthesis of compregnacite, $K_2U_6O_{16} \cdot 11H_2O(s)$ [13], was performed by adding stoichiometric amounts of potassium hydroxide to a solution of uranyl nitrate at room temperature. The vessel was sealed and placed in a low temperature incubator at 25 °C. After a week of reaction, a fine solid was observed. The precipitation process was accelerated by placing the reactor in an oven at 60 °C. Further treatment was done as described above for becquerelite.

Method

Experiments with schoepite

Certain amounts of the hydrated uranyl hydroxide were put in contact with the deaerated leaching solutions 1 m $CaCl_2$ and 1 m KCl at two different initial pH values: 3.97, 7.47 for the $CaCl_2$ system and 4.25, 6.00 in the case of the KCl solution. The experiments were performed in Teflon-PFA vessels (50 ml) which were sealed and placed in a water bath at 25.0 ± 0.5 °C. After 3, 5 and 9 months, aliquots were taken and filtered for further analysis of both solid and aqueous phases. The experimental details have been described elsewhere [10].

Since no major pH changes were observed after 9 months of contact, it was decided to increase the pH in one of the reactors for each system, i.e., $CaCl_2$ and KCl solutions, whereas the other two were left to continue the reaction. In the latter, final samples were taken after 13 months. In the former, the pH was increased stepwise by adding TMAHP. Equilibrium was assumed to be attained when the pH remained constant within ±0.01 units over a 24 hours period. The results showed that the system reached equilibrium in 2–3 weeks. After equilibrium was attained, a sample was taken, filtered and analyzed. The duration of the experiments was 14 months.

Solubility experiments with becquerelite and compregnacite

A given amount of becquerelite and compregnacite was put in contact with 1 m $CaCl_2$ and 1 m KCl solutions, respectively, at 3 different initial pHs, (4, 16,

4, 46, 5, 85 for the Ca system and 3, 12, 4, 46, 5, 83 in the case of the K system), following the procedure described elsewhere [10]. Duplicate experiments were performed in Teflon-PFA vessels (50 ml), which were sealed and placed in a low temperature incubator at 25 °C. Based on the experiments described above, equilibrium was assumed to be achieved after a month. At this time, aliquots were taken and filtered for further analysis of both solid and aqueous phases. A week later, the solution was completely withdrawn from the reactors. They were then refilled with fresh deaerated solutions of the corresponding ionic medium at the given pH. On termination of the tests, further samples were taken for analysis. These experiments were performed over a 3 months period.

Analysis

In order to check the possible influence of colloids, the samples were filtered through 0.05 and/or 0.2 µm membranes (Millipore). No variations between samples filtered with the two different membranes were observed. The pH was measured by a Ross electrode (Orion 8-02) which was calibrated daily using standard buffer solutions. Measured pH values were corrected for liquid junction potentials by calibrating the electrode against molality of the hydrogen ion by adding known amounts of HCl to pure $CaCl_2$ or KCl solutions [14]. The uranium, calcium and potassium concentrations in solution were determined by ion coupled plasma spectrophotometry (ICP-AES). These analyses were performed using an ARL-3580 spectrophotometer. Selected solid samples were analyzed by X-ray Powder Diffraction, XPD. The X-ray patterns were recorded on a Siemens-D500 diffractometer using $CuK\alpha$ radiation. The solid phases were also examined by Scanning Electron Microscopy and Energy-Dispersive Analysis, SEM-EDX, in a JEOL-35C scanning electron microscope. Chemical analysis of the solid samples were also performed. The amount of water in the samples were determined by thermogravimetric methods.

Results

Schoepite transformation

The analysis of the solid samples indicated that the initial solid transformed to a Ca - and a K -bearing phase after 3 months contact time with the 1 m $CaCl_2$ and 1 m KCl solutions, respectively. These phases were identified as becquerelite and compregnacite, based on the following results: the XPD patterns of the solids were in excellent agreement with the patterns given in the literature for these two phases (see Figure 1b–1c–1d); the SEM micrographs obtained showed the characteristic morphology of these solids (see Figure 2), especially in the case of becquerelite [6]; EDX and chemical analysis yielded good quanti-

