EUROPEAN COMMISSION

nuclear science and technology

Understanding and Physical and Numerical Modelling of the Key Processes in the Near Field and their Coupling for Different Host Rocks and Repository Strategies

(NF-PRO)

Contract FI6W-CT2003-002389

Final report

Project co-funded by the European Commission under the Euratom research and training programme on nuclear energy within the Sixth Framework Programme (2002-2006)
Area: Management of radioactive waste

Directorate-General for Research
2008 Euratom EUR 23730

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Project partners

The NF-PRO consortium consisted of 40 organisations:
http://www.nf-pro.org/eng/partners

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PART 1: Executive summary

Abstract

Most EU Member States depending on nuclear power pursue geological disposal as the preferred option for the long-term management of long-lived and high-level radioactive waste. During the past 25 years, considerable progress has been made in the establishment of a scientific basis for the final disposition of radioactive waste.

Repository concepts under development in the EU put strong emphasis on the performance of the engineered barriers surrounding the disposed waste. The near field is an essential part of the disposal system as its principal function is to contain and to minimise the release of radionuclides over extended periods of time. Accordingly, the properties, the behaviour and the evolution of the near-field system are fundamental in the evaluation of the overall performance of a geological repository for radioactive waste disposal.

The integrated project NF-PRO (Sixth Euratom Framework Programme) has investigated key processes in the near field of a geological repository for the disposal of high-level vitrified waste and spent fuel. This final activity report provides a concise overview of the project scope and content and summarises key achievements and advances made by the project.

Introduction

Since 1984, the European Commission has supported research related to the management of radioactive waste. R&D projects are funded by Euratom through multiannual framework programmes. In 2002, the Commission launched the Sixth Framework Programme (FP6). The Sixth Framework Programme represented a major step forward relative to previous Community-supported programmes since the scope and the ambition of research as well as the average level of funding of individual projects increased substantially.

NF-PRO is one of the integrated projects forming part of the FP6 Euratom programme. NF-PRO is a multinational European research project investigating processes affecting the barrier performance of the near field of geological repositories for high-level waste disposal. The NF-PRO consortium consists of 40 leading nuclear research organisations, radioactive waste management agencies/implementing organisations, universities and consulting companies.

The near-field system

The near field of a geological repository for the disposal of high-level radioactive waste and spent nuclear fuel plays a key role in ensuring the long-term safety of disposal: The principal safety function of the near field is to confine radionuclides and to minimise/retard radionuclide release from the waste to the host rock. The near field is a complex environment consisting of multiple engineered barriers and repository components. These include the waste form, the waste canisters, backfills, seals, plugs, and the disturbed zone of the host rock. Repository construction and operation as well as waste emplacement will disturb ambient conditions of the disposal site. After repository closure, the near-field environment will evolve as a result of

geochemical interactions between various repository components, heat generation, and radiation effects. The combined effects of processes occurring in the near field will affect radionuclide transport and retardation.

In recent years, substantial progress has been made in the scientific understanding of individual near-field processes. The main scientific undertaking now is to integrate results from detailed process investigations (experimental studies in surface and underground laboratories and detailed process modelling) into evaluations of the overall near-field system.

Scope of the research addressed by NF-PRO

The scope of the integrated project NF-PRO involves the near field of a repository for the geological disposal of vitrified high-level radioactive waste and spent fuel. NF-PRO's project scope includes various repository concepts/designs that are currently under investigation in EU Member States. The host rocks addressed by NF-PRO are salt, granite and clay.

Research as part of NF-PRO has concentrated on the investigation of detailed processes taking place in the near field as well as their couplings in view of integration in performance assessment. In doing so, work within NF-PRO focused on outstanding issues and a strong link has been established between laboratory and *in situ* experiments, modelling and assessments of the overall system performance.

NF-PRO acknowledges that a large body of scientific data and information on the near-field system is available from previous Community-supported programmes as well as from national research programmes in the EU Member States. Research by NF-PRO has built on this knowledge and has deepened and strengthened the scientific basis for geological disposal. Given the broad subject scope, it was not NF-PRO's ambition to carry out an encompassing R&D programme on all processes and materials interactions occurring in the near-field system. Neither NF-PRO aspired to provide a comprehensive assessment of the near-field system taking into account various repository designs and host rock types. Instead, NF-PRO has reviewed the current status on near-field research and concentrated its programme of work on outstanding key issues. This allowed reducing remaining uncertainties with respect to processes and interactions of near-field components that might affect the long-term performance of the disposal system. Accordingly, NF-PRO's work programme is to a certain extent topical and complements national R&D performed in the EU Member States.

A distinctive feature of NF-PRO lies into the fact that NF-PRO has integrated European R&D on the near-field system by bringing together scientific disciplines and research teams that largely worked independently in the past (integration at the scientific level). Also, NF-PRO has strengthened communication between major R&D organisations and radioactive waste management agencies/implementing organisations throughout Europe (integration at the organisational level). The strong interaction between researchers investigating detailed processes and investigators assessing the overall performance of the near-field system (performance assessment) is another unique quality of NF-PRO. More specifically, this level of integration of different disciplines, fields of expertise and methodological approaches required for the assessment of the near field has not been achieved in previous EU-supported framework programmes. In this sense, the scientific output and the achiements by the integrated project NF-PRO constitute a prominent milestone in EU-funded research on the safe disposal of radioactive waste. Future European research programmes can build on these foundations and scientific achievements by NF-PRO. In addition, results obtained by NF-PRO are transferred and applied in national repository development programmes. In particular, new

insights in the near-field system and advances made by NF-PRO can contribute to evaluate, improve, and optimise repository designs. Consequently, NF-PRO has made major contributions to the European and national programmes on the safe management of radioactive waste.

Project objectives

The principal objective of NF-PRO is to contribute to the establishing of a scientific basis for evaluating the safety function "containment and minimisation of release" of the near field. More specifically, the detailed objectives of NF-PRO are:

- To resolve a number of outstanding issues with respect to the key processes controlling the dissolution of the vitrified waste/spent fuel matrix including processes related to the release of radionuclides from the waste matrix to the geological environment;
- To establish a comprehensive insight in the chemical processes and materials interactions taking place in the near field of a geological repository for high-level watste (HLW) and spent-fuel disposal;
- To investigate the evolution of the thermal, the hydrological and the mechanical processes taking place in the near field and their influence on the total system;
- To assess the impact of the evolution in the disturbed zone (EDZ) (from repository construction till T-H-M equilibration) on the physico-chemical conditions of the near field including waste matrix alteration processes, radionuclide mobilisation/immobilisation, and mass transfer;
- To identify and to provide key data on critical processes and their couplings determining the evolution of the near field and affecting radionuclide release to the geosphere;
- To translate models and data on complex and coupled near-field processes to concise but accurate models and data as input to assessments of the overall system performance.

Project components and structure

To understand the performance of the overall near-field system, an adequate insight in the performance of the individual near-field sub-systems as well as their interactions is essential. Accordingly, the integrated project NF-PRO has been structured in five research and technology development components (below referred to as "RTD components"), each representing a major near-field sub-system (Figure 1).

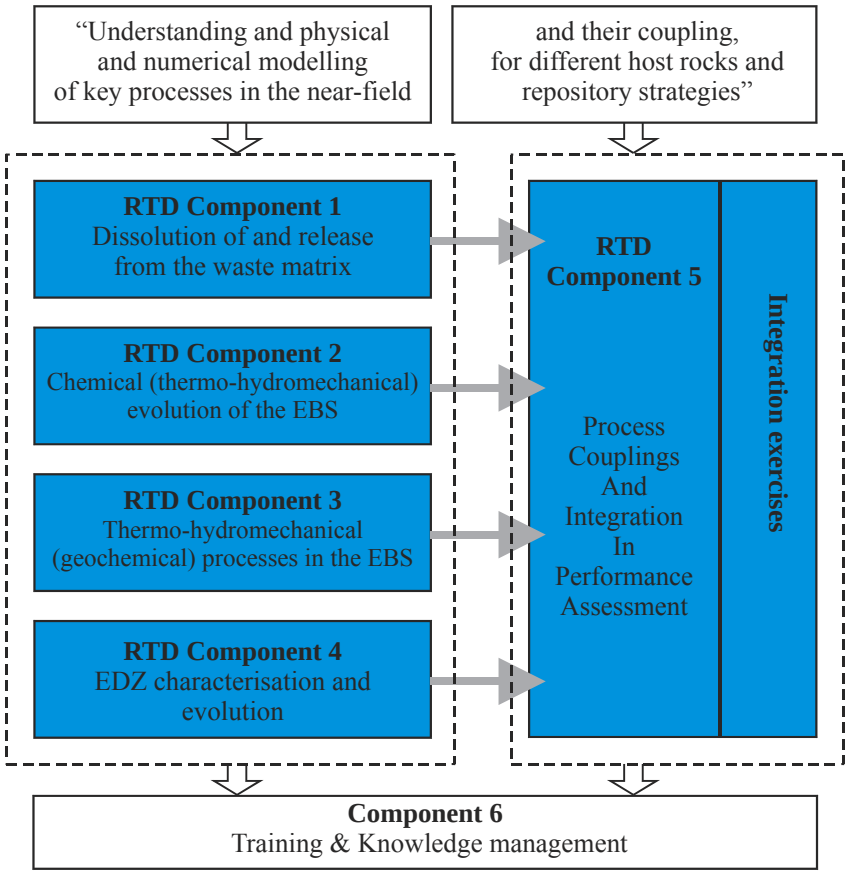

Figure 1: The NF-PRO project structure indicating the different RTD components and their interaction. Figure 1 gives an overview of the main research areas covered by NF-PRO. Research by NF-PRO addresses the following sub-components or key processes in the near-field system: processes affecting the waste matrix (vitrified high-level waste and spent fuel), chemical processes and interactions in the engineered barrier system, coupled thermo-hydro-mechanical processes, and the initiation and evolution of the excavation-disturbed zone

RTD Components 1 to 4 address key processes controlling dissolution of and release from the waste matrix, chemical processes taking place in the engineered barrier system (EBS), the thermo-hydro-mechanical (THM) evolution of the EBS and the characteristics and the evolution of the excavation-disturbed zone (EDZ), respectively. Process couplings and integration in performance assessment are dealt with in RTD Component 5. In previous and ongoing Community-supported research programmes as well as in national programmes, topics covered by these RTD components were studied in self-standing projects while R&D teams have operated to a great extent independently. The level of integration aimed at by NF-PRO, in particular the development of a comprehensive and phenomenological insight in the overall near-field system behaviour and its evolution in time and space has not yet been achieved in preceding framework programmes.

Component 6 brings together all activities concerning training (including knowledge management and transfer). In addition to the scientific-technical objectives, the NF-PRO consortium has made the acquired data, knowledge and expertise available and accessible to the broad scientific community within the EU, uses its expertise for public information purposes, and promotes knowledge and technology transfer through training.

Composition of the NF-PRO consortium

The type and complexity of the research subject covered by NF-PRO calls for multidisciplinary expertise: To achieve the scientific-technical objectives of NF-PRO and to guarantee the relevance of the research and the use of its results, the project required a strong multidisciplinary team involving both the major European radioactive waste management organisations and the main nuclear research institutes supported by other research institutions, universities, industrial partners and consultancy companies (SMEs). The NF-PRO consortium includes 40 participating organisations that are endowed with a wide variety of highly specialised skills, competences and responsibilities and that have access to nuclear research infrastructures needed to perform the multidisciplinary R&D work proposed within NF-PRO. The Belgian Nuclear Research Centre, SCK•CEN, acts as the overall and scientific coordinator of the integrated project (IP) NF-PRO.

The following radioactive waste agencies/end users participate in NF-PRO: ANDRA (France), BGR (Germany), ENRESA (Spain), NAGRA (Switzerland), NIRAS/ONDRAF (Belgium), NIREX (United Kingdom), POSIVA (Finland), and SKB (Sweden). The role of the waste management organisations within NF-PRO is to:

- ensure as end-user that the outcome of the IP is of direct use for their waste disposal implementation programme (including performance assessment) and their interaction with different stakeholders;
- integrate the results of the IP with those from the national programmes;
- set priorities in types of waste, engineered barriers, repository designs and host rocks that shall be considered in the IP;
- manage research performed in underground research laboratories;
- perform parts of the proposed R&D within their competence.

The following large nuclear research organisations take part in NF-PRO: SCK•CEN (Belgium), CEA (France), CIEMAT (Spain), the EC Joint Research Centre, ITU (European Commission), FZK-INE (Germany), GRS (Germany), IRSN (France), NRG (the Netherlands), NRI (Czech Republic), PSI (Switzerland), Serco (United Kingdom), Studsvik (Sweden), and VTT (Finland). The role of these nuclear research organisations is to:

- bring together a multidisciplinary and complementary expertise in laboratory experiments, including the capacity to work with actinides, long-lived fission products and real high level waste, *in situ* testing in URLs, modelling, and safety assessments for the different research domains;
- ensure the dissemination of knowledge and technology within the scientific community;
- ensure the accessibility of the results derived from the IP for the intended end-use
- manage and preserve the knowledge and expertise acquired by the IP.

The following other organisations, including universities, industrial and governmental partners and consultancy companies including SMEs contributed to NF-PRO's work programme: AITEMIN (Spain), ARMINES (France), BUTEC (Germany), Chalmers University (Sweden), CIMNE (Spain), CNRS DR10 (Centre de géochimie de la surface, France), Enviros Spain, Charles University (Czech Republic), Forschungszentrum Rossendorf (Germany), University of Nîmes (France), Geoenvironmental Research Centre Cardiff (United Kingdom), Galson Sciences Ltd (United Kingdom), Institute for Rock Mechanics Leipzig (Germany), INERIS (France), British Geological Survey (United Kingdom), Quintessa (United Kingdom), Technical University Clausthal (Germany), the Catalunia University (Spain), Univer-

sity of Sheffield (United Kingdom), Utrecht University (the Netherlands), and Uppsala University (Sweden). These organisations complemented the skills and experience of the core partners with specific competences needed within NF-PRO typically related to:

- high-tech "state-of-the-art" analytical techniques and (*in situ*) monitoring techniques;
- high-tech "state-of-the-art" experimental set-ups;
- advanced (coupled) modelling;
- engineering.

This broad participation of organisations is a decisive factor for the success of the project given the large number of complementary scientific disciplines that are required in investigations related to near-field processes, i.e. nuclear chemistry and physics, geochemistry, hydrogeology, mineralogy, geomechanics of clay, hard rock and rock salt, thermomechanics, mining engineering, *in situ* instrumentation, and modelling concerning all these disciplines.

Summary of advances made by the integrated project NF-PRO

Advances in research related to key processes affecting the waste form (vitrified high-level waste and spent fuel)

Introduction and overall objectives

In a geological repository, the waste matrix constitutes the first barrier confining the disposed radionuclides. The overall objective of NF-PRO's RTD component 1 was to improve the scientific basis and predictive capacities on key-processes affecting matrix dissolution and radionuclide release from vitrified high-level waste (HLW) and spent nuclear fuel in the near field of a geological repository.

Summary of key activities and achievements

NF-PRO has investigated radionuclide release from disposed vitrified waste and spent fuel taking into account the dominant near-field processes controlling the alteration of and the release from the waste matrix, their couplings and their evolution As part of RTDC 1, NF-PRO has investigated the interaction of vitrified waste with water in view of the parameterisation of UK glass performance in pure water and the investigation of glass dissolution kinetics under near field conditions in clay water.

Within NF-PRO, experiments have been conducted to study the dissolution of vitrified waste in the presence of various compacted near-field media. These experiments have allowed measuring the diffusion of radionuclides through different near-field media. The simultaneous measurement of several critical coupled processes has made it possible to calibrate and to improve glass dissolution models. As a result, more accurate glass source term data have been established and data have been produced and interpreted for input to performance assessment.

Another important area of research within NF-PRO concerns experimental studies on the evolution of spent fuel prior to water ingress (normal evolution scenario) and during the transient period (early failure scenario). Various studies have been performed to expand knowledge on grain boundary characterisitcs/inventories and grain boundary stability in spent fuel. Amongst others, the effect of helium on the spent fuel microstructure and diffusion processes

has been re-evaluated. This has allowed diminishing the conservatism of former 'instant release fraction' values of key safety relevant radionuclides for PWR UO_2 fuels.

NF-PRO has made important contributions to insights in the quantitative understanding of key processes affecting the spent fuel source term in geological repository conditions. Amongst others, NF-PRO has elaborated on a radiolysis model for near-field/spent fuel interactions and has investigated the effect of secondary phases on spent fuel dissolution and alteration including radionuclide retention in the UO_2 matrix. NF-PRO has investigated the effect of hydrogen gas on the dissolution of UO_2. Experiments have been conducted to investigate whether the dissolution of UO_2 is inhibited in the presence of hydrogen gas. Data from these experiments are highly relevant to performance assessments: If the inhibiting effect of H_2 on the dissolution of the spent fuel matrix is confirmed, very low matrix dissolution rates have to be taken into account for the normal evolution scenario. However, trace constituents present in groundwater such as bromide may counteract at low concentrations. The effect of bromide on radiation-induced corrosion of UO_2 has also been investigated by NF-PRO.

The chemical evolution of the engineered barrier system

Introduction and overall objectives

The engineered barrier system (EBS) isolates the disposed radioactive waste from the undisturbed host rock. The uptake of groundwater as well as chemical interactions between various near-field components will have an impact on the confinement properties of the EBS. NF-PRO investigates processes affecting the barrier performance of the EBS, in particular the evolution of the porewater composition in the near-field system, chemical alteration processes, the formation of secondary phases and corrosion products, and the impact of new-formed phases on sorption and radionuclide mobility.

Summary of key activities and achievements

Clay-based (bentonite) buffer materials are widely applied in repository concepts in granite and clay host rocks. Bentonite buffer materials will progressively hydrate and act as a low-permeability barrier thereby controlling and limiting the migration of radionuclides released from the disposed waste after repository closure. An important part of work by NF-PRO has been dedicated to the investigation of the evolution of the porewater composition and chemistry in the bentonite barrier. Laboratory experiments have been carried out to assess the extent of the zone affected by oxidising porewater upon the hydration of compacted bentonite. Experimental results show that the zone affected by the uptake of oxidising porewater is very limited. Similar observations have been made with respect to the effects of alkaline porewater. These experimental observations indicate that redox and pH conditions are buffered very effectively in compacted bentonite.

NF-PRO has conducted laboratory experiments to investigate the effect of temperature and porewater composition (salinity) on the hydration of FEBEX bentonite. Column experiments show that the increase in calcium is due to the dissolution of calcite leading to oversaturation of the porewater with respect to gypsum, which precipitates in the upper part of the column, and which results in a decrease in sulphate concentration. Observations from these experiments confirm that pH buffering can be explained by dissolution/precipitation reactions.

Experimental work by NF-PRO includes investigations on water absorption in different types of bentonite (MX-80 and FEBEX bentonite). More specifically, the amount of water absorbed has been measured as a function of porewater salinity. It was found that the distribution of the water among external and internal (interlamellar) sites depends on the pore water salinity. This has been tested by fixing pore water in FEBEX bentonite at three different ionic strengths: 0.01, 0.1 and 1 M NaCl. Results from experimental work indicate that the amount of internal water decreases with increasing salinity. Additional experiments have led to the conclusion that the amount of water absorbed in bentonite depends on the dominant cation in the smectite exchanger. Experimental results with homoionised FEBEX bentonite show that maximum water absorption occurs with magnesium or calcium as the dominant exchangeable cations. Minimum water absorption was observed with potassium as dominant exchangeable cation.

NF-PRO has investigated the evolution of bentonite swelling properties. Earlier studies have shown that the swelling pressure in bentonite varies with ionic strength of the porewater. This has been confirmed by experimental work by NF-PRO on MX-80 bentonite and on FEBEX bentonite. Notwithstanding different experimental initial conditions, in both bentonite types the swelling pressure decreases with increasing ionic strength. In addition, experiments performed on FEBEX bentonite confirm that the lower is the salinity of pore water the largest is the absorption of water in the interlamellar space, which will lead to a higher swelling pressure as basal spacing of the smectite will increase.

Work by NF-PRO involves investigations on interactions between bentonite and corrosion products from carbon steel canisters, or in the case of the KBS-3 concept, copper canisters with cast iron inserts, and the effects of these interactions on the engineered barrier system. A literature review on the nature of corrosion products undertaken within NF-PRO showed that the composition of the corrosion products does not only depend on the redox conditions and the time of reaction but also on the chemical composition of the porewater and interacting materials. This has been confirmed by experiments performed by NF-PRO.

As concerns corrosion rates, experiments performed at different temperatures, have demonstrated that (under a range of experimental conditions), the corrosion rate rapidly decreases with time to values of approximately 1 μm/yr. A temperature effect is only observed in the initial phase during which the corrosion rate of carbon steel plates increases with temperature. When using iron powder, the corrosion rate also increases due to the larger reactive surface. However after 400 hours, the corrosion rate decreases to values of 1 μm/yr. For the long-term, no effect has been observed due to changes in temperature or water composition. It seems that the corrosion rate is mainly controlled by the thickness and composition of the corrosion product layer. Additional experiments have shown that after an initial phase of faster corrosion rates, the corrosion rate decreases to values below 5 μm/yr. This observation is explained by the formation of the corrosion product film on the surface.

Experimental work within NF-PRO on bentonite alteration has led to conclusive results with respect to the alteration of bentonite in the presence of iron corrosion products. Results indicate that there is no evidence for the transformation of the montmorillonite into an iron-rich clay mineral phase.

NF-PRO has produced a large body of data and new information on interactions of bentonite and concrete degradation, the understanding of radionuclide main transport processes, sorption and diffusion.

Results from work by NF-PRO have lead to a better insight in key processes affecting radionuclide mobility in the EBS system under realistic repository conditions. These data are particularly important to performance assessment since they contribute to the reducing of parameter uncertainties regarding the near-field source term.

Thermo-hydro-mechanical and coupled processes affecting the near-field system

Introduction and overall objectives

In most repository concepts considered by EU Member States, buffer or backfill materials are emplaced around the disposed waste canisters. In granite and clay host rocks, bentonite is applied as buffer material while in rock salt, crushed salt is used. An important part of the work performed by NF-PRO concentrated on the investigation of the combined effects of thermal, geomechanical and hydrological processes on the performance of bentonite buffer and crushed-salt backfill. A comprehensive analysis of the THM (C) processes in the EBS has been carried out as part of NF-PRO, taking into account various types of buffer material (bentonite, salt), different scales (from laboratory to real scale), and several degrees of saturation and thermal states.

Summary of key activities and achievements

As part of NF-PRO, experiments and modelling studies have been performed to evaluate the parameters and processes influencing hydration kinetics and moisture transfer in the clay barrier, especially with respect to its long-time evolution (low hydraulic and temperature gradients) and scale effects (from small-scale laboratory tests to real-scale *in situ* experiments). In addition, the impact of temperature on the hydro-mechanical properties of the bentonite has been determined as well as the reversibility of the observed modifications including influence on the microstructure of bentonite hydration.

The FEBEX mock-up and *in situ* test investigate the long-term behaviour of the bentonite barrier under realistic repository conditions. As part of work under NF-PRO, the *time domain reflectometry* (TDR) technique, which is applied for the long-term monitoring the hydration of the buffer in the FEBEX experiments, has been improved and optimised. Numerical analyses of the experimental results derived from the FEBEX experiments have led to the conclusion that further enhancement of the classical THM formulations were required. Accordingly, a threshold hydraulic gradient has been introduced in THM models and thermo-osmotic effects and the evolution of the micro-fabric have been taken into account in these models.

The migration of gas through the buffer is a key issue with respect to the long-term safety of disposal. In a deep repository, gases are generated as a result of radioactive decay and the corrosion of steel. The LASGIT *in situ* experiment at Äspö aims to resolve outstanding questions with respect to the migration of gas through the clay following pressure-induced pathways. LASGIT is a full-scale demonstration experiment operated by SKB at the Äspö Hard Rock Laboratory, Sweden, at a depth of 420 m. High-quality test data from this large-scale gas injection test were used to test and to validate modelling approaches. The test was used to examine issues relating to upscaling and to provide additional information on the process of gas migration. Data from the LASGIT experiment are highly relevant to performance assess-

ment since they will contribute to reducing data uncertainties and will allow for the calibration of models on gas migration in a saturated bentonite buffer.

An important part of work within NF-PRO focuses on the investigation of crushed-salt backfill. The crushed salt backfill will only attain its low permeability through either compaction by drift convergence or by pre-compaction before emplacement. Work by NF-PRO includes the optimization of the compaction process and the study of the long-term compaction development at low differential stresses. The use of bentonite as additive to crushed salt to ease the compaction and reduce permeability has been tested. Experimental work has demonstrated that adding about 15 to 20 percent of bentonite reduces the permeability of crushed salt by four orders of magnitude and considerably eases compaction. The application of this type of backfill is restricted to low temperature (< 100 °C) areas. Alternatively, pre-compacted salt bricks can be used as backfill. The performance of the salt bricks mainly depends on the characteristics of the interfaces between the bricks and between the bricks and the surrounding rock salt. These characteristics have been determined by shear tests and modelling. Moisture seems to accelerate the healing of interfaces with time.

Compaction experiments have been performed to investigate the long-term behaviour of compacted salt at low differential stresses and low porosity (< 5 %). Experiments on the compaction of 'wet' crushed salt indicate that pressure solution creep (IPS) is the prevailing process while the experiments on 'dry' crushed salt (with only the natural amounts) indicate a mixed process of IPS and dislocation glide. The permeability significantly decreases in the 'annealing' period after the compaction. Microphysical models have been developed to explain the compaction and permeability behaviour.

Research on the initiation and the development of the excavation-damaged zone

Introduction and overall objectives

The host rock forms a natural barrier isolating the geological repository from the biosphere. However, repository construction will lead to the development of a damaged (EDZ) and/or a disturbed zone (EdZ). The extent and the characteristics of the affected zone may vary significantly. The confinement properties of the host rock can be locally altered, especially in the vicinity of the disposal galleries and access shafts, providing higher permeability for water and gases. This potential preferential pathway for radionuclides represents one of the key issues which may affect the overall performance of a repository, particularly in scenarios with early canister and seal failure.

Summary of key activities and achievements

In situ measurements, laboratory tests on rock samples, together with desktop studies and modelling exercises carried out as part of NF-PRO have provided new information on the different phases of the damaged zone, in particular from its initiation (during, and just after the excavation period), through its intermediate evolution phase (during the exploitation of the repository) up to its long-term evolution (after the repository closure).

In parallel to the in-depth study of the different processes involved in the EDZ development and evolution (fracturing, fissuring, deformation, desaturation, thermo-hydro-mechanical damages, hydraulic release, creep and relaxation, expansion, resealing processes, etc.), existing methods and instrumentation for EDZ characterisation have been applied and

evaluated (including non destructive methods like tomography, acoustic waves, ultrasonic logging, seismic imaging techniques, etc.). Also, new *in situ* EDZ characterisation techniques such as seismic-acoustic monitoring, ultrasonic logging, seismic and geoelectric tomography and very-high-resolution ultrasonic logging, were improved and developed

In general, results from experimental work by NF-PRO indicate that for the indurated and soft clay rocks, the extent of the host rock that has been affected by geomechanical processes and/or chemical alterations is very limited, varying from a maximum of some tens of centimetres in the Ventilation II experiment in the Opalinus clay at Mont Terri and in the experimental gallery at – 445 m in the Callovo-Oxfordian formation at the Meuse/Haute-Marne URL (underground research laboratory) in Bure up to less than one metre around the experimental galleries of the HADES URL in the Boom clay.

This information, in combination with data on fracture resealing processes, water and gas properties in the damaged zone, data on radionuclide mobility in the chemically altered zone, are being integrated to assess the impact of the damaged zone on the overall performance of the near-field system. Preliminary performance assessment calculation on indurated clay (Callovo-Oxfordian argillites in France and Opalinus clay in Switzerland) have shown that the EDZ impact is in fact very limited and will not affect the overall repository safety.

Process couplings and integration in performance assessment

NF-PRO has carried out integrated analysis of the near-field evolution. These analyses have been performed for different European geological disposal concepts and host rocks and have resulted in new insights in the release of radionuclide from the waste matrix and radionuclide transport in the near field. Results from these calculations have confirmed that the near field displays a high degree of robustness and redundancy.

The studies of near-field evolution cover various processes in the context of diverse near-field disposal systems (carbon steel and copper canisters; bentonite or salt backfill) in clay, crystalline and salt host rocks. One major emphasis of the work in this area has been the focus on phenomenology, i.e. obtaining a good understanding of how the various systems evolve over time, including thermal, hydraulic (including gas), chemical and mechanical processes. Such understanding provides a foundation for evaluating the completeness of system understanding, in particular the question of what features, events and processes need to be considered in adequately describing repository evolution and in abstracting assessment models that evaluate containment and release of radionuclides. An additional aspect involves sensitivity analyses for different near-field disposal systems, which explore how various processes that influence radionuclide retention (canister isolation time, waste form dissolution, precipitation of insoluble phases, diffusion and retardation in bentonite, and hydraulic boundary conditions), along with their associated uncertainties, affect release from the near field. Such calculations provide some insights regarding the significance of the various phenomena when considered from the radionuclide retention perspective. When combined with an assessment of the scientific foundations of the various models, the results of such performance assessment studies provide valuable guidance regarding the research areas that require greatest attention in future research.

The inclusion of a strong performance-assessment perspective within the structure of a project that is predominantly focused on process understanding achieved through experimental studies and detailed modelling has proven to be challenging but rewarding. The benefits accrue from increasing the awareness of process specialists in relation to overall system behav-

iour, in addition to forcing performance-assessment specialists to examine how various detailed processes may influence the key features in the system that contribute to safety (i.e. the safety functions).

