
Chapter 2

Disposal of spent nuclear fuel: uranium as main radionuclide

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2.1 Disposal of spent nuclear fuel in deep geological formations

In the past, the Belgian strategy concerning spent nuclear fuel and nuclear waste management was based on reprocessing. Nowadays, the Belgian Agency for Radioactive Waste and Enriched Fissile Materials is also considering the direct disposal of spent fuel as a possible alternative. The solution recommended at international level for the long-term management of this high-level and long-lived waste is to isolate it from humans and the environment, namely to dispose of it in a stable geological formation with appropriate characteristics. A fundamental concern in safety assessments of nuclear waste repositories is the potential release of radionuclides to the environment as dissolved constituents in aquifers.

The safety of high-level waste disposal in a geological formation is mainly based on its ability to efficiently delay the migration of radionuclides. The objective is that, whenever they reach the biosphere, the concentration levels will be low enough to prevent any health consequence for human beings. The long-term safety of the nuclear waste repository relies on the principle of multiple barriers. Engineered and natural barriers are placed between the waste and the biosphere for a period of time that is long enough to allow a sufficient decrease in the activity of the radionuclides before their release into the biosphere in the long term.

The physical containment of the waste is achieved by an engineered barrier, the waste container. The purpose of the container is to prevent contact with water at least during the thermal phase, *i.e.* the period during which the waste presence in the disposal system significantly increases the temperature. A container lifetime of 2000 years is generally considered. Other engineered barriers are the backfill material and the disposal gallery seals.

Since it is not possible to guarantee that the radioactivity has decayed to a harmless level before the degradation of the engineered barriers, the safety of the nuclear waste repository is primarily ensured by the natural barrier. The natural barrier is the main barrier and consists of the geological host formation that surrounds the engineered barriers. Its function is to delay the migration of the radionuclides leached from the waste packages to allow their maximum radioactive decay within the formation.

The aquifers and the biosphere are not considered to be part of the disposal system. Their function is to dilute and disperse within the underground and surface flows of water the release of radionuclides to the biosphere in the very long term.

2.2 The Boom Clay as a candidate host formation

The main barrier ensuring the long-term safety of the disposal system is the geological formation which will delay and spread the release of radionuclides towards the biosphere. In Belgium, research is concentrated on argillaceous formations because of their expected favourable properties and their presence at an accessible depth. Since 1974, the Boom Clay is studied for site characterisation and is currently considered as a potential host formation. Under the facilities of the SCK•CEN at Mol, the Boom Formation is about 100 m thick and is located at a depth of -190 m to -293 m. The Boom Clay separates the overlying Neogene aquifer from the underlying Ruisbroek-Berg and Lede-Brussel aquifers (Figure 2.1).

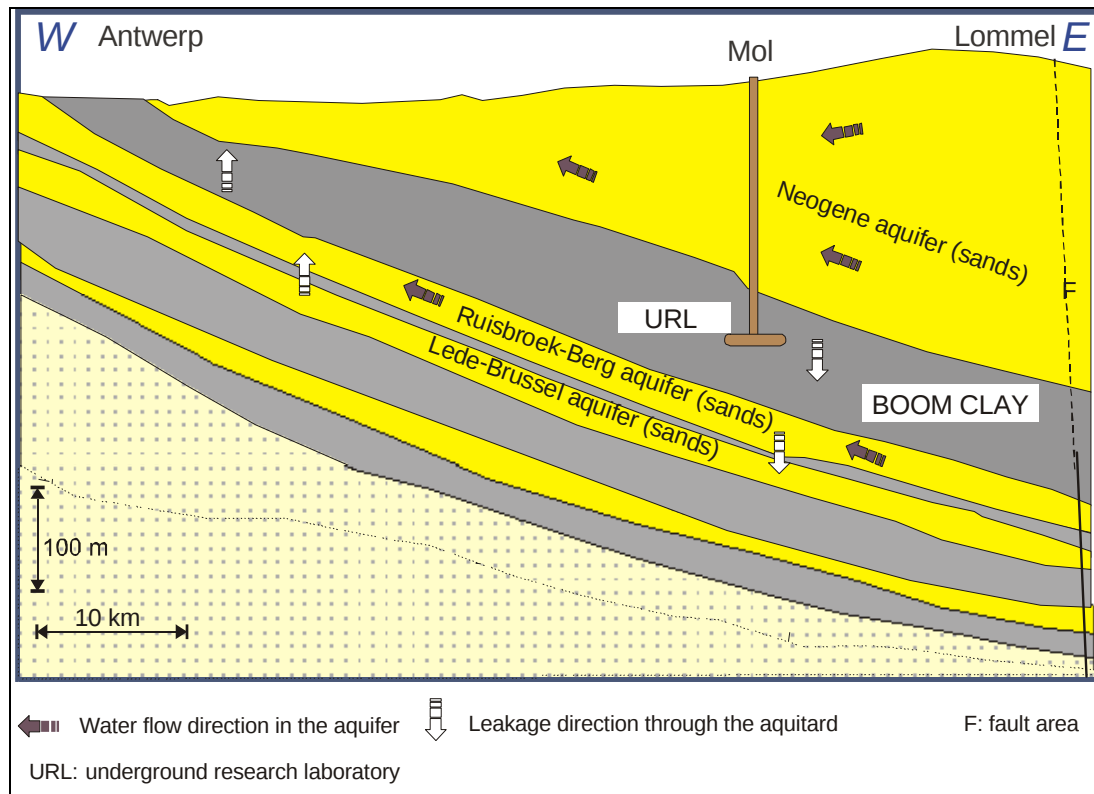


Figure 2.1. Hydrogeological cross-section of the regional Mol area (from Wemaere *et al.*, 2000)