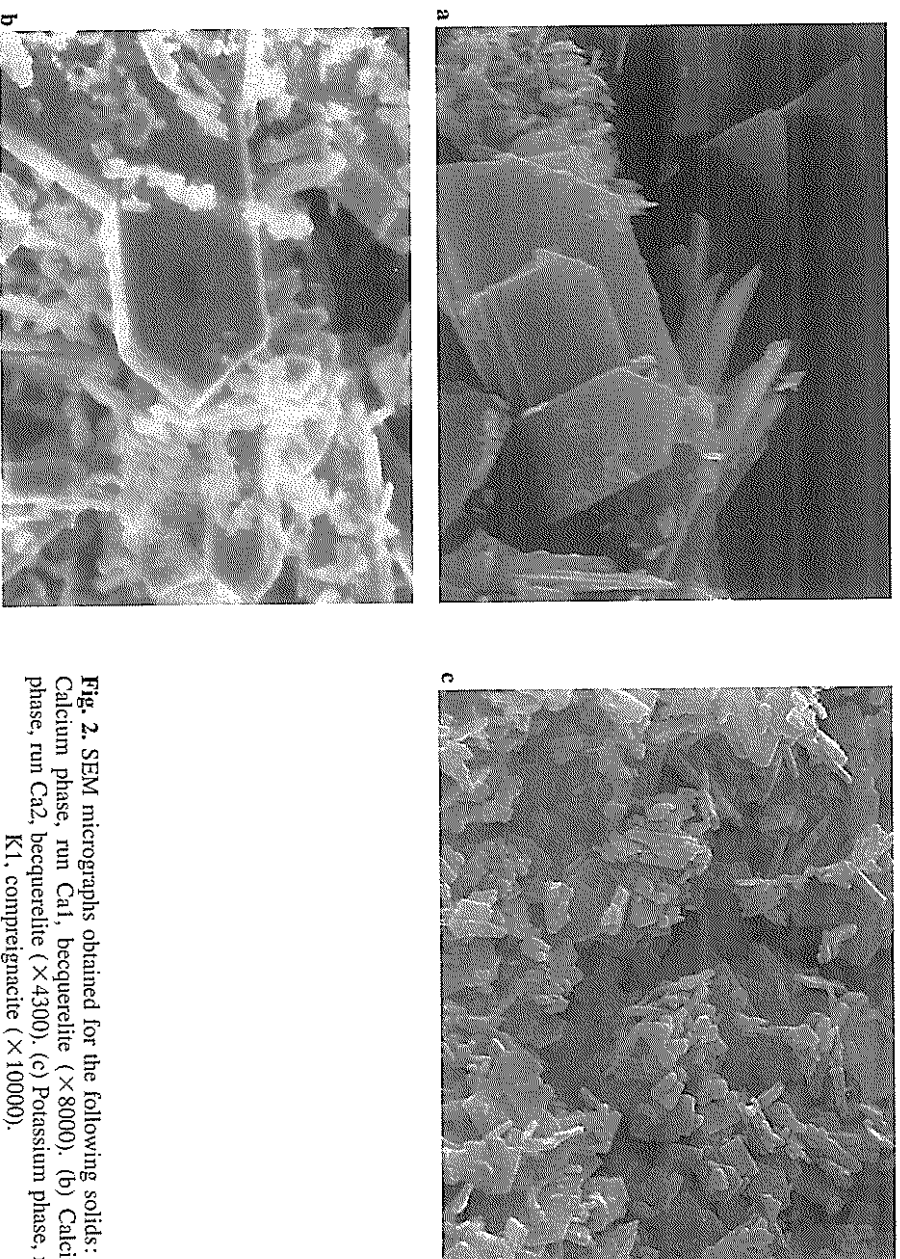


Fig. 2. SEM micrographs obtained for the following solids: (a) Calcium phase, run Ca1, bequerelite ($\times 8000$), (b) Calcium phase, run Ca2, bequerelite ($\times 4300$), (c) Potassium phase, run K1, compraignacite ($\times 10000$).