During the final year of NF-PRO, the developments in process understanding within the project were evaluated, both at the detailed process level by the appropriate specialists and by the performance-assessment specialists. This evaluation provides the basis for the present synthesis report, in which the progress in the project is placed in the context of the performance of the different near-field disposal systems and the most important areas of future research for these systems are identified.

Conclusion

The integrated project NF-PRO has investigated processes affecting the confinement of radioactive waste in the near field of a geological repository. Experimental work by NF-PRO as well as information derived from modelling studies have provided new qualitative and quantitative information on key process affecting the performance of the near-field system.

NF-PRO has brought together scientific disciplines and research teams that essentially worked independently in previous Community-supported programmes. Within NF-PRO, a strong link has been established between detailed process investigations and assessments of the overall near-field system performance: Results and conclusions derived from detailed process modelling and from experimental studies in surface and underground laboratories were applied in assessments of the overall near-field system.

NF-PRO represents an important milestone in Community-supported research on the safe geological disposal of radioactive waste and has a major strategic impact since it has strengthened the scientific-technical basis for geological disposal. Conclusions from NF-PRO have contributed to reducing remaining uncertainties. Information generated by the project is particularly significant for the assessment and the optimisation of repository designs under investigation in the European Union.

PART 2: Project execution

1 RTDC 1: Dissolution and release from the waste matrix

1.1 WP 1.1: Critical review of information and integration in NF-PRO

1.1.1 Overall objective of work package 1.1

The main objective of WP1.1 was to draft a reference document on the state of knowledge in waste form properties, key processes for waste form alteration and their couplings, in models and in source term development as well as on waste form evolution scenarios under long-term storage and disposal conditions. Information derived from this work package was applied to bring in the project existing information, to critically review this information, to establish consensus among RTDC 1 participants on remaining key uncertainties, and to adapt NF-PRO's programme of work, if appropriate.

1.1.2 Overview of work performed

1.1.2.1 Reference report on the state of waste matrix properties and alteration during long-term storage and under disposal conditions: Part 1: Reference report on the state of the art of spent fuel properties and spent fuel alteration under long-term storage and disposal conditions, and Part 2: Reference report on the state of the art of spent fuel properties and spent fuel alteration under long-term storage and disposal conditions

Participants

SCK-CEN, CEA, ARMINES

Goals/objectives of the research

The main objective of WP1.1 was to draft a reference document on the state of knowledge in waste form properties, key processes for waste form alteration and their couplings, in models and in source term development as well as on waste form evolution scenarios under long-term storage and disposal conditions. Information derived from this work package was applied to bring in the project existing information, to critically review this information, to establish consensus among RTDC 1 participants on remaining key uncertainties and to adapt NF-PRO's work programme, if appropriate.

Key results/achievements over the full duration

Based on a critical review of information on waste form/groundwater interactions with and without presence of near-field materials of the Fourth and Fifth Euratom Framework Programmes as well as from other national and international programs, two reports with reference data are created, one for spent fuel, the other for glass. SCK, ARMINES and CEA drafted a detailed description of the state of the art, which summarises the knowledge with respect of the glass and spent fuel alteration under near-field conditions. This work benefits from the synthesis reports which are currently under writing in France on the long-term evolution of glass (VESTALE) and spent fuel (PRECCI). Laboratory and *in situ* tests data as well as mechanistic and source term models are reviewed. The various current views on the key process couplings relevant to the long-term evolution of spent fuel and HLW glass under dry conditions and in presence of ground water and near field materials are documented. A quantification of remaining uncertainties of models and their parametrisation is pursued.

Detailed report

A detailed report on the execution of this part of NF-PRO's work programme is available on the NF-PRO consortium website as Deliverable D1.1.1.

1.2 WP 1.2: Experimental studies on dissolution of and release from vitrified HLW

1.2.1 Overall objective of work package 1.2

The overall objective of WP 1.2 was to assess the key processes controlling radionuclide release from HLW glass due to the interaction with groundwater and different components of the near-field sub-system. In addition, it was intended to develop a common understanding, reduce uncertainties, and quantify these key processes with their associated parameters. Information derived from this work package allowed providing the necessary input data for conceptual and mathematical model development in WP1.3.

1.2.2 Overview of work performed

1.2.2.1 Joint modular integral material experiment

Participants

CEA

Goals/objectives of the research

The overall objective of the experiments performed by CEA was to reduce remaining key uncertainties in relation to the dissolution of the vitrified HLW matrix, and the radionuclide release from this matrix, in a complex (multi-component) near-field environment. More in particular, these tests were designed to study the effect on the glass corrosion of:

- the distance between glass and clay or canister corrosion products, and
- the clay-solution equilibria.

The experiments were designed to validate existing knowledge and to make semi-quantitative observations, rather than to determine specific parameter values. For this purpose, the experiments were simulated in WP1.3 using the codes Hytec (CEA) and Phreeqc (ARMINES). This allowed for a better phenomenological description of glass dissolution in integrated conditions. Besides this, the experiments were compared with the predictions of source-term models which take into account the interaction between the glass and the near-field materials. As a result, a better evaluation and understanding of the key processes affecting the corrosion of vitrified waste in a multi-barrier near-field system, as input to RTDC5 of NF-PRO.

Key results/achievements

The deliverable report describes the following achievements:

- Realisation of the tests
    - A total of 15 integral modular tests was realised with various near-field system combinations: SON68 glass/clay, glass/magnetite/clay, glass/magnetite/clay plus silica additives,
    - Duration of the tests: 12 months (April 2006 to April 2007) for 5 tests, 24 months (April 2006 - April 2008) and more for 10 tests,
    - Solution analyses by ICP/AES and ICP/MS on 16 elements every 2 months, allows to track the evolution of the glass alteration and the physico-chemical transformation of the near-field,
    - Solid analyses of 4 of the 5 tests stopped in 2007: longitudinal sections observed with SEM/EDS
    - A total of 10 integral modular tests was realised under similar conditions at partner SCK.CEN (18 months duration). All tests were finished and analyses on were performed on transverse slices (SEM and XRD)
    - Analyses of solution: The boron and lithium release, which are tracers of glass alteration, are as expected in terms of impact of magnetite (enhances glass corrosion), clay and silica additives (slow glass corrosion) ; the comparison with SCK.CEN tests also gives coherent results, with some impact of the differing protocols (CEA tests have higher flow rates than SCK•CEN tests).

- Results
  - Glass corrosion rates: 5.10-3 to 10-2 g/m².d for glass+clay tests, 5.10-2 to 10-1 g/m².d for glass+magnetite+clay tests. Glass + magnetite + clay tests show sustained corrosion rates, which cannot be explained by the silicon sorption on magnetite (only 0.2 to 0.3 mg Si/g magnetite) and clay. They can account to a glass mass loss less than 10 g/m², much lower than the observed mass losses (40-50 g/m² after 18 months).
  - Analyses of solids: coherent with analyses of solution for glass corrosion thicknesses but fracturing observed on the glass powder grains might impact significantly the total glass surface area.
  - Evolution of pH: show marked trends but weakly correlates to the glass corrosion rates (pH plume effect) or carbonate concentrations,
  - Observations of other elements in solution: (i) Si concentrations at the outlet differ markedly for each system, being highest (80-160 mg/l) in the presence of silica additives, and lowest (10-20 mg/l) for glass+magnetite+clay. The differences are sustained in the tests from CEA, whereas they tend to converge to a constant concentration around 40 mg/l after 1 year in the tests from SCK-CEN(ii) other elements, such as Cs and Mo (present only or mostly in the glass) or Ca and Mg (mostly or only in the clay and the inlet solution), have different behaviours in the tests in the presence of silica additives, compared with the absence of silica additives. The silica additives lead to higher concentrations of Ca, Mg and Cs in the outlet solution, suggesting inhibition of precipitation. On the other hand, Mo is congruent to B in the absence of silica additives, and is retained in the solids (gel layer, precipitates) in the presence of silica additives.
  - Comparison with modelling (WP 1.3, see Deliverable D1.3.8): Good agreement between the tests and the predictions of the coupled geochemical-transport code Hytec. Nevertheless the agreement is qualitative and several mechanisms still have to be integrated especially for the description of clay behaviour. Moreover the mechanisms leading to the sustained corrosion rates in the presence of magnetite, are still to be identified and integrated.

Publications

Internal deliverables: D1.2.1 (description of the tests) and D1.2.5 (first results).
Y. Minet, J.E. Lartigue, K. Lemmens, "Study of nuclear glass - canister corrosion products - clay system by means of integral modular material tests", Poster presented at the conference "Clays in natural and engineered barriers for radioactive waste confinement", Lille, 17-20 September 2007

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D1.2.7.

1.2.2.2: Long-term corrosion tests with the HLW glass GP WAK1 with two synthetic clay pore solutions: Release behaviour of soluble and less soluble elements and identification of secondary phases

Participants

FZK-INE

Goals/objectives of the research

The long-term corrosion behaviour of simulated and high-active glass R7T7 and of the simulated HLW glass GP WAK1 has been investigated in previous EU projects by numerous corrosion tests in brines. Besides salt formations, also granite and clay formations are newly discussed in Germany as a potential repository. Even if many data already exist about the long-term corrosion behaviour of simulated and radioactive HLW glasses in aqueous solutions of clay formations, there is still need for future research. The clay formation contains besides clay minerals also Calcite. The interstitial clay water, which is in chemical equilibrium with the Calcite, could contain high carbonate concentrations. The corrosion experiments should reveal particularly the effect of the carbonate concentration on the glass corrosion, especially the release behaviour of rare earth elements and U. High CO_3^{2-}/HCO_3- concentrations in the solution may increase the solubility of these elements at high pH (> 7) due to the formation of non-sorbing anionic carbonate complexes. The results of the experiments should refine the estimated radionuclide release from the glass package into the near field. The objective of these experiments is also to enhance the exactitude of models and modelling calculations used for long-term nuclear waste glass performance assessment and to substantiate them.

Key results/achievements

Long-term corrosion tests were started in May 2004 with the glass GP WAK1 in two synthetic clay pore solutions based on the composition of the Opalinus clay water and Konrad water. Both solutions contain high salt contents, above all the Konrad water, and are rich in sulphate. The corrosion tests are performed at 50° and 90°C with and without $NaHCO_3$ and Calcite added to the solutions. Solution samples have been taken after 14, 60, 130 and 365 days and analysed by ICP-MS and ICP-AES. The pH in Opalinus clay water ranged between 8.2 and 8.6 and in Konrad water between 6.8 and 6.5 over 2 years. The Si saturation concentration at 90 °C amounts to about 90 mg/L in Opalinus water and about 50 mg/L in Konrad water. The lower saturation concentration of Si in Konrad water is caused by the high $MgCl_2$ concentration. The release of the soluble elements Li, B, Cs and Sr is rather similar both in Opalinus and Konrad water and remains nearly constant after 130 days (corrosion rates with r lower than or equal to 10^{-4} g/m^2.d). The release of Mo depends strongly on the pH value in the solution. At the lower pH conditions in Konrad water, the Mo release is clearly lower than in Opalinus water. An effect of the added carbonates on the release of Ce, Nd and U (and the rest of the elements) was not clearly visible due to the low CO_3^{2-} concentrations in the solutions even if carbonates were added. Also the different temperature of 50 and 90°C had only a small effect on the release of most of the elements investigated. The corrosion behaviour of the HLW glass in the clay pore solutions resembles the behaviour found in pure water and NaCl-rich solution at corresponding temperatures. In all these solutions the pH remains between about 7 and 9 and the pH value determines mainly, besides the temperature, the glass corrosion behaviour. The crystalline secondary phases found on the surface of the glass chips leached in Opalinus clay and Konrad water consist mainly of Powellite, Barite, Calcite, $CaSO_4$ and above all of clay-like Mg(Ca,Fe) silicates. EXAFS investigations indicate a re-

duced U coordination symmetry in the corrosion layer. Both the symmetry decrease and O_2 number increase in the corrosion layer can be explained by additional coordinated water molecules within this layer.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D1.2.8.

1.2.2.3: Joint integrated test on magnox – UO_2 glass dissolution in combination with near-field materials

Participants

UFSD

Goals/objectives of the research

The overall objective of the experiments described in this report was to determine the effect of near-field materials on the corrosion behaviour of a UK simulant HLW glass, MT2575 and to provide data for comparison with a more extensive study of SON68 glass. The experimental set up utilises a percolation cell containing various combinations of glass, clay and canister corrosion product (magnetite). The experiments were undertaken as part of the Joint Modular Integral Material Experiment at SCK-CEN, which was designed to allow qualitative and semi-quantitative validation of the present understanding of glass corrosion in the presence of near field materials.

Key results/achievements

The effect of MT2575 glass dissolution on the local pH in the near field interface was found to be small in these experiments and effectively buffered by the corrosion product and/or clay layer under the experimental conditions. The forward rate of MT2575 glass dissolution, based on B release, is a factor of ~10 greater under these test conditions, compared to batch dissolution experiments conducted at similar pH and 90 degrees Celsius. This would suggest that secondary phase formation, involving silica removal from solution, may be important in these experiments, requiring greater cumulative glass dissolution in order to maintain silica saturation. The initial glass dissolution rate was found to be greater in the presence of the magnetite corrosion product, consistent with the presence of unsaturated silica adsorption sites on the surface of this material reducing the dissolved silica concentration. At longer timescales the effect of the magnetite corrosion product on the stability of the gel-layer may also contribute to controlling the long-term glass dissolution rate, further experiments with longer duration are required to validate this hypothesis. The magnetite corrosion product layer may also be important in adsorption of other dissolved glass species, such as molybdenum. The experiments discussed here provide qualitative support for the silica concentration gradients in the near field. In combination with our previous batch dissolution studies the experiments described here have provided the first quantitative and qualitative appreciation of the dissolution behaviour of the UK MT2575 glass composition.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D1.2.9.

1.2.2.4: Joint modular integral material experiment by SCK-CEN

Participants

SCK-CEN

Goals/objectives of the research

The general objective of the experiments was to reduce the remaining key uncertainties of the dissolution of the vitrified HLW matrix, and the radionuclide release from this matrix, in a complex (multi-component) near field environment. More in particular, these tests were designed to study the effect on the glass corrosion of:

- the distance between glass and clay or canister corrosion products, and
- the clay-solution equilibria.

The experiments have been designed to validate existing knowledge, and to make semi-quantitative observations, rather than to determine specific parameter values. For this purpose, the experiments were simulated in WP1.3. This should allow a better phenomenological description of glass dissolution in integrated conditions. Besides this, the experiments have been compared with the predictions of source-term models which take into account the interaction between the glass and the near-field materials. This should allow a better evaluation of the key processes, as input to RTDC5 of NF-PRO.

Key results/achievements

The following key results are reported:

- The experiments show that the system, consisting of compact materials, is sufficiently pH buffered to avoid a pH gradient due to glass dissolution in the considered test conditions. A confirmation by tests with a better CO_2 control would be useful, but difficult to realize. Comparison with the geochemical modelling (NF-PRO report D1.3.7) shows that the experimental pH can in general be reproduced within 0.5 pH units, but this is already sufficient to cause important changes in the system. Especially the effect of magnetite is difficult to model.
- The glass dissolution rate was measured, using the mass loss of the glass pieces and the boron concentrations in solution as indicators. The results are in good agreement with the known dominating glass dissolution mechanisms, involving matrix dissolution and sorption of silica on the near field solids. The dissolution rate can be modelled relatively well, but for long-term extrapolations, the uncertainty remains large.
- Silica concentration evolutions are a key factor in understanding the impact of near field materials on glass dissolution behaviour. The experiments confirm that the concentration of dissolved silica in the pore water is a key factor in understanding the glass dissolution rate. The effect is particularly clear in the case of the addition of magnetite, where Si sorption clearly leads to lower Si concentrations in solution, and faster glass dissolution. The results also suggest, however, that other effects need to be taken into account to explain the dissolution rate in the considered systems, such as the formation of a protective layer. Whether this needs to be taken into account for source term calculations, it will depend on the details of the disposal concept (type of materials). The added amorphous silica could not impose high silica concentrations for a long time. More in general, this suggests that the addition of siliceous additives or

glass frit to the near field cannot guarantee high silica concentrations for a long time. Long-term predictions, based on models making such assumption, are therefore insufficiently validated. The quantitative understanding of the Si/clay and Si/magnetite interactions in the considered complex system is still insufficient.

- The experiments allow estimating the silica concentrations in the pores of the various component layers in the reactor, assuming that the evolution in the upstream compartments is not much influenced by the evolution in the downstream compartments. At the interfaces, concentration gradients will occur. It appears that silica concentration gradients develop as expected in most cases, with the higher concentrations in the compartments with the most soluble silicates (or glass). Hence, we can conclude that concentration gradients through the various near field layers have been experimentally confirmed.
- The experiments suggest that the effect of the magnetite will be only of short duration. The overall impact of the presence of a metallic overpack is probably favourable for the glass life time, rather than penalizing.
- The XRD analyses on the glass-, magnetite and clay plugs at the end of the test showed only minor mineralogical changes. There were no indications for the formation of iron rich clay at the magnetite/clay interface, or for the formation of crystalline secondary glass phases. The formation of chalcedony (predicted by the models) could evidently not be proved by the XRD (chalcedony is amorphous).

Publications

Karel Lemmens, Christelle Cachoir, Elie Valcke, Karine Ferrand, Marc Aertsens, Thierry Mennecart,
"The strategy of the Belgian Nuclear Research Centre in the area of High-level waste form compatibility research" , Proceedings of ICEM2007, September 2-6, 2007, Oud Sint-Jan Hospital Conference Center, Bruges, Belgium.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D1.2.10

1.3 WP 1.3: Assessment of the glass source term by geochemical and kinetical modelling

1.3.1 Overall objective of work package 1.3

The principal objective of NF-PRO's Work Package 1.3 was to confirm, to adapt and to develop models for a mechanistic source term for glass corrosion and associated radionuclide release under near-field conditions, including model for secondary solid solution formation and compilation of a dataset for modelling solid solution formation under near field conditions.

1.3.2 Overview of work performed

1.3.2.1 Adaption of long-term behaviour of the coupled system Clay + Corrosion products + Glass

Participants

ARMINES

Goals/objectives of the research

The objective of the contribution of SUBATECH was to adapt a glass dissolution model to near field constraints caracterised by the presence of iron corrosion products and clay and to apply the model both to the experimental data gathered in WP1.2 and to the long-term performance of nuclear waste glass;

Key results/achievements

It was initially planned to use the model GM2003/4 for the project. However, even if this model describes the glass corrosion process in the simple glass water system very accurately (the model was tested in the project GLAMOR) it was decided to base the modelling on the coupled geochemical and transport code PHREEQC, since this code, even if less accurate for the glass, provides a much better representation of near field equilibria, transport and mass balance constraints. So a glass dissolution model for the simple glass/water system was developed on the basis of PHREEQC governing glass dissolution by a first order rate law and describing gel layer formation by a solid solution model. In the same way sub models were calibrated for the clay/water system and the iron/iron corrosion product/water system. All subsystems were calibrated with pertinent data. The coupling of the various sub systems to one overall system considering as well transport processes allowed application of the model to the experimental data from WP1.2 (joint modular experiment) and as well long-term predictions. Key experimental observations were described qualitatively correct: important role of dissolved silica in slowing down reaction rates, sorption of dissolved silica on magnetite increasing reaction rates, stabilising effect of silica additives, pH evolution) but a detailed quantitative agreement of experimental data and model was not always achievable due to (1) an inadequate representation of the hydrodynamic conditions in the flow through reactor by a constant permeability and porosity, (2) due to missing temperature dependent data for silica sorption on magnetite and for clay water interactions as a function of temperature.

Publications

The results are summarized in 2 deliverables:
D1.3.1 on "Selected models and modelling predictions on the joint modular experiment in WP1.2" by S. Ribet and B. Grambow (the deliverable exists in an updated version from the 15th Dec. 2007)
and
D1.3.4 on "modelling of corrosion, sorption and diffusion processes in the near field" by S. Ribet and B. Grambow. (this deliverable contains the long-term predictions by the model and it exists as a updated version from 15th Dec; 2007.
Some preliminary results have been presented at the MRS conference 2005 in Gent: The contribution is published : Grambow, Giffaut, "Coupling chemical processes in the near field" Mat Res. Soc. Symp. Proc. 932, 421-432 (2006) Warendale, PA, USA

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D1.3.7

D1.3.2.2: Modelling of integral modular material experiments using the Hytec geochemical code - Proposition of a source term

Participants

CEA

Goals/objectives of the research

The main objectives of research performed by CEA in the framework of NF-PRO's WP 1.3 were:

- To reproduce and explain the results and observations of joint integral glass corrosion tests performed by SCK.CEN and CEA in the framework of Workpackage 1.2, using the coupled geochemistry-transport model Hytec
- To make propositions of a source term model based.

Key results/achievements

The current report includes the following main results and achievements:

- The main goal of the first study is the simulation, by means of a coupled geochemistry-transport model, of the results of glass corrosion tests in presence of model near-field materials : magnetite as a substitute for corrosion products of metallic canisters, and engineered barrier clay. The tests, realised jointly at SCK.CEN and CEA Marcoule, are described in Deliverable D1.2.7. The simulations have been done using the code HYTEC (van der Lee, 2004), which couples chemical reactions and transport in porous media. The different stages of the construction of the model gave been detailed. They consist in describing the reactivity of each material used in the tests. The reactions considered in the simulations are extracted from published data for each individual material, yet generally studied in isolation. The effect of each new reaction added to the physicochemical system is illustrated with respect to the change of glass corrosion rate such change causes. When the clay layer is described in terms of acido-basic properties and silica sorption capacity, and the magnetite layer is described in terms of silica sorption capacity, the evolution of silicon and boron concentration in solution as measured in the tests is fairly well reproduced. Nevertheless those simulation results should be considered as preliminary since the interpretation of the experimental data is still underway. Different proposition for improvement of the model are discussed.
- The second part are propositions for a preliminary source model based on the “V0 --> Vr” model are updated in the light of the studies of sorption isotherms of magnetite performed by CEA and SCK.CEN, and in order to make some simplifications when taking into account the period of saturation of the metallic corrosion products at high glass alteration rate.

Publications

Trotignon L., Lartigue J.-E., Bilstein O. et De Combarieu G. (2005). Modélisation géochimique des argilites du Callovo-Oxfordien : élaboration et application d’un modèle utilisable dans des scénarios de champ proche simplifiés (contribution au projet NFPRO), CEA internal document.

Lartigue J.-E., Trotignon L. et de Combarieu G., Modélisation préliminaire des expériences intégrales NFPRO à l'aide d'un code couplé chimie-transport(2006), CEA internal document
Lartigue J.-E., Modelisations à l'aide du code Hytec d'expériences intégrales menées dans le cadre du programme européen NFPRO. Contribution au rapport final (2007), CEA internal document.
Y. Minet, J.E. Lartigue, K. Lemmens, "Study of nuclear glass - canister corrosion products - clay system by means of integral modular material tests", Poster presented at the conference "Clays in natural and engineered barriers for radioactive waste confinement", Lille, 17-20 September 2007

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium deliverable D1.3.8.

D1.3.2.3: Final report on the contribution by FZK-INE to NF-PRO's WP1.3

Participants

FZK-INE

Goals/objectives of the research

The aim of the contribution by FZK-INE to NF-PRO's WP 1.3 was to outline the status of knowledge of solid solution formation with trivalent actinides and two key secondary phases with respect to HLW glass corrosion in clay pore water. Rather than providing an exhaustive list of phenomenological observation of actinide containing secondary phases that form during long-term HLW glass corrosion experiments, here Powellite ($CaMoO_4$) and Calcite ($CaCO_3$) have been selected. Powellite is a prominent secondary phases that seems to be capable of incorporating significant amounts of trivalent actinides. Calcite is considered a reference compound at this stage, since it is expected that carbonate based secondary phases will form during HLW glass corrosion in carbonate rich clay pore water (RTDC WP1.2 , INE-FZK contribution).
The focus of this study is on molecular level understanding of the substitution mechanisms and deriving thermodynamic mixing data. However, at first some further details on solid solution aqueous solution equilibria are introduced.

Key results/achievements

Deriving thermodynamic data on solid solution formation as a consequence of structural incorporation of trivalent actinides into a crystal lattice of a host mineral is a challenging task. It requires (1) a molecular level understanding of the actual incorporation, (2) deriving thermodynamic mixing data and (3) considering kinetic effects for SSAS equilibria at repository relevant temperature conditions. At this stage it is not possible to derive the activity coefficients in the powellite and calcite solid phase as a function of the actinide/lanthanide content. Clearly, there are ways to determine the missing data experimentally.
The understanding of structural incorporation of trivalent actinides and lanthanides could be significantly improved. It seems reasonable to expect that sufficient thermodynamic mixing data will be derived for these two selected key secondary phases within NF-PRO, to be able to describe actinide/lanthanide uptake during secondary phase formation quantitatively. It should also be emphasized that in principle, the same concepts can be expanded to secondary solid solution phases which form during spent fuel corrosion (WP1.1).

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium deliverable D1.3.9

D1.3.2.4 Adaption of source term model and introduction of automatic fitting routine

Participants

SCK-CEN

Goals/objectives of the research

The main objective of the task was to couple a glass dissolution model (the GM model) with a fit program so that automatic fits can be obtained for this model.

Key results/achievements

A new code has been written for an improved GM model, called Brag, allowing obtaining automatically optimal fit parameter values. Due to remaining conceptual uncertainties of the underlying models, these parameter values need to be regarded with care. The code has been made available on the NF-PRO portal.

Publications

Aertsens M., *The BRAG and GM2003 models for glass dissolution.* Accepted for publication in the proceedings of MRS 2006

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium deliverable D1.3.10

1.4 WP 1.4: Evolution of spent fuel prior to water ingress (normal evolution scenario) and during the transient period (early failure scenario) and impact on radionuclide release

1.4.1 Overall objective of work package 1.4

WP 1.4 included research on the assessment of the evolution of spent fuel prior to water access (normal evolution scenario) and the early failure scenario and impact on radionuclide release in view of providing a description of the initial condition of spent fuel that is intended for disposal in a geologic repository

Information derived from this work package will allow quantifying the instant radionuclide release fraction and its evolution with time. Emphasis will be on fission products and actinides that are available for rapid release on first contact by water and on the evolution of the micro structural stability of spent fuel as a function of time.

1.4.2 Overview of work performed

1.4.2.1 Grain boundaries characteristics in spent nuclear fuel after irradiation: Literature review

Participants

CEA

Goals/objectives of the research

The objectives of this contribution by CEA to NF-PRO were to establish a review of published and unpublished data on the grain boundaries properties in irradiated fuel after removal from reactor. This initial state will condition the evolution of grain boundaries in disposal before water ingress in the container.

Key results/achievements

There are very few data reported in literature on the mechanical state of grain boundaries after irradiation. Most data focus on the presence of fission gases and fission products in grain boundaries. The presence of fission gas bubbles and metallic precipitates can be correlated to the mode of failure, inter- or intra-granular observed by SEM on fractographs. Various modes of failure are observed as a function of the radial position in the fuel pellet. Most part of data reported in this report is issued from CEA examinations. The literature available data do not allow correlating the mechanical state of grain boundaries in the spent nuclear fuel pellet with the irradiation history.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium deliverable D1.4.1

1.4.2.2: Description of the analytical model of grain boundary evolution

Participants

CEA

Goals/objectives of the research

The release of radionuclides by spent fuel assemblies under disposal conditions is classically described by two terms: an Instant Release Fraction (IRF) which quantifies the rapid release of activity when water arrives and contacts the fuel surface, and a Matrix Alteration Model, which quantifies a slower release rate of activity in water. The IRF has been defined as the fraction of activity which is located within the regions of the spent fuel rod with low long-term confinement properties. Presently, there is not an international consensus on the evolution of restructured zones and grain-boundaries, and different values of IRF have been proposed to the end users.
In the framework of the French PRECCI project, studies have been focusing for some years on helium diffusion and solubility in spent fuel. However helium fate in the spent fuel remains to be assessed. The first part of this report briefly presents the state of knowledge concerning the grain-boundaries properties of spent fuel after removal from the reactor. These data are based on post-irradiation examinations. Furthermore, fast heating of spent fuel may lead to the loss of grain boundaries (GB) cohesion in high burn up fuels. This behaviour is considered possible as due to the over-pressurization of the inter-granular fission gas bubbles during these experiments.

Key results/achievements

In order to quantify the long-term effect of helium on the spent fuel microstructure, many questions have to be addressed, such as:

- *Can fission gas bubbles be pressurized by helium?*
- *What is the effect of cumulated a-decay damage on helium diffusion?*
- *What is the condition for micro-crack initiation and propagation in grains?*
- *How to relate classical mechanical tests of rupture to a critical pressure in grain boundaries bubbles?*

The behaviour of fission gases (FG) in fuel during irradiation has been widely studied and is relatively well known. A comparison between in-reactor and out-of-reactor conditions will be used to identify mechanisms of helium migration in spent fuel under repository conditions. The potential evolution of FG intra-granular bubbles with helium accumulation as well as the stress conditions for spent fuel rupture is given. Results are presented for UO2 spent fuels at different burn up.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D1.4.3

1.4.2.3: Report on the first characterisation of grain boundary stability within irradiated fuels

Participants

CEA

Goals/objectives of the research

In repository, a fraction of the radionuclides (RN) inventory will be rapidly released from the spent fuel rod. In the framework of the European "*Spent Fuel Stability under Repository Conditions*" project [1] the so-called Instantaneous Release Fraction (or IRF) has been defined as the fraction of the inventory of safety-relevant radionuclides, which is located in fuel microstructures for which no confinement properties is anticipated or can be demonstrated at the time of canister breaching.
Hence, the IRF depends on (1) the intrinsic evolution of the spent fuel pellet microstructure before the canister breaching (i.e. during~10 ky.); (2) RN distribution within the spent fuel rod after discharge from the reactor and (3) its evolution with time before canister breaching.
IRF best and pessimistic estimates have been proposed by Johnson *et al.* [2005] for PWR UO_2 fuels. These values take into account uncertainties on the spent nuclear fuel (SNF) evolution during a confinement phase of 10,000 years prior to the canister breaching. The IRF values of the key-safety-relevant radionuclides are updated considering the recent results issued from the European NF-PRO and French PRECCI projects on (1) the diffusion processes in spent fuel, (2) evolution of the pellet microstructure with helium accumulation and (3) leaching data.

