Chapter 5
Complexation of U(VI) by humic acids

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5.1 Introduction

The strong complexing and redox interactions of humic materials with metal ions are very important in the migration of radionuclides in geological media (Choppin, 1988). Already in 1951, Szalay concluded that the insoluble humic acids (HA) were responsible for the accumulation of uranium in bioliths via a cation exchange process (Szalay, 1964). In Boom Clay, the spatial association between naturally occurring uranium is ascribed to the reduction of U(VI) to U(IV) during early diagenesis (Chapter 2). If organic matter is involved in uranium accumulation, it may also play a role in migration of this element as water soluble complex (Munier-Lamy *et al.*, 1986). Therefore a question arises: "Can the high concentration of dissolved organic carbon (about 115 $mg \cdot l^{-1}$) in Boom Clay pore water play an important role in the mobility of uranium ?". If uranium is complexed by mobile organic matter molecules and forms a stable complex, the transport of uranium may be enhanced. This topic is of crucial importance for performance assessment of a radioactive waste repository when considering the impact of natural organic matter on the uranium migration. An assessment of the U(VI) complexation by HA is therefore necessary by considering that the hexavalent oxidation state of uranium dominates under Boom Clay conditions.

The complexation of metal such as uranium by HA is an arduous subject. In the introduction, we will expose the difficulty to express the interaction between metal ions and HA in a thermodynamic sense. Afterwards, we will give a review of the available complexation constant of U(VI) by HA. Most of these complexation constants are determined at low *p*H and can not be extrapolated to the Boom Clay conditions. Finally, we will remind the main results of the previous studies about the extent of the interaction between uranium and HA under Boom Clay conditions.

5.1.1 Metal complexation by humic acids

From a thermodynamic point of view, humic acids (HA) cannot be treated as simple organic or inorganic ligands. Simple ligands are ligands with fully characterised nature, structure and properties (*e.g.* Cl^-, CO_3^{2-}, acetate, ...).
Complexation of a cation M with a simple ligand L is commonly described as:

$$M + L \rightleftharpoons ML \qquad \text{Eq. 5.1}$$

The corresponding complexation constant[1], β, is defined as:

$$\beta = \frac{[ML]}{[M] \cdot [L]} \qquad \text{Eq. 5.2}$$

where [ML] is the metal bound to the ligand concentration, [M] and [L] are the metal free and ligand free concentrations, respectively.

[1] Considering that the concentration is equal to the activity under given conditions.

Complexation reaction of a cation M by HA can be described as:

$$M + HA \rightleftharpoons MHA \qquad \text{Eq. 5.3}$$

The corresponding complexation constant is defined as:

$$\beta = \frac{[MHA]}{[M]\cdot[HA]} \qquad \text{Eq. 5.4}$$

where [MHA] is the metal bound to the HA concentration, [M] and [HA] are the metal free and HA free concentrations, respectively.

Although equations 5.2 and 5.4 closely resemble, there are two fundamental differences (Hummel, 1997). First, simple ligands in equation 5.2 are ligands with well characterised molecular structure, nature and number of functional groups. In contrast, HA are ill-defined substances. Their molecular structure is poorly characterised. The nature and number of functional groups involved in metal binding are uncertain and the stereochemistry is largely unknown. A complex of stoechiometry 1:1 in the case of HA is defined as a metal ion bound to an unknown number of functional groups within the same humic molecule. The second difference between equations 5.2 and 5.4 is closely related to the first one, and concerns the estimation of the concentration of HA involved in the reaction. This value is model-dependent. Sometimes, the HA concentration is given in $g\cdot l^{-1}$ (Glaus *et al.*, 2000). More commonly, the concentration is expressed as a functional group content and $equivalent\cdot l^{-1}$ is used. One way to convert the mass of HA added per unit volume of solution into the equivalent concentration of binding sites available for complexation with the metal ion is to determine the proton exchange capacity of HA, *i.e.* the total amount of dissociable protons per unit mass of HA. The latter can be measured by *p*H titration.

Besides the problems to express the interaction between metal ions and HA in a thermodynamic sense, several properties of HA can influence the complexation reaction: their polyfunctional, polyelectrolyte and polydispersive properties. The polyfunctionality of HA results from the multiplicity of the functional groups. Humic acids mainly contain carboxylic and phenolic groups, but also amino and quinone groups among others (Stevenson, 1982). Identical functional groups are present in different configurations and thus have somewhat different binding properties. Although there is a variety of functional groups in their structures, HA complex metals via their carboxyl or phenolic groups (Kříbek and Podlaha, 1980; Choppin, 1985; Stumm and Morgan, 1996). The polyelectrolyte properties originate from the ionic character of HA (mainly from the carboxylic groups). As *p*H increases, the increased deprotonation makes the HA more negatively charged. This negative charge creates an electrical field which influences the complexation reaction. The polydispersive properties of HA come from their structures which are random coils which expand and shrink in reaction to the *p*H, to the ionic strength and to the binding of cations (Choppin, 1992).

Humic acids being heterogeneous mixture of polyelectrolytes containing different functional groups, they present a broad distribution of complexation constants. Several models of varying complexity have been developed to mathematically describe the interaction between metal ions and HA. A comprehensive review of the common models is proposed by Dierckx (1995) and Hummel (1997). It is obvious that the resulting numerical values of the complexation

constants are different depending on the model used. They cannot be always compared and must be considered with caution.

In the present research, we have used the discrete sites non-electrostatic approach by assuming the formation of a 1:1 complex. The proton concentration is not included as a variable and the influence of the electrostatic forces is not taken into account. Using this model, the effects resulting from the variations of parameters such as *p*H and ionic strength are neglected. Consequently, the resulting complexation constants are highly conditional since they are only valid under given experimental conditions. That is why the term of conditional complexation constant is employed. The selected model provides a valuable and simple tool for the purpose of this study, *i.e.* the determination of a conditional constant for the complexation of U(VI) by HA under geochemical conditions representative for the Boom Clay.

5.1.2 State of the art on the complexation of U(VI) by humic acids

Several experimental and modelling studies existing in the literature have examined the complexation of U(VI) by HA (Table 5.1). These studies concluded that HA have a strong affinity for U(VI). The affinity was shown to vary as a function of the experimental method, the HA used and the model.

Table 5.1. Published results on the complexation constants (β) of U(VI) with HA.

***p*H**	**Ionic strength** mol·l^{-1}	**Log β 1:1 complex** L/mol or L/eq	**Log β 1:2 complex** L/mol or L/eq	**References**
3.5 - 7	0.1	7.8	—	Kříbek and Podlaha, 1980
6	0.01	4.72 §	—	Li *et al.*, 1980
		6.73 #	—	
4	0.1	5.11	8.94	Shanbhag and Choppin, 1981
4.5 - 6	0.1	5.0 + 4.8 α*	8.5 + 4.5 α*	Choppin, 1985
4.5	0.01	6.5	—	Giesy *et al.*, 1986
3.5 – 4.5	0.1	4.0 – 5.2	8.1 – 9.3	Munier-Lamy *et al.*, 1986
4.7 - 5.6	?	7.2 - 8.3	—	Choppin, 1992
4	0.1	6.16	—	Czerwinski *et al.*, 1994
4 - 6	0.1	7.2 - 7.8	—	Moulin and Moulin, 1995
3.9	0.1	6.16	—	Pompe *et al.*, 1998
4 - 5	0.1 – 0.004	6.08	—	Montavon *et al.*, 2000
4 - 5	0.1	6.75 – 7.57	—	Lenhart *et al.*, 2000
		4.75 – 5.38	8.39 – 9.59	
		7.59 – 7.64#	—	

§: constant for "weak affinity" binding sites
#: constant for "strong affinity" binding sites
*: α is degree of ionisation of HA functional groups

From Table 5.1, it clearly appears that most of the data reported in the literature were determined under conditions that are irrelevant for most of nuclear waste repositories: low *p*H and high ionic strength. The main reason for this is that the hydrolysis and carbonate complexation of uranium are negligible at low *p*H. Under these conditions, mainly two species are present in solution: the U(VI)-HA complex and the free uranyl cation (UO_2^{2+}). All authors agree that the complexing capacities are sensitive to *p*H, ionic strength and metal concentration. Therefore, applying these complexation constants to conditions of alkaline *p*H is basically wrong (Van Loon *et al.*, 1992). However, such extrapolation was performed by Moulin and Moulin (1995). They concluded that under Boom Clay conditions humate complexes dominate the

speciation of trivalent actinides while hexavalent actinides are present as carbonate complexes. Although the HA complexation constants are of the same order of magnitude for trivalent actinides and U(VI), the hydrolysis and carbonate complexation constants of U(VI) are much higher (Table 5.2). Sensitivity studies show that some *p*H variations or a reduced CO_2 partial pressure will modify these conclusions in favour of organic complexation (Moulin and Moulin, 1995).

Table 5.2. First order constant for HA, hydrolysis and carbonate complexation of Eu, Cm, Am and U at an ionic strength of 0.1M.

Radionuclides	Log K_{MHA}	Log K_{MOH}	Log K_{MCO3}	References
Eu	6.7	6.5	6.57	Dierckx (1995); Yun *et al.* (2001); Kim *et al.* (1994)
Cm	6.24	5.76	6.65	Czerwinski *et al.* (1996); Fanghänel *et al.* (1994); Kim *et al.* (1994)
Am	6.24	6.21	6.81	Czerwinski *et al.* (1996); Guillaumont *et al.* (2003)
U	6.16	8.36	9.15	Czerwinski *et al.* (1994); Guillaumont *et al.* (2003)

As mentioned previously, only very few data on the complexation of U(VI) by HA that are relevant for performance assessment of an underground repository for radioactive waste are available. Conditional complexation constants for the formation of complexes of HA with U(VI) from *p*H 5 to 10 and at ionic strength varying between 0.02 and 0.2 M were measured by Glaus (Glaus *et al.*, 1995; Glaus *et al.*, 2000). The logarithm of the complexation constant increases markedly with increasing *p*H, from 6 L/g at *p*H 5 to about 12 L/g at *p*H 10. The influence of ionic strength is of less importance.

5.1.3 Uranium interaction with humic acids under Boom Clay conditions

The studies on the interaction between uranium and HA under Boom Clay conditions provide contradictory results.

Dierckx *et al.* (2000) carried out complexation experiments to gain a rough idea about the extent of uranium-Boom Clay HA interaction. The results indicate no obvious evidence for the formation of U(VI) complexes with Boom Clay HA. Further results were obtained from sorption experiments of U(VI) on Boom Clay as a function of the Boom Clay to SBCW ratio (Dierckx *et al.*, 2000). As the solid-liquid ratio increases, the concentration of organic matter in solution increases. For many radionuclides (Np, Tc, Pu, Eu and Am), the sorption always decreases as the organic matter content in solution increases. This observation suggests that the formation of complexes with organic matter in solution hinders the sorption of these radionuclides. On the contrary, the sorption of U(VI) increases as the dissolved organic matter concentration increases. These results indicate that U(VI) does not form strong complexes with soluble organic matter; probably because of the competition with the very stable carbonate complexes (Dierckx *et al.*, 2000).

The absence of interaction between uranium and HA was also noticed by Thang and Geckeis (1999). They investigated the size distribution of humic/fulvic bound to metal species in BCW. The results point out that uranium is not associated with the main fraction of humic/fulvic acids. However, data obtained from analysis on BCW collected from piezometers are in contradiction with the previous findings. By plotting the uranium concentration as a function of the dissolved organic carbon, it is

obvious that the uranium concentration is increasing as the organic carbon concentration increased. Although the linear correlation is poor, this observation suggests that natural uranium is associated with Boom Clay organic matter (Wang *et al.*, 2000a).

Because of the contradictory findings on the interaction of Boom Clay organic matter and uranium and the lack of data on complexation constant of U(VI) by HA under Boom Clay conditions, further studies are very much needed. Therefore, we have conducted experiments to investigate the extent of U(VI) complexation by HA and to determine conditional complexation constant. Dialysis experiments were performed in SBCW under the *in situ* partial pressure of CO_2 ($pCO_2 = 10^{-2.4}$ atm). The *p*H was about 8.2 and the ionic strength of 1.5×10^{-2} M. The O_2 content was approximately 5 ppm but sometimes increased up to 8 ppm. The U(VI) concentration was held constant at 4.5×10^{-7} mol·l^{-1} while the HA concentration was varied, from 90 to 1220 mg·l^{-1}.

5.2 Experimental

5.2.1 Concentration and purification of humic acids

Three different batches of HA were used: commercially available Aldrich HA, oxidised Boom Clay HA extracted under atmospheric conditions and non-oxidised Boom Clay HA concentrated under anaerobic conditions (Table 5.3). This last batch is considered as the most representative of Boom Clay natural organic matter.

