Chapter 4
Experimental conditions

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4.1 Introduction

The data gathered from a study conducted with the Boom Clay are the global result of various processes occurring in its different constituents. Indeed, the mobility of uranium in the Boom Clay is determined by its solubility, its interactions with inorganic and organic solid surfaces and its complexation with inorganic and organic ligands. In addition, uranium is a redox-sensitive element and its oxidation state controls all its geochemistry. Working on a simplified synthetic system instead of the natural one has the main advantage that the most important mechanisms such as complexation, solubility, reduction and sorption can be studied separately. Studies on a simplified synthetic system consist in batch experiments (Table 4.1):

- complexation of U(VI) by humic acids (HA),
- solubility of U(IV) amorphous precipitate at various concentrations of HA,
- sorption of U(VI) onto Boom Clay pyrite and U(IV) onto pure constituents of the Boom Clay mineral assemblage.

Table 4.1. Overview of the batch experiments performed for the study of the mechanisms controlling the uranium migration; SBCW: synthetic Boom Clay water, BCW: Boom Clay water, HA: humic acids.

Process	Test	Water	Radionuclide		Atmosphere[#]
Complexation				***HA***	
	Cp-2	SBCW	U(VI)	Aldrich	Ar–0.4% CO_2
	Cp-3	SBCW	U(VI)	Aldrich	Ar–0.4% CO_2
	Cp-5	SBCW	U(VI)	Boom Clay	Ar–0.4% CO_2
	Cp-6	SBCW	U(VI)	Boom Clay	Ar–0.4% CO_2
	Cp-7	SBCW	U(VI)	Boom Clay	Ar–0.4% CO_2
	Cp-8	pure water	U(VI)	Boom Clay	air
	Cp-9	pure water	U(VI)	Boom Clay	air
Solubility				***Added HA***	
	S-2	BCW	U(IV)	—	Ar–0.4% CO_2
	S-2'	BCW	U(IV)	—	Ar–0.4% CO_2
	S-3	BCW	U(IV)	—	Ar–0.4% CO_2
	S-5	SBCW	U(IV)	—	Ar-5% H_2-0.4% CO_2
	S-6	BCW	U(IV)	—	Ar-5% H_2-0.4% CO_2
	S-7	SBCW	U(IV)	Boom Clay	Ar-5% H_2-0.4% CO_2
	S-8	SBCW	U(IV)	Boom Clay	Ar-5% H_2-0.4% CO_2
	S-9	SBCW	Th(IV)	Aldrich	Ar-5% H_2-0.4% CO_2
	S-10	SBCW	Th(IV)	Boom Clay	Ar-5% H_2-0.4% CO_2
	S-11	BCW	U(IV)	—	Ar-5% H_2-0.4% CO_2
	S-12	SBCW	U(IV)	Boom Clay	Ar-5% H_2-0.4% CO_2
	S-13	SBCW	U(IV)	Boom Clay	Ar-5% H_2-0.4% CO_2
Sorption				***Mineral***	
	Sp-1	SBCW	U(VI)	pyrite	Ar-5% H_2-0.4% CO_2
	Sp-2	BCW	U(VI)	pyrite	Ar-5% H_2-0.4% CO_2
	Sp-4	BCW	U(IV)	various	Ar-5% H_2-0.4% CO_2

volume %

The batch experiments were conducted under conditions representative for the Boom Clay, *i.e.* anaerobic and slightly alkaline. Anaerobic conditions were ensured by working inside glove boxes containing very low level of oxygen (a few ppm). The slightly alkaline conditions were achieved by conducting the experiments in Boom Clay pore water or in synthetic Boom Clay water under the *in situ* partial pressure of CO_2 at $10^{-2.4}$ atm. The extreme reducing conditions required for the handling of U(IV) were imposed by the utilisation of reducing agents such as dithionite, sulphide, Fe powder and/or by conducting the experiments under an atmosphere containing 5% H_2.

4.2 Anaerobic glove boxes

The use of glove boxes aims to perform experiments under conditions representative for the Boom Clay: absence of O_2 (anaerobic) and representative partial pressure of CO_2.

The experiments were carried out inside two glove boxes filled with two different atmospheres (Figure 4.1):

- Jacomex (BS 531 NMT4NMT) glove box with controlled Ar-0.4%CO_2 atmosphere
- Braun (MB 150B-G) glove box with a controlled Ar-5%H_2-0.4%CO_2 atmosphere.