Key results/achievements

The effect of He accumulation on the spent fuel pellet microstructure and diffusion processes have been re-assessed. It allows diminishing the conservatism of the former IRF values of key safety relevant radionuclides for PWR UO_2 fuels.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D1.4.4

1.4.4.24: Final activity report for CEA, WP1.4

Participants

CEA

Goals/objectives of the research

CEA coordinated NF-PRO's Work Package 1.4, in which the spent fuel evolution prior to the canister breaching and full re-saturation is investigated. As part of Work Package 1.4, CEA:

- performed a literature review on grain boundaries characteristics in spent nuclear fuel after irradiation. This work is reported as NF-PRO project deliverable D1.4.1;
- assessed the evolution of the spent fuel microstructure with the accumulation of helium under geological disposal conditions. To this end, CEA performed Vickers indentation tests in order to correlate the fracture type (intra- or inter-granular) to the local burn up of the UO_2 spent fuels. This work is reported as NF-PRO project deliverable D1.4.3.
- performed R&D on the in repository spent fuel source term. In particular, the Instant Release Fraction was updated.

Key results/achievements

This report summarises the contributions by CEA to NF-PRO's Work Package 1.4. A detailed report on R&D by CEA is available through the following links:

- Literature review on grain boundaries characteristics in spent nuclear fuel after irradiation (NF-PRO deliverable D1.4.1);
- Evolution of the spent fuel microstructure with the accumulation of helium under geological disposal conditions (NF-PRO Deliverable D1.4.3);
- Update of the Instant Release Fraction/spent fuel source term under geological repository conditions (NF-PRO project deliverable D1.4.4)

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D1.4.12

1.4.4.25: Final activity report for CIEMAT, WP1.4 on spent fuel evolution

Participants

CIEMAT

Goals/objectives of the research

CIEMAT investigated co-precipitation phenomena of dissolved spent fuel in different media, and focuses on the results obtained from precipitation and co-precipitation tests performed with simulated spent fuel saturated solution of granitic-bentonitic groundwater. This scenario would take place after »10.000 years of disposal following contact between the groundwater and the spent fuel. The α-radiation field will also have a major effect on the spent fuel alteration process, and also as regards assessment of the influence of this a radiation field on the U secondary phases formed and the final concentration value obtained for U and Pu.

Key results/achievements

The presence of low alpha radiation field in solution has a strong influence on the solubility of the matrix (uranium concentration). This fact, extrapolated to performance assessment studies, could have a critical influence on the alteration rate extrapolated and, of course, in the stability of the matrix considered. Whether from leaching studies the existence threshold of alpha radiation field has been proposed, when the influence of radionuclides dissolved on the groundwater radiolysis is considered this affirmation is not so clear. Because the results obtained show a clear increase of the uranium solubility with a low amount of alpha radionuclide in solution (10-13 mol·kg-1 of H_2O in 238Pu). An increase in more than three order of magnitude on the U mean concentration achieved were observed for experiments performed in similar conditions (as a function of pH) with and without low alpha radiation field presence.
Microstructural characterization by XRD, SEM-EDX, and TEM-EDX allow us to specify, the following:

- In anoxic conditions and in the absence of ionization radiation fields, sodium uranate and schoepite (absence Fe) formation was characterized. On the other side, when Fe was present, the secondary phase formed was a calcium sodium uranate.
- SEM and TEM characterization studies revealed the formation of precipitates with none larger than 3 mm grain size. Morphology for this precipitate is laminar, and shows habits of facetted growth.
- In absence of Fe, grain size processes were not observed because precipitation happened due to the coalescence of different grains of smaller size.
- In the presence of Fe, the growth of U phase over the surface of Fe, is observed without discontinuity between these materials.

Publications

J. Quiñones, E. Iglesias, J. M. Cobo, A. Martínez Esparza, and J. M. Gomez de Salazar, "Microstructural characterization of U coprecipitated phases formed in bentonitic-granitic groundwater and under anoxic conditions," in *Scientific Basis for Nuclear Waste Management XXX*. vol. 985, D. Dunn, C. Poinssot, and B. Begg, Eds. Warrendale, Pennsylvania. USA: Material Research Society, 2007, pp. 123-128

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D1.4.13

1.4.4.26: Final activity report for work performed by EC-JRC-ITU on spent fuel evolution

Participants

EC-JRC-ITU

Goals/objectives of the research

The work out at the Institute of Transuranium Elements (ITU) in WP1.4' relates to the evolution of spent fuel prior to water ingress (normal evolution scenario) and during the transient period (early failure scenario) and impact on radionuclide release' in the frame of NF-PRO.
ITU has contributed to WP1.4 with source term investigations to determine the fraction of inventory of fission products and actinides that might be released rapidly when spent fuel comes in contact with water. In particular the grain boundary inventory of MOX fuel was investigated as an important component of the so-called instant release fraction (IRF). For these studies an innovative approach combining Knudsen cell effusion measurements and leaching experiments was implemented to get additional information (see chapter 3).
A further objective of WP1.4 was to improve knowledge on the microstructural properties of spent fuel and their possible changes in the normal evolution scenario and during the early failure scenario. Here the mechanical stability of spent fuel is important because it affects the surface area of fuel available for leaching. The effects of alpha decay damage on the mechanical stability of spent fuel was investigated using alpha doped UO_2 and $(U,Pu)O_2$ (see chapter 4). The techniques used were SEM/TEM and XRD combined with annealing steps.
Finally, also potential alteration processes of the spent fuel during the transient phase between initial breach of the canister and water ingress in the canister (early failure scenario) were investigated. This work involved experiments with fuel segments that contained intentionally manufactured defects in the cladding and the exposure of these segments to a water-saturated atmosphere containing argon and/or hydrogen to simulate the atmosphere inside the canister emplaced in a geologic repository. The condition of the fuel inside the cladding was evaluated at the end of the experiments (see chapter 5) by SEM/EDS while gas and liquid phase were examined by mass spectrometry.

Key results/achievements

Grain boundary inventory and instant release fractions for MOX
An estimation of the grain boundary inventory of species belonging to the so called "labile fraction" for MOX fuel was carried out performing leaching tests on fragment and powder samples of SBR MOX. The experimental results indicate that fractions typically $\leq$1 % are released from grain boundary for the species showing fractional release higher than U, i.e. Rb, Sr, Mo, Cs, Tc, Ba, if only the amounts released after removing pre-existing oxidized layers on the sample are considered. By including also the amounts released during the initial "washing" cycles, the highest observed release falls typically between 1 and 2 % for all these species except Ba; the highest value for the fraction released was determined for Cs-133 (2.3%).
These values are generally lower than labile inventory values reported in literature from tests on UO_2 including also gap contributions. They are in satisfactory agreement with the data reported specifically for grain boundary inventory of low to medium burn-up UO_2. A good convergence was observed between the results obtained from leaching and those produced by

annealing studies. This is very promising in view of extending and deepening this type of investigation, especially if one considers the complementarities of the techniques.
From the point of view of the applicability of these results to the determination of IRF for spent fuel in a geologic repository, the findings confirm the conservative nature of the approaches adopted so far to define IRF values, and contribute to a better understanding of specific properties and behaviour of irradiated MOX fuel in terms of initial corrosion stages upon exposure to groundwater.
Alpha decay damage evolution
The UO_2 lattice is able to dissolve only low quantities of helium, but the gas in excess of the solubility limit will be accommodated in the porosity or bubbles present in irradiated fuel. The damage evolution due to alpha-decay will affect locally the microstructure. The recovery of the lattice parameter occurs at temperature higher than expected during storage and a lattice swelling of 2 % can be expected. The studies on alpha-doped UO_2 have been performed on samples up to 3 dpa of damage corresponding to a standard irradiated UO_2 fuel after 10000 years of storage. Regarding the stability of the spent fuel, the preliminary conclusion is that the alpha-damage and the precipitation of helium in regions with low porosity or few pre-existing trapping sites (bubbles) produced during irradiation could lead to a potential micro-cracking and local loss of cohesion. This may be the case e.g. for the high temperature region of irradiated fuels.
Evolution of spent fuel in steam
The complete experimental equipment including an autoclave, an oven, a gas-sampling system and all the electrical connections were installed inside a hot cell during normal operation and adapted to remote handling by tele-manipulators. Three experiments were carried out at 90°C in humid atmosphere composed of, respectively, 1) pure Ar, 2) mixture of Ar and H_2, and 3) pure H_2.
SEM investigations show a significant surface change in the area of the intentionally set defect only under Ar. On both rodlets exposed to a moist hydrogen-containing atmosphere, no fuel surface alteration could be seen.
EDS analysis of the hydrogen-exposed surfaces showed, in addition to uranium, only the presence of fission products caesium and barium at the outer periphery of the fuel pellet, near the fuel cladding. Here also zirconium traces were found.
In addition to surfaces, also gaseous and aqueous phases were analysed by mass spectrometry. A gas pressure increase was observed in all cases. It was 0.3 – 0.5 bar during the test under argon Under hydrogen, the total pressure increase was ~2 times lower (0-0.2 bar (H_2/Ar), 0.1-0.2 bar (H_2)). The main component was in all experiments fission gas Xe. Under argon also radiolytically produced H_2 was detected. A possible explanation for the high fission gas release could be the opening of pathways for release from pressurized gas bubbles in the fuel. The oxygen content in all gas samples was below the detection limit (<10 ppm).
Due to the high humidity in the autoclave, the fuel rodlet was covered by a thin water film. Also condensation near the top cover of the autoclave can not be excluded. This water film allowed the transport of released nuclides into the water reservoir at the bottom of the autoclave. ICP-MS analysis of water samples after the test confirmed that significant dissolution occurred for the mobile fission products Cs and I. Other fission products were also detected, but their concentration was orders of magnitude lower. In the case of redox-sensitive technetium, the release decreased from Ar to H_2/Ar to pure H_2. Mo showed a slight decrease in solution going from Ar to H_2.
The presence of relatively large amounts of Cs and I in solution is not an indication that matrix corrosion occurred. Mobile fission products Cs and I are not only located in the fuel matrix, but also at grain boundaries, in the fuel-cladding gap and on fuel surfaces. Here they are easily accessible to water and are released as part of the instant release fraction. Moreover, the

very low concentrations of matrix species would support the conclusion that very limited or no matrix dissolution occurred. This is also supported by the lower gas pressure increase in presence of H_2, and the correspondingly lower release of Tc and Mo. SEM investigations show a significant surface change only under Ar.
These experiments have produced evidence that the presence of hydrogen leads to a reduced matrix alteration also under moist atmosphere conditions.

Publications

Vincenzo V. Rondinella, Detlef Wegen, Joaquin Cobos, Daniel Serrano, Dimitri Papaioannou, T. Wiss, *MOX CHARACTERIZATION*, NF-PRO Deliverable (D-N°: 1.4.5), 2006

D.H. Wegen, D. Papaioannou, J.P. Glatz, P. Carbol, P. Fors, S. van Winckel, D. Serrano-Purroy, *Condition of spent fuel and cladding after exposure to a steam atmosphere*, NF-PRO Deliverable (D-N°: 1.4.6), ITU Technical Report Nr. JRC-ITU-TPW-2007/04

Vincenzo V. Rondinella, Jean-Pol Hiernaut, Detlef H. Wegen, Dimitri Papaioannou, *DETERMINATION OF GRAIN BOUNDARY INVENTORY OF VOLATILE SPECIES IN SBR MOX FUEL USING THE KNUDSEN CELL TECHNIQUE*, NF-PRO Deliverable (D-N°: 1.4.7), ITU Technical Report Nr. JRC-ITU-TPW-2007/05

T. Wiss, D. Staicu, V.V. Rondinella, R. Jardin, J-P. Hiernaut, *TEM analysis and XRD annealing study on alpha-doped UO2*, NF-PRO Deliverable (D-N°: 1.4.8), ITU Technical Report Nr. JRC-ITU-TPW-2007/06

Daniel Serrano-Purroy, Detlef Wegen, Vincenzo V. Rondinella, *CHARACTERISATION OF IRRADIATED MOX FUEL: CHARACTERISATION OF MOX CRUSHED SAMPLES*, NF-PRO Deliverable (D-N°: 1.4.9), ITU Technical Report Nr. JRC-ITU-TPW-2007/07

Daniel Serrano-Purroy, Vincenzo V. Rondinella, Detlef Wegen, *CHARACTERIZATION OF IRRADIATED MOX: STATIC LEACHING REPORT*, NF-PRO Deliverable (D-N°: 1.4.10), ITU Technical Report Nr. JRC-ITU-TPW-2007/37

D.H. Wegen, D. Papaioannou, P. Carbol, P. Fors, S. van Winckel, J.P. Glatz, K. Spahiu, *DEFECT RODLETS IN STEAM UNDER Ar AND Ar/H2: REPORT ON THE CONDITION OF SPENT FUEL AND CLADDING AFTER EXPOSURE TO HUMID Ar/H2 AND H2 ATMOSPHERE*, NF-PRO Deliverable (D-N°: 1.4.11), ITU Technical Report Nr. JRC-ITU-TPW-2007/21

D.H. Wegen, V.V. Rondinella, T. Wiss, D. Serrano-Purroy, J.P. Glatz, D. Staicu, D. Papaioannou, J-P. Hiernaut, P. Fors, S. van Winckel, P. Carbol, R. Jardin, FINAL ACTIVITY REPORT (EC-JRC-ITU), NF-PRO Deliverable (D-N°: 1.4.14), ITU Technical Report Nr. JRC-ITU-TPW-2007/35

C. Ferry, A. Poulesquen, C. Poinssot, B. Grambow, K. Lemmens, C. Cachoir, *Part 2: Synthesis report 2005 (spent fuel)*, NF-PRO Deliverable (D-N°: 1.6.1), 2006

B. Grambow, K. Lemmens, Y. Minet, C. Poinssot, K. Spahiu, D. Bosbach, Ignasi Casas, J. de Pablo, Javier Giménez, S. Gin, J.P. Glatz, N.C. Hyatt, E. Iglesias, B. Kienzler, B. Luckscheiter, A. Martinez-Esparza, V. Metz, A. Ödegaard-Jensen, K. Ollila, J.Quiñones, Alexandra Rey, S. Ribet, N. Rodriguez, G. Skarnemark, D. Wegen, V.V. Rondinella, T. Wiss, F. Clarens, E. Gonzalez-Robles, D. Serrano-Purroy, *Final Synthesis Report, RTD Component 1: Dissolution and release from the waste matrix*, NF-PRO Deliverable, 2007

D.H. Wegen, S. Van Winckel and P. Fors, *Behaviour of Defect Fuel Rodlets in Humid Inert Gas Atmosphere*, Spent Fuel Workshop 2007, September 11 – 12, 2007 – Böttstein, Switzerland

D.H. Wegen, V.V. Rondinella, D. Serrano-Purroy, T. Wiss, J.-P. Hiernaut, *Spent Fuel Research at ITU*, NF-PRO's Fourth Workshop, October 15-17, 2007 - Brussels, Belgium

V.V. Rondinella, T. Wiss, J.-P. Hiernaut, "*Dose Rate Effects on the Accumulation of Radiation Damage*", Proc. ICEM'07-11th International Conference on Environmental Remediation and Radioactive Waste Management, 2-6 September 2007 Bruges (B) ASME / TiV / BNS.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D1.4.14

1.4.4.27: Final activity report on the contribution by ENRESA to WP1.4

Participants

ENRESA

Goals/objectives of the research

The main goal of the research is to show the effect of the BU and irradiation history on Instant release fraction of radionuclides included into the spent fuel matrix. This fraction is the most important at short and long-term storage. There aren't data or are very scarce on high burnup LWR spent fuel instant release fraction.
The depth of the layer, known as the High Burn-Up Structure (HBS), grows with the BU and depends on the irradiation history [Walker et al., 2006]. The main objective of this ENRESA contribution was to quantitatively assess the initial IRF(t=0) as a function of burn-up (BU) with an emphasis on the effect of HBS. For these reasons, in the present work, two samples, one prepared from the centre of the pellet (labelled Core) and the second from the fuel pellet periphery, enriched with HBS (labelled Out), has been used to study the confinement properties of the HBS to better assess the IRF and long-term matrix dissolution rates. Different leaching conditions, i.e. synthetic (BW) bicarbonate and Bentonite Granitic Groundwater (BGW) will be used in static reactors under oxidising conditions.
The main objectives deal with the following matters or activities:

- Review of the state of the art on spent fuel fast release of radionuclides and generation of activation products from pellet and cladding impurities.
- Selection of an irradiation History and BUs for study the influence on the release.
- Selection and cutting of the fuel specimens to test.
- Radionuclide Inventory measure in the different areas: core (inner) and rim (outer) regions.
- Inventory of some radionuclides which for different reasons can't be quantified experimentally as: Se-79, Cl-36, C-14, Cl-36 as a first step for modelling their fast release fraction.
- Characterization of spent fuel specimens before leaching by SEM analysis.
- To correlate the surface available for leaching with the total grain boundary (or HBS pores), factors had been calculated based on SEM analysis (at least on three images) and geometrical considerations between particle and grain size.
- Effect of the groundwater composition on instant release fraction.
- Dynamic and static test at different atmospheres.
- Tests at different atmosphere conditions.
- Evaluation and discussion of the results of fast release and matrix release.

A summary of the samples studies of HBU (high burn-up) and MBU (medium burn-up) is summarised in Table 1 hereafter:

Experiment	*Fuel*	*Leaching solution*	*Sample weight (g) (S/V (m-1))*	
Core	Out			
I	HBU	BW	0.2529 (132)	0.2579 (113)
II	HBU	BGW	0.2468 (131)	0.2544 (112)
III	MBU	BW	0.2669 (108)	0.2650 (70)
IV	MBU	BGW	0.2545 (106)	0.2503 (197)

BW bentonitic water
BGW Bentonitic granitic water

Key results/achievements

The Fast Release Table on core and out area for two spent fuels of high burnup and medium burnup based in experimental measures are given hereafter:

Summary of IRF (t=0) as a function of BU in % of total inventory(conservative approach based on 3 weeks determination)

	MBU-Bic		***MBU-BGW***		***HBU-Bic***		***HBU-BGW***	
Element	**Core**	**Out**	**Core**	**Out**	**Core**	**Out**	**Core**	**Out**
Rb	7.0	0.4	3.5	1.8	0.8	0.7	2.2	1.0
Sr	4.0	0.1	2.1a	0.03a	1.0	0.9	2.1	0.6
Y	1.1	0.01	0.9	0.1	0.4	0.2	1.3	0.5
Zr	0.01	0.001	0.1	0.02	0.13	< 0.001	0.01	< 0.001a
Mo	1.9	0.1	1.1	0.4	1.5	0.9	2.5	0.9
Tc	0.9	0.3	0.9	0.7	0.9	0.4	0.9	0.4
Ru	0.02	0.01	0.01	0.01	0.03	0.03	0.03	0.04
Rh	0.02	0.01	0.02	0.02	0.1	0.1	0.1	0.1
Cs	5.6	0.6	2.7	1.4	1.1	0.7	1.6	1.1
Ba	2.1	0.3	2.2	0.4	1.8	1.0	2.1	0.8
La	0.1	0.004	0.5	0.1	0.1	0.1	0.7	0.3
Nd	0.2	0.002	0.3	0.04	0.1	0.1	0.3	0.2
U	0.1	0.001	0.1	0.03	0.1	0.1	0.1	0.03
Np	1.2	0.04	0.9	0.2	0.8	0.2	1.0	0.3
Pu	0.2	0.02	0.1	0.04	0.3	0.1	0.1	0.1
Am	0.1	0.003a	0.1	0.02	0.2	0.05	0.03	0.1
Cm	0.1	< 0.001a	0.1	0.03	0.3	0.1	0.2	0.1

For more details on inventories and concentrations and uncertainties of the measures see the D.1.4.15 report.
Lower release is observed for the Out sample than for the Core sample. This can be explained by the fact that during irradiation soluble volatile elements migrate to the grain boundary. This effect is higher in Core area fuel due to higher temperatures.
The effect of Burn-Up needs a further more detailed study as no clear tendencies can be found. In general, higher release of Cs and Rb can be observed for MBU; while other RN shown lower release, especially in the case of Out sample.
With the exception of results from Core MBU fuel, slightly higher release is observed for BGW compared to Bicarbonate water. Influence of water leaching solution means that IRF (t=0) should depend also slightly on the surrounding conditions.
Partitioning of inventory radionuclides into the different parts is dependent of the burnup too.

Cladding inventory and fission gas release has been measured for both spent fuel specimens, but it's not included in the scope of this report.
Some relevant radionuclides which can't be quantified by ICP-M analysis as
Se-79, Cl.36, C-14 and Sn-129 has been quantified by calculation as a first step for develop of a release model or try to develop an analytical method adequate for measuring in its range.
Results of calculated inventory have showed an effect of burnup on the inventory and of the irradiation history made by calculation (see D1.4.15 for more details).

Publications

Publications/Meetings
Results obtained within this task had been discussed and presented in several meetings.

- Frederic Clarens, Daniel Serrano-Purroy, Aurora Martínez-Esparza, Jean Paul Glatz, Joan de Pablo, Detlef Wegen, Birgit Christiansen, Ignasi Casas Poster contribution: "Instant Release of Spent Fuel as a function of Burn-up. Studies with High Burn-up Fuel: Preliminary Results" to the Third NF-PRO workshop held in EL Escorial, (Madrid, Spain) on 14-17 November, 2006.
- NF-PRO RTDC1. Final Meeting on SF. 22-23 January, 2007. Saclay, France.
- Oral presentation and proceedings submitted. F. Clarens, D. Serrano-Purroy, A. Martínez-Esparza, D. Wegen, E. Gonzalez-Robles, J. de Pablo, I. Casas, B. Christiansen and J.P. Glatz "RN fractional release of High Burn-Up fuel: effect of HBS and estimation of accessible Grain Boundary." In XXXI Scientific Basis for Nuclear Waste Management. MRS Conference. 18-21 November. Sheffield, England.
- F. Clarens, D. Serrano-Purroy, A. Martínez- Esparza, J.-P. Glatz, J. de Pablo, .H. Wegen, B. Christiansen, I. Casas, E. González-Robles, J.A.Gago "RN fractional release of Spent Fuel as a function of Burn-up: Effect of RIM". Poster contribution to the Foruth NF-PRO workshop held in Brussels, (Belgium) on 15-17 November, 2007.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D1.4.15

1.5 WP 1.5: Quantification of key processes affecting the source term for the spent fuel matrix under geological repository conditions.

1.5.1 Overall objective of work package 1.5

Assessment the effect of alpha radiolysis on spent fuel and UO2 dissolution so that it can be understood whether radicals or molecular radiolysis products are rate determining. The effects of sample surface area, presence and absence of hydrogen gas, Fe(II) ions and chloride in solution, and actively corroding Fe metal will be investigated. The conditions shall be determined under which hydrogen gas can act as a reducing agent limiting the effect of radiation enhanced spent fuel dissolution. Particular emphasis will be on the impact of a number of key environmental parameters and engineered barrier materials of the near-field on the performance of the spent fuel waste form and the release of radionuclides. The knowledge gained on the source term shall provide bounding conditions and input parameter for RTD C5.

1.5.2 Overview of work performed

1.5.2.1 Report on final radiolysis model for near field /spent fuel interactions

Participants

ARMINES

Goals/objectives of the research

The overall objective of the contribution of SUBATECH in WP 1.5 was to provide/adapt a model for the dissolution of spent nuclear fuel under near field constraints, characterized by dose and concentration gradients of groundwater species (HCO_3^-, O_2, species formed by container corrosion (H_2) and species formed by the radiolytic decomposition of water (hydrogen peroxide, radicals...) and to apply this model (1) to explain certain known trends governing spent fuel dissolution and (2) to explain certain experimental data.

Key results/achievements

The electrochemical radiolysis model which was developed in the SFS project has been incorporated into the radiolytic transport code TraRaMo and has been fully calibrated with experimental data from literature to describe the effect of H_2, O_2, pH, pCO_2, H_2O_2 and initial surface oxidation on spent fuel dissolution. The effect of hydrogen stabilising spent fuel dissolution against the oxidative effect of alpha radiolysis is represented in the model by the action of hydrogen on the corrosion potential at the fuel surface. The model explains as well the dose threshold, which was observed in the SFS project. This dose threshold is very important for performance analyses of spent fuel under near field conditions since it implies that there is no effect of alpha radiolysis on the long-term corrosion rate of spent nuclear fuel if the specific alpha activity is lower than a value of about 30 MBq/g. High hydrogen concentrations push this dose threshold to higher values.
An important result for near field conditions is also that there will not be a redox front at the fuel surface if hydrogen is provided by container corrosion. For long time it was thought that even under overall reducing near field conditions there might remain an oxidized surface, hence, solution and secondary phase chemistry of oxidized valence state of radionuclides remained relevant. The new data show that only reduced radionuclide valence states are relevant.

Publications

The results of the work of SUBATECH are summarized in the deliverable 1.5.14.
The results of the present work have been presented at the spent fuel workshop 2007 in Switzerland and as well at the MRS conference 2007 in Sheffield.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D1.5.15

1.5.2.2: Dissolution of ^{233}U-doped UO_2 under inert and reducing conditions - Final Activity Report Chalmers University

Participants

Chalmers

Goals/objectives of the research

During recent years a relatively large number of studies both with spent fuel and alpha doped UO_2 (s) have indicated an unexpectedly large effect of the presence of dissolved hydrogen in decreasing considerably the oxidative dissolution of fuel caused by radiolysis of water. These systems are complicated and attempts to understand them necessarily include efforts to understand both processes that occur in the interface solid-solution as well as processes that occur in the bulk solution under the influence of radiation. The present work addresses the second group of processes and more specifically the case of alpha radiolysis in hydrogen saturated solutions.

Key results/achievements

The production of oxidants increases as expected linearly with the radiation dose. It is not possible to conclude, within the experimental uncertainties, if there is any difference between H_2 and Ar atmosphere. This result indicates clearly that dissolved hydrogen does not, within the uncertainties of the experiment, affect the production of hydrogen peroxide measured through the product of its decomposition in acidic ^{238}Pu solutions during homogeneous alpha radiolysis, i.e. the amount of radiolytic oxidants produced in Ar atmosphere remains the same under H_2 atmosphere. Thus apparently there is no measurable consumption of the oxidants produced by alpha radiolysis in the bulk solution even by the presence of dissolved hydrogen at concentrations as high as 8 mM. If one considers the dissolution tests with alpha doped UO_2 or spent fuel carried out in the presence of high concentrations of dissolved hydrogen, the present experiments indicate that no consumption of hydrogen peroxide occurs in the bulk solution. The observed absence of oxidants or of oxidized uranium in these tests should be mainly due to interfacial processes.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D1.5.17

1.5.2.3: Study of crystallinity of studtite at different temperatures

Participants

ENRESA

Goals/objectives of the research

The goal of the research was to show the effect of the secondary phases formed on spent fuel in the dissolution/alteration of the UO_2 matrix and in retention of radionuclides:
The main objectives deal with the following matters:

- UO_2 dissolution rate as a function of phosphate concentration in solution
- Secondary solid phase's formation on the UO_2 surface in phosphate media.
- Influence of the groundwater composition on the formation of secondary phases on UO_2 in phosphate media
- Influence of temperature on the uranyl peroxides stability
- Effect of ionizing radiation on the uranyl peroxides stability
- Effect on the secondary phases on retention of Cs.

Key results/achievements

- The UO_2 dissolution rates as a function of phosphate concentration in solution have been determined, and an empirical equation that relates dissolution rate and phosphate concentration has been deduced.
- Chernikovite formation on the UO_2 surface in contact with a 10-4 M phosphate solution has been observed, and its precipitation rate has been determined.
- The importance of the carbonate concentration on the uranyl-phosphate secondary phase formation on UO_2 has been established.
- The temperature-depending transformation studtite-metastudtite-schoepite-UO_3-UO_8 has been quantified.
- The enthalpies of the different solid transformations have been calculated.
- The amorphization of natural and synthetic studtite by an ionizing radiation has been demonstrated, as well as the formation of nanoparticles of UO_2.

The results obtained in this work have shown that caesium sorption is a very fast process. Cesium in solution is sorbed in less than one hour at pH around 5 on studtite formed as secondary phase.

Publications

Journals and books

A. Rey, J. Giménez, I. Casas, F. Clarens, J. de Pablo. *UO_2 dissolution in phosphate media. Dissolution rates and secondary-phase formation.* Submitted to Applied Geochemistry
J. Giménez, A. Rey, M. Rovira, J. de Pablo, I. Casas, A. Martínez-Esparza, X. Martínez-Lladó. *"Sorption of cesium on freshly precipitated studtite (UO4·4H2O). Kinetics of sorption and sorption isotherm."* NEA Book, in press.

Conferences

A. Rey, S. Utsunomiya, J. Giménez, I. Casas, J. de Pablo, R. C. Ewing. *"Stability of synthetic uranium (VI) peroxide hydrates under ionizing radiation".* Migration 2007. Munich, Germany (2007).

J. Giménez, A. Rey, M. Rovira, J. de Pablo, I. Casas, A. Martínez-Esparza, X. Martínez-Lladó. *"Sorption of cesium on freshly precipitated studtite (UO4·4H2O). Kinetics of sorption and sorption isotherm."* International Workshop on Mobile Fission and Activation Products in Nuclear Waste Disposal. La Baule, France (2007).

J. Giménez, A. Rey, F. Clarens, I. Casas, V. Martí, J. de Pablo *"SFM study of the secondary phase formation on UO2 in contact with phosphate solutions".* Migration 2005. Avignon, France (2005).

