Migration Case Study:
Transport of radionuclides in a reducing Clay Sediment (TRANCOM-II)

Final Scientific and Technical report of the EC TRANCOM-II project

Norbert Maes (coordinator, SCK-CEN, Belgium)

L. Wang, G. Delécaut, T. Beauwens, M. Van Geet, M. Put, E. Weetjens, J. Marivoet (SCK•CEN, Belgium)
J. van der Lee (Ecole des Mines de Paris, France)
P. Warwick, A. Hall, G. Walker (University of Loughborough, UK)
A. Maes, C. Bruggeman (KULeuven, Belgium)
D. Bennett, T. Hicks, J. Higgo, D. Galson (Galson Sciences Ltd., UK)

September 2004

SCK•CEN-BLG-988

Work performed as part of the European Atomic Energy Community (EURATOM)
Specific programme on "Nuclear Energy" (1988-2002), Key Action on Nuclear Fission
Area: "Safety of the Fuel Cycle – Waste and spent fuel management and disposal"
Migration Case Study:
Transport of radionuclides in a reducing Clay Sediment (TRANCOM-II)

Final Scientific and Technical report of the EC TRANCOM-II project

Norbert Maes (coordinator, SCK-CEN, Belgium)

L. Wang, G. Delécaut, T. Beauwens, M. Van Geet, M. Put, E. Weetjens, J. Marivoet (SCK•CEN, Belgium)
J. van der Lee (Ecole des Mines de Paris, France)
P. Warwick, A. Hall, G. Walker (University of Loughborough, UK)
A. Maes, C. Bruggeman (KULeuven, Belgium)
D. Bennett, T. Hicks, J. Higgo, D. Galson (Galson Sciences Ltd., UK)

September 2004

SCK•CEN-BLG-988

Work performed as part of the European Atomic Energy Community (EURATOM) Specific programme on "Nuclear Energy" (1988-2002), Key Action on Nuclear Fission Area: "Safety of the Fuel Cycle – Waste and spent fuel management and disposal"
Preface

The TRANCOM-II project is conducted as part of the European Atomic Energy Community (EURATOM) 5th Framework Programme, specific programme on “Nuclear Energy” (1988-2002), Key Action on Nuclear Fission Area: “Safety of the Fuel Cycle – Waste and spent fuel management and disposal” under contract N° FIKW-CT-2000-00008. The project is a continuation of the TRANCOM-CLAY project under the 4th Euratom Framework programme.

The purpose of this final scientific and technical report is two-fold: first, to present a comprehensive overview of the scientific work and results obtained and secondly, to compile all relevant and detailed technical information gathered throughout the project.

The report consists of 3 parts:
2. Technical annexes with detailed information to back-up the final report. Part of these annexes are reports (technical notes, topical reports) which acted as deliverables towards the EC for which most were constricted to the consortium during the period of the contract.
3. CD-ROM with the raw data structered according to the work-package structure of the project.

Acknowledgement

- The EC is acknowledged for financing the Trancom-II project which is performed as part of the European Atomic Energy Community (EURATOM) Specific Programme on “Nuclear Energy” (1988-2002), Key Action on Nuclear Fission Area: “Safety of the Fuel Cycle – Waste and spent fuel management and disposal”. The critical follow-up of Mr. Henning Ritter Von Maravic (EC-DG RTD/J4) was highly appreciated.

- NIRAS/ONDRAF is acknowledged for the co-financing of SCK-CEN’s part in the Trancom-II project. The critical follow-up by, and fruitful discussions with, Mrs. A. Dierckx and Mr. R. Gens are very much appreciated.

- Dr. Fr. Béhar from IFP (France) and Dr. J. Schwarzbauer from RWTH-Aachen (Germany) are thanked for their assistance in the experimental work on natural organic matter characterisation.

- We like to thank Prof. K. Janssen and C. Proost of the University of Antwerpen (UA) for performing/interpretation of speciation measurements with µ-XANES on some Uranium samples.

- We like to thank Dr. M. Denecke of the ANKA synchrotron radiation facility of Forschungszentrum Karlsruhe (FzK) for performing/interpretation of EXAFS measurements on U(VI)-OM samples.
Executive Summary

In Europe, clay formations become more and more important as candidate geological formations (e.g. Boom Clay, Callovo-Oxfordian, Opalinus,...) for the deep disposal of High-Level radioactive Waste (HLW). In demonstrating the suitability of a geological site for the disposal of radioactive waste, it is essential to consider the potential mobility of critical radionuclides through the relevant “rock” types. This project addresses the migration behaviour of radionuclides, identified as important for the long term safety (U, Se, Pu, Am), in a reducing clay environment, with special emphasis on the role of the Natural Organic Matter (NOM). In such reducing environments, the solubility limit is considered as the most important mechanism to lower the mobile concentration of these radionuclides and the speciation is most likely neutral or negatively charged so a low retardation is expected. However, the presence of NOM may jeopardise the expected low concentration and sorption: by solubility enhancement due to complexation/colloid formation with NOM or by influencing the sorption behaviour. The objective is to develop and demonstrate a conceptual model for the description of the migration of radionuclides in a reducing, NOM rich clay environment that can be implemented in performance assessment (PA) models.

The main questions are: (i) does the NOM increase the radionuclide concentration in solution due to complex formation and (ii) what is the possible role of mobile NOM as radionuclide carrier?

To answer these questions, following research strategy was adopted taking the Boom Clay Formation as a Case Study. Prior to any experimental work, speciation and solubility’s for the considered radionuclides were calculated not accounting for NOM. The mechanisms determining the overall behaviour of the radionuclides in the clay environment are then studied in solution in presence of NOM (solubility, complexation) and with respect to the solid phase (retention by immobilisation, sorption). Modelling is used to interpret and derive interaction constants which can be implemented in a geochemical “clay” database. Understanding and quantifying the interaction mechanisms in the clay environment should allow to model and interpret migration experiments with mixtures of the radionuclides and ¹⁴C-labelled NOM. Separately, methodologies were developed to identify the source of mobile organic matter. The obtained results are translated into conceptual models which can be used to evaluate the performance of Boom Clay as potential host rock.

Batch experiments revealed that the solubility of amorphous UO₂ is ~10⁻⁸ mol dm⁻³ with no effect of NOM complexation. However, it was evidenced that the presence of NOM facilitated the formation of uranium colloids upon dissolution of UO₂. The formation of colloids, with molecular size between 2 nm and 0.45 µm, accounts for a total uranium concentration, three orders of magnitude higher than the solubility of the amorphous UO₂. Uranium colloids were also found being dominant in leaching experiments of natural uranium from Boom Clay samples. These colloids, only evidenced in batch experiments, are unlikely to be mobile in the compact natural Boom Clay. Electromigration experiments showed that U(VI) reduces to U(IV) and precipitates. This U(IV) precipitated phase constantly releases positive or neutral charged U-species. Furthermore, classical migration experiments with U(IV) mixed with ¹⁴C-labelled NOM showed that U(IV) migrates independently of the NOM through the Boom Clay. The migration of uranium in the Boom Clay is governed by strong retention due to precipitation (solubility limit) and sorption and is not enhanced by the mobile organic matter.
Oxidised selenium species, as might be present in the waste forms, undergo a slow reduction in the Boom Clay. $\text{SeO}_4^{2-}$, although thermodynamically not stable under the Boom Clay conditions, remains fairly stable (no reduction was observed in batch experiments for periods up to several months), and migrates unretarded through the Boom Clay. $\text{SeO}_3^{2-}$ shows a more complex behaviour which is described as a kinetically controlled sorption-reduction process resulting in a constant Se concentration of $\sim 3 \times 10^{-9}$ mol dm$^{-3}$ similar to the concentration in equilibrium with a prepared Se(0) phase. Upon reduction of $\text{SeO}_3^{2-}$, part of the Se in solution is found to be associated with OM as colloids but with no pronounced effect on the Se(0) solubility. Synthetically prepared reduced Se solid phases showed solubility’s varying over 3 orders of magnitude ($10^{-10} – 10^{-7}$ mol dm$^{-3}$) but no effect of NOM on the solubility was observed. The relative high Se concentration in the Boom Clay water ($\sim 2 \times 10^{-8}$ mol dm$^{-3}$) compared to the observed solubility is puzzling and needs further attention.

Solubility experiments of Pu(IV) in absence and presence of Boom Clay organic matter were not conclusive (possible presence of Pu(VI)); Pu concentrations ($< 30 \text{,000 MWCO}$) of $4 \times 10^{-8}$ mol dm$^{-3}$ up to $8 \times 10^{-7}$ mol dm$^{-3}$ were measured with increasing Pu concentration as a function of NOM concentration suggesting that NOM may increase the Pu(IV) solubility by an order of magnitude. Migration experiments with Pu(IV) showed that the spiking solution contains Pu-OM associated species. But no enhanced transport of Pu by OM, in terms of mobile Pu-OM species (complexes or colloids) was noticed. These are either filtered or instable with respect to the clay phase. The Pu transport mechanism can be described by an immobilisation (solubility or quasi irreversible interaction with the solid phase) followed by a constant release of Pu and resembles the behaviour of the trivalent Am.

In the previous EC TRANCOM-Clay project (FI4W-CT95-0013, EUR19135) the idea developed that Am-OM complexes dissociate, almost instantaneously, when contacted with Boom Clay and only a small portion persists as “stabilised” Am-OM complex leading to a constant bleeding of Am. Further investigations in the present project showed that these “stabilised” Am-OM complexes also dissociate upon travelling through the clay but this dissociation is controlled by slow kinetics. The constant bleeding of Am, $[\text{Am}] \sim 10^{-13} – 10^{-12}$ mol dm$^{-3}$, is caused by an Am “source” which is not associated to OM (inorganic Am-“solid phases”) acting as a continuous source of Am to form “stabilised” Am-OM complexes which results in a constant release of Am. This immobilisation/constant release resembles a solubility like process. The experimentally observed constant concentration of mobile Americium is treated in PA as a constant concentration source released from immobilised Am, which diffuses through the Boom Clay with a similar migration parameters as the mobile OM.

A transport model, POPCORN, is developed to describe and evaluate the influence of OM on radionuclide transport in clay. It accounts for attachment/detachment rates of OM to clay surfaces, the kinetics of radionuclide complexation to, and destabilisation from, OM. The model described well the Am-OM transport behaviour and offers potential means of extrapolating parameter values for application of the model to larger-scale.
Methodologies were developed to identify the source of mobile NOM: leaching, discrete porewater sampling & OM isolation, characterisation of the kerogen. The Boom Clay kerogen makes up to 5% of the total sediment. Rock Eval and pyrolysis GC/MS analysis have shown that the kerogen is a mixture of terrestrial and marine OM. Some smaller molecules (e.g. polar oxygen-containing products) are entrapped into the 3D macromolecular network of the kerogen and are prone to release upon applying low thermal stress. The Boom Clay porewater contains around 100 to 200 mgC/L, but might be up to 400 mgC/L. Up to now, the DOC can not be linked to the neighbouring TOC as no correlation exists in their concentrations. Leached organic matter contains a higher amount of total organic carbon than the Boom Clay porewater and is predominantly composed of humic acids. The amount of leached organic matter is primarily controlled by the amount of Boom Clay solid phase used. Solving the question on the source of mobile NOM was however beyond the scope of the project, but the methodologies are proven to be useful and will be further explored.

The transport mechanism for the studied radionuclides (except for $\text{SeO}_4^{2-}$) is dominated by an immobilisation (precipitation or strong, quasi irreversible interaction with the solid phase) process followed by a constant release of a small fraction of the radionuclide. The transport of the released radionuclides is only in case of the trivalent Am (possibly also Pu) correlated with NOM. PA calculations are therefore performed with a limited set of parameters: concentration limit (or solubility limit), $D_{\text{pore}}$, $R$ and diffusion accessible porosity. The values are taken from experimental observations and interpretations. Examples of PA calculations for U and Se in BC are performed with a new parameter set based on the project outcome and compared with results based on former datasets. Special attention is given to selenate as possible species and the presence of inactive Se in the waste.

The methods, results and conceptual models developed in the TRANCOM-II project are of direct use for evaluating the performance of the Boom Clay as potential host rock for HLW disposal but they serve also as a reference for other clay formations and waste types (chemo toxic waste).
# TABLE OF CONTENTS

Foreword ................................................................................................................................ III

Acknowledgement .................................................................................................................. III

Executive Summary ........................................................................................................... V

1 Introduction ..................................................................................................................... 1

1.1 Background .................................................................................................................. 1

1.2 Objectives ..................................................................................................................... 1

1.3 Methodology ................................................................................................................ 2

2 Scientific and technical results ....................................................................................... 5

2.1 Predictions of speciation and solubility of the selected radionuclides in Boom Clay geochemical conditions ......................................................................................................... 5

2.2 Radionuclide interaction with NOM in solution........................................................ 7

2.2.1 Effect of organic matter on solubility's of U, Pu and Se under reducing conditions ................................................................................................................................. 7

2.2.1.1 Effect of NOM on U solubility ........................................................................ 7

2.2.1.2 Effect of NOM on Pu solubility ...................................................................... 11

2.2.1.3 Effect of NOM on the Se solubility .................................................................. 12

2.2.2 Uranium and selenium complexation with NOM .............................................. 13

2.2.2.1 U(IV)/U(VI)-NOM complexation ................................................................ 13

2.2.2.2 Se-NOM complexation ............................................................................. 16

2.2.3 Natural uranium concentration in Boom Clay .................................................... 16

2.2.4 Conclusions on the radionuclide interaction with NOM in solution ............... 17

2.3 Radionuclide solid phase interactions ....................................................................... 18

2.3.1 U solid phase interaction ....................................................................................... 18

2.3.1.1 Uranium(VI) interaction with Pyrite ................................................................. 18

2.3.1.2 Uranium(IV) interaction with selected BC components .................................. 20

2.3.2 Selenium solid phase interactions ...................................................................... 21

2.3.2.1 Selenium interaction with pyrite ................................................................. 21

2.3.2.2 Selenium interaction with Boom Clay ......................................................... 22

2.3.3 Conclusions on the radionuclide solid phase interactions .................................. 24

2.4 Geochemical modelling of the influence of NOM and update of geochemical clay database .......................................................................................................................... 25

2.4.1 Discussion on the theoretical basis of the side-reaction theory ...................... 25

2.4.2 Modelling of U(IV) solubility and complexation by Boom Clay Humic Acids .......................................................................................................................... 26

2.4.3 Modelling of U(VI) complexation by Boom Clay Humic Acids ..................... 27

2.4.4 Update of the thermodynamic database and its implications on the radionuclide speciation calculations ................................................................. 28

2.4.5 The concept of solubility increasing factor ...................................................... 31

2.5 Migration experiments with RN-NOM double labelled solutions .................... 32
1 Introduction

1.1 Background
Disposal in deep geological formations is at present the main option for long-lived radioactive waste disposal and spent fuel management. In Europe, clay formations become more and more prominent as candidate geological formations (e.g. Boom Clay, Callovo-Oxfordian, Opalinus,…). In establishing the suitability of a geological site for the disposal of radioactive waste, it is essential to consider the potential mobility of critical radionuclides through the relevant “rock” types.

This project addresses the migration behaviour of radionuclides, identified as important for the long term safety of a HLW repository, in a reducing clay environment, with special emphasis on the role of the Natural Organic Matter (NOM). The project is a continuation of the TRANCOM-CLAY project (Dierckx et al., 2000a) under the 4th Euratom Framework Programme.

In such reducing environments, the solubility limit is considered as the most important mechanism to lower the mobile concentration of these radionuclides and the speciation is most likely neutral or negatively charged so a low retardation is expected. However, the presence of NOM may jeopardise the expected low concentration and sorption: by solubility enhancement due to complexation/colloid formation with NOM or by influencing the sorption behaviour. The objective is to develop and demonstrate a conceptual model for the description of the migration of radionuclides in a reducing, NOM rich clay environment that can be implemented in performance assessment models.

The Boom Clay is taken as a case study since it is one of the first clay formations investigated for the purpose of radioactive waste disposal and therefore a lot of experience and knowledge is already available for use. Especially in the field of migration experiments on Boom Clay samples, a lot of information is available from long-term running experiments.

1.2 Objectives
The main scientific objectives are:

- to improve our understanding of the migration behaviour of U, Se, Pu and Am (as representative of trivalent actinides/lanthanides) under reducing conditions in an organic matter rich clay environment,
- the production of an internal coherent database for the interaction of radionuclides with NOM and clay under reducing conditions.
- the development and demonstration of a conceptual model for the description of the migration of radionuclides in a reducing, NOM rich clay environment that can be implemented in performance assessment models.

The laboratory batch and migration experiments are designed to improve the scientific basis for the safety assessment, because they intend to acquire a better insight in the mechanisms of radionuclide migration in clay. This way, modelling migration experiments will not lead to black-box parameters, but to scientific under built parameters. A higher credibility contributes to the acceptability of geological disposal of high-level radioactive waste.
The results and conceptual models developed are of direct use for evaluating the performance of the Boom Clay as potential host rock for HLW disposal and it therefore helps in demonstrating the effectiveness of clay formations in isolating radionuclides from a waste repository. The results, methods and model concepts can be transferred to other clay formations considered for radioactive waste disposal but also for other types of waste (chemo toxic waste).

1.3 Methodology

To answer the main questions:
(i) does the NOM increase the radionuclide concentration in solution due to complex formation and
(ii) what is the possible role of mobile NOM as radionuclide carrier;
the following research strategy was adopted taking the Boom Clay as a Case Study (see also the flow chart in figure 1):

- Prior to the experimental work, calculations have been carried out to bring forward expected solubility’s and dominating species under reducing Boom Clay conditions (Predictions of speciation and solubility of the selected radionuclides in Boom Clay geochemical conditions – WP1), as necessary input for the experimental studies conducted in following work packages.

- In order to understand the migration behaviour of the considered radionuclides in a reducing clay sediment, the speciation in the solution phase is first investigated (Radionuclide interaction with NOM in solution – WP2): determination of the solubility limits for the reduced forms (to compare them with predicted values) followed by the determination of the effect of NOM onto the solubility (complexation, colloid formation). Since it is anticipated that uranium might be present in the Boom Clay in its U(VI) redox state, the complexation of U(VI) with NOM is also investigated.

- Following the speciation studies in the solution phase, the interaction of U and Se with the solid phase is investigated in more detail (Radionuclide solid phase interactions – WP3) to determine the effect of solid phases (pyrite, BC, minerals) in combination with NOM on the retention of U and Se-species (starting from different redox states) in terms of immobilisation and sorption process.

- The existing database and conceptual models used for the initial predictive simulations are continuously updated with new data from the literature as well as with data that become available from the experimental work. Furthermore, a thorough analysis of the interpretation methods used to model the experimental results is done (Geochemical modelling of the influence of NOM and update of geochemical clay database – WP6).

- Based on the knowledge acquired during the previous work packages, radionuclide sources were prepared, as close as possible to their expected equilibrium speciation under in-situ BC conditions and in contact with $^{14}$C-labelled Boom Clay Organic Matter (BCOM) to be used in migration experiments (Migration experiments with RN-NOM double labelled solutions – WP5). By using double tracer solutions, both the fate of the radionuclide and the organic matter can be followed. The aim is to see whether the mobile BCOM facilitates the radionuclide (RN) migration, to formulate conceptual models, and deliver representative migration parameters, usable by performance assessment.
In the previous TRANCOM-Clay project (FI4W-CT95-0013, EUR19135), the idea developed that Am-OM complexes dissociate, almost instantaneously, when contacted with Boom Clay and only a small portion persists as “stabilised” Am-OM complex leading to a constant bleeding of Am. The aim is to see if kinetics of exchange of trivalent Am between mobile and immobile phase can explain differences in the Am-concentrations in water percolating from migration experiments and the occurrence of a fast –but small – breakthrough of Am accompanying the organic matter (OM)-breakthrough (Demonstration of the model concept for the migration behaviour of trivalent radionuclides – WP8).

The migration experiments will be modelled and interpreted using existing and new developed transport models to deliver parameters and understanding of the mechanisms for Performance Assessment (Modelling and interpretation of migration experiments – WP7).

Considering the relative high mobility of dissolved OM in the Boom Clay, it is surprising that OM is still observed in the pore water because all mobile organic matter should have diffused out unless immobile organic matter is continuously dissolved or secondly, the organic matter does not move at all. Methodologies are tested and developed which can be used to identify the source of mobile OM (Methodologies developed to identify the source of mobile Boom Clay Organic Matter – WP4).

All results obtained during the project are evaluated and translated in data and conceptual models useful for PA to describe the transport of radionuclides in a NOM rich clay environment (Conceptualisation of migration processes for PA and PA evaluation – WP9).

**WP1: Prediction of Radionuclide speciation and solubility**

**WP2: RN interaction with NOM in solution**

**WP3: RN interaction with the solid phase**

**WP4: Development of methodologies to identify the source of mobile BCOM**

**WP5: Migration experiments with RN-NOM double labelled solutions**

**WP6: Geochemical modelling of the influence of NOM Update of thermodynamic database**

**WP7: Transport Modelling**

**WP8: Demonstration of the migration behaviour of trivalent RN**

**WP9: Conceptualisation for PA and PA evaluation**

![Figure 1: Schematic representation of the project structure and interrelations.](image-url)
Within the project we bring together, at a European level, material specialists, modellers, engineers and experts from waste agencies responsible for development and implementation of radioactive waste disposal. The partners have been selected for their complementary expertise within the fields of radionuclide complexation, sorption, migration experiments, modelling and performance assessment. Part of this consortium has already been working together in the TRANCOM-CLAY project (under the 4th EURATOM framework programme) - SCK-CEN (B), KULeuven (B), Loughborough University (UK), Armines (F) - adding 2 new groups to enlarge the expertise: Galson Sciences Ltd. (UK) and ENSCP-LCBOP (F).
2 Scientific and technical results

2.1 Predictions of speciation and solubility of the selected radionuclides in Boom Clay geochemical conditions\(^1\) – WP1

In reducing or moderately oxidising environments, the solubility limit defines for the major part the source term of radionuclide mobility. Prior to the experimental work (Radionuclide interaction in solution: solubility and complexation experiments), calculations have been carried out to bring forward expected solubility’s and dominating species under reducing Boom Clay conditions. Solubility and speciation are calculated with geochemical computer codes without considering the effect of natural organic matter. The calculated solubility values will be compared/verified with experimental measurements in absence of NOM prior to experiments involving NOM. The effect of the organic matter complexation, \textit{i.e.}, an increase or a decrease of the solubility of radionuclides can be evaluated accordingly.

