Chapter 6
Solubility of UO_2(am)

Contents

6.1 Introduction

Migration and electromigration experiments conducted with uranium have been interpreted by Maes *et al.* (2002 and 2003) as a change in oxidation state: reduction of U(VI) and precipitation of U(IV) oxy-hydroxides. It is concluded that the migration of uranium in the Boom Clay is governed by strong retention mechanisms mainly due to precipitation. As a consequence, the uranium concentration in Boom Clay pore water is solubility limited. One possible scenario is that under the influence of alpha-radiolysis caused by the radioactivity of the spent fuel, a partial oxidation and dissolution of the UO_2 matrix and the subsequent U(VI) mobilisation occur. Mobile U(VI) will migrate away from the oxidising region and encounter the undisturbed clay where strongly reducing conditions are prevailing. There, the reduction of uranyl species to the tetravalent state would be possible. The precipitation of U(IV) will likely produce an amorphous or poorly crystallised solid. The re-crystallisation of this amorphous phase at low temperature may take relatively long time. According to Rai *et al.* (2003), UO_2(am) is the dominant and solubility limiting solid phase of U(IV) in neutral and alkaline solutions (*p*H>5), even after 24 days of heating at 900°C. Therefore, the solubility study of amorphous U(IV) is important to determine the maximum uranium concentration in Boom Clay pore water in contact with the spent fuel. Indeed, performance assessment studies clearly indicate that the uranium solubility is an important parameter influencing the long-term dose rate (Baudoin *et al.*, 2000; Sillen and Marivoet, 2002).

6.1.1 State of the art on the solubility of amorphous UO_2

Extensive effort has been spent on the determination of the solubility of amorphous uranium dioxide, UO_2(am). In the literature, the term "hydrous" is also used as synonym of "amorphous" to characterise the same solid, denoted $UO_2 \cdot xH_2O$. The solubility values of U(IV) hydrous oxide reported in the literature are extremely scattered. The variation over several orders of magnitude is due to the uncertainty involved in the solid phase and to the difficulty to maintain properly reducing conditions (Neck and Kim, 2001). There are considerable difficulties in ensuring that the aqueous solutions are sufficiently free of oxygen and that the precipitated solids contain only U(IV). Even traces of dissolved oxygen cause at least partly oxidation of U(IV) to U(VI). With oxygen contamination, the measured solubility becomes that of a mixed U(IV)-U(VI) oxide or that of an U(VI) solid. Furthermore, the solubility is expected to be dependent on the particle size and on the crystallinity of the precipitated solid (Grenthe *et al.*, 1992; Langmuir, 1997).

Gayer and Leider (1957) studied the solubility of U(IV) hydroxide in NaOH solution. They measured uranium concentration from 6.3×10^{-6} to 7×10^{-5} mol·l^{-1} in the *p*H range 12.9-13.8. Ryan and Rai (1983) obtained solubilities approximately 3.5 orders of magnitude lower, *i.e.* uranium concentration lower than 10^{-8} mol·l^{-1} in the *p*H range 12.7-13.9 and in presence of dithionite. According to these authors, the work by Gayer and Leider was questionable about the oxidation state of uranium. High solubility was also reported by Bruno *et al.* (1987). They measured uranium concentration above amorphous UO_2 of 4×10^{-5} mol·l^{-1} at *p*H 5.5-10. The solubility did not vary in that *p*H range and was attributed to the uncharged complex $U(OH)_4$(aq).

They determined a log K for the equilibrium reaction of the solubility of amorphous UO_2 at the *p*H range 5.5 to 10:

$$UO_2(am) + 2\ H_2O \rightleftharpoons U(OH)_4(aq) \qquad \log K = -4.4$$

Bruno *et al.* (1986 and 1987) claimed that the divergence between their results and those obtained by Ryan and Rai (1983) was based on differences in the crystallinity of the solid phases. According to Rai *et al.* (1990), Langmuir (1997) and Neck and Kim (2001), oxygen contamination apparently invalidates the results of Gayer and Leider (1957) and Bruno *et al.* (1987) who obtained solubilities roughly equal to that of $UO_3 \cdot H_2O$ as reported by Gayer and Leider (1955). Rai *et al.* (1990) determined the solubility of freshly precipitated $UO_2.xH_2O$ in dilute solution in the *p*H range from 2 to 12. They used Fe powder and Eu^{2+} to eliminate dissolved oxygen and to maintain reducing conditions. The uranium concentrations were around 10^{-8} mol·l^{-1} and essentially independent on *p*H at *p*H above 4. Their solubility data yielded values of the logarithm of the solubility product for the reactions:

$$UO_2.xH_2O(am) \rightleftharpoons U(OH)_4(aq) + (x\text{-}2)\ H_2O \qquad \log K = -8$$

and,

$$UO_2.xH_2O(am) \rightleftharpoons U^{4+} + 4OH^- + (x\text{-}2)\ H_2O \qquad \log K = -52$$

Rai *et al.* (1997) reviewed the value of the logarithm of the solubility product for the above reaction. The best value that described their solubility data was -53.45. Yajima *et al.* (1995) reported solubility for UO_2(am) 0.5 to 2 orders of magnitude lower than the results of Rai *et al.* (1990). Beyond *p*H 2, the solubilities were constantly around 10^{-9} mol·l^{-1} and independent on *p*H. The dominant reaction in that *p*H region was estimated as:

$$UO_2(am) + 2\ H_2O \rightleftharpoons U(OH)_4(aq) \qquad \log K = -8.7$$

More recently, Fujiwara *et al.* (2003) determined the following solubility product for the reaction:

$$UO_2.xH_2O \rightleftharpoons U^{4+} + 4OH^- + (x\text{-}2)\ H_2O \qquad \log K = -53.9$$

Bicarbonate and carbonate are components of Boom Clay pore water which may increase the solubility of U(IV) hydrous oxide by the formation of U(IV)-carbonate complexes. However, Rai *et al.* (1995 and 1998) have shown that bicarbonate and carbonate do not increase the solubility of U(IV) hydrous oxide at concentrations lower than 4×10^{-2} and 0.1 mol·l^{-1}, respectively. The respective concentrations of bicarbonate and carbonate being about 10^{-2} and 10^{-4} mol·l^{-1} in Boom Clay pore water, the formation of U(IV)-carbonate complexes is not expected.

The solubility of crystalline uranium dioxide in simulated Boom Clay water was determined by Guilbert *et al.* (2002). They found a relatively high uranium concentration (3×10^{-6} mol·l^{-1}) after one month of equilibration. This high uranium concentration decreased afterwards and reached steady state around 10^{-8} mol·l^{-1} after 200 days. The authors explained the high solubility by the presence of oxygen traces in the atmosphere at the beginning of the test, resulting in oxidation of the uranium dioxide surface. The dissolution of crystalline UO_2 under Boom Clay conditions was also investigated by Cachoir *et al.* (2003). The uranium concentration also decreased in function of time suggesting the reduction of U(VI) to U(IV). The reduction

occurred faster in BCW than in SBCW, probably due to the presence of Fe(II) in BCW. At the end of the test (370 days), the uranium concentrations were around 4×10^{-8} mol·l^{-1}, both in BCW and SBCW. In contrast to the study of the crystalline UO_2, Dierckx *et al.* (2000) attempted to measure the solubility of U(IV) amorphous oxide in SBCW under conditions prevailing in the Boom Clay. The objective was to estimate an upper solubility limit for a freshly prepared U(IV) solid phase by using an electroreduced U(IV) source. The uranium concentrations, without any prior filtration, were about 10^{-4} mol·l^{-1} and probably resulted from the presence of U(VI) in the system.

6.1.2 Solubility calculations of amorphous UO_2 in Boom Clay

In the thermodynamic database of the Nuclear Energy Agency (NEA-TDB) released by Grenthe *et al.* (1992), the value for $U(OH)_4$(aq) reflects the work of Bruno *et al.* (1986 and 1987). As mentioned before, this work was criticised by several authors (*e.g* Rai *et al.*, 1990 and Langmuir, 1997). According to Langmuir (1997), there is strong evidence that the thermodynamic data for $U(OH)_4$(aq) is seriously in error in Grenthe *et al.* (1992). The likelihood of this error was acknowledged by Grenthe *et al.* (1995): "although it appears that the stability of $U(OH)_4$(aq) has been overestimated by orders of magnitude in Grenthe *et al.* (1992), the inconsistencies still remain unresolved, and a re-examination of this system is being undertaken". In the updated NEA-TBD (Guillaumont *et al.*, 2003), the stability constant for $U(OH)_4$(aq) is revised according to the literature review made by Neck and Kim (2001) which is based on the results from Rai *et al.* (1990 and 1997) and Yajima *et al.* (1995). An important change in the NEA-TDB 03 update is the decrease of more than five orders of magnitude of the stability constant of the aqueous species $U(OH)_4$(aq). Although $U(OH)_4$(aq) should dominate based on NEA-TDB 92, the recent NEA-TDB 03 update predicts that $UO_2(CO_3)_3^{4-}$ is the dominant species under Boom Clay conditions (Figures 2.4 and 2.5).

The impact of the NEA-TDB 03 update on the solubility of UO_2(am) was studied by Wang (2003). Unlike the NEA-TDB 92 where no thermodynamic constants were selected for UO_2(am), the NEA-TDB 03 gives the solubility product of UO_2(am) with a remark that it is selected as the value to be used to calculate the U(IV) concentration in the presence of UO_2(am). The selected values are those derived by Neck and Kim (2001):

$$UO_2(am) + 2\ H_2O \rightleftharpoons U(OH)_4(aq) \qquad \log K = -8.5 \pm 1$$

and,

$$UO_2(am) + 2\ H_2O \rightleftharpoons U^{4+} + 4\ OH^- \qquad \log K = -54.5 \pm 1$$

At E_h lower than -350 mV, the redox potential is low enough to keep uranium in its tetravalent state. The solubility of UO_2(am) is then given by the log K of the reaction:

$$UO_2(am) + 2\ H_2O \rightleftharpoons U(OH)_4(aq) \qquad \log K = -8.5$$

which corresponds to a solubility of 3×10^{-9} mol·l^{-1}. At higher E_h, the solubility is E_h dependent and can be calculated as:

$$UO_2(am) + 3\ CO_3^{2-} \rightleftharpoons UO_2(CO_3)_3^{4-} + 2\ e^- \qquad \log K = 14.30$$

In the Boom Clay (CO_3^{2-} ~10^{-4} mol·l^{-1} and E_h ~ -280 mV), the solubility of UO_2(am) is about 5×10^{-7} mol·l^{-1} which is about two orders of magnitude higher than the value obtained when the solubility is only controlled by $U(OH)_4$(aq).

The decrease of the stability constant for the species $U(OH)_4$(aq), as revised by the NEA-TDB 03, has important impact on the prediction of the solubility of U(IV) under a moderate reducing environment in the presence of carbonate. The calculated solubility of UO_2(am) varies over 2 orders of magnitude depending on the dominant species present in the Boom Clay, *i.e*. $U(OH)_4$(aq) or $UO_2(CO_3)_3^{4-}$. Therefore, experimental work is very much needed to validate or invalidate these modelling results. Our objective is to determine the solubility of U(IV) amorphous precipitate under conditions representative for the Boom Clay: reducing conditions and *in situ* partial pressure of CO_2 at $10^{-2.4}$ atm. In a first series of experiments, we have studied the time evolution of the solubility of U(IV) amorphous solid in BCW in the absence and in the presence of reducing agents. In a second series of tests, we have studied more in detail the influence of organic matter on the solubility of UO_2(am).

6.2 Time evolution of the solubility of amorphous U(IV) precipitate

6.2.1 Experimental

Because U(IV) is readily oxidised to U(VI), the precautions recommended by Rai *et al.* (1990) were taken: (i) the U(IV) stock solution was prepared in 1 M HCl; (ii) all solutions were freshly prepared under anaerobic conditions from degassed ultra-pure water (Milli-Q) and further deoxygenated by either bubbling with pure Ar just before use or by prior equilibration with Fe powder; (iii) the experiments were carried out in the presence of one of the reductants dithionite, sulphide, or Fe powder to maintain very low O_2 fugacity; (iv) the sample tubes were filled nearly to capacity to minimise gas space; (v) the sample tubes were sealed with a screw cap during equilibration to avoid O_2 diffusion; and (vi) all experiments were conducted at 25°C in an anaerobic glove box with a controlled Ar-0.4% CO_2 atmosphere (<5 ppm O_2).

Dithionite, Fe powder and sulphide were selected as reductants since they are efficient to maintain uranium in its tetravalent state in bicarbonate and carbonate medium although it is difficult and requires extreme precautions (Rai *et al.* 1995 and 1998; Cachoir *et al.*, 2003).

6.2.1.1 Reagents

U(IV) stock solution was obtained after the electrochemical reduction of 10^{-2} M U(VI) in 26 ml 1 M HCl at a constant cathodic potential of -200 mV *vs* Ag/AgCl reference electrode during 25 hours (Appendix 3). The electroreduction was performed under atmospheric conditions since the reduction of U(VI) is inhibited under anaerobic conditions by the formation of a black layer at the cathode. Afterwards, the U(IV) acidic solution was degassed by bubbling with pure Ar for at least 1 hour prior to its transfer to the anaerobic glove box. At this stage, the oxidation state of uranium was controlled by UV-Vis spectrophotometry (Varian Cary 500 spectrophotometer). The UV-Vis spectra show the typical absorption bands of U(IV) at 428, 495, 549, and 648 nm and no measurable peak of U(VI) at 414 nm as illustrated in Figure 6.1.

To avoid contamination by CO_2, the 1 M NaOH stock solution was prepared in a N_2 glove box (< 5 ppm O_2) by using degassed ultra-pure water and *pro-analysi*

grade pellets of NaOH coming from a new bottle opened and stored under the N_2 atmosphere. Degassed ultra-pure water was produced by the On-Line Degassing System (Alltech). The on-line degassing system with 4 channels operates with a vacuum pump and a Teflon gas permeable membrane to continuously remove dissolved gases from the liquid phase. The NaOH stock solution was further degassed by bubbling with pure Ar for 90 minutes just before use.

BCW was sampled under anaerobic conditions from the EG/BS piezometer in the underground research laboratory. The Total Organic Carbon (TOC) content of the BCW was 110 $mg \cdot l^{-1}$ (Appendix 1). Two BCW batches of about 500 ml were equilibrated with the CO_2 partial pressure of the glove box by bubbling with the Ar-0.4 % CO_2 mixture at 1 bar for 17 hours. The *p*H after equilibration was 8.3 in the two batches which is in fairly good agreement with the target *p*H of Boom Clay pore water. Nevertheless, the *p*H of the second batch decreased to 8.15 after 5 days of storing in the glove box indicating that *p*H was still evolving after the bubbling. The experiments were conducted either in the absence or in the presence of reducing agents: dithionite, sulphide and Fe powder. Two solutions of 250 ml and 100 ml containing 5×10^{-3} $mol \cdot l^{-1}$ $S_2O_4^{2-}$ were prepared by dissolving the right amount of $Na_2S_2O_4$ in BCW. Likewise, sodium sulphide ($Na_2S \cdot 9H_2O$) was dissolved in 100 ml of BCW to obtain 3×10^{-4} $mol \cdot l^{-1}$ total sulphur (10 $mg \cdot l^{-1}$).