The favourable physical characteristics of the Boom Clay as potential host formation are:

- its sufficient thickness (about 100 m) and depth (190 m),
- its location in an area of low seismic and tectonic activity,
- its adequate plasticity resulting in self healing of fissures,
- its very low hydraulic conductivity (about $2 \times 10^{-12} \text{ m} \cdot \text{s}^{-1}$),
- its specific surface area ($44 \text{ m}^2 \cdot \text{g}^{-1}$),
- its low diffusion constant for anions ($< 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$).

Besides its physical properties, the geochemical features of the Boom Clay are very interesting towards the retention of radionuclides:

- strongly reducing conditions as indicated by the presence of pyrite, siderite and organic matter (E_h about -300 mV),
- slightly alkaline environment ($\text{pH} \sim 8.2$, $\sim 10^{-2} \text{ M HCO}_3^-$, $\text{pCO}_2 \sim 10^{-2.4} \text{ atm}$),
- cation exchange capacity ($\sim 25 \text{ meq}/100 \text{ g}$ of rock).

Because of its very low hydraulic conductivity, the transport in the Boom Clay is practically limited to diffusion, *i.e.* transport due to concentration gradient. Moreover, the migration of radionuclides is delayed by several retention processes such as sorption (by cation exchange and surface complexation) on inorganic and organic solid surfaces and precipitation, especially of redox sensitive radionuclides like neptunium, uranium, plutonium, In Boom Clay pore water, the most important reactions for multivalent cations are hydrolysis and complexation with naturally occurring ligands such as carbonate and dissolved organic matter. By consequence, the effect of organic matter present in Boom Clay is twofold. On one hand, the retention of radionuclides by insoluble and immobile organic matter, which represents more than 99.9% of the total organic matter, will retard their migration. On the other

hand, the complexation of radionuclides by soluble and mobile organic matter (mainly humic acids) might increase their mobility.

2.3 Critical radionuclides for the disposal of spent fuel

Performance assessment (PA) studies aim to evaluate the long-term safety of deep disposal of nuclear waste on the basis of simulations using information on the repository design and migration parameters of the radionuclides within the Boom Clay. The International Commission on Radiological Protection (ICRP) recommends that the maximum permitted dose for deep repository should not exceed 0.3 mSv per year. By comparison, the mean exposure to ionising radiation in Belgium represents a dose of 3.6 mSv per year.

For example, the calculated dose rate received by man in the case of the disposal of spent fuel is shown in Figures 2.2 and 2.3 considering the reference scenario. The reference scenario describes the expected sequence of events and processes following the closure of the disposal facility. One also assumes that the dose rate comes from a well drilled into the overlying Neogene aquifer. The total dose rate results from the sum of the individual contribution of the radionuclides. Up to about 1 million years, the dose rate is controlled by the activation and fission products (I-129, Se-79, Cl-36, Tc-99, ...). Since we are dealing with uranium, the individual contribution of the activation and fission products are not represented in Figures 2.2 and 2.3, only the total dose rate is given.

Because of the uncertainties about the interpretation of the migration experiments and the lack of experimental data for actinides in the Boom Clay, several migration data sets are defined (Sillen and Marivoet, 2002). The main differences between the data sets concern the solubility limits and the retardation factor¹. Figure 2.2 is based on data set 1 in which the solubility limit and the retardation factor of uranium are $10^{-4} \text{ mol}\cdot\text{l}^{-1}$ and 300, respectively. At the very long term (about 1 million years), the dose rate is controlled by the actinides. The dose rate due to Ra-226 is controlled by the migration of its parent isotopes, *i.e.* U-238, U-234 and Th-230. Other relatively important actinides are Th-230, Pa-231 and U-236. Therefore, performance assessment studies clearly indicate that uranium isotopes and their daughters are the main contributors to the total dose rate at very long term when calculations are performed with migration data set 1. In migration data set 2', the solubility limit for uranium is $5 \times 10^{-10} \text{ mol}\cdot\text{l}^{-1}$ and its retardation factor is 40. Compared to set 1, the very long-term dose rate decreases by more than 2 orders of magnitude due to the lowered solubility of actinides defined in set 2' (Figure 2.3). The main dose contributor are Np-237 and its daughters U-233 and Th-229. Using set 2', the contribution of uranium isotopes and their daughters to the total dose rate is several orders of magnitude lower than the contribution determined with data set 1. In all cases, the total dose rate remains at least one order of magnitude lower than the dose constraint (Figures 2.2 and 2.3).

By comparing Figures 2.2 and 2.3, it is obvious that sound scientific explanations of the uranium behaviour (solubility limit, sorption, organic matter complexation, ...) are needed to gain confidence in the data on which assessments made for geological disposal of spent fuel are based. The general objective of the present research is to provide such scientific explanations.