Humic acids from the Aldrich Company (catalogue number: H1, 675-2) were used after purification. Two samples of respectively 70 g and 80 g were dissolved in 800 ml solutions containing 0.1 M NaOH and 0.01M NaF. After shaking overnight, the HA were precipitated by acidifying the solutions at *p*H 1 with concentrated HCl. The suspensions were centrifuged at 12100xg for 30 minutes. The coagulate was collected in Spectra/Por® regenerated cellulose membranes with a molecular weight cut-off (MWCO) of 6-8000 and dialysed against 0.1 M HCl for one week with regular change of the HCl solution. The HA in the protonated form were dialysed against demineralised water until Cl^- was removed, *i.e.* the conductivity of the water was less than 20 μS·cm^{-1}. Finally, they were freeze-dried and stored in the dark at a temperature of 4°C.

Oxidised Boom Clay 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). A volume of 50 ml of the concentrated organic matter was dialysed against demineralised water in 1000 MWCO Spectra/Por® regenerated cellulose membranes until the organic molecules smaller than the membrane pore size , mainly fulvic acids, were leached out. Afterwards, the HA were 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.

Non-oxidised Boom Clay HA were prepared by freeze-drying BCW under anaerobic conditions. The extraction and purification of the Boom Clay HA were performed in a N_2-glove box (O_2 < 3 ppm) and all solutions were prepared from ultra-pure water (Milli-Q) after prior degassing (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 flasks of the freeze-drier were filled several times in the glove box with a total volume of about 3.5 l of BCW sampled under anaerobic conditions from the EG/BS piezometer. After freeze-drying under vacuum, the flasks were opened in the glove box and the dried material was dialysed against degassed ultra-pure water. Spectra/Por® regenerated cellulose membranes of 1000 MWCO were used to allow the leaching of the salts and the fulvic acids. Once no leaching of organic matter was noticed, the Boom Clay HA were protonated, rinsed and freeze-dried according to the procedure followed for Aldrich and oxidised Boom Clay HA. The purified material (about 80 mg) was stored under anaerobic conditions.

Table 5.3. Types of humic acids (HA) used in the study of the U(VI) complexation**.**

HA	Oxidation	Source
Aldrich	oxidised	Aldrich company
Boom Clay	oxidised	concentration in air of dissolved organic matter in BCW with DEAE-cellulose
Boom Clay	non-oxidised	concentration under anaerobic conditions of dissolved organic matter in BCW by freeze-drying

5.2.2 Preparation of humic acids mother solutions

Mother solutions of HA were prepared by dissolving purified HA in SBCW to obtain a final concentration of about 1000 to 1500 $mg \cdot l^{-1}$. The *p*H was adjusted to the target *p*H of 8.2 with aliquots of 1M NaOH. Mother solutions of Aldrich HA were prepared under atmospheric conditions and afterwards allowed to equilibrate under the 0.4% partial pressure of CO_2 inside the glove box. On the other hand, mother solutions of Boom Clay HA were directly prepared inside glove box. The HA solutions at various concentrations were obtained by diluting the HA mother solutions with SBCW.

5.2.3 Parameters studied in the complexation experiments

The complexation experiments were performed in SBCW at *p*H about 8.2 under the *in situ* pCO_2 at $10^{-2.4}$ atm (Ar – 0.4% CO_2 glove box, ~ 5 ppm O_2). Several sets of complexation experiments (Cp-#) were conducted by considering several parameters which may influence the U(VI) complexation (Table 5.4).

Test Cp-2 was carried out with Aldrich HA and in the presence of hydrogen-phosphate at a concentration of 7.7×10^{-5} $mol \cdot l^{-1}$. This concentration is about two times higher than the HPO_4^- content in BCW reported by Dierckx (1997). The reason of such a high concentration is to investigate the possible competing effect of HPO_4^- with HA and carbonate. Indeed, phosphate is known to be a strong complexing agent for uranium (Langmuir, 1978).

Test Cp-3 was also conducted with Aldrich HA but in the absence of hydrogen-phosphate since more recent measurements have shown that the HPO_4^- content in BCW is below the detection limit, *i.e.* 2.5 ppm (Wang *et al.*, 2000b).

Test Cp-4 was performed with oxidised Boom Clay HA which are more representative of the Boom Clay organic matter than Aldrich HA.

Test Cp-5 was conducted with non-oxidised Boom Clay HA which are the most representative of dissolved natural organic matter in the Boom Clay.

Test Cp-7 was designed to study the effect of oxidation but also the influence of the U(VI) concentration. Humic acids solution was simply BCW. One batch of BCW was sampled under anaerobic conditions while the other was oxidised by

contact with air for two days and by bubbling with pure O_2 for two hours. Uranium concentration was varied from 10^{-7} to 10^{-4} mol·l^{-1}.

Tests Cp-8 and Cp-9 were performed under atmospheric partial pressure of CO_2 ($pCO_2 = 10^{-3.5}$ atm). By varying the pCO_2, the carbonate concentration in solution changes. Consequently, the competing effect of carbonate with HA for U(VI) complexation can be evaluated. These experiments were conducted at *p*H ~ 8 with oxidised Boom Clay HA. The *p*H in the first experiment was regularly adjusted by addition of NaOH or HCl (Cp-8) while the second experiment was carried out in Trizma buffer at *p*H 8.1 (Cp-9). The ionic strength was fixed at 1.5×10^{-2} M by $NaClO_4$ and the U(VI) concentration was about 4.5×10^{-7} mol·l^{-1}.

Table 5.4. Overview of the complexation experiments and the parameters studied; BCW: Boom Clay pore water, TOC: Total Organic Carbon.

Test Cp-#	Humic acids (HA)	TOC mg·l^{-1}	Atmosphere	Parameters
Cp-2	Aldrich HA	0 - 640	Ar – 0.4% CO_2	HPO_4^{2-}
Cp-3	Aldrich HA	0 - 414	Ar – 0.4% CO_2	HPO_4^{2-}
Cp-5	oxidised Boom Clay HA	0 - 590	Ar – 0.4% CO_2	oxidation
Cp-6	non-oxidised Boom Clay HA	0 - 560	Ar – 0.4% CO_2	oxidation
Cp-7	oxidised BCW non-oxidised BCW	~ 60	Ar – 0.4% CO_2	oxidation, U concentration
Cp-8	oxidised Boom Clay HA	0 - 790	air	pCO_2
Cp-9	oxidised Boom Clay HA	0 - 490	air	pCO_2

5.2.4 Dialysis technique

5.2.4.1 Principle

The dialysis technique has been described by Li *et al.* (1980), Van Loon *et al.* (1992), Dierckx *et al.* (1994) and Glaus *et al.* (1995). This technique allows to determine a conditional complexation constant over a broad range of *p*H and ionic strength. Basically, the equilibrium dialysis-ligand exchange technique measures the complexation constant of the metal-HA complex relative to a reference metal-ligand (L) complex of known stability. Equilibrium dialysis is used to distinguish between metal bound to the reference ligand and the metal bound to the HA (Van Loon *et al.*, 1992). Practically, this technique involves a physical separation, the membrane, to distinguish between metal-humate and other metal species (Figure 5.1). The metal humate species are hindered completely to pass the membrane while the other metal species diffuse freely through the membrane.

5.2.4.2 Experimental procedure

Dialysis experiments were performed in 50 ml Pyrex® culture tubes. All tubes and glassware were first cleaned with soap, followed by sequential base (1% NaOH) and acid baths (10% HCl), after which they were rinsed at least three times with deionised water. The dialysis bag (1000 MWCO Spectra/Por® regenerated cellulose) was filled with 10 ml of the HA solutions at concentrations varying between 0 and about 1300 mg·l^{-1}. Afterwards, the dialysis bag was immersed in a Pyrex tube containing 50 ml of SBCW spiked with U(VI) at a concentration of 5.4×10^{-7} mol·l^{-1}. The final concentration of U(VI) in the 60 ml total system was about 4.5×10^{-7} mol·l^{-1}. For each test, SBCW spiked with U(VI) was prepared by diluting 65 μl of a solution containing

5×10^{-3} mol·l^{-1} of $UO_2(NO_3)_2.6H_2O$ in 1M HCl into 600 ml of SBCW. If needed, the *p*H was adjusted by adding aliquots of 1M NaOH.

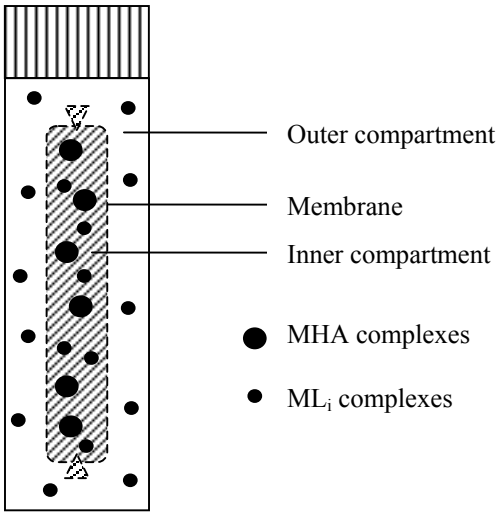

Figure 5.1. Schematic representation of the experimental setup. For simplicity, the free metal ion, the free reference ligand and the free HA are not included.

5.2.4.3 Measurements

After 10 days of equilibration, the tubes were opened and the *p*H was measured with a combined glass electrode (Metrohm) calibrated against *p*H buffers 7 and 9. The electrodes were good or excellent according to the performance test offered by the Metrohm 713 *p*H-meter. The absolute uncertainty on the *p*H values was ± 0.2. Afterwards, both the inner and the outer compartments were sampled. The uranium and HA concentrations were measured by Inductively Coupled Plasma-Mass Spectrometry (Sciex 5000, Perkin-Elmer ICP-MS) and Total Organic Carbon (TOC) analyser (Dohrmann, DC-190), respectively. The 95% confidence interval 2σ of the ICP-MS measurements was about 10% and all samples were above detection limit, *i.e.* 4×10^{-9} mol·l^{-1}. The detection limit of the TOC analyses was 10 mg·l^{-1}. The TOC is measured by subtracting the Total Inorganic Carbon (TIC) concentration from the Total Carbon (TC) concentration. The uncertainty on the TC and TIC concentrations was of maximum 5% which is the maximum deviation allowed for the calibration measurements. Therefore, the uncertainty on the TOC depends on the TC and TIC concentrations of the samples. For the experiments conducted under Boom Clay conditions, the maximum uncertainty on the TOC analyses varied between 6% for the highest TOC concentration (640 mg·l^{-1}) to 27% for the lowest TOC concentration (50 mg·l^{-1}). The maximum uncertainty was 5% for the experiments performed under the atmospheric conditions. All the data on the uranium and TOC concentrations in the inner and outer compartments are available in Appendix 2.

5.2.4.4 Mathematical development

The mathematical development explained below aims to calculate a conditional complexation constant for the formation of a metal-HA complex under given experimental conditions.

The dialysis system can be described in terms of the following series of mass balance equations in which the subscript "in" denotes the inner compartment which contains the HA, "out" the outer compartment which is free of HA and "tot" the total system. M denotes the metal, *i.e.* uranium in our case. The available experimental data are the measured metal and HA concentration inside and outside the dialysis bag as well as the volume of the inner and outer compartments.

$$M_{in} = M(aq)_{in} + MHA \qquad \text{Eq. 5.5}$$

$$M_{out} = M(aq)_{out} \qquad \text{Eq. 5.6}$$

where MHA represents the mass of humate-complexes, and M(aq) the other metal aqueous species. Therefore,

$$MHA = M_{in} - M(aq)_{in} \qquad \text{Eq. 5.7}$$

Since the left-hand side quantities of equations 5.5 and 5.6 are experimentally available quantities expressed as concentration ($[M]_{in}$ and $[M]_{out}$), they have to be converted in order to account for the difference in volume of the inner and outer compartments.

$$[MHA]_{tot} = MHA / V_{tot} \qquad \text{Eq. 5.8}$$

$$[MHA]_{tot} = ([M]_{in} \cdot V_{in} - [M(aq)]_{in} \cdot V_{in}) / V_{tot} \qquad \text{Eq. 5.9}$$

The equilibrium being assumed, the concentrations of the non-humate species are identical in both compartments:

$$[M(aq)]_{in} = [M(aq)]_{out} \qquad \text{Eq. 5.10}$$

where,

$$[M(aq)]_{out} = M(aq)_{out} / V_{out} = [M]_{out} \qquad \text{Eq. 5.11}$$

From equations 5.9, 5.10 and 5.11, the metal-HA complexes concentration at equilibrium in the total system becomes:

$$[MHA]_{tot} = ([M]_{in} - [M]_{out}) \cdot V_{in} / V_{tot} \qquad \text{Eq. 5.12}$$