A. Rey, S. Utsunomiya, J. Giménez, I. Casas, J. de Pablo, R.C. Ewing. *Stability of natural and syntehtic uranium (VI) peroxide hydrates under ionizing radiation.* American Mineralogist. Submitted.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D1.5.18

1.5.2.4: Report on Radiation induced UO2(s) /spent nuclear fuel corrosion in NaCl brine: effects of hydrogen and bromide. Report on investigations on Spent Fuel/Clay Contact: retention of Radionuclides in Compacted Bentonite Contacting high burnup Spent Fuel

Participants

FZK-INE

Goals/objectives of the research

Radiation induced UO_2(s) /spent nuclear fuel corrosion in NaCl brine: Effects of hydrogen and bromide

Spent fuel leaching tests and radiolysis experiments indicated that hydrogen both considerably inhibits corrosion of the UO_2(s) matrix and impedes radiolytic decomposition of the studied groundwater simulates The aim of the present study is to determine whether the protective effect of non-radiolytic hydrogen is significantly reduced - if not annihilated - by bromide.

Retention of Radionuclides in Compacted Bentonite Contacting High Burnup Spent Fuel

Aim of this work was to study the fate of compacted bentonite directly contacting spent fuel after the arrival of groundwater and the associated consequences. Special attention was directed on the concentrations of radionuclides in the aqueous phase and in the compacted bentonite as well, to assess the retention of radionuclides in the compacted bentonite during immersion in groundwater. Moreover, the impact of the radiation field resulting from the radionuclide inventory of the fuel on the crystalline state of the contacting area of the bentonite was studied by means of XRD techniques.

Key results/achievements

Radiation induced UO_2(s) /spent nuclear fuel corrosion in NaCl brine: Effects of hydrogen and bromide

Results of the complementary spent nuclear fuel corrosion and gamma-radiolysis experiments allow the conclusion that bromide traces reduce significantly the protective hydrogen effect with respect to the release of certain radionuclides and the yield of radiolytic products.

Retention of Radionuclides in Compacted Bentonite Contacting High Burnup Spent Fuel

After 4.5 years reaction time the amount of radionuclides encountered in the bentonite was found to be at a factor of 5 – 10 (Sr, Cs) and at a factor 20 - 50 (U, Pu) higher than in the surrounding groundwater used for the immersion of the reaction cell. No concentration gradient across the profile through the bentonite pellet was found for Cs and Sr. In contrast, the level of Pu close to the contact with the fuel was found to be roughly at 1.5 orders of magnitude higher than in the residual bentonite, whereas no pronounced concentration gradient was found for U. The results show clearly the ability of the bentonite to retain radionuclides, in particular Cs, Sr, U and Pu. XRD studies on the bentonite slice directly contacting the fuel surface have shown that no radiation damage (metamictization) was generated due to the radiation field of the fuel.

Publications

Kienzler, B., Loida, A., Müller,N., Metz, V.
High Level Waste Forms for Repositories in Rock Salt or Clay: Concepts for Future Investigations
E-MRS Spring Meeting 2006, May 29 – June 2, 2006, Nice, France,
Loida A., Kienzler B., Geckeis H., Kim,S.S.

Radionuclide retention in compacted bentonite contacting high burnup spent fuel E-MRS 2005 Spring Meeting, May31-June 3, 2005, Strasbourg, France
Loida, A., Kienzler, B., Metz,v.
High level waste forms for repositories in rock salt and argillaceous rocks: concepts for future investigations.
Jahrestagung Kerntechnik 2007, Karlsruhe, 22. - 24.5.2007
Loida A., Kienzler B., and Metz V. Alteration behavior of high burnup spent fuel in salt brine under hydrogen overpressure and in presence of bromide Scientific Basis for Nuclear Waste Management XXX . Mat. Res. Soc. Symp. Proc. 985, (2007) 15-20
Metz V., Bohnert E., Kelm M., Schild D., Reinhardt J., Kienzler B., and Buchmeiser M. R. Gamma-radiolysis of NaCl brine in the presence of UO2(s): Effects of hydrogen and bromide. Scientific Basis for Nuclear Waste Management XXX . Mat. Res. Soc. Symp. Proc. 985, (2007) 33-40
Metz, V.; Loida, A.; Bohnert, E.; Schild, D., Römer, J.; Dardenne, K.
Effects of hydrogen and bromide on radiation induced UO2(s) corrosion in NaCl brine.
11th Internat. Conf. on the Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere (Migration 2007), München, D, August 26-31, 2007
Metz, V., Loida, A., Bohnert, E., Müller, N., Kelm, M., Kienzler, B.
Radiation Induced UO2(s) Corrosion in Presence of H2 and Br- : Corrosion of Spent Fuel and Depleted UO2(s) in NaCl-Brine
International Conference on Radioactive Waste Disposal in Geological Formations
Braunschweig November 6 – 9, 2007

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D1.5.19

1.5.2.5: Discussion of some of the results on α-doped UO_2 and spent fuel leaching in the presence of a corroding container and comparison with literature data

Participants

SKB

Goals/objectives of the research

In this report an attempt to summarize most of the experimental and modelling results obtained in WP 1.5 of RTD1 of NF-PRO has been made by the WP leader. This is attempted by discussing the results of the different tasks together with literature data from previous research in the field.

Key results/achievements

The report summarizes and discusses the results of the different experimental tasks by concentrating mainly in their reciprocal influence. The results of VTT confirm previous data on the activity threshold and non-influence of the radiation field up to 10% 233U in the presence of 1 ppm sulphide and especially in the presence of an iron strip. The residual rates measured are very low and do not increase with doping level in the interval 0- 10 % 233U. The data of Chalmers on the influence of dissolved hydrogen in homogeneous alpha radiolysis make possible to understand the importance of surface processes in the fuel leaching tests in the presence of bromide carried out at FZK-INE or in the results obtained in the presence of hydrogen with high surface and high doping level powders of SCK.CEN.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D1.5.20

1.5.2.6: Dissolution of unirradiated UO_2 and UO_2 doped with ^{233}U in low- and high-ionic-strength NaCl under anoxic and reducing conditions

Participants

VTT

Goals/objectives of the research

The objective of these experimental dissolution studies with unirradiated UO_2 and UO_2 doped with 233 U was to investigate the role of solution composition and ionic strength in controlling reaction rates and equilibrium state in low- and high-ionic strength NaCl solution. Another objective was to study the effect of specific alpha activity on dissolution rate. The effect of the ratio of the UO_2 surface area to leachant volume (SA/V) was investigated in the tests with unirradiated UO_2 in 0.01 M NaCl. The dissolution rates were measured using the isotope dilution technique to decrease uncertainties due to precipitation and sorption effects.

Key results/achievements

The results with the isotope dilution method suggest that the dissolution rate of UO_2 in 0.01 to 1 M NaCl under anoxic conditions (N_2 , 1 ppm S_2-) is higher than the low concentrations measured in the aqueous phase suggest. The total 238U release, that was based on the change in the 233U/238U ratio during dissolution period, was higher than the measured [238U] in solution and did not reach steady state. This suggests that the UO_2 solid is continuing to dissolves and precipitates even though the solution concentration is constant. The 238U release increased with the SA/V being proportional to the SA/V difference. The results suggest the rate control for UO_2 dissolution under these conditions. The measurements under reducing conditions with Fe showed a similar trend. The [238U] in solution was below or close to the detection limit of the analytical method. The leaching solutions were shown to be inhomogeneous at the end of the contact periods containing precipitates and/or colloids. U was found sorbed or precipitated on the surfaces in the test vessels and on the surface of the iron strips. The U release increased as the SA/V increased also in the presence of iron. Tests with longer duration are needed to confirm the results.
No effect of alpha radiolysis could be observed on the dissolution rate results of the UO_2 samples doped with 0, 5, 10% 233U in 0.01 M NaCl ... 1 M NaCl under anoxic or reducing conditions. A relatively low SA/V ratio was used in these tests due to the small amount of solid phase available for the tests. Tests with higher SA/V would confirm results.
Dissolution rates were evaluated for the UO_2 samples (0, 5, 10% 233U) using the total 238U releases, which were calculated on the basis of the changes in isotopic ratios during contact periods.

Publications

Ollila, K. 2006, Dissolution of unirradiated UO2 and UO2 doped with 233U in 0.01 M NaCl under anoxic and reducing conditions, POSIVA Report 2006-08. Olkiluoto, Finland: Posiva Oy. 87 p.
Ollila, K. 2008, Dissolution of unirradiated UO2 and UO2 doped with 233U in low- and high-ionic-strength NaCl under anoxic and reducing conditions, to be published as Posiva Report.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D1.5.21

1.5.2.7: Quantification of key processes affecting the source term for the spent fuel matrix under geological repository conditions

Participants

Studsvik Nuclear

Goals/objectives of the research

Several experiments have suggested that a small amount of hydrogen dissolved in water slow down the oxidation of spent nuclear fuel considerably. It has been suggested that the UO_2 surface may act as a catalyst of the reaction between hydrogen and oxygen. The objective of the work of Studsvik was to test this hypothesis and to test if the radiation from the fuel itself would have any influence. A small amount of 18O was added to an autoclave with UO_2 powder under water, pressurized with a hydrogen/argon atmosphere. The reaction between oxygen and hydrogen was detected by the formation of 18O marked water.

Key results/achievements

Results from several tests with the experimental setup showed that the original idea had to be re-evaluated. A new setup was therefore designed. We also learned which type of autoclaves, o-rings etc works best and especially which manufacturer and seller of equipment you should choose. The new experimental equipment was installed and appropriate chemicals purchased. Due to the late delivery of the autoclaves, the experiments were not able to be completed before end of the project.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D1.5.22

1.5.2.8: The effect of H_2 on UO_2 dissolution in the presence of engineered barrier clay

Participants

SCK-CEN

Goals/objectives of the research

Recent results demonstrate the inhibiting effect of H_2 on UO_2 dissolution rate in absence of clay [1]. The SCK·CEN contribution to the NF-PRO project is to verify if this effect is also observed in the presence of clay. Indeed if the H2 effect is confirmed, this would imply for performance assessment studies that the dissolution rate in the normal evolution scenario would be very small. The dissolution rates measured in absence of H_2, and life time predictions based on these rates, would thus be conservative. To demonstrate this potential effect, SCK·CEN has performed static leach tests with a-doped UO_2 in Volclay in the presence of H_2 gas for 90 to 540 days at room temperature and in Ar/0.04% CO_2 atmosphere.

Key results/achievements

H_2 pressure will not much suppress the fuel dissolution rate in the presence of a surface with sufficient U sorption capacity, such as clay, as long as the sorption sites are not saturated. The presence of metallic iron from the overpack will have a corrosion suppressing effect on the UO_2 dissolution also in the presence of clay. The clay has an increasing effect on the initial UO_2 dissolution rate, but the "long-term" rate does not seem to be affected much. Precise long-term rates for integrated conditions cannot yet be given. Much longer tests, and tests in more realistic conditions are necessary to improve the estimations of the long-term rate. For the time being, the average rates of 50-150 µg.m-2.d-1 can be used as conservative estimations.
A more fundamental approach would require the explicit consideration of U(IV) or U(VI) sorption on the clay in the dissolution models. Confirmation of our results with real spent fuel would be useful, to see for the potential influence of the e- particles.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D1.5.23

1.6 WP 1.6: Synthesis of results and conclusions from RTD Component 1 and integration in RTD Component 5 (Performance assessment)

1.6.1: RTDC 1 synthesis reports (Part I: Vitrified waste and Part II: Spent fuel)

Participants

SCK-CEN, CEA, ARMINES, ENRESA, VTT, FZK-INE, EC-JRC-ITU

Goals/objectives of the research

Objectives and key questions addressed in the final activity report of RTDC1

WP1.1
Drafting of a reference document for the state of knowledge in waste form properties, key processes for alteration and their couplings, in models in and source term development, for evolution scenarios under long-term storage and disposal conditions.

WP1.2
Assessment of the key processes controlling radionuclide release from HLW glass due to the interaction with groundwater and different components of the near field sub-system. Develop a common understanding, reduce uncertainties and quantify these key processes with their associated parameters. Information derived from this work package will allow providing the necessary input data for conceptual and mathematical model development in WP1.3

WP1.3
To conform, adapt and develop models for a mechanistic source term for glass corrosion and associated radionuclide release under near-field conditions, including model for secondary solid solution formation and compilation of a dataset for modelling solid solution formation under near field conditions

WP1.4
Decrease the uncertainties in the assessment of the Instant Release Fraction of spent fuel by performing specific key experiments and modelling. Effort is focused on (i) the initial instant release fraction, IRF(0) by performing characterisation and leaching of irradiated fuels, (ii) the potential evolution of grain boundaries by developing a micromechanical model based on dedicated characterisation of MOX fuels, (iii) the potential consequence of any early breaching of the canister (evolution in steam).

WP1.5
The main objective of WP 1.5 is to assess the effect of alpha radiolysis on spent fuel and UO2 dissolution so that it can be understood whether radicals or molecular radiolysis products are rate determining. Also, the effects of sample surface area, presence and absence of hydrogen gas, Fe(II) ions and chloride in solution, and actively corroding Fe metal will be investigated. The conditions shall be determined under which hydrogen gas can act as a reducing agent limiting the effect of radiation enhanced spent fuel dissolution . Particular emphasis will be on the impact of a number of key environmental parameters and engineered barrier materials of the near-field on the performance of the spent fuel waste form and the release of radionuclides. The knowledge gained on the source term shall provide bounding conditions and input parameters for RTD C5.

WP1.6
Synthesis of results and conclusions from RTD Component 1 and integration in RTD component 5

Key results/achievements

Main outcome for the behaviour of HLW glass in clay

- Two basic dissolution parameters have been measured for the blended magnox-UO_2 glass, i.e. the forward and residual dissolution rate. These two parameters are essential parameter for the reference source term model (see section ..). This means that this source term model can now be applied for the blended magnox-UO_2 glass, provided sufficient data are available from literature concerning another important parameter, i.e. the cracking factor of the blended magnox waste glass.
- Regarding the potential effect of incorporation of radionuclides in secondary phases, the following was concluded:
    - Trivalent actinides (Am, Pu, Cm) can be structurally incorporated in to the host minerals powellite, calcite and clay minerals, forming solid solutions;
    - The quantitative understanding of this solid solution formation has improved, with a.o. the determination of activity coefficients for Eu in powellite;
    - More thermodynamic data for the aqueous – solid solution equilibria are necessary.

The fact that trivalent f-elements can be structurally incorporated into the host minerals powellite, calcite and clay minerals is a universal observation. In particular if the project succeeds in developing thermodynamic data for the aqueous – solid solution equilibria, these data will be relevant to every system since they represent thermodynamic data. This information represents the scientific basis for trustworthy evidence of long-term retention of radionuclides in the near-field.

- The trends observed in the integrated glass dissolution experiments could be explained qualitatively with the assumed key mechanisms and the related conceptual model of glass dissolution The quantitative reproduction of the data with the geochemical codes was nevertheless not always satisfying.
- The rate increasing effect of magnetite can be simulated, but a much better description of the combination of geometric, hydrodynamic, thermodynamic and kinetic constraints is necessary. The Silica/clay system must be better understood (kinetics, solubility, sorption, effect of temperature)
    - The hypothesis of instant sorption equilibrium on the magnetite must be revisited
    - In addition to silica sorption, silica precipitation on the magnetite may have to be considered
    - The pH evolution at the glass interface must be better understood
    - With the sorption parameters used in the calculations for the long-term predictions, the impact of the magnetite layer on the overall performance of the glass would be small. This is confirmed by the experiments. The sorption parameters of the real in situ corrosion products are, however, not known. For this reason, conservative sorption parameters should be used for the calculations.
    - The r_0 -r_r model can still be considered as a good reference source term model. The performed long-term calculations suggest that the first r_0 stage would be relatively unimportant, compared to the much longer r_{res} stage.

Publications

Presentation at the 4th NF-PRO workshop, Brussels, 15-17 October 2007

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as Deliverable D1.6.3

2 RTDC 2: Chemical (thermo-hydro-mechanical) evolution of the EBS

2.1 WP 2.1: Critical review of existing information

2.1.1 Overall objective of work package 2.1

All research works need background information to know and quantify what has been done in any specific field. The state-of-the-art report intends to be a platform for the integration of scientific and technical information by providing a critical review and incorporating the information available from EC, national and international programs to the research and technology development (RTD) Component 2.

This work package will establish a common knowledge reflecting the current status on the key near field geochemical processes to be investigated, the critical concepts to be developed and the missing parameters to be determined. This will enable to define the detailed scope of the experiments and modelling to be carried out in all the work packages. Also, based on the information compiled in this work package, the initial conditions needed by experiments in other work packages will be provided.

This work package will also provide a detailed test plan in order to define the experimental program at different stages along the project and will be updated on a yearly basis.

The participating organisations are CIEMAT, ENRESA, GRS and ENVIROS. CIEMAT will focuss on the review and integration of the experimental works in the engineered barrier system at process level. GRS will carry out the same kind of work but referred to the salt concept of a deep repository. ENVIROS will concentrate mainly on modelling aspects and ENRESA will act as integrator of the work package report and will ensure the final preparation of the test plan.

2.1.2 Overview of work performed

2.1.2.1: State of the Art Report

Participants

CIEMAT, ENRESA, ENVIROS, GRS

Goals/objectives of the research

Key results/achievements

2.2 WP 2.2: Porewater chemistry

2.2.1 Overall objective of work package 2.2

To main objectives of NF-PRO's Work Package 2.2 were:

- To know the quantity and composition of pore water and its evolution in the clay barrier for the granite, salt and clay host rock concepts, improving the knowledge of the processes taking place during hydration and heating.
- To improve the knowledge of the kinetics of bentonite hydration and its repercussion on the microstructure and hydro-mechanical properties of the barrier.
- To estimate the impact of saline pore waters on the chemical, mineralogical, hydrological and mechanical evolution of the clay EBS.

As a secondary objective, and as a means for achieving the main aims, it is considered necessary to get online measurement of key geochemical parameters of the system.

In order to get a complete understanding of the pore water evolution in the barrier, the information provided by this WP must be combined with that provided by WP23 and WP24. The information on corrosion products allows the knowledge of the final stages of barrier evolution, whereas the information on concrete degradation is necessary to define the pore water chemistry in the clay host rock concept. WP22 supplies information to WP26 and to WP25 concerning the geochemical environment in which the migration processes take place.

2.2.2 Overview of work performed

2.2.2.1: CIEMAT report on experimental work related to FEBEX bentonite

Participants

CIEMAT

Goals/objectives of the research

The main objective of this Work Package was to know the quantity and composition of pore water and its evolution in the clay barrier, improving the knowledge of the processes taking place during hydration and heating, as well as to improve the knowledge of the kinetics of bentonite hydration and its repercussion on the microstructure and hydro-mechanical properties of the barrier.

Key results/achievements

The approach taken by CIEMAT concerning the study of the bentonite pore water has included basically three types of experiments:

- the determination of the water sorption isotherms as a function of density, salinity, exchangeable cations and temperature;
- the performance of laboratory tests in which the compacted bentonite is subjected to conditions similar to those of the repository (tests in cells), and
- the analysis of the pore water and bentonite of an *in situ* test running for more than five years, the FEBEX test performed at Grimsel.

The first group of tests, combined with the determination of heat of immersion, has allowed the identification of the mechanism of adsorption of water in FEBEX bentonite, as well as the types of water and their distribution in the external surfaces and interlayer space. The hydration of interlamellar space proceeds in steps corresponding to the adsorption in external surfaces, and the intercalation of one, two and three water monolayers. The amount of water adsorbed depends on the type of interlayer cation and its hydration energy. The hydration of the cations and of the exposed clay surfaces occurs at low water contents, whereas the osmotic phenomenon is more effective at high water content. The salts hinder the swelling of the smectite particles at low and high water activity values. The amount of water at the three-layer hydrate and the total amount of water adsorbed decreases with temperature. The amount of external water at 20-30ºC would be slightly smaller than at 60ºC.
The second group of tests has included the performance of heating/hydration tests and infiltration tests in which different types of water and thermal gradients have been used. The online measurements and the postmortem analysis of the bentonite have allowed the identification of processes taking place: dilution of chlorides, dissolution/precipitation of carbonates and sulphates, and cation exchange reactions in the smectite. After 7.6-years, no significant alteration of the montmorillonite was observed.
Finally, the FEBEX *in situ* test provided bentonite submitted to repository conditions during five years and pore water obtained from bentonite which was being submitted to repository conditions. The analysis of both has allowed the knowledge of bentonite geochemistry and pore water composition under representative conditions.

Publications

Abstracts sent to conferences:

- Long-term geochemical evolution of the near field repository: insights from reactive transport modelling and experimental evidences. D.Arcos, F.Grandia, C.Domènech, A.M.Fernández, M.V.Villar, A. Muurinen, T. Carlsson, P.Sellin, P.Hernán. Goldschmidt 2007. Colonia (Alemania), 19-24 agosto 2007.
- Geochemical behaviour of a bentonite barrier: results up to 8 years of thermo-hydraulic treatment in the laboratory. A.M. Fernández, M. V. Villar, R. Gómez-Espina. Clays in natural & engineered barriers for radioactive waste confinement. ANDRA. Lille, 17-20 Sept 2007.
- Geochemistry and mineralogy of a bentonite subject to heating and hydration in an in-situ test after five years operation. A. M. Fernández, P. Rivas, A.M. Melón, M.V. Villar. Clays in natural & engineered barriers for radioactive waste confinement. ANDRA. Lille, 17-20 Sept 2007.
- Analysis of the water absorption in bentonites as a function of the salinity and their influence in the pore water composition. A.M. Fernández. Clays in natural & engineered barriers for radioactive waste confinement. ANDRA. Lille, 17-20 Sept 2007.

Books and journals:

- Villar, M.V., A.M. Fernández, R. Gómez, J.F. Barrenechea, F.J. Luque, P.L. Martín & J.M. Barcala. 2007. State Of A Bentonite Barrier After 8 Years Of Heating And Hydration In The Laboratory. In: D.S. Dunn, C. Poinssot, B. Begg (eds.): *Scientific Basis for Nuclear Waste Management XXX*. Mater. Res. Soc. Symp. Proc. **985,** 0985-NN11-19. Materials Research Society, Warrendale, PA.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D2.2.12

2.2.2.2 Swelling pressures of MX-80 bentonite in solutions of different ionic strength

Participants

GRS

Goals/objectives of the research

The overall objective of the GRS contribution to the NF-PRO RTDC2 WP2.4 and 2.2 was a better understanding and quantification of the reactions of bentonite with repository relevant solutions of different salinities and pH. The chemical compositions of the solutions used in the experiments are typical for repositories in salt, clay and granite formations. This comprehensive study included the monitoring of important parameters like fluid composition, cation exchange, interlayer spacing, chemical and mineralogical composition of montmorillonite and swelling pressure of bentonite after 7 days, 1,2 and 3 years of reaction.

Key results/achievements

All solutions change the bentonite properties, but to a different degree. Each solution affects the mineralogy and the swelling pressure differently. In all reactions with all solutions montmorillonite was partially dissolved but remained the dominant mineralogical phase. As a consequence Mg, Al and Si contents in the solutions rose and the chemistry of the montmorillonite particles changed. Mg was substituted by Al in the octahedral layer which led to a decrease of interlayer charge. The interlayer spacing of montmorillonite was high in water and low salinity solutions and lower in the high saline solutions. Cation exchange capacity, total charge, interlayer charge and interlayer spacing of the montmorillonite particles generally decreased with reaction time. A good correlation of the interlayer charge of montmorillonite and swelling pressure of bentonite was observed. Swelling pressures are strongly dependant on the salinity of solution and pH. Swelling pressures decreased with reaction time in low and high saline solutions. The observed reduction of total and interlayer charge of the montmorillonite particles suggest that the mineralogical changes will eventually lead towards the formation of pyrophyllite/kaolinite. A schematic diagram was generated which explains the correlation of swelling pressure and interlayer charge as well as the processes occurring in open and closed geologic systems. Under the conditions of a closed system which can be assumed in a repository in salt or in clay formations the transformation of montmorillonite into pyrophyllite/kaolinite is more likely than the transformation in illite. From the results of this study it can be concluded that the swelling pressures of bentonites will decrease in the long run.. High saline solutions may lead to an almost complete loss of swelling capacity. Low ionic strength cement pore solutions have a similar effect on bentonite than high saline solutions.

Publications

Herbert, H.-J.; Kasbohm, J.; Moog, H. C.; Henning, K. H. (2004): Long-term behaviour of the Wyoming bentonite MX-80 in high saline solutions, Applied Clay Science 26, 275-291.
Herbert, H.-J. (2005): Zum Kurz- und Langzeitverhalten von Bentonit als Dichtstoff in Salzformationen – Conference proceedings of Altbergbaukolloqium Clausthal 2005, 9p.
Herbert, H.-J., Kasbohm, J (2005): Alteration of Montmorillonites in Saline Solution. - Proceedings of the 3rd International Meeting on Clays in Natural & Engineered Barriers for Radioactive Waste Confinement, Lille, September 17.-20. 2007. 163-164.
Herbert, H.-J., Kasbohm, J., H. Sprenger H., Reichelt, Ch. and A. M. Fernandez, A. M. (2007): Swelling pressures of MX-80 bentonite in solutions of different ionic strength – Paper presented at the Conference 3rd International Meeting on Clays in Natural & Engineered Bar-

riers for Radioactive Waste Confinement, Lille, September 17.-20. 2007. Paper submitted for publishing in Applied Clay Technology.
.Kasbohm, J. and Herbert, H.-J. (2007): Mechanisms for mineralogical alteration of dioctahedral montmorillonite in saline solutions – a TEM study. – Repreints of the contributions to the workshop on Long-term performance of smectitic clays embedding canisters with highly radioactive waste, Lund, Sweden, November 26-28, 2007, 70-80

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D2.2.13

2.2.2.3: Eh and pH in compacted MX-80 bentonite

Participants

VTT

Goals/objectives of the research

The main objective of work performed by VTT as part of NF-PRO's work package 2.2 was to determine the evolution of the water composition (mainly pH and Eh) in the bentonite buffer.

Key results/achievements

The report summarises the following key achievements:

- On-line measurement method has been developed for pH and Eh measurement in compacted bentonite.
- Understanding of the determinants of pH and Eh in bentonite has improved.

Publications

Muurinen, A., Carlsson, T. 2007. Development of methods for on-line measurements of chemical conditions in compacted bentonite. J. Phys. Chem. Earth, 32, 2007, 241-246.
Carlsson, T., Muurinen, A. 2007. Measurements on Eh and pH in compacted MX-80 bentonite. In: Dunn, D.S., Poinssot, C., and Begg, B. (eds.) Scientific basis for Nuclear Waste Management XXX (Mater. Res. Soc. Symp. Proc., Vol. 985, Warrendale, PA, p. 533-541.
Muurinen, A., Carlsson, T. 2007. Eh and pH in the porewater of compacted bentonite. Poster presentation. Clays in Natural & Engineered Barriers for Radioactive Waste Confinement, Lille, France, September 17-20, 2007. Paper submitted for proceedings.
Muurinen, A., Carlsson, T. Experiences of pH and Eh measurements in compacted MX-80 bentonite. Presentation in Workshop on Long-Term Performance of Smectitic Clays Embedding Canister with Highly Radioactive Waste. Lund, Sweden, November 26-28, 2007. Paper submitted for proceedings.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D2.2.14

2.3 WP 2.3: Corrosion product interactions

2.3.1 Overall objective of work package 2.3

The Deep Geological Repository (DRG) is currently the most accepted option to bury high level radioactive waste. The DGR is based on a multi-barrier system, the main function of which is to minimize and/or retard the migration of radionuclides towards the biosphere. One of the barriers is the metallic container in which the spent fuel is stored. The container will be designed to have an expected life-time of at least 1 000 years. During this time, it will be exposed to corrosion, which will result in the formation of various corrosion products. The objective of the WP 2.3 is to study both the effect of bentonite on the corrosion behaviour of metal and the effect of the corrosion products on the characteristics of the bentonite.

Briefly, the work was restricted to copper and iron alloys (steel or cast iron). The work focused on, among other things, the interactions between bentonite and metal and/or corrosion products, hydrogen production caused by corrosion, and geochemical modelling.

The interactions between bentonite and corrosion products depend both on the pore water evolution (dealt with in WP2.2) and the effects from concrete degradation (dealt with in WP 2.4). The processes studied in WP 2.2, WP 2.3 and WP 2.4 may have a strong influence on the radionuclide transport in the EBS (dealt with in WP 2.5 and WP 2.6).

2.3.2 Overview of work performed

2.3.2.1 Experimental work (GAME) on bentonite-iron interactions

Participants

CIEMAT

Goals/objectives of the research

The aim of the experiments by CIEMAT in the framework of NF-PRO's Work Package 2.3 is to obtain information on the medium and long-term for the THG evolution in the near field, especially for those processes related to steel corrosion and THG coupled processes. CIEMAT continued work related to the design, set-up and instrumentation of several scale tests: small and medium cells, and a large-scale GAME experiment hydrated with Grimsel groundwater. In the two smallest scales, the experiments have two main objectives; on one hand, the study of the corrosion products generated in the canister/bentonite interface at the repository conditions and, on the other one, to establish how the corrosion affects the properties of the bentonite.