Table 1. Chemical analysis of bequerelite, $\text{CaU}_6\text{O}_{19} \cdot 11\text{H}_2\text{O}(\text{s})$ and compraignacite, $\text{K}_2\text{U}_6\text{O}_{19} \cdot 11\text{H}_2\text{O}(\text{s})$

Sample	UO ₃ %	CaO %	H ₂ O(a,b,c)	U/Ca
1c	86.54	2.81	10.65, 10.36, —	6.1
2c	87.57	2.92	9.51, 10.00, 9.21	5.94
3c	88.07	2.88	9.05, 9.88, 9.58	5.96
Ideal	87.10	2.84	10.1	6.0
Sample	UO ₃ %	K ₂ O %	H ₂ O(a,b,c)	U/K
1k	84.46	4.86	10.68, 9.59, 8.21	2.99
2k	84.16	4.71	11.13, 9.82, 9.91	2.94
3k	85.10	4.57	10.33, 9.64, —	3.08
Ideal	85.45	4.69	9.86	3.0

Water analysis: (a) by difference, (b) by thermogravimetry and (c) by DTG. U/M catio ratio.

tative results for the corresponding stoichiometries (see Tables 1 and 2). The composition and morphology of these solids were analyzed at different stages of the experiments. The solids did not exhibit any significant change during the course of the experiments (over a year), which shows the stability of these phases at the ionic medium investigated. Moreover, the aqueous data, pH and total uranium concentration, [U], obtained during the first 9 months of the experiments indicated that equilibrium was clearly attained, since these values did not exhibit any significant variation. The measured solubility data, ($\log[\text{U}]$, vs. pH), for the cal-

Table 2. EDX analysis of bequerelite, $\text{CaU}_6\text{O}_{19} \cdot 11\text{H}_2\text{O}(\text{s})$ and compraignacite, $\text{K}_2\text{U}_6\text{O}_{19} \cdot 11\text{H}_2\text{O}(\text{s})$

Sample	U %	Ca %	Sample	U %	K %
1c	88	11	1k	77	23
2c	87	12	2k	78	22
Ideal	86	14	Ideal	75	25

M is % atomic percentage.

cium and potassium systems are shown in Figures 3 and 4, for runs Ca1 and K1, respectively.

Solubility tests

The solubility data for bequerelite and compraignacite (runs Ca2 and K2), are presented in Figures 3 and 4. The composition and morphology of the solid phases were also investigated at different stages of the experiments. At all times, the obtained XPD patterns agreed with the literature data for both phases. However, a decrease in crystallinity was inferred based on the X-ray powder data and the SEM micrographs obtained when compared with the samples obtained in the transformation experiments described above. This finding has a clear relationship with the time scale of the experiments and is illustrated in the XPD patterns (width and intensity of the peaks), e.g., K system in Figure 1c–1d, and SEM micrographs (particle size),

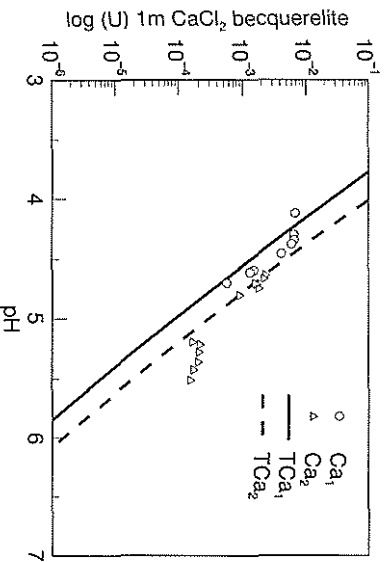


Fig. 3. Solubility data of becquerelite from the two runs, Ca1 and Ca2, at 1 m CaCl₂ and $T = 25^\circ\text{C}$. The models have been calculated with the corresponding constants given in Tables 3 and 4.

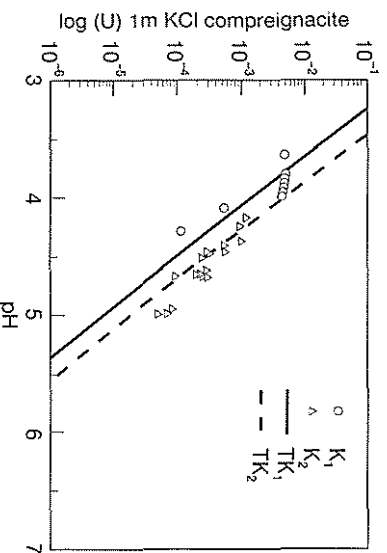
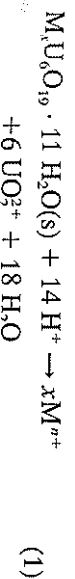


Fig. 4. Solubility data of compreignacite from the two runs, K1 and K2, at 1 m KCl and $T = 25^\circ\text{C}$. The models have been calculated with the corresponding constants given in Tables 3 and 4.

e.g., Ca system in Figure 2a–2b. The corresponding chemical and EDX analysis are given in Tables 1 and 2.