The Jacomex glove box is operational since 1997 and has typically an O_2 content around 5 ppm. This glove box was used to conduct the U(VI) complexation experiments and a part of the solubility experiments of U(IV). The Braun glove box is operational since 2003. It is specially designed to work with U(IV) which requires extremely low O_2 content and reducing conditions. In that glove box, the oxygen content is lower than 1 ppm. Very low values of O_2 are achieved by the principle of gas circulation and oxygen removal: the gas permanently circulates between the glove box and the oxygen purification system composed of two Cu-getter columns. The gas circulation is carried out by a turbo-blower. The presence of 5 % H_2 in the gas mixture ensures a reducing atmosphere. The Braun glove box was used to perform a part of the solubility experiments and all sorption tests.

Both glove boxes do not only guarantee to conduct the experiments under anaerobic conditions but also to work at a representative CO_2 partial pressure of the Boom Clay. As mentioned in Chapter 1, a CO_2 partial pressure of about $10^{-2.4}$ atm is considered as the reference value for the Boom Clay. Such partial pressure corresponds to a CO_2 concentration of 3800 ppm. Therefore, the glove boxes are filled with a gas mixture containing 0.4% CO_2 (4000 ppm) to simulate the *in situ* CO_2 partial pressure, which controls the carbonate concentration and the solution *p*H.

a.

b.

Figure 4.1. Pictures of the glove boxes. **a**: Jacomex (BS 531 NMT4NMT) glove box, Ar-0.4%CO_2 atmosphere. **b**: Braun (MB 150B-G) glove box, Ar-5%H_2-0.4%CO_2 atmosphere.

4.3 Boom Clay water

In the batch experiments, two different types of Boom Clay water were used: Boom Clay pore water (BCW) and synthetic Boom Clay water (SBCW).

4.3.1 Boom Clay water

Boom Clay pore water (BCW) is sampled under anaerobic conditions from the Extension Gallery/Bottom Shaft (EG/BS) piezometer in the underground research laboratory at a depth of about -250 m below the surface. This water is generally used as reference BCW in many laboratory experiments. The EG/BS water composition is reminded in Table 4.2 (see also Table 1.8). Boom Clay pore water is of the sodium bicarbonate type ($NaHCO_3$ ~ 1.5×10^{-2} mol·l^{-1}) and contains about 115 mg·l^{-1} of dissolved organic carbon (De Craen *et al.*, in preparation). During the sampling in 20 litres barrels, BCW undergoes severe degassing in terms of CO_2. Therefore, the water is re-equilibrated with the *in situ* partial pressure of CO_2 before use by bubbling with 0.4% CO_2 gas mixture until constant *p*H inside the glove box.

Table 4.2. Average composition of Boom Clay pore water form the EG/BS piezometer (Dierckx, 1997).

	mol·l^{-1}	**mg·l^{-1}**
HCO_3^-	1.4×10^{-2}	828
Cl^-	7.6×10^{-4}	27
F^-	1.9×10^{-4}	3.6
HPO_4^{2-}	4.0×10^{-5}	3.8
Br^-	6.1×10^{-6}	0.49
SO_4^{2-}	2.1×10^{-6}	0.2
Na^+	1.8×10^{-2}	408
K^+	2.8×10^{-4}	11
Mg^{2+}	1.2×10^{-4}	2.9
Ca^{2+}	9.9×10^{-5}	4.0
B	6.9×10^{-4}	7.5
Si	1.8×10^{-4}	5
Fe	1.6×10^{-5}	0.9
Al	2.9×10^{-6}	0.08
TOC	—	110
Log p_{CO_2}, atm	-2.42	
E_h, mV	-275	
*p*H	8.2	

Wang *et al.* (2000) mentioned that the phosphate concentration in EG/BS water is lower than 2.5 ppm.

The water analysis of BCW batches used in the experiments is given in Appendix 1.

4.3.2 Synthetic Boom Clay water

Synthetic Boom Clay water (SBCW) is prepared to obtain the same composition than BCW apart from the presence of dissolved organic matter.