Key results/achievements

A total number of 19 cells, 13 small and 6 medium ones, were working from mid-2005. Ten small cells were dismantled after different times of operation. Two medium cells were dismantling after 6 and 18 months of operation. The characterization of the corrosion products showed:

- Identification of the evolution of corrosion products during the lifetime of a DGR: FeOOH in the post-closure stage, haematite or magnetite during the transient state and ferrous hydroxide and magnetite when bentonite is fully saturated.
- Precipitation of iron phases in the cracks and voids of the bentonite compacted blocks.
- Possible movement of iron oxide particles along the bentonite blocks.
- Small enrichment of iron in bentonite: formation of iron oxide nanoparticles in iron-rich montmorillonite particles. Cation exchange does not seem to be as important as sorption or precipitation of iron phases.
- Ferrous ions seem to induce a change in the redox behaviour of the clay. The formation of Green Rusts or ferrous hydroxide may be relevant as well in this process.
  1. Slight decrease on CEC values: Na and Mg concentration decreases in the EC.
  2. Slight decrease on swelling capacity.
  3. Increase of specific surface and micro-porosity of the clay due to the precipitation of iron oxide nano-particles

  Influence of iron on the bentonite properties:
- Longer time and higher temperatures are required for the transformation of montmorillonite into new iron-rich phases: long-term experiments are necessary.

The GAME large scale experiment has demonstrated that installation of an EBS and the THG instrumentation in a large-scale experiment, with the hydration and heating infrastructures, is feasible for the HLW clay-repository concept:

- The experimental setup is installed and the corrosion processes are progressing in the experiment, which was flooded initially, in spite of the simultaneous heating and

hydration has been stopped.

- The integrity of the measure chain of GCh-parameters is a major issue to solve: problems in whichever of the components become measures fail.
- A longer saturation time can assures the continuity of the water phase around the sensors.
- Robustness of solid state electrodes is a critical issue still not solved.
- At the moment, the in-situ multi-parameter G-Ch measurements with solid state technology are unfeasible.
- The development and implementation of suitable sampling systems seems to be the best option to correct the problems.
- Continuation of the heating and hydration phase will be able to continue after, with a similar duration to that foreseen in the frame of NF-PRO.
- Comparison of the future data, from the post-mortem analysis of the GAME components, against the data currently obtained from other corrosion experiments in cells will be possible.

Publications

Proceedings of the MRS Fall Meeting 2006 “Geochemical processes at the C-steel/bentonite interface in repository conditions”. E. Torres, M.J. Turrero, P.L. Martín
SNE (Sociedad Nuclear Española) 2006 “Estudio experimental de la interacción hierro/bentonita: procesos geoquímicos en la interfase”. E. Torres, M.J. Turrero, P.L. Martín
Annual Report Legnaro National Laboratory 2006 “RBS study on the corrosion products interaction with bentonite under the conditions of a high-level waste repository”. U. Alonso, A. Patelli, E. Torres, T. Missana, M.J. Turrero, V. Rigato
3rd International Meeting on “Clays in natural and engineered barriers for radioactive waste confinement”, 2007.“TEM characterization of bentonite after two-years-contact with iron corrosion products”. E. Torres, M.J. Turrero, P.L. Martín, J.L. Baldonedo
VI Iberian Congress on Geochemistry,2007. “Formation and evolution of Green Rust in anoxic conditions”. E. Torres, M.J. Turrero, P.L. Martín, E. Baldonedo
Euroclay 2007. ²Location of iron at the bentonite/metal canister interface in a Deep Geological Repository². E. Torres, U. Alonso, M.J. Turrero, A. Patelli, P.L. Martín and A. Escribano.
Kinetic modelling of the iron corrosion attenuation by diffusive transport through layers of corrosion products.J. Peña, M.J. Turrero, E. Torres, P.L. Martín, A. (Submitted)

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D2.3.7

2.3.2.2 A study of anaerobic corrosion of carbon steel

Participants

NRI

Goals/objectives of the research

The main objective of NRI part of the project was to provide description of carbon steel container processes in granite host rock and processes occurring on the container/bentonite interface using literature data and limited set of new experimental work. Experimental work was focused mainly on study of evolution of hydrogen from reaction of carbon steel with water using sophisticated equipment developed in NRI and testing electrochemical noise analysis for corrosion monitoring. Limited work was also devoted to modelling transport of iron in near field and its possible effect on corrosion processes.

Key results/achievements

Comprehensive literature analysis focusing on characterization of corrosion products led to the following conclusions:

- In water with low concentration of carbonate species and negligible concentration of sulphides, the major corrosion products will be magnetite and ferrous hydroxide.
- In groundwaters with not negligible concentration of sulphides, all Fe^{2+} will be precipitated by sulphide until its depletion.

In groundwaters with very high concentration of carbonates (1 mol/l) siderite ($FeCO_3$) can be formed directly, and at lower concentration of carbonates carbonate green rusts ($GR(CO_3^{2-})$) are formed. The stability of these species is not, however, clear. At high concentration of sulphates or chlorides in a groundwater green rusts ($GR(SO_4^{2-})$ or GR(Cl-)) could be also formed.

- In the long-term at the interface of canister/bentonite iron silicates will be formed. Due to very slow kinetic of the reactions of iron with silicate species, it is, however, difficult to experimentally determine their nature.
- Carbon steel corrosion rate and consequently hydrogen evolution rate decreases significantly with time due to the formation of corrosion products on carbon steel surface until the values well below 1 mm/yr.
- Iron released from carbon steel could change porosity and sorption properties of bentonite.

Measurements of hydrogen evolution from anaerobic corrosion of steel showed that:

- Corrosion rates increase significantly with temperature in the initial phases of corrosion, but the effect of temperature will almost disappear in the long-term.
- Corrosion rates in bentonite porewater (derived in WP 2.5 by PSI) do not differ significantly from corrosion rates in distilled water and decrease in both cases in several weeks to values below 1 mm/yr. The impact of different nature of corrosion products layers formed in distilled and bentonite water on corrosion rate is visible.

The results of electrochemical noise analysis (ENA) showed that it could be used for monitoring corrosion of carbon steels and the behaviour of corrosion product layers, but it is difficult to use it for determination of corrosion rates.
An approach of modelling of corrosion of carbon steel was similar to modelling of corrosion rates of waste forms using mass transfer theory. The results showed that:

- Corrosion rates of carbon steel surrounded by bentonite will decrease for thousands of years until reaching steady state well below 0.1 mm/yr.
- In the transient period, bentonite will accelerate corrosion due to increasing gradient for iron ions diffusion by iron sorption on bentonite (pumping effect).

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D2.3.8

2.3.2.3: Interactions between iron corrosion products and bentonite (Final activity report for Serco Assurance and SKB, WP2.3)

Participants

Serco Assurance and SKB

Goals/objectives of the research

In Sweden and Finland, spent nuclear fuel will be encapsulated in sealed cylindrical canisters, consisting of a ferrous insert and a copper outer container, for disposal in a geologic repository. In the horizontal emplacement concept (KBS-3H) for the disposal of radioactive waste, copper canisters with cast iron inserts will be surrounded by bentonite buffer and mounted in perforated carbon steel support structures in boreholes within the bedrock. The natural groundwater conditions in the bedrock at the proposed repository depth in the crystalline bedrock are reducing. Oxygen will however be introduced into the repository during the construction phase. After a transient oxic period the conditions in the repository will become reducing due to different oxygen consuming processes (e.g. in the KBS-3H concept the large amount of steel present is expected to be one of the major oxygen consumers). The groundwater will be reducing, leading to anaerobic corrosion of the ferrous material which will liberate hydrogen, form a magnetite film on the surface and release iron ions into the surrounding matrix. It is important therefore to understand both the effect of bentonite on the corrosion behaviour of the steel and the effect of the corrosion products on the performance of the bentonite. This report presents the results from the work carried out by Serco, SKB and Posiva, together with a number of collaborators (principally Geological Survey of Finland, GSF, and Clay Technology, through the SKB-Posiva joint project for development of the horizontal emplacement concept) and the British Geological Survey, BGS, within WP2.3 of NF-PRO, with the aim of investigating the interactions between corroding iron and bentonite.

Key results/achievements

In order to measure the corrosion rates in bentonite, the rate of hydrogen generation of steel in bentonite was measured using a barometric gas cell technique. In addition, a range of analytical techniques was applied to study the composition and morphology of the corrosion products, the distribution and chemical state of iron released into the bentonite and the extent of changes induced in the basic physico-chemical properties of bentonite. The work programme consists in the following:

- In Stage I of the programme, samples for analysis were taken from long-term anaerobic corrosion tests of carbon steel or cast iron in compacted bentonite (Na/Ca-bentonite: Volclay MX-80, ~4% Fe_2O_3) in contact with a simple artificial groundwater at 30 ºC or 50 ºC. A range of analytical techniques was applied to samples of corrosion product on carbon steel and cast iron and to the bentonite surrounding the corroding specimens. Corrosion products and bentonite samples were analysed using scanning electron microscopy (SEM), electron microprobe analysis (EPMA), Raman spectroscopy, X-ray diffraction (XRD) and Mössbauer transmission spectroscopy. In addition, the bentonite samples were analysed using Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM) with energy dispersive spectroscopy (EDS) and selected area electron diffraction (SAED), exchangeable cation analysis and cation exchange capacity (CEC) measurements. Hydraulic conductivity and swelling pressure were also measured.

- In Stage II, a range of new experiments was set up to measure the anaerobic corrosion rate of steel under a wider range of conditions than those examined previously and additional corrosion cells were set up to provide further material for analysis. The experiments investigated the effects of alkaline plumes released from concrete support structures and the effect of chloride concentration and temperature on the corrosion rate of steel in bentonite. In addition, comparison was made between corrosion in compacted bentonite and artificial bentonite porewater with no bentonite mineral present. A selection of the additional cells set up were analysed using a range of techniques and the results of these measurements are presented in this report.
- In Stage III, geochemical modelling of the experimental data was performed. Preliminary modelling calculations reported previously were supplemented by a more detailed modelling exercise which is included in this report.

Publications

N.R. Smart, A.P. Rance, L. Carlson and L.O. Werme, *Further Studies of the Anaerobic Corrosion of Steel in Bentonite*, presented at MRS 2005, Ghent, 2005; Mat. Res Soc.Symp. Proc **932**, 813, 2006.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D2.3.9

2.3.2.4: Interactions between copper corrosion products and MX-80 bentonite

Participants

VTT

Goals/objectives of the research

The objective of VTT's contribution to NF-PRO's Work Package 2.3 was twofold. First, identify by means of a literature study those copper corrosion products that may form in a repository for nuclear waste. Second, study experimentally the interaction between wet MX-80 bentonite and two copper compounds that were selected on the basis of the results from the literature survey.

Key results/achievements

Compacted MX-80 samples were stored under anaerobic conditions and kept in contact with an NaCl solution. The samples were kept at room temperature and 75 ºC for 2.9 years and then analysed. The presence of either atacamite or the green copper corrosion product on the plates did not have any notable effects on the porewater chemistry. However, the copper concentration profiles indicated that the corrosion products did dissolve, and then diffused into the surrounding bentonite. Concentration profiles were found to be roughly the same, irrespective of whether the samples had been stored at room temperature or at 75 ºC.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D2.3.11

2.4 WP 2.4: Concrete-bentonite interactions

2.4.1 Overall objective of work package 2.4

In the frame of this WP the interactions between concrete and bentonite and their impact on the mineralogical chemical and hydraulic evolution of the clay engineered barrier system under the boundary conditions of repositories in argillaceous formations, crystalline formations and salt formations are investigated. In terms of the employed bentonitic materials and interacting solutions a number of experiments on different scales are set up in such a way as to obtain a maximum amount of information regarding:

- the bentonite-concrete interface in contact with high alkaline solutions with low and high salinity;
- the spatial extension of the mineralogical and geochemical modifications:
- the duration of high pH conditions in the system;
- geochemical modifications as a function of time and their influence on the behaviour oft the EBS.

2.4.2 Overview of work performed

2.4.2.1 Design, set-up and instrumentation of several scale tests: medium cells and a large-scale GAME experiment hydrated with synthetic RAF water

Participants

CIEMAT

Goals/objectives of the research

The aim of the CIEMAT's experiments as part of WP 2.4 is to obtain information on the medium and long-term for the THG evolution in the near field, especially for those processes related to steel corrosion, groundwater-concrete interaction and THG coupled processes. The work carried out by CIEMAT relates to the design, set-up and instrumentation of several scale tests: medium cells and a large-scale GAME experiment hydrated with synthetic RAF water.

Key results/achievements

Six medium cells are working from mid-2005. Three cells were dismantled after 6, 12 and 18 months of operation. A thin layer of white-precipitate was found at the concrete/bentonite interface in all cases.

- The precipitate consists of a superposition of different secondary minerals identified by means of SEM-EDS: portlandite (Ca(OH)2), C-S-H gels (Ca/Si = 0.6), brucite (Mg (OH)2) and ettringite (3CaO·AlsO3·3CaSO4·30H2O).
- XRD studies have confirmed the formation of a poorly crystalline trioctahedral phase similar to saponite.
- An increase of the BET specific area has been measured in the zones close to the interface.
- CEC values decrease near the interface: Na increases in the exchanger whereas magnesium decreases.
- The mineralogical composition of the bentonite at the interface changes slightly and a brucite-saponite-smectite mixture has been observed.

The GAME large scale experiment has demonstrated that installation of an EBS and the THG instrumentation in a large-scale experiment, with the hydration and heating infrastructures, is feasible for the HLW clay-repository concept:

- The experimental setup is installed and the corrosion processes are progressing in the experiment, which was flooded initially, in spite of the simultaneous heating and hydration has been stopped.
- The integrity of the measure chain of GCh-parameters is a major issue to solve: problems in whichever of the components become measures fail.
- A longer saturation time can assures the continuity of the water phase around the sensors.
- Robustness of solid state electrodes is a critical issue still not solved.
- At the moment, the in-situ multi-parameter G-Ch measurements with solid state technology are unfeasible.

- The development and implementation of suitable sampling systems seems to be the best option to correct the problems.
- Continuation of the heating and hydration phase will be able to continue after, with a similar duration to that foreseen in the frame of NF-PRO.
- Comparison of the future data, from the post-mortem analysis of the GAME components, against the data currently obtained from other corrosion experiments in cells will be possible.

Publications

Papers send to congress

M.J. Turrero, A. Escribano, E. Torres, P.L. Martín (2007): Concrete/FEBEX bentonite interaction: Preliminary results on short-term column experiments. Clays in natural & Engineered Barriers for radioactive waste confinement. Lille, Francia, 17-20 Septiembre.

A.M. Fernández, A. Melón, D.M. Sánchez, M.P. Galán, R. Morante, L. Gutiérrez-Nebot, M.J. Turrero, A. Escribano (2007): Changes of FEBEX bentonite mineralogy and physico-chemical properties from exposure to concrete pore fluids. Scientific Basis for Nuclear Waste Management - Materials Research Society, Sheffield, UK, 16-20 Septiembre.

A. Escribano, A.M. Melón, M.J. Turrero, A.M. Fernández, E. Torres, P.L. Martín (2007): Concrete-Febex bentonite interaction: results on column and infiltration experiments. NF-PRO Fourth Workshop, Brussels, Belgium, 15-17 October.

Publications

A.M. Fernández, A. Melón, D.M. Sánchez, M.P. Galán, R. Morante, L. Gutiérrez-Nebot, M.J. Turrero, A. Escribano (2007): Changes of FEBEX bentonite mineralogy and physico-chemical properties from exposure to concrete pore fluids. Scientific Basis for Nuclear Waste Management - Materials Research Society Symposium Proceedings (in press).

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D2.4.6

2.4.2.2 Reactivity/transport investigations on the detailed understanding of the chemical reactions at the bentonite-concrete interface

Participants

ENRESA

Goals/objectives of the research

- Detailed understanding of the bentonite-concrete interface in contact with the high alkaline solutions (REACTIVITY)

The scope of this objective is to acquire data and to develop basic knowledge on

1. Nature of the reactants and by-products (new-formed mineral phases)
1. Kinetics of dissolution/precipitation (d/p)

- Study of the spatial extension affected by mineralogical and geochemical modifications (TRANSPORT)

In turn, the scope of this objective is to acquire data and to give an interpretation on:

1. Extension of mineralogical transformations (d/p)
2. Extension of cationic exchange

Key results/achievements

Continuous reaction (reactivity)
pH 13-13.5 at 25 - 60 ºC:

- FEBEX bentonite reactivity is driven by montmorillonite dissolution: rates are equivalent to several other investigations (10-12 -10-13 mol m-2 s-1) 1mol in (O20(OH)4 2:1 phyllosilicate anion basis).
- By-products are zeolites (K- chabazite and K-filipsite (merlinoite)) and a Mg-rich mica and smectite clay minerals

pH 11-11.5 (Ca(OH)2/bentonite reaction pH) at 25 - 60 ºC:

- FEBEX bentonite reactivity is negligible. CSH-minerals have not been detected, but equilibrium calculations based on the speciation of the experimental aqueous phase are consistent with the achievement of an equilibrium state between montmorillonite and a tobermorite-type CSH-gel.

Diffusion (transport)
pH 13.5 at 60 ºC:

- The diffusion of the hiperalkaline plume through compacted bentonite (1.6 g/cm3 dry density) produces a mineralogical alteration front characterized by a cemented rim that affect 2 mm thickness. The thickness of the rim did not evolve with time. This means that diffusion is retarded by the reduction of porosity.
- The mineralogical composition of the rim is a mixture of poorly ordered clay materials, mainly brucite, hydrotalcite and Mg-sheet-silicate. Montmorillonite is

partially dissolved and a part of it remained trapped within the new-formed cements.

- Alkaline cations (mainly K+) have diffused far beyond the mineralogical alteration rim. The Mg^{2+} is displaced from the interlayer region of smectites.

pH 12.5 at 60 ºC:

- There was not detected any significant mineralogical alteration

Publications

J. Cuevas, R. Fernández, L. Sánchez, D. Ruiz de León, R. Vigíl, Leguey, S. (2006). Interacciones a corto y largo plazo en una barrera mineral compuesta por hormigón y bentonita (2006en: "Materiales Arcillosos: de la Geología a las Nuevas Aplicaciones". Editores: M. Suárez, M. A. Vicente, V. Rives y M. J. Sánchez. Salamanca, 2006.
12th Water-rock interaction, China (Kunming, August, 2007). *Alkaline diffusion in compacted bentonite. Experiments and modeling*. R. Fernández & U. Mäder. Rock-Water Interaction group, Institute of Geological Sciences, University of Bern, Switzerland, and L. Sánchez, R. Vigil de la Villa & J. Cuevas, Department of Geology and Geochemistry, University Autónoma of Madrid, Spain.
3rd International Meeting: Clays in Natural and Engineering Barriers for radioactive waste confinenment (Lille, 2007): *Reactive diffusion front driven by an alkaline plume in compacted Mg-homoionic bentonite*. Jaime Cuevas, Raúl Fernández, Laura Sánchez, Raquel Vigil de la Villa, Manuel Rodríguez and Santiago Leguey.
Jornada científica SEA'07. Sevilla (2007)**:** *Estudio termoquímico de la formación de zeolitas a partir de la reacción alcalina de una bentonita. Raquel Vigíl,* Jaime Cuevas y Santiago Leguey

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D2.4.7

2.4.2.3: Swelling pressures of MX-80 bentonite in solutions of different ionic strength

Participants

GRS

Goals/objectives of the research

The overall objective of the GRS contribution to the NF-PRO RTDC2 WP2.4 and 2.2 was a better understanding and quantification of the reactions of bentonite with repository relevant solutions of different salinities and pH. The chemical compositions of the solutions used in the experiments are typical for repositories in salt, clay and granite formations. This comprehensive study included the monitoring of important parameters like fluid composition, cation exchange, interlayer spacing, chemical and mineralogical composition of montmorillonite and swelling pressure of bentonite after 7 days, 1,2 and 3 years of reaction.

Key results/achievements

All solutions change the bentonite properties, but to a different degree. Each solution affects the mineralogy and the swelling pressure differently. In all reactions with all solutions montmorillonite was partially dissolved but remained the dominant mineralogical phase. As a consequence Mg, Al and Si contents in the solutions rose and the chemistry of the montmorillonite particles changed. Mg was substituted by Al in the octahedral layer which led to a decrease of interlayer charge. The interlayer spacing of montmorillonite was high in water and low salinity solutions and lower in the high saline solutions. Cation exchange capacity, total charge, interlayer charge and interlayer spacing of the montmorillonite particles generally decreased with reaction time. A good correlation of the interlayer charge of montmorillonite and swelling pressure of bentonite was observed. Swelling pressures are strongly dependant on the salinity of solution and pH. Swelling pressures decreased with reaction time in low and high saline solutions. The observed reduction of total and interlayer charge of the montmorillonite particles suggest that the mineralogical changes will eventually lead towards the formation of pyrophyllite/kaolinite. A schematic diagram was generated which explains the correlation of swelling pressure and interlayer charge as well as the processes occurring in open and closed geologic systems. Under the conditions of a closed system which can be assumed in a repository in salt or in clay formations the transformation of montmorillonite into pyrophyllite/kaolinite is more likely than the transformation in illite. From the results of this study it can be concluded that the swelling pressures of bentonites will decrease in the long run.. High saline solutions may lead to an almost complete loss of swelling capacity. Low ionic strength cement pore solutions have a similar effect on bentonite than high saline solutions.

Publications

Herbert, H.-J.; Kasbohm, J.; Moog, H. C.; Henning, K. H. (2004): Long-term behaviour of the Wyoming bentonite MX-80 in high saline solutions, Applied Clay Science 26, 275-291.
Herbert, H.-J. (2005): Zum Kurz- und Langzeitverhalten von Bentonit als Dichtstoff in Salzformationen – Conference proceedings of Altbergbaukolloqium Clausthal 2005, 9p.
Herbert, H.-J., Kasbohm, J (2005): Alteration of Montmorillonites in Saline Solution. - Proceedings of the 3rd International Meeting on Clays in Natural & Engineered Barriers for Radioactive Waste Confinement, Lille, September 17.-20. 2007. 163-164.
Herbert, H.-J., Kasbohm, J., H. Sprenger H., Reichelt, Ch. and A. M. Fernandez, A. M. (2007): Swelling pressures of MX-80 bentonite in solutions of different ionic strength – Paper presented at the Conference 3rd International Meeting on Clays in Natural & Engineered Bar-

riers for Radioactive Waste Confinement, Lille, September 17.-20. 2007. Paper submitted for publishing in Applied Clay Technology.
.Kasbohm, J. and Herbert, H.-J. (2007): Mechanisms for mineralogical alteration of dioctahedral montmorillonite in saline solutions – a TEM study. – Repreints of the contributions to the workshop on Long-term performance of smectitic clays embedding canisters with highly radioactive waste, Lund, Sweden, November 26-28, 2007, 70-80

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D2.4.8

2.5 WP 2.5: Transport

2.5.1 Overall objective of work package 2.5

The main aim of WP2.5 (Transport) is to get a better understanding of the basic processes important for radionuclide transport through a bentonite near-field of a repository for high-level radioactive waste. Because diffusion and sorption are the dominant processes, research activities of the work package focuss on these two aspects. For the diffusion/retention studies, both the complex bentonite and pure clay minerals (e.g. montmorillonite) are used. The priority questions for the diffusion/retention studies can be summarised as follows:

- are effective diffusion coefficients of anions and cations comparable with those of water (HTO)
- are Kd values measured in dispersed systems applicable to compacted systems (transferability)
- what is the effect of ionic composition of pore water on the transport (chemistry)
- coupling of chemistry and transport
- bottom-up approach.

Because corrosion of steel canisters produce corrosion products in the near-field, it is important to study the potential effects of these corrosion products. Priority questions for the sorption studies can be summarised as follows:

- what kind of corrosion products are formed (green rust, magnetite,...)
- are corrosion products important for sorption processes in the near-field
- what is the effect of iron on the sorption of other radionuclides
- what is the effect of corrosion products on diffusion

For the studies dealing with the iron corrosion products, a cooperation with WP2.3 is necessary.

2.5.2 Overview of work performed

2.5.2.1: Mass transport processes in the near field: Hyperfiltration of metal solutions through low-permeability material and Reactive transport of uncharged radionuclide complexes through clay membranes

Participants

BGR

Goals/objectives of the research

Two phenomena with special relevance for the transport of radionuclides in low-permeable media were investigated. Firstly, hyperfiltration (reverse osmosis) describes a transport process especially relevant for near field conditions. High pressure due to gas emanating from container corrosion leads to hyperfiltration mass transport. In the second part the transport behaviour of the Calcium-Uranyl-Carbonyl ($Ca_2UO_2(CO_3)_3$) complex was investigated. This radionuclide compound is uncharged under common environmental conditions and, therefore, may potentially be characterized to be highly mobile.

Key results/achievements

The two phenomena with special relevance for the transport of radionuclides in low-permeable media were investigated in the frame of two components which were carried out at both the BGR (Federal Institute of Geosciences and Natural Resources, Germany and ZSR (Center for radiation protection and radioecology, Germany). The results obtained were presented within two parts:
Firstly, hyperfiltration (reverse osmosis) describes a transport process especially relevant for near field conditions. High pressure due to gas emanating from container corrosion leads to hyperfiltration mass transport. Several experiments in the laboratories of BGR modelled this process and its contribution to a self-sealing of low permeable media.
In the second part focus the transport behaviour of the Calcium-Uranyl-Carbonyl ($Ca_2UO_2(CO_3)_3$) complex. This radionuclide compound is uncharged under common environmental conditions and, therefore, may potentially be characterized to be highly mobile. Its interaction with MX-80 bentonite has been studied in ZSR.
Major conclusions of the studies described above underline the significance of the observed phenomena for the mass transport within the near-field of radioactive waste repositories:
Hyperfiltration effects can cause mineral precipitation and thus decrease mobile pollutant mass. The precipitates decrease hydraulic conductivity and thus slow down solute transport. Precipitates of fully blocked pores may remain for extended periods of time. Overall, hyperfiltration processes can counteract transport of contaminants away from the near-field of leaky radioactive waster disposal sites through mineral precipitation and lowering of hydraulic conductivity. The quantitative aspect of this phenomenon is yet to be assessed.
Uranium(VI) in the uncharged ($Ca_2UO_2(CO_3)_3$) complex (CaUC) has revealed an enhanced mobility by a factor of ~2 in comparison of to solutions dominated by negatively charged U(VI) solutions. Ca-bentonite has been characterized to have a lower immobilisation ability for U(VI) than Na-bentonite for solutions with CaUC, possibly due to competitive cation exchange. However, Na-bentonite should be preferred instead of Ca-bentonite in the case of betonite application as a retention barrier in a deep geological repository.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D2.5.17

2.5.2.2: Final activity report on the retardation of Uranium and Caesium in clay rocks

Participants

FZR

Goals/objectives of the research

The objectives of work performed by ForschungsZentrum Rossendorf as part of NF-PRO was to check to which degree distribution coefficients derived from diffusion experiments could be compared with those derived from batch sorption experiments. Furthermore, ways to increase the quality of these parameters were explored. The systems investigated consisted of clay and related model components interacting with ceasium and uranium(VI).

Key results/achievements

Sorption parameters of U and Cs on bentonite (KWK) were studied at different dry bulk densities of the clay (1.3, 1.6, 1.9 g/cm3) in batch tests. An innovative approach to calculate the pore water chemistry at each density was used. The obtained parameters shall be used for long-term prognoses of diffusion processes in the near field of final repositories of nuclear waste. U and Cs sorption experiments were carried out as comparative tests on the pure mineral montmorillonite (Wyoming montmorillonite SWy-1) in 0.1 M $NaClO_4$.
The sorption was modelled using thermodynamic data of aqueous and solid species, protolysis data and surface complex constants from literature, and the characterization data of the solids. The modelled and measured sorption data are in a good agreement for pH-dependence, as well as for metal concentration dependence, including the precipitation of oversaturated minerals. Also the modelling with ion exchange models shows a good compliance between experiment and prediction in the case of sorption of Cs at various concentrations on montmorillonite and bentonite.
The K_D values obtained from the batch tests are 56.4, 49.2, and 44.9 mL/g at a Cs concentration of 1·10-6 mol/L for the pore water compositions calculated for the densities of 1.3, 1.6, and 1.9 g/cm3, respectively. We recommend the use of batch derived K_D values considering the pore water chemistry only for the prognosis of the diffusion process in slightly compacted bentonite. The diffusion derived K_D values are 61.7, 180.3, and 546.0 mL/g for the respective clay densities. The effective diffusion coefficients De of Cs are systematically higher than those of tritiated water, e.g., 15.8·10-11 m2/s and 5.8·10-11m2/s, respectively, at a density of 1.6 g/cm3. For a long-term prediction, the effective diffusion coefficient De is a crucial parameter. Using De from HTO diffusion experiments leads to a systematic underestimation of the diffusive flux, thus proving a weak point in risk assessment.
Concerning uranium(VI) the diffusion experiments posed serious problems. Due to a very slow migration of the uranium there was no break-through observed within the timeframe of this work package, not even at the lowest bulk density. Thus the experiments are continued beyond the NF-PRO timeframe. Results obtained later will be published in peer-reviewed journals.
The experiments performed with time-resolved laser-induced fluorescence spectroscopy (TRLFS) proved useful reveal the species actually occurring on mineral surfaces. In case of UO_2^{2+} surface species on alumosilicates, obviously TRLFS lifetimes are more suitable than peak positions to discriminate contributions of aluminol and silanol surface groups to the overall sorption. The present state of knowledge indicates that aluminol sites dominate uranyl sorption onto alumosilicates.