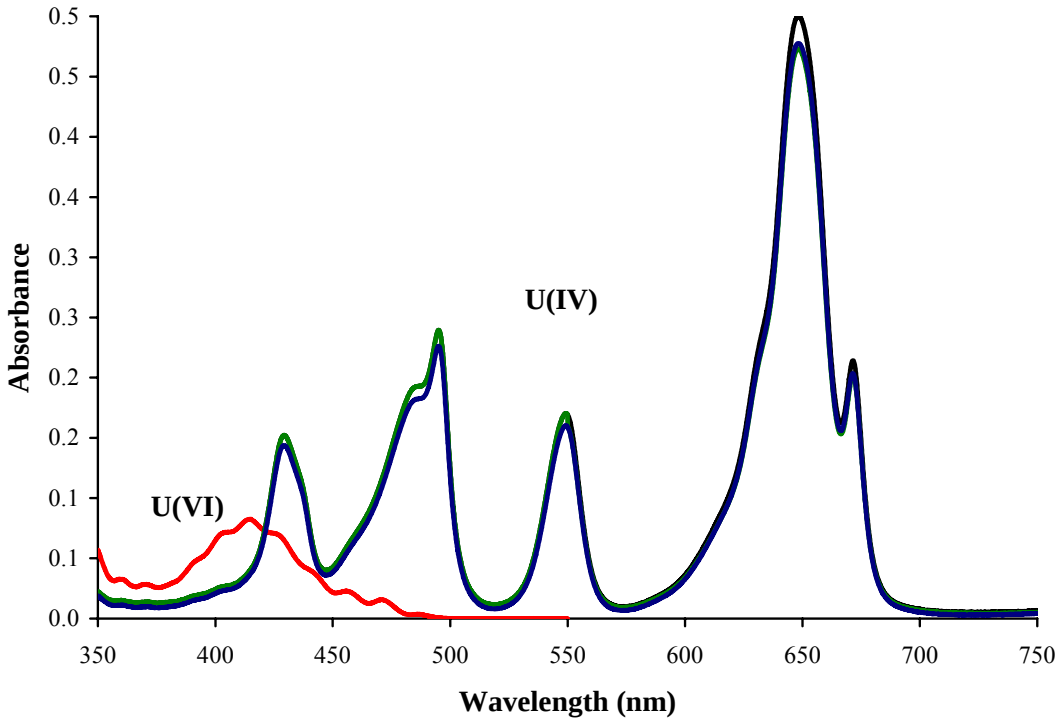

Figure 6.1. UV-Vis spectra of 10^{-2} M natural uranium in 26 ml 1M HCl before and after 25 hours of electroreduction at -200 mV *vs* Ag/AgCl electrode. The results are presented for the three electroreduced solutions used in the kinetic study.

6.2.1.2 Experimental procedure

Solubility of amorphous U(IV) was approached in all experiments from the undersaturation direction. The general procedure consisted in precipitating the amorphous U(IV) solid, washing the precipitate, suspending it in BCW, equilibrating the solutions, separating the solids from suspensions, and analysing the aqueous phase.

The U(IV) amorphous solid was precipitated by titrating the electroreduced U(IV) solution with about 25 ml of degassed 1 M NaOH to a *p*H of about 8.5. For each test (Table 6.1), a batch of U(IV) amorphous precipitate was freshly prepared. Upon titration, a black precipitate formed continuously. A volume of 6 ml of the precipitated U(IV) stock suspension was added to 16 ml polypropylene centrifuge tubes (Nalgene) and the solids were allowed to age overnight. Then, the precipitates were washed three times; successively with 8 ml and two times with 10 ml of the washing solution (Table 6.1). The washing step occurred inside the glove box by decanting the washing solutions and removing the supernatants. Afterwards, the washed U(IV) amorphous precipitates were suspended in 14 ml of BCW solutions for a period of two days to two months. Three sets of experiments were conducted and are detailed in Table 6.1.

Table 6.1. Detailed overview of the three experimental tests.

Test S-#	Washing solution	Added reductants	Samples	Time days
S-2	BCW containing 5×10^{-3} M $S_2O_4^{2-}$ §	none 5×10^{-3} M $S_2O_4^{2-}$	S 2-1 to S 2-4 S 2-5 to S 2-8	2 to 63
S-2'	ultra-pure water deoxygenated by prior equilibration with Fe powder	none 5×10^{-3} M $S_2O_4^{2-}$	S 2'-1 to S 2'-4 S 2'-5 to S 2'-8	3 to 61
S-3	ultra-pure water deoxygenated by prior equilibration with Fe powder	3×10^{-4} M S^{2-} 1 g·l^{-1} Fe powder	S 3-1 to S 3-4 S 3-5 to S 3-8	5 to 62

§ the last washing of the samples without addition of reductants was performed with 10 ml of pure BCW only.

The Fe powder used as reducing agent was washed to remove possibly formed ferric oxy-hydroxides. The washing was achieved with degassed 0.1 M HCl for 10 minutes and rinsing 5 times with degassed ultra-pure water. Approximately 15 mg of washed Fe powder were added to the tubes for which the uranium suspensions were equilibrated in presence of Fe powder as reducing agent.

6.2.1.3 Measurements

At the end of the equilibration period, the redox potential (E_h) was measured for at least 30 min with a combined platinum-Ag/AgCl electrode calibrated against quinhydrone buffers at *p*H 4, 7 and 9. Due to the relatively large uncertainty on the E_h measurements in BCW, the reported values in Table 6.2 are only given as an indication of the oxidising or reducing capacity of the solution. The *p*H was measured with a combined glass electrode (Metrohm) calibrated against *p*H buffers 7 and 9.

A 5 ml aliquot was sampled in each tube and micro-filtered at 0.45 μm (Millex-HA, Millipore). The first ml was used for conditioning the filter, *i.e.* saturation of possible adsorption sites on the filter and was afterwards discarded. The next filtered 4 ml were analysed for uranium concentration by Inductively Coupled Plasma-Mass Spectrometry (Sciex 5000, Perkin-Elmer ICP-MS). The 95% confidence interval 2σ was about 10%.

6.2.2 Results

In a preliminary set of experiments, the solubility of amorphous U(IV) was measured as 4×10^{-6} mol·l^{-1} after filtration at 0.45 μm under geochemical conditions representative for the Boom Clay. There was no notable effect of the added reducing agents (dithionite, sulphide or Fe powder) on the total uranium concentration after one week of equilibration (Delécaut *et al.*, 2002). The evolution of the uranium concentration above the U(IV) amorphous solid is given as a function of time in Figure 6.2 for the case using degassed ultra-pure water as rinsing solution (tests S-2' and S-3). Dithionite is most effective to reduce the uranium concentration in the shortest time. At a concentration of 5×10^{-3} mol·l^{-1} $S_2O_4^{2-}$ in BCW, the uranium concentration is 2.4×10^{-6} mol·l^{-1} after 3 days of equilibration and decreases to a constant concentration of 1.0×10^{-6} mol·l^{-1} within 10 days. The same uranium concentration is reached either in the presence of Fe powder or in BCW without addition of reductants (blank) but after longer times of equilibration, *i.e.* about 20 days and 2 months, respectively. Although the same uranium concentration is measured in presence of Fe powder and sulphide after 5 days of equilibration, the used concentration of sulphide is not efficient to reach a constant uranium concentration within the experimental period. The measured solubility is 6.0×10^{-6} mol·l^{-1} after 2 months despite the fact that sulphide was very effective to impose strongly reducing conditions as indicated by the measured E_h from -490 to -290 mV (Table 6.2). Dithionite and iron powder are able to keep the redox potential lower than – 200 mV after 2 months.

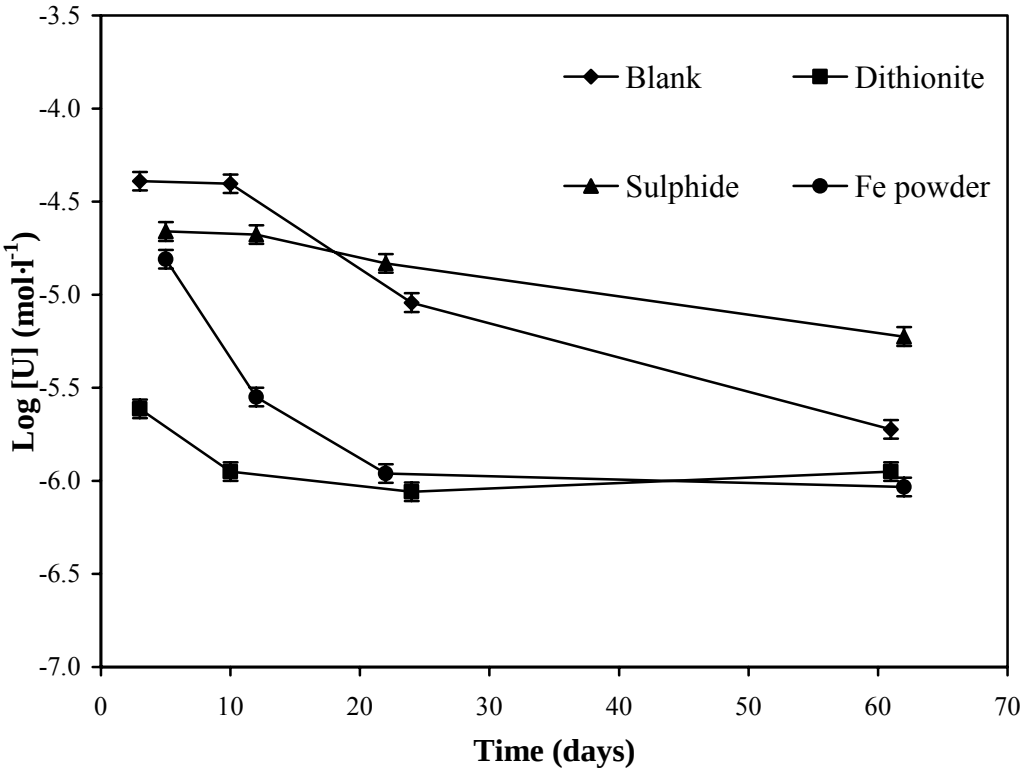

Figure 6.2. Effect of the added reducing agent on the uranium concentration above U(IV) amorphous precipitate as function of the time in BCW. The precipitates were washed with ultra-pure water equilibrated for 24 hours with iron powder.

In all experiments, the uranium concentration decreases with equilibration time. We ascribe this decrease either to the precipitates ageing or to a reduction of U(VI) traces present in the system despite the efforts made to avoid U(IV) oxidation. The effect of the crystallinity on the uranium solubility is not yet clear (Casas *et al.*, 1998). However, Yajima *et al.* (1995) observed that the progress of crystallization had little effect on the solubility. Neck and Kim (2001) reported that the U(IV) concentrations at pH > 5 was not significantly affected by the initial solid phases, either freshly precipitated or microcrystalline UO_2. This observation was confirmed by Rai *et al.* (2003) who show that UO_2(am) is the solubility limiting solid phase of U(IV) in neutral and alkaline solutions. Therefore, we surmise that the uranium concentration decrease results from a redox phenomena. The amorphous U(IV) solid has probably a partially oxidised surface layer despite the precautions taken during the U(IV) precipitation. The proposed mechanism is the following: complexation of the U(VI) sites of the oxidized layer of the U(IV) precipitate and detachment of the U(VI)-carbonate surface complexes (De Pablo *et al.*, 1999). Owing to the reductants or to the reducing capacity of BCW and the possible catalytic effect of precipitate surfaces, these U(VI)-carbonate complexes are reduced to U(IV) that subsequently precipitates. This freshly neo-formed phase would determine the final solubility. Depending on the kinetics of the reduction, a constant concentration of about 10^{-6} mol·l^{-1} is reached within a shorter or a longer time.

The effect of the washing solution on the solubility of amorphous U(IV) solids without added reductants or in the presence of dithionite is illustrated in Figures 6.3 and 6.4, respectively. Without addition of reducing agents, the lowest uranium concentration measured in BCW is 1.8×10^{-6} mol·l^{-1} (Figure 6.3). This value is reached within 30 days for the precipitates washed with BCW containing 5×10^{-3} M $S_2O_4^{2-}$ whereas it takes about 2 months to reach the same solubility for the solids washed with ultra-pure water equilibrated with Fe powder. By the use of dithionite during the washing step, the possible remaining U(VI) is reduced to U(IV), resulting in a constant uranium concentration in a relative short time. On the other hand, ultra-pure water equilibrated with Fe(0) does not contain high concentration of reducing species (Fe^{2+}) even if the dissolved oxygen is removed. The reduction of U(VI) traces would be therefore slower and could be due to the own reducing capacity of BCW and catalysed by the surfaces of U(IV) amorphous precipitate. Another likely explanation is the effect of the ionic strength of the washing solution. Due to the dissolved dithionite, the higher ionic strength can induce flocculation of the colloids. Therefore, there are less colloidal particles passing through the 0.45 μm filter.

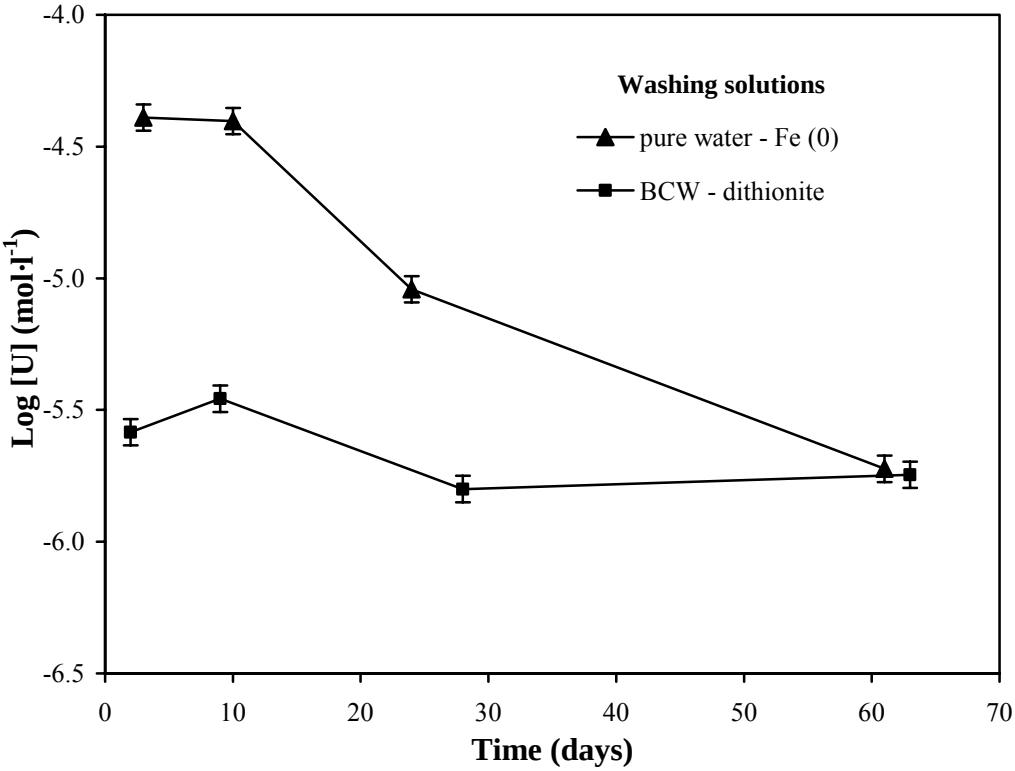

Figure 6.3. Effect of the washing solution on the U concentration above U(IV) amorphous precipitate as function of the time in BCW without addition of reducing agents.

In BCW containing 5×10^{-3} mol·l^{-1} $S_2O_4^{2-}$, the effect of the washing solution is less pronounced than in pure BCW only, showing the efficiency of dithionite as redox conditioner for solubility experiments with U(IV) (Figure 6.4). A steady state concentration of 3×10^{-6} mol·l^{-1} is reached within 2 days for the precipitates washed with BCW containing dithionite. This constant concentration is rapidly reached since the washing solution and the solution in which the precipitate was suspended are the same. On the other hand, it takes 10 days to obtain a plateau at 10^{-6} mol·l^{-1} for the precipitates rinsed with ultra-pure water equilibrated with metallic iron powder. The lower uranium concentration might be controlled by the neo-formed precipitate resulting from the reduction of the U(VI)-carbonate complexes released from the oxidised layer of the original U(IV) precipitate. The higher solubility obtained for the precipitate washed with BCW containing dithionite could be controlled by a more oxidised precipitate. Indeed, the precipitates respectively washed with deoxygenated pure water and BCW containing dithionite were prepared in two separate batches starting from different electroreduced U(IV) solutions.

