Chapter 7
Sorption of uranium

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7.1 Introduction

The study of the uranium sorption is an important part of the overall investigation required for the assessment of potential sites for spent fuel disposal. Sorption is a significant mechanism which contributes to the retention of uranium although precipitation is the primary process. In the environmental science literature, sorption is generally defined as a loss of a chemical species from a solution to a contiguous solid phase (Davis, 2002). The sorbate is the chemical species that becomes concentrated at the surface of some solid, the sorbent. Dissolved uranium will always partition itself between the water and the surfaces of contacting solids in the Boom Clay. There are several mechanisms by which a sorption process can occur, for example: adsorption, absorption, ion exchange, and surface precipitation.

The sorption of U(VI) and its modelling onto different geological materials is extensively documented in the literature. Ferric oxyhydroxides being generally the most important sorbents for U(VI) (Langmuir, 1997), several studies have been devoted to these minerals, *e.g.* Ames *et al.*, 1983a; Hsi and Langmuir, 1985; Waite e*t al.*, 1994; Bruno *et al.*, 1995; Ohnuki *et al.*, 1997; Gabriel *et al.*, 1998; Steele *et al.*, 2002. The sorption of U(VI) on clay minerals has also been investigated by numerous authors: Tsunashima *et al.*, 1981; Borovec, 1981; Ames *et al.*, 1983b; Sikalidis *et al.*, 1989; Zachara and McKinley, 1993; Morris *et al.*, 1994; Chisholm-Brause *et al.*, 1994; McKinley *et al.*, 1995; Turner *et al.*, 1996; Pabalan and Turner, 1997; Boult *et al.*, 1998; Thompson *et al.*, 1998; Sylwester *et al.*, 2000. Moreover, the sorption of U(VI) has been studied on carbonate (Morse *et al.*, 1984; Carroll and Bruno, 1991; Carroll *et al.*, 1992); on alumina (Prikryl *et al.*, 1994; Sylwester *et al.*, 2000); on zeolite (Pabalan *et al.*, 1993); on hydroxylapatite (Gauglitz *et al.*, 1992); on silica gel (Lieser *et al.*, 1992); on amorphous silica (Sylwester *et al.*, 2000); on quartz (Pabalan *et al.*, 1998; Prikryl *et al.*, 2001); on natural sands (Rosentreter *et al.*, 1998); on fracture-infilling minerals (Ticknor, 1993); and on complex substrate (Ticknor, 1994; Payne *et al.*, 1994; Arnold *et al.*, 1998 and 2001). This non-exhaustive list of references gives an idea about the extensive work performed on the sorption of U(VI) onto different geological materials.

The literature review indicates that the U(VI) sorption depends on various geochemical parameters, including aqueous solution properties (*p*H, ionic strength, concentration of ligands that form U(VI) complexes) and mineral characteristics as well as temperature and redox conditions. Generally, sorption maximum occurs at the near-neutral *p*H range. Experimental results can be effectively simulated by surface complexation models and, for clay minerals, by an ion-exchange mechanism at low *p*H. Of interest for the Boom Clay is the influence of carbonate and dissolved organic matter on the uranium sorption behaviour. All authors agree that the sorption of U(VI) significantly decreases in presence of carbonate due to the dominance in solution of poorly sorbed anionic uranyl carbonate species: $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ (Hsi and Langmuir, 1985; Lieser *et al.*, 1992; Pabalan *et al.*, 1993; Waite e*t al.*, 1994; Pabalan and Turner, 1997; Boult *et al.*, 1998; Payne *et al.*, 1998). In presence of carbonate, the data are modelled by assuming the formation of ternary complex involving UO_2^{2+}, CO_3^{2-} and the mineral surface (Hsi and Langmuir, 1985; Payne and Waite, 1991; Waite e*t al.*, 1994). In presence of natural organic matter, the sorption of uranium is enhanced at acidic *p*H values but reduced at more alkaline *p*H values (Beneš *et al.*, 1998; Lenhart and Honeyman, 1999; Schmeide *et al.*, 2000). Therefore,

the sorption of U(VI) in the Boom Clay should be low due to the presence of dissolved organic matter and to the slightly alkaline conditions under which U(VI) occurs as the weakly sorbed $UO_2(CO_3)_3^{4-}$.

As mentioned previously, the dominant mechanism proposed to interpret migration experiments is the reduction of uranium since the sorption of U(VI) is expected to be weak in the Boom Clay. It is reported in the literature that aqueous U(VI) is reduced after interaction with some solid phases under anoxic conditions. These solid phases are zero-valent iron (Gu *et al.*, 1998), corroded iron (Cui and Spahiu, 2002), magnetite (Missana *et al.*, 2003) and sulphide minerals (Wersin *et al.*, 1994). From this statement, the following question arises: "Can pyrite, the most abundant reducing mineral in the Boom Clay, reduce U(VI) under Boom Clay conditions ?". To answer this, we have studied the sorption of U(VI) on pyrite as a function of time under conditions representative for the Boom Clay.

Unlike U(VI), data on the sorption of U(IV) are very scarce. According to Baston *et al.* (1992), the sorption of U(IV) on geological material at *p*H 8 is much stronger than that of U(VI). Baston *et al.* (1995) also compared the sorption behaviour of U(IV) and U(VI) on bentonite, tuff and granodiorite at *p*H 8 and 10. For all rock types, the sorption of U(VI) is much weaker than the sorption under strongly reducing conditions (E_h about -400 mV) where uranium is predicted to be almost exclusively present in the tetravalent oxidation state. The U(IV) sorption is unaffected by the presence of cellulosic degradation products (Baston *et al.*, 1992 and 1997). U(IV) being expected in the Boom Clay, we have performed screening experiments with aqueous uranium present above UO_2(am) to determine the most important sorbent(s) among the Boom Clay minerals.

7.2 Sorption of U(VI) on pyrite

The sorption of U(VI) on Boom Clay pyrite was studied in SBCW and BCW at *p*H 8.2 under the *in situ* partial pressure of CO_2 ($10^{-2.4}$ atm). The batch experiments were conducted under anaerobic conditions in a glove box with a controlled Ar–5% H_2-0.4% CO_2 atmosphere (O_2 < 1 ppm). The ratio solution to solid was 20 (10 ml/0.5 g) and the suspensions were equilibrated for 1, 4, 8, 16, and 32 days. The aim of these experiments is to look into the possible redox processes which could result from the interaction between aqueous U(VI) and reducing mineral pyrite.

7.2.1 Experimental

7.2.1.1 Pyrite preparation

Pyrite was separated from Boom Clay samples. Slurries of clay were wet sieved and the fraction between 32 and 63 μm was collected. The heavy minerals of this fraction were extracted by sedimentation in heavy liquid (bromoform). The characterisation by x-ray diffraction (XRD) shows that the main constituents are pyrite and quartz. Besides, minor amounts of carbonates and Ti-oxides are also present as well as clay minerals traces. The recognised carbonates are calcite, siderite, dolomite and maybe hydrozincite ($Zn_5(CO_3)_2(OH)_6$). The mineral assemblage obtained was used without further treatment. The surface area measured by N_2-adsorption isotherms (Autosorb-1-MP, Quantachrome Corp.) is 5.23 $m^2 \cdot g^{-1}$. The analysis was performed at the Laboratory for adsorption and catalysis of the University of Antwerpen (Belgium).