Two different speciation models have been used, CHESS (Van der Lee, 1998) and the Geochemist's Workbench (Bethke, 2000). No significant differences were encountered with respect to the calculation results between these models.

The major uncertainty encountered with predictive solubility- and speciation calculations is therefore not related to the model used, but to the database the user selected to run the simulations. At the time of writing the topical report (Van der Lee \textit{et al.}, 2001) on the speciation/solubility calculations, we disposed of three distinct databases:

- the LLNL (EQ3/6) database, including NEA recommendations for uranium (1997),
- the NEA database, including the publicly available data at the time of writing (2000),
- the HATCHES database, used for Se only.

The databases have been compared with each other, mainly with respect to uranium (the NEA dataset did not contain information with respect to Pu or Se). No significant anomalies have been encountered. Plutonium data compiled in the NEA pre-review (Lemire \textit{et al.}, 2000) differs from the LLNL data concerning \(\text{Pu(OH)}_4(aq)\) species. The question whether Pu occurs at an oxidation state of III or IV is still open.

HATCHES database provides additional data for solid selenium while the data for the aqueous species seems to be identical to the LLNL database. We noticed, however, the absence of iron carbonate complexes, hence the total iron concentration may contain some error. Accordingly, the iron concentration can influence the solubility of iron containing Se solids. We also found errors in the HATCHES database that some reactions concerning Se are charge imbalanced.

\(^1\) This part has been described in detail in a topical report by Van der Lee \textit{et al.}, 2001 (R-3400, SCK-CEN) which is given in Annex 1: \textit{Topical report on speciation and solubility calculations for uranium, plutonium and selenium under Boom Clay conditions}.
Several conclusions have been drawn with respect to the expected solubilities and speciation under Boom Clay conditions (Eh= -275 mV, pH= 8.2, pCO₂= 10⁻².₃ atm). They are summarized in Table 1.

- Uranium is predicted as U(OH)₄(aq) species in Boom Clay with various solubility values depending on the solubility controlling phases. UO₂(c) leads to a solubility of 2-4 10⁻¹⁰ molal, UO₂.₂₅(c) to 4 10⁻⁸ to 2 10⁻⁷ molal.

- Species Pu(OH)₄(aq) predominates for plutonium with a solubility of 10⁻¹⁵-10⁻¹⁷ molal based on PuO₂(c) as the controlling phase.

- Selenium is expected to be present in the form of selenide HSe⁻ (solubility = 3-8 10⁻⁹ molal). The solubility of selenium is very sensitive to the redox conditions and the total amount of iron available in the system. A lower solubility is expected in presence of non-negligible amounts of iron due to the formation of FeSe(c), but a wide range of thermodynamic values for the formation of this phase makes an estimate of the expected solubility uncertain.

Table 1: Solubility’s and predominant species of U, Pu and Se under strongly reducing conditions (in molal).

<table>
<thead>
<tr>
<th>Solubility</th>
<th>U(IV)</th>
<th>Pu(IV)</th>
<th>Se(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO₂(c):</td>
<td>2-4 10⁻¹⁰</td>
<td>PuO₂(c): 10⁻¹⁵ – 10⁻¹⁷</td>
<td>Se(c): 3 – 8 10⁻⁷</td>
</tr>
<tr>
<td>UO₂.₂₅(c):</td>
<td>4 10⁻⁸ - 2 10⁻⁷</td>
<td>Pu(OH)₄(c): 2 10⁻⁹</td>
<td>FeSe₂(c): 2 10⁻⁹</td>
</tr>
</tbody>
</table>

The thermodynamic database is still the most important source of uncertainty in geochemical modelling. This is particularly the case for speciation under reducing and slightly alkaline conditions. Several research projects are currently making considerable efforts to improve the situation, for example the NEA TDB-project, NAGRA-PSI, HATCHES and CTDP projects, to name only a few of them.

For the three selected radionuclides, the modelling results show a domination of the speciation by neutral or negatively charged hydroxylic species with little influence of the inorganic carbon content. This indicates that there might be no or weak sorption of these species on the negatively charged clay surfaces. Solubility is therefore likely the most important retention mechanism prevailing in Boom Clay.
2.2 Radionuclide interaction with NOM in solution – WP2

In order to understand the migration behaviour of the considered radionuclides in a reducing clay sediment, we first investigate the speciation in the solution phase: determination of the solubility limits for the reduced forms (to compare them with predicted values) followed by the determination of the effect of NOM onto the solubility (complexation, colloid formation). Since it is anticipated that uranium might be present in the Boom Clay in its U(VI) redox state, the complexation of U(VI) with NOM is also investigated.

The dissolved organic matter considered is Boom Clay Organic Matter (hereafter sometimes referred to as Boom Clay Humic Acid, BCHA). Mainly concentrated dissolved organic matter (coded TROM, TRancom Organic Matter) is used originating from an in-situ piezometer in the Boom Clay. In some experiments, OM is extracted by Synthetic Boom Clay Water (SBCW)\(^2\) from a Boom Clay sample, this is called a Boom Clay Extract (BCE).

2.2.1 Effect of organic matter on solubility's of U, Pu and Se under reducing conditions

2.2.1.1 Effect of NOM on U solubility.

The solubility of U(IV) was measured using the under saturation approach, using different preparation methods to obtain an amorphous U(IV)-phase: chemical reduction with dithionite (LU)\(^3\), electroreduction and U-metal dissolution (SCK-CEN)\(^4\).

Experiments conducted at LU to determine the effect of Boom Clay humic acid (BCHA) on U solubility under reducing conditions, used a method based on procedures described by Ryan et al. (1983) and Rai et al. (1990). Two series of experiments were conducted.

In a first phase, U(IV) was prepared by reducing uranyl nitrate solution (UO\(_2\)(NO\(_3\))\(_2\)) under alkaline conditions, with sodium dithionite (Na\(_2\)S\(_2\)O\(_4\)). \(^{233}\)U was included as a tracer. The black / brown precipitate that formed was assumed to be amorphous UO\(_2\).2H\(_2\)O. In the second phase, elemental Fe was included as an additional O\(_2\) ‘getter’. The aged precipitates were equilibrated with increasing concentrations of HA and the uranium concentrations were determined using liquid scintillation counting (LSC).

Method development took place during the first phase and involved investigations into precipitate aging, the use of filtration or centrifugation to separate the dissolved phase, and the use of HEPES buffer. Also the solubility of the oxide in SBCW, in the presence and absence of BCHA, was determined and the solubilising effects of BCHA and Aldrich HA (AHA) were compared.

Details of the method that evolved are as follows: Uranium oxide was precipitated by mixing solutions of NaOH (2.5 cm\(^3\); 0.4 mol dm\(^{-3}\)), Na\(_2\)S\(_2\)O\(_4\) (5.0 cm\(^3\); 0.10 mol dm\(^{-3}\)) and UO\(_2\)(NO\(_3\))\(_2\) (2.5 cm\(^3\); 0.01 mol dm\(^{-3}\); containing \(^{233}\)U tracer). The solid was aged for 2 weeks, centrifuged off, then washed with Na\(_2\)S\(_2\)O\(_4\) solution (0.05 mol dm\(^{-3}\)) and re-centrifuged. The washings were discarded and the washed precipitates were treated with: Na\(_2\)S\(_2\)O\(_4\) solution (2.5 cm\(^3\); 0.20 mol dm\(^{-3}\)), HEPES buffer (2.5 cm\(^3\), 0.4 mol dm\(^{-3}\), pH = 8.2), HA (x cm\(^3\); increasing concentrations), H\(_2\)O (5 – x cm\(^3\)). The mixtures were equilibrated for 2 weeks, then supernatant samples were taken, by filtering through 0.45 µm membranes, and uranium concentrations were determined using LSC. pH and E\(_h\) values were monitored and the experiments were performed in a N\(_2\) glove box.

---


\(^3\) Annex 3: Effect of NOM on the U and Pu solubility under reducing conditions.

Generally when HA was absent the U concentration in solution fell in the range 1 \times 10^{-6} to 1 \times 10^{-5} \text{ mol dm}^{-3}. In the presence of HA at concentrations comparable to Real Boom Clay Water, RBCW (TOC 80 – 150 mg dm^{-3}), U concentrations lay at the upper end of the range or higher. The solubilising effects of BCHA and AHA were similar. However the U concentrations in the absence of HA were high compared to accepted literature solubility values of \sim 10^{-8} to 10^{-9} \text{ mol dm}^{-3} (Neck et al., 2001). One possible explanation of the high concentrations was U colloid formation. Consequently typical mixtures with HA absent were ultra-filtered, using 500 MWCO membranes, to test for colloids. A reduction of \sim 2/3 in the U concentration was noted. However the reduction may have been due to simple sorption by the membrane not filtration, even then the U concentration remained well above the 10^{-8} \text{ mol dm}^{-3} level.

The favoured explanation for the high U-concentrations was partial oxidation of U(IV) to U(VI), due to traces of O_2. Rai et al. (1990) state that the O_2 fugacity must be < 10^{-65} atmospheres to prevent U(IV) oxidation. Consequently a second phase of experiments was undertaken using Fe as an additional O_2 getter.

Inclusion of Fe lowered U concentration by variable amounts. The evidence suggested that O_2 was entering the mixtures at various stages. The small amount present (<1 ppm) in the glove box atmosphere facilitated U(VI) formation. Consequently a mixed oxide was suspected containing U(IV) and U(VI). At pH = 13 when all further manipulation was avoided, the U content was found to be \sim 3.1 \times 10^{-9} \text{ mol dm}^{-3}, agreeing with the ‘best’ literature values. The derived solubility product was identical to the value calculated by Neck et al. (2001) i.e. \log K_{sp} = -54.5. Also a UV – visible spectroscopic study, conducted by dissolving oxide samples in HCl acid, provided further evidence of U(VI). The U(IV) absorbance peak at 429 nm contained a U(VI) contribution. The proportions corresponded to the proposed stoichiometry i.e. UO_2.25 or UO_3.3UO_2.

In the first series of experiments conducted by SCK-CEN, the solubility of amorphous uranium(IV) oxide was measured as a function of time in RBCW (which contains NOM). The \emph{in situ} CO_2(g) partial pressure of 10^{-2.4} atm. was applied, by conducting the experiments in a glove box with a controlled Ar – 0.4% CO_2 atmosphere (< 5 ppm O_2). The required uranium(IV) was obtained by electrochemically reducing uranium(VI). The precipitated phase was produced by titrating the uranium(IV) solution with degassed NaOH (1.0 mol dm^{-3}) to a pH of about 8.5. The experiments were conducted in the absence and presence of dithionite (5 \times 10^{-3} \text{ mol dm}^{-3}), sulphide (3 \times 10^{-4} \text{ mol dm}^{-3}) and Fe powder (1g dm^{-3}). U concentrations were measured after filtration at 0.45 \mu m.

Generally uranium concentrations decreased with time reaching approximately 1 \times 10^{-6} \text{ mol dm}^{-3} after 10 days in the presence of dithionite, 20 days in the presence of Fe powder and 2 months in the absence of reducing agents (Fig. 2). The decrease was notably less in the sulphide containing system and a constant uranium concentration was not reached even after 2 months. The decreases were postulated to be due to the presence of uranium(VI) in the original U(IV) precipitate. Dissolution of U(VI) followed by reduction-precipitation of a neo-formed phase of U(IV) gradually lowered the U concentration. However the observed U concentrations were two or three orders of magnitude higher than the solubility’s predicted by the solubility product (Neck et al., 2001). Possible explanations were considered including: formation of uranium(IV)-organic matter complexes, formation of soluble uranium(VI)-carbonato complexes and / or the presence of inorganic/organic U-colloids.
Figure 2: Effect of different reducing agents on the uranium concentration (0.45 µm filtered) above U(IV) amorphous precipitate as a function of the time in RBCW. The solids were washed with ultra-pure water equilibrated for 24 hours with iron powder.

In the second series of experiments, U solubility was investigated in SBCW, with and without added OM, and in RBCW. Dissolved U concentrations were determined after micro-filtration (0.45 µm) and ultra-filtration (30 000 MWCO). The tests were designed to obtain evidence for or against the existence of inorganic or organic U colloids and/or organic complexes due to U complexation by OM. The experiments were conducted anaerobically, in a controlled Ar – 5% H₂ – 0.4% CO₂ atmosphere (< 1 ppm O₂). Due to persisting problems with electrochemical reduction, a uranium(IV) stock solution was prepared by dissolving uranium metal in concentrated HCl acid. The U(IV) phase was precipitated from this solution and the precipitate was identified as being poorly crystallised UO₂ after characterisation by XRD, SEM and µ-XANES. The experiments were conducted in the presence of dithionite (5 10⁻³ mol dm⁻³) for 2 weeks and Fe powder (1g dm⁻³) for 4 weeks. The results are presented in Figure 3. In the samples with HA absent, the micro-filtered uranium concentration averaged 1.6 10⁻⁶ mol dm⁻³, whilst the ultra-filtered concentration was 2.9 10⁻⁸ mol dm⁻³. The decrease of 2 orders of magnitude was taken as evidence of inorganic uranium(IV) colloids.

In the experiments using BCHA (TOC 15 to 850 mg dm⁻³), typically more than 60 % of the HA was removed by micro-filtration (Fig. 4). Therefore it was surmised that the U-HA interaction had produced particles larger than 0.45 µm. The micro-filtered uranium concentration increased with TOC, from 4 10⁻⁶ mol dm⁻³ to about 1 10⁻⁴ mol dm⁻³. However this increase was ascribed to the presence of inorganic U colloids rather than U-organic colloids. Indeed, a significant decrease between micro- and ultra-filtered HA only became apparent when the remaining TOC after micro-filtration was higher than 75 mg dm⁻³. The micro-filtered uranium(IV)-HA organic colloids only contributed to a small extent to the uranium concentration increase (Fig. 5). Figure 3 shows that increasing amounts of HA did not significantly increase the ultra-filtered U solubility by formation of uranium(IV)-HA complexes.
Figure 3: Uranium concentration above amorphous UO₂ after micro- and ultra-filtration plotted as a function of the initial TOC concentration.

Figure 4: Percentage of TOC removed after micro-filtration at 0.45 µm plotted as a function of the initial TOC concentration.

Figure 5: Uranium concentration above amorphous UO₂ plotted as a function of the TOC concentration after micro-filtration.
Similar experiments were conducted with crystalline ThO$_2$ as an analogue for tetravalent uranium. Ultra-filtration decreased the HA concentration and the ThO$_2$ concentration significantly. Micro-filtered Th(IV) concentrations increased by up to three orders of magnitude upon increasing the HA content. Therefore, this increase was attributed to the formation of Th organic colloids.

The difference in solubility and colloidal behaviour reported by LU and SCK-CEN may be due to variation in the precipitated oxide phase, i.e. degree of oxidation and crystallinity and on the effect of the ionic strength. According to the literature, the carbonate at the Boom Clay concentration did not complex uranium(IV) but dominate the speciation of uranium(VI).

2.2.1.2 Effect of NOM on Pu solubility

Initial analysis of a $^{239}$Pu-nitrate stock solution, believed to contain Pu(IV) only, showed mixed Pu oxidation states. Subsequently Pu(IV) was purified from the mixture by column chromatography, using a Dowex ion exchanger column and eluting with nitric acid.

The purified Pu(IV) solution was titrated with NaOH to pH = 13 forming a hardly visible grey Pu(IV) precipitate/gel. Aliquots of the Pu(IV) suspension were immersed in pure water/SBCW containing different concentrations of BCHA and in RBCW. The solutions were bubbled with argon for ~2 hours prior to use and the experiments were conducted in a glovebox with an Ar/0.4% CO$_2$ atmosphere. Supernatant samples were taken, ultrafiltered at 30 000 MWCO and counted after 15 and 84 days equilibration. After 84 days Pu solubility was 50% of that observed at 15 days, suggesting that a slow coagulation/precipitation process was occurring. The results are displayed graphically in Figure 6.

![Figure 6: Evolution in Pu(IV) concentrations (after filtration at 30 000 MWCO) in H$_2$O, SBCW (with increasing concentrations of BCHA) and in RBCW. Measurements after 15 and 84 days.](image)

Relatively high Pu solubility’s were noted in the blank samples (no BCHA), $[\text{Pu}]_{\text{aq}} \approx 1.5 \times 10^{-6}$ mol dm$^{-3}$, possibly due to the presence of Pu(VI) formed by oxidation or disproportionation of Pu(IV) (positive $E_h$ values were measured, $\sim 300$ mV vs. SHE). But upon adding BCHA, the Pu concentration dropped so it was hypothesised that treatment with BCHA probably reduced Pu(VI) back to Pu(IV) and lowered the solubility ($E_h$ values were positive but lower for samples without OM, $\sim 200$ mV vs. SHE). Raising the BCHA concentration from 20 to 500 mg dm$^{-3}$ raised the initially lowered Pu solubility by about an order of magnitude from $\sim 1 \times 10^{-7}$ to $1 \times 10^{-6}$ mol dm$^{-3}$ which can be explained by an increased complexation with OM. The solubility in RBCW ($\sim 100$ ppm TOC) was $2.6 \times 10^{-7}$ mol dm$^{-3}$.

To some of the samples (those with 200 ppm C) dithionite was added to obtain strong reducing conditions, eliminating the possible presence of oxidised Pu-species. This not only resulted in a $E_h$ drop ($\sim -300$ to $-400$ mV vs. SHE) but also in a pH drop to pH$\sim$6-7 and all Pu became solubilised ($\sim 2 \times 10^{-6}$ mol dm$^{-3}$). According to speciation calculations, Pu(III) aqueous species are dominant under these conditions.

2.2.1.3 Effect of NOM on the Se solubility

Theory suggests that Se may be present as an equilibrium mixture of Se, FeSe and FeSe$_2$ under the reducing conditions imposed by FeS$_2$ in BC. Experiments have therefore been conducted to investigate Se speciation under BC conditions, starting from SeO$_4^{2-}$ and SeO$_3^{2-}$ (over saturation approach in presence of pyrite, see also paragraph 2.3.2.2) and from Se$^0$ and Se$_2^-$ solid phases (under saturation approach).

A number of methods were investigated for the reduction of Se oxyanions to more reduced forms:
- chemical reduction using $\text{N}_2\text{H}_4$, $\text{Na}_2\text{S}$, FeS, Zn, and Fe;
- electro-reduction;
- isotopic exchange between FeSe and a $^{75}\text{Se}_2\text{O}_3^{2-}$ spike.

The chemical reduction systems provided amorphous red and crystalline black elementary selenium (Se$^0$), using $\text{Na}_2\text{S}$ and $\text{N}_2\text{H}_4$, and metal-selenides, using $\text{Na}_2\text{S}+\text{Fe}$, Fe and Zn. However XRD measurements on the selenides were not conclusive. These reduced products were contacted with SBCW containing $2.37 \times 10^{-5}$ mol dm$^{-3}$ Fe$^{2+}$ and the Se solubility’s were determined after 12 days. Solubility was found to be dependent on the reducing system and the solid phase. $^{75}\text{Se}$ concentrations in solution fell in three solubility ranges, consistent with different solid phases i.e. amorphous Se$^0$: $2.2 \times 10^{-8}$ - $9.1 \times 10^{-8}$ mol dm$^{-3}$, crystalline Se$^0$: $1.5 \times 10^{-9}$ - $8.1 \times 10^{-9}$ mol dm$^{-3}$ and amorphous M$_x$Se$_y$: $4.8 \times 10^{-10}$ - $9.7 \times 10^{-10}$ mol dm$^{-3}$, where M = Fe and Zn.

After removal of the supernatant SBCW solution, half of each solid phase was re-contacted with SBCW (+ $2.37 \times 10^{-5}$ mol dm$^{-3}$ Fe$^{2+}$) and the other half was contacted with BCE. The systems were allowed to equilibrate for 2 months and were then analysed for: total $^{75}\text{Se}$ concentration in solution; $^{75}\text{Se}$ concentration in solution after precipitation of dissolved OM using $\text{La}^{3+}$; UV absorbance at 280 nm; $E_h$ and pH. The total initial $^{75}\text{Se}$ concentrations ranged from $1.1 \times 10^{-9}$ to $2.0 \times 10^{-7}$ mol dm$^{-3}$. The results showed no direct relationship between the total $^{75}\text{Se}$ concentration in solution and the dissolved OM. After addition of $\text{La}^{3+}$ and removal of the precipitate, the $^{75}\text{Se}$ concentration ranged from $2.8 \times 10^{-10}$ to $2.1 \times 10^{-9}$ mol dm$^{-3}$. In the presence and absence of dissolved OM, the addition of $\text{La}^{3+}$ resulted generally in the loss of 70-95% Se from solution, suggesting that Se colloids were present but not particularly associated with OM.
Electro-reduction of inactive SeO$_3^{2-}$ using a galvano-potentiostat was also used. Solid Se phases were precipitated on the surface of metallic (Pt, Ni) scraps. Amorphous and crystalline Se$^0$ solid phases were again identified. Equilibration of the metal scrap / $^{75}$Se alloys, with SBCW, confirmed amorphous and crystalline Se solid phases. The solubility's were similar to those noted above i.e. $8.0 \times 10^{-8} - 2.0 \times 10^{-7}$ mol dm$^{-3}$ and $4.0 \times 10^{-9} - 5.3 \times 10^{-9}$ mol dm$^{-3}$.

The electro-reduced systems were treated with SBCW and BCE as above and allowed to equilibrate for 2 months before analysing. Again no significant interaction with dissolved OM was noted. Initial Se concentrations ranged from $3.06 \times 10^{-9}$ to $3.06 \times 10^{-8}$ mol dm$^{-3}$ but after addition of La$^{3+}$ and centrifugation, the concentrations decreased to $1.2 - 3.3 \times 10^{-9}$ mol dm$^{-3}$. Se colloids were again suspected.