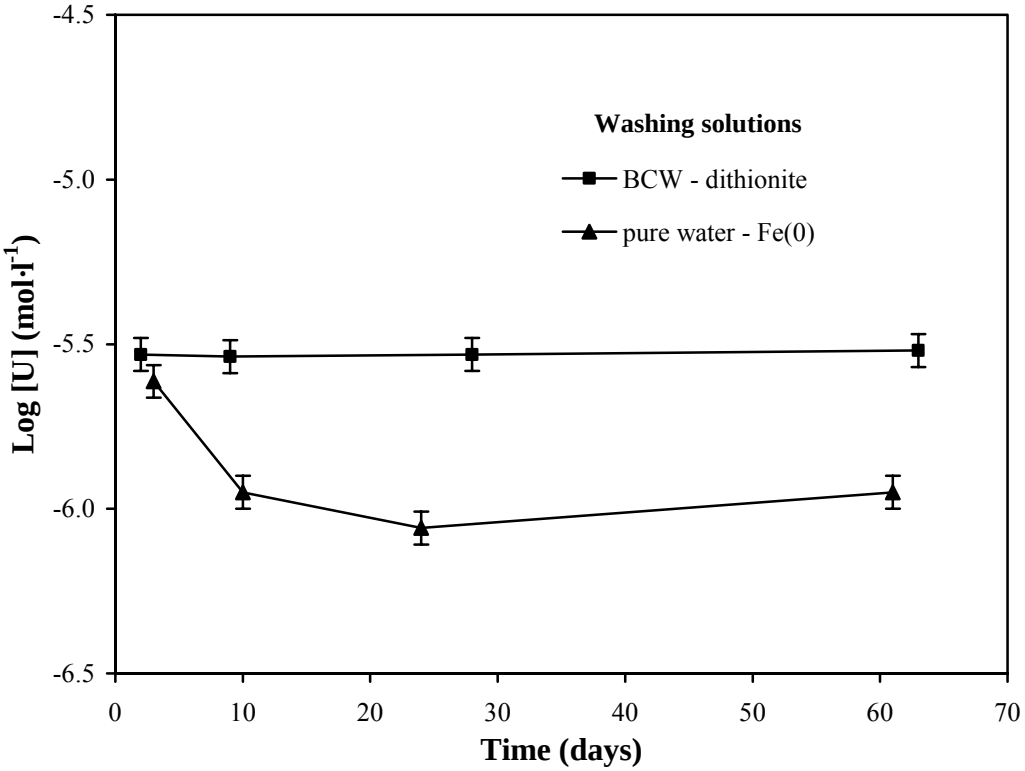

Figure 6.4. Effect of the washing solution on the U concentration above U(IV) amorphous precipitate as function of the time in BCW containing 5×10^{-3} mol·l^{-1} $S_2O_4^{2-}$.

The addition of reductants to BCW affects the *p*H (Table 6.2). Without addition of reducing agents, the *p*H was constant during the experimental period at a value of 8.1. By the addition of dithionite, the *p*H of BCW decreased from 8.3 to about 7.4 but slightly increased afterwards until 7.8 after two months. The *p*H decrease is explained by the dithionite oxidation which acidifies the system:

$$S_2O_4^{2-} + 2\ H_2O \rightleftharpoons 2\ SO_3^{2-} + 4\ H^+ + 2e^-$$

On the other hand, the *p*H was increasing from 8.2 up to 8.9 after two months in presence of iron powder. The proposed mechanism is the water dissociation by anaerobic corrosion of metallic iron:

$$Fe(0) + 2H_2O \rightleftharpoons Fe^{2+} + H_2(g) + 2\ OH^-$$

The presence of sulphide did not change the *p*H which remained stable around 8.3.

Table 6.2. *p*H, E_h and uranium concentrations of the solubility experiments with uranium(IV) amorphous precipitate in BCW.

Samples S#-#	*p*H	E_h (mV)	[U] ($mol \cdot l^{-1}$)	Log [U] ($mol \cdot l^{-1}$)	Reducing agents	Time (days)
S2-1	8.1	-231	2.61 E-06	-5.58	—	2
S2-2	8.1	-305	3.49 E-06	-5.46	—	9
S2-3	8.1	-357	1.58 E-06	-5.80	—	28
S2-4	8.1	-357	1.79 E-06	-5.75	—	63
S2-5	7.6	-470	2.94 E-06	-5.53	dithionite	2
S2-6	7.6	-418	2.90 E-06	-5.54	dithionite	9
S2-7	7.7	-335	2.94 E-06	-5.53	dithionite	28
S2-8	7.9	-263	3.03 E-06	-5.52	dithionite	63
S2'-1	8.1	54	4.08 E-05	-4.39	—	3
S2'-2	8.1	-361	3.95 E-05	-4.40	—	10
S2'-3	8.0	4	9.08 E-06	-5.04	—	24
S2'-4	8.1	-240	1.89 E-06	-5.72	—	61
S2'-5	7.4	-450	2.44 E-06	-5.61	dithionite	3
S2'-6	7.6	-438	1.12 E-06	-5.95	dithionite	10
S2'-7	7.6	-318	8.74 E-07	-6.06	dithionite	24
S2'-8	7.8	-338	1.12 E-06	-5.95	dithionite	61
S3-1	8.3	-493	2.18 E-05	-4.66	sulphide	5
S3-2	8.2	-488	2.10 E-05	-4.68	sulphide	12
S3-3	8.2	-388	1.47 E-05	-4.83	sulphide	22
S3-4	8.3	-288	5.97 E-06	-5.22	sulphide	62
S3-5	8.2	-480	1.55 E-05	-4.81	Fe(0)	5
S3-6	8.2	-348	2.82 E-06	-5.55	Fe(0)	12
S3-7	8.2	-226	1.10 E-06	-5.96	Fe(0)	22
S3-8	8.9	-362	9.29 E-07	-6.03	Fe(0)	62

6.2.3 Discussion

Excluding the high solubilities reported by Gayer and Leider (1957) and Bruno *et al.* (1987) which are presumably caused by oxidised U(VI) species (Neck and Kim, 2001), our results are about two and three orders of magnitude higher than the solubility values reported by Rai *et al.* (1990) and Yajima *et al.* (1995), respectively. Although these results were obtained in carbonate-free system, they can be compared with our data since the expected dominant aqueous species of U(IV) in Boom Clay interstitial water is $U(OH)_4$(aq) as well.

One possible reason for this difference could be a contamination of our system by U(VI) despite the use of reductants and the precautions taken. The difficulty to maintain uranium in the tetravalent state in presence of low bicarbonate concentrations was already observed by Rai *et al.* (1998). The measured values of redox potential (E_h) generally range from – 450 to -200 mV *vesus* SHE (Table 6.2). At *p*H between 7.4 and 8.9, these values are very close to the boarder of the E_h-*p*H stability region for hexavalent uranium (Figure 6.5). Our uranium concentrations are similar to those measured for natural uraninites from Oklo and Jachymov in synthetic granitic groundwater, data interpreted by the probable presence of U(VI)-carbonate complexes (Casas *et al.*, 1998).

Another possibility to explain our higher solubility is the presence of colloids. Indeed, the solubility value of about 10^{-8} $mol \cdot l^{-1}$ determined by Rai *et al.* (1990) was obtained after ultra-filtration of the samples at 25000 MWCO. After ultra-filtration at 10000 MWCO, a solubility of one order of magnitude lower was measured by Yajima *et al.* (1995). This shows that a clear relation exists between the measured solubility and the filter pore size. The use of a 0.45 μm filter does not allow to determine the

solubility, *i.e.* only the dissolved uranium species. It also includes the colloidal fractions. These colloids could be either inorganic or organic.

A third hypothesis is that the dissolved organic matter present in BCW may increase the solubility of U(IV) amorphous precipitate through the formation of U(IV)-organic matter complexes. To the best of our knowledge, no data are available on the effect of organic matter on the solubility of amorphous U(IV).

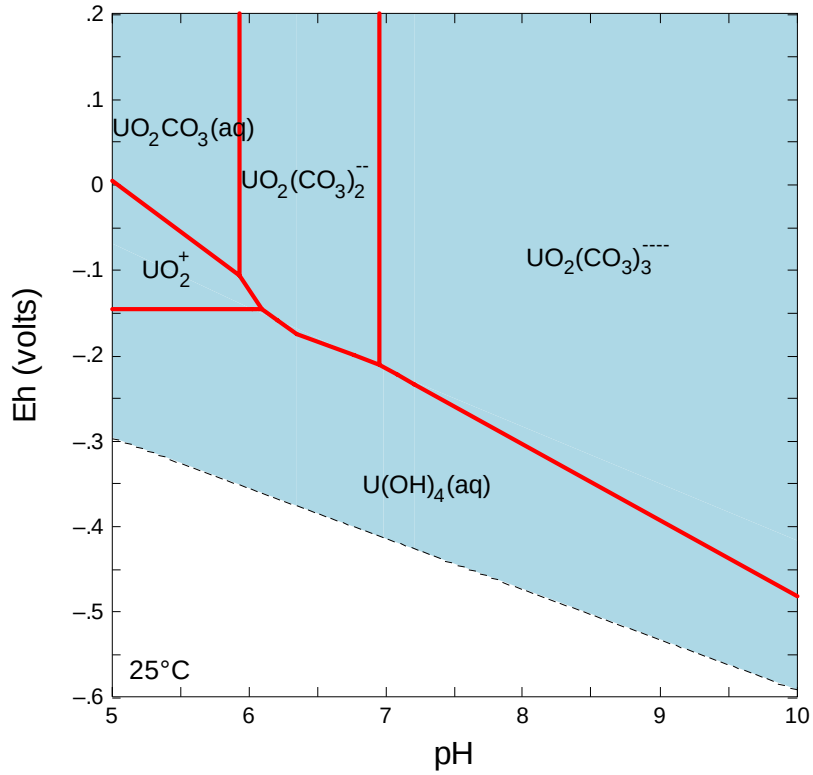

Figure 6.5. E_h-*p*H diagram of uranium (10^{-8} mol·l^{-1}) based on the NEA-TDB 03 (Guillaumont *et al.*, 2003). Boom Clay pore water composition as given in Table 4.2 of Chapter IV. The HCO_3^- concentration is fixed at 0.014 mol·l^{-1}. No organic matter taken into account.

To summarise, the aqueous uranium concentration in BCW above U(IV) amorphous precipitate is decreasing as a function of time under geochemical conditions representative for Boom Clay; *i.e.* reducing conditions and CO_2 partial pressure of $10^{-2.4}$ atm. An apparent solubility of about 10^{-6} mol·l^{-1} is reached after 10 days in the presence of dithionite, after 20 days in the presence of Fe powder and after 2 months without the addition of reducing agent. Although it imposes strongly reducing conditions, the used concentration of sulphide (3×10^{-4} mol·l^{-1} S^{2-}) does not allow to reach a constant uranium concentration within a period of 2 months. The decrease in uranium concentration with time is ascribed to a redox process: the precipitation of secondary U(IV) solid phase after the reduction of U(VI)-carbonate complexes released from the oxidised layer of the original U(IV) precipitate. Compared to the literature, our results are two or three orders of magnitude higher than the reported values. The higher concentration could be attributed to the presence of U(VI)-carbonate complexes, inorganic or organic colloids, or U(IV)–organic matter complexes.

6.3 Influence of organic matter on the solubility of amorphous UO_2

In a reducing environment like the Boom Clay, solubility is considered to be the main limiting factor controlling the mobile concentration of uranium. However, the presence of natural organic matter may increase the solubility due to complexation or colloid formation. To our knowledge, no study has been carried out up to now on the effect of organic matter on the solubility of amorphous U(IV) precipitate. The complexation of U^{4+} by humic and fulvic acids is expected to be strong. Nevertheless, the extent of U^{4+} binding depends on *p*H and hydrolysis reactions (Tipping, 1993). According to Choppin (1992), the tetravalent actinides form strong humate complexes but their hydrolysis is much stronger. However, the humic colloids can serve as a host to sorption of hydrolysed actinides ions onto colloidal surfaces (Choppin, 1988). We have performed experiments to study in detail the influence of organic matter on the solubility of UO_2(am). The solubility of U(IV) amorphous precipitate was determined in BCW and in SBCW at various concentrations of humic acids (HA). The presence of colloids was assessed by measuring the uranium concentration after micro-filtration at 0.45 μm and ultra-filtration at 2 nm (30000 MWCO). The inorganic and organic nature of the colloids was investigated by analysing the distribution of the total organic carbon (TOC) in the samples before and after micro- and ultra-filtrations.

6.3.1 Experimental

Improved precautions with respect to those used for the study of the time evolution of solubility were taken to minimise oxidation during preparation of the U(IV) stock solution and during the equilibration period. These precautions included (Rai *et al.*, 1990): (i) preparing the concentrated U(IV) stock solution (~ 600 $gU \cdot l^{-1}$) in approximately 2M HCl where U(IV) is relatively stable, storing it under inert gas in a sealed container, and treating it with uranium metal immediately before use to ensure the absence of U(VI), (ii) conducting the experiments in low-redox potential solutions obtained by equilibration with Fe powder (calculated O_2 content reduced to $< 10^{-75}$ atm), and (iii) conducting the experiments at 25°C in a glove box with a controlled reducing and anaerobic Ar-5% H_2-0.4% CO_2 atmosphere, O_2 content lower than 1 ppm.

6.3.1.1 Reagents

Unexpected problems were met with the electrochemical reduction technique. The spectrophotometric controls of the acidic U(IV) solution showed that the absorbance at 648 nm was about 30-40 % lower than the value measured for the electroreduced U(IV) stock solutions used in the previous experiments. A systematic study of the different parameters was performed: change of electrodes, solutions, potentiostat, stirring velocity, addition of hydrazine, ... Unfortunately, we did not succeed in solving the problem. Therefore, we tried another way to produce U(IV) that consisted in dissolving uranium metal in concentrated HCl. Uranium metal is attacked by concentrated hydrochloric acid with remarkable rapidity. The reaction appears to be complex, since variable amounts of the metal are converted into an insoluble black material. It has been suggested that this product is a hydrated uranium oxide. In 12M hydrochloric acid practically all of the metal is oxidized to the tetravalent state (Katz and Rabinowitch, 1951). The U(IV) stock solution was obtained by dissolving a piece of 45 g uranium metal in 75 ml concentrated HCl under atmospheric conditions. A single 45 g piece of metal was placed in a Pyrex glass bottle in an ice-water bath.

Concentrated HC1 was added in 2.5 ml aliquots for the two first increments and in 10 ml increments afterwards over a period of 6 hours. Between additions the cap was allowed to set loosely on the top of the bottle to minimize air diffusion to the solution surface. A total of 75 ml of concentrated HC1 was added. After all HC1 had been added, the bottle containing the solution was loosely capped and the water bath was heated slowly to 90-100ºC for about an hour and a half. The solution was centrifuged the next day at 1500g for 100 minutes and the supernatant was filtered at 0.22 μm (Millex-GS, Millipore). The final solution volume was about 50 ml. Afterwards, the U(IV) stock solution was degassed by bubbling with pure Ar for 45 minutes in the laboratory and for 1 hour in the glove box (< 1 ppm O_2). The degassed solution was tightly capped under an Ar atmosphere and stored in the glove box. To eliminate any oxidised uranium species that might have been present, the U(IV) stock solution was treated with uranium metal before each use.

The 2 M NaOH stock solution was prepared under N_2 atmosphere to avoid CO_2 contamination from deoxygenated pure-water and *pro-analysi* grade pellets. The NaOH pellets came from a new bottle opened and stored under N_2 atmosphere. Ultra-pure water was degassed by the On-Line Degassing System (Alltech) and further deoxygenated by equilibration with Fe powder. The NaOH stock solution was transferred into the Ar-5% H_2-0.4% CO_2 glove box just before use.

BCW was sampled under anaerobic conditions from the EG/BS piezometer in the underground research laboratory. The total organic carbon (TOC) content was about 110 $mg \cdot l^{-1}$ (Appendix 1). The *p*H of 9.4 indicated that BCW underwent CO_2 degassing. Therefore, two batches of about 500 ml were equilibrated with a gas mixture containing 0.4% CO_2 for at least 16 hours. The *p*H after equilibration was 8.2 in both batches.