7.2.1.2 U(VI) stock solutions

U(VI) stock solutions were prepared at two different concentrations, *i.e.* 10^{-3} and 10^{-5} M. Solutions of 10^{-3} M U(VI) were obtained by diluting 200 μl of 0.1 M U(VI) mother solution into 19.8 ml of either SBCW or BCW. The mother solution was prepared by dissolving 0.502 g of $UO_2(NO_3)_2.6H_2O$ into 10 ml of SBCW. The *p*H of this solution was 2.9. Prior to its dilution, the 200 μl aliquot of the acidic uranyl nitrate solution was titrated with aliquots of 1 M NaOH to avoid the perturbation of the carbonate equilibrium of Boom Clay water. Afterwards, the mixture was shaken to dissolve the U(VI) precipitate formed upon titration with 1 M NaOH. The *p*H was then adjusted at about 8.3. Solutions of 10^{-5} M U(VI) were obtained by diluting 700 μl of the 10^{-3}M U(VI) solution into 70 ml of either SBCW or BCW.

7.2.1.3 Pyrite equilibration

The purpose of this washing step is to establish chemical equilibrium between pyrite and the solution used in the sorption experiments. Half a gram of pyrite was weighed into 16 ml polypropylene centrifuge tubes (Nalgene) inside the glove box. A volume of 10 ml of SBCW or BCW was added to each tube. The tubes were placed on a shaker for a gentle agitation. After 24 hours of contact, the mixtures were centrifuged at 2500g for 5 minutes to separate solid and liquid. The washing solution was removed with a pipette to prevent removal of the sediment (some liquid remains in the tube). Fresh SBCW or BCW was added in order to maintain a solution volume of about 10 ml. The equilibration cycle was repeated twice more for a total of three washes. After removal of the third wash solution, each tube was reweighed. The weight was recorded to determine the volume of residual solution left in each sample.

7.2.1.4 Batch experiments

About 10 ml of the 10^{-5} M U(VI) stock solutions were added to each sample tubes containing 500 mg of washed pyrite. In addition, 10 ml of U(VI) stock solutions were placed in two empty centrifuge tubes (blank). The blank tubes are needed to detect uranium sorption by centrifuge tube walls. The suspensions were gently shaken and equilibrated for periods varying from 1 to 32 days. The samples with an initial U(VI) concentration of 10^{-3} M were contacted for 46 days at the same solution-solid ratio of 20 (Table 7.1).

At the end of the equilibration period, the aqueous and the solid phase were separated by centrifugation at 2500g for 5 minutes. The *p*H and the potential redox (E_h) were determined. The *p*H was measured with a combined glass electrode (Metrohm) calibrated against *p*H buffers 7 and 9. The E_h was measured for at least 30 minutes with a combined platinum-Ag/AgCl electrode calibrated against quinhydrone buffers at *p*H 4, 7 and 9. Two aliquots of 5 ml and 4.5 ml were sampled for parallel filtrations at 0.22 μm (Millex-HA, Millipore) and at 2 nm (Microsep 30k, Omega), respectively. For both filtrations, a volume of 1 ml of the samples was first passed through the filters to saturate any possible adsorption sites. This filtrate was discarded before filtering the solution for analyses. For filter conditioning, ultra-filtration was accomplished by centrifugation at 2500g for 30 minutes. Afterwards, the remaining aliquots of 4 and 3.5 ml were filtered at 0.22 μm and 2 nm, respectively. The micro-filtration was achieved by passing the 4 ml sample through the 0.22 μm filter with a syringe. The ultra-filtration was accomplished by centrifuging the 3.5 ml sample at 2500g for 60 minutes. The filtrates were analysed

for uranium by Inductively Coupled Plasma-Mass Spectrometry (Perkin-Elmer ICP-MS, Elan 5000) with a 95% confidence interval 2σ of about 10%.

Table 7.1. Detailed overview of the experiments performed to study the interaction between U(VI) and pyrite; SBCW: synthetic Boom Clay water; BCW: Boom Clay water.

Samples	Solution	[U] $mol \cdot l^{-1}$	Time days	Solution/solid $l \cdot g^{-1}$
Blank	SBCW	10^{-5}	32	20
Sp 1-1	SBCW	10^{-5}	1	20
Sp 1-2	SBCW	10^{-5}	4	20
Sp 1-3	SBCW	10^{-5}	8	20
Sp 1-4	SBCW	10^{-5}	16	20
Sp 1-5	SBCW	10^{-5}	32	20
Sp 1-6	SBCW	10^{-3}	46	20
Blank	BCW	10^{-5}	32	20
Sp 2-1	BCW	10^{-5}	1	20
Sp 2-2	BCW	10^{-5}	4	20
Sp 2-3	BCW	10^{-5}	8	20
Sp 2-4	BCW	10^{-5}	16	20
Sp 2-5	BCW	10^{-5}	32	20
Sp 2-6	BCW	10^{-3}	46	20

7.2.2 Results

All results relating to the sorption study of U(VI) on pyrite are given in Appendix 2.

7.2.2.1 Uranium sorption on the tube walls and on the filters

Prior to data interpretation, the absence of uranium sorption on the tubes walls and on the filters is verified. Sorption on tube walls is controlled by measuring the uranium concentration in blank samples, *i.e.* samples without pyrite. These measured concentrations are compared with the uranium concentration in the 10^{-5} M U(VI) stock solutions (Table 7.2). No sorption on the tube walls is detected by considering the analytical error of 10 % on the measurements.

Table 7.2. Study of the uranium sorption on the tube walls; SBCW: synthetic Boom Clay water; BCW: Boom Clay water.

Filtration	solution	U(VI) stock solutions $mol \cdot l^{-1}$	Blank $mol \cdot l^{-1}$	Difference relative to initial concentration %
Without	SBCW	8.91×10^{-6}	1.06×10^{-5}	19
	BCW	9.24×10^{-6}	8.95×10^{-6}	3
2 nm	SBCW	9.45×10^{-6}	9.29×10^{-6}	2
	BCW	9.87×10^{-6}	9.20×10^{-6}	7

The sorption on the filter is checked by comparing the uranium concentrations measured in the U(VI) stock solutions and in the blank samples without filtration, after filtration at 0.22 μm and after filtration at 2 nm (Tables 7.3 and 7.4). The difference between the concentrations is negligible in comparison to the analytical error.

Table 7.3. Study of the uranium retention by the 0.22 μm filter; SBCW: synthetic Boom Clay water; BCW: Boom Clay water.

Samples	Solution	[U] mol·l^{-1}	[U] mol·l^{-1}	Difference relative to initial concentration
		without filtration	0.22 μm filtration	%
10^{-3} M U(VI) stock solution	SBCW	9.29×10^{-4}	9.20×10^{-4}	1
10^{-5} M U(VI) stock solution		8.91×10^{-6}	8.91×10^{-6}	0
10^{-3} M U(VI) stock solution	BCW	9.20×10^{-4}	9.33×10^{-4}	1
10^{-5} M U(VI) stock solution		9.24×10^{-6}	9.20×10^{-6}	0

Table 7.4. Study of the uranium retention by the 2 nm filter; SBCW: synthetic Boom Clay water; BCW: Boom Clay water.