Isotopic exchange was tested. After one and a half years a reddish precipitate appeared, probably amorphous $^{75}$Se pointing to simple reduction of $^{75}$SeO$_3^{2-}$ and not isotopic exchange. Consequently the systems were not investigated further.

2.2.2 Uranium and selenium complexation with NOM

2.2.2.1 $U$(IV)/$U$(VI)-NOM complexation

As a pre-cursor to the U(IV) complexation experiments, U(VI)-BCHA and U(VI)-AHA constants were determined using the Schubert approach under carbonate free conditions (LU)$^6$, by applying the method as developed by Dierckx et al. (1994), and by the conventional dialysis method under in-situ carbonate conditions (SCK-CEN)$^7$.

For the Schubert approach, $^{233}$U(VI) tracer was contacted with a cation exchange resin (Na form), in the presence and absence of varying amounts of HA. The required $D$ and $D_0$ values i.e. the distribution coefficients ([U]$_{\text{resin}}$/[U]$_{\text{solution}}$) in the presence and absence of HA were derived from supernatant activity measurements. The $\beta_{\text{exp}}$ values were calculated using the following relationship:

$$\log \beta_{\text{exp}} = \log_{10} A(\frac{D_0}{D} - 1) - n \log [HA]$$

“A” is a side reaction coefficient term, included to take account of competition from hydroxide ions, and “n” is the stoichiometric ratio of HA to U(VI) in the complex.

BCHA and AHA solutions purged with N$_2$, carbonate free NaOH solution and HEPES buffer were equilibrated with tracer for 1 – 2 weeks in a N$_2$ atmosphere at various pH values. The micro-filtered supernatant $^{233}$U activities were determined using LSC. BCHA was assumed to contain 50% TOC and a maximum proton exchange capacity (PEC) of $4.0 \times 10^{-3}$ mol g$^{-1}$ was taken irregardless of the pH (Dierckx et al., 2000). The AHA PEC was assumed to be $5.3 \times 10^{-3}$ mol g$^{-1}$ (Dierckx et al., 2000). Since carbonate was absent, U(VI)-carbonato species did not interfere and the side reaction coefficients were calculated using the expression given below. The $\beta$ values were adjusted to reflect the ionic strengths (I.S.) of the mixtures:

$$A = 1 + \beta_{UO_2(OH)^+} [OH^-] + \beta_{UO_2(OH)_{12}} [OH] + \beta_{UO_2(OH)_{13}} [OH]^2 + \beta_{UO_2(OH)_{14}} [OH]^3$$

The BCHA and AHA Schubert plots had unit slopes implying 1:1 U(VI) to HA stoichiometries i.e. $n = 1$. Graphical interpolations of the U(VI)-BCHA and AHA data provided identical stability constants i.e. $\log \beta = 9.69$ (s.d. ± 0.39) at pH = 8.2.

---

$^6$ Annex 5: Complexation studies of U(VI) and U(IV) with NOM using the Schubert method.

$^7$ Annex 6: Complexation studies of U(VI) with NOM using the dialysis method (Delécaut, 2004).
The dialysis experiments were conducted to investigate the complexation of uranium(VI) by BCHA and AHA, in SBCW under the in situ CO$_2$ partial pressure condition of $10^{-2.4}$ atm (4000 ppm CO$_2$). The U(VI) concentration (~ 4.2 $10^{-7}$ mol dm$^{-3}$) was held constant whilst the HA concentration was varied i.e. TOC from 0 to 640 mg dm$^{-3}$. The 1000 MWCO dialysis bags were filled with 10 ml of the HA solution and immersed in Pyrex tubes, containing 50 ml of SBCW spiked with uranium. After 10 days of equilibration, the bags were opened and samples taken from inside and outside the bags. The uranium and HA concentrations were measured by ICP-MS and TOC analyses, respectively.

The effect of BCHA oxidation was observed because the OM batch (TROM 28) was in contact with air during the concentration process, whereas the other was prepared by freeze-drying BC interstitial water, under anaerobic conditions. Further experiments were conducted using AHA in the presence and absence of phosphate ($8 \times 10^{-5}$ mol dm$^{-3}$ HPO$_4^{2-}$). Two additional experiments were conducted using BCHA at a different pCO$_2$ value (air atmosphere), to investigate the effect of carbonate. The pH in the first experiment was controlled by addition of NaOH or HCl and in the second by including Trizma buffer at pH 8.1. The ionic strength was fixed using 1.5 $10^{-2}$ mol dm$^{-3}$ NaClO$_4$ and the uranium concentration was ~ $3.5 \times 10^{-7}$ mol dm$^{-3}$.

The complexation reaction may be represented simply as:

$$UO_2^{2+} + HA \Leftrightarrow UO_2HA$$

Hence the conditional constant is given by:

$$\beta = \frac{[UO_2HA]}{[UO_2^{2+}][HA]_{\text{free}}}$$

However calculations using the NEA data base and the Geochemist’s Workbench code indicated that the main uranium species were UO$_2$(CO$_3$)$_3^{4-}$ (>95 %) and UO$_2$(CO$_3$)$_2^{2-}$ (<5 %). Hence the concentration of UO$_2^{2+}$ present is given by:

$$[UO_2^{2+}] = \frac{[U_{\text{tot}}]}{1 + \beta_{13} \cdot [CO_3^{2-}]^3 + \beta_{12} \cdot [CO_3^{2-}]^2}$$

where \(1 + \beta_{13} \cdot [CO_3^{2-}]^3 + \beta_{12} \cdot [CO_3^{2-}]^2\) is the side reaction coefficient (A).

Consequently $\beta_{\text{exp}}$ values were calculated from the dialysis results using following equation, with the A term included.

$$\beta_{\text{exp}} = \frac{[U_{\text{in}}] - [U_{\text{out}}]}{[U_{\text{out}}] \cdot [HA]_{\text{free}}} \times A$$

The results are displayed graphically in Figure 7. Under BC conditions (TOC from 50 – 150 mg dm$^{-3}$), less than 10% of the uranium was complexed by Aldrich HA and less than 5 % by BCHA. The difference between AHA and BCHA is explained by the PEC, $4.3 \times 10^{-3}$ mol g$^{-1}$ and $2.9 \times 10^{-3}$ mol g$^{-1}$ for AHA and BCHA (for a pH of 8.1), respectively. Under CO$_2$ atmosphere partial pressure, the percentage of uranium-humate complexes increased to 65-90 % in the TOC range of Boom Clay pore water. However, under BC conditions, the speciation was dominated by U(VI) carbonate-complexes as noted above. At the in situ pCO$_2$, the concentration of carbonate is about $1.3 \times 10^{-4}$ mol dm$^{-3}$ while in air saturated solution the carbonate concentration is about $6 \times 10^{-6}$ mol dm$^{-3}$, at pH 8.1. The derived log $\beta_{\text{exp}}$ values are given in Table 2. The constants are seen to be in close agreement and not dependent on the type of HA, it’s oxidised state or the presence of phosphate.
Table 2: Conditional complexation constants of uranyl HA complexes obtained for different systems (under in-situ CO₂ conditions). The quoted error corresponds to the standard deviation.

<table>
<thead>
<tr>
<th></th>
<th>Aldrich HA with HPO₄²⁻</th>
<th>Aldrich HA without HPO₄²⁻</th>
<th>Oxidised Boom Clay HA</th>
<th>Non-oxidised Boom Clay HA</th>
</tr>
</thead>
<tbody>
<tr>
<td>logβ̂_{exp}</td>
<td>12.2 ± 0.12</td>
<td>12.1 ± 0.11</td>
<td>12.3 ± 0.14</td>
<td>12.3 ± 0.08</td>
</tr>
</tbody>
</table>

The constants are higher than those reported in the literature (Czerwinsky et al., 1994) for non-hydrolysing conditions, for various reasons e.g.:

(i) the low concentration of ‘free’ UO₂^{2+} present i.e. ~10^{-17} mol dm^{-3}.
(ii) the increased ionisation of HA functional groups with pH.
(iii) possible formation of mixed-complexes involving carbonato and hydroxy ligands.

However, the constants obtained are conservative because they include all uranium humate species.

![Figure 7: Bound to total uranium ratio plotted as a function of the total organic carbon content (TOC) of the mixtures.](image)

The discrepancy of ~ 2 orders of magnitude between the SCK-CEN and LU U-HA stability constants may be attributed to several factors including the following:

(i) CO₂ was present in the SCK-CEN studies but not the LU studies. The resulting A terms which dominate the numerical value of the derived constants were different.
(ii) The experiments were carried out at different I.S. values.
(iii) LU assumed maximum PEC values whilst SCK-CEN used lower pH dependent values.
(iv) Different mixed-complexes may be involved.
Due to the presence of insoluble oxide phases the classical Schubert approach could not be applied to the U(IV) (or Pu(IV)) systems. Therefore a solubility product/side reaction coefficient approach was developed for deriving stability constants based on the experimental results of the solubility tests in presence of BCHA (see also the discussion on the side reaction coefficient in paragraph 2.4.1). However the U(IV) calculations relied on the formation of pure UO₂ and it’s solubility product. But as already pointed out, the U-phase formed in these experiments was presumably a mixed U(IV)-U(VI) phases as was indicated by a UV – visible spectroscopic study, conducted by dissolving oxide samples in HCl acid, The U(IV) absorbance peak at 429 nm contained a U(VI) contribution. The proportions corresponded to the proposed stoichiometry i.e. UO₂.₂₅ or UO₃.₃UO₂.

Consequently the results acquired in the first phase were modelled as UO₂.₂₅ (Van der Lee, 2003b, see also paragraph 2.4.2). A U(IV)-BCHA stability constant may be derived using speciation codes.

2.2.2.2 Se-NOM complexation
A meaningful study of selenium complexation with NOM was precluded because interaction of reduced Se solid phases with dissolved OM was negligible. Furthermore the SeO₃²⁻/OM observations suggested that Se colloids were formed leading to a Se colloid–OM colloid interaction.

2.2.3 Natural uranium concentration in Boom Clay
Study on natural uranium concentration is continuing. Batch leaching tests have been performed in NaHCO₃ media (0.01 to 1 mol dm⁻³) containing different amount of clay (20 to 800 g clay per litre of solution). Aqueous uranium concentrations after a centrifugation of 21,255 g constantly increases as the amount of clay increases. We interpreted this finding as being due to colloids formation by suspending clay into bicarbonate solution. Some isolated colloidal suspensions were found unstable after some months of storage in the refrigerator. Humic gels or precipitates were found in high or low ionic strength media. Ultrafiltration experiments indicated that uranium was present as colloids at the NaHCO₃ level similar as in Boom Clay. Natural uranium concentration determined by batch tests is in general 2 to 3 orders of magnitude higher than the uranium concentration in the pore waters collected through piezometers. Step-wise leaching resulted in similar level of uranium concentration up the 4th leaching suggesting a constant release of uranium colloids from clay surfaces (Wang et al. 2001, 2002). It is not clear at this stage of study if released uranium colloids are associated with NOM or not.

Experiments were also planned to estimate the retardation of uranium due to an isotopic fractionation/dilution between aqueous uranium released from waste (e.g., from spent fuel) and natural uranium present in Boom Clay. According to the definition, isotopic fractionation/dilution phenomena occur only among same chemical species containing different isotopes. This requires that the introduced radio isotope, for example ²³³U in this case, must be in a chemical form which is identical to the natural uranium species (containing ²³⁸U isotope) in Boom Clay. In other words, uranium species containing ²³³U must be in the tetravalent U(IV) oxidation state which is the controlling oxidation state of natural uranium in Boom Clay. This was however difficult to achieve as demonstrated by the work performed in the work package 2.1. Batch experiments showed that commercial ²⁵³U(VI) tracer cannot be reduced easily even in the presence of strong chemical reducing agents. Without a complete

---

8 Annex 10: Technical note: Theoretical analysis of U(IV) solubility and complexation with Boom-Clay organic matter (NT34/03, Armines).
reduction of U(VI) to U(IV), uranium distribution will be governed by oxidation/reduction kinetics rather than by isotopic exchange equilibrium. For this reason, we believe that it is difficult to demonstrate an isotope dilution mechanism in the case of uranium because it is difficult to control the speciation of the $^{233}$U tracer. It was therefore decided not to perform the isotopic dilution experiments at the current stage.

2.2.4 Conclusions on the radionuclide interaction with NOM in solution.

- **U interaction with NOM**

  Batch experiments revealed that the solubility of amorphous UO$_2$ is $\sim 10^{-8}$ mol dm$^{-3}$ with no effect of NOM complexation. However, it was evidenced that the presence of NOM facilitated the formation of uranium colloids upon dissolution of UO$_2$. The formation of colloids, with molecular size between 2 nm and 0.45 µm, accounts for a total uranium concentration, three orders of magnitude higher than the solubility of the amorphous UO$_2$. Uranium colloids were also found being dominant in leaching experiments of natural uranium from Boom Clay samples. These colloids, only evidenced in batch experiments, are unlikely to be mobile in the compact natural Boom Clay. See also the discussion in paragraph 2.4.5 on the U-solubility enhancement.

  Due to the uncertainties in the U(IV) oxide phase and the nature of the U(IV)-OM interaction, no complexation constants are derived. See also the discussion in paragraphs 2.4.1&2 on the U(IV) solubility.

  The complexation of U(VI) with OM was studied in detail under different conditions (different CO$_2$ conditions: no CO$_2$, atmospheric CO$_2$ and in-situ partial pressure CO$_2$) and conditional log$\beta_{\text{exp}}$ are derived. U(VI)-humate complexes are the dominant species under atmospheric pCO$_2$ conditions but under Boom Clay pCO$_2$ conditions, the speciation is dominated by carbonate complexes. The high log$\beta_{\text{exp}}$ value might indicate the presence of mixed complexes. See also the discussion in chapter 2.4 on the U(VI) complexation.

- **Pu(IV) solubility and interaction with NOM**

  No direct speciation techniques were done on the prepared reduced Pu(IV)-phase but the high solubility ($< 30 000$ MWCO) $\sim 8 \times 10^{-7}$ mol dm$^{-3}$ in absence of OM points to the presence of some oxidised Pu species. Solubility experiments of Pu(IV) in absence and presence of Boom Clay organic matter were therefore not conclusive; Pu concentrations ($< 30 000$ MWCO) of $4 \times 10^{-8}$ mol dm$^{-3}$ up to $8 \times 10^{-7}$ mol dm$^{-3}$ were measured with increasing Pu concentration as a function of the NOM concentration, suggesting that NOM may increase the Pu(IV) solubility by an order of magnitude.

- **Se interaction with NOM**

  Through chemical reduction and electro-deposition, different reduced Se solid phases were formed with different experimental solubility’s (see table below). Upon equilibration with Boom Clay organic matter, no interaction was observed. Observations suggested that Se colloids were formed leading to a Se colloid–OM colloid interaction. These colloids are probably not mobile in the Boom Clay.

<table>
<thead>
<tr>
<th>Se precipitate</th>
<th>Colour</th>
<th>Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous Se$_0^-$</td>
<td>Red</td>
<td>$\sim 2.2 \times 10^{-8}$ mol dm$^{-3}$</td>
</tr>
<tr>
<td>Crystalline Se$_0^-$</td>
<td>Black</td>
<td>$\sim 2.0 \times 10^{-9}$ mol dm$^{-3}$</td>
</tr>
<tr>
<td>Metal selenide (Zn, Fe)</td>
<td>Black</td>
<td>$\sim 4.8 \times 10^{-10}$ mol dm$^{-3}$</td>
</tr>
</tbody>
</table>
2.3 Radionuclide solid phase interactions – WP2

Following the speciation studies in the solution phase, the interaction of U and Se with the solid phase is investigated in more detail to determine the effect of solid phases (pyrite, BC, minerals) in combination with NOM on the retention of U and Se-species (starting from different redox states) in terms of immobilisation and sorption process.

2.3.1 U solid phase interaction

2.3.1.1 Uranium(VI) interaction with Pyrite

The sorption of uranium(VI) on Boom Clay pyrite was studied in SBCW and RBCW (pH ~8.2) at the *in situ* partial pressure of CO$_2$, i.e. $10^{-2.4}$ atm. The batch experiments were conducted under anaerobic conditions in a glove box with a controlled Ar – 5% H$_2$ - 0.4% CO$_2$ atmosphere (O$_2$ < 1 ppm). The pyrite was separated from Boom Clay samples. The characterisation by X-ray diffraction (XRD) showed that the main constituents were pyrite and quartz. Besides, carbonates and Ti-oxides were also present as well as clay minerals traces. Half a gram of pyrite was contacted with 10 ml of Boom Clay water containing $1 \times 10^{-5}$ mol dm$^{-3}$ of uranium(VI) and the suspensions were equilibrated for 1, 4, 8, 16, and 32 days. At the end of the equilibration period, two aliquots were sampled for U measurement (ICP-MS) after filtration at 0.22 $\mu$m and 30 000 MWCO, respectively.

In SBCW, the uranium concentration decreased as function of time, from $1.7 \times 10^{-6}$ mol dm$^{-3}$ after 1 day to $4.4 \times 10^{-8}$ mol dm$^{-3}$ after 16 days. Surprisingly, it was increased to $1.1 \times 10^{-7}$ mol dm$^{-3}$ after 32 days. The filtration at different sizes did not influence the uranium concentration indicating that there were no uranium-bearing colloids present in solution (Fig. 8). On the other hand, there was a notable effect of the filtration in the experiments performed with RBCW which contains, unlike synthetic water, about ~100 mgCl$^{-1}$ of dissolved organic matter. The uranium concentration decreased with time but was always higher after micro-filtration than after ultra-filtration (Fig 8). This behaviour indicates the presence of uranium-bearing colloids, presumably organic in nature since the only difference with the experiments conducted in SBCW is the OM.

After 32 days, the uranium concentration was decreased to $3.5 \times 10^{-7}$ mol dm$^{-3}$ after micro-filtration and $7.0 \times 10^{-8}$ mol dm$^{-3}$ after ultra-filtration. The uranium concentrations were lower in SBCW than in RBCW showing that the sorption was reduced by the presence of organic matter (Fig. 8). The suppression or the reduction of sorption in presence of organic matter at alkaline pH has been reported in the literature (Beneš *et al*., 1998 and references therein; Lenhart and Honeyman, 1999; Zuyi *et al*., 2000).

For each solution (SBCW and RBCW), one sample with an initial uranium(VI) concentration of $1 \times 10^{-3}$ mol dm$^{-3}$ was allowed to equilibrate for 46 days at the same solid-solution ratio. The final concentration (~ $2 \times 10^{-7}$ mol dm$^{-3}$) was about the same than that of the experiments with an initial uranium concentration of $10^{-5}$ mol dm$^{-3}$ (Fig. 8). The distribution coefficient calculations resulted into $K_d$ of 73 900 ml g$^{-1}$ in SBCW and 93 884 ml g$^{-1}$ in RBCW after ultra-filtration (27 647 ml g$^{-1}$ after micro-filtration). These unrealistic $K_d$ would indicate that sorption is not the only mechanism occurring.

---

9 Annex 7: U interaction with solid phases present in Boom Clay (Delècaut, 2004).
Figure 8: Evolution of the uranium concentration (mol dm$^{-3}$) from an initial concentration of $10^{-5}$ mol dm$^{-3}$ as function of contact time with pyrite. The data at 46 days were obtained for an initial uranium concentration of $10^{-3}$ mol dm$^{-3}$.

The sorption on the walls of the tubes being excluded, the phenomenon which is expected to happen is the reduction of uranium(VI) to uranium(IV) and its subsequent precipitation. Several information support this assumption. First, the reduction of uranium(VI) and the precipitation of a mixed U(VI)-U(IV) oxide in presence of pyrite under anoxic conditions was already demonstrated by the experimental study of Wersin et al. (1994). Second, the fact that the final concentrations tended to a constant value whatever the initial uranium(VI) concentration was would indicate a solubility control. According to the solubility of the uranium phases in Boom Clay water, UO$_2$3333(beta) may be the solubility controlling phase since its modelled solubility is $3.5 \times 10^{-7}$ mol dm$^{-3}$ (Wang et al., 2000; Van der Lee et al., 2001). Third, the presence of uranium-colloids in RBCW was noticed. It has been shown in chapter 2.2 that the complexation of uranium(VI) by organic matter under Boom Clay conditions is very limited while there exists a strong colloidal-interaction between uranium(IV) and organic matter. Fourth, the pH of the samples was always increasing, from 8.2 to 9 in SBCW and to 9.5 in RBCW while the $E_h$ was decreasing accordingly. Assuming the reduction of uranium(VI) to uranium(IV), that may be explained by the release of carbonates through the reaction:

$$\text{UO}_2(\text{CO}_3)_{34}^- + 2e^- \leftrightarrow \text{UO}_{2+x} + 3\text{CO}_3^{2-}$$

Finally, spectroscopic analyses ($\mu$-XANES, figure 9) confirmed the presence of uranium(IV) after interaction with pyrite in SBCW. Like iron powder, the spectrum of pyrite lacks the multiple scattering feature observed in the UO$_2$(Ac)$_2$ and goethite spectra, characteristic for uranium(VI). This indicates the reduction of uranium(VI) to uranium(IV). However, the energy of the pyrite white-line maximum is closer to that of the U$_3$O$_8$ than to that of the UO$_2$ reference. This is in agreement with the hypothesis that UO$_2$333 is the solubility controlling phase.
2.3.1.2 **Uranium(IV) interaction with selected BC components**  
The sorption of uranium(IV) on pure minerals was investigated in RBCW at the *in situ* partial pressure of CO$_2$ (10$^{-2.4}$ atm.) under anaerobic conditions in a glove box with a controlled Ar – 5% H$_2$ - 0.4% CO$_2$ atmosphere (O$_2$ < 1 ppm). The batch experiments were performed in duplicates. The aim of this study was to carry out screening sorption experiments to determine the most important sorbants for uranium(IV).

Nine minerals were selected and characterised by X-rays diffraction (XRD), X-rays fluorescence (XRF) and N$_2$-adsorption (specific surface area by BET method): kaolinite, illite, illite-smectite mixed-layers, montmorillonite, chlorite, rutile, calcite, apatite and pyrite.