The composition of SBCW used in this study is given in Appendix 1. SBCW was first bubbled with a gas mixture containing 0.4% CO_2 until the target *p*H of Boom Clay (~ 8.2) was reached. Then, traces of dissolved oxygen were removed by equilibration with Fe powder for at least 3 days. The calculated dissolved O_2 content is estimated lower than 10^{-75} atm (Rai *et al.*, 1990).

Based on the results from the study of the solubility evolution with time (Section 6.2.2.), dithionite and Fe powder were chosen to ensure low redox potential. The dithionite was added to BCW or SBCW at a concentration of 5×10^{-3} $mol \cdot l^{-1}$. The addition of dithionite lowered the *p*H to about 7.8. Iron powder was added at a concentration of about $1g \cdot l^{-1}$ once the precipitate was suspended in the appropriate solutions.

Boom Clay humic acids (HA) were obtained by concentrating the organic matter dissolved in BCW with di-ethyl-amino-ethyl-cellulose (DEAE-cellulose) according to the procedure described by Pirlet (2003). The concentrate of organic matter was shaken overnight in 0.1M NaOH and 0.01M NaF. The HA were precipitated and protonated by dialysis against a solution containing 0.1 M HCl for one week and rinsed from Cl^- by dialysis against demineralised water. Finally, they were freeze-dried and stored in the dark. Mother solutions of HA were prepared by dissolving HA either in SBCW containing dithionite or in SBCW alone when Fe powder was the reductant. The HA solutions at various concentrations were obtained by dilution of mother solutions. The *p*H was not adjusted.

6.3.1.2 Experimental procedure

Solubility of amorphous UO_2 was approached in all experiments from the undersaturation direction. The general procedure consisted in precipitating UO_2(am), washing the precipitate, suspending it in appropriate solutions, equilibrating the solutions, separating the solids from suspensions, and analysing the aqueous phase. All experiments were performed in glove box with a controlled atmosphere composed of Ar, 5% H_2 and 0.4% CO_2 which contained less than 1 ppm O_2. Amorphous UO_2 was precipitated by pipetting 7 ml aliquot of the U(IV) stock solution that was treated with pickled uranium metal in concentrated HNO_3 immediately before use. This 7 ml aliquot was titrated with more or less 40 ml of 2 M NaOH to *p*H ~ 8. Upon titration, a dark green solid appeared. Two batches of about 4.5 g of U(IV) amorphous precipitate were prepared for this study. A volume of 1 ml of the precipitated U(IV) stock suspension was added to 16 ml polypropylene centrifuge tubes (Nalgene) and was diluted by addition of 8 ml of deoxygenated ultra-pure water by prior equilibration with Fe powder. Then, the solids were allowed to age overnight. The next day, the U(IV) amorphous precipitates were centrifuged at 2500g for 15 minutes and were washed two times with 10 ml of deoxygenated ultra-pure water. The washing step occurred inside the glove box by centrifugation at 2500g for 15 minutes and removing the supernatants. The last centrifugation lasted 30 minutes. The centrifuge tubes were kept tightly capped with sealing caps as much as possible during these operations.

Several sets of experiments were carried out with these washed solids. These sets included determining the solubility of U(IV) amorphous precipitates in the following solutions (Table 6.3):

- SBCW containing 5×10^{-3} mol·l^{-1} dithionite,
- SBCW containing 1 g·l^{-1} Fe powder,
- BCW containing 5×10^{-3} mol·l^{-1} dithionite,
- BCW containing 1 g·l^{-1} Fe powder,
- SBCW containing variable HA concentrations and 5×10^{-3} mol·l^{-1} dithionite,
- SBCW containing variable HA concentrations and 1 g·l^{-1} Fe powder.

A 14 ml aliquot of the appropriate solution was added to each centrifuge tube containing the washed precipitates. Approximately 15 mg of Fe powder were also added to the tubes when Fe powder was the reductant.

Table 6.3. Detailed overview of the experiments performed in the framework of the study of the influence of organic matter on the solubility of amorphous UO_2.

Test S-#	Solution	Reductants	Samples
S-5	SBCW	5×10^{-3} mol·l^{-1} dithionite	S 5-1 to S 5-4
		1 g·l^{-1} Fe powder	S 5-5 to S 5-8
S-6	BCW	none	S 6-1 to S 6-3
		5×10^{-3} mol·l^{-1} dithionite	S 6-4 to S 6-6
		1 g·l^{-1} Fe powder	S 6-7 to S 6-9
S-7	SBCW + HA	5×10^{-3} mol·l^{-1} dithionite	S 7-1 to S 7-8
S-8	SBCW + HA	Fe powder	S 8-1 to S 8-8
S-11	BCW	5×10^{-3} mol·l^{-1} dithionite	S 11-1 to S 11-4
		1 g·l^{-1} Fe powder	S 11-5 to S 11-8
S-12	SBCW	5×10^{-3} mol·l^{-1} dithionite	S 12-1 to S 12-2
	SBCW + HA	5×10^{-3} mol·l^{-1} dithionite	S 12-3 to S 12-10
S-13	SBCW	1 g·l^{-1} Fe powder	S 13-1 to S 13-2
	SBCW + HA	1 g·l^{-1} Fe powder	S 13-3 to S 13-10

6.3.1.3 Measurements

The suspensions were equilibrated for a period of either 2 weeks or 1 month when using dithionite or iron powder, respectively. At the end of the equilibration period, the *p*H was measured with a combined glass electrode (Metrohm) calibrated against *p*H buffers 7 and 9. The suspensions were sampled for parallel filtrations at 0.45 μm (Millex-HA, Millipore) and at 2 nm (Microsep 30k, Omega). For both filtrations, an aliquot of 1 ml of the samples was first filtered to saturate any possible adsorption sites. The filter conditioning was performed with a syringe for filtration at 0.45 μm and by centrifugation at 2500g for 30 minutes for filtration at 2 nm. This filtrate was discarded before filtering the solution for analyses. Afterwards, aliquots of 4 and 3.5 ml were sampled for micro- and ultra-filtration, respectively. The micro-filtration was achieved by passing the 4 ml sample through the 0.45 μm filter with a syringe. The ultra-filtration was carried out by centrifuging the 3.5 ml sample at 2500g for 60 minutes. To study the colloidal effect, it was necessary to homogenise the samples before every sampling by gently hand shaking the centrifuge tubes.

The filtrates were analysed for uranium and total organic carbon (TOC). Uranium concentration in the filtrates was measured by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) with a 95% confidence interval 2σ of about 10%. The TOC content was determined by TOC analyser (Dohrmann, DC-190). The 99.7% confidence interval 3σ was varying between 6% for the highest TOC concentration (850 $mg \cdot l^{-1}$), 15% for BCW (TOC ~ 110 $mg \cdot l^{-1}$) and up to 82% for the lowest TOC concentration (15 $mg \cdot l^{-1}$). The initial TOC concentration, *i.e* before any filtration, was also measured in the experiments conducted in the presence of HA.

The possible release of organic carbon from the filters was controlled by measuring the TOC concentration in the filtrates of the suspensions in SBCW only (without added HA). To avoid such contamination, the 30k MWCO filters were rinsed before any use in ultra-pure water for two weeks with regular change of the washing solution. The possible retention of uranium and organic matter on the filter was also controlled for some samples. After filtration of a first aliquot, a second aliquot of the same suspension was passed through the same filter. The measured uranium and TOC concentrations in the first and in the second filtrates were then compared.

6.3.2 Results

6.3.2.1 Solid characterisation

Up to now, the solid obtained by the titration of the U(IV) mother solution was denoted "U(IV) amorphous precipitate", without further information. The solid used in the first study was not characterised although U(IV) amorphous oxide was considered as being the solubility controlling phase. This assumption is reasonable since UO_2(am) was the solid obtained by authors (*e.g.* Ryan and Rai, 1983; Yajima *et al.*, 1995) using the same precipitation procedure than that we followed. To guarantee that our precipitate was U(IV) amorphous oxide in the study of the influence of organic matter, it was characterised. The amorphous character was investigated by scanning electron microscopy (SEM) and x-ray diffraction (XRD). The chemical and mineralogical composition was studied by energy dispersive x-ray (EDX) analyses and x-ray diffraction (XRD), respectively. The most important thing when dealing with the solubility of U(IV) is to ensure that the uranium precipitate contains only tetravalent uranium. The oxidation state was controlled by micro-x-ray absorption near edge spectroscopy (μ-XANES).

Scanning electron microscopy

The SEM analyses were carried out at SCK•CEN in the Microstructure Research Group with a fully shielded Jeol 6310 Scanning Electron Microscope. The sample was prepared by pipetting aliquots of the precipitated U(IV) stock suspension after three washings with deoxygenated ultra-pure water. The suspension was allowed to evaporate overnight on carbon coated tapes fixed on the SEM sample holder. The evaporation occurred in an controlled Ar-5% H_2-0.4% CO_2 atmosphere with less than 1 ppm O_2. The sample was transported in a container filled with the inert atmosphere. The container was opened just before analyses. The contact of the sample with air was kept as short as the manipulations allowed. Nevertheless, the colour of the U(IV) amorphous solid turned from dark green to black within seconds in contact with air. Secondary electron images show that the precipitate is poorly crystallised but not amorphous (Figure 6.6). The precipitate presents polyhedral crystallites from 1 to 5 μm with irregular edges. These flakes are assembled forming xenomorphous randomly aggregated structures.

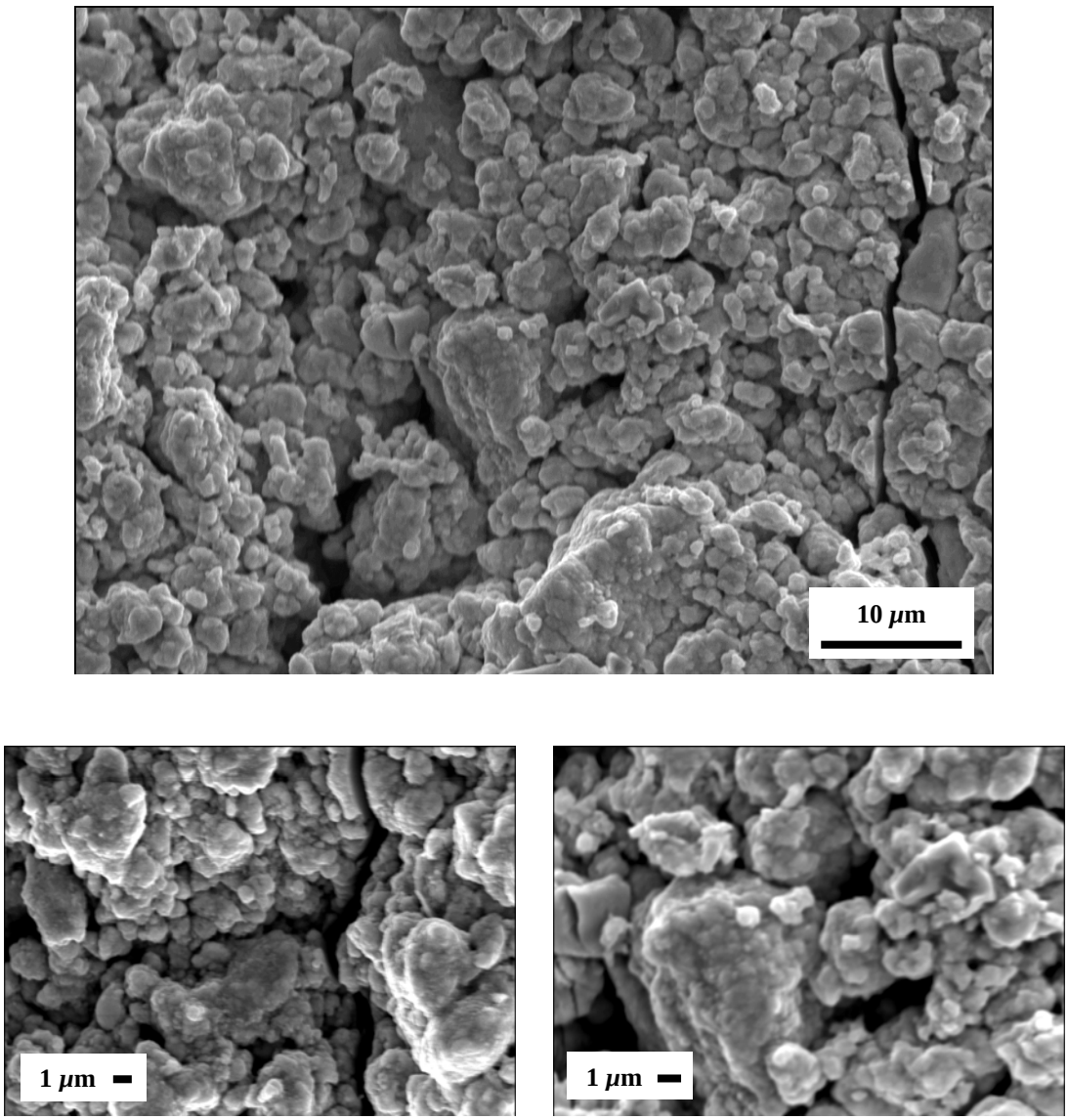

Figure 6.6. Micrographic images of the washed U(IV) precipitate illustrating the poorly crystallisation.

The elements reported by energy dispersive x-ray (EDX) analyses are C, O, Na, Cl and U (Figure 6.7a and b). The carbon comes from the tape on which the sample was fixed. The presence of sodium and chlorine results from the titration of U(IV) mother solution in about 2 M HCl by 2 M NaOH. The washing step is very important to remove the excess of salt as illustrated in Figure 6.7a. After washing, oxygen and uranium are the main components (Figure 6.7b).

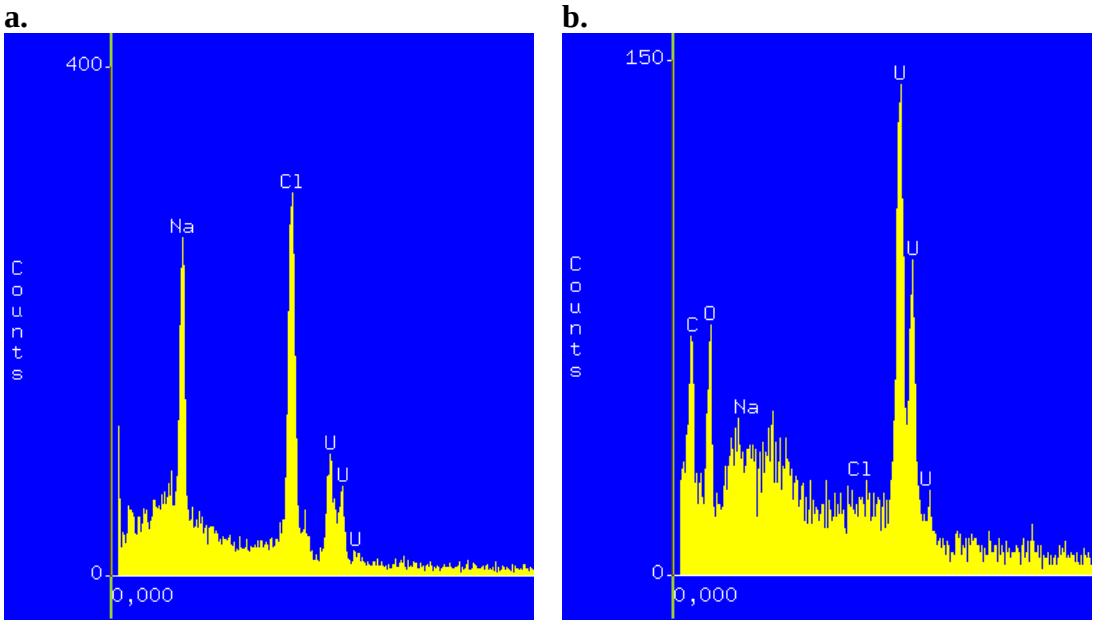

Figure 6.7. EDX spectra of the U(IV) precipitate before washing (a) and after washing (b).