Samples	Solution	[U] mol·l^{-1}	[U] mol·l^{-1}	Difference relative to initial concentration
		without filtration	2 nm filtration	%
10^{-5} M U(VI) stock solution	SBCW	8.91×10^{-6}	9.45×10^{-6}	6
Blank		1.06×10^{-5}	9.29×10^{-6}	12
10^{-5} M U(VI) stock solution	BCW	9.24×10^{-6}	9.87×10^{-6}	7
Blank		8.95×10^{-6}	9.20×10^{-6}	3

7.2.2.2 Evolution of uranium concentration

The evolution of the uranium concentration as function of contact time with pyrite is shown in Figure 7.1. The uranium concentrations are generally lower in SBCW than in BCW. This indicates that the sorption is reduced by the presence of organic matter. The reduction of sorption in presence of organic matter at alkaline *p*H is mentioned by Beneš *et al.*, 1998; Lenhart and Honeyman, 1999; and Schmeide *et al.*, 2000.

For initial U(VI) concentration of about 10^{-5} M, the uranium concentration is lower than 10^{-6} mol·l^{-1} after 4 days of equilibration both in SBCW and BCW. In SBCW, the uranium concentration decreases from 1.7×10^{-6} mol·l^{-1} after 1 day to 4.4×10^{-8} mol·l^{-1} after 16 days. Surprisingly, it increases to 1.1×10^{-7} mol·l^{-1} after 32 days. The filtration at different sizes (0.22 μm and 2 nm) does not influence the uranium concentration indicating that no uranium-bearing colloids are present in solution. On the other hand, there is a notable effect of the filtration in the experiments performed with BCW. The uranium concentration is always higher after filtration at 0.22 μm than after filtration at 2 nm. While the uranium concentration after micro-filtration reaches a plateau after 8 days, the uranium concentration measured after ultra-filtration continues to decrease. The difference between both filtrations increases with increasing equilibration time. After 32 days, the uranium concentrations are 3.5×10^{-7} and 7.0×10^{-8} mol·l^{-1} after micro- and ultra-filtration, respectively. This behaviour indicates the presence of uranium-bearing colloids but it

can not be concluded whether they are organic or inorganic. Nevertheless, the colloids occurrence is attributed to the presence of organic matter since the only difference between BCW and SBCW is that BCW contains 130 $mg \cdot l^{-1}$ of dissolved organic carbon.

After 46 days of contact with pyrite, the sample with an initial U(VI) concentration of about 10^{-3} M reaches a concentration of 2.3×10^{-7} $mol \cdot l^{-1}$ in SBCW, independent from the filter size. In BCW, the measured concentrations after 46 days are 6.3×10^{-7} and 1.8×10^{-7} $mol \cdot l^{-1}$ after filtration at 0.22 μm and 2 nm, respectively. It is interesting to note that these final concentrations are about the same than those measured in the experiments with an initial uranium concentration around 10^{-5} M after 32 days of equilibration.

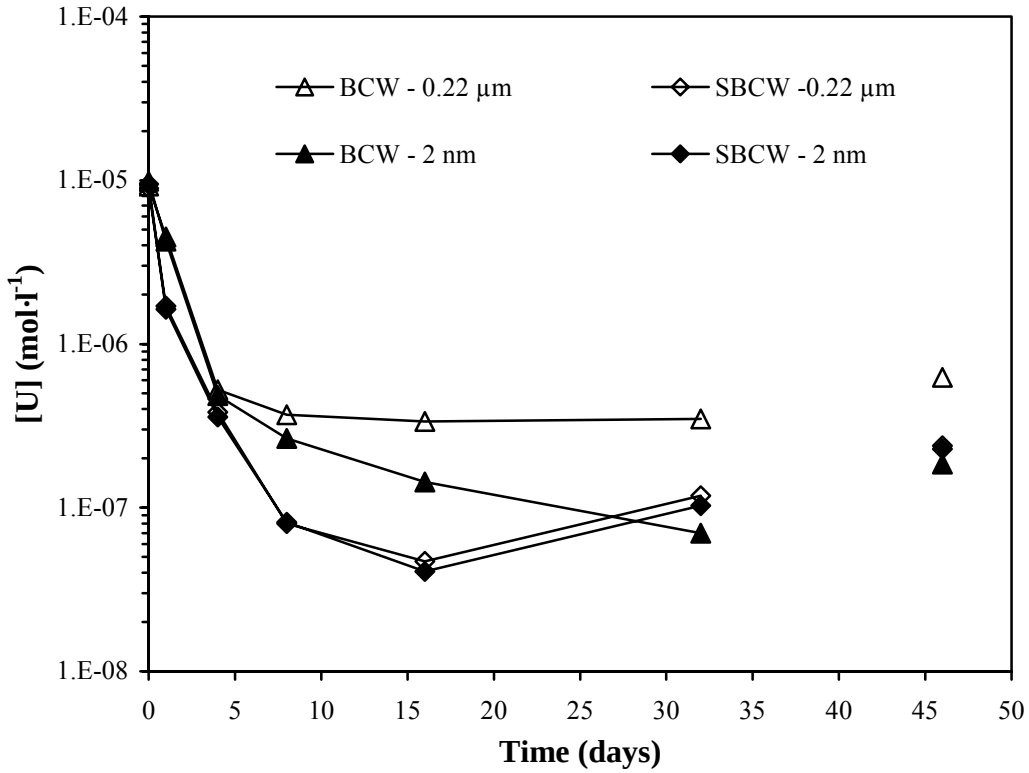

Figure 7.1. Evolution of the uranium concentration ($mol \cdot l^{-1}$) from an initial concentration of 10^{-5} $mol \cdot l^{-1}$ as function of contact time with pyrite. The data at 46 days were obtained for an initial uranium concentration of 10^{-3} $mol \cdot l^{-1}$.

7.2.2.3 Distribution ratio

The distribution coefficient (K_d) is a convenient empirical ratio for representation of sorption data. The K_d can be defined as:

$$K_d\ (ml \cdot g^{-1}) = \frac{equilibrium\ amount\ of\ uranium\ sorbed}{equilibrium\ amount\ of\ uranium\ in\ solution} \times \left(\frac{V}{m}\right) \qquad \text{Eq. 7.1}$$

where V is the volume of solution (ml) and m is the mass of solid (g). The use of K_d provides a means of normalizing sorption results to the solid mass to solution volume (M/V) ratio and of accounting for the decrease of uranium concentration in solution due to sorption. As discussed by Payne *et al.* (2001), the term K_d implies chemical equilibrium which may not be achieved in laboratory experiments. Therefore, we express the results of the uranium sorption experiments by the distribution ratio (R_d). The R_d is similar to the K_d but does not imply equilibrium between sorbed and aqueous uranium species. The distribution ratio (R_d, $ml \cdot g^{-1}$) in batch sorption experiments is determined by:

$$R_d = \frac{(C_i - C_f)}{C_f} \cdot \frac{V}{m} \qquad \text{Eq. 7.2}$$

where C_i is the initial concentration of the sorbate in the system, C_f is the remaining concentration of the sorbate after sorption, V is the volume of solution (ml), and m is the mass of the sorbent (g). In our experiments, the total volume of solution (V_{tot}) is the sum of the volume of the residual solution left from the third wash ($V_{residual}$) and the volume of the U(VI) stock solution (V_0) added to the washed pyrite:

$$V_{tot} = V_{residual} + V_0 \qquad \text{Eq. 7.3}$$

Due to the dilution by the residual washing solution, the initial concentration of uranium in the system, C_i, is given by:

$$C_i = \left(\frac{C_0 \cdot V_0}{V_0 + V_{residual}}\right) \qquad \text{Eq. 7.4}$$

where C_0 is the U(VI) concentration in the stock solution.