¹ Parameters for uranium in data set 1: solubility limit $S = 10^{-4} \text{ M}$ and retardation factor $R = 300$.
Parameters for uranium in data set 2': solubility limit $S = 5 \times 10^{-10} \text{ M}$ and retardation factor $R = 40$.

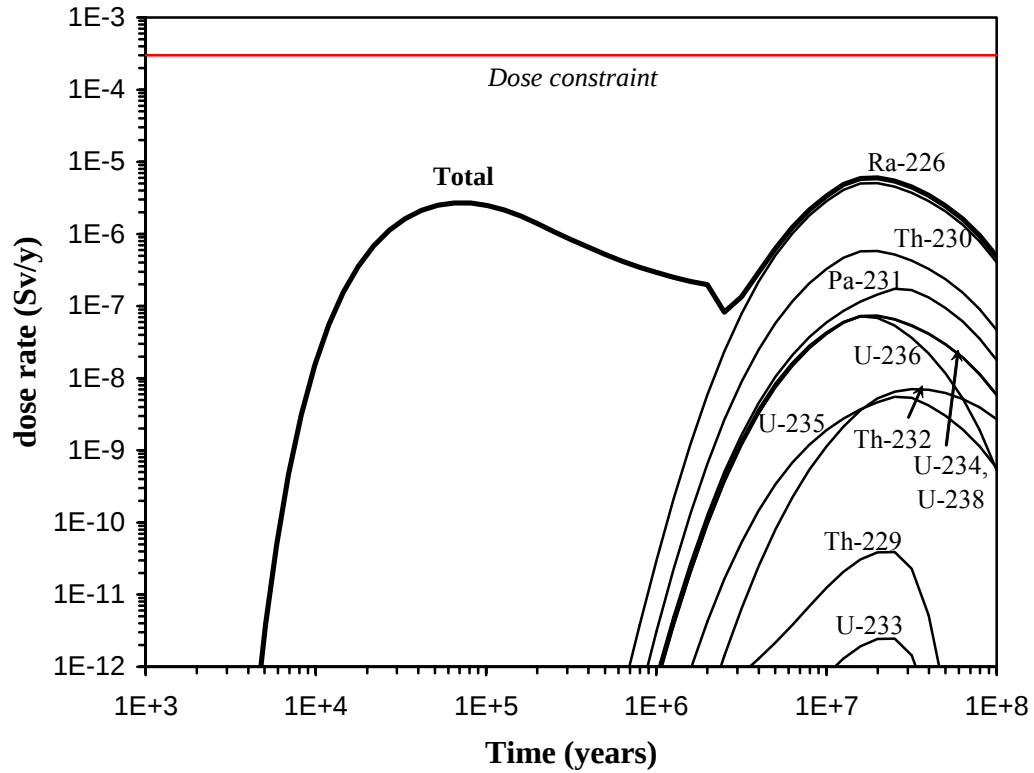


Figure 2.2. Total dose rate (bold curve) from a well in the Neogene aquifer and individual contribution of the actinide using migration parameters set-1 (Sillen and Marivoet, 2002).

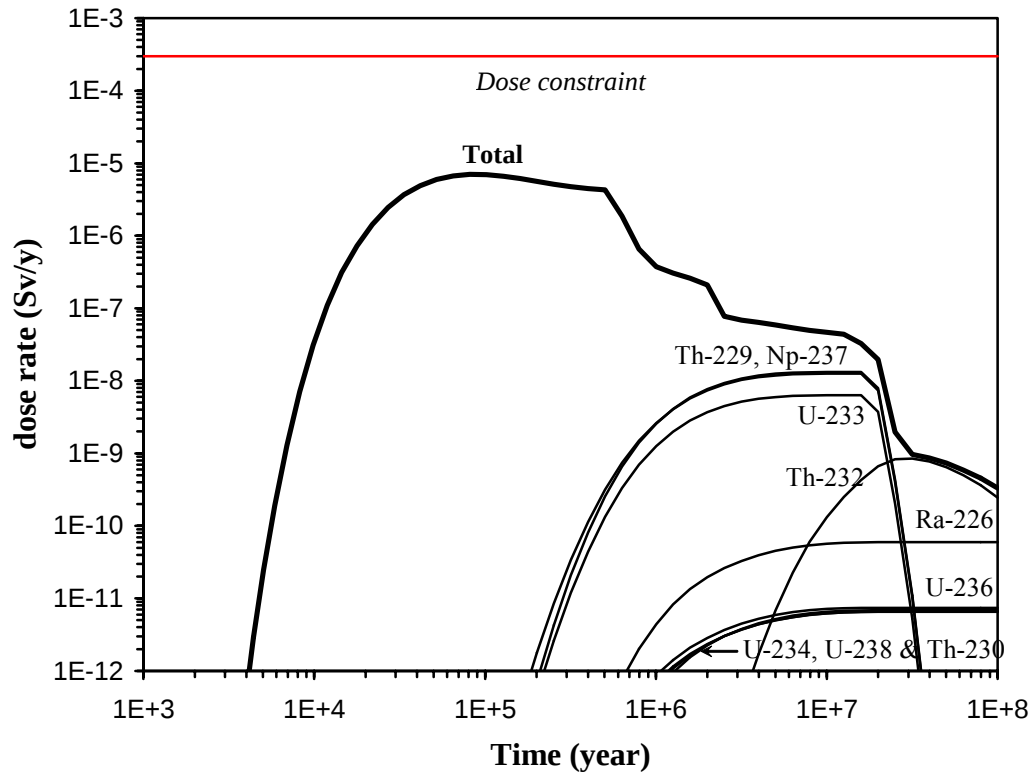


Figure 2.3. Total dose rate (bold curve) from a well in the Neogene aquifer and individual contribution of the actinide using migration parameters set-2' (Sillen and Marivoet, 2002).