The solution of uranium(IV) was prepared by suspending hydrous UO$_2$(am) in RBCW containing 5 $10^{-3}$ mol dm$^{-3}$ dithionite for 10 days. The measured uranium concentration was 2.9 $10^{-7}$ mol dm$^{-3}$ after micro-filtration at 0.22 µm. Afterwards, 10 ml of the filtered spiked RBCW were added to 500 mg of the minerals and allowed to equilibrate for 10 days. At the end of the equilibration period, an aliquot of 5 ml was sampled for U measurement (High-resolution ICP-MS) after filtration at 0.22 µm.

In the blank samples, about 40 % of the uranium was sorbed onto the walls of the centrifuge tubes. The distribution coefficient (K$_d$) was calculated for each duplicate and averaged without correction for the sorption onto the tubes (Table 3). The minerals can be ranked in order of increasing uranium(IV) distribution coefficients: montmorillonite < rutile < pyrite < apatite < kaolinite < calcite < chlorite < illite < illite-smectite mixed-layers. By normalising the K$_d$ values to the specific surface area, Chlorite is an important sink for uranium. When normalised to the abundance of the different minerals in the Boom Clay it is clear that illite and illite-smectite will be the dominant sorption sinks for uranium.
Table 3: Raw and normalised distribution coefficients \((K_d)\) for the sorption of uranium(IV) on pure minerals in RBCW.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Abundance</th>
<th>Normalised (K_d)</th>
<th>Wt. % normalised (K_d)</th>
<th>Surface area (BET)</th>
<th>Wt. % (ml·g⁻¹)</th>
<th>Surface Area normalised (K_d) (ml·m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Montmorillonite</td>
<td>15</td>
<td>~0</td>
<td>~0</td>
<td>30.72</td>
<td>30.72</td>
<td>~0</td>
</tr>
<tr>
<td>Rutile</td>
<td>&lt; 1</td>
<td>19</td>
<td>0.2</td>
<td>3.27</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Pyrite</td>
<td>2</td>
<td>44</td>
<td>0.9</td>
<td>4.84</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>Apatite</td>
<td>&lt; 1</td>
<td>62</td>
<td>0.6</td>
<td>1.02</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>Kaolinite</td>
<td>10</td>
<td>111</td>
<td>11</td>
<td>11.39</td>
<td>11.39</td>
<td>10</td>
</tr>
<tr>
<td>Calcite</td>
<td>3</td>
<td>130</td>
<td>4</td>
<td>2.38</td>
<td>2.38</td>
<td>55</td>
</tr>
<tr>
<td>Chlorite</td>
<td>2</td>
<td>363</td>
<td>7.3</td>
<td>3.49</td>
<td>3.49</td>
<td>104</td>
</tr>
<tr>
<td>Illite</td>
<td>20</td>
<td>380</td>
<td>76</td>
<td>27.32</td>
<td>27.32</td>
<td>18</td>
</tr>
<tr>
<td>Illite-smectite</td>
<td>15</td>
<td>688</td>
<td>103.2</td>
<td>25.02</td>
<td>25.02</td>
<td>27</td>
</tr>
</tbody>
</table>

2.3.2 Selenium solid phase interactions

Theory suggests that Se may be present as an equilibrium mixture of Se, FeSe and FeSe₂ under the reducing conditions imposed by FeS₂ in BC. Experiments have therefore been conducted to investigate Se speciation under reducing BC conditions after interaction with solid phases: pyrite and Boom Clay.

Since oxidised Se species will probably be present in the waste forms, both experiments starting from over saturation with selenium oxyanions and from under saturation with reduced Se solid phases were undertaken. (1) Firstly the interaction of \(\text{SeO}_4^{2-}\) and \(\text{SeO}_3^{2-}\) with pyrite (with or without OM) is studied; (2) then the interaction of \(\text{SeO}_3^{2-}\) and chemically reduced Se phases with Boom Clay is studied.

2.3.2.1 Selenium interaction with pyrite

A new method based on ion chromatography of radiolabelled \(^{75}\text{Se}\) solutions, followed by gamma-ray counting was developed to measure oxidised selenium species in solution (Bruggeman et al. 2002.) The identification of reduced selenium species (HSe⁻, Se⁰) was performed indirectly. The method has a detection limit of \(10^{-10}\) mol dm⁻³ for oxidised species.

For the over saturation experiments, different amounts of ground pyrite (FeS₂: < 100 µm, 2.5 g dm⁻³ and 10 g dm⁻³) were contacted with SBCW and spiked with \(^{75}\text{SeO}_3^{2-}\) and \(\text{SeO}_4^{2-}\) (\(5 \times 10^{-6}\) mol dm⁻³ and \(10^{-6}\) mol dm⁻³). The batches were allowed to equilibrate for up to two months in an oxygen-depleted glove box (99.6% N₂, 0.4% CO₂), then analysed.

In systems where \(\text{SeO}_3^{2-}\) was contacted with FeS₂ a steady decrease with time (60 days) was observed, until a final concentration in solution of \(3 \times 10^{-9}\) mol dm⁻³ was reached. However equilibrium was not attained in many samples. All the systems obeyed a single rate law, which was first-order with respect to selenium and FeS₂, and inversely proportional to the square root of FeS₂ site occupancy by selenium. The observations suggested that SeO₃⁻⁻ reduction occurred through sorption on FeS₂. A Se solid phase, probably crystalline elementary Se⁰, with a solubility of \(3 \times 10^{-9}\) mol dm⁻³ was formed.

In systems where \( \text{SeO}_4^{2-} \) was contacted with \( \text{FeS}_2 \), the \( \text{SeO}_4^{2-} \) concentrations decreased very slowly remaining approximately equal to the starting concentration, even after 60 days in many samples. The \( \text{SeO}_4^{2-} \) was not sorbed by \( \text{FeS}_2 \) or \( \text{Fe} \) oxides.

The above method was extended to SBCW/\( \text{FeS}_2 \) (10 g dm\(^{-3}\)) systems with OM included. Two sets were prepared, one with 100 mg dm\(^{-3}\) TROM29, and the other with BC extract (100 mg dm\(^{-3}\) and 30 mg dm\(^{-3}\)). Two initial \( \text{SeO}_4^{2-} \) concentrations were used (5 \( \times \) 10\(^{-6}\) mol dm\(^{-3}\) and 10\(^{-6}\) mol dm\(^{-3}\)). The TROM systems were analysed after 330 days and the BCE systems after 92 days. The BCE systems were analysed using GPC in addition to the ion chromatographic method (Bruggeman et al., 2002). In all the batches part of the added organic matter was sorbed onto the solid \( \text{FeS}_2 \) producing a linear sorption isotherm (log\( K_d \) = 4.26 \( \pm \) 0.05).

In the TROM batches (positive \( E_h \) values measured), the decrease in total Se concentrations with time was less than in the absence of OM. After 320 days, total Se concentrations were of the order of 1 \( \times \) 10\(^{-7}\) mol dm\(^{-3}\), indicating that \( \text{SeO}_4^{2-} \) reduction was slow.

In the BCE batches (negative \( E_h \) values measured), total Se concentrations decreased at the same rate as observed in the absence of OM, but remained constant after 14 days equilibration time.

A small proportion of the Se in solution (< 10%) was associated with OM. This “equilibrium” situation generated a sorption log\( K_d \) value for \( \text{SeO}_4^{2-} \) of 3.49 \( \pm \) 0.01. After “equilibrium” was established, \( \text{SeO}_4^{2-} \) concentrations were seen to decrease very slowly, whilst the Se concentrations associated with OM remained constant or even increased slightly. After 90 days in systems with an initial \( \text{SeO}_4^{2-} \) concentration of 1 \( \times \) 10\(^{-6}\) mol dm\(^{-3}\), up to 25% of total Se in solution was associated with organic matter. In the systems with an initial \( \text{SeO}_4^{2-} \) concentration of 5 \( \times \) 10\(^{-6}\) mol dm\(^{-3}\) the percentage was 2% - 17%. At the end of the experiments a constant log\( K_d \) = 3.57 \( \pm \) 0.01 was obtained for free Se in solution.

### 2.3.2.2 Selenium interaction with Boom Clay

First, the speciation of Se in presence of Boom Clay was studied starting from over saturation with \( \text{SeO}_4^{2-} \). In order to eliminate all possible \( O_2 \) interactions with the Se systems, various centrifuge tubes containing \( \text{SeO}_4^{2-} \) and Boom Clay were submerged into a larger container with Boom Clay suspension. Systems were prepared using two Boom Clay solid-to-liquid ratios (0.05 and 0.21 kg dm\(^{-3}\)), as well as two initial \( \text{SeO}_4^{2-} \) concentrations (5 \( \times \) 10\(^{-6}\) mol dm\(^{-3}\) and 10\(^{-6}\) mol dm\(^{-3}\)). These systems were allowed to equilibrate up to 9 months. The supernatant of the samples (after centrifugation, cut-off ~ 20 nm) was analysed for total \( \text{Se} \) concentration in solution, \( \text{Se} \) concentration in solution after La\(^{3+} \) precipitation of dissolved HS, Optical Density at 280 nm, \( E_h \) and \( pH \). Solutions were also injected on Anion Chromatographic and Gel Permeation Chromatographic columns.

Experimental results showed that the speciation procedures used were sufficiently quantitative for identification of several different \( \text{Se} \) species in the Boom Clay suspensions. \( \text{SeO}_4^{2-} \), \( \text{SeO}_3^{2-} \) and Se associated with organic matter could be readily determined; the detection of HS\( \text{Se}^- \) species however could not be achieved via a direct procedure. It is also possible that selenide species in solution were oxidised upon injection in the Ion Chromatograph or Gel Permeation Chromatograph and were measured as \( \text{SeO}_3^{2-} \). \( pH \) and redox measurements showed that the correct geochemical requirements were met for reduction of the added \( \text{SeO}_3^{2-} \) in the Boom Clay suspension.
Upon addition of $^{75}\text{SeO}_3^{2-}$ to the Boom Clay systems (Figure 10), it was shown that in the first few days, a distribution of Se between the solid and the liquid phase was seen to exist, attributable to the (inner-sphere) sorption of selenite onto broken edges of the clay particles ($\log K_{d} = 2.00 \pm 0.05$). After approximately 14 days (depending on the system studied) two “stable” concentrations of $^{75}\text{SeO}_3^{2-}$ were seen to exist: one being $1.4(\pm0.2) \times 10^{-7}$ mol dm$^{-3}$ and the other being $2.4(\pm0.2) \times 10^{-8}$ mol dm$^{-3}$. These two concentrations were (remarkably enough) identical to the plateau values of $\text{SeO}_3^{2-}$ observed in the experiment with FeS$_2$ and BCE. Hereafter, in some systems (after 3 months’ equilibration time) $^{75}\text{SeO}_3^{2-}$ concentrations in solution again lowered towards $3 \times 10^{-9}$ mol dm$^{-3}$, the experimental solubility observed in experiments using FeS$_2$ as a reductant. The amount of solid phase in the systems seemed to be the critical parameter for the reaction kinetics in the samples. In all systems $^{75}\text{Se}$ concentrations in solution tended to decrease, but the system with lowest initial Se conc. and largest solid/liquid ratio attained equilibrium most rapidly. Thus, adsorption of $\text{SeO}_3^{2-}$ onto the clay minerals seemed to act as a competitor for the reduction of $\text{SeO}_3^{2-}$ by FeS$_2$.

$^{75}\text{Se}$ in all systems was found to be associated with dissolved organic matter. This amount was initially low (10% - 30%) relative to the total Se solution concentration, but remained quite constant (although slightly decreasing) throughout the experiment. Thus, after nine months, in some samples the largest part (40% - 75 %) of selenium in solution was found to be associated with organic matter.

Figure 10: $\text{SeO}_3^{2-}$ concentration in solution (mol dm$^{-3}$) vs. Se concentration on the Boom Clay solid phase (mol g$^{-1}$) for the long-term experiment to study the Se speciation under Boom Clay geochemical conditions. The figure shows how $\text{SeO}_3^{2-}$ concentrations in solution initially decreased to two “plateau” values (of $1.35 \times 10^{-7}$ mol dm$^{-3}$ and $2.4 \times 10^{-8}$ mol dm$^{-3}$), and that only after three months’ equilibration time, $\text{SeO}_3^{2-}$ concentrations in the systems with highest solid-to-liquid ratio again lowered towards the previously observed experimental Se “solubility” value of $3 \times 10^{-9}$ mol dm$^{-3}$. 

23
In a second set of experiments, reduced $^{75}$Se solid phases –prepared beforehand- were contacted with Boom Clay phases in order to study the Se behaviour starting from under saturation. The same systems as described in paragraph 2.2.1.3 (on the one hand different chemically reduced $^{75}$Se solid phases, on the other hand electro-deposited $^{75}$Se) were contacted with Boom Clay suspensions (2 solid-to-liquid ratios, 0.05 kg dm$^{-3}$ and 0.21 kg dm$^{-3}$) and allowed to equilibrate up to two months. The supernatant of the samples (after centrifugation, cut-off $\sim$ 20 nm) was analysed for total $^{75}$Se concentration in solution, $^{75}$Se concentration in solution after La$^{3+}$ precipitation of dissolved OM, Optical Density at 280 nm, $E_h$ and pH.

$^{75}$Se concentrations in solution ranged from $5.8 \times 10^{-10}$ mol dm$^{-3}$ to $2.2 \times 10^{-8}$ mol dm$^{-3}$, which was overall lower than the concentrations observed in batch experiments where the same $^{75}$Se solid phases were contacted with SBCW and BCE. This probably means that either reduced $^{75}$Se species interact with the Boom Clay solid phase (and systems are kinetically not yet in equilibrium), or that during centrifugation, co-precipitation of reduced Se colloids by the clay particles present in the samples occurred. However, no relation with the organic matter concentration was found, thus providing no evidence for HSe$^-$ complexation with Boom Clay OM. Neither was any specific relationship observed with the amount of solid Boom Clay phase for the total $^{75}$Se concentration.

2.3.3 Conclusions on the radionuclide solid phase interactions

- **Uranium interaction with solid phases**

Both experimental and spectroscopic results indicate that pyrite is able to reduce U(VI), as UO$_2$(CO$_3$)$_3$$^{4-}$, under Boom Clay conditions. The solubility of the precipitated U(IV) phase is about $\sim$10$^{-7}$ mol dm$^{-3}$ and UO$_2.3333$ may be the solubility controlling phase. In the presence of organic matter (RBCW) colloids are formed, presumably U(IV)-HA since there are no colloidal particles of uranium in SBCW.

The aqueous U above UO$_2$(am) in RBCW can sorb onto pure minerals. Taking into account the relative abundance of the minerals in Boom Clay, the main sinks are illite and illite-smectite mixed layers.

- **Selenium interaction with solid phases**

Upon introduction of SeO$_4^{2-}$ to Boom Clay or pyrite, no considerable sorption or reduction was seen to occur over short experimental measuring periods (a few months). Its migration behaviour is therefore assumed to be (initially) almost unretarded. Association with Boom Clay organic matter is highly unlikely.

Upon reduction of SeO$_3^{2-}$ in the presence of FeS$_2$, a precipitate with a solubility of approximately $3 \times 10^{-9}$ mol dm$^{-3}$ was observed. This precipitate was probably crystalline Se$^0$, based on the measured solubility and the XRD evidence from chemically and electro-chemically reduced Se solid phases. In the presence of organic matter or Boom Clay minerals, the kinetics of reduction are decreased and an association with Boom Clay organic matter was found to exist, probably attributable to a stabilisation of Se colloids (which are formed upon reduction of SeO$_3^{2-}$) by the organic colloids present in solution. SeO$_3^{2-}$ migration is expected to be retarded, because of sorption onto FeS$_2$ and clay minerals.

Through chemical reduction and electro-deposition, different reduced Se solid phases were formed with different experimental solubility’s. Upon equilibration with Boom Clay organic matter, no interaction was observed. It remains unclear if HSe$^-$ species can interact with solid phases present in Boom Clay.
2.4 Geochemical modelling of the influence of NOM and update of geochemical clay database – WP6

This work-package is an extension of chapter 2.1. The existing database and conceptual models used for the initial predictive simulations in chapter 2.1 have been updated with new data from the literature (paragraph on database update) as well as with data which have become available from the experimental work in this project. Interpretation of the experimental results is tightly linked to the subject of database development (paragraphs on modelling of the U(IV) solubility, the U(VI) complexation with OM, the solubility increasing factor), and a thorough analysis of the interpretation methods (discussion on the side reaction coefficient) is presented. Full details are written in underlying technical notes of Van der Lee, (2003a,b,c) and Wang (2003) which are taken up as annexes 9 to 12.

2.4.1 Discussion on the theoretical basis of the side-reaction theory

The side-reaction coefficient method has been applied to establish the humate-complexation reaction mechanism with respect to U(IV). The advantage of this method is its simplicity: no geochemical model or specific humic-acid model is required, since the model reduces the system to the determination of the slope and the interception of a straight line.

One of the questions often raised is whether the slope of the logarithm of the experimental complexation constant versus pH does reflect the type of complex formed with the humic acid. It has been demonstrated that this is not the case: the slope merely reflects that the HA-U complex is in equilibrium with the solid phase UO$_2$, an assumption made a priori. Hence the slope is a result of the assumptions, and cannot be used to deduce a reaction mechanism. This has been demonstrated mathematically: the slope is a consequence of the solubility controlling phase and is unrelated to the actual complex formed. Indeed, using a solubility controlling phase with another stoichiometry with respect to H$^+$ will lead to a different slope.

Furthermore, it has been demonstrated that the side-reaction method in presence of a solubility-limited phase cannot be used to validate or corroborate any assumption with respect to the HA-U reaction mechanism. The method is not precise enough as a model to determine thermodynamic complexation constants.

In addition, the theoretical basis of the method becomes significantly more complex for non-linear expressions of the side-reaction coefficient and if the solubility-limiting phase has a non-trivial composition. It has been shown that the solid phase in one of the experiments was UO$_2.25$, a mixed redox species (see below). This phase leads to a dependence on E$_h$ which, in turn, depends on pH, a non-linearity which cannot be included in the simplified method.

The detailed theoretical analysis has demonstrated that the side-reaction method cannot be applied to the experiments of this project. Moreover, it followed that dissolution kinetics play a role as well. Therefore, only speciation models have been used for interpretation of the experiments.

---

11 Annex 9: Technical note: Note on the theoretical basis of the side-reaction theory (NT36/03, Armines).
2.4.2 Modelling of U(IV) solubility and complexation by Boom Clay Humic Acids

The discussion on the validity and precision of the thermodynamic constants for uranium IV is still ongoing, and forms part of an international debate. Experimental results (LU) concerning the solubility at in-situ conditions (pH = 8.2) in presence of sodium dithionite as reducing agent could be modelled using NEA database and the assumption that UO$_{2.25}$ was formed instead of UO$_2$. The presence of the former solid was considered after a detailed analysis of the UV spectroscopy results (we refer to paragraph 2.2.1.1).

Datasets have been made available by LU for apparent uranium solubility’s in presence of Boom Clay Humic Acids (BCHA), i.e. the amount of uranium passing through a filter of 0.45 um. The BCHA was obtained from the TROM 31 sample. A reduced U(IV)-oxyhydroxide phase was prepared by precipitation at high pH with varying aging times, typically from 1 to 14 days. The equilibrium time seemed to have a significant impact on the apparent solubility (i.e. solubility in presence of BCHA). This kinetic control of the dissolution process has been taken into account by the model. We were able to simulate the experimental findings with a single parameter configuration (i.e., thermodynamic constants) for different experimental data sets. Figure 11 illustrates the simulation with CHESS of experimental results (LU), assuming U$_{2.25}$ with kinetically controlled dissolution. The kinetic constant is relatively straightforwardly derived by a visual fit. The absolute value of this constant, however, is a function of the specific surface of the solid phase, which we ignore. The absolute value of the kinetic constant is therefore unknown.

![Figure 11: Apparent uranium solubility in presence of Boom Clay Humic Acid. Experimental results (LU) and modelling (CHESS) assuming UO$_{2.25}$ with kinetically controlled dissolution. exp3: pH = 7, equilibration time = 7 days; exp5: pH = 8.2, equilibration time =14 days.](image)

---

13 Annex 10: *Technical note: Theoretical analysis of U(IV) solubility and complexation with Boom-Clay organic matter (NT34/03, Armines).*
2.4.3 Modelling of U(VI) complexation by Boom Clay Humic Acids

Experimental data with regard the complexation of U(VI) by Boom Clay humic acids have been obtained by SCK-CEN. The experimental technique is based on dialysis. Prior to modelling, a technical note has been written on the interpretation of the experimental data obtained using the dialysis technique. Indeed, the typical experimental set-up requires some careful pre-treatment of the data before use and comparison with modelling results.

Summarizing the theoretical considerations, the use of a dialysis bag requires rescaling of the total humic acid concentrations and the bound uranium concentration with respect to the total volume of the system (bag + outside volume). The rescaling factor does not affect the classically derived complexation constant, due to a cancelling out of the factor; it has a significant impact, however, on the actually amounts of bound uranium. Rescaling is therefore an essential step if a thermodynamic speciation model is used for the interpretation of the experimental results.

The reaction constants obtained are strongly depending on the assumptions underlying the humate-U(VI) reaction. Assuming a simple and ad-hoc reaction,

\[ \text{UO}_2^{2+} \text{HA} = \text{HA-UO}_2^{2+} \]

leads to a constant of 12.2. Using a three-site humic acid model, as developed for Boom Clay Humic Acid in the previous TRANCOM-Clay project (Dierckx et al., 2000a)

\[ \text{UO}_2^{2+} \text{HA(1)-COOH} \rightleftharpoons \text{H}^+ + \text{HA(1)-COOUO}_2^{+} \]
\[ \text{UO}_2^{2+} \text{HA(2)-COOH} \rightleftharpoons \text{H}^+ + \text{HA(2)-COOUO}_2^{+} \]
\[ \text{UO}_2^{2+} \text{HA-OH} \rightleftharpoons \text{H}^+ + \text{HA-OUO}_2^{+} \]

and assuming identical constants for all types of functional groups (the data does not allow to discriminate between the constants), the results is 2.2. This constant is much smaller than 12.2 because the reaction affinity is significantly increased due to deprotonation, an important factor at these relatively high pH values. The model also includes electrostatic effects. Figure 12 shows a simulation obtained for two datasets and CHESS, illustrating the fit for the latter, three-site model. Identical could be obtained for the simple complexation model and a log(K) of 12.2. We nevertheless believe that the three-site model is more useful for chemists, since the values used are not (or, at least less) pH-dependent.