By introducing equations 7.3 and 7.4 in equation 7.2, it becomes:

$$R_d = \frac{\left(\frac{C_0 \cdot V_0}{V_0 + V_{residual}}\right) - C_f}{C_f} \cdot \frac{V_0 + V_{residual}}{m_{pyrite}} \qquad \text{Eq. 7.5}$$

where C_f is the concentration of uranium remaining in solution after contact with pyrite and m_{pyrite} is the mass of pyrite (g).

Rearranging equation 7.5, the equation used to calculate R_d in our experiments is finally obtained:

$$R_d = \frac{(C_0 \cdot V_0) - C_f \cdot (V_0 + V_{residual})}{C_f \cdot m_{pyrite}} \qquad \text{Eq. 7.6}$$

The U(VI) concentration of the stock solutions, C_0, considered in the calculations is the average value of the uranium concentrations measured without filtration and after filtrations. The R_d calculated for each sample are reported in Tables 7.5 and 7.6. The R_d is generally higher in SBCW than in BCW.

In SBCW, the R_d determined after micro- and ultra-filtration are very similar and a mean value is considered (Table 7.5). The R_d increases from 82 ml·g^{-1} after 1 day to 3752 ml·g^{-1} after 16 days but decreases to 1514 ml·g^{-1} after 32 days. The sample with an initial U(VI) concentration of about 10^{-3} M gives R_d as high as 73574 ml·g^{-1} after 46 days of equilibration.

Table 7.5. Distribution ratio (R_d) of uranium in contact with pyrite in SBCW as function of time, initial U(VI) concentration and filtration at 0.22 μm and 2 nm; C_0: U(VI) concentration in the stock solutions.

Samples	**Time** **days**	***p*H**	**C_0** **mol·l^{-1}**	**R_d** **0.22 μm** **ml·g^{-1}**	**R_d** **2 nm** **ml·g^{-1}**	**Mean R_d** **ml·g^{-1}**
Sp 1-1	1	8.2		79	84	82
Sp 1-2	4	8.3		423	455	439
Sp 1-3	8	8.5	9.09×10^{-6}	2110	2066	2088
Sp 1-4	16	8.6		3481	4022	3752
Sp 1-5	32	8.8		1407	1622	1514
Sp 1-6	46	9.0	9.24×10^{-4}	71983	75165	73574

In BCW, R_d determined after micro- and ultra-filtration are about the same for contact time up to 8 days (Table 7.6). The R_d calculated by considering uranium concentration remaining in solution after filtration at 0.22 μm are constant around 480 ml·g^{-1} after 8 days for initial U(VI) concentration of about 10^{-5} M. On the other hand, the R_d obtained after filtration at 2 nm continuously increases with contact time from 22 ml·g^{-1} after 1 day to 2482 ml·g^{-1} after 32 days. Similar to SBCW, the R_d determined after 46 days for the sample with initial U(VI) concentration of around 10^{-3} M are huge: 27840 and 94539 ml·g^{-1} after micro- and ultra-filtration, respectively.

Table 7.6. Distribution ratio (R_d) of uranium in contact with pyrite in BCW as function of time, initial U(VI) concentration and filtration at 0.22 μm and 2 nm; C_0: U(VI) concentration in the stock solutions.

Samples	**Time** **days**	***p*H**	**C_0** **mol·l^{-1}**	**R_d** **0.22 μm** **ml·g^{-1}**	**R_d** **2 nm** **ml·g^{-1}**
Sp 2-1	1	8.2		19	22
Sp 2-2	4	8.3		315	344
Sp 2-3	8	8.7	9.44×10^{-6}	456	645
Sp 2-4	16	9.1		507	1214
Sp 2-5	32	9.3		481	2482
Sp 2-6	46	9.5	9.26×10^{-4}	27840	94539

7.2.3 Discussion

The huge R_d obtained for initial U(VI) concentration of about 10^{-3} M would indicate that adsorption is not the only mechanism occurring during the interaction between aqueous U(VI) and pyrite. The sorption on the tube walls and filters being excluded, we surmise that the reduction of U(VI) to U(IV) and its subsequent precipitation may take place. Several observations support this assumption.

First, the reduction of U(VI) and the precipitation of a mixed U(VI)-U(IV) oxide in presence of pyrite under anoxic conditions have been already demonstrated by the experimental study of Wersin *et al.* (1994).

Second, the *p*H of the samples is always increasing with time, from 8.2 to 9 in SBCW and to 9.5 in BCW while the E_h is decreasing accordingly (Figure 7.2). Assuming the reduction of U(VI) to U(IV), the *p*H increase may result from the release of carbonate through the reaction:

$$UO_2(CO_3)_3^{4-} + 2e^- \rightleftharpoons UO_2 + 3\ CO_3^{2-}$$

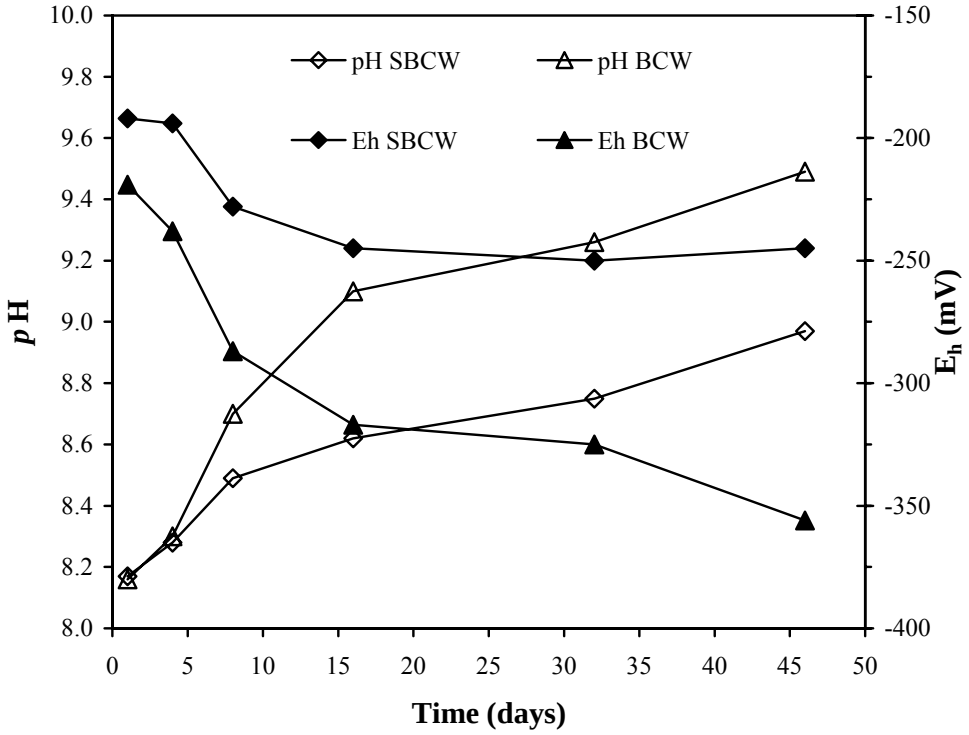

Figure 7.2. *p*H and E_h evolution as function of contact time between aqueous U(VI) and pyrite in SBCW and BCW.

Third, the occurrence of uranium-colloids in BCW would indicate that at least a part of uranium is present in the tetravalent oxidation state. It has been previously demonstrated that there exists a strong colloidal interaction between U(IV) and organic matter (Chapter 6). On the other hand, organic matter complexes or colloids of U(VI) are not significantly formed in the Boom Clay where the speciation of U(VI) is dominated by the carbonate complexes (Chapter 5).