Publications

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Mibus, J., Sachs, S., Pfingsten, W., Nebelung, C., Bernhard, G. “Laboratory Column Experiments on the Migration of Uranium (IV)/(VI) in the Presence of Humic Acids in Quartz Sand”. Journal of Contaminant Hydrology, 89(2007),199-217.
Baumann, N., Brendler, V., Arnold, T., Geipel, G. “Uranyl sorption onto gibbsite studied by Time-resolved Laser-induced Fluorescence Spectroscopy (TRLFS)”. Journal of Colloid and Interface Science, 290(2005), 318-324.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D2.5.18

2.5.2.3: Diffusion and retention of ^{36}Cl-, $^{22}Na^{+}$, $^{85}Sr^{2+}$ and $^{134}Cs^{+}$ in compacted Na-Bentonite (Part1) Sorption of Ni (II) and Eu(III) and U(VI) on montmorillonite and MX-80 bentonite: Experimental and sorption modelling studies (Part2)

Participants

PSI

Goals/objectives of the research

The main goals of the study were i) to obtain a better understanding of the diffusion of neutral, anionic and cationic species in compacted bentonite as a function of the degree of compaction and the composition of the pore water, ii) to obtain more information on the effect of compaction on the sorption behaviour of cations and iii) to quantify the effect of carbonate on the sorption of selected cations on montmorillonite and bentonite. Montmorillonite is the dominant clay mineral component of bentonite considered as backfill material for a high-level waste repository (Nagra, 2002). Carbonate is together with hydroxide one of the most important inorganic ligands for radionuclide complexation in natural groundwaters. The formation of strong carbonate complexes in the liquid phase can potentially lead to a decrease in metal ion sorption

Key results/achievements

1. Diffusion of anions and cations in bentonite

Diffusion of 36Cl- in compacted bentonite was studied using through-diffusion, out-diffusion and profile analysis techniques. Increasing the bulk dry density of the bentonite resulted in a decrease of both the effective diffusion coefficient and the Cl- accessible porosity. Increasing the ionic strength of the external solutions resulted in an increase of both the effective diffusion coefficient and the Cl-accessible porosity. This can be explained by anion exclusion effects (Donnan exclusion). At high ionic strength values (I 1 M NaCl) the Cl--accessible porosity approaches the interparticle porosity. This interparticle porosity is the difference between the total and interlayer porosity of the bentonite. The interlayer porosity was found to depend on the degree of compaction. Up to a bulk dry density of 1300 kg m^{-3} the interlayer is build up of three water layers. Between 1300 and 1800 kg m^{-3} the interlayer water is reduced from three to two layers of water. Above 1800 kg m^{-3} evidences for a further decrease to one layer of water were found. These findings are in agreement with X-ray data found in the literature showing a decrease of the basal spacing of montmorillonite (the main clay mineral in bentonite) with increasing degree of compaction. The relationship between the effective diffusion coefficient of Cl^{-} and the diffusion accessible porosity can be described by an empirical relationship analogue to Archie's law. To predict the effective diffusion coefficient of Cl^{-} in compacted bentonite, the diffusion coefficient of Cl^{-} in water, the bulk dry density and the ionic strength of the pore water have to be known.
The diffusion of the double-charged $^{35}SO_4^{2-}$ was found to be slower than that of the single-charged $^{36}Cl^{-}$. This can partly be explained by the smaller diffusion coefficient of SO_42- in free water, and by a higher degree of exclusion of the double-charged anion from the free pore space. The capacity factor, α, however, was higher than that of $^{36}Cl^{-}$ indicating that $^{35}SO_4^{2-}$ sorbs on bentonite. Such a sorption process might be explained by an isotopic exchange of $^{35}SO_4^{2-}$ with the stable SO_4^{2-} in celestite ($SrSO_4$) that is present in bentonite in trace amounts.
The diffusion of $^{22}Na+$ and $^{85}Sr^{2+}$ through compacted bentonite was studied using through- and out-diffusion measurements, and profile analysis. All three methods resulted in similar

values of the effective diffusion coefficient and rock capacity values. The effective diffusion coefficient of both $^{22}Na^{+}$ and $^{85}Sr^{2+}$ decreases with increasing degree of compaction of the bentonite. The values are in good agreement with those measured on pure compacted Na-montmorillonite (Glaus et al., 2007). The sorption values (Rd values) measured on compacted systems were compared with those measured in dispersed systems, and with geochemical calculations. There was a very good agreement between these three values. Because $^{22}Na^{+}$ and 85Sr2+ sorb via cation exchange, this observation indicate that compaction of bentonite does not cause a change in the accessibility of the cation exchange sites. This is in agreement with earlier measurements on Opalinus Clay (Van Loon et al., 2005). The sorption values, after being normalized to the fraction of montmorillonite in bentonite, are also in good agreement with those measured on pure compacted Na-montmorillonite (Glaus et al., 2007) at similar chemical conditions. The diffusion/retention behaviour of $^{22}Na^{+}$ and $^{85}Sr^{2+}$ in bentonite is determined by the montmorillonite clay fraction present. The sorption is an ion exchange process, which can be seen as a partitioning in the subaqueous interlayer water. The ions in the interlayer water are mobile and therefore result in interlayer diffusion. The concentration gradient of the cations in the interlayer is the driving force of this interlayer diffusion process.

2. Sorption of cations on compacted bentonite

A key discussion in radioactive waste disposal is the question whether the adsorption behaviour of radionuclides in dispersed and in highly compacted materials are similar. It is common practice to measure sorption data on dispersed systems and to use these data to predict the sorption in compacted systems. The latter represent the situation in a real deep geological repository system. The discussions focus mainly on items such as the effect of compaction on the accessibility of sorption sites, i.e. on sterical effects, and not on the effect of compaction on the thermodynamics of the sorption processes. As shown for $^{22}Na^{+}$ and $^{85}Sr^{2+}$, sorption on loose and compacted sodium bentonite is identical and shows that neither the site accessibility, nor the thermodynamics of the sorption process are affected by compaction. In the case of cesium, however, material compaction indeed affects the thermodynamics of the sorption process such that sorption increases. This increase is due to a reduction of the interlayer space leading to a lower ability of the interlayer water for cation hydration. Cations with a low hydration tendency such as cesium therefore accumulate in the interlayer space whereas highly hydrated cations such as sodium tends to accumulate in the bulk water where water is easily available for hydration. The fact that mechanical compaction affects the thermodynamics of ion exchange processes in clay is an important finding and brings in a new aspect in the discussion on the transferability of thermodynamic data from diluted to compacted systems. The common practice of applying chemical and thermodynamic concepts valid for diluted systems to compacted systems must be basically scrutinised.

3. Effect of carbonate on the sorption of radionuclides

Sorption edges/isotherm data for Ni(II), Eu(III) and U(VI) in the absence of inorganic carbonate on Na-montmorillonite were available and were modelled using the 2SPNE SC/CE model to obtain the corresponding surface complexation constants and selectivity coefficients. In a first attempt to scope the problem a modelling study was carried out in which the uptake of the three radionuclides was calculated for trace concentrations for a montmorillonite in equilibrium with the range of MX-80 porewater compositions. The calculations were carried out under the assumption that only metal cations and the hydrolysed metal species sorb, all other aqueous species were considered to be non-sorbing. This is a conservative approach, with relevance to performance assessment, and yielded first estimates of the possible influences of complexation in “realistic” water chemistries on sorption.

The influence of equilibrium carbonate concentration as a function of pH was focused on the sorption of Ni(II), Eu(III) and U(VI) in suspensions of purified and conditioned Na-montmorillonite. The experimental data indicate that Ni(II) sorption onto montmorillonite is rather insensitive to the presence of inorganic carbon at levels up to 20 mM and pH values below 9, within the experimental uncertainties associated with the measurements. Only at very high inorganic carbon concentrations (0.1 M) was a more pronounced effect on sorption observable. On the other hand, a clear effect of the presence of inorganic carbon on Eu(III) and an even more pronounced effect on U(VI) sorption on montmorillonite was obtained. Model predictions using the 2SPNE SC/CE model with the assumption that metal carbonate complexes do not sorb were carried out. In the case of Ni the data and the model predictions agree within the uncertainty of the data. For Eu(III) and U(VI) the model prediction underestimate the measured data. This result could be an indication that (hydroxy)carbonate complexes could also taken up by the montmorillonite. On the other hand such effects could, at least in part, be explained by the quality of the thermodynamic data used in the modelling i.e. carbonate complexation constants which are too strong. The wet chemistry investigations alone are not sufficient to resolve this problem. Further investigations on the influence of inorganic carbonate using synchrotron radiation and pulsed laser-light spectroscopy methods are necessary. Finally, sorption isotherm data for Ni(II), Eu(III) and U(VI) on MX-80 bentonite have been measured and modelled using the two site protolysis non electrostatic surface complexation and cation exchange sorption model. Sorption was calculated assuming that only metal cations and positively charged and neutral hydroxy complexes sorb. A further key assumption in the model was that the sorption is only taking place on the montmorillonite fraction of the bentonite. This procedure is based on the so-called “bottom-up” approach, and the final aim is to generate a thermodynamic sorption data base to be used in performance assessment. The results for Ni(II) at trace concentrations indicated that the presence of Mn(II) could play a competitive role in sorption. Inclusion of Mn(II) in the model calculations improved the predicted sorption isotherm. In the case of Eu(III) the model prediction was in good agreement with the measured data. From the modelling evidence presented for U(VI) it appeared plausible that a neutral $Ca_2UO_2(CO_3)_3(aq)$ complex exists in solution which is non-sorbing. These results are of direct relevance to performance assessment studies.

Publications

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L.R. Van Loon, M.A. Glaus, W. Müller. Anion exclusion effects in compacted bentonites: towards a better understanding of anion diffusion. Appl. Geochem. 22, 2536-2552 (2007).
M.A. Glaus, B. Baeyens, M.H. Bradbury, A. Jakob, L.R .Van Loon, A. Yaroshchuk. Diffusion of 22Na and 85Sr in montmorillonite: evidence of interlayer diffusion being the dominant pathway at high compaction. Environ. Sci. Technol. 41, 478-485 (2007).

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D2.5.20

2.5.2.4: On the interactions between iron canister material and fission product ^{79}Se and ^{99}Tc under simulated deep repository conditions

Participants

SKB, PSI, NAGRA, Studsvik Nuclear

Goals/objectives of the research

Iron metal will be used as canister or part of the canister material for high level nuclear waste disposal in some countries. Cement may also be used as a construction material for the repository.
To understand the fates of redox sensitive radionuclides, in this work, the kinetics of reductive immobilization of Se-79 and Tc-99 on iron surface in normal groundwater (pH 8.5) and cement contacting water (pH 11.5 to 10) were investigated under anoxic conditions. The immobilized Se and Tc in iron corrosion layer were analyzed by XRD, SEM-EDS and micro- XAS.
The scope of this experimental work is much bigger than the originally planned. Se(IV)-Se(VI) redox behaviours in cement contacting water and Se(IV) at normal groundwater were not included in the original plan.

Key results/achievements

The results indicated that both Se and Tc can be immobilized at all tested experimental conditions. The reaction rates sequenced as: Tc(VII) > Se(IV) > Se(VI). The iron corrosion layer was found to play important role on reductive immobilization of these two radionuclides. For instance, at the cement contacting water with increased pH, the rate of Se(IV) immobilization on polished iron is very slow, but that on the pre-corroded iron or that after the polished iron being corroded in the same high pH solution are much faster. Iron carbonate greenrust was identified by XRD method in most experiments unless the corrosion product was too little to measure.
The evidences collected in this work are important for bettering our understanding on the fates of redox sensitive radionuclides at the repository conditions.

Publications

The manuscript on the interactions between iron canister material and fission products 79Se and 99Tc under simulated deep repository conditions is ready to be published .

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D2.5.21

2.5.2.5: Report on reduction of Pu(VI) on Fe surfaces: soft-x-ray absorption and resonant inelastic scattering study

Participants

UUP

Goals/objectives of the research

The goal is to address the issue of reducibility of highly oxidized Pu on the level of changes in the electronic structure of systems in question by utilizing the spectroscopic tools, such as soft x-ray absorption and resonant inelastic scattering techniques.

Key results/achievements

As a part of the project work, spectroscopic experiments were performed by our group at the Advanced Light Source, Lawrence Berkeley National Laboratory (LBNL) and Swedish synchrotron radiation laboratory MAXLAB. The samples studied were iron films exposed to the Pu (VI) solution in ground water, which were prepared by the group from Chalmers University, and polycrystalline PuO2+x as a reference. The technique utilized was resonant inelastic soft x-ray spectroscopy (RIXS). The emphasis was on a study of excitations in the Pu 5f shell. RIXS profiles of f-f transitions were shown to be defined by the oxidation state of actinides in prior work by our group on a number of U and Np compounds. To help with interpretation of experimental data, calculations of x-ray scattering spectra were also performed in framework of atomic multiplet theory. This type of calculations was established to be a good approximation for the description of RIXS results obtained on U and Np systems.
To take advantage of large scattering cross-section and higher resolution for the same slits of spectrometer and monocromator, the RIXS measurements were conducted near the Pu 5d threshold by tuning the energy of the incident monochromatized photon beam throughout the Pu 5d absorption edge. The RIXS cross-section for the f-f transitions is enhanced when the excitation energy is tuned to so-called "pre-threshold" structure in the Pu 5d absorption spectrum which is below the ionization limit.
RIXS spectra of reference PuO2+x recorded at various energies of the incident photon beam were compared with calculated spectra for Pu (IV), Pu (V), and Pu (VI) ions. Analysis of the data suggests a presence of both Pu (IV) and Pu (V) oxidations states in the studied PuO2+x sample. The contribution of either Pu (IV) or Pu (V) signal in the RIXS spectra becomes dominant at certain energies of the incident photon beam due to significant difference in the absorption cross-section between Pu (IV) and Pu (V) at those energies.
On the other hand the results obtained for the Pu species sorbed on the Fe foil only showed signs of Pu (IV) present. This can be seen from a comparison of RIXS spectra of the Pu-on-Fe sample and reference. At the excitation energy, which leads to the dominant Pu (V) contribution in the reference spectra, RIXS spectrum of the Pu species on the Fe foil only shows structures of Pu (IV). Anyhow, these preliminary data suggest reduction of sorbed Pu on Fe surfaces as it was observed for Np (V) and U (VI) in our prior studies.

Publications

K.O. Kvashnina, S.M. Butorin, D.K. Shuh, K. Ollila, I. Soroka, J.-H. Guo, L. Werme and J. Nordgren, *"Studies of Actinides Reduction on Iron Surface by Means of Resonant Inelastic X-Ray Scattering"*, in *Speciation Techniques and Facilities for Radioactive Materials at Synchrotron Light Sources*, NEA No. 6288 (2007), p. 115

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D2.5.22

2.5.2.6: On the interactions between iron canister material and fission product ^{79}Se and ^{99}Tc under simulated deep repository conditions

Participants

SKB, NAGRA, Studsvik Nuclear

Goals/objectives of the research

The main objectives of this experimental work are to investigate:

- The kinetics of interaction between iron canister material and redox sensitive radionuclides Se-79 and Tc-99 at anoxic groundwater conditions.
- The mechanisms of the immobilization process. The distribution and chemical forms of the iron corrosion products and immobilized Se and Tc were investigated by Raman spectrum, XRD, SEM-EDS, EXAFS.
- The influences of corrosion layer and pH values of solution (8.5 to 11.5).

Key results/achievements

The major experimental results are summarized below:

- At both near-neutral groundwater pH and higher pH conditions, Se(IV) reacts faster with pre-corroded iron surfaces than with polished iron surfaces.
- The Fe-Se(IV) reaction is much faster than the Fe-Se(VI) reaction.
- At higher pH, Se(VI) reacts faster with polished iron coupons than with pre-corroded and $FeCO_3$ coated iron coupons.
- At near neutral pH, polished and pre-corroded (both covered by Fe_3O_4 and FeCO3) iron displays similar Se(VI) immobilization properties.
- Under anoxic conditions after one or several months reaction, both Se(IV) and Se(VI) in groundwater can be reduced by iron and/or iron corrosion products ($FeCO_3$, Fe_3O_4 and green rust) to insoluble phase, possibly dominated by Se(-I) as $FeSe_2$.
- The previously reported reduction of Se(IV) to Se(-II) by Fe(0) [Myneni and Tokunaga, 1997] is not observed by micro XRF/XAS surface analysis.
- Se(IV) may be reduced to Se(0) by the UO_2 surface, as the results of solution analysis and thermodynamic calculations suggest, but no direct evidences are collected in this work. More investigations are needed.
- Tc(VII) can be reduced by polished and pre-corroded iron at simulated groundwater conditions with faster kinetics that Fe-Se(IV) redox reaction and much faster than that of Fe-Se(VI) redox reaction. The immobilized Tc is unevenly distributed in the whole corrosion layer of the iron coupon: at several positions of iron corrosion layer, about 15 % of Tc present is observed.
- Unlike the observations of pure UO_2 particle on corroded iron surface in a previous Fe – U(VI) experiment [Cui and Spahiu 2002], neither mm sized pure $FeSe_2$ particles nor TcO_2 particles were observed on the corroded iron surface in this work.
- Se(IV), Se(VI) and Tc(VII) immobilization in a thick cotton like dark green coloured iron corrosion products on iron surface under normal groundwater conditions were observed. Carbonate green rust is identified as the main corrosion product by XRD

method.

The evidences observed in this work demonstrated that Se(IV), Se(IV) and Tc(VII) can be reduced and immobilized on iron canister surface at anoxic near-field conditions. The involving of cement at the near field may slow down the Se immobilization process but after the iron being corroded, Se(IV) and Se(VI) can be immobilized quickly. The results of thermodynamic calculations support the above conclusions.

Publications

The manuscript has been written and to be published.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D2.5.23

2.5.2.7: Diffusion and retention processes in a bentonite Near-Field: Thorium sorption onto MX-80 (Volclay KWK)

Participants

SCK-CEN

Goals/objectives of the research

One of the objectives within NF-PRO WP2.5 (*transport*) is to provide thermodynamically underbuild sorption data instead of values for distribution coefficients (Rd) in order to be able to predict the effect of geochemical evolutions of the near-field on radionuclide retention.
Interaction processes of tetravalent radionuclides with clays under natural conditions are still not well understood and data (e.g. sorption/surface complexation data) are scarce or even lacking. The objective of SCK-CEN within the project was to improve the understanding on these interaction processes.
Th sorption edge onto purified Na-montmorillonite and Th sorption isotherms onto Volclay bentonite in a representative clay porewater in presence and absence of NOM were measured and a surface complexation model used to describe and interpret the experimental data.

Key results/achievements

Interaction processes of tetravalent radionuclides with clays under natural conditions are still not well understood and data (e.g. sorption/surface complexation data) are scarce or even lacking. In order to improve our understanding on these interaction processes, the Th sorption edge onto purified Na-montmorillonite and Th sorption isotherms onto Volclay bentonite in a representative clay porewater in presence and absence of NOM were measured and a surface complexation model used to describe and interpret the experimental data.
The sorption edge of Th on Na-montmorillonite, representing the major clay component of the bentonite, was determined. The logRd-values determined in 0.01M NaCl background electrolyte for the pH range 3-10 are between ~4.0 and 5.5 with an average Rd of ~115500 (logRd ~5.0). These values are consistent with sorption edge data of Bradbury and Baeyens (2005) for the same clay type.
The Th sorption isotherms on Volclay (no NOM present) were measured over a concentration range between 10-7 and 10-10 mol/l. The obtained sorption data were quite scattered and erratic for thorium equilibrium concentrations (Theq) lower than 10-10 mol/l. Thus, only data with Theq > 10-10 mol/l were considered in the data interpretation. The sorption behaviour for the VC/Th system is linear with a logRd of 3.6 ± 0.01.
In order to investigate the influence of NOM (~50 ppm C) on the Th sorption on bentonite, two experiments (i.e. routes) were followed: in Route 1, the bentonite was first equilibrated with NOM containing clay water prior to Th sorption while in Route 2, Th was first equilibrated with NOM prior to sorption to the bentonite. In this way we could find out if kinetic effects (fast and slow association/dissociation of Th-NOM complexes) are playing a role.
Thorium sorption onto NOM equilibrated bentonite (V2 / Route 1 experiment) was shown to be higher than in the VC/Th experiment (no NOM). The sorption data could be fitted for linear sorption, which resulted in a logRd of 3.98 ± 0.01. During equilibration of the bentonite with the NOM solution, NOM was sorbed onto the bentonite with a distribution coefficient calculated for NOM (RdNOM) corresponding to 3.1 l/kg and mainly the large size NOM molecules (> 30 kD) interacted with the bentonite. However, during Th sorption, the initial TOC content (~50 ppm) did not change. It seems that the small amount of initial sorbed NOM on the bentonite acts as an extra sorbent for Th.

In the third experiment (V3 / Route 2) where Th was pre-equilibrated with NOM before the addition to bentonite, sorption of Th is lowest compared to the previously described systems. The sorption data could also be fitted for linear sorption and the derived logRd is equal to 2.93 ± 0.02. This lower Rd show, that formation of Th-HA complexes in solution is clearly favoured in the V3 experiment compared to the V2 experiment, which reduces the Th sorption by around 1 log unit. Although the Rd for Th is lower than in the Volclay 2 experiment, a higher RdNOM was calculated (i.e. 87 l/kg). This suggests that part of Th is adsorbed as Th-HA complex.

The above described results show that the influence of NOM on Th sorption depends strongly on the experimental conditions and shows opposite effects. NOM (large size fraction) sorbed onto bentonite or forming a surface layer acts as an extra sink, while complexation of Th with HA in solution has a lowering effect on the sorption.

In order to model the sorption behaviour of Th, the 1 **s**ite **p**rotolysis **n**on-**e**lectrostatic (1SPNE) model developed by Bradbury and Baeyens (1997) was used. The simulations were performed using different thermodynamic databases, i.e. the LLNL TDB (Wolery, 1992), the NAGRA/PSI (NAPSI) TDB (Hummel et al. 2002) and literature values (Bradbury and Baeyens, 2005). Major difference between these databases is the logβ value of the Th(OH)4,aq species which ranges between ~16 (LLNL) and 18.5 (NAPSI). As this species represents the major aqueous species under the studied pH conditions (in absence of carbonates), sensitivity calculations were performed to get insight to what extent the different values may affect the simulation results.

It was shown that sorption edge data < pH 6 could be well reproduced by the combined NAPSI/B&B dataset, but to obtain a good fit with the experimental data over the entire pH range, the logβ value of the 1:4 hydrolysed Th species needed to be increased by 1 log unit (from -17.5 to -16.5).

Modelling the Th/Volclay isotherms in presence and absence of NOM was performed using the so-called generalized composite approach, meaning that the bentonite was represented by surface complexation equilibria on Na-montmorillonite being its main component.

Whereas also for the sorption data of the Th/VC experiment for Theq < 10-10 mol/l could be quite well reproduced by either the LLNL or NAPSI/B&B dataset, in the higher concentration range adaptation of the aqueous and/or surface complexation constants was required to fit the experimental data. This is interpreted to be related to the increasing significance of $Th(OH)_4$,aq in the higher concentration range, as well as to the fact that the sorption capacity of montmorillonite in Volclay may be less than the one of purified clay and that surface complexation constants derived from sorption edge experiments may not be directly applicable to more complex systems where also other competing and complexing species may be present and reduce the sorption.

As described already above, the influence of NOM on Th-sorption showed opposite effects, which made the interpretation of the V2 and V3 experimental results difficult and the modelling has not been straightforward.

In order to model the Volclay 2 experiment, the so-called free-ligand approach was applied using Th-HA complexation data from Murphy et al. (1999). Results of these simulations revealed that despite the incorporation of Th-HA interaction, adaptation of the modelling parameters was necessary to fit the experimental data. The used Th humate formation constant – due to its low value – changed only slightly the aqueous speciation distribution, but had no influence on the Th sorption behaviour. Another approach was applied to reproduce the experimentally determined isotherm of the V3 experiment. Based on a publication of Reiller et al. (2003), a so-called global Th-HA interaction constant was calculated (i.e. logHAβ = 19.6) and found to be consistent with values determined by Reiller et al. (2003). Using this value in the modelling resulted however in a severe underestimation of the experimental data. The fit-

ted logHAβ value was around 4.5 to 5 orders of magnitude lower, reflecting that NOM in fact interacted with the clay surface, as was also revealed by the calculated RdNOM value. This shows that this approach is indeed restricted or only applicable to purely competitive systems where no NOM/surface interactions are occurring. In order to improve the modelling results, a reaction representing the sorption of a Th-HA complex onto the Na-montmorillonite surface was added into the model and a surface complexation constant (logKSC) derived/fitted with a value for the V3 experiment of ~19.3 and ~20.3 for the V2 experiment (using the beforehand calculated global interaction constant of 19.6).
The modelling attempts performed to reproduce the experimental sorption data of the V2 and V3 experiment made clear that due to the lack of natural clay/NOM and Th/NOM interaction data, the simulation of ternary Th/NOM/clay systems up to now remains a fitting exercise. Therefore, the surface complexation constants for Th-HA onto Volclay derived in this study are highly "conditional" and associated with a high uncertainty. Another general drawback is that most of Th(IV)-HA complexation data are obtained at pH conditions £ 5, which may not simply be extrapolated to a higher pH range. Thus, complexation studies of Th(IV) by HA under natural groundwater conditions where competing reactions exist (such as Th-carbonate complexation) are needed to derive also more appropriate aqueous Th-complexation data. Besides this, it is important to get more insight into the role of kinetic effects onto the sorption behaviour of Th.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D2.5.24

2.5.2.7: Sorption mechanisms of Cs on magnetite

Participants

CIEMAT

Goals/objectives of the research

The main aim of the work to be performed at CIEMAT in WP 2.5, was to identify and characterize the sorption mechanisms of Cs on magnetite, that, in anaerobic conditions, is expected to be one of the main corrosion products of steel containers. The modeling of Cs sorption data was also carried out. The initially planned experimental work was already finished in 2005. Beyond the initial work plan, the effects of the temperature on Cs sorption were analyzed.

Key results/achievements

Work by CIEMAT has led to the following conclusions and key results:

- Sorption studies in the pure nanocrystalline magnetite showed that Cs is able to interact with the oxide surface.
- Sorption is non negligible at pH higher than 8.5 and tend to increase when the ionic strength of the solution decrease.
- Desorption experiments showed that part of the Cs becomes irreversibly sorbed.
- Sorption data could be satisfactorily fit with a simple model but to understand the actual nature of the complex, more detailed spectroscopic analysis are needed.
- No particular effects on the temperature for Cs sorption on magnetite were observed in the range 20-80 ºC.

Publications

Granizo N. and Missana. T “Mechanisms of Cesium Sorption onto Magnetite”, Radiochim.Acta, 94, 1-7 (2006).
T. Missana and N.Granizo: Mechanisms of Cesium sorption onto magnetite. Technical Report CIEMAT/DMA/M2142/05/05. Madrid, 2005.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D2.5.25

2.6 WP 2.6: Synthesis

2.6.1 Overall objective of work package 2.6

The objectives of this work package are the integration of the outcomes of RTDC2 and provide the link for their integration in RTDC5. To fulfil these purposes a consistent set of modelling exercises will be developed, in three degrees of complexity.

- Secondary modelling of individual experiments, to help to ensure that conceptual and numerical outcomes of the lab experiments are transferable to the subsequent stages of the Project.
- Interpretation and modelling of the interim data provided by the mock up "GAME scale" experiments that would integrate the main coupled processes among the NF components.
    - Geochemical evolution coupled modelling in the three evolutionary stages of the NF
    - Integrate diverse types of conceptual and numerical modelling to produce radionuclide flux modelling data
    - Treatment of uncertainties, both in processes and parameters. Sensitivity analyses aimed to identify main variables affecting the outcomes of different approaches.
    - Input for PA modelling

There are clear relationships between RTDC2 WP´s and the rest of the components within NF-PRO in a twofold sense both providing information on chemical conditions for alteration processes of other components and taking their outputs as intervening agents for the chemical evolution of the engineered clay barrier.

2.6.2 Overview of work performed

D2.6.4: RTDC 2 Synthesis Report (Final Version)

Participants

Goals/objectives of the research

Key results/achievements

2.6.2.2: Reaction and diffusion of cementious water in bentonite

Participants

QUINTESSA

Goals/objectives of the research

The aim of this study was to simulate a laboratory experiment investigating the effects of cementitious water diffusing through bentonite. The numerical simulations aimed to replicate the experiments as closely as possible. The chemical processes included in the model include ion-exchange reactions within the montmorillonites and kinetic dissolution/precipitation of primary and secondary minerals. The modelling study described in this report was carried out before the results of the experiments were available, as an exercise in "blind" modelling. This version, produced at the end of NF-PRO, also includes a comparison with the experimental results.

Key results/achievements

A number of input parameters are subject to uncertainty, such as the precise nature of kinetic and ion-exchange reactions, diffusion coefficients, pore water composition, montmorillonite dissolution models. A sensitivity analysis was carried out to determine the impact of such uncertainties upon the ultimate fate of the bentonite sample. The experiments used two types of fluid; one consisting of $Ca(OH)_2$ showed little mineralogical alteration, which was predicted by the simulations (Case 9). A high pH K-Na-OH-based water however, caused alteration to a depth of ~2 mm in the bentonite after a period of 1 year. The altered bentonite was analysed and was found to contain large amounts of hydrotalcite, gibbsite and brucite. Evidence was also found for the blocking of pores, limiting the extent of the alteration front after 6 months. Experimental evidence showed that ion exchange of Mg-montmorillonite to K-montmorillonite was not confined to this thin region however, and was found to extend throughout the whole of the bentonite cylinder. This movement of ion exchange fronts through the bentonite was also accurately simulated by the model. The choice of dissolution model for montmorillonite plays a very important role in the outcome of the simulations. Sato's TST and Twin-Site models demonstrated moderate amounts of bentonite dissolution, whilst the Yamaguchi model resulted in no discernible dissolution at all. Of the simulation cases considered in the sensitivity study, Case 6 (Yamaguchi dissolution model) was clearly the best match, exhibiting all the main characteristics of the experiment including pore blocking, brucite precipitation, little montmorillonite dissolution and the replacement of Mg- by K-montmorillonite throughout the length of the bentonite. Other factors had a smaller impact upon the simulation results. These were the rate of the ion-exchange reactions, which did not discernibly alter the rate or extent of dissolution but did impact upon the montmorillonite species present within the bentonite sample during the early stages of the simulation. In the later stages, the rates of secondary mineral precipitation play a role; fast precipitation results in pore blockage at the end of the sample exposed to the reservoir containing the cementitious water, thus limiting the amount of alkaline water that can enter the sample. This aspect would benefit in future from a more realistic treatment of mineral growth by considering time-dependent surface areas, as suggested by Steefel and van Cappellen.Other factors that were investigated as part of the sensitivity analysis, included the exact composition of the bentonite pore water, the smectite surface area, variations in porosity, and the inclusion of trace minerals in the bentonite mineralogy. However, none of these factors played a large part upon the outcome of the simulations. This is perhaps surprising in the case of the smectite surface area,

as it might be expected that the available surface area would be one of the most important factors governing the rate of montmorillonite dissolution. However, because the surface area and the relative mass of montmorillonite in the bentonite are so large compared to other minerals, the variations considered in the surface area actually have little effect on the overall results.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D2.6.5

2.6.6.3: Geochemical evolution of near field process modelling

Participants

ENVIROS

Goals/objectives of the research

Increase the knowledge on the geochemical processes in the EBS.
Progress in the implementation of the previous process in reactive - transport models.