![Figure 12: Simulation of U(VI)-humate complexation data of the SCK-CEN using the TRANCOM-Clay humic acid discrete site model.](image)

14 Annex 11: Technical note: Modelling of U(VI) complexation with Boom-Clay organic matter (NT42/03, Armines).
2.4.4 Update of the thermodynamic database and its implications on the radionuclide speciation calculations

There has been an important update released by OECD-NEA (Guillaumont et al., 2003 and related personal communications with Federico Mompean from NEA) on the thermodynamic database for radionuclides. A new calculation has been performed for uranium and plutonium using the update and reported in this section. This new calculation should, in principle, update the calculations presented in chapter 2.1 and be used for interpretations of experiments.

Figure 13 and 14 show the new calculations of $E_h$-$pH$ diagrams for uranium using the NEA-TDB 03 update and the NEA-TDB 92 book (Grenthe et al., 1992) respectively. Comparing the two figures, it is apparent that different from the prediction made based on NEA-TDB 92 book (figure 14), the NEA-TDB 03 update predicts that U(VI) carbonato complex is dominant under the Boom Clay reducing condition. This is because of the stability constant of $\text{U(OH)}_4^{\text{aq}}$ was decreased by more than 5 orders of magnitude in the new NEA-TDB 03 update. The predicted result that U(VI) is dominant under a moderate reducing condition should have important effects on solubility, sorption and therefore the retention of uranium in Boom Clay. Figure 15 plots the solubility of $\text{UO}_2^{\text{am}}$ at $pH$ 8.2, total inorganic carbon of 14 mmol dm$^{-3}$ as function of $E_h$. It is seen that the solubility of $\text{UO}_2^{\text{am}}$ increases as function of $E_h$ due to the formation of uranyl carbonato complex. The solubility of $\text{UO}_2^{\text{am}}$ is calculated to be $5 \times 10^{-7}$ mol dm$^{-3}$ at $E_h$ -280 mV, which is two orders of magnitudes higher than the solubility ($3 \times 10^{-9}$ mol dm$^{-3}$) controlled by $\text{UO}_2^{\text{am}}$-$\text{U(OH)}_4^{\text{aq}}$ equilibrium for strong reducing conditions. The dominance of uranyl carbonato complex might also reduce the sorption of uranium onto clay since the negative charged $\text{UO}_2(\text{CO}_3)_3^{4-}$ is not significantly sorbed by natural sorbate, e.g., iron oxy-hydroxides.

Plutonium data also have been renewed in the NEA-TDB 03 update and the $E_h$-$pH$ diagram is calculated (figure 16). Comparing to the results in chapter 2.14, the new database confirms the formation constant for $\text{Pu(OH)}_4^{\text{aq}}$ and the reaction constant of $\text{PuO}_2^{\text{am}}$. From figure 16, it is seen that plutonium is present in two dominant oxidation states, Pu(IV) and Pu(III). The solubility of $\text{PuO}_2^{\text{am}}$ is in the range of $10^{-11}$ mol dm$^{-3}$ to $10^{-12}$ mol dm$^{-3}$ controlled by $\text{Pu(OH)}_4^{\text{aq}}$ and $\text{PuOH}^{2+}$ respectively. Different from the case of uranium, plutonium solubility is about 2 orders of magnitudes lower and the dominant $\text{PuOH}^{2+}$ species might be sorbed strongly by the negative charged, NOM rich Boom Clay.

---

Figure 13: $E_h$-$pH$ diagram for uranium based on the NEA-TDB 03 update. The total dissolved uranium concentration is $10^{-8}$ mol dm$^{-3}$. The total inorganic carbon concentration is 0.014 mol dm$^{-3}$. The open square represents the $E_h$-$pH$ condition of Boom Clay, i.e., $E_h = -280$ mV and $pH = 8.2$.

Figure 14: $E_h$-$pH$ diagram for uranium based on the NEA-TDB 92 book (Grenthe, et al., 1992). The total dissolved uranium concentration is $10^{-8}$ mol dm$^{-3}$. The total inorganic carbon concentration is 0.014 mol dm$^{-3}$. The open square represents the $E_h$-$pH$ condition of Boom Clay, i.e., $E_h = -280$ mV and $pH = 8.2$. 
Figure 15: Contribution of $\text{U(OH)}_4^{4-}$ (aq) and $\text{UO}_2(\text{CO}_3)_{3}^{4-}$ to the solubility of $\text{UO}_2$ (am) as function of redox potential ($E_h$) at $pH$ 8.2 and total inorganic carbon of 14 mmol dm$^{-3}$. Database NEA-TDB 03 update.

Figure 16: $E_h$-$pH$ diagram of plutonium based on the NEA-TDB 03 update. The total dissolved plutonium concentration is $10^{-3}$ mol dm$^{-3}$. The total inorganic carbon concentration is 0.014 mol dm$^{-3}$. The open square represents the $E_h$-$pH$ condition of Boom Clay, i.e., $E_h = -280$ mV and $pH = 8.2$. 
2.4.5 The concept of solubility increasing factor\textsuperscript{16}

The effect of NOM on the solubility of radionuclides has been evaluated through a solubility increasing factor. The factor is defined as the ratio between the solubility in the presence of NOM to the case in the absence of NOM. The factor significantly greater than unity suggests a strong increase of solubility of uranium by NOM. The factor close to unity merely means that NOM has no apparent effect on the solubility. Figure 17 shows results for the solubility experiments of uranium. In term of solubility, i.e., the uranium concentration measured after the ultrafiltration of 30 000 MWCO, SCK•CEN’s data show no effect of NOM on the solubility of UO\textsubscript{2} (am) since the solubility increasing factor is around 1. Both datasets, however, indicate formation of colloids upon dissolution of UO\textsubscript{2} (am) as indicated by the uranium concentration increase (U\textsubscript{NOM}/U\textsubscript{0} > 1) measured after filtration using 0.45 \textmu m filter. These results suggest that NOM will unlikely enhance the migration of uranium through formation of mobile complex. The effect of the observed colloids formation depends on what fraction(s) of colloids, in terms of size, is mobile in compact undisturbed Boom Clay.

\textsuperscript{16} Annex 12: Technical note: Reflection on the geochemical modelling of the RN-NOM interaction experiments (03/LWa/N-18, SCK-CEN).

Figure 17: The ratio of [U\textsubscript{NOM}]/[U\textsubscript{0}] upon dissolution of UO\textsubscript{2}\textsubscript{x} (am) as function of NOM concentration. The experiment of SCK was performed with the solid phase UO\textsubscript{2} (am) while the data of LU was possibly produced using UO\textsubscript{2:25} phase.
2.5 Migration experiments with RN-NOM double labelled solutions – WP5

The objective is to provide migration data sets for U, Pu and Se, using well prepared radionuclide sources, as close as possible to their expected equilibrium speciation under in-situ BC conditions and in contact with $^{14}$C-labelled Boom Clay Organic Matter (BCOM). By using double labelled solutions, both the fate of the radionuclide and the organic matter can be followed. The aim is to see whether the mobile BCOM facilitates the radionuclide migration, to formulate conceptual models, and deliver representative migration parameters, usable by performance assessment.

2.5.1 Production and stability testing of site specific $^{14}$C-labelled NOM

Due to uncertainties with regard to the stability of the previously used $^{14}$CH$_3$NH$_2$ labelled organic matter (OM), an alternative labelling technique was developed. BCHA was treated with $^{14}$C-formaldehyde (H$^{14}$CHO) in the presence of a reducing agent. The process is used to radiolabel proteins (Jentoft et al., 1979). The reaction which involves reductive methylation proceeds as follows:

\[
\begin{align*}
R_N^+H & \quad + \quad H_4C=CH_2 & \quad \rightarrow & \quad R_N^{=^{14}C}H \\
& & \quad \text{NaCNBH}_3 & \quad \text{H}_2\text{O} \\
& & & \quad \text{H} \\
& & & \quad \text{H} \\
\end{align*}
\]

Samples of TROM 33 and 34 were labelled. The products were analysed using gel permeation chromatography (GPC). A Sephadex-G10 gel column was used with 0.05 mol dm$^{-3}$ NaCl as the mobile phase. Activity and UV absorbance (254 nm) chromatograms were obtained using liquid scintillation counting (LSC) and UV-visible spectrophotometry, respectively. Comparison of the activity and UV profiles, before and after precipitation of the BCHA with HCl acid, indicated that the humic fraction of the OM had labelled successfully.

The purified $^{14}$C-BCHA was shown to be stable over the pH range from 4 to 10 and in contact with various minerals, including Boom clay; no releases of activity were recorded.

For the planned diffusion experiments, two samples of labelled BCHA were purified using HCl acid precipitation, followed by re-dissolution in dilute NaOH solution. The first sample was sent to SCK-CEN (642.2 kBq cm$^{-3}$; 7.5 cm$^3$) and the second was retained at LU (355.7 kBq cm$^{-3}$; 7 cm$^3$).

---

2.5.2 Migration experiments with $^{233}$U, Se, $^{239}$Pu - $^{14}$C-NOM double labelled solutions.

Different types of migration experiments were performed: back-to-back diffusion (LU)$^{18}$, percolation type and electromigration type migration experiments (SCK-CEN)$^{19}$.

Preliminary experiments using the electromigration technique were started to perform fast screening experiments with prepared $^{233}$U- and $^{75}$Se-sources to optimise conditions for migration tests. Experiments started by using prepared $^{233}$UO$_2$(CO$_3$)$_4^{4-}$ sources to first identify the behaviour of U(VI) species. It was noticed from these experiments (Maes et al., 2001 and 2002) that the uranyl-carbonate complex is not stable but is reduced by the clay to form U-hydrous oxide precipitates with the solubility limited release of an uranium species that was positive or neutral charged, presumably U(OH)$_4$ (Figure 18). From these experiments an estimate of the apparent diffusion coefficient for U(OH)$_4$ was made: $D_{app} \approx 6-12 \times 10^{-12}$ m$^2$ s$^{-1}$ which is in line with the results of a long-time running experiment with uranium which is re-evaluated in chapter 2.7 (see also Wang et al., 2001). The pore water U-concentration in the plateau region at the cathode side equals $4 \times 10^{-8}$ mol dm$^{-3}$, which is similar to the observations for the solubility of amorphous UO$_2$ made in chapter 2.

![Figure 18: Left: Schematic representation of an electromigration set-up. Right: Logarithmic activity distribution profile of $^{233}$U (applied as UO$_2$(CO$_3$)$_4^{4-}$) after electromigration for 674 h/5 mA/60 V m$^{-1}$). The horizontal line denotes detection limit.](image)

Experiments starting from $^{75}$SeO$_3^{2-}$ showed the presence of oxidised $^{75}$SeO$_4^{2-}$ species which remain stable in the clay and move fast. Most of the selenium remained at the initial position due to strong sorption of the selenite and due to reduction/precipitation. The formation of a negatively charged species, presumably HSe$^-$, is observed in the experiments. These observations are in line with the results obtained by batch Se experiments reported in chapter 2 and 3. It was decided to study in more detail the migration of selenate with electromigration since this species remains stable in the BC (no reduction observed) and it moves unretarded. A $D_{app} \approx 2-6 \times 10^{-11}$ m$^2$ s$^{-1}$ for SeO$_4^{2-}$ was determined with no retardation (Beauwens et al., 2003).

For the back-to-back diffusion experiments labelled $^{14}$C-BCHA was contacted with precipitated UO$_2$ for 1 week then an aliquot of the supernatant was taken using a 0.1 μm syringe filter. A small sample was placed between two halves of a core. The total α and β activities were 9.25 kBq and 20.6 Bq, respectively. Diffusion was allowed to proceed for 120 days. Afterwards the core sections were segmented, dispersed in H$_2$O and analysed for α and β activities.

---

$^{18}$ Annex 13: Double tracer migration experiments: Radiolabelling of Boom Clay organic Matter and back-to-back diffusion experiments.

$^{19}$ Annex 14: Migration experiments and demonstration of model concept for trivalent radionuclides
The diffusion profiles for the $^{14}$C-BCHA-U experiment can be seen in Figure 19. Very low levels of alpha activity were incorporated into the BCHA, hence the ‘noise’ is significant. However it appears that the uranium $\alpha$ activity did move away from the centre of the core.

![Figure 19: Top: Schematic view of the back-to-back migration set-up. Bottom: Diffusion profile of $^{14}$C-BCHA-U after 120 days (The $\alpha$ activities have been increased by a factor of 100 to facilitate comparisons).](image)

For the *percolation type migration experiments* (Figure 20), SCK-CEN has chosen to prepare and to work as much as possible under similar conditions as used in the solubility and complexation experiments conducted (and described in chapter 2). This has the benefit that results obtained correlate directly with the migration experiments. These new started experiments will be compared to long-term running experiments (8 years) at SCK-CEN with $^{233}$U and $^{238}$Pu single labelled solutions. These radionuclide sources were applied to the clay “as delivered by supplier”: uranyl nitrate and plutonium nitrate in HNO$_3$ and with concentrations above the solubility limit (> $10^{-6}$ mol dm$^{-3}$). Because of the fact that these radionuclide sources were initially not in equilibrium with the BC conditions, the evolution of the source is unsure and therefore the results of these migration experiments were always treated with suspicion.

Due to the problems we can have with detection of the solubility limited tracers (as observed in figure 19), suspensions (containing a solid phase) of the RN-$^{14}$COM were used as source. For the double labelled migration experiments, solutions containing solid phases of $^{239}$Pu(IV) (see the Pu(IV) solubility experiments), $^{233}$U(IV) (reduction with dithionite) and FeSe were added to SBCW and subsequently spiked with $^{14}$C-labelled BCHA to obtain a final concentration in organic carbon of 95 ppm (similar to RBCW).
Spikes of these suspensions were used as sources for percolation experiments. Besides the monitoring of the radionuclide solutions percolating through the clay cores, the radionuclide concentrations in the double label solutions are monitored in time and therefore compared to the solubility tests in chapter 2.2.

Figure 20: Schematic presentation of the percolation type experimental set-up used for the migration experiments in the TRANCOM-II project.

Gel electrophoresis techniques were tested and found useful as a relative simple speciation tool to have an idea on the redox state of the radionuclide (charge), and to check if an association between the radionuclide and NOM exists.

Although, no direct speciation of the radionuclide source solutions was done, a combination of experimental findings (filtration, electrophoresis, electromigration) and reasoning’s lead us to the conclusion that the conditions of the radionuclide-suspensions at the clay surface are: reduced solid phases (amorphous in the case of U and Pu) in equilibrium with their respective reduced aqueous species. The possible presence of some oxidised species will not jeopardise the results for U and Se:

- since it was shown that the Boom Clay will reduce the uranium (electromigration experiments),
- since we identified and quantified the oxidised Se-species present in the source and they are “washed” out rapidly without disturbing the system,

By gel electrophoresis we observed that the $^{239}$Pu(IV)-$^{14}$COM source solution contains Pu-OM associated species besides a Pu-solid phase, unfortunately we were unable to draw conclusions on that for U and Se.

The migration experiments (Figure 21) clearly show that, irregardless of the initial presence of RN-OM associated species, the radionuclide transport is not enhanced by the mobile OM. Most of the mobile $^{14}$C-labelled OM has percolated out while no significant U and Pu concentrations were detected (respectively detection limits for U and Pu: $10^{-11}$ and $10^{-12}$ mol dm$^{-3}$). For Se, a breakthrough of oxidised Se species (initially present in the FeSe source) was noticed, followed by a constant concentration of $2 \times 10^{-8}$ mol dm$^{-3}$ which is equal to the Se background concentration in RBCW. The source of Se in the Boom Clay is not identified but it was observed that the BC pyrite contains high levels of Se ($\sim 20$ µg g$^{-1}$).

The new experiments do not contradict with the long-term experiments (Figure 22) but due to higher detection limits some information is lost. For uranium we know now that applying a source initially not in equilibrium with the BC conditions will not jeopardise the results since reduction/precipitation occurs fast (days) with regards to the slow diffusion process.
Figure 21: Breakthrough curves of the different radionuclides and the $^{14}$C-labelled OM.

Figure 22: U and Pu breakthrough curves for the long-term running experiments with non equilibrated single labelled radionuclide sources.
2.5.3 Conclusions on the migration experiments
Diffusion coefficients for $\text{U(OH)}_4^-$ and $\text{SeO}_4^{2-}$ were derived from electromigration experiments.

From the classical migration experiments we are currently not able to determine migration parameters for the reduced radionuclide species but following conclusions can be made:

- Uranium reduces in the clay and diffuses through it as $\text{U(OH)}_4^-$ (not as a negatively charged OM associated species, as proven by electromigration). The current double labelled percolation experiments support the long-term migration experiment with $^{233}\text{U}$ (initially not in geochemical equilibrium), therefore the results of these experiments can now be used to obtain reliable migration parameters.

- No migration parameters for Pu could be derived, neither could we conclude on the redox state of the aqueous Pu (III or IV). Despite the presence of Pu-OM associated species, which enhanced the solubility to $10^{-7}$ mol dm$^{-3}$ (complexation), it did not lead to an enhanced transport. Neither did we observe a Pu breakthrough linked with the OM or increased Pu concentrations in the solutions percolating from the clay cores.

- For Selenium it is important to know the initial speciation of the selenium in the waste, if it is present in its highest oxidation state it is quite stable (no reduction is observed), highly soluble and moves unretarded through the clay. For the lower oxidation states, solubility will be the dominating effect. The presence of relative high concentrations of natural Se in the Boom Clay water and its abundance in Boom Clay phases (e.g. pyrite) needs a more detailed study.

It is evidenced that the transport of these reduced radionuclide species is not enhanced by the mobile OM in terms of RN-OM species (complexes or colloids). Even if such complexes or colloids exist, they are filtered or instable with respect to the clay phase. The dominating retention effect is immobilisation (solubility in case of U and Se and a solubility-like process for Pu).
Demonstration of the model concept for the migration behaviour of trivalent radionuclides – WP8

In the previous EC TRANCOM-Clay project (FI4W-CT95-0013, EUR19135, Dierckx et al., 2000a,b; Wang et al., 2001), the idea developed that Am-OM complexes dissociate, almost instantaneously, when contacted with Boom Clay and only a small portion persists as “stabilised” Am-OM complex leading to a constant bleeding of Am. The aim is to see if kinetics of exchange of trivalent Am between mobile and immobile phase can explain differences in the Am-concentrations in water percolating from migration experiments and the occurrence of a fast –but small – breakthrough of Am accompanying the organic matter (OM)- breakthrough.

The objective is to describe and demonstrate a conceptual model for the migration of trivalent radionuclides in an NOM rich clay environment. The obtained conceptual models will then be translated into a transport model described in chapter 2.7.

2.6.1 $^{241}$Am-$^{14}$COM double label migration experiments

As trivalent actinides have a great affinity for organic matter, it is of great concern to study their interaction and migration behaviour in presence of organic matter. As organic matter in soils and subsurface environments is a mixture of low and high molecular weight molecules, which do not necessarily share the same properties (such as affinity towards actinide elements, diffusion coefficient,...), it is relevant to study the migration of different size fractions. In previous phase (Trancom-Clay, Dierckx et al., 2000a) it was noticed that the used experimental migration set-up (pulse-injection, Figure 23) was not appropriate due to sorption effects of Am on the stainless steel injection loop and filter. These experiments showed a breakthrough peak of a tiny fraction of the Am (<0.1%) together with the OM size fractions followed by a constant release of Am, $[\text{Am}] \sim 0.8-3 \times 10^{-12} \text{ mol dm}^{-3}$ (Figure 23).

Figure 23: Experimental set-up used in the previous Trancom-Clay EC project with typical $^{241}$Am and $^{14}$C-OM breakthrough curves. The recoveries are respectively: $^{241}$Am<0.1%, $^{14}$COM~76%.

To investigate the possible kinetics of exchange of Am between mobile and immobile phase, experiments were done with varying clay plug length and Darcy velocity. These experiments were conducted using an newly prepared $^{14}$C-labelled OM, $^{14}$C-TROM34, with a distinct size distribution. In order to do a good interpretation, the radionuclide sources were characterised by ultrafiltration (size distribution, presence of Am inorganic phases), electrophoresis (existence of Am-OM complexes).

Annex 14: Migration experiments and demonstration of model concept for trivalent radionuclides.
The Am solubility was determined in synthetic Boom Clay Water (SBCW) \([\text{Am}]_{300\text{LD}} \sim 2 \times 10^{-8} \text{ mol dm}^{-3}\). We observed that the Am-OM double labelled solutions (Am-TROM6) used in the Trancom-Clay project contained quite some Am-“solid” phase (Figure 24-top), although they were prepared with Am concentrations below the Am solubility in RBCW (determined as \(10^{-6}\) mol dm\(^{-3}\) in Trancom-Clay).

Upon adding the \(^{14}\text{C}\)-labelled OM (TROM34), the Am is solubilised as an OM complex and the Am is distributed over the different size fractions (Figure 24-bottom). These complexes easily dissociate upon interaction with Boom Clay solid phase. Larger OM molecules form more kinetically stable Am-OM complexes.

**Figure 24:** *Top:* effect of filtration on the Am concentration for different Am containing solutions. Am-SBCW: Am added to synthetic Boom Clay Water (solubility measurement), Am-TROM6 and Am-TROM34: respectively the double labelled solutions used in Trancom-Clay and Trancom-II projects. *Bottom:* size distributions for the \(^{14}\text{C}\)-labelled OM batch (TROM34) and the double labelled \(^{241}\text{Am}^{14}\text{C}\)-TROM34 solution prepared for the diffusion experiments. Note that the \(^{241}\text{Am}\) follows the OM size distribution.
The migration experiments in current TRANCOM-II project were performed with an optimised percolation type set-up (Figure 20) using inert materials to avoid sorption effects of Am.