Similarly, the HA concentration is calculated from the following relation:

$$[HA]_{tot} = ([HA]_{in} \cdot V_{in}) / V_{tot} \qquad \text{Eq. 5.13}$$

The concentration of free HA is defined as:

$$[HA]_{free} = [HA]_{tot} - [MHA]_{tot} \qquad \text{Eq. 5.14}$$

At the trace concentration of the studied metal, the free HA concentration equals the initial HA concentration because $[MHA] <<< [HA]_{tot}$:

$$[HA]_{free} = [HA]_{tot} \qquad \text{Eq. 5.15}$$

The mass balance equation for the non-humate species is:

$$M(aq) = M(aq)_{in} + M(aq)_{out} \qquad \text{Eq. 5.16}$$

In terms of concentrations, equation 5.16 is written as:

$$M(aq) = [M(aq)]_{in} \cdot V_{in} + [M(aq)]_{out} \cdot V_{out} \qquad \text{Eq. 5.17}$$

According to equation 5.10, it becomes:

$$M(aq) = [M(aq)]_{out} \cdot V_{tot} \qquad \text{Eq. 5.18}$$

and applying equation 5.11, the following relation is obtained:

$$[M(aq)] = [M]_{out} \qquad \text{Eq. 5.19}$$

The concentration of the metal species outside the dialysis bag (outer compartment without HA) is equal to:

$$[M]_{out} = [M^{n+}] + \sum[ML_n] \qquad \text{Eq. 5.20}$$

where M^{n+} is the free metal cation concentration and ML_n the sum of all possible metal-competitive ligand species. Competitive ligand (L) are ligands for metal complexation different from HA, *e.g.* OH^-, CO_3^{2-}, ...
The complexation constant of metal by the competitive ligand is defined as:

$$\beta_{1n} = \frac{[ML_n]}{[M^{n+}] \cdot [L]^n} \qquad \text{Eq. 5.21}$$

where M^{n+} is the free metal cation concentration and L the competitive ligands for metal complexation other than HA. Therefore, the concentration of all possible metal-competitive ligand species, $\Sigma[ML_n]$, is obtained from the following equation:

$$\sum[ML_n] = \sum\beta_{1n} \cdot [M^{n+}] \cdot [L]^n \qquad \text{Eq. 5.22}$$

Combining equations 5.20 and 5.22, the concentration of metal species outside the dialysis bag becomes:

$$[M]_{out} = [M^{n+}] + \sum \beta_{1n} \cdot [M^{n+}] \cdot [L]^n \qquad \text{Eq. 5.23}$$

Isolating the free metal cation concentration, equation 5.23 is written as:

$$[M]_{out} = [M^{n+}] \times \left(1 + \sum \beta_{1n} \cdot [L]^n\right) \qquad \text{Eq. 5.24}$$

The free metal cation concentration is finally obtained by the following equation:

$$[M^{n+}] = \frac{[M]_{out}}{1 + \sum \beta_{1n} \cdot [L]^n} \qquad \text{Eq. 5.25}$$

The denominator of equation 5.25 is called the side reaction coefficient and is further represented by As:

$$As = 1 + \sum \beta_{1n} [L]^n \qquad \text{Eq. 5.26}$$

The side reaction coefficient accounts for the metal complexation with ligands different from HA. Since, trace metal quantities were used, the competitive ligand concentration, [L], equals the initial ligand concentration.

The complexation reaction of a cation M by HA is reminded in equation 5.27:

$$M + HA \rightleftharpoons MHA \qquad \text{Eq. 5.27}$$

The corresponding complexation constant is also reminded below:

$$\beta = \frac{[MHA]}{[M] \cdot [HA]} \qquad \text{Eq. 5.28}$$

Equation 5.28 shows that the concentration of metal-humate complexes [MHA], the metal free concentration [M] and the HA free concentration [HA] are needed to determine the complexation constant β. Similarly, the conditional complexation constant, β^{exp}, is determined in the dialysis system from equations 5.12, 5.15, and 5.25:

$$\beta^{exp} = \left(\frac{[M]_{in} - [M]_{out}}{[M]_{out} \cdot [HA]_{tot}} \right) \cdot As \qquad \text{Eq. 5.29}$$

In equation 5.29, the available experimental data are the metal (uranium) concentrations inside, $[M]_{in}$, and outside, $[M]_{out}$, the dialysis bag and the total HA concentration, $[HA]_{tot}$. The difference between the metal concentrations in the inner and outer compartments gives the concentration of metal-humate complexes. The

concentration of HA is derived from the TOC content in the dialysis bag. Both the metal-humate complexes and HA concentrations are obtained by considering the difference in volume of the inner and outer compartments. The metal concentration in the outer compartment gives the concentration of the non-humate metal species. The free metal cation concentration is calculated by using the side reaction coefficient which accounts for the metal complexation by ligands different from HA. The complexation constant β^{exp} is conditional since the side reaction coefficient, As, strongly depends on the experimental conditions.

5.3 Results

5.3.1 Intrinsic problems of the dialysis technique

The dialysis technique has some intrinsic problems:

- uranium may adsorb on the membrane;
- HA may leak through the membrane;
- the system has to be in equilibrium before sampling, *i.e.* the concentrations of non-humate complexes must be identical in the inner and outer compartments.

These problems are not encountered during our experiments (Table 5.5). The issue of uranium adsorption on the membrane is easily solved by sampling both in the inner and outer compartments. This allows to measure the actual concentration of uranium in both compartments. From these measurements, the uranium recovery is more than 90%, except for the tests conducted under atmospheric conditions for which the recovery is about 80%.

The leaking of HA is controlled from TOC analyses in the outer compartment. It is always smaller than 5 %. It is interesting to mention that no leaching of organic matter is noticed in the test Cp-7. This observation suggests that the organic matter dissolved in BCW has a size larger than 1000 dalton.

Finally, the equilibrium state is verified by measuring the uranium concentration in the inner and outer compartments in absence of HA. The $[U]_{in}$ to $[U]_{out}$ ratio is equal to one indicating that the concentrations of U(VI) aqueous species other than HA complexes are the same in both compartments (see Eq. 5.10).

Table 5.5. Control of the problems intrinsic the dialysis technique: uranium absorption on the membrane, HA leaking and equilibrium of the non humate complexes.

Tests Cp-#	Uranium recovery Average %	HA leaching %	$[U]_{in}/[U]_{out}$ ratio in absence of HA
Cp-2	91	3	1.0
Cp-3	95	below detection limit	1.0
Cp-5	94	2	1.0
Cp-6	94	below detection limit	1.0
Cp-7	100	below detection limit	1.0
Cp-8	79	3	0.9
Cp-9	77	4	1.0

5.3.2 Redox stability

Humic acids effectively reduce mercury, vanadium, iron and actinides like Np(VI) and Pu(VI) (Nash *et al.*, 1981 and references therein). Pirlet (2003) observed by UV-Vis spectroscopy the reduction of Np(V) to Np(IV) by BCW. However, HA do not reduce U(VI) in solution in the laboratory studies reported by Nash *et al.*, 1981; Czerwinski, 1994 and Moulin and Moulin, 1995. Based on these literature data, U(VI) is considered to be stable in presence of HA in solution under our experimental conditions.

5.3.3 Determination of humic acids concentration

The concentration of HA must be known to solve the equation that describes the uranium complexation by HA (Eq. 5.29). The only available experimental data are the TOC concentrations measured in the inner compartment of the dialysis system. This concentration is expressed in $mg \cdot l^{-1}$ of organic carbon and needs to be converted in $mg \cdot l^{-1}$ of HA. To perform this conversion, calibration curves are determined for Aldrich HA, oxidised and non-oxidised Boom Clay HA (Figure 5.2). Humic acids solutions were prepared at five or six different concentrations by weighing accurate amounts of HA with an analytical balance (0.1 mg). These HA were dissolved in SBCW and the solutions were analysed for TOC concentration. Due to the hygroscopic character of HA, they were weighed after freeze-drying and preservation in the dried anaerobic glove box. The HA to TOC ratio is 1.9 for Aldrich HA and 1.6 for Boom Clay HA. There is no difference between oxidised and non-oxidised Boom Clay HA.

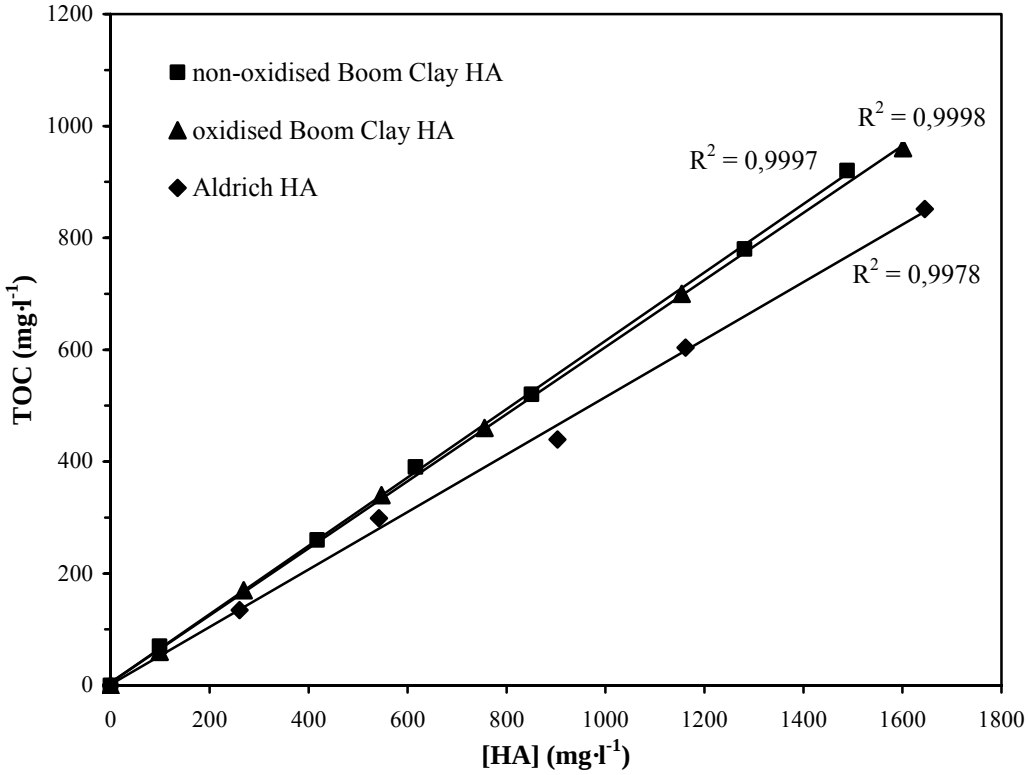

Figure 5.2. Calibration curves of Aldrich HA, non-oxidised and oxidised Boom Clay HA for the determination of the HA to TOC ratio.

Although the HA concentration can be expressed by the amount of HA ($mg \cdot l^{-1}$), the equivalent per litre is more commonly used. In this study the HA concentration is expressed by means of the proton exchange capacity (PEC) which is theoretically equal to the amount of dissociable protons (Dierckx, 1995). The charge of HA ($equivalent \cdot g^{-1}$) due to the deprotonation of the functional groups is calculated from titration data. Titrations of purified Aldrich HA were performed in a background of 3 M $NaClO_4$ by Dierckx *et al.* (1994). At this ionic strength, the dissociation behaviour of HA is no longer influenced by electrostatic effects. The proton exchange capacity is equal to 4.3 ± 0.1 $meq \cdot g^{-1}$ HA. Titration curves were acquired by Pirlet (2003) for HA extracted from BCW. The PEC determined at the working *p*H value (8.3) is equal to 2.9 ± 0.2 $meq \cdot g^{-1}$ HA.

5.3.4 Fraction of U(VI) complexed by humic acids

Besides the determination of the conditional complexation constant, dialysis experiments allow to determine the ratio of uranium complexed by HA to total uranium ($[U\text{-}HA]/[U_{tot}]$). This ratio gives the fraction of U(VI) which is complexed by HA. The concentration of U(VI)-humate complexes is given by equation 5.12. The total uranium concentration in the dialysis system is determined from the following equation:

$$[U]_{tot} = ([U]_{in} \cdot V_{in} + [U]_{out} \cdot V_{out}) / V_{tot} \qquad \text{Eq. 5.30}$$

The ratio $[U\text{-}HA]/[U_{tot}]$ is model independent because it is only derived from measured concentrations and volumes without any further development or assumptions. Therefore, this ratio provides a very reliable information on the extent of the U(VI) complexation by HA.