Key results/achievements

The main results are summarised in the Synthesis Report of Component 2, which is written and edited by Arcos, D., Hernán, P., de la Cruz, B., Herbert, H.-J., Savage, D., Smart, N.R., Villar, M.V. and Van Loon, L.R.

Publications

de la Cruz, B., Villar, M.V., Turrero, M.J., Peña, J., Fernández, A.M., Carlsson, T., Herbert, H.-J., Meyer, T. Vokál, A., Arcos, D. 2005. Critical review and incorporation of information of EC, national and international programmes in RTD component 2. State-of-the-Art Report. NF-PRO RTD2 Deliverable 2.1.1.
Arcos, D., Hernán, P., de la Cruz, B., Herbert, H.-J., Savage, D., Smart, N.R., Villar, M.V., Van Loon, L.R. 2008. RTDC-2 Synthesis Report. NF-PRO RTD2 Deliverable 2.6.4.
Arcos, D., Grandia, F., Domènech, C., Fernández, A.M., Villar, M.V., Muurinen, A. Carlsson, T., Sellin, P., Hernán, P. 2007. Long-term geochemical evolution of the near field repository: Insights from reactive transport modelling and experimental evidences. Abstract presented at the Goldschmidt Conference 2007.
Arcos, D., Grandia, F., Domènech, C., Fernández, A.M., Villar, M.V., Muurinen, A. Carlsson, T., Sellin, P., Hernán, P. 2008. Long-term geochemical evolution of the near field repository: Insights from reactive transport modelling and experimental evidences. Journal of Contaminant Hydrology (submitted).

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D2.6.6

3 RTDC 3: Thermo-hydro-mechanical (geochemical) processes in the EBS

The objectives of RTD component 3 are:

- to improve the understanding of the thermo-hydro-mechanical and geochemical (THM(C)) processes in the near-field in an integrated way.
- to enhance the predictive capability of the existing models, especially in relation with the long-term.

3.1 WP 3.1: State of the art

3.1.1 Overall objective of work package 3.1

The main objective of work package 3.1 is to compile and analyse existing information on backfill materials and in the evolution of the clay barrier subjected to thermal and hydraulic flows, especially those processes that may affect the hydration dynamic.

3.1.2 Overview of work performed

3.1.2.1: Integrated state of the art report

Participants

ENRESA

Goals/objectives of the research

This report seeks to establish the level of process understanding in the buffer and backfill for the different host rocks and disposal strategies and derive the open question that still need to be answered.

Key results/achievements

A number of issues have been identified and discussed throughout the report which still require to be further investigated for each one of the three geological media considered.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D3.1.5

3.2 WP 3.2: Basic THM (C) processes in clay barrier

3.2.1 Overall objective of work package 3.2

The main objectives of this WP are:

- To evaluate the parameters and processes influencing hydration kinetics and moisture transfer in the clay barrier (temperature, hydraulic gradient), especially with respect to its long-time evolution and scale effects.
- To determine the impact of temperature on the hydro-mechanical properties of the bentonite and the reversibility of the modifications observed.
- To study the repercussion on microstructure of bentonite hydration.

Inside Component 3, this WP is mainly related to WP3.3, since both provide data on the long-term behaviour of the barrier under realistic conditions: WP32 through the FEBEX mock-up test, and WP33 through the FEBEX *in situ* test. There is also a connection with the issue on gas effects on the barrier behaviour dealt with in WP34, since the laboratory tests performed at high temperature in the context of WP32 give place to the generation of water vapour

3.2.2 Overview of work performed

3.2.2.1 Final report on laboratory tests performed by CIEMAT in the context of WP3.2

Participants

CIEMAT

Goals/objectives of the research

The following objectives were proposed and intended to be accomplished by means of laboratory tests:

- To determine the impact of temperature on the hydro-mechanical properties of the bentonite and the reversibility of the modifications observed;
- To improve the understanding of water flow under low hydraulic gradients, determining the existence of threshold or critical gradients for different bentonite dry densities;
- To evaluate the parameters and processes influencing the hydration kinetics in the clay barrier and to understand it, especially with respect to its long-time evolution
- To study the repercussion on microstructure of bentonite hydration: evaluate the evolution of porosity and microstructure of the bentonite with time and saturation and its influence on the thermo-hydro-mechanical properties of the material, as well as the effect of chemical changes on mechanical properties, because both aspects are believed to be of fundamental importance for the long-term evaluation of barrier performance (in connection with NF-PRO Component 2 WP2.2).

Key results/achievements

The results of some of the laboratory studies performed by CIEMAT in the context of WP3.2 of the NF-PRO Project are presented. They refer to the effect of the hydraulic gradient on the permeability of bentonite, the effect of the thermal gradient on the hydration of bentonite, and the repercussion of temperature on the hydro-mechanical properties of the bentonite. The information obtained improves the knowledge on the behaviour of expansive clay and will help the development of constitutive models and the interpretation of the results obtained in the mock-up and the *in situ* tests.

The hydraulic conductivity of the FEBEX bentonite compacted at different dry densities between 1.4 and 1.65 g/cm3 has been determined under low hydraulic gradients. No clear effect of the hydraulic gradient employed on the permeability value obtained has been detected. In addition, no evolution of the permeability with time (up to 970 days) has been observed. The comparison of the new results with those obtained under higher hydraulic gradients during FEBEX I, points to the existence of a possible critical hydraulic gradient around 2000. The critical gradient is the hydraulic gradient below which flow occurs but it is not Darcian. The possible threshold hydraulic gradient would be below 200 or 1400, depending on the dry density. The dependence of the value of the threshold gradient on the density and injection pressure has been pointed out. The threshold gradient is higher as the dry density is higher and the injection pressure is lower.

Infiltration tests are being performed on the FEBEX bentonite compacted at dry density 1.65 g/cm3. One of them is performed under thermal gradient, whereas another one is performed at isothermal conditions (laboratory temperature). The infiltration test performed under thermal

gradient showed that the permeability to water vapour of dry bentonite is very high. The initial saturation of compacted bentonite takes place quicker under thermal gradient than at laboratory temperature. The increase of hydraulic conductivity with temperature would account for this. Afterwards, the water intake is higher for the sample tested under room temperature, as the hot zones of the sample tested under thermal gradient remain desiccated. In fact, both tests seem to have reached a steady state, since the relative humidity inside the bentonite barely changes, especially in test GT40, that reached a steady state much before. The weight changes of the cells have been controlled in the last 14 months, suggesting that the water intake is very low in both cases.
With respect to the effect of temperature on the hydro-mechanical properties of the clay, it has been measured the dependence of the swelling strains of bentonite compacted to dry densities of 1.6 and 1.5 g/cm3 on temperature in the interval from 30 to 80°C. At high temperatures the swelling capacity of the clay slightly decreases, the decrease being more important for the highest density and the highest vertical loads. On the other hand, a clear decrease of swelling pressure as a function of temperature was observed for the dry densities of 1.5, 1.6 and 1.7 g/cm3. Nevertheless the deformation of bentonite is more dependent on the stress than on temperature. It has been also detected an increase with the temperature of the water saturated permeability of FEBEX bentonite compacted to dry density of 1.5, 1.6 and 1.7 g/cm3.
In spite of this, FEBEX bentonite remains suitable as a sealing material in HLW repositories (from the hydro-mechanical point of view) for temperatures of up to 80°C, as it keeps its low permeability and self-healing ability. No data are still available for higher temperatures, although the extrapolation of results points out to the preservation of properties for at least up to 100°C.

Publications

Conference abstracts:

"State of the bentonite barrier and THM effects observed after five years of operation" M.V. Villar & A. Lloret. ANDRA, Tours 2005.
"Advances on experimental techniques for the characterization of THM behaviour of bentonite" M.V. Villar & A. Lloret. ANDRA, Tours 2005.
"Temperature effects on the swelling pressure of a compacted bentonite at different dry densities"R. Gómez-Espina & M.V. Villar. EUROCLAY 2007. Aveiro (Portugal), 22-27 July 2007.

Conference papers:

"Experimental evidence of the interaction between THM behaviour and geochemistry in bentonites" (M.V. Villar, E. Castellanos, E, Romero & A. Lloret) 2nd International Conference Geoproc2006 (Nanjing, China) 22-25 May 2006. 6 pp.
"Estado de la barrera de bentonita tras siete años de simulación en laboratorio de las condiciones de un almacenamiento geológico profundo" M.V. Villar & R. Gómez, Reunión Anual Sociedad Nuclear Española (Tarragona, octubre 2006). 8 pp.
"Modelling the effect of temperature on unsaturated swelling clays" Marcelo Sánchez, Antonio Gens, María Victoria Villar & Leonardo Guimaraes, Internacional Symposium on Numerical Models in Geomechanics (NUMOG X), Rhodes (Greece) April 2007. 6 pp.
"Effect of temperature on the retention capacity of FEBEX and MX-80 bentonites" M.V. Villar & R. Gómez-Espina. E-UNSAT 2008 (First European Conference on Unsaturated Soils, Durham, July 2008). 6 pp.

"Swelling pressure development in compacted bentonite at different temperatures: laboratory tests and modelling" M. Sanchez, M.V. Villar, R. Gómez-Espina, Antonio Lloret & Antonio Gens. E-UNSAT 2008 (First European Conference on Unsaturated Soils, Durham, July 2008). 6 pp.
"Behaviour of a bentonite barrier in the laboratory: experimental results up to 8 years and numerical simulation" M.V. Villar, M. Sánchez, A. Gens (ANDRA 2007, Lille).
"Chemical influence on the hydro-mechanical behaviour of high-density febex bentonite" E. Castellanos, M.V. Villar, E. Romero, A. Lloret, A. Gens (ANDRA 2007, Lille).

Books and journals:

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Lloret, A.& Villar, M.V. (2007): Advances on the knowledge of the thermo-hydro-mechanical behaviour of heavily compacted FEBEX bentonite. Physics and Chemistry of the Earth, Parts A/B/C, 32(8-14): 701-715.
Villar, M.V., A.M. Fernández, R. Gómez, J.F. Barrenechea, F.J. Luque, P.L. Martín & J.M. Barcala. 2007. State Of A Bentonite Barrier After 8 Years Of Heating And Hydration In The Laboratory. In: D.S. Dunn, C. Poinssot, B. Begg (eds.): *Scientific Basis for Nuclear Waste Management XXX*. Mater. Res. Soc. Symp. Proc. **985,** 0985-NN11-19. Materials Research Society, Warrendale, PA.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D3.2.13

3.2.2.2 Thermo-Hydro-Mechanical behaviour of expansive clays

Participants

CIMNE

Goals/objectives of the research

In this research an effort to advance in the understanding of the Thermo-Hydro-Mechanical behaviour of expansive clays has been made. For that, a computer code has been used to predict and reproduce the results of a mock-up test and of several THM laboratory tests. New processes not previously considered have been taken into account in order to better reproduce and understand the behaviour observed.

Key results/achievements

The activities performed have been addressed to clarify some questions pending to be solved for the understanding and modelling of the EBS saturation and the evolution of its final stages stated in the State of the Art, which are:

- The role of the thermal gradient on the saturation process, especially at high temperatures. Experimental results confirm that saturation is delayed when a thermal gradient exists, especially if the temperatures reached in the barrier are higher than 100°C.
- The possible existence of a threshold hydraulic gradient, which could prevent the movement of water in the final stages of the buffer maturation, when suction is very low and the only driving force is the hydraulic pressure.
- The influence of thermal effects on swelling properties of bentonites.

In addition, the work has been oriented to check the capability of 'standard' THM models to predict the long-term behaviour of a heating and hydration tests at almost full scale (FEBEX mock-up).
The main new processes investigated have been the existence of threshold hydraulic gradient and the presence of thermo-coupling effects. In addition, the inclusion of the thermal effects on a double structure model (considering micro and macro structure) has been proposed. 'Standard' THM formulations do not include these phenomena in the analysis. Specific laboratory tests performed in the context of the NF-PRO project have been used to analyse these processes. The new developments have been proposed based on strong physical basis. Therefore, the better description of the clay behaviour obtained by using the new mathematical formulation is not due to the simple fitting of experimental data, but it is the results of the development of a more complete and reliable formulation. A better understanding of the clay barrier behaviour has been gained using a consistent framework based on sound physical laws.
As for the analysis of the mock-up test, the main activity has been the critical analysis of the comparisons between the evolution of the main THM variables of the mock-up test and the corresponding model predictions. The heating and hydration of the experiment has been maintained for 10 years, approximately. The finite element model used in the analysis was defined at the beginning of the test, no changes in the constitutive laws or model parameters have been introduced. Therefore, the model results presented in this report are actual predictions. It has been observed that standard THM formulations are able to predict the behaviour of a large scale heating test in the short and medium term (i.e. up to 3 years, approximately).

Qualitative long-term predictions have also been obtained with such standard formulation. But, to obtain reliable long-term predictions an enhanced THM formulation (including additional THM phenomena) has to be used. Finally, failure of a particular formulation to achieve a good reproduction of observed behaviour is a strong indication of lack of real understanding and a powerful argument towards further research work in that particular deficient area. Particularly, the improvements of the basic formulations described above have been proposed.

Publications

Sánchez M., Gens A. & Olivella S. (*under revision*) "Implementation algorithm of a generalized plasticity model for swelling clays' *Computer and Geotechnics.*
Villar M.V., Sánchez M. & Gens A. *(under revision).* "Behaviour of a bentonite barrier in the laboratory: Experimental results up to 8 years and numerical simulation". Physics and Chemistry of the Earth.
Sánchez M., Gens A. & Olivella S. (2007) "Behaviour of an expansive clay submitted to heating and hydration". Invited lecture: IUTAM Symposium on Swelling and Shrinking of Porous Materials From Colloid Science to Poromechanics. Rio de Janeiro, Brazil. August 2007.
Sánchez M., Villar M.V., Lloret A. & Gens A. (2007). "Analysis of the expansive clay hydration under low hydraulic gradient". International Conference: Mechanics of Unsaturated Soils. Weimar, Germany. 7-9 March, 2007.
Sánchez M., Gens A Guimarães L. &. Olivella S. (2007) "A generalised plasticity model for swelling clays: formulation, implementation and validation". Invited conference paper International Workshop on Constitutive modelling – Development, Implementation, Evaluation, and Application. Hong Kong, China. 12-13. January, 2007.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D3.2.14

3.2.2.3: Calibration of models of the THM(C) behaviour of buffer materials regarding moisture flow under thermal, hydraulic and thermo-hydraulic gradients

Participants

UWC

Goals/objectives of the research

Work has focused on processes that require investigation leading to calibration of models of the THM(C) behaviour of buffer materials. In particular, moisture flow under thermal, hydraulic and thermo-hydraulic gradients is considered. The key objectives are i) an improved understanding of the processes of thermally induced moisture migration in the buffer, ii) development of confidence in the ability of the theoretical formulation to accurately predict transient behaviour under laboratory conditions leading to improved predictive ability in large scale repository experiments, iii) validated computer software to accommodate these advances and iv) identification and quantification of a key process in the THCM behaviour of the buffer.

Key results/achievements

The programme of work by UWC as part of Work Package 3.2 is based on a series of the small scale thermal and hydraulic gradient laboratory experiments on MX-80 bentonite. These tests have enabled an investigation of heat and moisture movement in unsaturated clays under different wetting and heating paths to be made. The processes in these experiments has also been investigated via numerical simulation of the tests

A new apparatus termed a thermo-hydraulic (TH) cell has been designed, fabricated and calibrated to perform thermal gradient, thermo-hydraulic gradient and isothermo-hydraulic gradient tests on MX-80 bentonite. The TH cell is capable of measuring the transient temperature, relative humidity, volume flow rate of incoming water and swelling pressure. It also facilitates the determination of moisture content, dry density and chemical composition (anions and cations concentration) of the soil samples at the end of the tests. In the thermal test, the clay sample is subjected to fixed temperatures of 85 °C at the bottom end and 25 °C at the top end. In the thermo-hydraulic test, the same thermal gradient is used with the addition of deionised and de-aired water being supplied at the top end under a pressure of 0.6 MPa. In the isothermal test, the clay sample is supplied deionised and de-aired water from the top end under a pressure of 0.6 MPa and the temperature kept at 25 °C at both ends of the clay sample.

The test results show that there is a cycle of vapour and liquid moisture movement within the clay sample, with vapour moving from the hot to cooler regions, condensing and then moving as liquid moisture back towards the hotter regions. The observation of the accumulation of chloride ions near the hot end clearly indicates this phenomenon.

An empirical method has been developed to calculate the vapour fluxes using the variation of chloride ions concentration and moisture content with time. The vapour fluxes calculated empirically are found to be much lower than that determined by existing vapour theories. Therefore, the existing vapour theory has been modified to more closely predict the observed vapour fluxes. The new modified vapour model has been incorporated within a transient finite element code and applied to simulate the experimental work carried out in this study. The numerically simulated results match reasonably with the experimental heat and mass results offering a significant improvement on the original model.

Publications

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Cleall, P.J., Melhuish, T.A and Thomas, H.R., 2006 "Modelling the three-dimensional behaviour of a prototype nuclear waste repository", Engineering Geology Volume 85(2):212-220
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P. J. Cleall, R. M. Singh, N. Y. Do and H. R. Thomas 2006 "An experimental study of moisture movement due to thermal and thermo-hydraulic gradients in clays" Proceedings of the 5th Intl Congress on Environmental Geotechnics (5th ICEG) Cardiff, UK, 26-30 June, Vol 1, pp 693-700 ISBN 07277-3472-5.
S. C. Seetharam, P. J. Cleall and H. R. Thomas 2006 "On the inclusion of geochemical effects in coupled processes in soils" Proceedings of the 5th Intl Congress on Environmental Geotechnics (5th ICEG) Cardiff, UK, 26-30 June, Vol 1, pp 781-788 ISBN 07277-3472-5.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D3.2.16

3.2.2.4: THM investigations related to the FEBEX mock-up

Participants

CIEMAT and ENRESA

Goals/objectives of the research

The following objectives were proposed and intended to be accomplished by means of laboratory and mock-up tests:

- To determine the impact of temperature on the hydro-mechanical properties of the bentonite and the reversibility of the modifications observed.
- To improve the understanding of water flow under low hydraulic gradients, determining the existence of threshold or critical gradients for different bentonite dry densities.
- To evaluate the parameters and processes influencing the hydration kinetics in the clay barrier and to understand it, especially with respect to its long-time evolution and scale effects.
- To study the repercussion on microstructure of bentonite hydration: evaluate the evolution of porosity and microstructure of the bentonite with time and saturation and its influence on the thermo-hydro-mechanical properties of the material, as well as the effect of chemical changes on mechanical properties, because both aspects are believed to be of fundamental importance for the long-term evaluation of barrier performance (in connection with NF-PRO Component 2 WP2.2).

In addition, the continuation of the FEBEX mock-up at CIEMAT facilities provides information to know and understand the long-term behaviour of a clay barrier submitted to thermal and hydraulic gradients, and to validate and verify the near field THM models under controlled boundary conditions.

Key results/achievements

The results of some of the laboratory studies performed by CIEMAT in the context of WP3.2 of the NF-PRO Project are presented. The processes studied were selected in collaboration with ENRESA taking into account their relevance to PA. They refer to the effect of the hydraulic gradient on the permeability of bentonite, the effect of the thermal gradient on the hydration of bentonite, and the repercussion of temperature on the hydro-mechanical properties of the bentonite. The information obtained improves the knowledge on the behaviour of expansive clay and will help in the development of constitutive models and in the interpretation of the results obtained in the mock-up and the *in situ* tests.
The hydraulic conductivity of the FEBEX bentonite compacted at different dry densities between 1.4 and 1.65 g/cm3 has been determined under low hydraulic gradients. No clear effect of the hydraulic gradient employed on the permeability value obtained has been detected. In addition, no evolution of the permeability with time (up to 970 days) has been observed. The comparison of the new results with those obtained under higher hydraulic gradients during FEBEX I, points to the existence of a possible critical hydraulic gradient around 2000. The critical gradient is the hydraulic gradient below which flow occurs but it is not Darcian. The possible threshold hydraulic gradient would be below 200 or 1400, depending on the dry density. The dependence of the value of the threshold gradient on the density and injection pres-

sure has been pointed out. The threshold gradient is higher as the dry density is higher and the injection pressure is lower.
Infiltration tests are being performed on the FEBEX bentonite compacted at dry density 1.65 g/cm3 . One of them is performed under thermal gradient, whereas another one is performed at isothermal conditions (laboratory temperature). The infiltration test performed under thermal gradient showed that the permeability to water vapour of dry bentonite is very high. The initial saturation of compacted bentonite takes place quicker under thermal gradient than at laboratory temperature. The increase of hydraulic conductivity with temperature would account for this. Afterwards, the water intake is higher for the sample tested under room temperature, as the hot zones of the sample tested under thermal gradient remain desiccated. In fact, both tests seem to have reached a steady state, since the relative humidity inside the bentonite barely changes, especially in test GT40, that reached a steady state much before. The weight changes of the cells have been controlled in the last 14 months, suggesting that the water intake is very low in both cases.
With respect to the effect of temperature on the hydro-mechanical properties of the clay, it has been measured the dependence of the swelling strains of bentonite compacted to dry densities of 1.6 and 1.5 g/cm3 on temperature in the interval from 30 to 80°C. At high temperatures the swelling capacity of the clay slightly decreases, the decrease being more important for the highest density and the highest vertical loads. On the other hand, a clear decrease of swelling pressure as a function of temperature was observed for the dry densities of 1.5, 1.6 and 1.7 g/cm3. Nevertheless the deformation of bentonite is more dependent on the stress than on temperature. It has been also detected an increase with the temperature of the water saturated permeability of FEBEX bentonite compacted to dry density of 1.5, 1.6 and 1.7 g/cm3.
In spite of this, FEBEX bentonite remains suitable as a sealing material in HLW repositories (from the hydro-mechanical point of view) for temperatures of up to 80°C, as it keeps its low permeability and self-healing ability. No data are still available for higher temperatures, although the extrapolation of results points out to the preservation of properties for at least up to 100°C.
The FEBEX mock-up has been running and providing THM data on the behaviour of the bentonite barrier for more than ten years. The swelling pressure values measured agree with those determined in the laboratory for similar bentonite densities and temperatures. It seems that the physico-chemical processes controlling the evolution of the measured parameters suffer deviations related to the temperature field generated in the barrier, either as thermal gradient-driven processes (thermo-hydraulic coupled phenomena), or as temperature-driven processes (chemical or Arrhenius ones).

Publications

Abstracts sent to conferences:

“State of the bentonite barrier and thm effects observed after five years of operation” M.V. Villar & A. Lloret. ANDRA, Tours 2005.
"Advances on experimental techniques for the characterization of thm behaviour of bentonite" M.V. Villar & A. Lloret. ANDRA, Tours 2005.
“Temperature effects on the swelling pressure of a compacted bentonite at different dry densities”R. Gómez-Espina & M.V. Villar. EUROCLAY 2007. Aveiro (Portugal), 22-27 July 2007.

Papers sent to conferences whose abstracts had been previously accepted:

"Experimental evidence of the interaction between thm behaviour and geochemistry in bentonites" (M.V. Villar, E. Castellanos, E, Romero & A. Lloret) 2nd International Conference Geoproc2006 (Nanjing, China) 22-25 May 2006. 6 pp.
"Estado de la barrera de bentonita tras siete años de simulación en laboratorio de las condiciones de un almacenamiento geológico profundo" M.V. Villar & R. Gómez, Reunión Anual Sociedad Nuclear Española (Tarragona, octubre 2006). 8 pp.
"Modelling the effect of temperature on unsaturated swelling clays" Marcelo Sánchez, Antonio Gens, María Victoria Villar & Leonardo Guimaraes, Internacional Symposium on Numerical Models in Geomechanics (NUMOG X), Rhodes (Greece) April 2007. 6 pp.
"Effect of temperature on the retention capacity of febex and mx-80 bentonites" M.V. Villar & R. Gómez-Espina. E-UNSAT 2008 (First European Conference on Unsaturated Soils, Durham, July 2008). 6 pp.
"Swelling pressure development in compacted bentonite at different temperatures: laboratory tests and modelling" M. Sanchez, M.V. Villar, R. Gómez-Espina, Antonio Lloret & Antonio Gens. E-UNSAT 2008 (First European Conference on Unsaturated Soils, Durham, July 2008). 6 pp.
"Behaviour of a bentonite barrier in the laboratory: experimental results up to 8 years and numerical simulation" M.V. Villar, M. Sánchez, A. Gens (ANDRA 2007, Lille).
"Chemical influence on the hydro-mechanical behaviour of high-density febex bentonite" E. Castellanos, M.V. Villar, E. Romero, A. Lloret, A. Gens (ANDRA 2007, Lille).

Books and journals:

R. Gómez & M.V. Villar. (2006). Estudio de la bentonita febex sometida a las condiciones de un almacenamiento geológico profundo. Macla 6: 221-224.
M.V. Villar & A. Lloret (2006). Experimental Investigation on the Mechanical Behaviour of Unsaturated Bentonite at High Temperature. Unsaturated Soils 2006. Geotechnical Special Publication 147. Vol 2: 1719-1730. ASCE.
M. Sánchez, M.V. Villar, A. Lloret & A. Gens (2007) "Analysis of the expansive clay hydration under low hydraulic gradient" Experimental Unsaturated Soil Mechanics. Springer Proceedings in Physics. Vol. 112: 309-318.
M.V. Villar & R. Gómez (2007) "Retention curves of two bentonites at high temperature" Experimental Unsaturated Soil Mechanics. Springer Proceedings in Physics. Vol. 112: 267-274.
Villar, M.V. & Lloret, A. (2007): Dismantling of the first section of the febex in situ test: THM laboratory tests on the bentonite blocks retrieved. Physics and Chemistry of the Earth, Parts A/B/C, 32(8-14): 716-729.
Lloret, A.& Villar, M.V. (2007): Advances on the knowledge of the thermo-hydro-mechanical behaviour of heavily compacted FEBEX bentonite. Physics and Chemistry of the Earth, Parts A/B/C, 32(8-14): 701-715.
Villar, M.V., A.M. Fernández, R. Gómez, J.F. Barrenechea, F.J. Luque, P.L. Martín & J.M. Barcala. 2007. State Of A Bentonite Barrier After 8 Years Of Heating And Hydration In The Laboratory. In: D.S. Dunn, C. Poinssot, B. Begg (eds.): *Scientific Basis for Nuclear Waste Management XXX*. Mater. Res. Soc. Symp. Proc. **985,** 0985-NN11-19. Materials Research Society, Warrendale, PA.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D3.2.17

3.2.2.5 Integrated THM (C) experimental at real scale

Participants

AITEMIN and ENRESA

Goals/objectives of the research

The main objective of the work carried out by AITEMIN within WP 3.3 was to collaborate to a better understanding of the main THM processes taking place in the clay barrier for a high level radioactive waste repository in crystalline host rock (horizontal in-drift) under natural conditions (the FEBEX in-situ test): those referring to its hydration and to the establishment of the thermal gradient and the couplings between them.

Key results/achievements

Temperature at the Heater surface remains constant at 100 ºC. In general experiment temperatures seem to be stabilised but in the bottom part of the drift continue being higher than those in the sides and upper part for each section. Clay temperatures range from 80ºC close to the Heater up to 35 ºC close to the rock.
The water content in the clay buffer continues increasing at all points but the values at the outer and intermediate rings were almost 100% everywhere. The biggest differences were appreciated in the inner ring where values range from 100% far from the Heater area to 47-65% in the middle of the Heater. The hydration of the buffer has progressed more or less as initially expected although the rate of hydration became slower than predicted by THM models after approximately the first 3 years.
As for the water content, the total pressure continues increasing in all points in the buffer although at a slower rate lately, and also in the contact bentonite/rock. For the first time from the start of the experiment, the total pressure in one point has risen above the theoretical 6 MPa, reaching 6.03 MPa.
NF-PRO has extended the in-situ test data base for three years more (up to eleven), what helped to assert the previous observations as well as the comparison with the computational model for a longer period of time. However the information provided is still very limited for judging the long-term performance of the clay buffer due to its slow evolution.
More than 81% of the 534 sensors installed remains operative in spite of the harsh environmental conditions. After almost 11 years of operation, the accuracy of the “in-situ” instrumentation and therefore of the obtained data can not be determined/assured. Nevertheless, the redundancy of installed sensors and the consistence of the data trends do not indicate the existence of significant errors.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D3.3.5

3.3 WP 3.3: Integrated THM (C) experiment at real scale

3.3.1 Overall objective of work package 3.3

NF-PRO's work package 3.3 deals with the study of the THM (thermo-hydro-mechanical) processes in the near field for crystalline rock under natural conditions. For the horizontal concept the data from the FEBEX “in-situ” experiment is used for the validation of mathematical models for prediction of the THM behaviour. For the vertical concept (KBS-3V) a general model for multiphase porous media was used to provide a description of the evolution of the key macroscopic THM parameters.