Mathematical treatment of the data

The solubility reactions involved in these chemical systems can be expressed by the following general equilibrium,



where $M = Ca^{2+}$ or K^+ and $x = 1$ or 2, respectively. The solubility data from runs Ca1, Ca2, K1 and K2 have been evaluated using the computer program C-Letagrop [15] to obtain the corresponding solubility constants, $\log K_{so}$, for reaction (1). Due to the possible differences in solubility between the synthesized phases and the solids formed by the transformation of schoepite, the experimental data for each run, (aqueous uranium concentration and pH), were evaluated separately. The equilibrium constants of the aqueous spe-

Table 3. Thermodynamic data base used for the aqueous phase, at $I = 0$ and at 1 m KCl and CaCl₂ solutions

Species	$\log K_{so}^0$	$\log \beta_{r,n}$ 1 m KCl	$\log \beta_{r,n}$ 1 m CaCl ₂
$(UO_2)_3(OH)_3^{3+}$	-5.62a	-6.04	-6.13
$(UO_2)_3(OH)_3^{2+}$	-11.9 a	-12.32	-12.08
$(UO_2)_3(OH)_7^+$	-21.9 a	-23.35	-23.48
$(UO_2)_3(OH)_8^+$	-15.55a	-16.81	-17.08
$(UO_2)_3(OH)_7^-$	-32.2 b	-32.39	-32.01
$UO_2(OH)_5^-$	-19.74b	-19.55	-19.45
UO_2Cl^+	0.17a	-0.40	-0.31
$UO_2Cl_2(aq)$	-1.1 a	-1.62	-1.17
OH^-	-14.0 a	-13.80	-14.13

a: [16], b: [21].

cies used for these calculations are given in Table 3. They have been extrapolated to both ionic media, 1 m CaCl₂ and 1 m KCl solutions, by means of the specific interaction theory, SIT [16], following the application to uranium(VI) chemistry used in the OECD/NEA review of the chemical thermodynamics of uranium [17]. We have already addressed [10], the uncertainty in the hydrolysis of uranium(VI), specifically with regard to some of the species, e.g., $UO_2(OH)_2(aq)$ and UO_2OH^+ . Since these species are not predominant under these experimental conditions, they have not been included in the aqueous model to reduce the sources of error. Furthermore, chloride complexation in the chemistry of uranium(VI) in chloride medium is not well understood. In the NEA review [17], uranium-(VI) chemistry in chloride medium is treated similar as in perchlorate medium, and the differences between the uranium(VI) chemistry in the two media are attributed exclusively to chloride complexation. Alternatively to the SIT approach [16], chloride complexation may indirectly be accounted for in the activity coefficients calculated for the uranyl ion in chloride medium using the Pitzer theory. In order to include chloride complexation into the activity coefficients to allow a comparison between the Pitzer and the SIT approaches, one has to divide the activity coefficient of the free (uncomplexed) uranyl ion by $(1 + \beta_1 \cdot [Cl^-] + \beta_2 \cdot [Cl^-]^2)$, where β_1 and β_2 are the equilibrium constants for the chloro complexes, UO_2Cl^+ and $UO_2Cl_2(aq)$, respectively. Differences between the two methods are less than 15% for 1 m KCl and 1 m CaCl₂ solutions. Hence, the simplest approach, SIT, is used in the present communication.

The results of the calculations, $\log K_{so}$, are given in Table 4 for the four runs along with the corresponding values at zero ionic strength. In Figures 3 and 4, the theoretical models calculated using the obtained solubility constants are compared with the experimental data.