X-ray diffraction

XRD analyses were also performed at SCK•CEN in the Microstructure Research Group. A Philips X'Pert θ-θ diffractometer equipped with a Cu tube ($K\alpha_{1,2}$ = 0.1541 nm), was configured for standard powder diffraction measurements (Bragg-Brentano geometry). Scans of the various diffraction peaks in the 5°-120°2θ range were recorded with the X'Celerator, an X-ray area detector based on RTMS (Real Time Multiple Strip) technology. The step-size is 0.05°2θ, measuring a total of 400 seconds per step. To eliminate the Cu Kβ contribution, a nickel filter is used and to reduce the background, a small anti-scatter shield is mounted in front of the detector.

The sample was prepared by the same way than those analysed by SEM, *i.e.* pipetting aliquots of the precipitated U(IV) stock suspension after washing and evaporation on the XRD sample holder inside the glove box (< 1ppm O_2). Once the container used to transport the sample under inert atmosphere was opened, the U(IV) precipitate became black.

The XRD pattern of the washed U(IV) precipitate is given in Figure 6.8. The precipitate is not amorphous since diffraction peaks are visible. However, these peaks are broad, not intense indicating a poorly crystallisation. The sharp peak at about 44.4°2θ is that of iron and comes from the sample holder. Apart from the Fe peak, the most intense peak is present at 28.4°2θ with a shoulder about 33°2θ. The occurrence of broad peak around 30 to 35°2θ are characteristic of the amorphous solid studied by Bruno *et al.* (1987); Rai *et al.* (1990; 1997; 1998). These authors identified their solids

as amorphous UO_2. Our XRD pattern presents two other peaks at 48.2 and 57.4°2θ, respectively. The peaks of our U(IV) precipitate correspond in position and relative intensity to the peaks of crystalline UO_2 (Figure 6.8). Therefore, the U(IV) precipitate is identified by XRD as poorly crystallised U(IV) oxide.

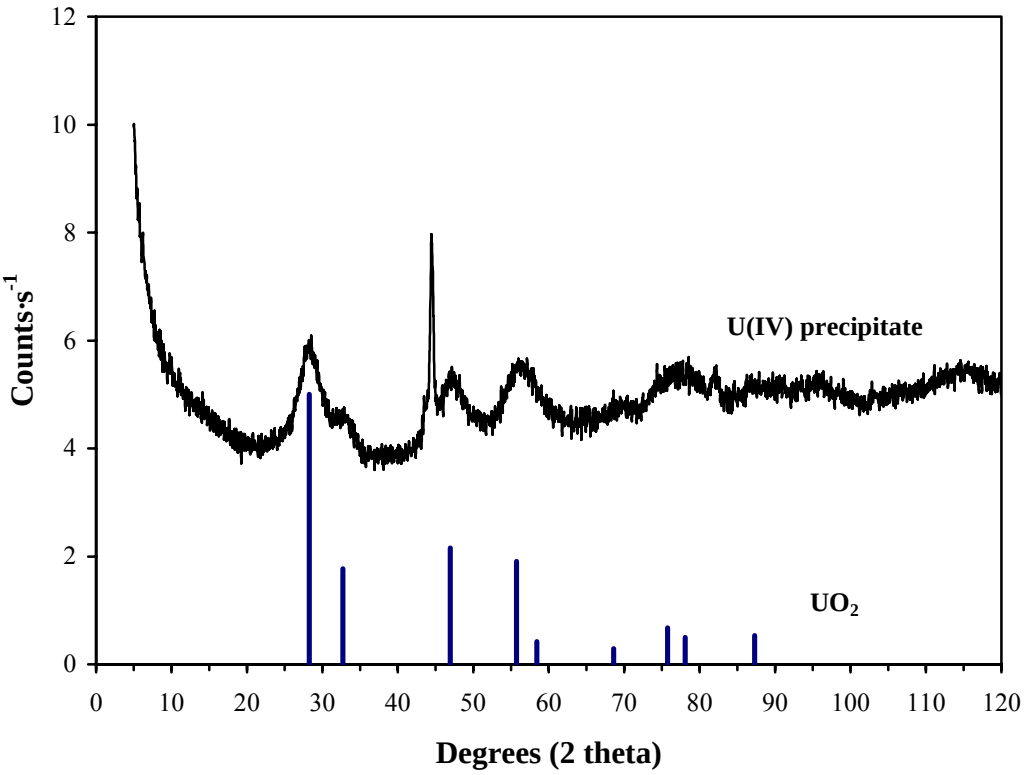

Figure 6.8. X-Ray diffraction pattern of the washed u(IV) precipitate. UO_2 reference pattern from JCPDS-international Centre for Diffraction data (76-1118).

micro-x-ray absorption near edge spectroscopy

The principle of a x-ray absorption fine structure (XAFS) experiment is given in Chapter 5 (section 5.5). With XANES, one is concerned with the intensity of the absorption coefficient as a function of energy at energies at and about 50 eV above the absorption edge. An important and common application of XANES is to use the shift of the edge position to determine the oxidation state.

The analyses were performed at the HASYLAB synchrotron facility, Hamburg in Germany. The measurements and their evaluation were realised by Professor K. Janssens and Drs K. Proost (University of Antwerpen).

Two samples were analysed. The first one is the U(IV) amorphous precipitate after washing with deoxygenated ultra-pure water and is named UO_2(am). The second one is the same precipitate but after a 55 days equilibration period with SBCW containing 1500 $mg \cdot l^{-1}$ HA and $5 \times 10^{-3} mol \cdot l^{-1}$ dithionite. This sample is identified as UO_2(am)-55 days. Both samples were prepared in the anaerobic glove box (< 1 ppm O_2) by pipetting aliquots of the suspensions into polypropylene centrifuge micro-tubes (400 μl). The samples were transported in a container filled with air atmosphere. As the micro-tubes were not fully airtight, an oxidation of the samples may have occurred between the samples preparation and the μ-XANES analyses.

The μ-XANES profile shape and absorption maximum of our samples were compared with those of well defined uranium oxidation state standards: UO_2, U_3O_8 and uranyl acetate ($UO_2(AcO)_2 \cdot 2H_2O$) as shown in Figure 6.9. The UO_2 and U_3O_8 reference spectra show a shift of the absorption maximum (A) towards higher energy for increasing oxidation sate. The absorption maximum of the reference UO_2 occurs at 17.173 keV compared to 17.176 keV for U_3O_8. The shoulder (B) at about 10 eV above the absorption maximum of the uranyl acetate results from multiple scattering interference between the absorber (uranium) and the axial oxygen atoms of the linear uranyl unit (Denecke, 1998 and references therein). This feature is characteristic of U(VI). The energy of the absorption maxima of our samples lines up with that of the UO_2 reference + 1eV, *i.e.* at 17.174 keV. Within the uncertainty of the measurements (1 eV increment), this indicates that they are both tetravalent. Our sample spectra also both lack the multiple scattering feature (B) observed in the $UO_2(AcO)_2$ spectrum, characteristic for U(VI). Moreover, the value of the energy difference between the absorption maximum (A) and the first absorption feature (C) above the absorption maximum is comparable for both samples and the UO_2 reference. It is not the case for U_3O_8 reference spectrum. This energy difference is in a good approximation a function of the U-O bond distance (Denecke, 1998). This means that the U-O bond distance are comparable in our precipitates and in the UO_2 reference. The largest difference between our samples and UO_2 reference is in the amplitude of the absorption features indicating an increase in ordering about uranium going from UO_2(am), UO_2(am)-55 days and UO_2 reference. Therefore, the crystallinity increases in the order UO_2(am), UO_2(am)-55 days and UO_2 reference.

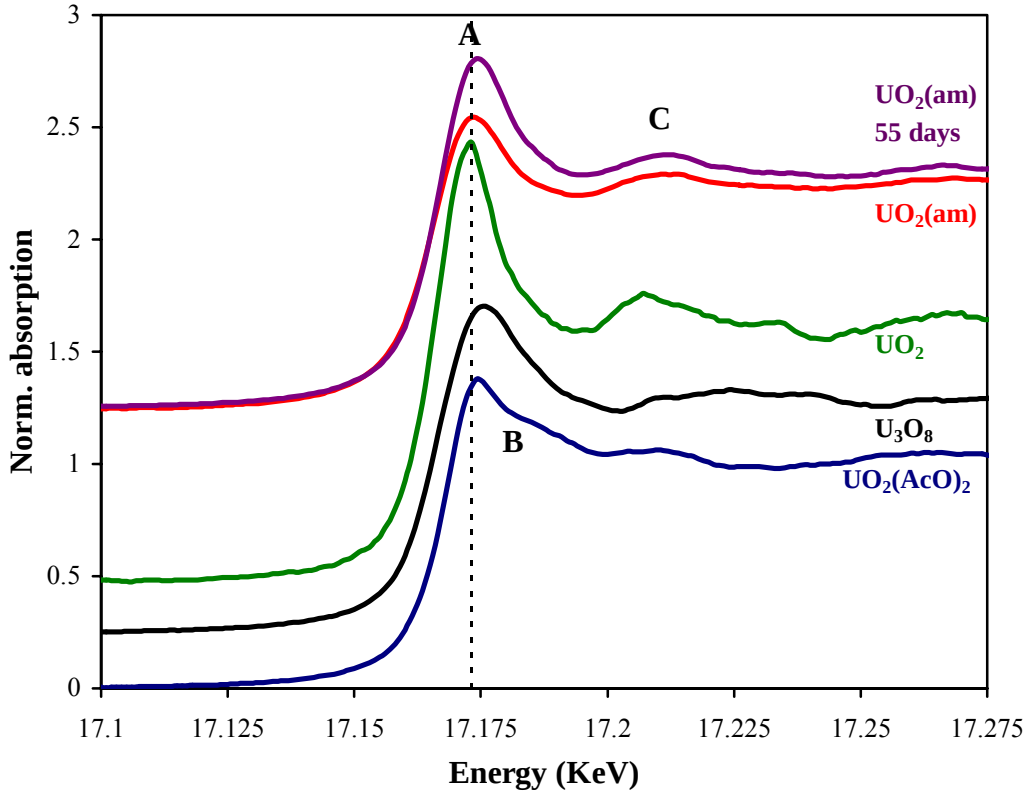

Figure 6.9. UL_{III} edge XANES spectra for U(IV) amorphous precipitate and reference compounds. The dashed line is a guide showing the absorption maximum for UO_2 reference. For clarity, the spectra were shifted along the y-axis. A, B and C mark UL_{III} edge XANES features and are described in the text.

Conclusion

EDX analyses show that the U(IV) amorphous precipitate is composed of uranium and oxygen. SEM and XRD indicate that this solid is poorly crystallised. Finally, both XRD and μ-XANES point out that our precipitate has the same features than reference UO_2 and consequently the oxidation state of uranium is tetravalent. To resume, the U(IV) amorphous precipitate is clearly identified as poorly crystallised U(IV) oxide, UO_2(am).

6.3.2.2 Possible artefacts linked to the use of filters

The use of filters to separate the solids from suspensions may cause some artefacts. The two main likely problems are the release of organic carbon from the filter in the filtrates and the retention of uranium and organic matter on the filter. The concentration of organic carbon is controlled by measuring the TOC in the filtrates of the SBCW suspensions in the absence of HA. The TOC content in the filtrates after micro- and ultra-filtration is always lower than the detection limit (< 9 $mg \cdot l^{-1}$). The contamination by organic carbon is avoided by conditioning the 0.45 μm and 2 nm filters with 1 ml of the suspensions to filtrate. Before conditioning, the filters of nanometer pore size were rinsed for two weeks in ultra-pure water with regular change of the water.

The retention of uranium and organic matter on the filters is investigated by comparing the uranium and TOC concentrations of two aliquots from the same suspensions: the second aliquot is passed through the same filter than that used to filtrate the first aliquot. If the conditioning of the filter with 1 ml of the suspension is sufficient to saturate all adsorption sites of the membrane, the uranium and TOC concentrations should not vary upon filtration. If not, these concentrations should be higher in the second filtrate than in the first filtrate, the possible remaining adsorption sites on the filter being at least partially saturated after the first filtration. The comparison of uranium and TOC concentrations in first and second filtrate is given in Figures 6.10 and 6.11, respectively. The figures 6.10a and b give the logarithm of the uranium concentration ($mol \cdot l^{-1}$) in the second filtrate (s.f.) as function of the logarithm of the uranium concentration in the first filtrate (f.f.) after filtration at 0.45 μm and 2 nm, respectively. The solid line represents the line for which uranium concentration is the same in both filtrates. The experimental points are scattered on both sides of the solid line but are mainly situated on or below the solid line indicating that: (i) the uranium retention on the filter is negligible; (ii) the uranium concentration is generally higher in the first filtrate than in the second filtrate. The same trend is observed for both filters (0.45 μm and 2 nm). The explanation for such behaviour lays in the sampling method. As mentioned in the "measurements" section (6.3.1.3), the centrifuge tubes were gently hand shaken to homogenise the suspensions before sampling. The uranium concentration in both filtrates is different since the aliquots of a same suspension are probably not equivalent. Depending on the sampling, the aliquots contain more or less uranium colloids. The sampling affects much more the results than the uranium retention on the filter. Therefore, only the data obtained after the first filtration at 0.45 μm or 2 nm will be presented in the results. On the other hand, nor retention on the filter nor sampling effect are observed for the TOC concentration (Figure 6.11). The TOC concentration is the same in both filtrates within the error measurement. The pore size has no influence since the same trend is obtained for micro- and ultra-filtration. Therefore, uranium and organic matter do not behave similarly and are probably not associated.

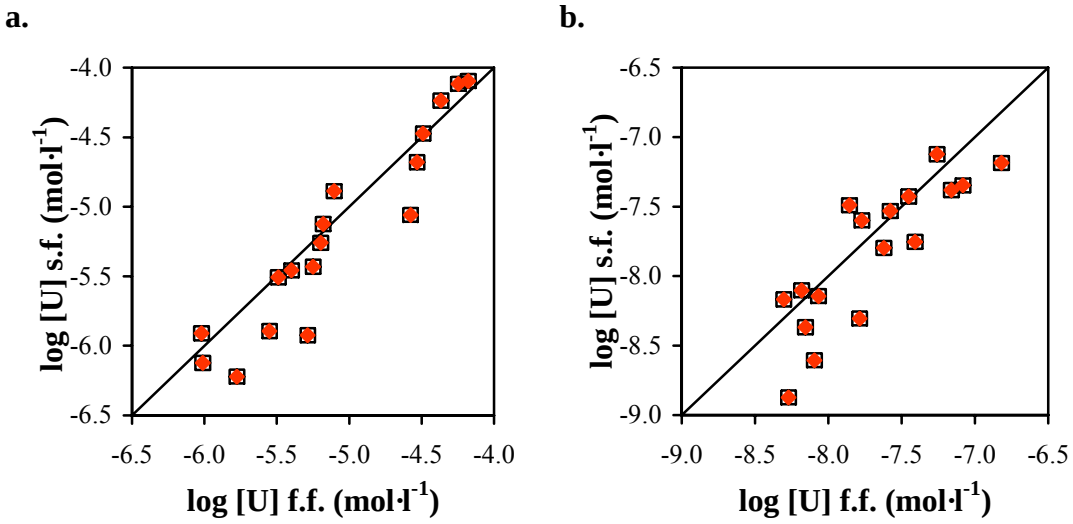

Figure 6.10. Comparison of the uranium concentration in the first filtrate (f.f) and in the second filtrate (s.f) obtained by passing successively two aliquots of the same suspension through the same filter. The solid line represents the 1:1 line. a: 0.45 μm filter, b: 2 nm filter. The error bars give the absolute uncertainty on the logarithm of the uranium concentration.