5.3.4.1 Under in situ conditions

The ratio $[U\text{-}HA]/[U_{tot}]$ is always lower than 25% even at TOC concentrations as high as 650 $mg \cdot l^{-1}$ (Figure 5.3). This low ratio indicates that the U(VI) complexation by HA is weak under geochemical conditions representative for the Boom Clay (*p*H~ 8.2, $\log pCO_2 = -2.4$). Aldrich HA complex more U(VI) than Boom Clay HA. This difference is explained by the larger PEC of Aldrich HA (4.3 $meq \cdot g^{-1}$) compared to that of Boom Clay HA (2.9 $meq \cdot g^{-1}$). In the experiments conducted with Aldrich HA, the presence of HPO_4^{2-} at a concentration of 8×10^{-5} M does not markedly affect the results. This observation points out that phosphate at this concentration does not significantly complex U(VI) under Boom Clay conditions. The oxidation of Boom Clay HA does not influence their complexing behaviour judged from the similar results obtained with oxidised and non-oxidised batches of Boom Clay HA. At the HA concentration of BCW, *i.e.* TOC between 50 and 150 $mg \cdot l^{-1}$, less than 5% of U(VI) occurs as humate complex. Therefore, the speciation of U(VI) under Boom Clay conditions is greatly dominated by the carbonate complexes.

The same conclusions are obtained from the experiment Cp-7 in which the dialysis bag was filled with BCW. The organic matter concentration was constant while the uranium concentration was varying from 10^{-7} to 10^{-4} $mol \cdot l^{-1}$. The possible effect of oxidation of organic matter was also studied by using two batches of BCW, one sampled under anaerobic conditions and the other one oxidised by contacting the water with air for two days and bubbling with pure O_2 for two hours. In BCW, the

fraction of U(VI) complexed by organic matter is negligible (less than 2 %), regardless to the U(VI) concentration and oxidation of BCW (Table 5.6).

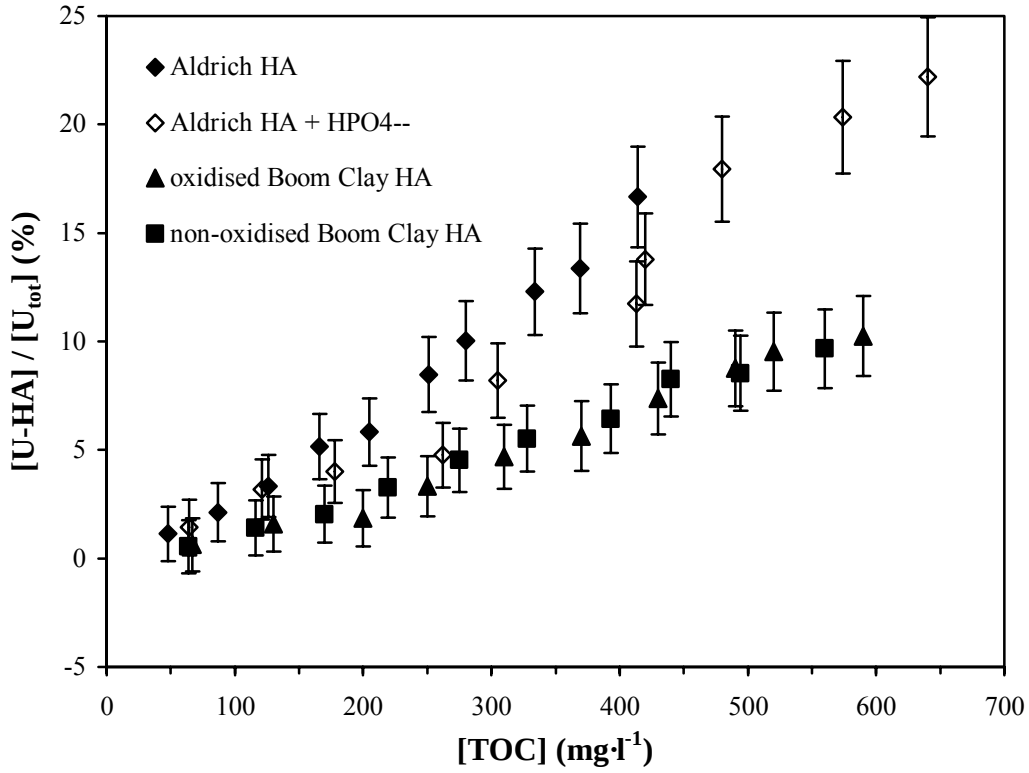

Figure 5.3. Fraction of U(VI) complexed by HA under conditions representative for Boom Clay as a function of the total organic carbon (TOC). The error bars give the absolute uncertainty on the ratio.

Table 5.6: Ratio of U(VI)-organic matter complexes to total U(VI) at different U(VI) concentration in non- and oxidised BCW.

Samples Cp 7-#	BCW	[U] mol·l^{-1}	TOC mg·l^{-1}	[U-HA] / [U$_{tot}$] %
Cp 7-1	non-oxidised	1.0×10^{-7}	60	0
Cp 7-2	non-oxidised	2.5×10^{-7}	61	0
Cp 7-3	non-oxidised	5.0×10^{-7}	60	2
Cp 7-4	non-oxidised	7.5×10^{-7}	62	0
Cp 7-5	non-oxidised	1.0×10^{-6}	63	0
Cp 7-6	non-oxidised	1.0×10^{-5}	60	0
Cp 7-7	non-oxidised	1.0×10^{-4}	62	0
Cp 7-8	oxidised	1.0×10^{-7}	67	1
Cp 7-9	oxidised	1.0×10^{-6}	61	0
Cp 7-10	oxidised	1.0×10^{-5}	66	0
Cp 7-11	oxidised	1.0×10^{-4}	62	0

From the ratio of U(VI)-humate complexes to total U(VI), it is clear that U(VI) is not significantly complexed by HA under conditions representative for Boom Clay, probably because of the competition with the very stable carbonate complexes.

5.3.4.2 Under atmospheric conditions

Under the atmospheric partial pressure of CO_2 (log pCO_2 = -3.5), the [U-HA]/[U_{tot}] is much higher than under Boom Clay conditions (Figure 5.4). The humate-complexes dominate largely the U(VI) speciation over the experimental TOC concentration range. The percentage of U(VI)-humate complexes varies between 65 and 95 % at the TOC concentration range of BCW. This observation evidences that the formation of uranyl carbonate complexes is responsible for the low complexation of U(VI) by HA under *in situ* partial pressure of CO_2. Indeed, the concentration of carbonate (CO_3^{2-}) is about 1×10^{-4} mol·l^{-1} in SBCW containing 4.5×10^{-7} mol·l^{-1} of U(VI) at *p*H 8.2 and under a log pCO_2 = -2.4. At the same U(VI) concentration, the CO_3^{2-} concentration is 6×10^{-6} mol·l^{-1} in air saturated solutions at *p*H 8.1.

The data under atmospheric conditions are scattered but the general trend shows a decrease of the U(VI)-HA complexes with increasing TOC. Such behaviour is unexpected and might involve the polydispersive character of HA. With increasing HA concentration, the increasing molecular repulsion would cause a shrinkage of the HA structure resulting in a decrease of the sites number available for the complexation.

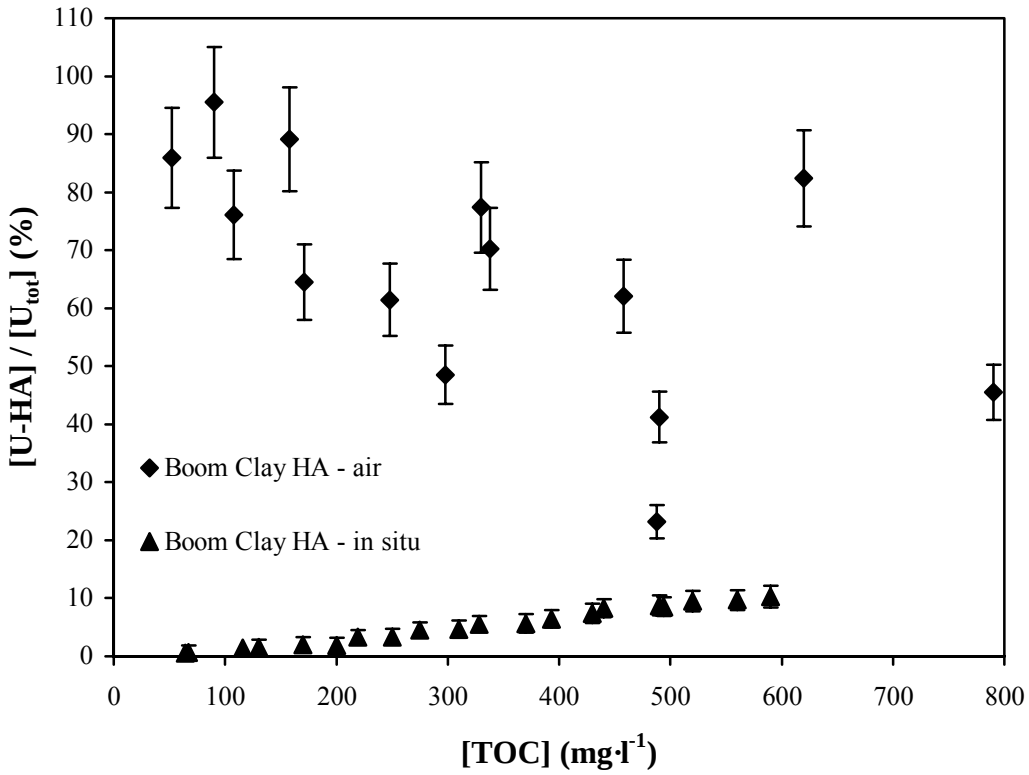

Figure 5.4. Fraction of U(VI) complexed by HA under atmospheric conditions as a function of the total organic carbon (TOC). The error bars give the absolute uncertainty on the ratio.

The competing effect of carbonate with HA for uranium complexation was already demonstrated by Zeh *et al.* (1997) who studied the sorption behaviour of the uranyl cation (UO_2^{2+}) on humic colloids at different CO_2 partial pressures from *p*H 1 to 10 (Figure 5.5). Under 100% CO_2 atmosphere, a desorption begins near *p*H 4.5 whereas the desorption starts near *p*H 7 under an atmosphere containing 0.035% CO_2.

The desorption is attributed to carbonate complexation which forms stable complexes with the uranyl cation in solution.

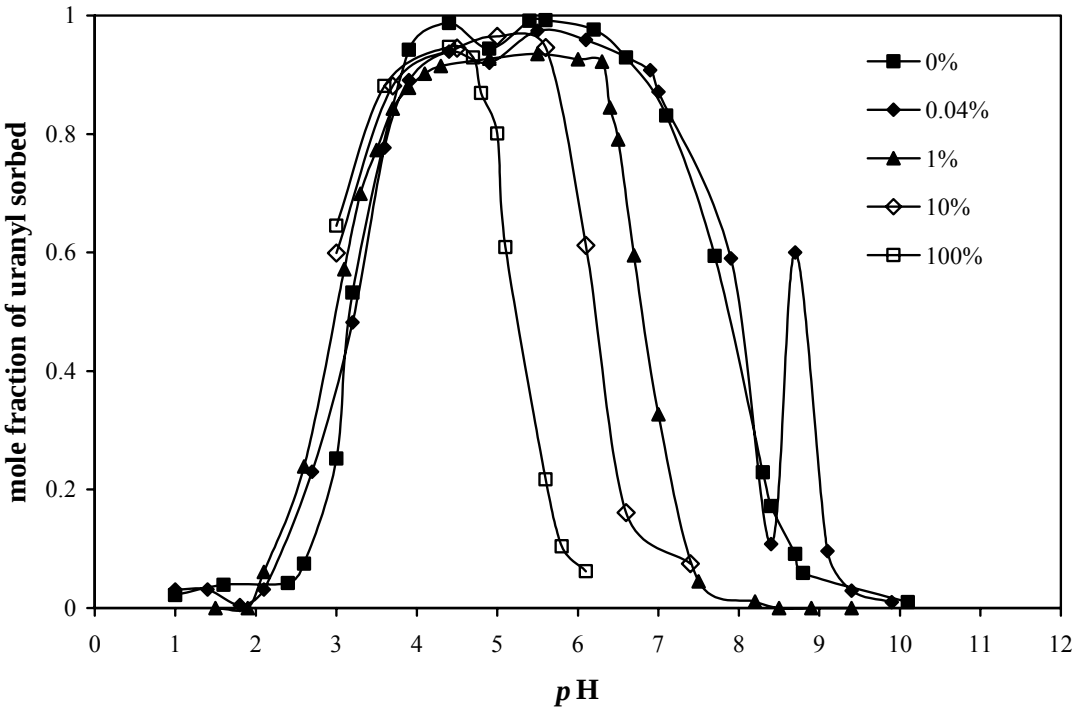

Figure 5.5. Mole fraction of uranyl sorbed on humic colloids as a function of *p*H for different CO_2 partial pressures (from Zeh *et al.*, 1997).

