

General conclusions

Despite the reprocessing policy adopted by Belgium for about 25 years concerning the radioactive waste management, about 4400 tons of spent fuel will remain from the electricity production by the seven nuclear power plants over an operational period of 40 years. A likely option for the management of this spent fuel at very long term is its direct disposal as highly and long-lived radioactive waste in deep geological formation. The Boom Clay is considered as a potential host rock in Belgium because of its favourable properties such as a low hydraulic conductivity, a reducing redox potential and a slightly alkaline pH. At very long term (after about 1 million years), uranium isotopes and their daughters are significant contributors to the dose rate resulting from the direct disposal of spent fuel. Consequently, it is important to understand in a correct and reliable way the migration behaviour of uranium in the host rock, which constitutes the main barrier of the whole disposal system. The main objective of the present PhD research was to acquire a better knowledge about the uranium speciation and retention in the Boom Clay.

To better characterise naturally occurring uranium in the Boom Clay, we have determined the uranium content in several rock-forming or accessory Boom Clay minerals. Uranium is concentrated in authigenic iron-bearing minerals such as siderite, ankerite and glauconite and in detritic heavy minerals such as zircon, xenotime, monazite and Ti-oxide. Furthermore, uranium is also associated with the surfaces of clay minerals. The clayey fraction ($< 2 \mu\text{m}$), which represents up to 60 wt. % of the rock, contains 4 ppm uranium and is the main contributor to the total uranium content. Despite its reducing capacity, pyrite is depleted in uranium. The role of calcite in concentrating uranium is not clearly established.

The most important and well-known factor controlling the geochemical behaviour of uranium is its oxidation state. Tetravalent uranium has a very low solubility whereas the hexavalent state is much more soluble and mobile as uranyl ion (UO_2^{2+}) and its complexes, especially carbonate complexes. Because of the difference in solubility between the reduced and the oxidised forms of uranium, reduction and the subsequent precipitation are very effective processes to immobilise uranium within the host formation. The uranium concentration in Boom Clay pore water is about $10^{-9} \text{ mol}\cdot\text{l}^{-1}$. Unfortunately, this concentration is too low to directly determine the uranium oxidation state and speciation using existing spectroscopic techniques. Moreover, no pure uranium minerals have been detected up to now in the Boom Clay which contains on average 4 ppm uranium.

Speciation calculations based on the most recent version of the Nuclear Energy Agency (NEA) database give $\text{UO}_2(\text{CO}_3)_3^{4-}$ as the dominant species in Boom Clay pore water. If uranium occurs as uranyl carbonate complexes, there is no concentration limitation by solubility and the uranium transport is only limited by anionic diffusion. Moreover, the complexation of U(VI) by dissolved organic matter present in the Boom Clay pore water might increase its mobility towards the biosphere. Therefore, the complexation of U(VI) by humic acids (HA) was studied by the conventional dialysis technique. Under Boom Clay conditions ($\text{pCO}_2 = 10^{-2.4} \text{ atm}$), less than 5% of U(VI) occurs as humate complexes in Boom Clay pore water (about 115 ppm of dissolved organic carbon). The U(VI) speciation is clearly dominated by the inorganic carbonate complex $\text{UO}_2(\text{CO}_3)_3^{4-}$. We have determined a conditional constant ($\log \beta^{\text{exp}}$) of 12.4 ± 0.2 for the complexation of U(VI) by HA. The logarithm

of β^{exp} is independent of the concentration of HA, the type of HA, the presence of hydrogen-phosphate and the oxidation of HA. The high $\log \beta^{\text{exp}}$ value relative to literature data determined at lower pH may indicate the formation of mixed complexes. The conditional complexation constants have been determined for two hypothetical mixed complexes: $\text{UO}_2(\text{CO}_3)\text{HA}$ and $\text{UO}_2(\text{CO}_3)_2\text{HA}$. However, the presence of such complexes was not evidenced by EXAFS measurements. EXAFS shows that the tricarbonato complex of U(VI) dominates the U(VI) speciation even for HA concentration as high as $1600 \text{ mg}\cdot\text{l}^{-1}$. These conclusions change in favour of organic complexation at lower partial pressures of CO_2 . Under the atmospheric partial pressure of CO_2 ($10^{-3.5} \text{ atm}$), humate complexes dominate the U(VI) speciation.