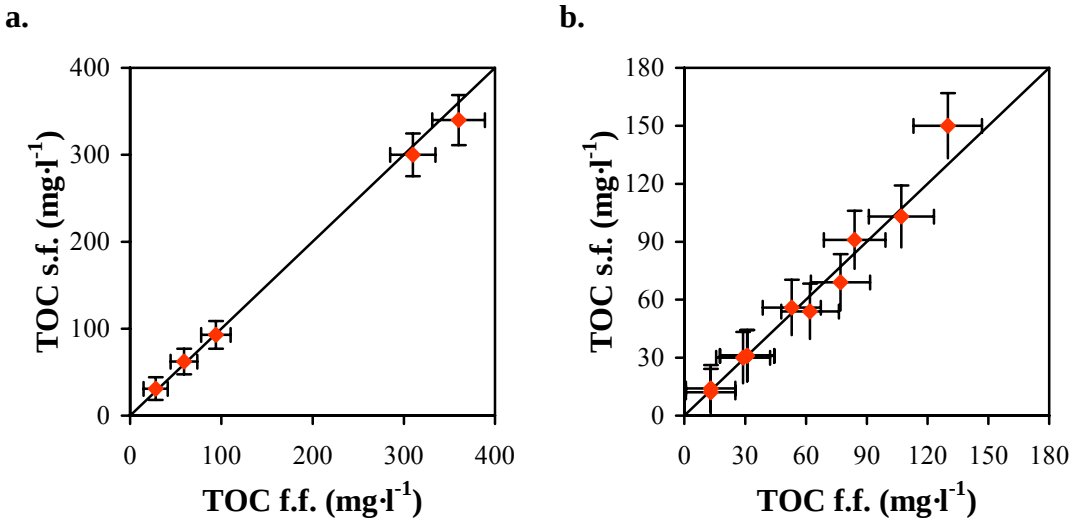

Figure 6.11. Comparison of the TOC concentration in the first filtrate (f.f) and in the second filtrate (s.f) obtained by passing successively two aliquots of the same suspension through the same filter. The solid line represents the 1:1 line. a: 0.45 μm filter, b: 2 nm filter. The error bars give the absolute uncertainty on the TOC concentration.

All the data relative to the study of the effect of HA on the solubility of UO_2(am) are available in Appendix 2.

6.3.2.3 Solubility of UO_2(am) in SBCW

The solubility of UO_2(am) is first determined in SBCW in the absence of HA. The uranium concentration measured after ultra-filtration at 2 nm is on average 2.9×10^{-8} mol·l^{-1} (Figure 6.12). This value is in the range of solubility values recommended by the recent NEA-TDB 03 (Guillaumont *et al.*, 2003), *i.e.* a solubility of 3×10^{-9} mol·l^{-1} with an uncertainty of ± one order of magnitude.

The uranium concentration is greatly affected by the pore size of the filter used for phase separation. The uranium concentration increases up to 1.6×10^{-6} mol·l^{-1} on average if the suspensions is filtered at 0.45 μm (Figure 6.12). The increase in uranium concentration evidences the presence of inorganic colloids of UO_2(am) with a size between 0.45 μm and 2 nm. The colloidal uranium concentration is 2 orders of magnitude higher than the solubility of UO_2(am). Because of their high electric charge, tetravalent uranium ions have a strong tendency towards hydrolysis in aqueous solution and undergo polynucleation and further formation of colloids which are known as real colloids (Kim, 1991). Similarly to hydrous U(IV) oxide, hydrated $TcO_2.xH_2O$ is also known to form $TcO_2.xH_2O$ polymers or colloids which enhance the Tc concentration compared to the solubility value (Maes *et al.*, 2004).

The use of dithionite or iron powder does not influence the measured uranium concentration. Therefore, the ageing of the precipitate has no effect on the solubility since the equilibration periods were different for the experiments conducted in the presence of dithionite and Fe powder, two and four weeks respectively.

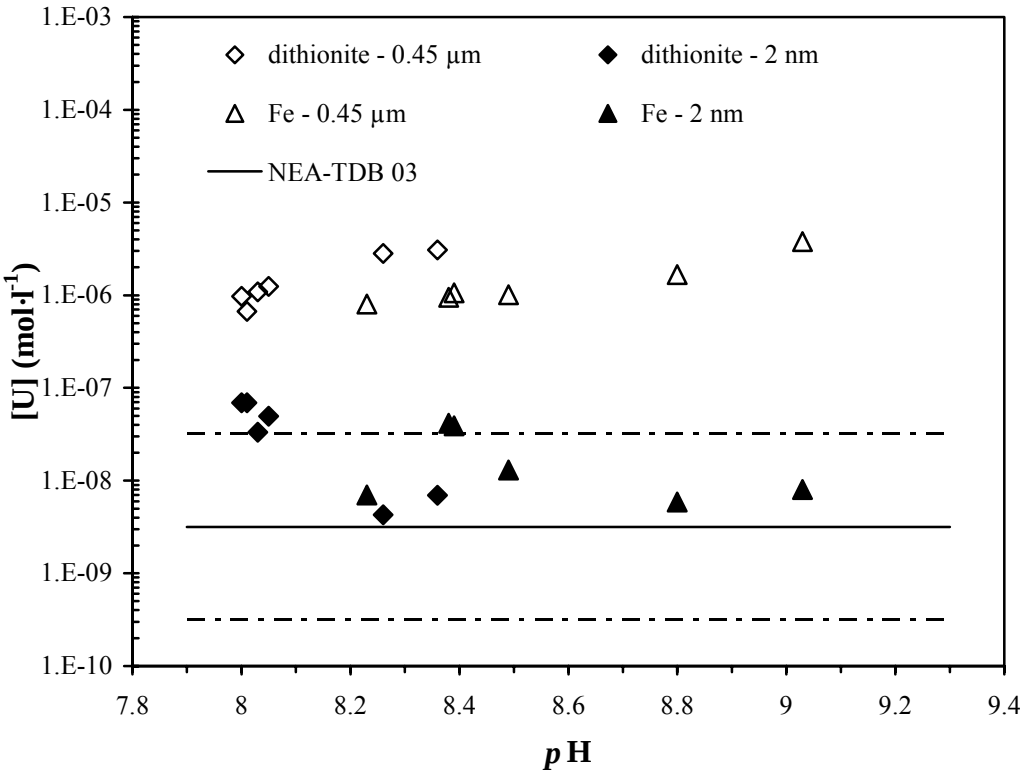

Figure 6.12. Solubility of UO_2(am) in SBCW in the presence dithionite and iron powder (Fe) as reducing agents. Open and filled symbols represent the measured uranium concentration after filtration at 0.45 μm and 2 nm, respectively. Solid line gives the solubility value recommended by NEA-TDB 03 and the dashed lines indicate the uncertainty mentioned in the same database.

6.3.2.4 Solubility of UO_2(am) in BCW

Unlike SBCW, Boom Clay pore water (BCW) contains dissolved organic matter. The TOC concentration in the two batches used was 110 and 120 $mg \cdot l^{-1}$ which corresponds to about 180 mg $HA \cdot l^{-1}$. The average uranium concentration in BCW is 2.9×10^{-8} $mol \cdot l^{-1}$ after ultra-filtration, in accordance with the values recommended by NEA-TDB 03 (Figure 6.13). The identical measured solubility of UO_2(am) in SBCW and BCW leads to the conclusion that HA do not increase the solubility of UO_2(am) by the formation of U(IV)-HA complexes in solution. The experiments conducted in the absence of reductant were sampled after one month of equilibration. The reducing capacity of BCW alone is sufficient to maintain the solubility of UO_2(am) at about 10^{-8} $mol \cdot l^{-1}$.

The uranium colloids concentration in BCW is 1.4×10^{-5} $mol \cdot l^{-1}$, *i.e.* 3 orders of magnitude higher than the solubility of UO_2(am) (Figure 6.13). In BCW, the colloidal uranium concentration (~10^{-5} $mol \cdot l^{-1}$) is enhanced by about one order of magnitude compared to SBCW (~10^{-6} $mol \cdot l^{-1}$, Figure 6.12). This increase in colloids concentration suggests the formation of U(IV)-organic colloids (pseudocolloids) besides the inorganic real colloids of UO_2(am). An increase of Tc concentration above $TcO_2.xH_2O$ in the presence of humic substances compared to the absence of humic substances is also observed by Geraedts *et al.* (2002) and Maes *et al.* (2004).

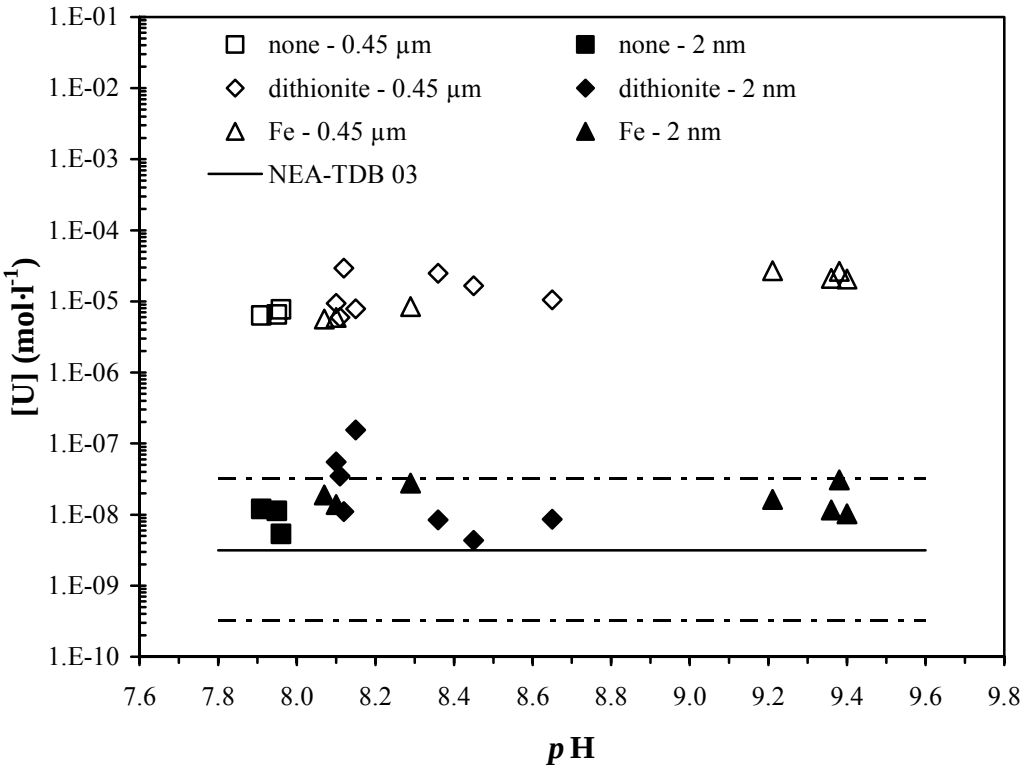

Figure 6.13. Solubility of UO_2(am) in BCW in the absence (none) or in the presence of reducing agents (dithionite and iron powder, Fe). Open and filled symbols represent the measured uranium concentration after filtration at 0.45 μm and 2 nm, respectively. Solid line gives the solubility value recommended by NEA-TDB 03 and the dashed lines indicate the uncertainty mentioned in the same database.

Uranium concentration as high as 10^{-5} mol·l^{-1} are measured after micro-filtration at 0.45 μm even for UO_2(am) solubility as low as 10^{-8} mol·l^{-1}. Based on this observation, the high uranium concentration (~10^{-6} mol·l^{-1}) that was measured in the first series of experiments after filtration at 0.45 μm (Section 6.2) may result from the presence of inorganic or organic colloids of uranium.

6.3.2.5 Solubility of UO_2(am) in SBCW at various HA concentrations

The mean uranium concentration measured above UO_2(am) in SBCW containing up to 1350 mg·l^{-1} HA is 4.0×10^{-8} mol·l^{-1} after ultra-filtration at 2 nm (Figure 6.14). This measured solubility is the same as that obtained in SBCW and BCW. Within the variability of the data, the uranium concentration remains independent of the dissolved HA concentration. This experimental fact confirms that the solubility of amorphous UO_2(am) is not increased by the formation of U(IV)-HA complexes.

The colloidal uranium concentration is up to 4 orders of magnitude higher than the solubility of UO_2(am), *i.e.* 1.5×10^{-4} mol·l^{-1}. The uranium colloids concentration increases from about 3×10^{-6} to about 6×10^{-5} mol·l^{-1} with increasing TOC concentration. This behaviour suggests that organic pseudocolloids of U(IV) are formed. The increase of the colloidal concentration mainly occurs at initial TOC concentrations lower than about 300 mg·l^{-1}. At higher TOC concentrations, the uranium colloids concentration reaches a plateau.

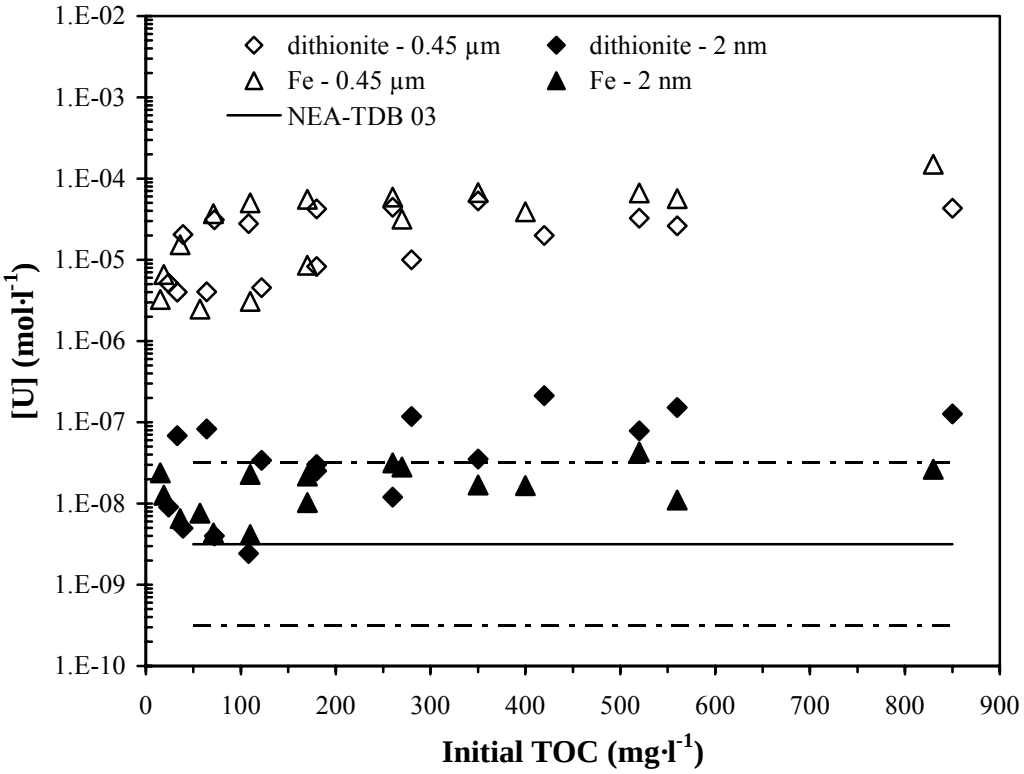

Figure 6.14. Solubility of UO_2(am) in SBCW at various HA concentrations in the presence of reducing agents (dithionite and iron powder, Fe). Open and filled symbols represent the measured uranium concentration after filtration at 0.45 μm and 2 nm, respectively. Solid line gives the solubility value recommended by NEA-TDB 03 and the dashed lines indicate the uncertainty mentioned in the same database.

6.3.2.6 Distribution of HA and nature of colloids

In the presence of UO_2(am), between 10 and 95 % of the initial TOC concentration is removed from the suspension by filtration at 0.45 μm (Figure 6.15). For initial TOC concentration up to 850 mg·l^{-1}, the highest TOC concentration remaining in solution after micro-filtration is 360 mg·l^{-1}. Therefore, an important interaction exists between HA and UO_2(am) particles larger than 0.45 μm. The association of Tc(IV) colloids with humic substances was evidenced by Geraedts *et al.* (2002). Maes *et al.* (2003b) called the interaction mechanisms between $TcO_2.xH_2O$ polymers and humic substance "hydrophobic sorption" to distinguish it from complexation. By analogy with Tc(IV), we assume that the mechanism of interaction between HA and UO_2(am) particles larger than 0.45 μm is a hydrophobic adsorption resulting in the removal of dissolved HA from the solution.