5.3.4.3 Conclusion

The fraction of U(VI) complexed by HA at two different partial pressures of CO_2 shows the importance of the carbonate concentration. Under Boom Clay conditions, the speciation of U(VI) is greatly dominated by the carbonate complexes. These complexes are very strong and the HA are not able to compete with them. For instance, less than 5% of U(VI) occurs as humate-complexes in BCW. Therefore, the dissolved natural organic matter will not increase the U(VI) mobility through the formation of stable complexes. However, a decrease of the partial pressure of CO_2 changes these conclusions in favour of HA complexes. Under atmospheric partial pressure of CO_2, between 65 and 95% of U(VI) are present as HA-complexes in BCW. The decreasing formation of U(VI)-HA complexes with increasing concentration of HA observed under the atmospheric partial pressure of CO_2 is not understood.

5.4 Determination of conditional complexation constant

5.4.1 Evaluation of the conditional complexation constant

Although the complexation of U(VI) by HA is very weak under Boom Clay conditions, it is possible to determine a conditional complexation constant, β^{exp}, according to equation 5.29. Such conditional complexation constant cannot be extrapolated to other conditions. Nevertheless, β^{exp} can be implemented in a specific database for the Boom Clay and used to determine the U(VI) speciation. β^{exp} is calculated for the experiments carried out under conditions representative for Boom Clay with:

- Aldrich HA (Cp-2 and Cp-3);
- oxidised and non-oxidised Boom Clay HA (Cp-5 and Cp-6).

The equation allowing the determination of the conditional complexation constant is reminded below:

$$\beta^{exp} = \left(\frac{[U]_{in} - [U]_{out}}{[U]_{out} \cdot [HA]_{tot}} \right) \cdot As \qquad \text{Eq. 5.31}$$

The concentration of HA, $[HA]_{tot}$, is calculated by the following relationship:

$$[HA] = TOC \cdot x \cdot PEC \qquad \text{Eq. 5.32}$$

where TOC is the concentration of total organic carbon measured inside the dialysis bag and x is equal to 1.9 and 1.6 for Aldrich and Boom Clay HA respectively. The PEC is 4.3 meq·g^{-1} for Aldrich HA and 2.9 meq·g^{-1} for Boom Clay HA. The U(VI) concentration inside, $[U]_{in}$, and outside, $[U]_{out}$, the dialysis bag are experimentally available data. The concentration of free uranyl cation (UO_2^{2+}) is calculated by introducing the side reaction coefficient (As) which accounts for the U(VI) complexation by ligands other than HA. Speciation calculations using "*The Geochemist's Workbench*" (Bethke, 2001) and the NEA database (Guillaumont *et al.*, 2003) indicate that U(VI) speciation is dominated for 98% by $UO_2(CO_3)_3^{4-}$ under our experimental conditions, $UO_2(CO_3)_2^{2-}$ contributes for only 2% (Table 5.7).
Similarly to equation 5.20, the concentration of the uranium species outside the dialysis bag is thus equal to:

$$[U]_{out} = [UO_2^{2+}] + [UO_2(CO_3)_2^{2-}] + [UO_2(CO_3)_3^{4-}] \qquad \text{Eq. 5.33}$$

where the UO_2^{2+} concentration is negligible.
The complexation constants of uranium by carbonate are defined as:

$$\beta_{12} = \frac{[UO_2(CO_3)_2^{2-}]}{[UO_2^{2+}] \cdot [CO_3^{2-}]^2} \qquad \text{Eq. 5.34}$$

and,

$$\beta_{13} = \frac{\left[UO_2(CO_3)_3^{4-}\right]}{\left[UO_2^{2+}\right]\cdot\left[CO_3^{2-}\right]^3} \qquad \text{Eq. 5.35}$$

Using equations 5.34 and 5.35 in equation 5.33, the concentration of metal species outside the dialysis bag becomes:

$$\left[U\right]_{out} = \left[UO_2^{2+}\right] + \beta_{12}\cdot\left[UO_2^{2+}\right]\cdot\left[CO_3^{2-}\right]^2 + \beta_{13}\cdot\left[UO_2^{2+}\right]\cdot\left[CO_3^{2-}\right]^3 \qquad \text{Eq. 5.36}$$

Rearranging equation 5.36 with respect to UO_2^{2+}:

$$\left[U\right]_{out} = \left[UO_2^{2+}\right]\times\left\{1 + \beta_{12}\cdot\left[CO_3^{2-}\right]^2 + \beta_{13}\cdot\left[CO_3^{2-}\right]^3\right\} \qquad \text{Eq. 5.37}$$

The free UO_2^{2+} concentration is finally obtained from the following equation:

$$\left[UO_2^{2+}\right] = \frac{\left[U\right]_{out}}{\left\{1 + \beta_{12}\cdot\left[CO_3^{2-}\right]^2 + \beta_{13}\cdot\left[CO_3^{2-}\right]^3\right\}} \qquad \text{Eq. 5.38}$$

The denominator of equation 5.38 is called the side reaction coefficient, As.

$$As = \left\{1 + \beta_{12}\cdot\left[CO_3^{2-}\right]^2 + \beta_{13}\cdot\left[CO_3^{2-}\right]^3\right\} \qquad \text{Eq. 5.39}$$

The side reaction coefficient must be determined to calculate the free UO_2^{2+} concentration according to equation 5.38, the concentration of uranium in the outer compartment being experimentally measured. The complexation constant of the di- and tri-carbonate complexes of U(VI), β_{12} and β_{13} respectively, are available in the literature (*e.g.* Guillaumont *et al.*, 2003). Since they depend on the ionic strength, they have to be extrapolated at the ionic strength of interest. The carbonate concentration can be calculated from *p*H and pCO_2 values.

In practice, the side reaction coefficient is not directly determined with equation 5.39. Geochemical code and database such as "*The Geochemist's Workbench*" and the NEA database are used to directly calculate the concentration of UO_2^{2+} in the experimental system. The advantage of the geochemical code is that it takes into account:

- all the species implemented in the database;
- the effect of ionic strength.

The concentration of UO_2^{2+} and that of carbonate (CO_3^{2-}) are calculated for each samples of the four experiments (Table 5.7). The input parameters are:

- the bicarbonate concentration derived from the Total Inorganic Carbon (TIC) concentration. We consider that all inorganic carbon occurred as HCO_3^- at *p*H 8.2;
- the measured *p*H;
- the analysed composition of SBCW (see Appendix 1);
- the measured concentration of U(VI) in the outer compartment, $[U]_{out}$.

Once the UO_2^{2+} concentration is known, the side reaction coefficient (As) is indirectly determined from equation 5.38:

$$As = [U]_{out} / [UO_2^{2+}] \qquad \text{Eq. 5.40}$$

The results of the modelling are given in Table 5.7.

Table 5.7. Results of the modelling exercise using "*The Geochemist's Workbench*" (Bethke, 2001) and the NEA database (Guillaumont *et al.*, 2003): calculation of the uranyl and the carbonate concentrations, the side reaction coefficient and the uranium speciation.

Samples	*p*H	$[U]_{out}$ 10^{-7} mol·l^{-1}	$[UO_2^{2+}]$ 10^{-17} mol·l^{-1}	As	$[CO_3^{2-}]$ 10^{-4} mol·l^{-1}	$UO_2(CO_3)_3^{4-}$ %	$UO_2(CO_3)_2^{2-}$ %
Cp 2-1	8.1	2.95	3.31	8.93×10^{9}	1.08	98	2
Cp 2-2	8.1	3.11	3.49	8.92×10^{9}	1.08	98	2
Cp 2-3	8.1	3.18	3.57	8.92×10^{9}	1.08	98	2
Cp 2-4	8.1	3.33	3.74	8.93×10^{9}	1.08	98	2
Cp 2-5	8.1	3.46	3.88	8.92×10^{9}	1.08	98	2
Cp 2-6	8.1	3.57	4.00	8.91×10^{9}	1.08	98	2
Cp 2-7	8.1	3.71	4.16	8.91×10^{9}	1.08	98	2
Cp 2-8	8.1	3.79	4.25	8.90×10^{9}	1.08	98	2
Cp 2-9	8.1	3.74	4.19	8.91×10^{9}	1.08	98	2
Cp 2-10	8.1	3.95	4.43	8.92×10^{9}	1.08	98	2
Cp 3-1	8.1	3.55	3.84	9.23×10^{9}	1.09	98	2
Cp 3-2	8.1	3.68	3.98	9.23×10^{9}	1.09	98	2
Cp 3-3	8.1	3.73	4.04	9.24×10^{9}	1.09	98	2
Cp 3-4	8.1	3.84	4.16	9.23×10^{9}	1.09	98	2
Cp 3-5	8.1	3.90	4.22	9.24×10^{9}	1.09	98	2
Cp 3-6	8.1	4.05	4.38	9.25×10^{9}	1.09	98	2
Cp 3-7	8.1	4.00	4.33	9.23×10^{9}	1.09	98	2
Cp 3-8	8.1	4.14	4.48	9.24×10^{9}	1.09	98	2
Cp 3-9	8.1	4.14	4.48	9.24×10^{9}	1.09	98	2
Cp 3-10	8.1	4.29	4.64	9.23×10^{9}	1.09	98	2
Cp 5-1	8.2	3.82	1.60	2.39×10^{10}	1.50	99	1
Cp 5-2	8.2	3.81	1.60	2.39×10^{10}	1.50	99	1
Cp 5-3	8.2	3.86	1.62	2.39×10^{10}	1.50	99	1
Cp 5-4	8.1	3.88	3.24	1.20×10^{10}	1.19	98	2
Cp 5-5	8.1	3.94	3.29	1.20×10^{10}	1.19	98	2
Cp 5-6	8.1	4.06	3.39	1.19×10^{10}	1.19	98	2
Cp 5-7	8.1	4.10	3.43	1.20×10^{10}	1.19	98	2
Cp 5-8	8.1	4.19	3.50	1.20×10^{10}	1.19	98	2
Cp 5-9	8.2	4.20	3.51	1.20×10^{10}	1.50	98	2
Cp 5-10	8.1	4.22	3.53	1.20×10^{10}	1.19	98	2
Cp 6-1	8.1	3.87	3.24	1.19×10^{10}	1.19	98	2
Cp 6-2	8.1	3.90	3.26	1.20×10^{10}	1.19	98	2
Cp 6-3	8.1	3.88	3.24	1.20×10^{10}	1.19	98	2
Cp 6-4	8.1	3.99	3.34	1.20×10^{10}	1.19	98	2
Cp 6-5	8.1	4.00	3.34	1.20×10^{10}	1.19	98	2
Cp 6-6	8.1	4.07	3.40	1.20×10^{10}	1.19	98	2
Cp 6-7	8.1	4.11	3.44	1.20×10^{10}	1.19	98	2
Cp 6-8	8.2	4.19	1.76	2.39×10^{10}	1.50	98	1
Cp 6-9	8.2	4.19	1.76	2.39×10^{10}	1.50	98	1
Cp 6-10	8.2	4.22	1.77	2.39×10^{10}	1.50	99	1

All the terms to solve equation 5.31 being determined, the conditional complexation constant, β^{exp}, is calculated for each sample (Table 5.8 and Figure 5.6). The mean value and the standard deviation of the logarithm of β^{exp} from the different experiments are given in Table 5.8. The logarithm of β^{exp} is very consistent within the same experiment as shown by the standard deviation ($\pm \sigma$) which is always lower than 0.3. Therefore, log β^{exp} is independent from the HA concentration.

The calculated grand mean value of log β^{exp} for the complexation of U(VI) by HA under Boom Clay conditions is:

$$\mathbf{Log\ \beta^{exp} = 12.4 \pm 0.2}$$

Taking into account all experimental points, the standard deviation is 0.2 and indicates that the logarithm of β^{exp} is very constant between the different experiments. Consequently, the conditional complexation constant is not influenced neither by the type of HA (Aldrich or Boom Clay), nor by the presence of hydrogen- phosphate, and nor by the oxidation of HA.

Table 5.8. Logarithm of the interaction constant (log β) for the complexation of U(VI) by HA determined by the dialysis technique under Boom Clay conditions; σ: standard deviation.