Figure 25: $^{241}$Am and $^{14}$C-OM breakthrough curves measured for Am-OM double labelled migration experiments for different Darcy velocity and clay plug length ($L$ denotes clay plug length, in $10^{-2}$ m; $V_d$ denotes Darcy velocity, in $10^{-9}$ m s$^{-1}$).

The breakthrough of a tiny Am peak (<0.1%) together with the OM is again observed (figure 25) but by increasing the travel time (by lowering the Darcy velocity or by using a longer clay plug), this Am breakthrough peak is suppressed and the concentration disappears under detection limit ($5 \times 10^{-14}$ mol dm$^{-3}$). Also for the other experiments the Am concentrations are decreasing towards detection limit and it seems that there is no establishing of a constant Am-concentration (Figure 25).
By plotting the ratio of the plug length/\(D_{\text{arcy}}\) (dimension of time = travel time) to the Am recoveries or the ratio of the Am/OM recovery an exponential decrease is noticed which can be fitted by a decay function (Figure 26).

\[
y = 1.25 \times 10^{-1} e^{-8.37 \times 10^{-8} x}
\]

\[R^2 = 8.48 \times 10^{-1}\]

Figure 26: Influence of the “travel time” on the Am recovery, showing an exponential “decay” of the breakthrough of the mobile Am-OM complex upon interaction with the Boom Clay.

When Am-OM complexes are contacted with Boom Clay they dissociate instantaneously, and the bulk of Am is immobilised (as Am complexed to OM_{immob} or sorbed) and only a small portion persists as “stabilised” Am-OM complex which move through the clay. These “stabilised” Am-OM complexes further dissociate upon travelling through the clay but this is controlled by a slow kinetic.

When Am is present in the source as an inorganic phase, not associated with NOM (when applied above solubility limit), then there is a continuous source of Am to form “stabilised” Am-OM complexes and this results in a constant concentration in the experiments.

The results obtained by the experiments covering both phases, Trancom-Clay and Trancom-II, can consistently be subdivided according to differences in source conditions, and can be described by 2 concepts depending on the initial source condition.
Concept when initially only Am-OM complexes are present:
Only one source of stabilised mobile Am-OM complexes that dissociate (controlled by slow kinetics) upon travelling through the clay.

Concept when initially an inorganic Am “solid phase” is present
If no Am-OM complexes are initially present: 1 source [Am], giving Am-OM stabilised complexes: [Am]$_{perco}$~1-4 $10^{-13}$ mol dm$^{-3}$.
If the source contains also Am-OM complexes, 2 sources giving Am-OM stabilised complex: [Am]$_{perco}$~$10^{-12}$ mol dm$^{-3}$.
2.6.2 $^{14}$C-labelled OM in-situ migration experiment (follow-up of Trancom-Clay)

During the Trancom-Clay project (Dierckx et al., 2000a) a large-scale in-situ migration experiment with $^{14}$C-labelled BCOM was initiated in the HADES Underground Research Laboratory of SCK-CEN at Mol (Belgium). Two experiments were started: one diffusion experiment in the horizontal direction -parallel with clay stratification- (June 1997) and one in the vertical direction -perpendicular to the clay stratification- (June 1998). The aim of the experiments was the up scaling of the lab migration experiments with mobile OM to a large in-situ scale. These experiments are intended to be monitored for many years. In figure 27 the breakthrough of $^{14}$C labelled BCOM is shown for the filters nearest to the injection filter (at a distance of 0.35 m). No activity has been observed in filters further away from the source position.

![Diagram of piezometers](image)

**Figure 27: Left:** Schematic representation of the emplacement of the piezometers in the HADES URL (SCK-CEN, Mol, Belgium) for the migration experiment with $^{14}$C-labelled Natural Organic Matter. **Right:** Measured $^{14}$C-activity in the sampling filters nearest to the injection filters.

The in-situ experiments demonstrate on a larger scale the mobility of natural organic matter. However, we are currently unable to consistently model the experimental breakthrough curves. This can be attributed to the complex mechanisms behind the OM transport as will be further discussed in chapter 2.7 on transport modelling.

2.6.3 Conclusions on the conceptual model for the migration behaviour of trivalent radionuclides

The Am transport mechanism can be described by an immobilisation (quasi irreversible interaction of Am with the solid phase) followed by a constant release of Am which migrates associated with mobile OM. This immobilisation/constant leaching resembles solubility like mechanism and can be implemented as a constant concentration source, and transport of the immobilised Am through the Boom Clay occurs with a similar $D_{app}$ and $R$ as the mobile OM.

The immobilisation process of Am by the solid phase is currently unknown: is it due to the immobile OM or due to the minerals, and needs further attention.
2.7 Modelling and interpretation of migration experiments – WP7

Despite the valuable information obtained from the double labelled migration experiments with U, Pu and Se, it was currently not possible to derive migration parameters from them. However, the experiments performed with uranium confirm long-term experiments with single labelled $^{233}$U (still on-going at SCK-CEN) (Wang et al., 2000) and are therefore re-evaluated (Weetjens, 2003a – Annex 15).

Earlier modelling studies simulated organic matter migration experiments using a standard advection-diffusion model, enhanced to include a range of velocities representing different size fractions of OM (Dierckx et al., 2000a). In a new approach, the potential for characterising OM behaviour by assuming a distribution of retardation coefficients for OM, is investigate as a preliminary descriptive approach (Weetjens, 2003b – Annex 16). This has been further developed through the development of a model, POPCORN that accounts for the kinetics of OM attachment and detachment (representation of filtration) on the clay surface and of radionuclide complexation to and destabilisation from, OM (Hicks and Bennett, 2003 – Annex 17).

2.7.1 Modelling of the $^{233}$U migration in Boom Clay

The migration experiments performed with uranium seem to confirm long-term experiments with single labelled $^{233}$U started some 8 years ago at SCK-CEN. Because of the fact that the used radionuclide sources initially were not in equilibrium with the BC conditions, the evolution of the source was unsure and therefore the results of these migration experiments were always treated with suspicion (Wang et al., 2000). New experiments of different nature (batch, electromigration), however evidenced that applying a uranium source initially not in equilibrium with the BC conditions will not jeopardise the results since reduction/precipitation occurs fast (days) compared to the slow diffusion process (see also chapter 2.5).

Therefore, this long-term running experiment is re-evaluated to obtain uranium migration parameters (for more details see the technical note by Weetjens, 2003a). The uranium breakthrough curve was fitted by eye, with a numerical code PORFLOW (Runchal 1997) taking a zero-gradient boundary condition and a constant concentration source (solubility).

An optimal fit was obtained with following parameters (Figure 28):

- $S = 6 \times 10^{-10}$ mol dm$^{-3}$
- $D_p = 2 \times 10^{-10}$ m$^2$ s$^{-1}$; $D_{app} = D_p/R = 2.1 \times 10^{-12}$ m$^2$ s$^{-1}$
- $R = 95$

The solubility is in line with the calculated solubility of UO$_2$(c) and the $D_{app}$ is coherent with the parameter obtained from the electromigration experiment.

---

2.7.2 Modelling of the $^{14}$C-labelled organic matter migration in Boom Clay$^{22}$

Preliminary modelling of the $^{14}$C-OM breakthrough curves for the $^{241}$Am-$^{14}$C labelled NOM (described in chapter 2.6) was done with PORFLOW version 3.07 (Runchal, 1997), a software tool for multiphase fluid flow, heat and mass transport in fractured porous media. Transport is modelled based only on the classical advection-dispersion equation in one dimension and no reactive transport was taken into account. The transport parameters used to fit the curves are the porosity, the pore diffusion coefficient, the retardation factor (to account for sorption processes) and the fraction immobile OM.

In a new approach we made use of different classes of $^{14}$C-labelled OM by considering different retardation factors (for more details we refer to the technical note of Weetjens, 2003b). Generally, the breakthrough curves show only little retardation and large mass losses. The large mass loss is believed to be the result of ultrafiltration by the Boom Clay. This retardation mechanism has nothing to do with sorption, and is dependent on particle size. The pore diffusion coefficient was assumed to be $5 \times 10^{-11}$ m$^2$ s$^{-1}$, a value close to those reported by previously (Dierckx et al., 2000a; Put et al., 1992; 1998). The porosity was assumed to be 0.13 (taken from data set 2; Marivoet et al., 1999).

The fitting procedure was as follows:

- Breakthrough data were linearly interpolated to have a value for every time output of the model.
- Various runs with 100% of the inventory using different retardation coefficients.
- Fractions of these curves are added up to fit the experimental data, minimising the sum of squared errors by means of the solver tool in excel. Each time, combinations of 2 runs with different R coefficients were made, for which the sum of fractions was not necessarily equal to one. This corresponds to a convolution of three classes: two with different retardation coefficients and one representing the mass loss.

---

$^{22}$ Annex 16: Technical note: Modelling of the $^{241}$Am and $^{14}$C labelled organic matter in Boom Clay (03/EWe/N-23, SCK-CEN).
Five experiments with different Darcy velocities and plug lengths were conducted (see table 4). 'HiPAmCOM', 'MePAmCOM' and 'LowPAmCOM' are experiments subject to different pressures. There is however no clear relationship between the Darcy velocity and the imposed pressure, because the clay samples had different hydraulic conductivities.

Table 4: Overview of the different $^{241}$Am-$^{14}$C labelled OM percolation experiments

<table>
<thead>
<tr>
<th>Exp. code</th>
<th>Darcy velocity (mm/day)</th>
<th>plug length(^1) (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ShortAmCOM</td>
<td>0.147</td>
<td>12</td>
</tr>
<tr>
<td>LongAmCOM</td>
<td>0.171</td>
<td>60</td>
</tr>
<tr>
<td>HiPAmCOM</td>
<td>0.164</td>
<td>36</td>
</tr>
<tr>
<td>MePAmCOM</td>
<td>0.362</td>
<td>36</td>
</tr>
<tr>
<td>LowPAmCOM</td>
<td>0.278</td>
<td>36</td>
</tr>
</tbody>
</table>

\(^1\) The total length of all clay cores was 72 mm long, but the position of the Am-OM source with respect to the back end of the migration cell was differed and is referred to as the “plug length” (see figure 20 for a schematic set up).

Figure 29: Fittings of the $^{14}$C-labelled OM breakthrough curve of the LowPAmCOM migration experiment.

As an example, only the fitting of the LowPAmCOM experiment is described here (Figure 29). For all fits, the tailing is significantly underestimated. Generally, the breakthrough curves of the $^{14}$C-labelled OM showed little retardation. The best fits were obtained using fractions of the fits for retardation factor 2 and 4. Fits with combinations of $R=\times$ and $R=\times+2$ gave in general better results than combinations of $R=\times$ and $R=\times+1$. In most of the cases, the tailings were underestimated. It is clear that, the more classes of differently retarded OM are modelled, the better is the fit. The ultrafiltration process, responsible for the observed particle-size dependent retardation mechanism and mass loss, was indirectly modelled using a class of immobile particles. Still, the recovery of $^{14}$C was sufficient to derive meaningful parameters.

The relevance of the absolute value of the deduced transport parameters is of limited importance for Performance Assessments, due to the large uncertainty that is inherent to the relative low recoveries and the limitations of the model concept. But these fits give at least an indication of the order of magnitude of the transport characteristics of the mobile fraction and they are coherent with previous reported modelling attempts (Dierckx et al. 2000a).
2.7.3 Description of a radionuclide transport model including the interaction with NOM

A model, POPCORN (POPulations of COlloids on RadioNuclide transport), is developed which accounts for attachment and detachment of OM to the clay surfaces, the kinetics of radionuclide complexation to, and destabilisation from, OM. The model is described in more detail in the topical report by Hicks and Bennett (2003) given in annex 17.

The equations for transport of concentrations of dissolved radionuclides, \( c_s \), radionuclides attached to mobile OM, \( c_m \), and radionuclides attached to immobile OM, \( c_f \), in a porous medium are:

\[
R \frac{\partial c_s}{\partial t} = D_s \frac{\partial^2 c_s}{\partial x^2} - u_s \frac{\partial c_s}{\partial x} - R \lambda c_s - \kappa_m \left( K_m c_s - c_m \right) - \kappa_f \left( K_f c_s - c_f \right)
\]

\[
\frac{\partial c_m}{\partial t} = D_m \frac{\partial^2 c_m}{\partial x^2} - u_m \frac{\partial c_m}{\partial x} - \lambda c_m + \kappa_m \left( K_m c_s - c_m \right) - (s_m c_m - s_f c_f)
\]

\[
\frac{\partial c_f}{\partial t} = -\lambda c_f + \kappa_f \left( K_f c_s - c_f \right) + (s_m c_m - s_f c_f)
\]

The key features of the model, illustrated in Figure 30, are:

- Separate linear kinetic representations of radionuclide adsorption (complexation) to, and desorption (destabilisation) from, mobile and immobile OM. The terms \( \kappa_m (K_m c_s - c_m) \) and \( \kappa_f (K_f c_s - c_f) \) represent the rates of mass transfer between the dissolved phase and the sorbed phase on mobile and immobile OM, respectively.

- A component \( (s_m c_m - s_f c_f) \) representing the effective rate of transfer of radionuclides from mobile to immobile OM that results from the attachment to, and release from, the rock of radionuclide-bearing OM.

The TRANCOM II project has included two experiments aimed at studying the diffusion of OM in the Boom Clay (Back-to-back diffusion experiments by LU, described in chapter 2.5). Each experiment involved measuring the migration of \(^{14}\text{C}\)-labelled OM following its injection between two Boom Clay cores. The POPCORN model was used to evaluate these experiments. The best model fits were obtained by assuming diffusion and filtration of OM by attachment to the surface of the clay matrix. The key parameter values were an OM diffusion coefficient of \( 3 \times 10^{-11} \text{ m}^2 \text{s}^{-1} \) with \( s_m = 1 \times 10^{-6} \text{ s}^{-1} \) (Figure 31).

The POPCORN code was also used to analyse the \(^{14}\text{C}-^{241}\text{Am}\)-OM percolation migration experiments (experiments by SCK-CEN, described in chapter 2.6). These experiments aimed to investigate the kinetics of exchange of Am between mobile and immobile phases by using clay plugs of different lengths with different Darcy velocities.

---

23 Annex 17: Topical Report on: Modelling the effects of organic matter on radionuclide transport (9918-2 v. 1.0, GSL Ltd.).
Figure 30: Processes represented in the POPCORN radionuclide transport model.

Reasonable matches to the $^{14}$C-OM migration data were achieved for each of the experiments considered by assuming attachment of $^{14}$C-OM to the clay, followed by its gradual detachment. In each case, an OM dispersion coefficient of $3 \times 10^{-11}$ m$^2$s$^{-1}$ and a diffusion accessible porosity, $\phi$, of between 0.3 and 0.35 gave good results with different values of the terms $s_m$ and $s_f$. The results of the LowPAmCOM (low pressure) migration experiment and modelling are shown in Figure 31; values of $s_m = 2.4 \times 10^{-7}$ s$^{-1}$ and $s_f = 2.4 \times 10^{-8}$ s$^{-1}$ achieved the best results (case LowPC_4).

Subsequently, the behaviour of the $^{241}$Am-OM complex was studied. Less than 0.1% of the injected $^{241}$Am activity was recovered during the course of each experiment, indicating that the $^{241}$Am-OM complex is highly susceptible to dissociation in the clay cores. The modelling assumed that the released $^{241}$Am was free to sorb to other mobile OM or to the greater proportion of immobile OM and mineral surfaces in the clay. The stability properties of the $^{241}$Am-OM were characterised by the kinetic constants, $k_m$ and $k_f$. Good matches to the $^{241}$Am-OM migration data were achieved for each of the experiments. An $^{241}$Am-OM dispersion coefficient of $3 \times 10^{-12}$ m$^2$s$^{-1}$ and a porosity of 0.35 gave the best results, with different values of the terms $s_m$ and $s_f$.

Figure 31: Results of $^{14}$C-OM diffusion experiments and modelling studies: (a) $D_m = 3 \times 10^{-11}$ m$^2$s$^{-1}$, $s_m = 0$ s$^{-1}$; (b) with $D_m = 3 \times 10^{-11}$ m$^2$s$^{-1}$ and $s_m = 1 \times 10^{-6}$ s$^{-1}$.
Figure 32: Migration experiment LowPAmCOM (a) $^{14}$C concentrations and (b) percentage recovery, with the following simulations: LowPC_1 ($D_m = 3 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$, $\phi = 0.3$, $s_m = 0 \text{ s}^{-1}$, $s_f = 0 \text{ s}^{-1}$); LowPC_2 ($D_m = 3 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$, $\phi = 0.3$, $s_m = 3.5 \times 10^{-7} \text{ s}^{-1}$, $s_f = 0 \text{ s}^{-1}$); LowPC_3 ($D_m = 3 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$, $\phi = 0.3$, $s_m = 3.5 \times 10^{-7} \text{ s}^{-1}$, $s_f = 3.5 \times 10^{-8} \text{ s}^{-1}$); LowPC_4 ($D_m = 3 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$, $\phi = 0.35$, $s_m = 2.4 \times 10^{-7} \text{ s}^{-1}$, $s_f = 2.4 \times 10^{-8} \text{ s}^{-1}$).

Figure 33: Migration experiment LowPAmCOM (a) $^{241}$Am concentrations and (b) percentage recovery, with the following simulations: LowPAm_1 ($D_m = 3 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$, $s_m = 1.7 \times 10^{-7} \text{ s}^{-1}$, $s_f = 1.7 \times 10^{-8} \text{ s}^{-1}$, $k_m = 3.6 \times 10^{-6} \text{ s}^{-1}$); LowPAm_2 ($D_m = 3 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$, $s_m = 3.5 \times 10^{-6} \text{ s}^{-1}$, $s_f = 3.5 \times 10^{-7} \text{ s}^{-1}$, $k_m = 0.65 \times 10^{-6} \text{ s}^{-1}$); LowPAm_3 ($D_m = 3 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$, $s_m = 2.45 \times 10^{-6} \text{ s}^{-1}$, $s_f = 2.45 \times 10^{-7} \text{ s}^{-1}$, $k_m = 0.45 \times 10^{-6} \text{ s}^{-1}$).

Results of the LowPAmCOM migration experiment and model analyses are shown in Figure 33; a reasonable match was achieved with $k_m = k_f = 0.45 \times 10^{-6} \text{ s}^{-1}$, $s_m = 2.45 \times 10^{-6} \text{ s}^{-1}$, and $s_f = 2.45 \times 10^{-7} \text{ s}^{-1}$ (Case LowPAm_3). These findings suggest that a small sub-population of the original $^{241}$Am-OM is the most stable, and that this sub-population has specific transport characteristics, including low dispersivity and a greater potential for filtering. Such characteristics may be representative of larger, more stable, but less mobile $^{241}$Am-OM complexes.
General conclusions regarding $^{14}$C-OM and $^{241}$Am-OM transport were drawn from the analysis of the modelling attempts:

- The key processes governing OM transport and $^{241}$Am-OM stability appear to be the rates of attachment and detachment of OM on the clay surfaces and the rate of complexation destabilisation, indicating that it is important to evaluate the kinetics of the system.

- Best results are obtained with a rate of OM attachment to the rock that is about an order of magnitude less than the rate of detachment.

- There is an apparent correlation between the inverse of the rate of OM attachment to the rock, the inverse of the kinetic constant for the stability of mobile $^{241}$Am-OM, and the peak advection-driven OM breakthrough time (see Figure 34).

The relationships derived offer a potential means of extrapolating parameter values for application of the model to larger-scale problems. The POPCORN model has proved tractable, with run times of a few seconds for the studies described in this report, and would be suitable for use in repository performance assessments alongside standard advection-dispersion models.

Figure 34: Relationship between the core length divided by the fluid velocity and the terms $1/s_m$ and $1/k_m$ for the experiments analysed. Least squares fit trend lines and $R^2$ values are shown.
2.8 Methodologies developed to identify the source of mobile Boom Clay Organic Matter – WP4

The Boom Clay formation contains relatively large levels of organic matter (ca. 2-5 %). Previous measurements based on piezometer waters indicated that only a small fraction (0.01%) of this total OM is present in the interstitial solution. However, the rules governing the partitioning of Boom Clay OM into a mobile and non-mobile fraction are unknown. This work package is only regarded as a first step in understanding the source of mobile organic matter. The objective is therefore limited to the development of methodologies to investigate the different possible pathways of mobile organic matter formation. These methodologies are described in detail in a topical report by Maes et al. 2003 given in annex 1824.

2.8.1 Leaching tests with synthetic clay water

Leaching tests were performed on Boom Clay samples by equilibrating the solid clay phase with organic matter-free Synthetic Boom Clay water (pH 8.3). One would expect that the Boom Clay organic matter pool would play as a reservoir to replenish the organic matter concentration in solution. However the present results as well as observations from the TRANCOM-Clay project (Dierckx et al., 2000a) all indicate that the concentration of organic matter in the first extract at different solid-to-liquid ratios corresponds to a simple dilution of a rather constant amount of a soluble organic matter pool. Further dilution of this pool due to increasing extraction steps with SBCW (without organic matter) leads to decreasing amounts of organic matter in solution, although there is some replenishment from the solid phase. Finally a more or less constant organic matter release from the solid phase is observed.

Based on the amount of organic matter leached from the solid Boom Clay phase with OM-free SBCW, distribution values of organic matter between the solid and the liquid phase (RdOC) can be calculated. The organic carbon concentration in solution ([OC]) was calculated from Optical Density (OD) (UV-VIS absorbance at 280 nm) measurements combined with the relationship from Henrion et al. (1985): [OC] = 23.2×OD. The total amount of organic carbon in Boom Clay was taken at 2.2% (Henrion et al., 1985). The distribution coefficient of organic matter between the solid and the liquid Boom Clay phase (RdOC) was seen to increase inversely proportional to the decreasing amount of Boom Clay used in the suspensions.