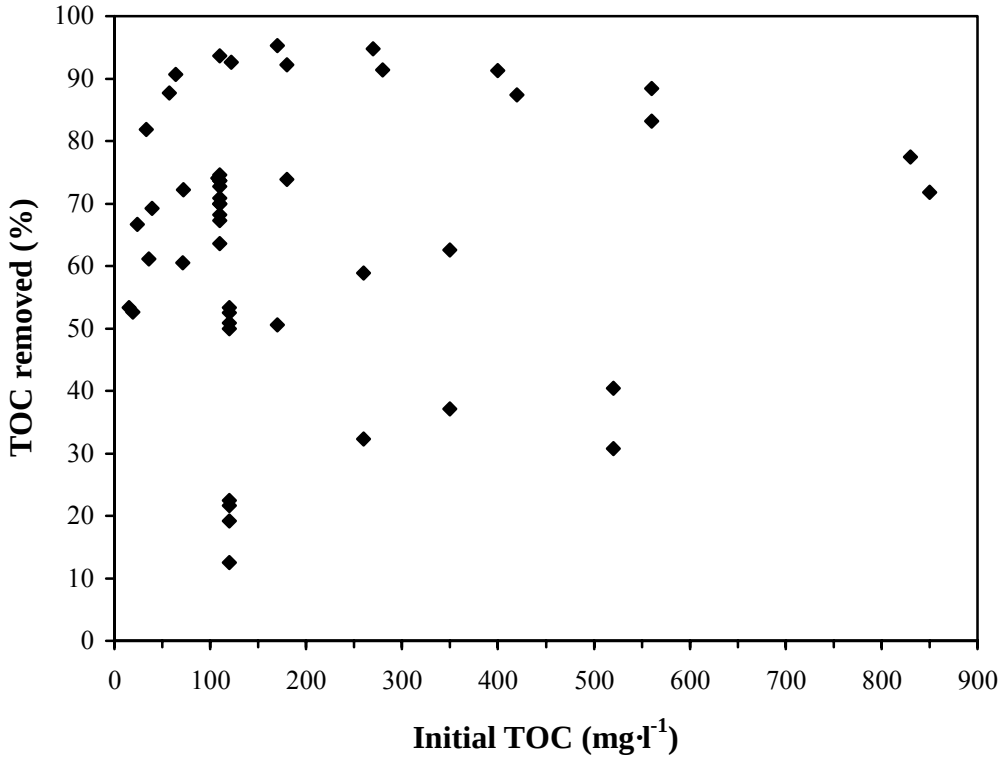

Figure 6.15. Percentage of TOC removed by micro-filtration at 0.45 μm as a function of the initial TOC concentration. The solid line gives the general trend.

As previously discussed, the presence of colloids with a size between 2 nm and 0.45 μm in the suspensions is clearly demonstrated. These colloids account for a total uranium concentration up to three orders of magnitude higher than the solubility of UO_2(am). In the absence of HA, real colloids of UO_2(am) increase the solubility by 2 orders of magnitude. In the presence of HA, the colloidal uranium concentration increases with increasing TOC concentration (Figure 6.16). The uranium colloids concentration mainly increases at TOC concentrations lower than about 75 mg·l^{-1} and reaches a plateau afterwards. The apparent increase of the colloidal uranium concentration with increasing TOC observed in Figure 6.16 suggests that organic pseudocolloids of U(IV) are formed.

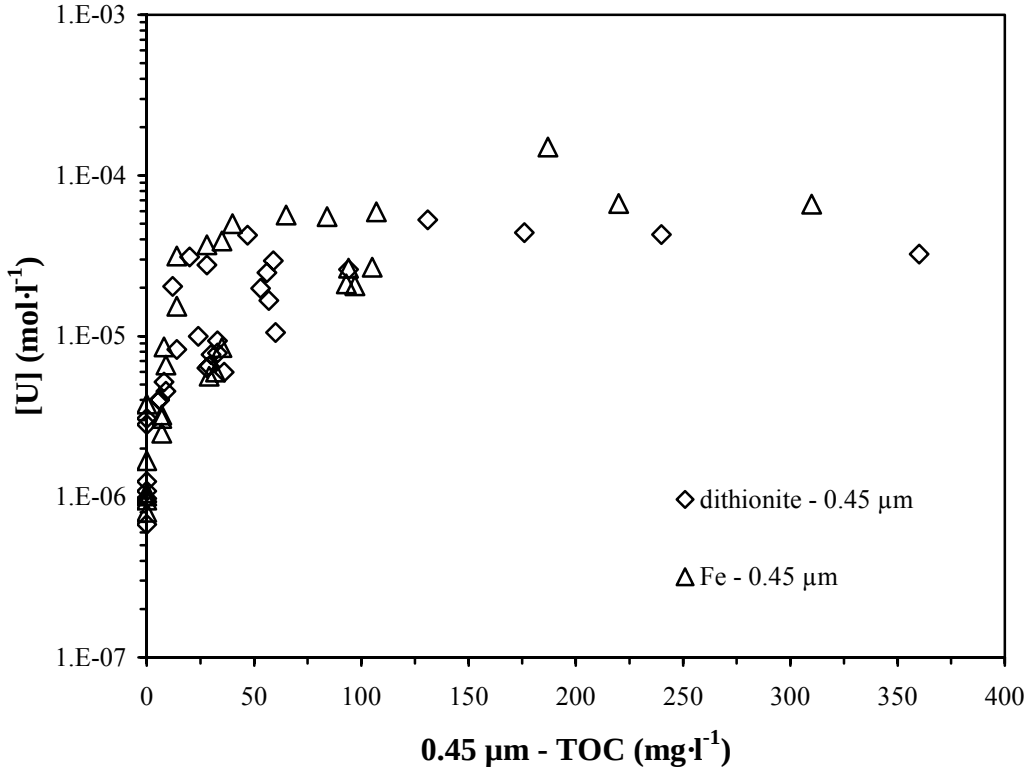

Figure 6.16. Colloidal uranium concentration as a function of the TOC concentration after micro-filtration at 0.45 μm in the presence dithionite and iron powder (Fe) as reducing agents.

The presence of organic colloids is verified by comparing the TOC concentrations in the filtrates obtained after micro- and ultra-filtrations (Figure 6.17). If organic colloids are formed, the TOC concentration should decrease after filtration at 2 nm as the uranium concentration decreases. If HA are not associated with the uranium colloids, the TOC concentration should remain the same after ultra-filtration. In Figure 6.17, identical TOC concentrations in both filtrates are represented by a solid 1:1 line. At TOC concentrations lower than about 75 $mg \cdot l^{-1}$, the data follow the 1:1 line. Therefore, the TOC content remains unchanged after ultra-filtration indicating that HA are not associated with the uranium colloids. At higher TOC concentrations, the data clearly deviate from the 1:1 line showing that HA are significantly removed by ultra-filtration and behave like colloids. Consequently, organic colloids are obviously formed at TOC concentrations remaining in solution after filtration at 0.45 μm higher than about 75 $mg \cdot l^{-1}$. As illustrated in Figure 6.16, these organic colloids only contribute to a small extent to the colloidal uranium concentration. Indeed, the increase in uranium colloids concentration mainly occurs at TOC concentration lower than ~75 $mg \cdot l^{-1}$. Therefore, the presence of dissolved HA has a stabilising effect on the presence of real colloids of UO_2(am).

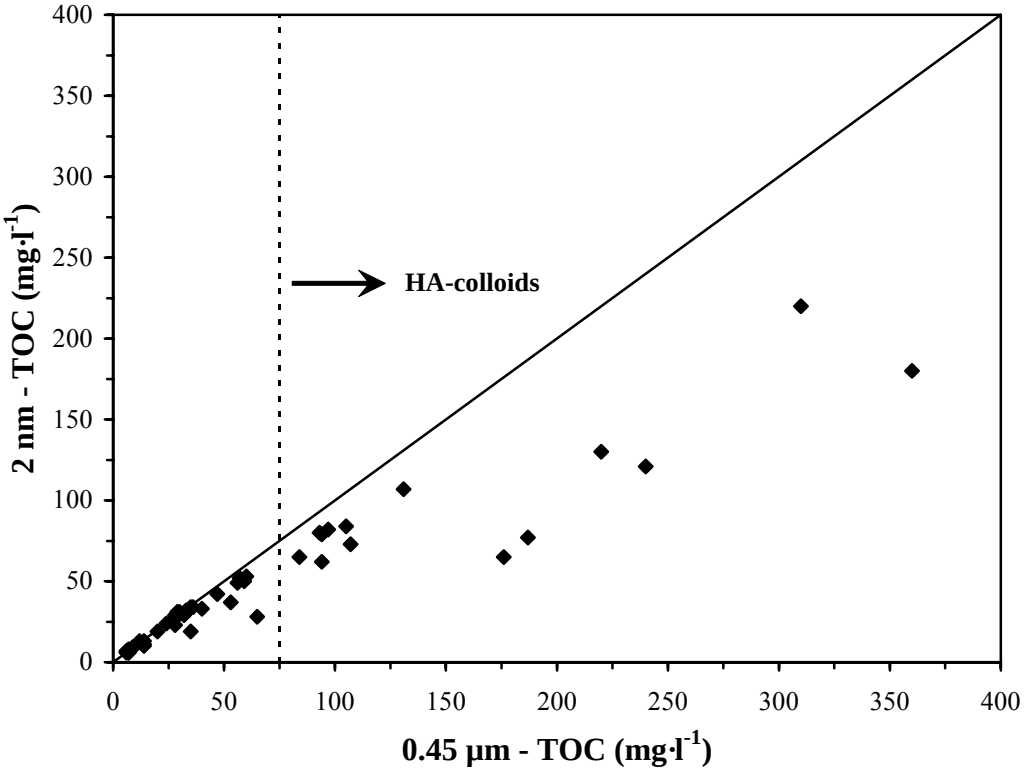

Figure 6.17. TOC concentration after ultra-filtration at 2 nm as a function of the TOC concentration after micro-filtration at 0.45 μm. The solid line is the 1:1 line representing identical TOC concentrations in both filtrates.

6.3.2.7 Solubility of ThO_2(cr) in SBCW at various HA concentrations

Besides UO_2(am), the effect of HA on the solubility of crystalline thorium oxide, ThO_2(cr), was also studied. The main advantage of Th is that it only exists in the tetravalent state while tetravalent uranium can readily oxidise to the hexavalent state. Thorium was used as analogue for U(IV). The experiments were carried out during the period where problems were encountered with the electrochemical reduction of U(VI). The solubility of ThO_2(cr) was determined in SBCW in the absence and at various HA concentrations. Aldrich HA and Boom Clay HA were used. The experiments were conducted in a glove box with a controlled Ar-5% H_2-0.4% CO_2 atmosphere (< 1 ppm O_2).

When starting from a crystalline oxide, the formation of real colloids is not observed. Indeed, Th concentrations are identical after micro- and ultra-filtration in the absence of HA (Figure 6.18). The measured Th concentration by ICP-MS is below the detection limit of 4.3×10^{-9} mol·l^{-1} (1 ppb). Therefore, this concentration value is given as an upper limit for the solubility of ThO_2(cr). Like UO_2(am), the solubility of ThO_2(cr) is independent from the TOC concentration after filtration at 2 nm (Figure 6.18). The dissolved HA do not form soluble organic complexes with Th(IV). On the other hand, the Th concentration is strongly affected by the pore size of the filter. The colloids concentration is up to 7×10^{-6} mol·l^{-1}, *i.e.* about 3 orders of magnitude higher than the solubility of ThO_2(cr). Real colloids of Th(IV) being absent in the suspension, the colloidal Th concentration likely results from the formation of organic pseudocolloids.

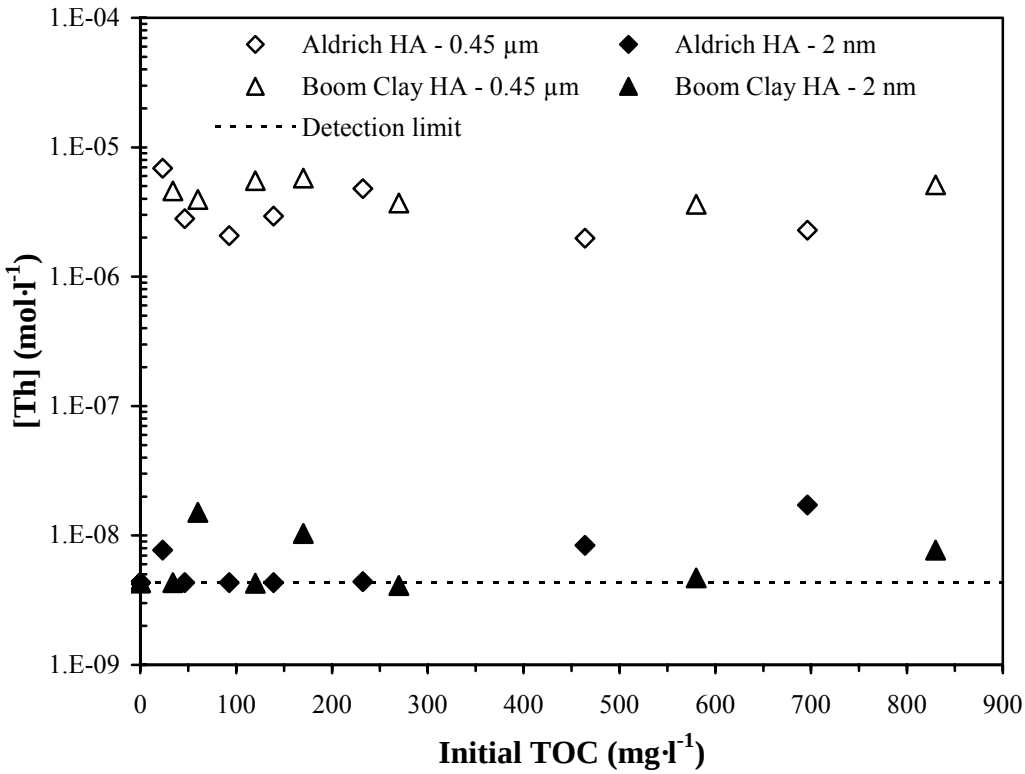

Figure 6.18. Th concentration in SBCW after 0.45 μm and 2 nm filtrations as a function of the initial TOC concentration. Dashed line gives the detection limit.

The formation of organic colloids is checked by measuring the TOC concentrations after filtration at 0.45 μm and 2 nm, respectively. The TOC concentration after micro-filtration is very similar to the initial concentration (Figure 6.19). The strong hydrophobic sorption of HA on particles larger than 0.45 μm that was observed in the presence of amorphous U(IV) oxide is not found in the ThO_2(cr) system. This observation suggests that the amorphous character of the solid favours the adsorption of HA. The difference in TOC concentration in the filtrates after micro-and ultra-filtration confirms the formation of Th(IV)-organic complexes. The TOC concentration clearly decreases after filtration at 2 nm pointing out the colloidal behaviour of HA (Figure 6.19). Respectively from 33 to 85 and from 22 to 56% of Aldrich and Boom Clay HA are removed by the 2 nm pore size filter. The stronger concentration decrease of Aldrich HA than Boom Clay HA is attributed to a larger particle size of Aldrich HA.

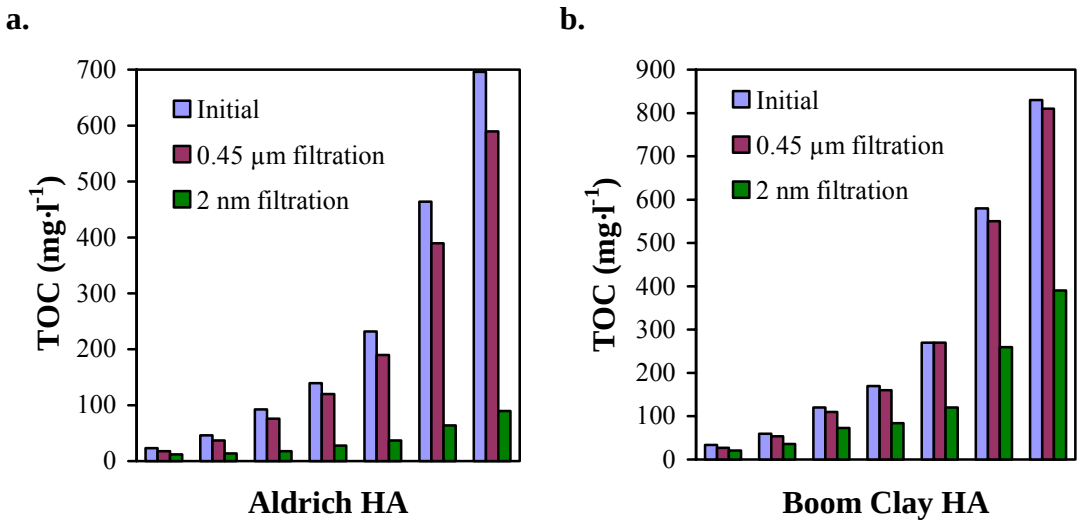

Figure 6.19. Distribution of the TOC concentration in the initial solution, after 0.45 μm and 2 nm filtrations. a: Aldrich HA, b: Boom Clay HA.