2.4 Uranium geochemistry

To explain and to model its migration in the Boom Clay, it is essential to know the geochemical features of uranium and especially its speciation, *i.e.* the particular form in which uranium exists in water or as solid phases. First, we will present the general characteristics of the uranium geochemical behaviour. Afterwards, we will focus on the uranium speciation in the Boom Clay.

2.4.1 General behaviour

The general features of the geochemical cycle of uranium are well known. The description of the uranium geochemistry given below is mainly based on the reference publications of Langmuir (1978 and 1997).

Uranium is the most abundant of naturally occurring actinides with values averaging 1.2 ppm in sedimentary rocks, and ranging from 2.2 to 15 ppm in granites and from 20 to 120 ppm in phosphate rocks. Seawater contains 2 to 3.7 $\mu\text{g}\cdot\text{l}^{-1}$ uranium. The possible oxidation state of uranium are 3+, 4+, 5+ and 6+, which are usually written as U(III), U(IV), U(V), and U(VI). Most important in nature are the tetravalent and hexavalent oxidation states. The chemistry of uranium in environmental and geological fluids is dominated by the difference in behaviour of the predominant tetravalent and hexavalent ions. The tetravalent form generally has low solubility whereas the hexavalent form is relatively soluble as the uranyl ion (UO_2^{2+}) and its complexes.

Uranous ion (U^{4+}) and its aqueous complexes predominate in groundwater of low redox potential. Because of its high electric charge, tetravalent uranium ions has a strong tendency towards hydrolysis in aqueous solution. The main aqueous complex of U(IV) is $\text{U}(\text{OH})_4(\text{aq})$. Carbonate complexes of U(IV) are formed at bicarbonate and carbonate concentrations higher than 4×10^{-2} and $0.1 \text{ mol}\cdot\text{l}^{-1}$, respectively (Rai *et al.*, 1998). U(IV) is the major oxidation state in the most common uranium ore minerals uraninite (UO_2) and coffinite (USiO_4). The U(IV) concentrations in groundwater at low E_h are usually less than $10^{-8} \text{ mol}\cdot\text{l}^{-1}$ because of the extremely low solubilities of these solids. Uraninite is the most common U(IV) mineral species, and is the main ore mineral in many uranium deposits. Most natural uraninites are probably always at least partially oxidised, with the formula UO_{2+x} with x in the range 0.0 to 0.25 (Burns, 1999).

In oxidised surface and ground waters, uranium is transported as highly soluble uranyl ion and its complexes. Depending on the pH and solution composition a wide variety of uranyl complexes may form. The most important are the carbonate complexes. Organic complexes can also be particularly important in determining the uranium speciation. In absence of CO_2 , the uranyl ion is the dominant species at pH lower than about 5. Above about pH 5, U(VI) generally occurs as hydroxyl complexes. Uranyl ion forms strong carbonate complexes in most natural waters. At atmospheric CO_2 pressure ($10^{-3.5} \text{ atm}$) and for a typical groundwater CO_2 pressure (10^{-2} atm), the carbonate complexes largely replace the U(VI) hydroxyl complexes above pH 6 to 7. The carbonate complexes are extremely important because they greatly increase the solubility of uranium minerals, facilitate U(IV) oxidation, and also limit the extent of uranium adsorption in oxidised waters, thus increasing uranium mobility. Other important U(VI) complexes are formed with fluoride, phosphate and sulphate ligands, for example. Because uraninite dissolution can be rapid in oxidising, aqueous environments, the oxidative dissolution of uraninite

caused by the weathering commonly leads to the development of a complex array of U(VI) minerals.

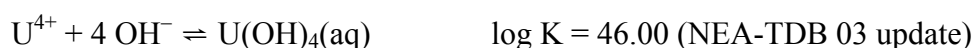
2.4.2 Behaviour in the Boom Clay

The direct determination of the uranium speciation in the Boom Clay by spectroscopic techniques is currently not possible since the uranium concentration is in the range of 10^{-10} to 10^{-8} mol·l⁻¹ in the pore water and about 4 ppm in the solid phase. Moreover, no uranium phases have been recognised up to now. Therefore, the uranium speciation is predicted by geochemical modelling, and indirectly deduced from field observations, literature data and migration experiments.