Fourth, the concentrations after contact time longer than one month tend to a constant value around 2×10^{-7} mol·l^{-1} independently from the initial U(VI) concentration (Figure 7.1). This behaviour would indicate a solubility control of the

uranium concentration. According to Wang *et al.* (2000), the solubility of $UO_{2.3333}$(beta) is 3.5×10^{-7} mol·l^{-1} under Boom Clay conditions. Therefore, this solid may be the solubility controlling phase formed upon U(VI) interaction with pyrite.

Several indirect evidences support the assumption that the interaction between aqueous U(VI) and pyrite results in the reduction of U(VI) under Boom Clay conditions. To independently verify this hypothesis, spectroscopic analyses are performed.

7.2.4 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). An important and common application of micro-x-ray adsorption near edge spectroscopy (μ-XANES) is to use the shift of the edge position to determine the oxidation state (see also Chapter 6, section 6.3.2.1). Therefore, this technique can give spectroscopic evidences for the reduction of U(VI) to U(IV).

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

Three solid samples were analysed after interaction with SBCW containing about 10^{-3} M U(VI) under Boom Clay conditions: pyrite, goethite and iron powder. The ratio solution/solid was 20 (10 ml/0.5 g) and the equilibration times were 7 days for the experiments conducted with goethite and iron powder and 78 days for pyrite. The samples were prepared in the anaerobic glove box (< 1 ppm O_2) by collecting the minerals 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 measurements.

As shown in Figure 7.3, the μ-XANES profile shape and absorption maximum of our samples are compared with those of well defined uranium oxidation state standards: UO_2, U_3O_8, uranyl acetate ($UO_2(AcO)_2{\cdot}2H_2O$). Similar to that of iron powder, the spectrum of pyrite lacks the multiple scattering feature (B) observed in the $UO_2(AcO)_2$ and goethite spectra. This demonstrates the reduction of U(VI) to U(IV) after interaction with pyrite and iron powder since the multiple scattering feature (B) is characteristic for U(VI). Indeed, the shoulder (B) results from the interference between uranium and the axial oxygen atoms of the linear uranyl unit (Denecke, 1998 and references therein). 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 energy of the absorption maxima of the iron powder sample lines up with that of the UO_2 reference indicating that they are both tetravalent. The reductive precipitation of U(VI) by iron powder has been already reported in the literature (*e.g.* Gu *et al.*, 1998). The energy of the absorption maxima of the pyrite sample is closer to that of U_3O_8 reference sample since it occurs at 17.175 keV. However, the value of the energy difference between the absorption maximum (A) and the first absorption feature (C) above the absorption maximum is comparable for pyrite and UO_2 reference spectra but not 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 the pyrite sample and in the UO_2 reference. In summary, the pyrite sample shows features which are characteristic for both UO_2 and U_3O_8. Therefore, we conclude that

the interaction between U(VI) and pyrite under Boom Clay conditions leads to the precipitation of a mixed U(VI)-U(IV) oxide. The composition of this mixed oxide is likely between that of UO_2 and $UO_{2.6667}$ (U_3O_8). This intermediate composition is in agreement with the hypothesis that $UO_{2.3333}$ is the solubility controlling phase.

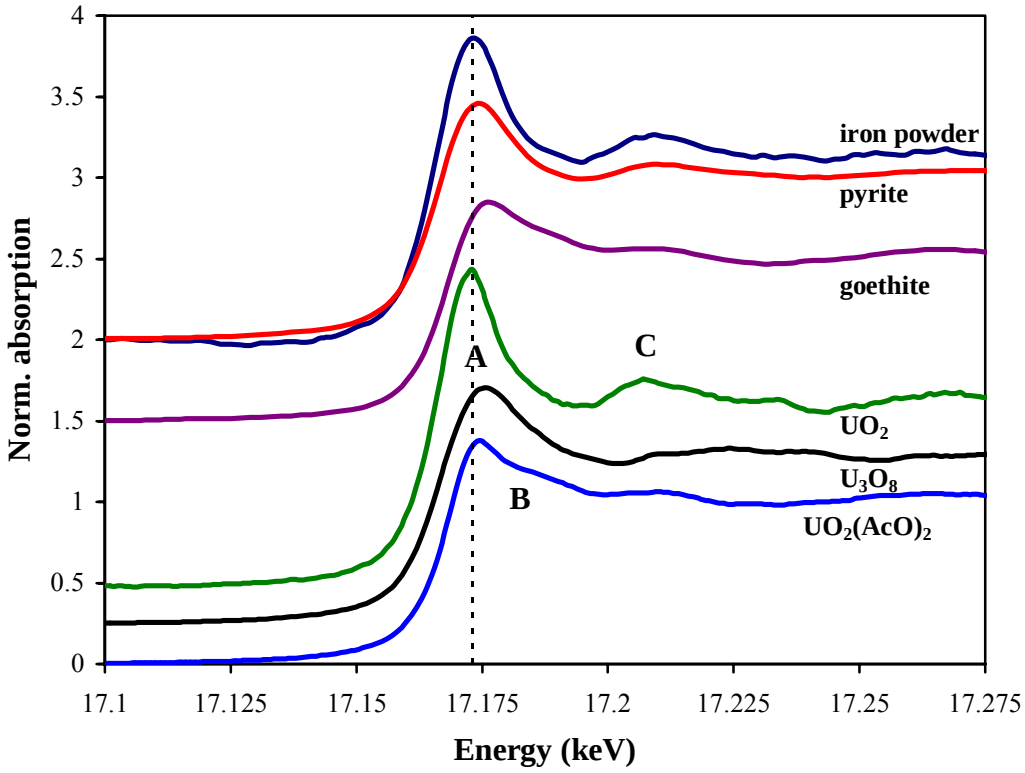

Figure 7.3. UL_{III} edge XANES spectra of uranium after sorption on goethite, pyrite, iron powder and of reference compounds. The dashed line is a guide showing the absorption maximum for UO_2 reference. For clarity, the spectra were shifted along the y-axis. A, B and C mark UL_{III} edge XANES features and are described in the text.

Both experimental and spectroscopic results indicate that pyrite is able to reduce U(VI), occurring as $UO_2(CO_3)_3^{4-}$ under Boom Clay conditions. The precipitate would have an intermediate composition between UO_2 and $UO_{2.6667}$. The solubility of this mixed U(IV)-U(VI) solid is about 10^{-7} mol·l^{-1} and corresponds to the calculated solubility of $UO_{2.3333}$ in the Boom Clay. In the presence of organic matter (BCW), uranium-bearing colloids are formed, presumably U(IV) colloids since there are no colloidal particles of U(VI) neither in SBCW nor in BCW as shown by the filtration of the U(VI) stock solutions.

7.3 U(IV) sorption on various pure minerals

In the Boom Clay, the uranium migration is governed by strong retention mainly due to precipitation (Maes *et al.*, 2003). Therefore, the aqueous concentration of uranium is limited by the solubility of U(IV), about 10^{-8} mol·l^{-1} if UO_2(am) is the solubility controlling phase (see Chapter 6). The migration of this mobile fraction may be retarded by sorption on Boom Clay constituents. Working with bulk Boom Clay samples does not allow to determine which are the constituents responsible for the sorption since the data result from the different components. Therefore, we have performed screening sorption experiments on various pure minerals of the Boom Clay mineral assemblage to determine the most important sorbent(s). The sorption of aqueous uranium present above UO_2(am) was studied in BCW in the presence of reducing agent and under the *in situ* partial pressure of CO_2 ($10^{-2.4}$ atm). The experiments were conducted in a glove box with a controlled Ar–5% H_2-0.4% CO_2 atmosphere (O_2 < 1 ppm).