6.3.3 Discussion

The complexation of U(IV) by the dissolved organic matter present in the Boom Clay is a potential process which may increase its solubility and its mobility. To validate or invalidate this hypothesis, we have studied the effect of organic matter on the solubility of UO_2(am). Batch experiments show that the solubility of UO_2(am) is 3.4×10^{-8} mol·l^{-1} on average (Figure 6.20). No effect of HA complexation is observed. The measured solubility is generally in fair agreement with the range of solubility values recommended by NEA-TDB 03 (Guillaumont *et al.*, 2003). Over the TOC concentration range remaining in solution after ultra-filtration (0 to 225 mg·l^{-1}), the uranium concentration is independent of the HA concentration. Therefore, the solubility is not increased by the formation of mobile U(IV)-HA complexes in solution.

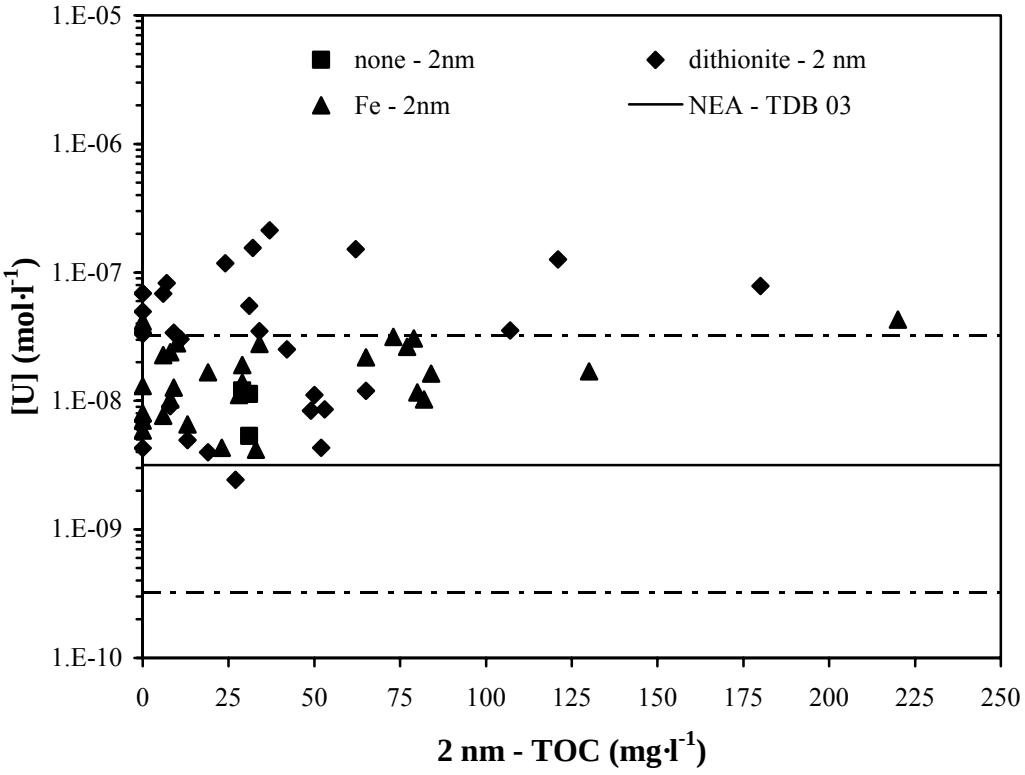

Figure 6.20. Solubility of UO_2(am) as a function of the TOC concentration after ultra-filtration at 2 nm in the absence (none) or in the presence of reducing agents (dithionite and iron powder, Fe). Solid line gives the solubility value recommended by NEA-TDB 03 and the dashed lines indicate the uncertainty mentioned in the same database.

The effect of organic matter on the solubility of UO_2(am) is also evaluated by introducing the notion of "solubility increasing factor" (Wang, 2003b). The solubility increasing factor measures the increase on U(IV) solubility due to the formation of U(IV)-HA complexes. The factor is defined as:

$$f_{sol.} = S/S_0$$

where, S is the solubility in the presence of HA and S_0 the solubility measured under the same condition but in the absence of HA.

The solubility increasing factor as function of the TOC concentration after filtration at 2 nm is given in Figure 6.21. The reference level ($f_{sol.}$ = 1) is defined by the average solubility of UO_2(am) in SBCW after ultra-filtration, *i.e.* 3×10^{-8} mol·l^{-1}. A factor significantly greater than unity indicates a strong increase of the UO_2(am) solubility by HA while a factor close to unity merely means that HA have no apparent effect on the solubility. Figure 6.21 clearly demonstrates that the solubility of UO_2(am) is not affected by dissolved HA since the solubility increasing factor is around 1. The scatter of the data is about ± 1 order of magnitude which is in line with the usually observed uncertainty of UO_2 (am) solubility.

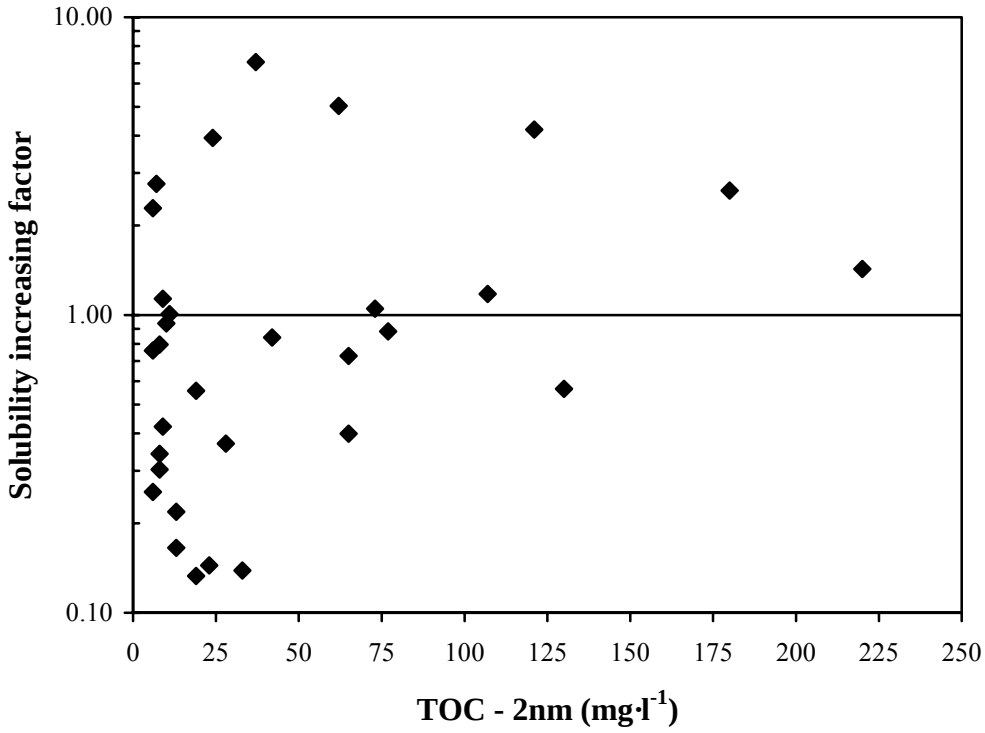

Figure 6.21. Solubility increasing factor as function of the TOC concentration after 2 nm ultra-filtration.

Similarly defined as the solubility increasing factor, the "colloids formation factor" is introduced to evaluate the colloidal effect of organic matter on the solubility of UO_2(am). The "colloids formation factor" is a measure for the formation of colloids in solubility experiment:

$$f_{\text{coll}} = C/S_0$$

where, C is the concentration of uranium colloids (2 nm - 0.45 μm) in the absence or in the presence of HA and S_0 the concentration of uranium under the same conditions but after 2 nm ultra-filtration.

The colloids formation factor as function of the TOC concentration after filtration at 0.45 μm is presented in Figure 6.22. The reference level ($f_{coll.}$ = 1) is defined by the average solubility of UO_2(am) in SBCW, SBCW at various concentrations of HA and BCW after ultra-filtration, *i.e.* 3.4×10^{-8} mol·l^{-1}. Unlike solubility increasing factors, colloids formation factors are all and significantly greater than unity indicating the presence of uranium colloids in the system. Uranium colloids

increase the uranium concentration by about 3 orders of magnitude compared to the solubility of UO_2(am). The colloids formation factor increases from 20 to about 1000 at TOC concentration lower than about 75 mg·l^{-1}. At these TOC concentrations, the HA remain in solution after filtration at 2 nm and the colloids are therefore mainly real colloids of UO_2(am). This implies that the Boom Clay HA enhances the formation of real colloids of UO_2(am); the mechanism behind it is not understood at the present stage. Organic colloids are formed at TOC contents higher than 75 mg·l^{-1} and do not significantly increase the colloidal uranium concentration as illustrated by the plateau value of about 1000 reaches by the colloids formation factor.

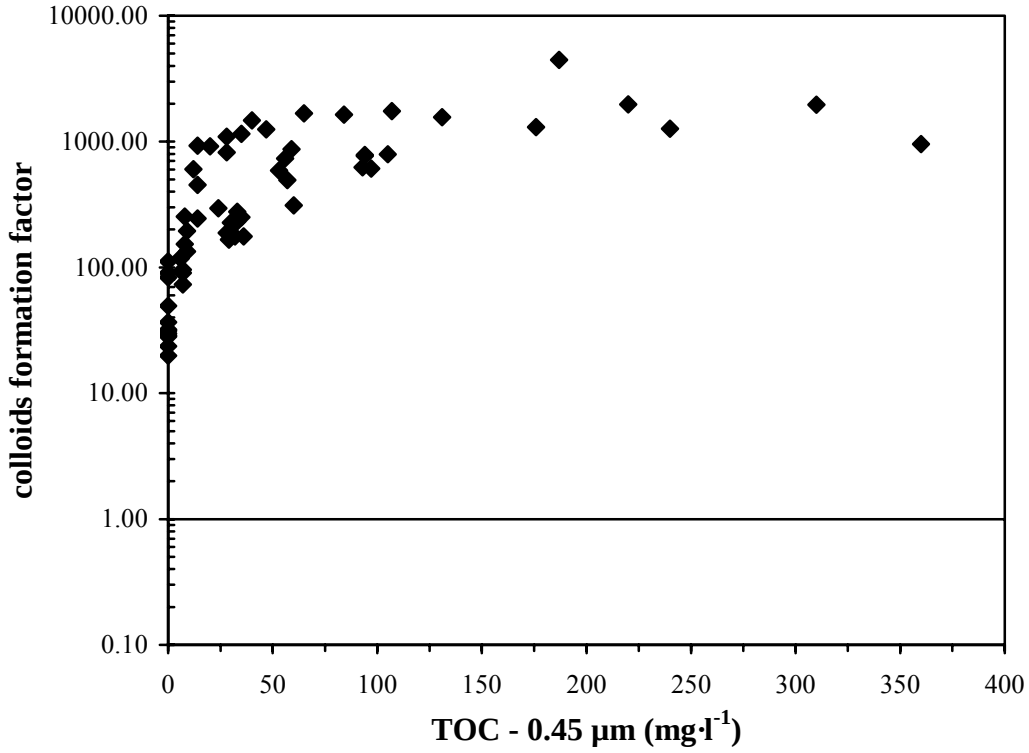

Figure 6.22. Colloids formation factor as function of the TOC concentration after 0.45 μm micro-filtration.

To summarize the U(IV) solubility experiments, it is found that the effect of Boom Clay HA on the solubility of UO_2(am) is negligible. Migration experiments performed in the framework of the TRANCOM-II project also reveal that reduced uranium migrates independent from Boom Clay organic matter (Maes *et al.*, 2003). The solubility of U(IV) hydrous oxide is not increased by the mobile organic matter through the formation of U(IV)-organic matter complexes. However, the formation of colloids, with a size between 2 nm and 0.45 μm, is obvious. These colloids increase the total uranium concentration up to 3 orders of magnitude beyond the UO_2(am) solubility. These colloids are not expected to increase the uranium mobility since they will be ultra-filtered by the Boom Clay.

6.4 Conclusions

The solubility of U(IV) amorphous precipitate was determined in Boom Clay pore water (BCW) in the presence of reducing agents and under the *in situ* partial pressure of CO_2 at $10^{-2.4}$ atm. The total aqueous uranium concentration measured after two-months equilibrating time and 0.45 μm filtration is about 10^{-6} mol·l^{-1}. The uranium concentration decreases as a function of time within the experimental period. This decrease is ascribed to the reduction of U(VI)-carbonate complexes released from an oxidised layer of the original U(IV) precipitate and the subsequent precipitation of neo-formed U(IV). Owing to its reducing capacity and the possible catalytic effect of the U(IV) precipitate surfaces, BCW is able to achieve this redox process. The high measured concentrations compared to the literature suggest a contamination of the system by U(VI), the presence of colloids, or U(IV)–organic matter complexes.

To evaluate the contribution of the colloids and the role of organic matter, the solubility of U(IV) amorphous precipitate was determined in BCW and in SBCW at various HA concentrations after micro-filtration at 0.45 μm and ultra-filtration at 2 nm. The precipitate obtained from uranium metal dissolution was identified as U(IV) poorly crystallised and hydrous oxide, UO_2(am) ($UO_2.xH_2O$). Batch experiments show that the solubility of UO_2(am) is more or less 10^{-8} mol l^{-1}. This solubility is in accordance with the range of values recommended by NEA-TDB 03 for the $U(OH)_4$(aq) concentration in aqueous solutions equilibrated with UO_2(am). The solubility of UO_2(am) is independent of the HA presence. The formation of U(IV)-HA complexes which was expected to possibly enhance the dissolution of UO_2(am) is negligible.

Generally, more than 50% of dissolved HA are removed from the solution by hydrophobic adsorption on UO_2(am) particles larger than 0.45 μm. The presence of colloids with a size between 2 nm and 0.45 μm in the system is clearly demonstrated. These colloids account for a total uranium concentration up to three orders of magnitude higher than the solubility of UO_2(am). Therefore, ultra-filtration with filter of nanometer pore size must be used to measure the concentration of dissolved species determining the solubility. The distribution of the TOC concentrations after filtration at 0.45 μm and 2 nm suggests that the uranium colloids are mainly inorganic *i.e.* real uranium colloids which are stabilised in presence of organic matter. Humic acids behave like colloids at TOC concentration higher than about 75 mg·l^{-1} after micro-filtration but they do not increase significantly the colloidal uranium concentration.

The effect of crystallinity was studied by conducting solubility experiments with crystalline ThO_2 as analogue for tetravalent uranium. Like UO_2(am), ultra-filtration at 2 nm decreases the Th concentration significantly. There is no effect of HA complexation on the solubility. Micro-filtered Th(IV) concentrations increase by up to 3 orders of magnitude upon increasing the HA content. Different from UO_2(am), this increase is attributed to the formation of Th organic pseudocolloids. Both the absence of real inorganic colloids and the removal of HA by ultra-filtration support this idea.

These results indicate that organic matter does not enhance the migration of uranium through the formation of mobile U(IV)-organic complexes in solution. The dominant effect of organic matter on the solubility of UO_2(am) is the formation of colloids. These colloids are expected to be immobilised in the host formation by ultra-filtration.

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