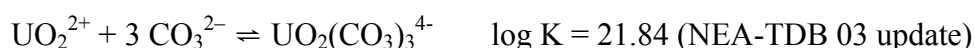
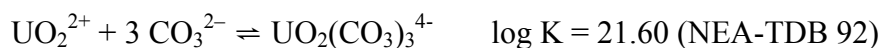
2.4.2.1 Geochemical predictions

Speciation calculations allow to predict the uranium species under given geochemical conditions. The calculations are computed with the code "The Geochemist's Workbench" (Bethke, 2001) and the Nuclear Energy Agency thermodynamic databases (NEA-TDB): NEA-TDB 92 (Grenthe *et al.*, 1992) and NEA-TDB 03 update (Guillaumont *et al.*, 2003). The diagrams of uranium speciation in Boom Clay pore water are produced using the EG/BS water composition (Table 1.8) and by fixing the bicarbonate concentration at 1.4×10^{-2} mol·l⁻¹. The total uranium concentration in solution is fixed at 10^{-8} mol·l⁻¹.

According to NEA-TDB 92, U(IV) is expected to be the dominant oxidation state under the conditions prevailing in the Boom Clay, *i.e.* pH ~ 8.2, E_h ~ -280 mV (Figure 2.4). Therefore, the uranium concentration is solubility limited and U(OH)₄(aq) is the main aqueous species. However, the recent NEA-TDB 03 update predicts that UO₂(CO₃)₃⁴⁻ is the dominant uranium species in the Boom Clay (Figure 2.5). Comparing the two figures, it is apparent that the stability field of U(OH)₄(aq) shrinks when using the NEA-TDB 03 update. An important change in this updated database is the decrease of more than five orders of magnitude of the stability constant of the aqueous species U(OH)₄(aq):



On the other hand, the stability constant for the uranyl tri-carbonate complex does not change, *i.e.*:



Therefore, the change in the dominant speciation of uranium is attributed to the change on the stability of U(OH)₄(aq).

According to the NEA-TDB 03 update (Figure 2.5), a repository having a pH around 8 and a redox potential higher than -300 mV will encounter uranyl tri-carbonate complex as the dominant species instead of neutral charged U(OH)₄(aq) (Figure 2.4). This should have important effects on the migration of uranium and result in an increase of the uranium mobility: solubility increase, sorption and retardation decrease.

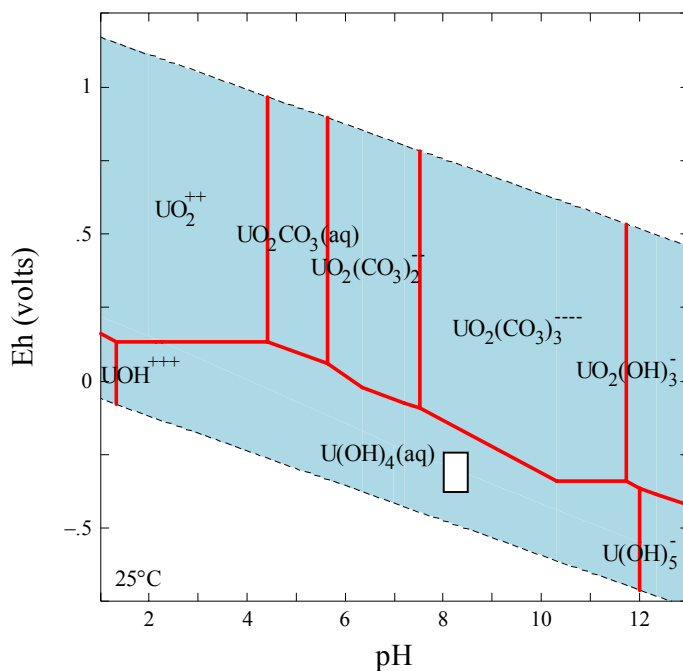


Figure 2.4. Eh-pH diagram of uranium ($10^{-8} \text{ mol}\cdot\text{l}^{-1}$) based on the NEA-TDB 92 (Grenthe *et al.*, 1992). Boom Clay pore water composition as given in Table 1.8. The HCO_3^- concentration is fixed at $0.014 \text{ mol}\cdot\text{l}^{-1}$. The square represents the Boom Clay conditions.

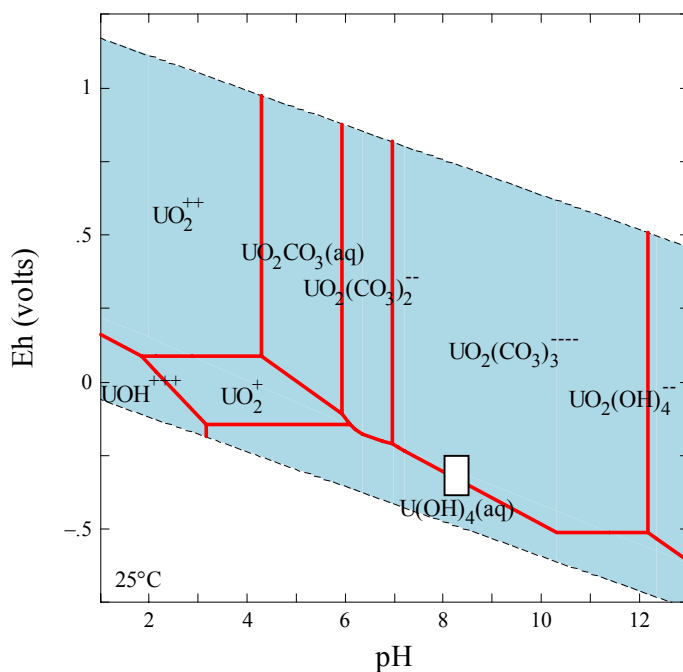


Figure 2.5. Eh-pH diagram of uranium ($10^{-8} \text{ mol}\cdot\text{l}^{-1}$) based on the NEA-TDB 03 (Guillaumont *et al.*, 2003). Boom Clay pore water composition as given in Table 1.8. The HCO_3^- concentration is fixed at $0.014 \text{ mol}\cdot\text{l}^{-1}$. The square represents the Boom Clay conditions.

