

General introduction

The proposed disposal of spent fuel (largely UO_2) from nuclear power plants in a geological repository and the evaluation of the long-term risk is of concern in many countries. In Belgium, the reprocessing of spent fuel in COGEMA plants at La Hague (France) was the privileged option for the nuclear waste management until the end of the eighties. Until then, the research on highly radioactive waste disposal focused essentially on vitrified high-level waste resulting from the reprocessing of spent fuel. In the beginning of the nineties, the extension of the reprocessing contracts with COGEMA became questionable because of the low prices of fresh uranium making the economical benefit of this option debatable. In 1998, the contract concerning the reprocessing for the period post-2000 was cancelled. Therefore, the direct disposal of spent fuel without reprocessing is considered as a likely option in Belgium, *i.e.* to treat spent fuel as nuclear waste. The total amount of spent nuclear fuel resulting from the electricity production by the seven Belgian nuclear reactors over a period of 40 years is estimated at about 5000 tons of heavy metals (tHM). The reprocessing contracts which have been signed with COGEMA cover 630 tHM, or about 13% of the total amount of spent fuel. It means that the remaining spent fuel would be disposed of directly if no additional reprocessing contracts are concluded.

Spent fuel is classified as long-lived and very high-level heat emitting waste (category C). Presently, the disposal in deep geological formations is promoted at international level as the most promising option for the management of highly radioactive waste. In Belgium, research is focused on argillaceous formations because of their expected favourable properties and their presence at an accessible depth. The Boom Clay is currently studied as a potential host formation.

After the degradation of the engineered barriers and the release of radionuclides from the waste packages, radionuclides will migrate in the Boom Clay mainly by diffusion, advection playing only a secondary role. Up to about one million years, the assessed dose rate resulting from the disposal of spent fuel is controlled by activation and fission products, chiefly by three isotopes: Se-79, Tc-99, I-129. At very long term (after about 1 million years), uranium, which constitutes about 95 % of the spent fuel, and its daughters are significant contributors to the total dose rate. Although the dose rate strongly depends on the uranium mobility, the migration behaviour of this redox-sensitive radionuclide is not well understood in the Boom Clay.

The comprehension of the mobility of radionuclides with a complex chemistry such as uranium in reducing clay environment still poses problems. The uranium migration is the result of complex chemical-coupled transport processes involving different constituents of the Boom Clay. The uranium migration is controlled by solubility, interactions with inorganic and organic solid surfaces and complexation with inorganic ligands such as carbonate. Moreover, Boom Clay pore water contains about 115 ppm of dissolved organic carbon. Because of its complexing capacity, natural organic matter may play an important role in the fate and the mobility of uranium. In addition, uranium is a redox-sensitive element and its geochemistry mainly depends on its oxidation state. According to geochemical calculations, both hexavalent and tetravalent oxidation states may exist or co-exist under the reducing conditions prevailing in the Boom Clay.

Because of the complex geochemistry of uranium in the Boom Clay, it is not trivial to clearly distinguish the contributions of solubility, sorption, and complexation by mobile organic matter in the migration behaviour of uranium. A number of questions are still unresolved. What is the oxidation state of uranium in the Boom Clay? What are the uranium-bearing minerals in the Boom Clay? What is the solubility of uranium? What is the extent of uranium sorption? What is the importance of uranium complexation by organic matter?

Fundamental knowledge to reach a sufficient level of understanding of the uranium behaviour in the Boom Clay is needed. The **main objective** of this PhD thesis is to provide sound scientific explanations about the uranium speciation and about the mechanisms controlling the uranium mobility in the Boom Clay, *i.e.* solubility, sorption, and complexation by organic matter. The general aim is to gain confidence in the data on which the performance assessment is based for the geological disposal of spent fuel. To achieve these objectives, we have compiled the information acquired from literature review and from the study on naturally occurring uranium in the Boom Clay. We have also designed specific laboratory experiments conducted under conditions representative for the Boom Clay. These conditions are those expected to prevail in the undisturbed Boom Clay (far-field). The perturbations induced by the repository such as radiolysis, oxidation, alkaline plume (from the use of cement) and temperature are not considered in the present work.

Chapter 1 gives an overview of the geological and the geochemical features of the Boom Clay, the reference host formation currently studied in Belgium.

Chapter 2 introduces the problematic of the spent fuel disposal and presents the general geochemical behaviour of uranium in the environment. Then, the uranium speciation in the Boom Clay is discussed on the basis of literature review, geochemical modelling, field observations and experimental results.

Chapter 3 deals with uranium naturally present in the Boom Clay. The emphasis is placed on the determination of the uranium content in some Boom Clay minerals.

Chapter 4 describes the experimental conditions under which the batch tests have been conducted.

Chapter 5 is devoted to complexation of U(VI) by humic acids under Boom Clay *in situ* partial pressure of CO₂ and under atmospheric conditions. The fraction of uranium complexed by humic acids is determined as well as a conditional complexation constant. The nature of the humate complexes is investigated by extended x-ray absorption fine-structure spectroscopy (EXAFS).

Chapter 6 presents the study on the solubility of U(IV) amorphous oxide under Boom Clay conditions. First, the solubility is measured as function of time in presence of various reducing agents and in Boom Clay pore water. Secondly, the influence of organic matter on the solubility is studied. The presence of colloids is investigated by using two different membrane pore-sizes, *i.e.* micro-filtration at 0.45 μm and ultra-filtration at 2 nm. The characteristics of the colloids is assessed by analysing the distribution of organic matter before and after both filtrations.

Chapter 7 starts with the study of the U(VI) interaction with pyrite, the main reducing mineral present in the Boom Clay. Afterwards, the sorption of dissolved uranium released by amorphous UO₂ is examined on different pure minerals typical of the Boom Clay.