Sample	$[HA]_{tot}$ $eq \cdot l^{-1}$	Log β^{exp}	Sample	$[HA]_{tot}$ $eq \cdot l^{-1}$	Log β^{exp}
Cp 2-1	8.85×10^{-4}	12.46	Cp 5-1	4.63×10^{-4}	12.77
Cp 2-2	7.94×10^{-4}	12.46	Cp 5-2	4.05×10^{-4}	12.79
Cp 2-3	6.64×10^{-4}	12.47	Cp 5-3	3.81×10^{-4}	12.78
Cp 2-4	5.83×10^{-4}	12.39	Cp 5-4	3.35×10^{-4}	12.45
Cp 2-5	5.71×10^{-4}	12.32	Cp 5-5	3.04×10^{-4}	12.37
Cp 2-6	4.22×10^{-4}	12.28	Cp 5-6	2.41×10^{-4}	12.39
Cp 2-7	3.62×10^{-4}	12.09	Cp 5-7	1.95×10^{-4}	12.33
Cp 2-8	2.46×10^{-4}	12.18	Cp 5-8	1.56×10^{-4}	12.16
Cp 2-9	1.67×10^{-4}	12.24	Cp 5-9	1.01×10^{-4}	12.28
Cp 2-10	8.91×10^{-5}	12.16	Cp 5-10	5.21×10^{-5}	12.16
mean ± σ		**12.30 ± 0.14**	mean ± σ		**12.45 ± 0.25**
Cp 3-1	5.69×10^{-4}	12.51	Cp 6-1	4.38×10^{-4}	12.46
Cp 3-2	5.07×10^{-4}	12.45	Cp 6-2	3.84×10^{-4}	12.46
Cp 3-3	4.59×10^{-4}	12.45	Cp 6-3	3.42×10^{-4}	12.50
Cp 3-4	3.85×10^{-4}	12.43	Cp 6-4	3.06×10^{-4}	12.43
Cp 3-5	3.45×10^{-4}	12.39	Cp 6-5	2.55×10^{-4}	12.44
Cp 3-6	2.82×10^{-4}	12.31	Cp 6-6	2.14×10^{-4}	12.42
Cp 3-7	2.28×10^{-4}	12.34	Cp 6-7	1.71×10^{-4}	12.37
Cp 3-8	1.80×10^{-4}	12.25	Cp 6-8	1.32×10^{-4}	12.58
Cp 3-9	1.22×10^{-4}	12.22	Cp 6-9	8.98×10^{-5}	12.58
Cp 3-10	6.55×10^{-5}	12.21	Cp 6-10	4.98×10^{-5}	12.42
mean ± σ		**12.36 ± 0.11**	mean ± σ		**12.47 ± 0.07**

To calculate the absolute uncertainty on log β^{exp} (Figure 5.6), the analytical uncertainties on the PEC, on the uranium and TOC concentrations are taken into account. The uncertainty on the side reaction coefficient cannot be directly measured. Since the side reaction coefficient is mainly sensitive to *p*H, the uncertainty on it is estimated by calculating the effect of a 0.2 *p*H variation, the uncertainty on a *p*H measurement.

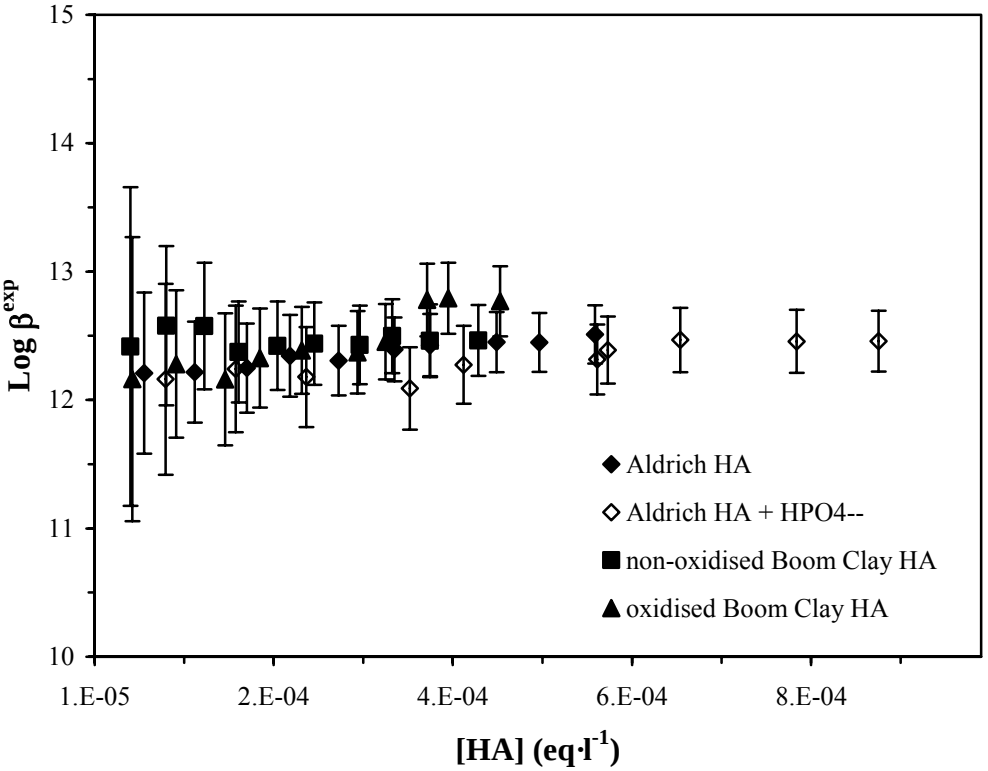

Figure 5.6. Log β^{exp} as function of the HA concentration. The error bars give the absolute uncertainty on the individual logarithm.

As mentioned in the introduction, there are only few studies to which our complexation constant can be compared. Glaus *et al.* (2000) studied by the dialysis technique the complexation of U(VI) at varying *p*H and in presence of carbonate concentrations of 10^{-3} to 3×10^{-3} mol·l^{-1}. They determined a complexation constant of about 9.8 L/g at *p*H 8.2 and ionic strength of 0.02 M. However, these authors express the HA concentration in g·l^{-1} in their calculations. By introducing the HA concentration in g·l^{-1} in equation 5.31, the average value of log β^{exp} becomes 9.9 which is in very good agreement with the Glaus's study.

5.4.2 Discussion

The conditional complexation constant β^{exp} determined under Boom Clay conditions (12.4) is much higher than the reported values at acidic *p*H where the hydrolysis of UO_2^{2+} is avoided (Table 5.1). Several reasons may explain this difference: the effect of *p*H and metal concentration and the formation of mixed complexes.

For a given metal concentration, complexation constants increase with increasing *p*H. This is explained by the increased ionisation of acidic functional groups with increasing *p*H and thereby the number of sites available for binding (Choppin and Allard, 1985; Munier-Lamy *et al.*, 1986, Choppin, 1988.). Since most carboxylic functional groups have pK_a values between 4 and 6, they are more than 99 % ionised at *p*H around 8. On the contrary, carboxylic functional groups are protonated at acidic *p*H.

With decreasing metal concentration (and all other parameters held constant) an increase in the complexation of the radionuclide with HA is observed (Glaus *et al.*, 2000). At low metal concentration, only the most strongly binding groups are

involved. With increasing metal concentration, the strong sites reach saturation and weaker binding sites determine the metal uptake resulting in an overall decrease of metal-humate interaction (Hummel *et al.*, 1999; Munier-Lamy *et al.*, 1986). In our experiments, the calculated concentration of UO_2^{2+} is as low as 10^{-17} mol.l^{-1}.

The formation of mixed complexes increases the value of the complexation constant. Mixed complexes are metal-humate complexes containing an additional ligand (L) other than HA. Dierckx *et al.* (1994) reported the formation of mixed complex of Eu^{3+} with HA and a competing ligand such as carbonate and hydroxide. Panack *et al.* (1996) and Morgenstern *et al.* (2000) presented spectroscopic evidence for the existence of ternary complexes of trivalent actinide with HA and hydroxide or carbonate. Zeh *et al.* (1997) interpreted their data by assuming the formation of the mixed complex $UO_2(OH)HA$. According to Glaus *et al.* (1995b), the complexation of a metal ion with HA in presence of an additional ligand can be better modelled if mixed complexes are also included. Pirlet (2003) observed in BCW two Np(IV)-humate species by UV-Vis spectroscopy which are interpreted as mixed hydroxo-humate complexes. Under Boom Clay conditions, the speciation of U(VI) is dominated by inorganic carbonate complexes. In presence of HA, both ligands (HA and CO_3^{2-}) compete with each other for the complexation of U(VI). Dialysis experiments show that less than 5% of uranium is complexed by HA in BCW. Although it is not possible to ascertain their presence by the dialysis technique, the formation of mixed U(VI) complexes with carbonate and HA may explain the very low complexation of U(VI) by HA observed under Boom Clay conditions. Indeed, the anionic ligand (CO_3^{2-}) and axial uranyl oxygens of the inorganic carbonate complexes repulse the anionic charge of HA functional groups. Due to the polyelectrolyte character of HA, this repulsion is stronger than the repulsion between carbonate ligands and the formation of inorganic carbonate complexes is favoured. The formation of mixed U(VI) carbonate-humate complexes is discussed more in detail in the next paragraph by considering two mixed complexes:

- $UO_2(CO_3)_2HA$;
- $UO_2(CO_3)HA$.

5.4.3 Mixed complexes formation of U(VI) with HA and carbonate.

If only pure humate complex are formed, the complexation reaction is described by:

$$UO_2^{2+} + HA \rightleftharpoons UO_2HA^{2} \qquad \text{Eq. 5.41}$$

The corresponding complexation constant is defined by:

$$\beta_{101} = \frac{[UO_2HA]}{[UO_2^{2+}]\cdot[HA]} \qquad \text{Eq. 5.42}$$

We have demonstrated in equation 5.12 that the difference between the uranium concentrations in the inner and outer compartments gives the concentration of U(VI)-humate complexes:

$$[U]_{in} - [U]_{out} = [UO_2HA] \qquad \text{Eq. 5.43}$$

[2] The charge balance is not indicated in the equation because of the nature of the humic acid ligand.

If mixed complexes are formed, the complexation reaction is described by:

$$UO_2^{2+} + iL + HA \rightleftharpoons UO_2(L)_iHA \qquad \text{Eq. 5.44}$$

where L is a competing ligand different from HA for the U(VI) complexation, *e.g.* carbonate according to our assumption.
The corresponding complexation constant is defined by:

$$\beta_{1i1} = \frac{\left[UO_2(L)_i HA\right]}{\left[UO_2^{2+}\right]\cdot\left[L\right]^i\cdot\left[HA\right]} \qquad \text{Eq. 5.45}$$

In the case that mixed complexes occur, equation 5.43 becomes:

$$[U]_{in} - [U]_{out} = [UO_2HA] + [UO_2(L)_iHA] \qquad \text{Eq. 5.46}$$

The formation of the mixed complex ($UO_2(L)_iHA$) can also be defined by the stepwise reaction:

$$UO_2HA + iL \rightleftharpoons UO_2(L)_iHA \qquad \text{Eq. 5.47}$$

with the corresponding stepwise complexation constant (K_{1i1}):

$$K_{1i1} = \frac{\left[UO_2(L)_i HA\right]}{\left[UO_2HA\right]\cdot\left[L\right]^i} \qquad \text{Eq. 5.48}$$

Therefore rearranging equation 5.46 by expressing the concentration of UO_2HA and $UO_2(L)_iHA$ with equations 5.42 and 5.48, respectively:

$$[U]_{in} - [U]_{out} = \beta_{101}\cdot[UO_2^{2+}]\cdot[HA] + K_{1i1}\cdot[L]^i\cdot[UO_2HA] \qquad \text{Eq. 5.49}$$

Isolating the product $[UO_2^{2+}]\cdot[HA]$, equation 5.49 becomes:

$$[U]_{in} - [U]_{out} = \beta_{101}\cdot[UO_2^{2+}]\cdot[HA]\cdot\{1 + K_{1i1}\cdot[L]^i\} \qquad \text{Eq. 5.50}$$

Dividing both members of equation 5.50 by the product $[UO_2^{2+}]\cdot[HA]$, the following equation is obtained:

$$\beta^{exp} = \beta_{101}\cdot\{1 + K_{1i1}\cdot[L]^i\} \qquad \text{Eq. 5.51}$$

Equation 5.51 shows that below a certain threshold concentration of additional ligand, the β^{exp} values can be considered to remain constant and can be identified with β_{101}. On the other hand, if the product $K_{1i1}\cdot[L]^i >> 1$, mixed complexes are predominant.
From the equations 5.42 and 5.48, it is established that:

$$\beta_{1i1} = \beta_{101}\cdot K_{1i1} \qquad \text{Eq. 5.52}$$

Therefore, equation 5.51 can also be written as:

$$\beta^{exp} = \beta_{101} + \beta_{1i1}\cdot[L]^{i} \qquad \text{Eq. 5.53}$$

It is demonstrated from equations 5.51 and 5.53 that β^{exp} overestimates β_{101} if mixed complexes occurs. Nevertheless, β^{exp} is a conservative value since it takes into account all possible humate-complexes. Consequently, it can be used in speciation calculations to determine the extent of U(VI) complexation by HA under Boom Clay conditions whatever the humate complexes are.