The geochemical modelling yields conflicting results about the oxidation state of uranium in the Boom Clay. Depending on the database used, either tetravalent or hexavalent uranium may be the dominant uranium species and govern the uranium behaviour.

2.4.2.2 Field observations and literature review

Besides the geochemical modelling, information on the uranium chemistry in the Boom Clay is available from field observations and literature data.

Field studies indicate that natural uranium present in the Boom Clay is spatially associated with immobile organic matter as illustrated in Figure 2.6 (De Craen *et al.*, 2000).

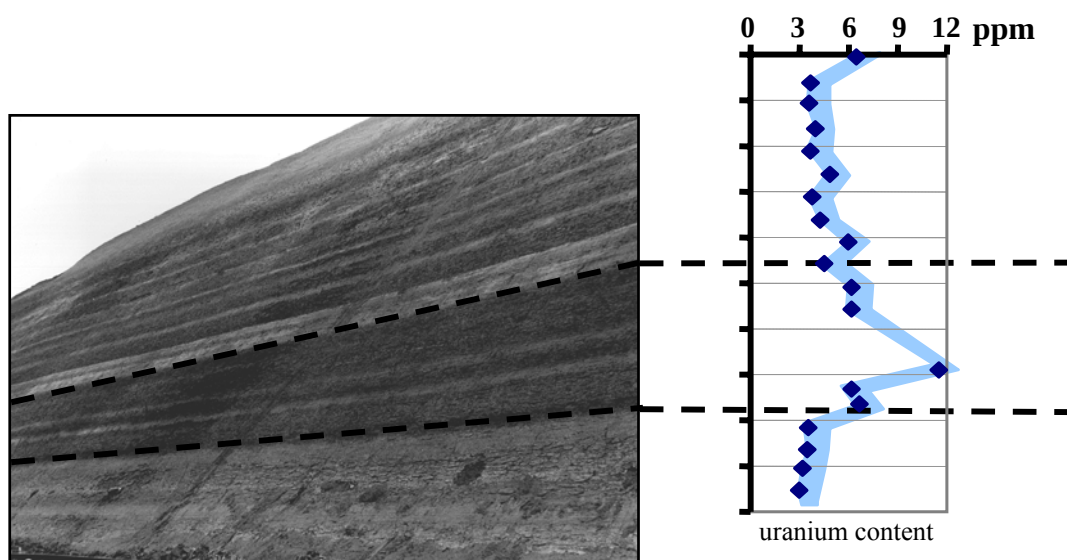


Figure 2.6. Picture showing an outcrop of Boom Clay and the corresponding uranium content which is higher in the black organic-rich layers.

Organic matter has long been known to be associated with many types of uranium deposits (Spirakis, 1996; Mossman, 1999; Min *et al.*, 2000). A direct proportionality between percentage of organic carbon and uranium is also observed in anoxic marine sediments. This association has produced much speculation on the relationship between organic matter and uranium. Two mechanisms are proposed to explain the uranium organic matter associations under reducing conditions: either as a result of complexation or adsorption of U(VI), or as a result of reduction of U(VI) to U(IV) after burial (Mo *et al.*, 1973; Anderson, 1982; Colley *et al.*, 1984; Colley and Thomson, 1985; Cochran *et al.*, 1986; Scott *et al.*, 1991).

The uranium fixation by organic matter is probably due largely to a reduction to the tetravalent state rather than association with organic fractions in higher oxidation states (Choppin, 1985). According to Spirakis (1996), reduction is the most important chemical process involving organic matter in the genesis of uranium deposits. It is not certain how adsorption is important. It is likely that concentration of uranium by adsorption onto organic matter or mineral surface precedes reduction and accelerates the process (Langmuir, 1978). The same reduction mechanism is suggested as the cause of enhanced uranium contents in marine sediments by Bonatti

et al., 1971; Anderson, 1982; Yamada and Tsunogai, 1984; Colley and Thomson, 1985 and Anderson *et al.*, 1989. Uranium occurs in seawater as a stable, anionic carbonate complex, $\text{UO}_2(\text{CO}_3)_3^{4-}$ (Langmuir, 1978). Mobile U(VI) may diffuse from oxygenated bottom waters into sediments where it then may be precipitated by reduction to insoluble U(IV) if the E_h is sufficiently low. Reducing conditions are often produced by anaerobic decomposition of organic matter just below the sediment sea-water interface in sediments with high organic matter contents (Anderson, 1982).