7.3.1 Experimental

The major difficulty of these experiments is to maintain uranium in its tetravalent oxidation state because U(IV) is readily oxidised to U(VI). We have taken the following precautions to avoid U(IV) oxidation: (i) the experiments were carried out in the presence of dithionite to maintain reducing conditions in the solution for the duration of the experiment, (ii) the U(IV) stock solution was prepared by suspending amorphous U(IV) oxide in BCW; (iii) all experiments were conducted at 25°C in a glove box with a controlled anaerobic and reducing Ar-5% H_2-0.4% CO_2 atmosphere, O_2 content lower than 1 ppm, (iv) all solutions were freshly prepared under anaerobic conditions, and (v) the sample tubes were sealed during equilibration to avoid O_2 diffusion.

Dithionite was selected as reducing agent since it is soluble. Solid reducing agent such as metallic zinc or ion powder also produces reducing conditions, but the solid added to the system is likely to sorb the species being studied.

7.3.1.1 Mineral preparation

The mineralogical composition of the Boom Clay mainly consists of clay minerals (up to 60 wt. %), quartz, feldspars, pyrite and carbonates. The clay mineralogy is dominated by illite, smectite, illite-smectite mixed-layer, kaolinite and chlorite. Other detrital minerals which occur in minor amounts are micas and heavy minerals. Consequently, the following constituents were selected to carry out the screening sorption experiments: kaolinite, illite, illite-smectite mixed-layer, montmorillonite, chlorite, rutile, calcite, apatite and pyrite (Table 7.7).

The clay minerals were obtained form the Source Clay Minerals Repository[1] (University of Missouri-Columbia, USA):

- kaolinite well-ordered (KGa-1b), Washington County, Georgia, USA;
- illite (IMt-2), Silver Hill, Montana, USA;
- Na-montmorillonite (SWy-2), Crook County, Wyoming, USA;
- 70/30 ordered illite-smectite mixed layer (ISCz-1), Czechoslovakia;
- ripidolite (CCa-2), Flagstaff Hill, El Dorado County, California, USA.

[1] http://cms.lanl.gov/sourcecl.html

Illite, illite-smectite mixed layer and ripidolite, which are not supplied as powder, were ground in an agate jar containing 8 agate balls by centrifugation at 400 rpm (Centrifugal Ball Mill S 100, Retsch). For all clay minerals, the less than 63 μm size-fraction, used in the experiments, was separated by dried sieving (As 200 control "g", Retsch).

Titanium(IV) oxide (predominantly rutile) was purchased from Aldrich (22,422-7). It was supplied as a powder with grain size smaller than 5 μm. The calcium carbonate was provided by Belmeco s.a. (Grez-Doiceau, Belgium). The rock is a Belgian Visean carbonate delivered as a powder smaller than 15 μm. The apatite was obtained from Prayon (Engis, Belgium). It originated from the deposits located in the Kola peninsula (East of Finland). The size fraction smaller than 63 μm, which was used in the experiments, was separated by dried sieving (As 200 control "g", Retsch). Pyrite was separated from Boom Clay slurries by wet sieving at 1.25 mm. The fraction bigger than 1.25 mm was collected, dried with acetone to avoid oxidation and ground. To minimise contact with air, the ground pyrite was not sieved and directly stored in an anaerobic glove box.

Table 7.7. Minerals selected to study the sorption of U(IV) and their grain-size.

Minerals	Grain-size
Kaolinite	< 63 μm
Illite	< 63 μm
Na-montmorillonite	< 63 μm
Illite-smectite mixed layer	< 63 μm
Ripidolite (chlorite)	< 63 μm
Rutile	< 5 μm
Ca-carbonate (Belgium)	< 15 μm
Apatite	< 63 μm
Pyrite (Boom Clay)	—

7.3.1.2 U(IV) stock solution

A batch of 250 ml of BCW was equilibrated with the CO_2 partial pressure of the glove box by bubbling a gas mixture containing 0.4% CO_2 for 17 hours. The water was then stored in the glove box under the 0.4% partial pressure of CO_2 for 13 days. After this period, the *p*H was 8.2. Sodium dithionite was then added to BCW to obtain a solution containing 5×10^{-3} mol·l^{-1} of dithionite. This reducing agent was used to maintain very low redox conditions. The addition of dithionite resulted in a *p*H of 7.8. About 1.5 g of amorphous UO_2 (see 6.3.1.2) were suspended in BCW containing dithionite for 10 days. After this equilibration period, the *p*H was decreased to 7.5. The solid was separated from suspensions by filtration at 0.22 μm. The filtrate was used as stock U(IV) solution to perform the sorption experiments. The measured uranium concentration in the filtrate was 2.87×10^{-7} mol·l^{-1}. This value is in agreement with the values reported in Chapter 6 for the solubility of amorphous UO_2 in BCW, *i.e.* about 10^{-8} and 10^{-5} mol·l^{-1} after filtration at 2 nm and at 0.45 μm, respectively.

7.3.1.3 Mineral equilibration

The purpose of this washing step is to establish chemical equilibrium between the minerals and the solution used in the sorption experiments. Half a gram of the selected minerals was weighed into 16 ml polypropylene centrifuge tubes (Nalgene) inside the glove box. A volume of 10 ml of BCW containing 5×10^{-3} M dithionite was added to each tube. The tubes were placed on a shaker for a gentle agitation. After 24 hours of contact, the mixtures were centrifuged at 2500g for 60 minutes to separate solid and liquid. The washing solution was removed with a pipette to prevent removal of the sediment (some liquid remains in the tube). Fresh BCW containing 5×10^{-3} M dithionite was added in order to maintain a solution volume of about 10 ml. The equilibration cycle was repeated twice more for a total of three washes. After removal of the third wash solution, each tube was reweighed. The weight was recorded to determine the volume of residual solution left in each sample.

7.3.1.4 Batch experiments

The batch experiments were performed in duplicates. About 10 ml of the U(IV) stock solutions were added to each sample tubes containing 500 mg of the washed minerals. In addition, 10 ml of U(IV) stock solution were placed in an empty centrifuge tube (blank) to detect sorption of uranium by centrifuge tube walls. The suspensions were gently shaken and equilibrated for 10 days.

At the end of the equilibration period, the aqueous and the solid phase were separated by centrifugation at 2500g for 60 minutes. The *p*H was measured with a combined glass electrode (Metrohm) calibrated against *p*H buffers 7 and 9. One aliquot of 5 ml was sampled in each tube for filtrations at 0.22 μm. A volume of 1 ml of the sample was first filtered to saturate any possible adsorption sites. This filtrate was discarded before filtering the solution for analyses. Afterwards, the remaining 4 ml were passed trough the conditioned filter at 0.22 μm with a syringe. The filtrates were analysed for uranium by High-Resolution Inductively Coupled Plasma-Mass Spectrometry (Royal Museum for Central Africa, Tervuren, Belgium) with an analytical error of about 5 %.

7.3.2 Results and discussion

All results relating to the sorption study of U(IV) on various pure minerals are given in Appendix 2.

7.3.2.1 Mineral characterisation

The mineral characterization is essential to verify their purity. All minerals were characterised by x-ray diffraction (XRD), x-ray fluorescence (XRF) and surface specific area.

XRD and XRF analyses were performed at the Cellule Interdépartementale d'Analyse of the University of Louvain-la-Neuve (Belgium). The characterisation study indicates that the selected minerals are sufficiently pure to be used as representative components of the Boom Clay. The XRD patterns and the chemical composition are given and discussed in Appendix 4.