We have shown that U(VI) is not stable in the presence of pyrite in Boom Clay pore water. Both experimental and spectroscopic results indicate that pyrite is able to reduce U(VI), initially present as $\text{UO}_2(\text{CO}_3)_3^{4-}$. The solubility of the precipitated U(IV) phase is about $\sim 10^{-7} \text{ mol}\cdot\text{l}^{-1}$ and UO_2 might be the solubility controlling phase. Moreover, field observations and literature data suggest that natural uranium present in the Boom Clay is reduced to the tetravalent oxidation state, in contradiction with speciation calculations. The correlation observed in the formation between uranium and organic matter probably results from the uranium reduction and its subsequent immobilisation during the early diagenesis. U(VI) may have been reduced either by organic matter; or by hydrogen sulphide produced by the bacterial sulphate reduction, the reaction being catalysed by mineral surfaces and bacteria; or by the bacteria themselves. Electromigration experiments performed by other authors also suggest that U(VI) is not stable in the Boom Clay. The present interpretation of these experiments considers the reduction of U(VI) and the precipitation of U(IV) oxide which limits the concentration of a species moving towards the cathode (-), presumably $\text{U}(\text{OH})_4(\text{aq})$. The possible mechanisms of reduction are for example: U(VI) reduction by organic matter or pyrite and surface-catalysed U(VI) reduction by dissolved Fe(II).

The hexavalent oxidation state of uranium being not stable in the Boom Clay, the migration behaviour of uranium is mainly solubility controlled by U(IV) solid phases. Precipitation is the most important mechanism to lower the concentration of the mobile fraction of uranium migrating through the host rock. We have first measured the solubility of U(IV) amorphous precipitate in Boom Clay pore water in the presence of reducing agents such as dithionite, sulphide and iron powder. The total uranium concentration measured after two-months equilibrating time and $0.45 \mu\text{m}$ filtration is about $10^{-6} \text{ mol}\cdot\text{l}^{-1}$ or higher. This concentration is about 3 orders of magnitude higher than literature data for the U(IV) solubility and suggests the existence in the system of U(VI) species, colloids and/or U(IV)-organic matter complexes. Further experiments were performed to elucidate the role of organic matter and the contribution of colloids. After ultra-filtration at 2 nm, the measured solubility of $\text{UO}_2(\text{am})$ is about $10^{-8} \text{ mol}\cdot\text{l}^{-1}$ in Boom Clay pore water. This solubility value is in agreement with the range of values recommended by the most recent NEA thermodynamic database concerning the $\text{U}(\text{OH})_4(\text{aq})$ concentration equilibrated with $\text{UO}_2(\text{am})$. The formation of U(IV)-HA complexes in solution which was expected to possibly enhance the dissolution of $\text{UO}_2(\text{am})$ is shown to be negligible. Filtration tests have demonstrated that more than 50% of dissolved HA are generally removed from the solution by adsorption on $\text{UO}_2(\text{am})$ particles larger than $0.45 \mu\text{m}$. Colloids, with molecular size between 2 nm and $0.45 \mu\text{m}$, account for a total uranium concentration three orders of magnitude higher than the solubility of amorphous UO_2 . The uranium colloids are mainly real colloids, *i.e.* U(IV)-oxide polymers and not organic

pseudocolloids. Dissolved organic matter has a stabilising effect on these U(IV) real colloids. Organic colloids are observed at total organic carbon concentration higher than $\sim 75 \text{ mg}\cdot\text{l}^{-1}$ but do not significantly increase the colloidal uranium concentration. Colloids are expected to be immobile in the host rock since they are ultra-filtered by the Boom Formation.

The migration of the mobile fraction of which the concentration is solubility limited may be retarded by sorption on Boom Clay constituents. Screening sorption experiments with aqueous uranium above $\text{UO}_2(\text{am})$ in Boom Clay pore water show a significant sorption onto several minerals present in the Boom Clay (R_d up to $\sim 600 \text{ ml}\cdot\text{g}^{-1}$). Due to their high specific surface area and abundance, clay minerals are the most efficient sorbents for uranium.

From the results acquired in the frame of this PhD thesis, we conclude that the migration of uranium is hindered by strong immobilisation and retention processes. The uranium immobilisation results from the U(VI) reduction and the subsequent precipitation of U(IV). The uranium concentration in equilibrium with $\text{UO}_2(\text{am})$ is about $10^{-8} \text{ mol}\cdot\text{l}^{-1}$. Dissolved uranium at this concentration is not significantly complexed by soluble natural organic matter. Moreover, the migration of this mobile fraction of uranium is retarded due to sorption onto Boom Clay solid phases, mainly clay minerals.

These conclusions are drawn for the geochemical behaviour of uranium in the undisturbed Boom Clay that constitutes the far-field. In the near-field of the waste canisters, the effects of radiolysis, oxidation and temperature must be assessed and could alter the migration behaviour of uranium described in the present study within a few meters of clay around the disposal galleries. The uncertainties related to the near-field are currently treated in a conservative way by safety studies by considering, for the undisturbed clay barrier, a thickness that is smaller than the effective thickness of the Boom Clay.