Leaching tests of solid Boom Clay phase with OM-free SBCW were compared to experiments which studied the interaction between mobile Boom Clay OM and the immobile fraction by allowing to equilibrate a spike of (mobile) 14C-OM (14C-labelled TROM batch) with Boom Clay suspensions of different solid-to-liquid ratio. It was observed that the amount of 14C remaining in the supernatant decreased linearly with increasing Boom Clay solid-to-liquid ratio. The same observation was made in the TRANCOM-Clay programme (Dierckx et al., 2000a). The distribution coefficient of 14C-organic matter between the solid and the liquid Boom Clay phase (RdC-14) demonstrates a similar trend as observed for the total organic matter pool (RdOC). Otherwise stated, RdC-14 was seen to increase inversely proportional to the decreasing amount of Boom Clay used in the suspensions. This points to the fact that the 14C spike used, behaves in the same way as the “bulk” dissolved organic matter. The observed value of RdC-14, however, was about 200 times smaller than RdOC, in line with the observations from the TRANCOM-Clay programme (Dierckx et al., 2000a). This result indicates that part of the organic matter pool is not involved in the 14C distribution. This observation is in line with the characterisations performed on immobile organic matter, which identified a large part of this immobile fraction as kerogen organic matter, containing no functional groups. The real

sorption mechanism of the dissolved organic matter (and $^{14}$C-OM spike) (hydrophobic sorption and/or ligand exchange) is unknown.

### 2.8.2 Exploration of methodologies for the characterisation of porewater OM

The characterisation of the porewater OM is a very complicated task which goes beyond the current project but under the TRANCOM-II project different methodologies are explored which can be used for characterisation. The work comprises several parts: discrete sampling of OM, methods for detailed chemical analysis of the mobile OM and methods for a more detailed analysis of the kerogen fraction. An overview of the current knowledge of Boom Clay organic matter can be found in Van Geet et al. (2003).

#### 2.8.2.1 Mobile OM

The sampling of mobile organic matter from Boom Clay can be performed in three ways. Firstly, pore water can be extracted in-situ from the clay by means of piezometers. Secondly, Boom Clay samples can be squeezed to extract the water content. Finally, OM can be leached from Boom Clay samples at different solid/liquid ratios. Different amounts of TOC are measured for the three techniques. Piezometer water is thought to be the most representative and gives TOC values between 40 and 250 mg C dm$^{-3}$ (De Craen et al., 2002).

For a detailed characterisation of the dissolved organic matter present in Boom Clay pore water, a non-metallic piezometer (MORPHEUS, May 2001) was installed in the HADES URL at SCK•CEN. The pore water was frequently sampled to follow up the evolution of the TOC content. The measurements have shown that the several filters have different amounts of TOC. It was also found that the TOC content is seriously varying in time. A general decrease in TOC is noticed during about 2 years after installation of the piezometer. From then a more or less stable TOC content is registered. Apart from the TOC measurements, UV-VIS absorption tests at 280 nm have also been performed in time. Surprisingly, these values are constant in time. Consequently, TOC and UV measurements cannot be correlated when originating from different horizons of the Boom Clay. Probably, some non-absorbing molecules are present within the pore water and especially these are fluctuating in time. On the contrary, such a correlation between TOC and UV was found when diluting leached organic matter from one sample of clay (Maes et al., 2002).

Next to the pore waters, the sediments along this piezometer have been characterised as well. Total TOC content within the sediment varies between 0.85 and 4.13%. However, the TOC content of the pore water is not correlated with the TOC content of the neighbouring sediment.

Finally, a more detailed characterisation of the dissolved organic matter is ongoing. First, it was tried to isolate the OM by liquid – liquid extraction with Dichloromethane. The extracted fractions were then analysed by means of Gas Chromatography – Mass Spectrometry (GC-MS). However, some plasticizer was present and obscured most of the GC profile. This plasticizer is probably originating from the non-metallic piezometer (constructed in PVC). New tests are now going on to extract the OM by means of freeze drying and to use Pyrolysis GC-MS for characterisation. As this technique is not focussing on the trace molecules present in the dissolved organic matter, it is hoped that the plasticizer will not obscure the whole profile, so that a general characterisation can be performed.
2.8.2.2 **Immobile OM**

The kerogen isolated from a sample, considered as representative of the Boom Clay, was examined via a combination of spectroscopic (FTIR, solid state $^{13}$C NMR) and pyrolytic (off-line pyrolyses with GC/MS analysis of the effluents) methods. Examination of the whole rock and of the kerogen by scanning and transmission electron microscopy provided additional information on the source organisms and organic matter preservation pathway in the Boom Clay.

It was found that the organic matter of type II exhibits a rather high aliphaticity and its chemical structure is chiefly based on a macromolecular network of long, normal alkyl chains probably cross-linked by ether bridges located at various positions on the chains. However, a substantial amount of aromatic structures also occurs in the kerogen along with minor branched hydrocarbon chains. Some alcohol and acid moieties, slightly degraded, when compared to biological compounds, were also detected in the kerogen.

This chemical structure points to a major contribution of phytoplanktonic material with a low input of terrestrial and bacterial components. Microscopic observations reveal that the bulk of the organic matter is nanoscopically amorphous (AOM) and does not exhibit any regular organisation with respect to clay minerals. Taken together, these observations and the aforementioned chemical structure, point to a major role for the degradation-recondensation mechanism in the formation of this kerogen, along with a substantial contribution of oxidative incorporation of lipids.

In contrast, no specific role for clay minerals in organic matter preservation could be evidenced. The selective preservation and the natural sulphurisation pathways were, at most, minor preservation processes.

Based on the behaviour of the Boom Clay kerogen upon analytical pyrolysis, a relatively high in situ production of liquid and gaseous products can be expected on heating which would result from long-term disposal of high level radionuclide waste. In addition to hydrocarbons, a number of functionalised compounds would be produced including acids and polar compounds. Such production could thus be associated with modification in the physico-chemical parameters of the surrounding clay and/or complexation of radionuclides.

2.8.3 **Conclusions on the methodologies**

Methodologies were developed to identify the source of mobile NOM. The Boom Clay kerogen makes up to 5% of the total sediment. Rock Eval and pyrolysis GC/MS analysis have shown that the kerogen is a mixture of terrestrial and marine OM. Some smaller molecules (e.g. polar oxygen-containing products) are entrapped into the 3D macromolecular network of the kerogen and are prone to release upon applying low thermal stress. The Boom Clay porewater contains around 100 to 200 mgC/L, but might be up to 400 mgC/L. Up to now, the DOC can not be linked to the neighbouring TOC as no correlation exists in their concentrations. Leached organic matter contains a higher amount of total organic carbon than the Boom Clay porewater and is predominantly composed of humic acids. The amount of leached organic matter is primarily controlled by the amount of Boom Clay solid phase used. Solving the question on the source of mobile NOM was however beyond the scope of the project, but the methodologies are proven to be useful and will be further explored.
2.9 Conceptualisation of migration processes for PA and PA evaluation – WP9

All results obtained during the project are evaluated and translated in data and conceptual models useful for PA to describe the transport of radionuclides in a reducing, NOM rich clay environment.

2.9.1 Summary of the results: parameters and conceptual models

Tables 5 and 6 give an overview of the obtained results from predictions, batch and migration experiments on solubility and migration parameters.

Following conclusions concerning the transport behaviour of the studied radionuclides in the OM rich Boom Clay could be made:

- Only for Pu and Am an increase in solubility was observed due to interaction with NOM. Colloids were observed in many cases and are very prominent in case of Uranium.
- Despite the possible enhanced solubility due to OM complexation and the increased radionuclide concentrations in solution due to colloid formation, no increased radionuclide concentrations after migration through clay cores were observed.
- The measured constant concentrations are of the same order of magnitude as the predicted solubility values or lower.
- In all cases, an immobilisation process governed the transport of the radionuclides, with one important exception: \( \text{SeO}_4^{2-} \) which is not immobilised and moves unretarded.
- Only for Am we observed undoubtedly that the transport of the mobile Am fraction was linked with mobile OM.

These observations were translated into conceptual models:

- **Selenium**
  The selenate transport mechanism can be described as a diffusion process of an unretarded anionic species.
  The selenite transport mechanism can be described as an immobilisation, by a kinetic controlled sorption-reduction followed by a solubility limited release of Se which diffuses unretarded and independent of NOM through the BC.
  The selenide transport mechanism can be described as an immobilisation/solubility limited release of Se which diffuses unretarded and independent through the BC.

- **Uranium**
  The uranium transport mechanism can be described as an immobilisation, precipitation of an U(IV) solid phase, followed by a solubility limited release of U for which the diffusion is independent of NOM but retarded due to sorption onto the BC solid phase.

- **Americium** (as representative of trivalent actinides and lanthanides)
  The Am transport mechanism can be described by an immobilisation (quasi irreversible interaction of Am with the solid phase) followed by a constant release of Am which migrates associated with mobile OM. This immobilisation/constant leaching resembles a solubility like mechanism and can be implemented as a constant concentration source, and transport of the mobilised Am through the Boom Clay occurs with a similar \( D_{app} \) and R as the mobile OM.

---

25 Annex 20: Note on: Treatment of colloids in Performance Assessment (9918-3, GSL Ltd.).
## Plutonium

The Pu transport mechanism can be described by an immobilisation (solubility or quasi irreversible interaction with the solid phase) followed by a constant release of Pu. This immobilisation/constant release resembles a solubility like mechanism and can be implemented as a constant concentration source. Due to the observed association with NOM, we consider that the mobilised Pu migrates through the Boom Clay with similar $D_{\text{app}}$ and $R$ as for the mobile OM.

### Table 5: Comparison of the predicted and experimental observed solubility’s for the Boom Clay conditions ($E_h=-275$ mV, $pH=8.2$, $p\text{CO}_2=10^{-2.4}$ atm).

<table>
<thead>
<tr>
<th></th>
<th>Calculated S at start of the project [mol dm$^{-3}$]</th>
<th>Calculated S at end of project (NEA-TDB03) [mol dm$^{-3}$]</th>
<th>Measured S (in presence of NOM) [mol dm$^{-3}$]</th>
<th>Measured C in migration experiments [mol dm$^{-3}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>$\text{UO}_2$ (c)= $2.4 \times 10^{-10}$</td>
<td>$\text{UO}_2$ (c)= $4 \times 10^{-7}$</td>
<td>filtered at 30kD: $\text{UO}_2$ (am)$\sim 10^{-8}$</td>
<td>$\sim 10^{-8}$ (short term)</td>
</tr>
<tr>
<td></td>
<td>$\text{PuO}_2$ (c)= $10^{-12}$-$10^{-17}$</td>
<td>$\text{PuO}_2$ (am)$\sim 10^{-11}$-$10^{-12}$</td>
<td>$3 \times 10^{-7}$</td>
<td>$\sim 10^{-13}$ (constant conc.)</td>
</tr>
<tr>
<td>Se</td>
<td>$\text{Se}$ (c)=$3.8 \times 10^{-7}$</td>
<td>$\text{Se}$ (am)$\sim 10^{-9}$</td>
<td>$\sim 10^{-8}$ (background conc. In RBCW)</td>
<td>$\sim 10^{-13}$ (constant conc.)</td>
</tr>
<tr>
<td>Am</td>
<td>$\text{Am}$</td>
<td>$\text{Am}$</td>
<td>$\sim 10^{-13}$</td>
<td>$\sim 10^{-13}$ (constant conc.)</td>
</tr>
</tbody>
</table>

$^a$ The high solubility is due to the dominance of uranylcarbonate species in equilibrium with $\text{UO}_2$ at mildly reducing conditions while the low solubility reflects $\text{U(OH)}_4$ in equilibrium with $\text{UO}_2$ at strong reducing conditions.

$^b$ The calculated values for Se are obtained using the data from the HATCHES database (because NEA database has only limited data).

### Table 6: Summary of the derived migration parameters (note that $D_{\text{app}}$=$D_p/R$)

<table>
<thead>
<tr>
<th>Migration parameters obtained from EM tests</th>
<th>Fitted parameters from percolation tests</th>
<th>Observations for exp. where no parameters were obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$\text{Se}^-$</td>
<td>---</td>
<td>background concentration of Se in RBCW, $[\text{Se}]\sim 2 \times 10^{-8}$ mol dm$^{-3}$</td>
</tr>
<tr>
<td>Se$\text{O}_4^{2-}$</td>
<td>$D_{\text{app}}=2.6 \times 10^{-11}$ m$^2$s$^{-1}$ $R=1$</td>
<td>---</td>
</tr>
<tr>
<td>$\text{U(OH)}_4$</td>
<td>$D_{\text{app}}=6-12 \times 10^{-12}$ m$^2$s$^{-1}$ $R&gt;10$</td>
<td>$D_p=2 \times 10^{-10}$ m$^2$s$^{-1}$ $R=95$ $n=0.3$ $S=6 \times 10^{-10}$ mol dm$^{-3}$</td>
</tr>
<tr>
<td>NOM</td>
<td>---</td>
<td>$D_p=5 \times 10^{-11}$ m$^2$s$^{-1}$ $R=1-5$ $n=0.13$</td>
</tr>
<tr>
<td>Am</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Pu</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>
2.9.2 PA parameter selection and evaluation

The transport mechanism for the studied radionuclides (except for SeO₄²⁻) is dominated by an immobilisation process with a constant release of radionuclides. In case of U and Se the constant release is controlled by a solubility limit of the precipitated phases and the transport is independent of NOM. Colloids were in most cases evidenced but found to be either unstable in or filtered by the Boom Clay. For Am – as representative of trivalent actinides/lanthanides - the constant release is due to a strong interaction with the solid phase (immobile OM?) and not determined by a solubility limit. The transport is correlated with NOM. For Pu the underlying processes are not understood but resemble that of Am.

PA calculations can therefore be performed with a limited set of parameters: concentration limit (or solubility limit), Dₚore, R and diffusion accessible porosity. The values are taken from experimental observations and interpretations and are summarised in Table 7 together with a motivation.

Table 7: Selected parameters for PA

<table>
<thead>
<tr>
<th>Solubility or concentration limit</th>
<th>Dₚ (pore diffusion coefficient)</th>
<th>R (Retardation)</th>
<th>n (diffusion accessible porosity)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility limit [mol dm⁻³]</td>
<td>Dₚ [m²s⁻¹]</td>
<td>R [-]</td>
<td>n [-]</td>
</tr>
<tr>
<td>HSe⁻</td>
<td>2 x 10⁻⁸</td>
<td>2 x 10⁻¹⁰</td>
<td>1</td>
</tr>
<tr>
<td>SeO₄²⁻</td>
<td>----</td>
<td>5 x 10⁻¹¹</td>
<td>1</td>
</tr>
<tr>
<td>U</td>
<td>6 x 10⁻¹⁰</td>
<td>2 x 10⁻¹⁰</td>
<td>95</td>
</tr>
<tr>
<td>Pu</td>
<td>1 x 10⁻¹³</td>
<td>5 x 10⁻¹¹</td>
<td>1</td>
</tr>
<tr>
<td>Am</td>
<td>1 x 10⁻¹³</td>
<td>5 x 10⁻¹¹</td>
<td>1</td>
</tr>
<tr>
<td>OM</td>
<td>----</td>
<td>5 x 10⁻¹¹</td>
<td>1</td>
</tr>
</tbody>
</table>

- **Selenium**
  Migration data with selenate were derived from migration experiments and this species is not solubility limited. No migration data for selenide were derived, and since it considers a monovalent anion, the migration parameters (Dₚ, n, R) for monovalent anions were taken (e.g. iodide). The natural background concentration of Se in the clay water was taken as concentration limit.

- **Uranium**
  Migration parameters were derived from different types of migration experiments and give consistent data. The predicted solubility of 5 x 10⁻⁷ mol dm⁻³ (based on the latest NEA data) is attributed to U(VI) in equilibrium with UO₂, but exp. evidence show that the species in solution in the BC pore water is U(IV). The selected solubility or concentration limit for the PA calculations is the one obtained from fitting concentration limit in the long-term migration experiment.

- **Americium (as analogue for trivalent actinides/lanthanides)**
  Due to the observed interaction with OM, the migration parameters for Am are set equal to those of the NOM. Since Am solubility is clearly not useable to describe the immobilisation, the constant concentrations measured in migration experiments are considered as the most representative measurements of a concentration limit.
o Plutonium

No migration parameters for Pu could be derived. Due to the observed similarities with Am, and geochemical modelling predicts possible formation of Pu(III), the same migration parameters were adopted. Due to the uncertainties on the speciation (solubility, complexation, …), the constant concentration measured in the long-term migration experiment is considered as the most representative measurement of a concentration limit.

The influence of the new parameter values are evaluated for U and Se as PA modelling cases in the BC (for more details we refer to the technical note of Weetjens, 2003c – Annex 19). The fluxes into the Neogene aquifer for the old and new parameter dataset will be evaluated with special attention to selenate as possible species and the presence of inactive Se in the waste. As waste type, spent fuel with a high burn up (UOX-55) is chosen. A comprehensive PA study for all types of spent fuel is recently described in the SPA+ report (Sillen and Marivoet, 2002).

Modelling of the radionuclide transport through the Boom Clay host rock is done with PORFLOW version 3.07 (Runchal, 1997). For details about the modelling assumptions, such as initial and boundary conditions, the model geometry and the radionuclide source term, the reader is referred to Sillen and Marivoet (2002).

2.9.2.1 PA calculations for $^{79}\text{Se}$

An overview of the different migration datasets used in this PA case study for selenium is given in Table 8. The SPA+ study considered migration parameter dataset 2 (Marivoet et al., 1999). An evaluation was made for $^{79}\text{Se}$ in a non-solubility-limited form and $^{79}\text{Se}$ as precipitate, respectively #1 and #2 in Table 8. In TRANCOM-II, only the value for the solubility limit was updated and 2 values are used for the calculation: $3 \times 10^{-9} \text{ mol dm}^{-3}$ (#3) (=exp. determined solubility in batch) and $2 \times 10^{-8} \text{ mol dm}^{-3}$ (#4) (=measured Se concentration in RBCW and considered as the new reference solubility limit for Se, Table 7).

However, if the considerable amount of stable Se in the waste is taken into account, the effective solubility limit will be approximately five times lower (#5 in Table 8).

In previous datasets, $^{79}\text{Se}$ is assumed to migrate as HSe$^-$ (selenide). In a last case (#6), $^{79}\text{Se}$ is assumed to migrate as selenate $\text{SeO}_4^{2-}$, which is not solubility limited, but shows a lower pore diffusion coefficient.

Table 8: Overview of the different migration parameter values for $^{79}\text{Se}$, used in the PA modelling case study. The values for datasets 2 and 4 (in bold face) are reference values. The other datasets are variants.

<table>
<thead>
<tr>
<th>isotope/speciation</th>
<th>parameter dataset</th>
<th>$C_i$ (mol dm$^{-3}$)</th>
<th>$\eta$ (-)</th>
<th>$D_p$ (m$^2$s$^{-1}$)</th>
<th>R (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1 $^{79}\text{Se undef}i nite$</td>
<td>set 2 unlimited (1999)</td>
<td>-</td>
<td>0.13</td>
<td>$2 \times 10^{-10}$</td>
<td>1</td>
</tr>
<tr>
<td>#2 $^{79}\text{Se as selenide}$</td>
<td>set 2 (1999)</td>
<td>$5.5 \times 10^{-8}$</td>
<td>0.13</td>
<td>$2 \times 10^{-10}$</td>
<td>1</td>
</tr>
<tr>
<td>#3 $^{79}\text{Se as selenide}$</td>
<td>TRANCOM2</td>
<td>$3 \times 10^{-7}$</td>
<td>0.13</td>
<td>$2 \times 10^{-10}$</td>
<td>1</td>
</tr>
<tr>
<td>#4 $^{79}\text{Se as selenide}$</td>
<td>TRANCOM2</td>
<td>$2 \times 10^{-8}$</td>
<td>0.13</td>
<td>$2 \times 10^{-10}$</td>
<td>1</td>
</tr>
<tr>
<td>#5 $^{79}\text{Se as selenide}$</td>
<td>TRANCOM2</td>
<td>$4 \times 10^{-7}$</td>
<td>0.13</td>
<td>$2 \times 10^{-10}$</td>
<td>1</td>
</tr>
<tr>
<td>#6 $^{79}\text{Se as selenate}$</td>
<td>TRANCOM2</td>
<td>-</td>
<td>0.13</td>
<td>$5 \times 10^{-11}$</td>
<td>1</td>
</tr>
</tbody>
</table>

*This is the “effective solubility” accounting for isotopic dilution of $^{79}\text{Se}$ by inactive Se in the waste. Note that in all numerical simulations a half-life of 1.1 $\times 10^6$ years is used for $^{79}\text{Se}$.

26 Annex 19: Technical note: PA case study for new parameters for Se and U (03/EWe/N21, SCK-CEN)
The resulting nuclide fluxes out of the Boom Clay into the Neogene aquifer for these cases are shown in Figure 35.

The effect of the imposed solubility limit is clearly visible in Figure 35. The solubility limited and unlimited version of the formerly applied dataset 2 result in the highest peak fluxes and the largest cumulative fluxes. The TRANCOM2 updated parameter set and its variants all result in smaller peak fluxes. Furthermore, although selenate is not solubility limited, its peak flux is still about a factor 3 smaller than that of dataset 2, because of the lower pore diffusion coefficient.

It is advisable to further examine the origin of the Se in the clay water to verify if it is caused by a solubility limited mineral source. If not, the lower experimentally determined solubility limit can be adopted. Accounting for the inactive selenium in the waste, the effective solubility will further decrease to 6 \(10^{-10}\) mol dm\(^{-3}\) which will decrease the peak flux by one order of magnitude. Furthermore it is advisable to acquire information on the possible speciation of selenium in the source term.

Figure 35: \(^{79}\)Se fluxes to the upper aquifer for the parameter datasets summarised in Table 8.
2.9.2.2 PA calculations for the 238U decay chain

Uranium is present in large quantities in spent fuel and in this case study we selected the decay chain of the 238U isotope as the most relevant one for a PA evaluation. The full decay chain is reduced to four long-lived members (238U → 234U → 230Th → 226Ra) to be incorporated in the PA model, the masses of the short-lived chain members being accounted for. Because the half-life of the 238U is at least 4 orders of magnitude larger than that of its daughters, and the transport time of U and its daughters is longer than their half lives, the fluxes out of the near field are in secular equilibrium. Therefore, additional sources for the daughters are not accounted for in the model, and the solubility limit is only applied on the parent uranium isotope. For more details about this source term, the reader is referred to the SPA+ report (Sillen et al., 2002). The parameter datasets considered here are represented in Table 9.