The bulk sample of kaolinite contains about 1 wt. % of TiO_2, mainly anatase. Quartz is the only mineral present besides the clay minerals in the bulk sample of illite, illite-smectite mixed-layer, Na-montmorillonite and ripidolite. The bulk sample of illite also contains minor amounts of feldspar. The presence of quartz and feldspar

is not considered as a problem since they are common minerals in the Boom Clay. The XRD patterns of the clayey fraction of the clay minerals confirm the purity of kaolinite, illite, ripidolite and illite-smectite mixed layer of which the ratio illite to smectite is 70/30. About 10% of illite could be present in the clayey fraction of Na-montmorillonite.

The purity of the non-clay minerals is also verified. The rutile sample is composed for more than 99 wt. % of TiO_2. Rutile is the predominant TiO_2 polymorph but anatase is detected by XRD in minor amounts. The calcium carbonate consists for more than 99 wt. % of a pure calcite. The apatite sample is identified by XRD as a fluoro-apatite which constitutes more than 92 wt. % of the sample. Finally, the Boom Clay pyrite sample mainly contains pyrite (~91 wt. %), quartz being the main impurity (6 wt. %).

The measurement of the surface area was carried out at the Laboratory for adsorption and catalysis of the University of Antwerpen (Belgium). The N_2-adsorption isotherms were recorded on Autosorb-1-MP (Quantachrome Corp.). The results are given in Table 7.8. When available, they are compared with the values of surface area given on the website of the Source Clay Minerals Repository (http://cms.lanl.gov/chem.htm).

Table 7.8. Surface area of the selected minerals determined by N_2-adsorption. SCMR: data given on the website of the Source Clay Minerals Repository.

Mineral	Surface area $m^2 \cdot g^{-1}$	Surface area SCMR $m^2 \cdot g^{-1}$
Kaolinite	11.39	10.05
Illite	27.32	—
Na-montmorillonite	30.93	31.82
Illite-smectite mixed layer	25.02	—
Ripidolite (chlorite)	3.49	—
Rutile	3.27	—
Ca-carbonate	2.38	—
Apatite	1.02	—
Pyrite (Boom Clay)	4.84	—

7.3.2.2 Uranium sorption on the tube walls and on the filters

The uranium sorption on the tube walls and on the filters is verified. Sorption on tube walls is controlled by measuring the uranium concentration in the blank sample. The measured concentration is compared with the uranium concentration of the stock solution (Table 7.9). About 40 % of uranium is sorbed on the tube walls at *p*H 7.5.

Table 7.9. Study of the uranium sorption on the tube walls

U(IV) stock solution $mol \cdot l^{-1}$	Blank $mol \cdot l^{-1}$	Difference relative to initial concentration %
2.87×10^{-7}	1.62×10^{-7}	43

The uranium sorption on the filter is checked by comparing the uranium concentrations measured in the blank sample after two filtrations at 0.22 μm. The first filtration was done after filter conditioning with 1 ml of the solution while the second filtration was performed after filter conditioning with 5 ml. The similar concentrations measured in both filtrates mean that filter conditioning with 1 ml is sufficient to saturate any sorption site of the filter membrane (Table 7.10).

Table 7.10. Study of the uranium retention by the 0.22 μm filter. Filtrate 1 and 2 refer to filtrates obtained after filter conditioning with 1 and 5 ml, respectively.

Sample	[U] filtrate 1	[U] filtrate 2	Difference relative to filtrate 1 concentration
	mol·l^{-1}	**mol·l^{-1}**	**%**
Blank	1.62×10^{-7}	1.68×10^{-7}	3.6

7.3.2.3 Distribution ratio

The distribution ratios (R_d) are calculated using equation 7.6. This equation is reminded below:

$$R_d = \frac{(C_0 \cdot V_0) - C_f \cdot (V_0 + V_{residual})}{C_f \cdot m_{mineral}} \qquad \text{Eq. 7.7}$$

where C_0 is the uranium concentration in the U(IV) stock solution; V_0 is the volume of the U(IV) stock solution (ml) added to the washed minerals; C_f is the concentration of uranium remaining in solution after sorption; $V_{residual}$ is the volume of the residual solution left from the third wash (ml); and $m_{mineral}$ is the dry weight of the mineral (g). The dried weight of the minerals is calculated by taking into account their moisture content (wt. % H_2O).

$$m_d = m_w - \left(m_w \times \frac{H_2O(\%)}{100} \right) \qquad \text{Eq. 7.8}$$

where m_d is the dried weight and m_w is the wet weight, *i.e.* the mass of the mineral weighed in the centrifuge tube. The moisture content is determined by weighing a given amount of the mineral before and after heating at 110°C for 48 hours. The measurements were performed in duplicates and averaged. The moisture content is less than 1 wt. % in non-clay minerals, kaolinite and ripidolite. It is considered as negligible for pyrite (Table 7.11).

Table 7.11. Determination of the moisture content (wt.% H_2O) in the selected minerals.

Mineral	Wet weight g	Dried weight g	H_2O in the wet mineral wt.%	Mean H_2O content wt.%
Kaolinite	1.4987	1.4930	0.38	0.39
Kaolinite	1.4073	1.4017	0.40	
Illite	3.8625	3.7883	1.92	1.87
Illite	4.0915	4.0169	1.82	
Na-montmorillonite	3.9309	3.7503	4.59	4.61
Na-montmorillonite	3.7746	3.6002	4.62	
Illite-smectite mixed layer	3.4621	3.3658	2.78	2.79
Illite-smectite mixed layer	3.5201	3.4218	2.79	
Ripidolite (chlorite)	2.9048	2.8981	0.23	0.20
Ripidolite (chlorite)	2.9460	2.9408	0.18	
Rutile	3.9587	3.9574	0.03	0.03
Rutile	4.7924	4.7908	0.03	
Ca-carbonate	4.8831	4.8804	0.06	0.06
Ca-carbonate	5.5618	5.5580	0.07	
Apatite	3.6069	3.6056	0.04	0.03
Apatite	2.2918	2.2913	0.02	
Pyrite (Boom Clay)	—	—	—	—
Pyrite (Boom Clay)	—	—	—	

The R_d can be overestimated if uranium is sorbed by the tube walls. In that case, the decrease of uranium concentration in solution is not only due to sorption on minerals but also to sorption on the tube walls. The blank sample shows that about 40% of uranium is sorbed by the centrifuge tube. Nevertheless, this percentage can be much lower in presence of minerals if the uranium affinity towards the minerals is much higher than that towards the tube walls. A possible option is to determine the uranium concentration sorbed on the minerals by chemically remove it from the sorbent and measure it. However, the method is often subject to incomplete removal of the element sorbed or loss of material during additional steps required for extraction, or both. Therefore, we prefer to determine minimum and maximum R_d according to that the sorption on the tube walls is taken into account or not. Minimum R_d is calculated by considering that the uranium concentration remaining in solution after sorption (C_f) should be 40% higher than the concentration effectively measured. Maximum Rd is determined by using the concentration effectively measured in solution at the end of the sorption test. The R_d is calculated for each duplicate and averaged (Table 7.12).