Discussion

The transformation of schoepite into becquerelite is ubiquitously observed in nature; its transformation

Table 4. Set of the solubility constants for reaction (1) obtained at 1 m CaCl₂ and KCl solutions at $T = 25^\circ\text{C}$ and the corresponding extrapolated values to the infinite dilution standard state

Run	$\log K_{so} \pm \sigma$	$\log K_{so}^\circ \pm \sigma^*$
Ca1	42.88±0.24	41.89±0.52
Ca2	44.69±0.12	43.70±0.47
K1	38.19±0.23	36.82±0.32
K2	40.53±0.21	39.16±0.31

* The uncertainty assigned to the extrapolated values was calculated using the following equation, $\sigma_{reg,De}^\circ = ((\sigma_{reg,De})^2 + (m_{Cl} \cdot \sigma_{De})^2)^{1/2}$ where De represents the increment of the interaction coefficients.

into compreignacite is also found but to a minor extent [6, 18]. Under laboratory conditions, Vochten [9] has reported the synthesis of becquerelite by the reaction of Ca²⁺ ions with schoepite at 60°C. The work presented here demonstrates the spontaneous transformation of the uranyl hydroxide phase into the two secondary phases under the given experimental conditions at room temperature. It seems, that the kinetics of these reactions are reasonably fast.

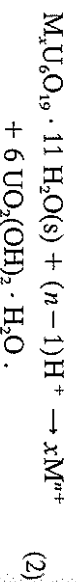
In order to describe the thermodynamic stability field of a solid phase, a knowledge of its solubility constant is required. We have calculated this value for reaction (1), with $M = \text{Ca}^{2+}$ and K^+ . The scatter of the experimental data around the calculated models (see Figures 3 and 4), reflects the magnitude in the error of the corresponding solubility constants. However, considering the various sources of error in the calculations, especially with respect to the aqueous model and the method for ionic strength corrections, the values for becquerelite are in fair agreement with the solubility constant reported by Vochten, $\log K_{so} = 43.2$, in pure water at 25°C [9]. In the literature, there is another value for the solubility of becquerelite [19]. In this study, the stability field of this phase was reported as a function of temperature and calcium concentration. A value for the solubility of becquerelite was given ($8.40 \cdot 10^{-6}$ mol dm⁻³ in H₂O at 20°C), but a comparison is not possible since exact experimental details were not specified. In the case of compreignacite, no literature data are available.

The differences in the solubility constants of the two runs, for both becquerelite and for compreignacite (see Table 4), may be attributed to differences in crystallinity. It is generally known that the degree of crystallinity influences the solubility of the solid [20]. We have not been able yet to quantify this parameter. A detailed investigation of the effect of crystallinity on solubility will be presented in a forthcoming publication.

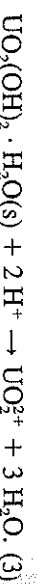
During the course of this study, no attempt has been made to derive stability constants for the aqueous species of the uranyl ion. In the pH range of our study, the monochloro complex, UO₂Cl⁺, and the uranyl hydroxide, (UO₂)₂(OH)₂²⁺, appear to be the dominant

solution species. The complete validation of these findings remains to be demonstrated.

The existence of different solubility constants depending on the degree of crystallinity, strongly influences the stability boundaries of the solid phases. The solid phase transformation can be expressed as,



The corresponding equilibrium constant, K_{ss} , is only dependent on the cation concentration and pH. Its numerical value can be calculated from a combination of reaction (1) and the solubility reaction of schoepite,



Taking various values reported in the literature for the solubility of schoepite of different crystallinity [10, 17, 21], the obtained $\log K_{ss}$ values vary considerably: in the case of becquerelite between 3.91 and 14.84, and in the compreignacite system from -1.16 up to 10.30. Hence, the equilibrium constant for the transformation reaction of schoepite into becquerelite or compreignacite depends largely on the degree of crystallinity.

Amorphous hydrated uranyl hydroxide will undergo transformation at a much lower pH value or calcium concentration than well crystalline schoepite. Under natural conditions formation of highly crystalline phases is expected. Using the solubility constant for schoepite given by NEA [17], along with the constants obtained for the most crystalline phases reported here (see Table 4), the values for $\log K_{ss}$ are 13.03 and 7.96, for becquerelite and compreignacite transformation reaction, respectively. Assuming that, typical calcium and potassium concentrations in granitic groundwater are 10^{-3} and 10^{-4} mol dm⁻³ respectively, schoepite will transform to either becquerelite or compreignacite at pH values higher than 8. Nevertheless, this pH boundary will move toward lower values as the crystallinity of becquerelite or compreignacite increases. The same effect will be observed with higher calcium or potassium aqueous concentration. This factor is particularly relevant for the natural conditions encountered in a deep geological repository in a salt formation.