Table 9: Overview of the different migration parameter values for 238U, used in the PA modelling case study.

<table>
<thead>
<tr>
<th>isotope</th>
<th>parameter dataset</th>
<th>Ci (mol dm⁻³)</th>
<th>η (-)</th>
<th>D_p (m² s⁻¹)</th>
<th>R (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1 238U</td>
<td>set 2’ unlimited (1999)</td>
<td>-</td>
<td>0.3</td>
<td>2 10⁻¹⁰</td>
<td>40</td>
</tr>
<tr>
<td>#2 238U</td>
<td>set 2’ (1999)</td>
<td>1 10⁻⁹</td>
<td>0.3</td>
<td>2 10⁻¹⁰</td>
<td>40</td>
</tr>
<tr>
<td>#3 238U</td>
<td>TRANCOM2 unlimited</td>
<td>-</td>
<td>0.3</td>
<td>2 10⁻¹⁰</td>
<td>95</td>
</tr>
<tr>
<td>#4 238U</td>
<td>TRANCOM2 unlimited</td>
<td>6 10⁻¹⁰</td>
<td>0.3</td>
<td>2 10⁻¹⁰</td>
<td>95</td>
</tr>
</tbody>
</table>

The retardation factors used for the daughters Th and Ra are respectively 500 and 50 (Sillen et al., 2002) and kept constant in the calculations for the different datasets. The retardation factor for the 234U daughter nuclide is adjusted to the one used for 238U.

The resulting fluxes to the Neogene aquifer for the old parameter values are shown in Figure 36 (top). It is clear that imposing a solubility limit lowers the fluxes by about five orders of magnitude for all chain members. The same plot for the new migration parameter values is given in Figure 36 (bottom). Especially the influence of the higher retardation is clearly visible: the peak fluxes now occur later.

To clearly see the influence of the different parameter values for every chain member, we grouped the fluxes for the four cases in one plot for every nuclide (see figure 37). Although the higher retardation factor and lower solubility limit are both in favour of a better confinement of the nuclides, the 230Th peak flux for the new dataset is higher than the one for dataset 2’. This seems somewhat contradictory, but it is in fact an example of the mathematical consistency of the model. In the case of R=40, when 40 nuclides reach point x, 39 attach to the sorption complex and 1 stays in solution. However, in the case of R=95, 94 are sorbed and 1 stays in solution. The production of daughter nuclides from the sorbed complex is thus somewhat larger in the latter case. The ratio between the (solubility limited) peak fluxes for 230Th is about 1.4 which is exactly the ratio between new and old parameter values:

\[
\frac{R_4 \cdot C_{S_4}}{R_2 \cdot C_{S_2}} = \frac{95 \cdot 6 \times 10^{-10}}{40 \cdot 1 \times 10^{-9}} = 1.4
\]

Furthermore, as expected, the time delay between 'new' and 'old' fluxes is exactly equal to the ratio of the retardation coefficients.

In general, the fluxes to the Neogene aquifer are somewhat smaller compared to the old values. Only the peak fluxes for 230Th and 226Ra are slightly higher.

59
Figure 36: $\text{^{238}U}$, $\text{^{234}U}$, $\text{^{230}Th}$ and $\text{^{226}Ra}$ fluxes to the upper aquifer for the dataset 2’ (top) and the dataset TRANCOM2 (bottom), with and without a solubility limit applied for $\text{^{238}U}$. 
Figure 37: Fluxes for the $^{238}$U chain into the Neogene aquifer according to the four considered cases.
3 Assessment of the results and conclusions

The TRANCOM II project addresses the migration behaviour of U, Se, Pu, Am, in a reducing clay environment (Boom Clay as case study), with special emphasis on the role of the Natural Organic Matter (NOM). The main scientific objectives were:

- to assess the effect of NOM on the radionuclide solubility and sorption due to the formation of complexes and/or colloids,
- to produce an internal coherent database for the interaction of radionuclides with NOM and clay under reducing conditions,
- to develop and/or demonstrate a conceptual model for the description of the migration of radionuclides in a reducing, NOM rich clay environment that can be implemented in performance assessment models.

The conclusions and assessment of the results are written with respect to the above objectives.

Uranium

Conditional complexation constants for U(VI) with NOM under different pCO₂ conditions were derived and pointed in the direction of mixed complexes. But under the BC conditions the carbonate complexes are dominant. However, U(VI) is found to be unstable under the Boom Clay conditions, it reduces and precipitates to an U(IV) oxide phase. A solubility of UO₂ (am) of ≈10⁻⁸ mol dm⁻³ is determined. The solubility was not enhanced by the NOM: no complexation with NOM was observed only colloid formation (organic and inorganic) increasing the U concentration in solution (> 30 000 MWCO) by 3 orders of magnitude. Distribution coefficients for U(IV) onto different pure minerals were measured showing considerable sorption onto some mineral phases present in the Boom Clay. When normalising the distribution coefficients to the abundance of the different minerals in the Boom Clay, the main mineral sorption sinks for U(IV) will be Illite and Illite/smectite.

Migration experiments reveal that U migrates independent from the NOM and there was no evidence that the U-colloids enhanced the transport. Migration parameters were derived and the uranium transport mechanism can be described as an immobilisation, precipitation of an U(IV) solid phase, followed by a solubility limited release of U for which the diffusion is retarded due to sorption onto the BC solid phase.

Selenium

As oxidised selenium species might be present in the waste forms, the behaviour of selenate and selenite were studied besides the reduced forms. SeO₄²⁻, although thermodynamically not stable under the Boom Clay conditions, remains fairly stable (no reduction was observed in batch experiments for periods up to several months), and migrates unretarded through the Boom Clay. No sorption and/or reduction by pyrite or BC was observed. Migration experiments show that SeO₄²⁻ moves unretarded through the Boom Clay and migration parameters were derived. The migration process can be described by diffusion, unaffected by reduction or retardation.

SeO₃²⁻, shows a more complex behaviour which is described as a kinetically controlled sorption-reduction process ending in a constant Se concentration of ≈ 3 10⁻⁹ mol dm⁻³ similar to the concentration in equilibrium with a prepared Se⁰ phase. Part of the Se in solution is found to be associated with OM as colloids but with no pronounced effect on the Se⁰ solubility. The observed “slow” sorption-reduction kinetics are still fast compared to geological time-scales used in PA, only the mobility of the solubility limited phase is
regarded. The migration process is governed by an immobilisation with a solubility limited release of Se (not influenced by NOM) and presumed unretarded.

Synthetically prepared reduced Se solid phases showed solubility’s varying over 3 orders of magnitude (10^{-10}-10^{-7} mol dm^{-3}) but no effect of NOM on the solubility was observed. Migration experiments with the reduced form of selenium, HSe^-, were inconclusive since they were jeopardised by the rather high natural Se concentration in the BC pore water which is one order of magnitude higher than the measured solubility. The presence of this relative high natural Se concentration needs further attention.

**Plutonium**

Solubility experiments of Pu(IV) in absence and presence of Boom Clay organic matter were not conclusive (possible presence of Pu(VI)); but they suggest that NOM may increase the Pu(IV) solubility by an order of magnitude (~ 10^{-7} mol dm^{-3}). Migration experiments with Pu(IV) showed that the spiking solution contains Pu-OM associated species besides a Pu(IV)-“solid” phase. Despite the presence of Pu-OM associated species in the “source” and the observed increased Pu solubility, no enhanced transport of the Pu was observed. The low constant concentration, leaching from a long-term experiment resembles the behaviour of Am. We are still unsure on the redox state of the aqueous Pu-species in the Boom Clay.

The Pu transport mechanism can be described by an immobilisation (solubility or quasi irreversible interaction with the solid phase) followed by a constant release of Pu. This immobilisation/constant release resembles a solubility like mechanism and can be implemented as a constant concentration source. Due to the observed association with NOM, we consider that the mobilised Pu migrates through the Boom Clay with similar D_{app} and R as for the mobile OM. Due to the large uncertainties on the experimental findings, Pu needs further study.

**Americium (as representative for trivalent actinides/lanthanides)**

In SBCW, an Am solubility of ~ 2 \times 10^{-8} mol dm^{-3} was measured. Interaction with OM brings the Am into solution as Am-OM complexes (distributed evenly over different size fractions), but these complexes are kinetically unstable. Larger OM molecules form more kinetically stable Am-OM complexes. When Am-OM complexes are contacted with Boom Clay they dissociate instantaneously and the bulk of Am becomes immobilised (as Am complexed to OM_{immob} or sorbed) and only a small portion persists as “stabilised” Am-OM complexes which are mobile. These “stabilised” Am-OM complexes further undergo dissociation upon travelling through the clay but this dissociation is controlled by slow kinetics. The constant bleeding of Am, [Am]~10^{-13} - 10^{-12} mol dm^{-3}, is caused by an Am “source” which is not associated to OM (inorganic Am-“solid phases”) acting as a continuous source of Am to form “stabilised” Am-OM complexes which results in a constant release of Am. The Am transport mechanism can be described by an immobilisation (quasi irreversible interaction of Am with the solid phase) followed by a constant release of Am which migrates associated with mobile OM. This immobilisation/constant leaching resembles a solubility like mechanism and can be implemented as a constant concentration source, and transport of the mobilised Am through the Boom Clay occurs with a similar D_{app} and R as the mobile OM.

A transport model, POPCORN, is developed to describe and evaluate the influence of OM on radionuclide transport in clay. The key processes governing OM transport and 241Am-OM stability appear to be the rates of attachment and detachment of OM on the clay surfaces and the rate of complexation/destabilisation, indicating that it is important to evaluate the kinetics of the system. Best results are obtained with a rate of OM attachment to the rock that is about an order of magnitude less than the rate of detachment. There is an apparent correlation
between the inverse of the rate of OM attachment to the rock, the inverse of the kinetic constant for the stability of mobile $^{241}$Am-OM, and the peak advection-driven OM breakthrough. The relationships derived offer a potential means of extrapolating parameter values for application of the model to larger-scale problems. The POPCORN model has proved tractable, with run times of a few seconds for the studies described in this report, and would be suitable for use in repository performance assessments alongside standard advection-dispersion models.

**Methodologies** were developed to identify the source of mobile NOM: leaching, discrete porewater sampling & OM isolation, characterisation of the kerogen. The Boom Clay kerogen makes up to 5% of the total sediment. Rock Eval and pyrolysis GC/MS analysis have shown that the kerogen is a mixture of terrestrial and marine OM. Some smaller molecules (e.g. polar oxygen-containing products) are entrapped into the 3D macromolecular network of the kerogen and are prone to release upon applying low thermal stress. The Boom Clay porewater contains around 100 to 200 mgC/L, but might be up to 400 mgC/L. Up to now, the DOC can not be linked to the neighbouring TOC as no correlation exists in their concentrations. Leached organic matter contains a higher amount of total organic carbon than the Boom Clay porewater and is predominantly composed of humic acids. The amount of leached organic matter is primarily controlled by the amount of Boom Clay solid phase used. Solving the question on the source of mobile NOM was however beyond the scope of the project, but the methodologies are proven to be useful and will be further explored.

The **transport mechanism for the studied radionuclide** (except for $\text{SeO}_4^{2-}$) is dominated by an immobilisation process with a constant release of radionuclides. In case of U and Se the constant release is controlled by a solubility limit of the precipitated phases and the transport is independent of NOM. For Am – as representative of trivalent actinides/lanthanides - the constant release is due to a strong interaction with the solid phase (immobile OM?) and not determined by a solubility limit. The transport is correlated with NOM. For Pu the underlying processes are not understood but resemble that of Am. PA calculations are therefore performed with a limited set of parameters: concentration limit (or solubility limit), $D_{\text{pore}}$, $R$ and diffusion accessible porosity. The values are taken from experimental observations and interpretations. PA calculations for U and Se in BC are performed with the new parameter set based on the project outcome and compared with results based on formerly used datasets. Special attention is given to selenate as possible species and the presence of inactive Se in the waste.

The methods, results and conceptual models developed in the TRANCOM-II project are of direct use for evaluating the performance of the Boom Clay as potential host rock for HLW disposal but they serve also as a reference for other clay formations and waste types (chemo toxic waste).
4 List of abbreviations

*AHA*: Aldrich Humic Acid

*AOM*: Amorphous Organic Matter

*Armines*: Association pour la recherche et le développement des méthodes et processus industriels

*BC*: Boom Clay

*BCE*: Boom Clay Extract. OM extracted from BC with SBCW

*BCHA*: Boom Clay Humic Acid (obtained by concentrating RBCW collected from a piezometer –reference EG/BS- in the HADES URL (SCK-CEN, Mol, Belgium), synonym for BCOM and TROM

*BCOM*: Boom Clay Organic Matter

*13C-NMR*: 13C-Nuclear Magnetic Resonance spectroscopy

*D_{app} or D_a*: Apparent Diffusion Coefficient

*D_{pore} or D_p*: Porewater Diffusion Coefficient

*E_h*: Redox potential versus Standard Hydrogen Electrode (SHE)

*ENSCP*: Ecole Nationale Supérieure de Chimie de Paris

*ENSMP*: Ecole Nationale Supérieure des Mines de Paris

*FTIR*: Fourier Transform Infra Red spectroscopy

*GC*: Gas Chromatography

*GC-MS*: Gas Chromatography – Mass Spectrometry

*GPC*: Gel Permeation Chromatography

*GSL*: Galson Sciences Ltd.

*HA*: Humic Acid

*HADES URL*: High Activity Disposal Experimental Site Underground Research Laboratory (SCK-CEN, Mol, Belgium)

*HLW*: High-Level radioactive Waste

*HS*: Humic Substances

*IS*: Ionic Strength

*ICP-MS*: Inductive Coupled Plasma – Mass Spectrometry

*K_d*: Distribution coefficient

*kD*: kiloDalton = 1000 Dalton = 1000 MWCO

*KULeuven*: Katholieke Universiteit Leuven

*LCBOP*: Laboratoire de Chimie Bioorganique & Organique Physique

*LLNL*: Lawrence Livermore National Laboratory

*LSC*: Liquid Scintillation Counting

*LU*: Loughborough University
**MORPHEUS:** Name of a piezometer in the HADES URL (SCK-CEN, Mol, Belgium) to sample Boom Clay water at different depths with distinctive OM horizons, acronym for Mobile ORganic matter Pore water Extraction in the HADES Experimental Underground Site

**MWCO:** Molecular Weight Cut-Off

**NEA:** Nuclear Energy Agency

**NOM:** Natural Organic Matter

**OC:** Organic Carbon

**OD:** Optical Density

**OM:** Organic Matter

**PA:** Performance Assessment

**PEC:** Proton Exchange Capacity

**POPCORN:** POPulations of COlloids on RadioNuclide transport

**R:** Retardation coefficient

**RBCW:** Real Boom Clay Water. Collected from a piezometer –reference EG/BS- in the HADES URL (SCK-CEN, Mol, Belgium)

**Rd:** Distribution coefficient

**RN:** Radionuclide

**SBCW:** Synthetic Boom Clay Water

**SCK-CEN:** StudieCentrum voor Kernenergie – Centre d’Etudes de l’énergie Nucléaire, Belgium Nuclear Research Centre

**SEM:** Scanning Electron Microscopy

**SHE:** Standard Hydrogen Electrode

**TOC:** Total Organic Carbon

**TRANCOM:** TRANsport of radionuclides due to Complexation with Organic Matter in clay formations

**TROM:** TRancom Organic Matter: Concentrated Boom Clay OM batches

**UV-VIS:** UltraViolet – Visual light spectroscopy

**µ-XANES:** micro X-ray Absorption Near Edge Spectroscopy

**XRD:** X-Ray Diffraction
5 References


Weetjens, E: Technical note on PA case study for new parameters of Se and U. Technical note prepared within the EC TRANCOM-II project contract No FIKW-CT-2000-00008, 03/EWe/N-21, SCK-CEN, Mol, Belgium (2003c).

List of Annexes

Annex 1 to WP-1
   Topical report on speciation and solubility calculations for uranium, plutonium and selenium under Boom Clay conditions (R-3400, SCK-CEN)

Annex 2 to WP-2
   Preparation of synthetic Boom Clay water

Annex 3 to WP-2
   Effect of NOM on the U and Pu solubility under reducing conditions

Annex 4 to WP-2
   Influence of NOM on the solubility of amorphous UO₂ (Delécaut, 2004)

Annex 5 to WP-2
   Complexation studies of U(VI) and U(IV) with NOM using the Schubert method

Annex 6 to WP-2
   Complexation studies of U(VI) with NOM using the dialysis method (Delécaut, 2004)

Annex 7 to WP-3
   U interaction with solid phases present in Boom Clay (Delécaut, 2004)

Annex 8 to WP-3
   Selenite reduction in Boom Clay: effect of FeS₂, Clay minerals and dissolved organic matter

Annex 9 to WP-6
   Technical note: Note on the theoretical basis of the side-reaction theory (NT36/03, Armines)

Annex 10 to WP-6
   Technical note: Theoretical analysis of U(IV) solubility and complexation with Boom-Clay organic matter (NT34/03, Armines)

Annex 11 to WP-6
   Technical note: Modelling of U(VI) complexation with Boom-Clay organic matter (NT42/03, Armines)

Annex 12 to WP-6
   Technical note: Reflection on the geochemical modelling of the RN-NOM interaction experiments (03/LWa/N-18, SCK-CEN)

Annex 13 to WP-5 and WP8
   Double tracer migration experiments: Radiolabelling of Boom Clay organic Matter and back-to-back diffusion experiments
Annex 14 to WP-5 and WP8
Migration experiments and demonstration of model concept for trivalent radionuclides

Annex 15 to WP-7
Technical note: Modelling of the $^{233}$U transport in Boom Clay (03/EWe/N-20, SCK-CEN)

Annex 16 to WP-7
Technical note: Modelling of the $^{241}$Am and $^{14}$C labelled organic matter in Boom Clay (03/EWe/N-23, SCK-CEN)

Annex 17 to WP-7
Topical Report on: Modelling the effects of organic matter on radionuclide transport (9918-2 v. 1.0, GSL Ltd.)

Annex 18 to WP-4
Topical report on: Methodologies developed to identify the source of mobile Boom Clay Organic Matter (BLG-967, SCK-CEN)

Annex 19 to WP-9
Technical note: PA case study for new parameters for Se and U (03/EWe/N21, SCK-CEN)

Annex 20 to WP-9
Note on: Treatment of colloids in Performance Assessment (9918-3, GSL Ltd.)
Contents of the CD-ROM

**Final S&T report BLG-988**

**Annexes**


**Main text BLG-988**

BLG-988.pdf

**Project outcome**

**WP1 speciation and solubility calculations**

R-3400.pdf or Annex 1.pdf

**WP 2 RN interaction with NOM in solution**

Datasets

- Se-FeS2-KUL
  - Chem reductionKUL.xls
  - KUL_Se reduction in presence of FeS2.xls
- U(IV) solubility-LU
  - U(IV) solubility Lboro.xls
- U(IV) solubility-SCK
  - U(IV) solubility-kinetic SCK.xls
  - U(IV) solubility – OM SCK.xls
- U(VI) complexation-SCK
  - U(VI)-OM-SCK.xls

**Text**

- LU
  - Annex 3.pdf
  - Annex 5.pdf
- SCK-CEN
  - Annex 4.pdf
  - Annex 6.pdf

**WP3 RN solid phase interaction**

Datasets

- Se-Boom Clay-KUL
  - KUL_Se in Boom Clay suspensions.xls
- U-Minerals-SCK
  - Mineral characterisation.pdf
  - U-minerals interaction-data.pdf

**Text**

- KULeuven
  - Annex 8.pdf
- SCK-CEN
  - Annex 7.pdf

**WP4 Methodologies to identify source of NOM**

BLG-967.pdf or Annex 18.pdf
WP5-WP8 migration experiments

Migration data sets

...........................................Overview migration datasets – SCK.pdf

Non-trancom experiments

Single label RN experiment

Americium

..........................................................Am241m3c7.xls

Plutonium

..........................................................Pu238m2c6.xls

Uranium

..........................................................U233m2c8.xls

Trancom-Clay

Am-OM double labelled experiments

Full spectrum MCWO OM

.......................................................14c48F2.xls

High MWCO OM 100000

.......................................................14c47H2.xls

Low MWCO OM 10000

.......................................................14C46L2.xls

Labelled OM experiments

Full spectrum MCWO OM

.......................................................14c43F.xls

High MWCO OM 100000

.......................................................14c42H.xls

Low MWCO OM 10000

.......................................................14C41L.xls

Trancom-II

Am-OM double labelled experiments

30000 MWCO OM (new batch)

.......................................................HiPAmCOM.xls

.......................................................LongAmCOM.xls

.......................................................LowPAmCOM.xls

.......................................................MePAmCOM.xls

.......................................................ShortAmCOM.xls

Full spectrum MWCO OM

.......................................................FAm3.8.xls

Low MWCO OM 10000

.......................................................LAm3.6.xls

RN-OM double labelled experiments

Plutonium-OM DL

.......................................................PuCOM1.xls

.......................................................PuCOM2.xls

Selenium-OM DL

.......................................................SeCOM1.xls

.......................................................SeCOM2.xls

UraniumM –OM DL

.......................................................UraCOM1.xls

.......................................................UraCOM2.xls

Text

...........................................................................................................Annex 13.pdf
WP6 Geochemical modelling

...............................................
Lwa-n18.pdf or Annex 12.pdf
...............................................
NT34-03.pdf or Annex 10.pdf
...............................................
NT36-03.pdf or Annex 9.pdf
...............................................
NT42-03.pdf or Annex 11.pdf

WP7 modelling & interpretation of migration experiments

.........9918-2v1d2.pdf or Annex 17.pdf
.............ewe-n20.pdf or Annex 15.pdf
...............ewe-n23.pdf or Annex 16.pdf

WP9 Conceptualisation and PA

.............................................
9918-3v1d1.pdf or Annex 20.pdf
.............................................