To prepare one litre of SBCW, the soluble salts given in Table 4.3 are dissolved into one litre of ultra-pure water (Milli-Q, 18 MOhm cm). Na_2SO_4 is added by pipetting 10 ml from a 30 ppm solution; a weight of 0.3 mg being too low to be accurately weighed. A volumetric flask of one litre is first cleaned thoroughly and rinsed with deionised water. Then, each pure salt is weighted separately in an aluminium cup with an analytical balance (0.1 mg). They are transferred one by one into the volumetric flask which already contains about 0.5 litre of ultra-pure water and 10 ml of the 30 ppm Na_2SO_4 solution. The aluminium cup are rinsed 3 times with ultra-pure water. After the transfer of all the salts, the flask is filled to the one litre mark.

Table 4.3. Weight of salts needed for the preparation of one litre of synthetic Boom Clay water.

Salt	Quantity (mg)	MW	(mol·l^{-1})
$NaHCO_3$	1 170mg	83.996	1.39 E-02
H_3BO_3	43 mg	61.834	6.95 E-04
KCl	25 mg	74.555	3.35 E-04
$MgCl_2 \cdot 6\ H_2O$	22 mg	203.218	1.08 E-04
NaF	11 mg	41.988	2.62 E-04
NaCl	10 mg	58.443	1.71 E-04
Na_2SO_4	0.3 mg	142.041	2.11 E-06
Total Dissolved Salts		—	1.55 E-02

MW: Molecular Weight

As the calcium concentration is expected to be controlled by the solubility of calcium carbonate in the Boom Clay (about 4 ppm), calcium carbonate is added in excess to the solution and the suspension is allowed to equilibrate for at least 10 days under continuous magnetic stirring. After this period, the supernatant solution is filtered through a 0.22 μm filter (Millipak-60, Millipore) to remove any residual particles of $CaCO_3$. A general overview of the chemical composition of SBCW is given in Table 4.4.

Table 4.4. Chemical composition of SBCW.

	(mol·l^{-1})	MW	(mg·l^{-1})
Na^+	1.44 E-02	22.990	330.3
K^+	3.35 E-04	39.098	13.1
Mg^{2+}	1.08 E-04	24.305	2.6
Ca^{2+}	—	40.078	—
Sum cations (eq.g.)	*1.48 E-02*		*346*
HCO_3^-	1.39 E-02	61.017	849.9
Cl^-	7.70 E-04	35.453	27.3
F^-	2.62 E-04	18.998	5.0
SO_4^{2-}	2.11 E-06	96.064	0.2
Sum anions (eq.g.)	*1.49 E-02*		*882.4*
$B(OH)_3$	6.95 E-04	61.834	43.0

After preparation, the *p*H of SBCW is about 8.5. To obtain the *in situ p*H of 8.2, it is necessary to equilibrate the water with an inert gas mixture containing 0.4 % CO_2. 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.

An important element regarding to the composition of BCW which is not present in the SBCW recipe is iron. Iron can be included by dissolving 3 mg·l^{-1} of ferrous chloride ($FeCl_2 \cdot 4\ H_2O$). This imposes to work under anaerobic conditions with deoxygenated water because the oxidation of Fe(II) to Fe(III) and the subsequent precipitation of oxyhydroxide can occur. In the frame of the study of U(VI) complexation by humic acids, no Fe was added to SBCW for the following reasons:

- Fe can form complexes with humic acids and can thus compete with U(VI),
- Fe(II) can be oxidised to Fe(III). The Fe(III) formed will precipitate as ferric oxyhydroxide on which U(VI) is strongly sorbed and,
- Fe(II) is able to reduce U(VI) in presence of hematite (Liger *et al.*, 1999).

In the solubility and sorption experiments, iron was added via equilibration of SBCW with metallic Fe-powder for at least 6 days. The dissolved oxygen content of the Fe-equilibrated water is estimated to be lower than 10^{-75} atm, many orders of magnitude lower than the 10^{-6} atm generally achievable by bubbling pure inert gas (Rai *et al.*, 1990). By doing this, the concentration of Fe in SBCW is limited by the dissolution of Fe-powder. For example, the Fe concentration was 0.15 $mg \cdot l^{-1}$ and 1.31 $mg \cdot l^{-1}$ after 4 and 14 days of equilibration with Fe-powder, respectively.

The water analysis of the different batches of SBCW prepared for the experiments is given in Appendix 1.

4.4 References

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