Conclusions

The transformation of schoepite into becquerelite and compreignacite at room temperature has been shown. The solubilities of these two phases have been measured in 1 m CaCl₂ and 1 m KCl solutions, respectively. An attempt has been made to determine the equilibrium constants for the solid phase transformation reaction. However, the inherent uncertainties in the knowledge of crystallinity of the solid phases involved do not really permit the quantification of the phase stability. In order to describe thermodynamically and kinetically this chemical process, systematic studies of the dependence of the solubility on the degree of crystallinity must be performed.

Acknowledgements

We acknowledge assistance from our colleagues: Mrs. Diel (ICP analysis), Mrs. Schlieker (XPD analysis), Dr. Bernotat, Dr. Römer and Mr. Spieler (SEM-EDX analysis) and Mrs. Nesovic (DTG analysis).

References

1. Johnson, L. J., Shoensmith, D. W.: In *Radiactive waste for the future* (eds. Lutze and Ewing), Elsevier Sci. Publish., Amsterdam (1988).
2. Wang, R., Katayama, J. B.: Nucl. Chem. Wast. Manag. **3**, 83 (1982).
3. Suroes-Gascogne, S., Johnson, L. J., Beeley, P. A., Selinger, D. M.: Mat. Res. Soc. Symp. Proc. **50**, 317–326 (1985).
4. Finch, R. J., Ewing, R. C.: SKB Technical Report 91-15 (1991).
5. Vochten, R., In *Primary radioactive minerals* (ed. Barot-Kyriakidis), Theophrastus Publish., Athens (1991).
6. Deltens, M., Piret, P., Comblian, G.: in *Les minéraux secondaires d'uranium du Zaïre*, Musée Royal de l'Afrique centrale, Tervuren, Belgique, D/1981/0254/7 (1981).
7. Bates, J. K., Tani, B. S., Veleckis, E., Wronkiewicz, D. J.: Mat. Res. Soc. Symp. Proc. **176**, 499–506 (1990).
8. Wronkiewicz, D. J., Bates, J. K., Gerding, T., Veleckis, E., Tani, B. S.: J. Nucl. Mater. **190**, 107–127 (1992).
9. Vochten, R., Van Haverbeke, L.: Mineral. Petrol. **43**(1), 65–72 (1990).
10. Torroero, M. E., Casas, I., de Pablo, J., Sandino, M. C. A., Granbow, B., Radiochim. Acta **66/67**, 29–35 (1994).
11. Finch, R. J.: personal communication.
12. Protas, J.: Bull. Soc. Fr. Mineral. Cristallogr. **82**, 239–272 (1959).
13. Brindley, G. W., Bastovanov, M.: Clays, Clay Miner. **30**(2), 135–142 (1982).
14. Granbow, B., Müller, R.: Mat. Res. Soc. Symp. Proc. **176**, 229 (1990).
15. Osthois, E.: The C-Letagrop program system. Tita-OK-2051, KTR/RTT, Stockholm (1991).
16. Grenthe, I., Wanner, H.: *Guidelines for the extrapolation to zero ionic strength*, TDB-2.1, OECD/NEA, Nuclear Energy Agency, France (1989).
17. Grenthe, I., Fuger, J., Konings, R., Lemire, R., Müller, A., Nguyen-Trung, C., Wanner, H.: in *Chemical thermodynamics of uranium* (eds. Wanner and Forest). OECD/NEA, North-Holland (1992).
18. Finch, R. J., Ewing, R. C.: J. Nucl. Mater. **190**, 133–156 (1992).
19. Atkins, M., Beckeley, A. N., Glaser, F. P.: Radiochim. Acta **44/45**, 255–261 (1988).
20. Schindler, P.: in *Equilibrium concepts in natural water systems* (ed. Stumm, W.), Adv. Chem. Ser. n° 67, American Chemical Society, Washington DC, p. 196 (1967).
21. Sandino, M. C. A., Bruno, J.: Geochim. Cosmochim. Acta **56**, 4135–4145 (1992).