Organic matter can reduce U(VI) either directly by oxidation of CH_2O molecules and organic carbon atoms or indirectly by hydrogen sulphide (H_2S), produced by bacterial sulphate reduction (Min *et al.*, 2000). Early diagenetic reactions involving sulphate reduction clearly occurred in the Boom Clay and resulted in the formation of framboidal pyrite. Although the reduction of U(VI) should occur in seawater in presence of H_2S (Langmuir, 1978), Anderson *et al.* (1989) demonstrate that the reducing agents naturally present in anoxic Black Sea water, including $4 \times 10^{-4} \text{ mol} \cdot \text{l}^{-1}$ total H_2S , do not reduce U(VI). The dominant removal process of uranium must involve precipitation of uranium within the sediments rather than the chemical reduction of U(VI) by H_2S in anoxic water column. Since chemical conditions are not significantly more reducing in the sediments than in anoxic bottom waters, the proposed explanation is that the mineral surfaces catalyse the thermodynamically favoured reduction of U(VI) to U(IV) by H_2S . The reduction of U(VI) by H_2S is also shown to be catalysed by the sulphate-reducing bacteria (Mohagheghi *et al.*, 1985). However, certain bacteria are capable of catalyzing the reduction of uranium without involving hydrogen sulphide (Abdelouas *et al.*, 1998 and references therein).

Literature data also suggest that naturally occurring uranium in the Boom Clay is present in its tetravalent form. The experimental study by Wersin *et al.* (1994) has conclusively demonstrated the reduction of U(VI) and the precipitation of a mixed U(VI)-U(IV) oxide in presence of pyrite under anoxic conditions. Based on this result, we expect that the pyrite present in the Boom Clay (up to 5 wt. %) is capable of reducing uranium. Moreover, Liger *et al.* (1999) consider that surface-catalysed U(VI) reduction by Fe(II) is a major pathway of uranium immobilisation in a wide range of redox-stratified environments. This mechanism of reduction is likely to occur in the Boom Clay which contains about $10^{-5} \text{ mol} \cdot \text{l}^{-1}$ Fe(II) in pore water.

To resume, natural uranium present in the Boom Clay is expected in its tetravalent oxidation state. Indeed, the reduction of U(VI) to U(IV) during early diagenesis is probably the main mechanism responsible for the association observed between organic matter and uranium in the Boom Clay. U(VI) may be reduced either by organic matter; or by hydrogen sulphide produced by the bacterial sulphate reduction, the reaction being catalysed by minerals surfaces and bacteria; or by the bacteria themselves. Other possible mechanisms are U(VI) reduction by pyrite and surface-catalysed U(VI) reduction by Fe(II).

2.4.2.3 Experimental evidences

Experimental evidences for uranium reduction in the Boom Clay are provided by electromigration experiments (Maes *et al.*, 2002). Electromigration accelerates the migration process by applying an electrical field to enhance the transport of the charged species towards the electrode of opposite charge. The radionuclide source is spiked and confined between two clay cores. A potential difference is applied over the system (Figure 2.7). After a specified time, the clay is cut in slices and the activity distribution profile in the clay is measured.

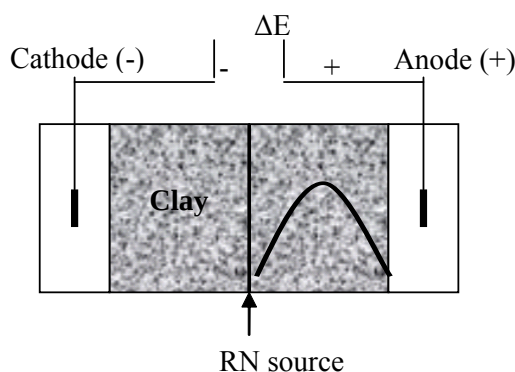


Figure 2.7. Schematic representation of the an electromigration experimental set-up. The curve symbolises the theoretical activity profile of an anionic radionuclide.

Electromigration has the advantage that it provides information on the speciation since the movement of the species towards the electrode depends on their charge. Electromigration experiments have been performed with $^{233}\text{UO}_2(\text{CO}_3)_3^{4-}$ sources to identify the migration behaviour of U(VI), starting from the hypothesis that this species should migrate without retardation towards the anode (+). Despite relatively long electromigration times, sufficient to displace strong retarded species such as Cs^+ , no displacement of the migration profile towards the anode is observed. Indeed, the activity profile of uranium remains centred around the source position (Figure 2.8). The electropherograms clearly shows the presence of species moving towards the cathode as indicated by the shoulder in the activity profile in the cathodic compartment. This points out the presence of neutral or positively charged uranium species. These observations are interpreted by the authors as a change in uranium oxidation state: reduction of $\text{UO}_2(\text{CO}_3)_3^{4-}$ and precipitation of U(IV) oxy-hydroxides near the source position. Therefore, the uranium concentration in solution is solubility limited. The uranium concentration in the plateau region at the cathode side equals $4 \times 10^{-8} \text{ mol} \cdot \text{l}^{-1}$ (Maes *et al.*, 2003). This concentration is similar to the solubility of amorphous UO_2 measured by Rai *et al.* (1990). As it could be the solubility controlling phase under Boom Clay conditions, the solubility value of amorphous UO_2 is studied in detail in the Chapter 6. The dominant uranium aqueous species moving towards the cathode is presumably $\text{U}(\text{OH})_4(\text{aq})$, in accordance with the speciation calculations for U(IV). The mechanisms of U(VI) reduction in the Boom Clay may be for example surface-catalysed reduction by organic matter, by pyrite, or by Fe(II).