The determination of the conditional stepwise interaction (K_{1i1}) and complexation (β_{1i1}) constants strongly depends on the value of β_{101} (see equations 5.51 and 5.53). β_{101} is the complexation constant for the formation of the pure complex UO_2HA. We have chosen β_{101} among the available data in the literature concerning the studies conducted at the non-hydrolysing *p*H where only two species are present in solution: the free uranyl cation (UO_2^{2+}) and the U(VI)-humate complex UO_2HA. Czerwinski *et al.* (1994) studied the complexation of the uranyl ion with HA by three different methods at *p*H 4 where the hydrolysis of UO_2^{2+} was negligible. They determined a log β_{101} of 6.16. However, this complexation constant is obtained with the charge neutralisation model (Kim and Czerwinski, 1996). In this model, the complexation reaction of a given metal ion with HA is considered as a metal ion charge neutralisation process. The metal ion occupies the number of proton exchange sites equal to its charge. To remain consistent with the model used so far in this research, the data of Czerwinski *et al.* (1994) are recalculated according to our model which does not consider the charge neutralisation. The recalculated log β_{101} is 5.51.

5.4.3.1 Conditional complexation constant of $UO_2(CO_3)_2HA$

Dierckx *et al.* (1994) studied the dependence of the logarithm of the HA complexation constant of UO_2^{2+} on the free carbonate concentration at 0.1 M ionic strength and varying *p*H. A slope of more or less 2 was found and indicated the formation of $UO_2(CO_3)_2HA$ mixed complex.
The complexation reaction of this mixed complex is described by:

$$UO_2^{2+} + 2\ CO_3^{2-} + HA \rightleftharpoons UO_2(CO_3)_2HA \qquad \text{Eq. 5.54}$$

The corresponding complexation constant is defined by:

$$\beta_{121} = \frac{\left[UO_2(CO_3)_2HA\right]}{\left[UO_2^{2+}\right]\cdot\left[CO_3^{2-}\right]^2\cdot\left[HA\right]} \qquad \text{Eq. 5.55}$$

The conditional complexation constant for $UO_2(CO_3)_2HA$ is determined for each sample according to the equation developed from equation 5.53:

$$\beta_{121} = \frac{\beta^{exp} - \beta_{101}}{\left[CO_3^{2-}\right]^2} \qquad \text{Eq. 5.56}$$

By introducing the carbonate concentration obtained by geochemical modelling (Table 5.7), the conditional complexation constant determined under Boom Clay

conditions (β^{exp}) and the recalculated β_{101}, the average logarithm of the complexation constant is:

$$\mathbf{\log \beta_{121} = 20.3 \pm 0.1}$$

The formation of the mixed complex can also be defined by the stepwise reaction:

$$UO_2HA + 2\ CO_3^{2-} \rightleftharpoons UO_2(CO_3)_2HA \qquad \text{Eq. 5.57}$$

The corresponding stepwise complexation constant is described by:

$$K_{121} = \frac{[UO_2(CO_3)_2HA]}{[UO_2HA]\cdot[CO_3^{2-}]^2} \qquad \text{Eq. 5.58}$$

The conditional stepwise complexation constant for $UO_2(CO_3)_2HA$ is also calculated for each sample according to the equation developed from equation 5.51:

$$K_{121} = \frac{\frac{\beta^{exp}}{\beta_{101}} - 1}{[CO_3^{2-}]^2} \qquad \text{Eq. 5.59}$$

By introducing the same data in equation 5.59 than those used for the calculations of the conditional complexation constant (β_{121}), the average logarithm of the conditional stepwise complexation constant is:

$$\mathbf{\log K_{121} = 14.7 \pm 0.1}$$

5.4.3.2 Conditional complexation constant of $UO_2(CO_3)HA$

If the formation of $UO_2(CO_3)HA$ is assumed, the complexation reaction is described by:

$$UO_2^{2+} + CO_3^{2-} + HA \rightleftharpoons UO_2(CO_3)HA \qquad \text{Eq. 5.60}$$

The corresponding complexation constant is defined by:

$$\beta_{111} = \frac{[UO_2(CO_3)HA]}{[UO_2^{2+}]\cdot[CO_3^{2-}]\cdot[HA]} \qquad \text{Eq. 5.61}$$

Similarly to the calculations performed for the mixed complex $UO_2(CO_3)_2HA$, the conditional complexation constant for $UO_2(CO_3)HA$ is calculated for each sample:

$$\beta_{111} = \frac{\beta^{exp} - \beta_{101}}{[CO_3^{2-}]} \qquad \text{Eq. 5.62}$$

By introducing the carbonate concentration obtained by geochemical modelling (Table 5.7), the conditional complexation constant determined under Boom Clay

conditions (β^{exp}) and the recalculated β_{101} in equation 5.62, the average logarithm of the complexation constant is:

$$\mathbf{\log \beta_{111} = 16.3 \pm 0.1}$$

The formation of the mixed complex can also be defined by the stepwise reaction:

$$UO_2HA + CO_3^{2-} \rightleftharpoons UO_2(CO_3)HA \qquad \text{Eq. 5.63}$$

The corresponding stepwise complexation constant is described by:

$$K_{111} = \frac{[UO_2(CO_3)HA]}{[UO_2HA]\cdot[CO_3^{2-}]} \qquad \text{Eq. 5.64}$$

The conditional stepwise complexation constant for $UO_2(CO_3)HA$ is also determined for each sample:

$$K_{111} = \frac{\frac{\beta^{exp}}{\beta_{101}} - 1}{[CO_3^{2-}]} \qquad \text{Eq. 5.65}$$

The average logarithm of the conditional stepwise complexation constant is:

$$\mathbf{\log K_{111} = 10.8 \pm 0.1}$$

Glaus *et al.* (1995b) also determined the logarithm of the stepwise complexation constant (K_{111}). They calculated a log K_{111} of about 5, *i.e.* five orders of magnitude lower than our value. As mentioned before, log K_{1i1} strongly depends on β_{101}. In their study, Glaus *et al.* assumed that β_{101} is the complexation constant determined between *p*H 8 and 10 and in presence of EDTA (Glaus *et al.*, 1994). In such system, the hydrolysis of U(VI) and the competition between HA and EDTA may happen. These possible artefacts would explain the difference between our value and that obtained by Glaus *et al*. We prefer to use a β_{101} determined in conditions where the only mechanism occurring is the complexation of UO_2^{2+} by HA to form UO_2HA (e.g. Czerwinski *et al.*, 1994).

5.4.4 Conclusion

The dialysis technique allows to calculate a conditional complexation constant, β^{exp}, for the formation of U(VI)-humate complexes under Boom Clay conditions. The constant is conditional since it depends on the experimental conditions. Therefore, the value of β^{exp} is only valuable for Boom Clay conditions. The logarithm of β^{exp} is **12.4 ± 0.2** with no effect of the concentration of HA, the type of HA, the presence of hydrogen-phosphate and the oxidation of HA. This complexation constant is conservative since it accounts for all possible humate-complexes formed. Our value of β^{exp} is rather high in comparison with the complexation constant determined for the uranyl cation (UO_2^{2+}) at acidic *p*H. The proposed reasons to explain this difference are the effect of *p*H and metal concentration as well as the formation of mixed complexes. Indeed, mixed complexes may occur under Boom Clay conditions where

the main species of U(VI) is the tri-carbonate complex $UO_2(CO_3)_3^{4-}$. Nevertheless, it is not possible to ascertain the formation of mixed complexes nor to determine their nature by the dialysis technique. We surmise the formation of mixed complexes of U(VI) with HA and carbonate which are the most likely to occur in Boom Clay according to us: either $UO_2(CO_3)_2HA$ or $UO_2(CO_3)HA$.

By assuming the formation of the mixed complex $UO_2(CO_3)_2HA$, the following conditional complexation constants are derived:

$$UO_2^{2+} + 2\ CO_3^{2-} + HA \rightleftharpoons UO_2(CO_3)_2HA \qquad \log \beta_{121} = 20.3 \pm 0.1$$

$$UO_2HA + 2\ CO_3^{2-} \rightleftharpoons UO_2(CO_3)_2HA \qquad \log K_{121} = 14.8 \pm 0.1$$

If the formation of the mixed complex $UO_2(CO_3)HA$ is postulated, the conditional complexation constants are:

$$UO_2^{2+} + CO_3^{2-} + HA \rightleftharpoons UO_2(CO_3)HA \qquad \log \beta_{111} = 16.3 \pm 0.1$$

$$UO_2HA + CO_3^{2-} \rightleftharpoons UO_2(CO_3)HA \qquad \log K_{111} = 10.8 \pm 0.1$$

5.5 Extended x-ray absorption fine-structure spectroscopy

Since the formation of mixed complexes is surmised, extended x-ray absorption fine-structure spectroscopy (EXAFS) was performed to obtain information on the nature of the U(VI)-humate complexes formed under Boom Clay conditions. EXAFS is used to determine the distances, coordination number, and type of neighbours surrounding the absorbing atom (uranium in our case). The measurements were conducted at the XAS beamline of ANKA, the synchrotron radiation facility constructed and operated by the Forschungszentrum Karlsruhe (FZK) in Germany. The measurements and their evaluation were realised by Dr. Melissa Denecke and her staff members (Institut für Nukleare Entsorgung, FZK, Germany). As the use of such spectroscopy requires specific skills, our contribution was limited to the preparation of the samples, to be present during the beam-time and to discuss and integrate the results in the context of the research field.

5.5.1 Principle

The basic physical principle of EXAFS is given here. The reader is referred to Koningsberger and Prins (1988) and Newville (2003) for a comprehensive description of the technique.

A x-ray absorption fine structure (XAFS) experiment measures the energy dependence of the absorption coefficient at and above the binding energy of a known core level of a known atomic species. Electrons tightly bound in a quantum core level of an atom are excited through the photoelectric effect due to the absorption of an x-ray photon. When the incident x-ray has an energy equal to that of the binding energy of a core-level electron, there is a sharp rise in absorption. These are referred to absorption edges and correspond to the promotion of this core level to the continuum. Any energy in excess of the electronic binding energy is given to a photon-electron that is ejected from the atom. The XAFS technique is elemental specific; the element to be probed can be selected by tuning the x-ray energy to an appropriate absorption edge. The variation of the absorption coefficient at energies well above the edge is

characterised by an oscillatory pattern of decreasing amplitude. This region of the spectrum, from about 50 eV to about 1 keV above the edge, is called the EXAFS region. The origin of EXAFS oscillations is best understood in terms of photo-electron waves created in the absorption process. If neighbouring atoms are present, the photo-electron wave can scatter on the electrons of these neighbouring atoms. Scattering is most likely at the forward and backward directions. EXAFS results from the interference of an outgoing photo-electron wave from the absorbing atom, with a wave that has been scattered on the neighbouring atoms. The interferences between these waves are at the origin of the sinusoidal variation of the x-ray absorption coefficient with energy. The oscillatory pattern in an EXAFS spectrum can be considered as an interferogram of the local environment surrounding the absorber.
In a simplified form, the EXAFS for a *k* edge can be described as:

$$\chi(k) = \sum_i \frac{N_i F_i(k) e^{-2k^2\sigma_i^2} e^{-2R_i/\lambda(k)}}{kR_i^{\,2}} \cdot \sin\left[2kR_i + \varphi_i(k)\right] \qquad \text{Eq. 5.66}$$

$\chi(k)$ is the primary quantity for EXAFS: the oscillations as function of photo-electron wave number and $\chi(k)$ is often referred to simply as "the EXAFS". In equation 5.66, k is the wave factor, N the coordination number, R the bond distance between absorber and backscattering atoms, σ^2 is the mean square displacement of atoms at the neighbour distance (Debye-Waller factor), λ is the mean free path of the excited electrons, F and φ are the element specific backscattering amplitude and phase shift functions. The sum (Σ) is over the various coordination shells, i. The EXAFS equation allows to determine N, R and σ^2 knowing the scattering amplitude F(k) and phase shift φ(k).

5.5.2 Samples

Four samples were prepared for the EXAFS measurements (Table 5.9). The first sample, sample 1, was a reference sample where only the species $UO_2(CO_3)_3^{4-}$ was present. The other samples, samples 2, 3 and 4, were representative for Boom Clay conditions, *i.e.* use of SBCW and preparation inside a glove box with a controlled 0.4% CO_2 atmosphere. Sample 2 was prepared to verify the speciation of U(VI) under Boom Clay conditions in absence of HA. Samples 3 and 4 contained HA.

Sample 1 was obtained by mixing 2.5 ml of a 0.1 M $NaHCO_3$ solution with 2.5 ml of 0.1 M Na_2CO_3 solution. A volume of 0.5 ml of 0.1 M uranyl nitrate solution was then added, resulting in a solution containing 9.1×10^{-3} mol·l^{-1} U(VI). The final *p*H of the mixture was 9.6.