Except montmorillonite, clay minerals sorb more uranium than the non-clay minerals. The most efficient sorbents are: illite-smectite mixed layer, illite and ripidolite. The negative R_d values obtained with montmorillonite are questionable. Indeed, the sorption properties of illite-smectite mixed layer are higher than those of illite alone indicating that the presence of smectite favours the retention of uranium. Although uranium contamination during the manipulations in the glove box can not be excluded, the absence of uranium sorption on montmorillonite is ascribed to the swelling properties of this mineral. The formation of a kind of gel is noticed in the samples tubes containing montmorillonite while the other minerals occur as particles dispersed throughout the solution by shaking. This gel greatly reduces the surface contact between the mineral and the solution resulting in a low uranium retention. The R_d values of kaolinite and calcite are similar. The less efficient sorbents are apatite, pyrite and rutile.

Table 7.12. Distribution ratio (R_d) for the sorption of U(IV) on pure minerals in BCW after 10 days. The concentration of the U(IV) stock solution is 2.9×10^{-7} mol·l^{-1}. Min.: uranium sorption on the tubes walls considered; max: uranium sorption on the tubes walls not considered.

Samples	Mineral	pH	Min. R_d ml·g^{-1}	Max. R_d ml·g^{-1}	Mean min. R_d ml·g^{-1}	Mean max. R_d ml·g^{-1}
Sp 4-1	kaolinite	8.2	125	183	74	111
Sp 4-2	kaolinite	8.1	22	39		
Sp 4-3	illite	8.1	314	447	344	489
Sp 4-4	illite	8.1	374	531		
Sp 4-5	montmorillonite	7.7	- 17	-13	-9	-2
Sp 4-6	montmorillonite	7.7	- 1	10		
Sp 4-7	illite-smectite m.l.§	8.0	502	712	500	707
Sp 4-8	illite-smectite m.l.§	7.9	497	703		
Sp 4-9	ripidolite	8.2	281	402	254	364
Sp 4-10	ripidolite	8.3	227	326		
Sp 4-11	rutile	8.1	10	22	8	19
Sp 4-12	rutile	8.1	7	16		
Sp 4-13	Ca-carbonate	8.2	77	115	88	130
Sp 4-14	Ca-carbonate	8.2	100	146		
Sp 4-15	apatite	8.3	40	63	39	62
Sp 4-16	apatite	8.3	38	60		
Sp 4-17	pyrite	8.2	27	46	26	44
Sp 4-18	pyrite	8.1	25	42		

§: m.l. for mixed layer.

R_a is obtained by normalizing R_d to the measured surface area (S_A) of the minerals:

$$R_a\ (ml\cdot m^{-2}) = R_d/S_A \qquad \text{Eq. 7.9}$$

The determination of R_a shows that the sorption properties of the clay minerals towards U(IV) are lower than that of apatite and calcite, except ripidolite which becomes the most important sorbent (Table 7.13). These results indicate that the sorption properties of the clay minerals are mainly due to their high surface area. Pyrite and rutile remain the less efficient sorption sinks.

Table 7.13. R_a for the sorption of U(IV) on pure minerals in BCW after 10 days. The concentration of the U(IV) stock solution is 2.9×10^{-7} mol·l^{-1}. Ra is the distribution ratio (R_d) normalised to surface area (S_A). Min.: uranium sorption on the tubes walls considered; max: uranium sorption on the tubes walls not considered.

Mineral	S_A m^2·g^{-1}	Min. R_d ml·g^{-1}	Max. R_d ml·g^{-1}	Min. R_a ml·m^{-2}	Max. R_a ml·m^{-2}
Kaolinite	11.39	74	111	6	10
Illite	27.32	344	489	13	18
Montmorillonite	30.93	~0	~0	0	0
Illite-smectite mixed layer	25.02	500	707	20	28
Ripidolite	3.49	254	364	73	104
Rutile	3.27	8	19	2	6
Ca-carbonate	2.38	88	130	37	55
Apatite	1.02	39	62	38	61
Pyrite	4.84	26	44	5	9

To determine the most important sorbents of U(IV) in the Boom Clay, the R_d is also normalised to the abundance of the minerals:

$$\text{Wt. \% normalised } R_d = R_d \times \left(\frac{\text{wt. \%}_{\text{mineral}}}{100} \right) \qquad \text{Eq. 7.10}$$

By normalising the R_d to the abundance of the different minerals in the Boom Clay, it is clear that illite and illite-smectite mixed-layer are the dominant sorbents for uranium in solution above UO_2(am) under reducing conditions (Table 7.14).

Table 7.14. Distribution ratio (R_d) normalised to the abundance of the minerals for the sorption of U(IV) in BCW after 10 days. The concentration of the U(IV) stock solution is 2.9×10^{-7} mol·l^{-1}. Min.: uranium sorption on the tubes walls considered; max: uranium sorption on the tubes walls not considered.

Mineral	**Abundance** wt. %	**min. R_d** ml·g^{-1}	**max. R_d** ml·g^{-1}	**Wt.% normalised min. R_d** ml·g^{-1}	**Wt.% normalised max. R_d** ml·g^{-1}
Kaolinite	10	74	111	7	11
Illite	20	344	489	69	98
Montmorillonite	15	~0	~0	0	0
Illite-smectite mixed layer	15	500	707	75	106
Ripidolite	5	254	364	13	18
Rutile	< 1	8	19	0	0
Ca-carbonate	max. 5	88	130	4	7
Apatite	< 1	39	62	0	1
Pyrite	max. 5	26	44	1	2

7.4 Conclusion

From the literature review, the sorption of U(VI) is expected to be weak under Boom Clay conditions. Indeed, U(VI) occurs as a carbonate complex ($UO_2(CO_3)_3^{4-}$) which was shown to be weakly sorbed by previous authors. Moreover, the presence of humic acids reduces the sorption at alkaline *p*H. Nevertheless, the interaction of U(VI) with pyrite, the most abundant reducing mineral in Boom Clay, leads to the reduction of U(VI) and the subsequent precipitation of U(IV)-U(VI) mixed oxide. Both experimental and spectroscopic results evidence that pyrite is able to reduce $UO_2(CO_3)_3^{4-}$ under Boom Clay conditions. The solubility of the precipitated U(IV)-U(VI) phase is about $\sim 10^{-7}$ mol·l^{-1}. The measured uranium concentration and the μ-XANES results would indicate that $UO_{2.3333}$ is the solubility controlling phase. In BCW, the presence of organic matter favours the formation of uranium-bearing colloids upon interaction of U(VI) and pyrite.

Sorption experiments on various pure phases of the Boom Clay mineral assemblage demonstrate that aqueous uranium above UO_2(am) in BCW is significantly sorbed on minerals (R_d up to ~600 ml·g^{-1}). The distribution ratio normalised to the mineral surface area shows that ripidolite, apatite and calcite present the best properties to sorb U(IV). However, due to their high surface area and abundance, clays minerals are the most efficient sorbents for U(IV) in the Boom Clay. Among the clay minerals, illite and illite-smectite mixed layer are of special importance. Montmorillonite is expected to play a significant role in the retention of uranium since illite-smectite mixed layer sorbs more uranium than illite alone. Unfortunately, the results do not verify this statement, probably because of experimental problems. Pyrite and rutile are the less important sorption sinks.

This study confirms that uranium migration in the Boom Clay is governed by a strong retention. A likely mechanism is the reduction by pyrite of mobile U(VI) to sparingly soluble U(IV)-U(VI) mixed precipitate. Moreover, the transport of the mobile fraction above the U(IV) solubility controlling phase, presumably $U(OH)_4$(aq), is retarded by significant sorption on some Boom Clay minerals, mainly clay minerals which represent up to 60 wt. % of the Boom Clay.

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