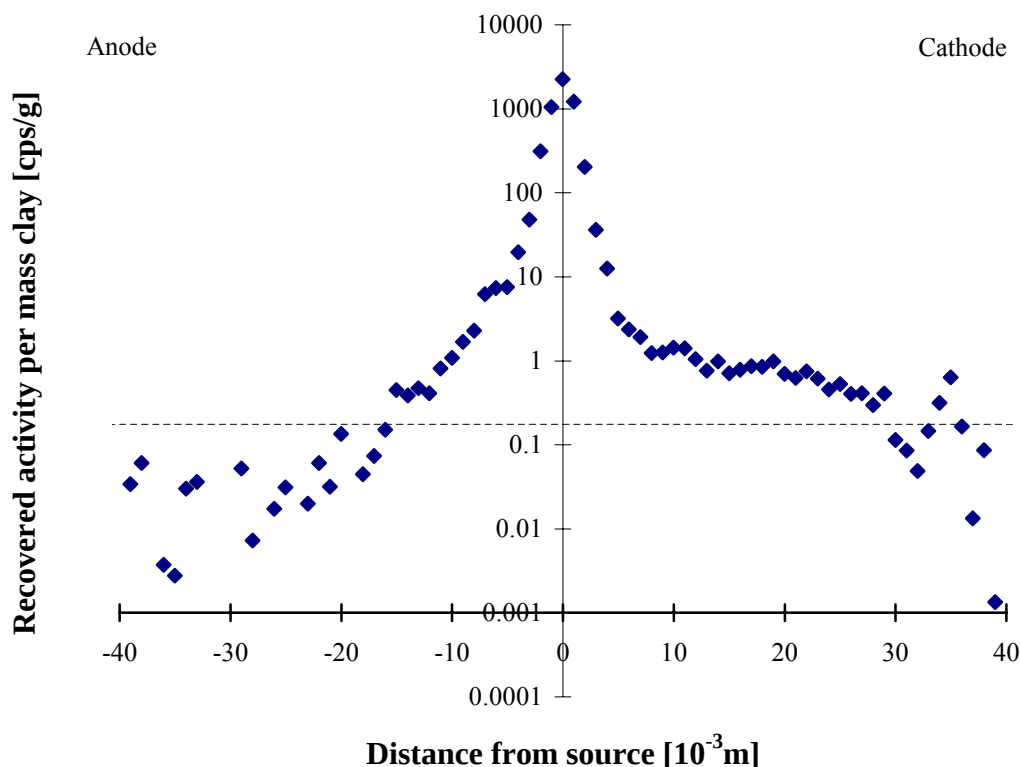


Figure 2.8. Logarithmic activity distribution profile of ^{233}U spiked as $\text{UO}_2(\text{CO}_3)_3^{4-}$ after electro-migration. The horizontal line denotes the detection limit (from Maes *et al.*, 2003).

Long-term migration experiment of the percolation type with ^{233}U started some 8 years ago at SCK•CEN. The driving force of the percolation experiment is a hydraulic gradient. This migration experiment was always carefully interpreted since the uranium source was not in equilibrium with the Boom Clay conditions: uranium was spiked as uranium nitrate in 5 M HNO_3 . However, electromigration experiments evidence that applying an uranium source initially not in equilibrium with the Boom Clay conditions will not compromise the results since reduction occurs within days (Maes *et al.*, 2003). Therefore, this long-term running experiment has been recently re-evaluated to determine uranium migration parameters (Maes *et al.*, 2003). The optimal value for the solubility parameter is $6 \times 10^{-10} \text{ mol} \cdot \text{l}^{-1}$. This solubility is in agreement with the calculated solubility of crystalline UO_2 in the Boom Clay (Wang *et al.*, 2000). The solubility value derived from the long-term migration experiment also indicates that U(VI) is not stable and is reduced to the tetravalent state in the Boom Clay.

2.5 Conclusion

In Belgium, the direct disposal of spent nuclear fuel as long-lived very high level radioactive waste is considered as an actual option. Because of its favourable properties resulting in a low mobility, a high sorption and a low solubility of radionuclides, the Boom Clay is a potential host formation studied.

Performance assessment studies on the direct disposal of spent fuel show that the total dose rate remains lower than the dose constraint in all cases. However, further experimental work is needed to narrow the range of uncertainty in the migration parameters. Therefore, the objective of this PhD thesis is to improve the fundamental knowledge about the migration behaviour of uranium in the Boom Clay on the basis of sound explanations derived from field observations and laboratory experiments.

The migration behaviour of uranium depends on its geochemistry which is controlled by its oxidation state. Tetravalent uranium precipitates as sparingly soluble minerals such as uraninite and coffinite, and is therefore immobile. On the other hand, hexavalent uranium and its complexes are much more soluble and mobile. Because of the detection limit, existing spectroscopy techniques do not allow to directly determine the speciation of uranium in the Boom Clay. Geochemical calculations provide contradictory results. Depending on the thermodynamic database used, either tetravalent or hexavalent oxidation state of uranium is predicted. However, field observations show that the tetravalent oxidation state of uranium should dominate in the Boom Clay. Moreover, electromigration and migration experiments conducted with uranium are currently interpreted as a reduction of U(VI), the subsequent precipitation of U(IV) oxide which releases solubility limited concentration of a positive or neutral species, presumably $\text{U}(\text{OH})_4(\text{aq})$.

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