Samples representative for Boom Clay were obtained by diluting 200 μl of 0.1 M uranyl nitrate solution into 19.75 ml of SBCW bubbled for four hours with an inert gas containing 0.4% CO_2. The final U(VI) concentration was 10^{-3} mol·l^{-1}. Prior to the dilution in SBCW, the 200 μl aliquot of acidic uranyl nitrate solution was titrated with 40 μl 1 M NaOH to avoid the perturbation of the carbonate equilibrium in SBCW. Afterwards, the mixture was shaken for two hours to dissolve the U(VI) precipitate formed upon titration with 1 M NaOH[3]. Sample 2 was prepared by

[3] At U(VI) concentrations higher than 10^{-3} M, the U(VI) precipitated upon titration with 1 M NaOH remains stable, even after *p*H adjustment. The carbonate concentration in SBCW is probably too low to complex and redissolved the U(VI) precipitate.

sampling an aliquot of 5 ml from 10^{-3} mol·l^{-1} U(VI) in SBCW. The *p*H was further adjusted by the addition of 10 μl of 1 M NaOH and the solution was bubbled with a gas mixture of Ar-0.4% CO_2 for three hours. The final *p*H was 8.2. Sample 3 and 4 were prepared the same way, except that Aldrich HA were added to the 5 ml aliquot of SBCW containing 10^{-3} mol·l^{-1} U(VI). The HA concentration was 920 mg·l^{-1} for sample 3 and 1600 mg·l^{-1} for sample 4. The *p*H of the mixture was adjusted with aliquots of 1M NaOH or 0.1 M HCl before bubbling for three hours with the gas mixture of Ar-0.4% CO_2. The final *p*H of samples 3 and 4 was 8.2 and 8.3 respectively. Samples 2, 3 and 4 had very similar *p*H and therefore, the only variable parameter was the concentration of HA.

Table 5.9. Samples prepared for the EXAFS measurements.

Samples	[U] mol·l^{-1}	[HA] mg·l^{-1}	*p*H	Uranium species	Characteristic
Sample 1	9.1×10^{-3}	—	9.6	$UO_2(CO_3)_3^{4-}$	Reference sample
Sample 2	1.0×10^{-3}	—	8.2	$UO_2(CO_3)_3^{4-}$?	Boom Clay conditions
Sample 3	1.0×10^{-3}	920	8.2	?	Boom Clay conditions
Sample 4	1.0×10^{-3}	1600	8.3	?	Boom Clay conditions

5.5.3 Experimental conditions

The storage ring was operated at the nominal energy of 2.5 GeV with an electron beam current of 180 mA. The uranium L_{III}-edge (17.166 keV) was measured using a Si(311) double-crystal monochromator. Uranium L_{III}-edge EXAFS transmission spectra were measured for sample 1 whilst uranium L_{III}-edge EXAFS fluorescence spectra were considered for samples 2, 3 and 4. The spectra were recording using argon filled ionisation chambers for the measurements in transmission and a 5-pixel high purity Ge detector (Canberra) for fluorescence measurements. Scattering amplitude and phase-shift functions were theoretically calculated using feff 8.0 modelling code by considering a complex of the type $UO_2(CO_3)_3^{4-}$. Data reduction and analysis were performed using the suite of programs UWXAFS.

5.5.4 Results

The four samples show very similar EXAFS patterns up to *k* equal 10 Å^{-1} (Fig. 5.7a). The observed similarities are also reflected in the corresponding Fourier transforms shown in Figure 5.7b. The most intense peak at about 1.35 Å corresponds to the axial oxygen atoms, O_{ax}, of the uranyl unit. The next peaks at about 1.95 and 2.55 Å represent the equatorial oxygen atoms, O_{eq}, and the carbon atoms, C, coordinated to uranium, respectively. The weak peak at 3 Å results from multiple scattering along the uranyl unit. The peak at 3.5 Å arises from both simple and multiple scattering involving the distal oxygen atoms, O_{dis}.

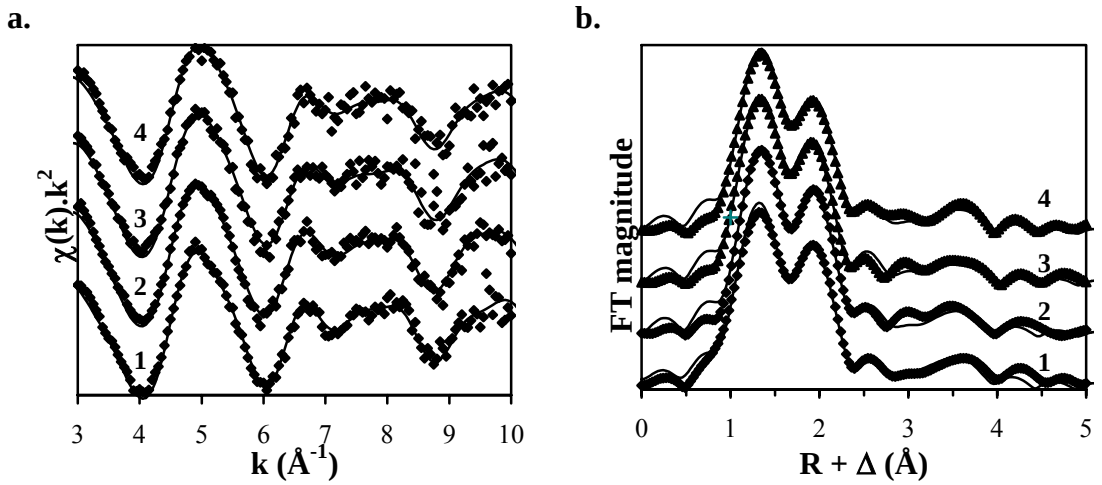

Figure 5.7. k^2-weighted uranium L_{III}-edge EXAFS spectra (a) and corresponding Fourier transforms (FT) without phase shift correction, R+Δ (b). The dots are the experimental data and the solid lines are the fits. For clarity, the spectra were shifted along the y-axis. Numbers refer to samples described in the text.

The EXAFS oscillations are fitted to the EXAFS equation using a structural model of type $UO_2(CO_3)_3^{4-}$. In addition to single scattering events on O_{ax}, O_{eq}, C, and O_{dis}, multiple scattering involving O_{ax} and O_{dis} are considered in the fit. The coordination number (N) for the axial oxygen is held constant at 2. The Debey-Waller factors (σ^2) are also held constant. Fit results are listed in Table 5.10. The fits are satisfactory as indicated by the residues lower or equal to 1%.

Fit results for the sample 1 are in accordance with a complexation by three bidendate carbonate ligands, *i.e.* $UO_2(CO_3)_3^{4-}$ complex. In this configuration, uranium is surrounded by two axial oxygen atoms, six equatorial oxygen atoms, three carbon atoms and three distal oxygen atoms (Figure 5.8). The bond distances are in good agreement with ones reported in the literature for the tricarbonatodioxouranate (*e.g.* Docrat *et al.*, 1999; Bargar *et al.*, 1999; Gagliadi *et al.*, 2001; Bernhard *et al.*, 2001).

The fit parameters for sample 2 are very similar to those of sample 1 indicating that U(VI) occurs as the tricarbonate-complex in SBCW as expected according to the geochemical calculations. The addition of HA (samples 3 and 4) does not alter significantly the values of the coordination number (N) and distances (R). There is a trend of decreasing N with addition of HA to the solutions which could indicate HA complexation. However, the large error in the determination of this parameter (~20 %) does not allow to consider this trend as significant. Results show that the tricarbonate-complex of U(VI) remains dominant in all samples. The humate complexes are not formed in sufficient amounts to detect structural changes in average U(VI) coordination.

Table 5.10. Fit parameters of U L_{III}-edge EXAFS data for the four samples. Estimated standard deviation are given in parentheses. Oax: axial oxygen, Oeq: equatorial oxygen, C: carbon, Odis: distal oxygen, R: distance, N: coordination number, σ^2: Debye-Waller factor.

Samples		Oax	Oeq	C	Odis	Residue
Sample 1	R (Å)	1.78 (0.01)	2.43 (0.01)	2.92 (0.01)	4.16 (0.02)	0.5 %
	N#	2*	6	3	3	
Sample 2	R (Å)	1.80 (0.01)	2.45 (0.01)	2.92 (0.01)	4.18 (0.02)	1.0 %
	N#	2*	6.1	3.0	2.4	
Sample 3	R (Å)	1.79 (0.01)	2.44 (0.01)	2.89 (0.02)	4.17 (0.03)	0.8 %
	N#	2*	5.8	2.6	2.2	
Sample 4	R (Å)	1.79 (0.01)	2.44 (0.01)	2.92 (0.02)	4.18 (0.02)	0.8 %
	N#	2*	5.5	2.8	2.3	
σ^2 (Å^2)		0.0017*	0.0075*	0.0022*	0.0047*	

error in coordination number was ± 20%
* held constant during the fit

The analysis of the EXAFS spectra give independent and spectroscopic evidences that:

- the tricarbonate-complex dominates the speciation of U(VI) in SBCW in absence of HA;
- this complex remains the dominant species under Boom Clay conditions even for HA concentration as high as 1600 mg·l^{-1}.

They do not, however, demonstrate the formation of mixed complexes of U(VI) with HA and carbonate.

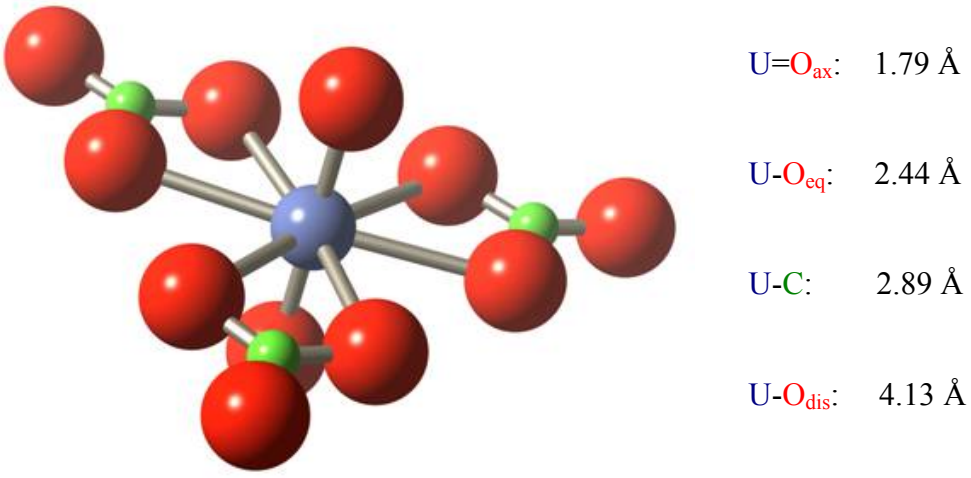

Figure 5.8. schematic tri-dimensional representation of the $UO_2(CO_3)_3^{4-}$ structure.

5.6 Conclusions

The complexation of U(VI) by humic acids (HA) was studied in synthetic Boom Clay water (SBCW) by the conventional dialysis technique at *p*H 8.2 and under the *in situ* partial pressure of CO_2 at $10^{-2.4}$ atm. The fraction of U(VI) complexed by Boom Clay HA in Boom Clay pore water is less than 5%. Therefore, the U(VI) speciation is clearly dominated by the inorganic carbonate complexes, and especially $UO_2(CO_3)_3^{4-}$. The complexation of U(VI) by HA is probably prevented by the repulsion between the anionic ligand (CO_3^{2-}) of the inorganic carbonate complexes and the anionic charge of HA functional groups. Under the atmospheric partial pressure of CO_2, the humate complexes dominate the speciation of U(VI) indicating that the low complexation of U(VI) by HA under Boom Clay conditions results from the competing effect of carbonate.

The dialysis technique allows to determine a conditional complexation constant (β^{exp}). Under our experimental conditions, log β^{exp} is **12.4 ± 0.2** and independent from the concentration of HA, the type of HA, the presence of hydrogen-phosphate and the oxidation of HA. This constant is conservative since it takes into account all possible humate-complexes. Therefore, it can be used to calculate the speciation of U(VI) in Boom Clay conditions. The formation of mixed complexes of U(VI) with HA and carbonate is assumed on the basis of the high β^{exp} value compared to the value determined at low *p*H by previous authors. The conditional complexation constants are determined for two hypothetical mixed complexes: $UO_2(CO_3)$HA and $UO_2(CO_3)_2$HA. However, the presence of mixed complexes can not be evidenced by EXAFS. EXAFS provides independent results showing that the tricarbonate-complex of U(VI) dominates the U(VI) speciation in SBCW even for HA concentration as high as 1600 $mg \cdot l^{-1}$.

Dialysis experiments and EXAFS analyses clearly show that the complexation of U(VI) by HA is weak under Boom Clay conditions. The implication of this study for the direct disposal of spent fuel in Boom Clay is that mobile organic matter does not increase U(VI) migration by complexation in solution.

5.7 References

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