3.3.2 Overview of work performed

3.3.2.1: Thermo-hydro-mechanical (geochemical) processes in the engineered barrier system - Integrated THM (C) experimental at real scale

Participants

NAGRA

Goals/objectives of the research

The FEBEX project at Nagra's Grimsel Test Site (GTS) is a large-scale experiment focused on demonstrating the technology of engineered barrier emplacement and the evaluation of the long-term evolution of the engineered barrier system (EBS) under natural conditions. The experimental procedure consists of emplacing two heaters in a 17 m long dead-end tunnel section, which is backfilled with bentonite blocks and sealed with a concrete plug. Extensive instrumentation of the FEBEX site has been realised, allowing measurements of e.g. temperature, volumetric water content and pressures in the bentonite. Another main objective of the project is to test and improve the predictive capability of coupled thermo-hydro-mechanical (THM) and thermo-hydro-geochemical (THG) codes.
The report under reference ("*Water content measurements using the TDR technique*") is the final report summarising the contribution by NAGRA to NF-PRO's Work Package 3.3 . The report summarises the water content measurements made using the time-domain reflectometry (TDR) technique for both the bentonite probes and the probes installed in the granite for the time period February 1997 to December 2007; an analysis of the data for the time period from January 2005 to December 2007 (NF-PRO) is also provided. The present report complements the Nagra Internal Reports (NIB) which was delivered to ENRESA and to the Swiss Federal Office of Education and Science, BBW (Table 1.1). In the above-mentioned reports, the objectives of the water content TDR measurements, the probe manufacture and calibration and the installation process are documented in detail.

Key results/achievements

The goals of the TDR laboratory experiment were:

- to develop and conduct TDR laboratory experiments,
- to gain more experience with TDR experiments,
- to increase the resolution of the measured water content and
- to improve the location of water content anomalies along the probes in low porosity applications.

In a first step, the experimental configuration successfully developed, installed and further optimized to help effective and simultaneous desaturation of two rock samples under controlled conditions. Desaturation experiments were performed on two granitic rock samples, one was relatively homogeneous, and the other was intersected by a shear zone. A relatively low water content of ~0.15 % and 0.025 % was extracted by drying the two rock samples. Such water contents are more than one magnitude lower than the typical porosity of granitic rock (~1 %). Reasons for this discrepancy may come from samples that were not fully saturated when excavated. It is further possible that the samples were not fully desaturated during the experiment. Samples with smaller diameters could probably reduce the time required for full desaturation.

The accompanying TDR measurements appear to be only slightly affected by the desaturation process. It was therefore difficult to estimate the sample's water content from TDR and relate it to the gravimetric water content. The measured water contents from the TDR pulse widths provided limited information that could not fully explain the desaturation process. Additional information on the water content in the rock sample may be expected from analysis of the TDR reflectivity. TDR is widely used in soil physics, where reflectivity negatively correlates with water content. Future experiments may concentrate on TDR reflectivity to investigate this correlation in low porosity rocks.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D3.3.7

3.3.2.2: Final activity report for POSIVA, WP3.3

Participants

POSIVA

Goals/objectives of the research

see D3.3.9

Key results/achievements

see D3.3.9

Publications

Posiva has continued, mainly outside the NF-Pro activities but closely related and relevant to WP3.3, the modelling work to improve the technical capabilities of the modelling and to reassess, support and confirm the results presented in D3.3.9. This has been described in a set of Posiva Working Reports available at Posiva's home pages www.posiva.fi:
Antti Lempinen. *Freefem++ in THM Analyses of KBS-3V Deposition Hole.* Working Report 2006-76, Posiva, December 2006
Antti Lempinen. *Swelling of the Buffer of KBS-3V Deposition Hole.* Working Report 2006-77, Posiva, December 2006
Antti Lempinen. *Working Report 2006-78*, Posiva, Simulations for EBS Task Force BMT 1, December 2006
Antti Lempinen. *Working Report 2006-79, Posiva, THM Model Parameters for Compacted Bentonite,* December 2006

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D3.3.8

3.3.2.3 Thermo-hydro-mechanical analyses of a deposition hole for spent nuclear fuel

Participants

VTT

Goals/objectives of the research

The aim of this study was to contribute to the thermo-hydromechanical analysis of the deposition holes for the canisters in a KBS-3V type repository.

Key results/achievements

First, a general model for multiphase porous media with more than one species in each phase was introduced. The general model was then simplified according to the knowledge about the behaviour of the bentonite. This model was discretised with the finite element method and implemented with a general-purpose solver programme. The simulations were repeated with various sets of boundary conditions, which are assumed to represent different scenarios and variation in the bedrock properties.
The hydraulic response to variation of the geometrical distribution of the water sources is strong. With inflow of water from a narrow band or from the backfill only it would take hundreds of years to complete the resaturation phase. If the flow is uniform from the backfill and also from the rock around the canister the resaturation phase takes 30 to 40 years. The availability of ground water in rock has minor importance as the ability of bentonite to take up water dominates the process. Taking into account the effect of trapped pore air prolongs the resaturation phase significantly, although the volume of the compressed pore air is small. If a 95 % or 99 % degree of saturation is considered to be full saturation, then the effect of trapped air is small. With low uniform inflow, low initial moisture in bentonite and a constant gas pressure the calculated resaturation time is 14 years.
The ability of the bentonite buffer to do mechanical work is not strong enough to make the buffer to swell into the deposition tunnel.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D3.3.9

3.3.2.4 Numerical modelling of the coupled Thermo-Hydro-Mechanical of the in-situ test at Grimsel underground laboratory

Participants

CIMNE

Goals/objectives of the research

The underlying aim of work described in this report is to validate the conceptual model for deep geological disposal in granite with the following scope of work:

- The activity has been focused on numerical modelling of the coupled THM (Thermo-Hydro-Mechanical) processes observed in the in-situ test that is being carried out at Grimsel underground laboratory.
- Analysis of THM processes and couplings in clay barrier and hosted media (granite) at full scale, in a natural media and under actual conditions.
- Critical study of the main THM variables by comparing model outputs and experimental data in the clay barrier and near field.

The specific goals were:

- To check the capabilities of an existent coupled THM formulation to predict the behaviour of a clay barrier and the natural rock submitted to heating and hydration under actual conditions.
- To validate the mathematical formulation and computers code using actual field data.

Key results/achievements

- The modelling of the *in-situ* test has contributed to the understanding of the main THM processes and phenomena that take place in the clay barrier and near field of a repository for high level radioactive waste under actual field conditions.
- Despite the problem complexities (i.e. heterogeneities and uncertainties inherent to a natural system), it was observed that the mathematical formulation and the operational model were able to reproduce quite well the global behaviour observed in the experiment both in the clay barrier and in the host rock.
- It seems that, in spite of the fact of the presence of heterogeneities in the host medium, a homogeneous axisymmetric model can predict satisfactorily the main tendencies observed in the rock.

Publications

Sanchez, M., Gens, A., Olivella, S. Guimares, L. do N. (2006). Modelling the behaviour of expansive clays. 6th European Conf. Num. Methods Geotech. Engng., Taylor and Francis, London: 11-17

Gens, A., Olivella, S. Guimares, L. do N. (2006). On modelling coupled phenomena in porous media. Int. Conf. Computational anad Exp. Engng and Sciences. Indian Institute of Technology. Chennai: 121-126

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D3.3.10

3.4 WP 3.4: Gas effects on the THM behaviour of clay buffer

3.4.1 Overall objective of work package 3.4

The main objective of work package 3.4 is to improve process understanding and to test/validate modelling approaches on gas movement and buffer performance, which may be used in performance assessment. High-quality test data from a large-scale gas injection test will be used to test/validate modelling approaches. The test will be interpreted to examine issues relating to up scaling and to provide additional information on the process of gas migration.

3.4.2 Overview of work performed

3.4.2.1: Hydraulic Tests with Surface Packer Systems

Participants

BGR

Goals/objectives of the research

For the hydraulic characterization of the excavation damaged zone BGR has developed surface packer systems. This packer type is fixed directly on the gallery wall, for this reason it is very qualified as a tool to characterize the area that is most damaged by excavation where borehole packers are not applicable. The surface packer systems were used in the HRL Äspö in galleries that were excavated by drill and blast and by TBM, also in deposition holes. Hydraulic tests with water, air, and Helium as test fluids were conducted to investigate the hydraulic properties of the EDZ.

Key results/achievements

Hydraulic tests were conducted mainly on test locations were no fracture or crack was visible. The permeability values that have been derived from these tests are based on the comparison of measured and calculated pressure at the end of the test. These values do not indicate a cohesive network of microcracks in the rock matrix, but this does not mean that such networks nowhere exist: especially in one test (which has not been evaluated with respect to a permeability value due to a leakage) gas flow in microcracks was observed. For the early time period of the tests the measured pressure drop is quicker, which can be seen even more clearly in the pressure derivative. This can be explained by dead-end microcracks with slightly increased permeability that are connected to the testing volume, but not connected to a cohesive network that forms a pathway between the open gallery wall (or the natural fracture network) and the testing volume.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D3.4.7

3.4.2.2: Large-scale gas injection test (Lasgit)

Participants

NERC (BGS) and SKB

Goals/objectives of the research

The objective of this experimental programme is to undertake a large-scale gas injection test (Lasgit) to provide data to improve process understanding and test/validate modelling approaches, which might be used in performance assessment. Specific objectives are: (1) perform and interpret a large-scale gas injection test based on the KBS-3 repository design concept, (2) examine issues relating to up-scaling and its effect on gas movement and buffer performance, (3) provide additional information on the process of gas migration, and (4) provide high-quality test data to test/validate modelling approaches. The project will be undertaken in the Äspö HRL. The basic idea is to instrument a KBS-3 type deposition hole (existing) and deposit a full-scale canister equipped with gas injection filters.

Key results/achievements

The deposition hole was closed on the 1st February 2005 signifying the start of the hydration phase. Groundwater inflow through a number of conductive discrete fractures resulted in elevated porewater pressures leading to the formation of conductive channels (piping), the extrusion of bentonite from the hole and the discharge of groundwater to the gallery floor. This problem was addressed by drilling two pressure-relief holes in the surrounding rock mass.
Artificial hydration began on the 18th May 2005 after 106 days of testing. Initial attempts to raise porewater pressure in the artificial hydration arrays often resulted in the formation of preferential pathways. These pressure dependent features were not focused in one location but occurred at multiple sites at different times in the test history. These pathways appear to be relatively short lived, closing when water pressure is reduced.
It was determined that both pressure relief holes should remain open until the bentonite had generated sufficient swelling pressure to withstand the high water pressure in the system when these holes are closed. Packers were installed into the pressure relief holes on 23rd March 2006 and sections in them closed off over the period to 5th July 2006. There was no repeat of the formation of piping through discrete channels so, on 20th November 2006, pressures to the artificial hydration filters on the canister were increased to 2350 kPa.
Pressure data from a number of sensors including FR901, RW901 and most of the porewater pressure sensors mounted on the borehole surface, seem to suggest some form of time dependent (temporal) evolution in the hydraulic characteristics of the rock mass adjacent to the Lasgit deposition hole. Monitored discharge rates from the pressure relief holes show a slow progressive reduction in value with time. These effects could be caused by a number of reasons from clogging and permeability reduction along conductive fractures near the Lasgit deposition hole, to operational activities performed at different locations within the site.
Monitored porewater pressures within the bentonite remain low, ranging from 230 kPa to 635 kPa. This is in contrast to the water pressure measured at the face of the deposition hole which ranges from 1055 kPa to 2510 kPa. Suction pressures recorded at psychrometers embedded within the bentonite show that suction is declining, confirming that resaturation is progressing, although the rate of hydration does appear to be slowing.
Monitored radial stress around the clay continues to increase steadily ranging in value from 1685 kPa to 5515 kPa, with an average value of 4230 kPa. In the absence of hydraulic piping the rate at which radial stress increases appears insensitive to the absolute value of porewater

pressure applied to the filter assemblies, confirming the modelling work described in this report. Analysis of the distribution in radial stress shows a narrow expanding zone of elevated stress propagating vertically upwards to around 3.5m.
Stress measurements on the canister surface indicate radial stresses in the range 4800 kPa and 5030 kPa, which is comparable with the average value of radial stress monitored on the rock face. Axial stress is significantly lower at 4380 kPa.
Axial stress within the clay ranges from 4910 kPa to 6230 kPa (excluding sensor PB901). Axial stress is non-uniformly distributed across the major axis of the emplacement hole and generally exhibits only minor sensitivity to changes in porewater pressure.
The axial force acting on the steel lid initially reduced after the deposition hole was closed but has risen again following the closure of the pressure relief holes. The continuum axial swelling pressure within the bentonite is now greater than the initial pre-stress applied by the lid. The slight reduction in force prior to the closure of the pressure relief hole packers can be explained by convex deformation of the steel lid in response to the uneven distribution in axial stress.
Displacement sensors indicate a fairly uniform drop in lid height relative to the gallery floor during the early part of the test history, mirroring the relaxation in the initial pre-stressing applied to the lid. Analysis of the subsequent displacement data suggests a slight distortion of the lid may have occurred as it deforms to accommodate the uneven distribution in axial stress. Since the installation and closure of packers into the pressure relief holes the lid has moved significantly upwards with an increasing disparity in displacements at different locations, indicating an increased distortion, probably linked to the uneven distribution of the axial force across the deposition hole.
Analysis of the volumetric flow rate data indicates a disproportionably large flux into the bentonite around the canister, indicating a higher permeability value in this region of the system. Volumetric flow rate through the artificial hydration filters is not particularly sensitive to the modest pressures applied to the filters.
Analysis of the volumetric flow rate data indicates that in general the proportion of flux into the clay from the various hydration sources (i.e. mats and canister filters) remains fairly constant with time, suggesting a general reduction in clay permeability as the clay hydrates.
The resaturation phase of the Lasgit experiment has been examined using numerical models developed with the TOUGH2 code and the EOS3 equation of state module. Model runs found that the impact of a single flowing fracture on the overall resaturation process was likely to be limited. In contrast, flow through the general rock mass and associated minor fractures could have a significant effect on the resaturation process depending on the permeability value selected.
A second group of models incorporating explicit representation of the individual bentonite rings and cylinders found that the rings around the canister were the most difficult to resaturate fully within the timescale of the experiment. In particular, if the gap between canister and bentonite rings seals quickly and effectively then full resaturation could take many years.
The effectiveness of the seal between canister and bentonite appears to be a critical parameter in determining the overall time taken to resaturate the facility.
A preliminary set of hydraulic and gas injection tests were started on the 25th May 2007 with the isolation of the lower canister filters FL901 to FL904 while artificial hydration continued through all other canister filters and filter mats. After a period of 27 days a constant head test was initiated on filter FL903, raising its pressure to 4.3 MPa for 28 days and then reducing it to 560 kPa for a further 19 days. Gas injection to FL903 was then begun with an initial volume of gas being compressed at a steady rate for 13 days, a period of 22 days with gas pressure held constant and then a further period of 22 days during which pressures were raised

again. Compression of the gas was then halted and the pressure monitored as it decayed for a further 4 weeks.
Preliminary modelling of the hydraulic test has been carried out using a 2D axisymmetric variably saturated finite element porewater flow model. Fits were obtained to the initial pressure decay data for the four filters that were isolated using values for hydraulic conductivity ranging from 9x10-14 to 1.6x10-13 ms-1 and specific storage values ranging from 5.5x10-5 to 4.4x10-4 m-1. The constant pressure test on filter FL903 was fitted with a hydraulic conductivity of 7.5x10-14 ms-1 and a specific storage of 2.5x10-5 m-1. The modelling done to set the initial conditions also shows that a significant zone around each of the canister filters remains unsaturated.
Analysis of the gas injection data suggest that gas starts to flow into the buffer at a pressure of about 775 kPa, which is much lower than the expected gas entry pressure for intact bentonite. It therefore seems likely that gas is flowing between the bentonite and the canister and possibly between bentonite blocks. The sudden reduction in gas flow when injection pressure was held constant is strongly indicative of pathway rather than visco-capillary flow within the original porosity of the clay.
Upon restarting gas injection pathway propagation continues at the outset. Gas flux into the clay gradually increases as the pressure in the system rises. At a gas pressure marginally greater than the local total stress measured on the rock wall (but a little smaller than the radial and axial stresses measured on and near the canister surface respectively), flux into the clay rapidly increases. Gas pressure continues to rise reaching a peak pressure of 5.66 MPa, which is marginally greater than the axial stress measured at PB902. This is followed by a small spontaneous negative transient leading to a quasi steady state. The post peak gas flux exhibits dynamic behaviour (over and undershooting flux into the system) suggestive of unstable gas flow. This general behaviour is reminiscent of the responses observed in laboratory scale tests reported by Horseman et al. (1999) and Harrington and Horseman (2003).
Following the cessation of injection, the pressure drops rapidly initially but then decays very slowly towards an asymptotic capillary threshold pressure, which is estimated to be about 4900 kPa, close to the average radial stress measured on the canister surface of 4900 kPa.
Following peak gas pressure a well pronounced increase in radial stress occurs around the entire base of the deposition hole, with the highest increase noted in the vertical plane below the point of injection. Porewater pressure data from the deposition hole wall exhibit similar behaviour, though initial results suggest that the pulse in porewater pressure dissipates at a faster rate than that of the radial stress.
Porewater pressure sensors located within the buffer show no obvious sensitivity to the injection of gas. In contrast, axial stress sensors located beneath and above the canister appear to register the passage of gas providing evidence for the time dependent propagation of gas pathways.
While it is difficult to make definitive statements regarding the exact direction and number of gas flow paths, it seems highly that the gas moved generally downwards away from the injection filter and then along the interface between blocks C1 and R1 and/or R1 and R2. This is logical as there is a clear axial stress gradient running from high to low from the top of the deposition hole to the lowest stress sensor. Under most conditions gas would propagate along such a stress vector. The fact that the gas pressure asymptotes at a value close to the local total stress, may suggest that the small amount of gas injected during the test remained resident in the buffer/deposition hole.
However, the general coupling between gas, stress and porewater pressure at the repository scale is extremely important and can readily be explained through concepts of pathway dilatancy. The reduction in flux when gas pressure was held constant supports this hypothesis. These observations are qualitatively similar to those reported by Horseman et al. (2004).

During the hydration phase, Lasgit has yielded high quality data relating to the hydration of the bentonite and the evolution in hydrogeological properties adjacent to the deposition hole. The limited preliminary hydraulic and gas injection tests confirm the correct working of all control and data acquisition systems. Lasgit has been in successful operation for in excess of 1000 days. The decreasing rate of change in sensor outputs demonstrates that significant progress in the hydration of the bentonite has been made.

Publications

Birchall, D.J., Harrington, J.F., Noy, D.J., Cuss, R.J. and Sellin, P. (2007). Lasgit (large scale gas injection test), 3rd International Meeting on Clays in Natural & Engineered Barriers for Radioactive Waste Disposal, Lille, France. **Poster presentation**

Sellin, P. and Harrington, J.F. (2006). Large-Scale Gas Injection Test (Lasgit): Current Status. American Nuclear Society High Level Waste Meeting, Las Vegas.

Horseman, S.T., Birchall, D.J., Harrington, J.F. and Sellin, P. (2005). Large scale gas injection test (Lasgit) at the Äspö Hrad Rock Laboratory in Sweden, 2rd International Meeting on Clays in Natural & Engineered Barriers for Radioactive Waste Disposal, Tours, France. **Poster presentation**

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D3.4.8

3.4.2.3: Numerical modelling in relation to LASGIT

Participants

CIMNE

Goals/objectives of the research

The main objectives of the work described in this report were:

- To develop a numerical formulation capable of simulating the migration of gas through an engineered barrier incorporating the possibility of opening of discontinuities due to gas pressure;
- To check the capabilities and performance of the model in a simulation of a large scale gas migration test: LASGIT;
- To generate an enhanced understanding of the processes taking place in gas migration from the critical examination of the numerical modelling results.

Key results/achievements

The report describes the following key results and achievements:

- A numerical formulation has been developed in which the buffer material can develop discontinuities at any point in a smeared way. Discontinuities are represented by a higher intrinsic permeability calculated as a function of a notional aperture which changes with deformations.
- The capability of the numerical formulation and associated numerical code has been proved via the modelling of the large scale LASGIT test
- Gas migration process understanding has been enhanced from the results of a series of sensitivity analyses demonstrating the effect of parameters such as initial suction, intrinsic permeability function and retention curve

Publications

Olivella, S. and E.E. Alonso, 2008, Gas flow through clay barriers, Geotechnique, vol 58, 3, pp 157:176.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D3.4.10

3.5 WP 3.5: Crushed salt engineered barrier behaviour

3.5.1 Overall objective of work package 3.5

An essential part of the EBS is the backfill used to fill cavities. In continuation to earlier investigations, special questions on various backfill components are processed in WP 3.5.

The BGR investigations are focused on the compaction behaviour of crushed salt with added bentonite. Bentonite is used as additive to accelerate the long-term process of compaction and to reduce the permeability of the crushed salt backfill in better time.

IfG analyses the HTM-behaviour of highly pre-compacted crushed salt bricks. IfG achieves triaxial compression and permeability tests at different confining pressures, shear-test at increasing normal pressures between highly pre-compacted crushed salt blocks and between the pre-compacted blocks and the host rock (rock salt) including brine injection.

NRG/UTR investigates on the compaction behaviour of crushed salt with low porosity under normal conditions and after brine intrusion. The results are analysed using a multi-mechanism model.

3.5.2 Overview of work performed

3.5.2.1: Report on adaptation of the material laws to the laboratory results

Participants

IfG

Goals/objectives of the research

With respect to an alternative concept for backfilling of remaining openings, the reported investigations were aiming to investigate both the mechanical compaction behaviour and the evolution of transport properties in salt bricks (artificial pressed granular salt with a porosity of ~8%), as a prerequisite to develop mechanism-based constitutive models describing these processes in the low porosity region (10 - 1%). A key factor is the role of water, since it affects in a complex manner the coupled hydraulical/mechanical properties of granular salt. Additionally, the experimental compaction results are discussed related to various modelling concepts.

Key results/achievements

The focus of this experimental study is divided into two topics:
Laboratory investigations were aiming at a comprehensive data basis regarding compaction and hydraulical behaviour of the pre-compacted salt bricks (initial porosity <10%) with respect to the numerical description of their long-term behaviour if they are used as sealing elements. Special account is given to humidity effects, affecting both, mechanical and hydraulical properties. The investigations were focusing on the following issues:

- Triaxial compression and permeability tests at different confining pressures on highly precompacted crushed salt samples.
- Gas injection tests on fluid saturated salt bricks with respect to 2-phase properties (e.g. permeability and threshold pressure).
- Long-term hydrostatic compaction tests with and without added brine, respectively.
- Shear-tests at increasing normal pressure between highly pre-compacted crushed salt blocks and host rock (rock salt) including wetting with brine.

Adaption and evaluation of appropriate material laws: The objective of this numerical modelling study was to examine existing material models appropriate for describing long-term salt brick compaction and to provide background on the research and development status of this type of backfill material, including model development that has been done to date focusing generally on granular salt. Four constitutive models were investigated in more detail as candidates to describe the deformation of salt bricks:

- Empirical formulations, e.g the Itasca crushed-salt constitutive model, the Hein-Model and the Zhang-Model
- Micromechanism-based models, e.g. the Spiers-Model

Our investigations on artificial saltbricks cover a wide field of relevant rock-mechanical and hydraulical properties. Remarkably, the load bearing capacity and dilatancy behaviour of the saltbricks (‘dry’ state) differ significantly from the behaviour of the compact natural rock salt due to reachable larger deformations and relatively high load bearing capacities whereby local

dilatancy is overlapped by the decrease of porosity during loading. Creep tests clearly show the faster creep of crushed salt in the range of small sdiff < 15 MPa than natural rock salt.
However, it is important to note that the strength of the salt bricks is drastically reduced when moisture is present. Hydrostatic compaction experiments clearly demonstrate that besides the loading conditions the water content is the key factor for the compaction processes. After one year only in the wet samples a final porosity in the order of 2% was reached. The efficiency of the compaction depends on the stress but in each case the compaction rates are decreasing when a saturation state at around 4% remaining porosity is passed.
During the stress induced compaction permeability decreases whereby the observed permeability/porosity relationship fits very well in the generally observed variation field for the compaction of granular salt. If water is present at the grain boundaries two-phase flow will occur associated with capillary effects. Threshold pressures determined for wet salt brick are slightly higher than the relationship estimated by Davies (1991), which may be due to the not sufficient test duration resulting in an overestimation of the threshold pressure. However taking the overall data scatter in the literature into account it can be argued that due to the difficulties of gas threshold measurements associated with lithological rock differences a unique relationship for describing capillary pressure effects seems not to be realistic.
Shear tests were performed to investigate contact properties between saltbrick surfaces and the rock salt. Whereas at dry conditions only some friction occurs, significant strengthening is observed when moisture is present because of activation of cohesion. This observation offers a direct proof of healing in salt rocks.
As a result of the numerical modelling study, we can conclude that at the present state the phenomenological founded ZHANG crushed-salt constitutive law is the most suitable constitutive law to describe the compaction behaviour of the pre-compacted crushed-salt bricks in a first approximation. Regarding backfill compaction as simulated in our compaction creep tests (dry and wet conditions) it came out that this approach satisfactorily simulates the experimental conditions and thus obtains satisfactory agreement between experimental and numerical results. However an implementation in commercial available code is necessary allowing prognosis calculations for real underground situations. Nevertheless, the potential of the SPIERS mechanism based pressure solution-model for future modelling is obvious but requires more experimental work.
Suggestions for future work: Summarizing our experimental and modelling results we can conclude that the principal challenges remaining in relation to the salt backfill materials are:

- Understanding of physical processes which control the efficiency of granular salt compaction especially with respect to humidity effects.
- Development of generally agreed constitutive models for compaction in granular salt that allow reliable extrapolations to in-situ conditions.

Publications

Deliverables (2005 - 2007)

- D3.5.3 (IfG, 2004): Report on triaxial compression and permeability tests (2004-10-31).
- D3.5.3 (IfG, 2004): Report on triaxial compression and permeability tests (2004-10-31).
- D3.5.4 (IfG, 2005): Report on shear-test (2004-12-31).
- D3.5.5 (IfG, 2006): Report on long-term creep test (2006-02-28).
- D3.5.6 (IfG, 2007): Final Activity Report: Report on adaptation of the material laws to

the laboratory results - Note, the 3 independent parts:

Contributions NF-PRO Workshops

- SALZER, K., T. POPP & H. BÖHNEL (2006): Mechanical and permeability properties of highly pre-compacted granular salt bricks.. 3th NFPRO-Workshop, El Escorial, Spain, Nov 14-16 2006. Poster.
- SALZER, K., T. POPP & H. BÖHNEL (2007): Mechanical and permeability properties of highly pre-compacted granular salt bricks. 4th NFPRO-Workshop, Brussels, 15-17 October 2007. Poster.

Conferences and Conference Proceedings

- Salzer, K., T. Popp & H. Böhnel, (2007): Mechanical and permeability properties of highly precompacted granular salt bricks. In K.-H. Lux, W. Minkley, M. Wallner, & H.R. Hardy, Jr. (eds.), Basic and Applied Salt Mechanics; Proc. of the Sixth Conf. on the Mech. Behavior of Salt. Hannover 2007. Lisse: Francis & Taylor (Balkema). 239 – 248.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D3.5.6

3.5.2.2: Final report on deformation processes at low porosity and the evolution from the permeable to impermeable state

Participants

NRG, UTR

Goals/objectives of the research

Limited knowledge exists regarding the process that converts permeable salt grit backfill into an impermeable backfill similar in properties to natural rock salt. In past studies (e.g. BAMBUS-II, PAGIS, PACOMA, EVEREST, etc.) it has been assumed that salt grit will eventually become impermeable and disconnection of the pore network due to ongoing compaction. The threshold is traditionally set at a porosity of about 1%, because this is the average porosity of (impermeable) rock salt. This purely empirical approach must be supported by understanding of the relevant microphysical processes and its quantification to improve the safety case for disposal in rock salt.

Key results/achievements

Experiments carried out within NF-Pro on (1) the compaction of 'wet' salt grit of low porosity (< 5 %) indicate the dominance of pressure solution creep (IPS), and (2) the experiments on 'dry' salt grit (with only the natural amounts) indicate a mixed process of IPS and dislocation glide. The permeability significantly decreases in the 'annealing' period after the compaction.
Microphysical models to explain the compaction and permeability behaviour have been developed. These offer a fundamental basis to determine the convergence and permeability of compacting salt grit.
At relatively low pressure (10-20 MPa) in most in situ conditions the water content in granular salt is high enough to allow compaction caused by pressure solution. Experiments point in the direction that in these conditions pressure solution may be the dominant deformation mechanism. A multi-mechanism compaction model is established, though the mechanistic basis not yet fully understood.
In natural rock salt the permeability is virtually zero at 1% porosity. Granular salt compacted in a laboratory has a relatively high permeability at 2%. Experiments have shown that the permeability of the laboratory samples slowly decreases in time. A model similar to the pressure solution model for compaction has been used to explain this behaviour. The rate of pore radius reduction, however, is much slower than predicted by the model. Moreover, at lower conductivity, the reduction rate decreases more and more. This suggests that there is some mechanism that inhibits full closure of pores. The qualitative agreement between experiment and model is good, but quantitatively the agreement should be improved.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D3.5.7

3.5.2.3 Compaction and permeability of backfill

Participants

BGR

Goals/objectives of the research

The BGR investigations in NF-PRO WP3.5 are focused on the compaction behaviour of crushed salt with added bentonite. Crushed salt is the preferred backfill material in a final repository of radioactive waste in salt formations. Its initial porosity reduces gas pressure built-up in the repository. The intended long-term barrier effect of crushed salt, however, is only achieved after the porous material has been compacted and its permeability has been sufficiently reduced. Compaction occurs as a result of drift convergence caused by the pressure of the overburden. The anyway slow convergence will be reduced moreover by the resistance of the compacting backfill, which increases with increasing density. Added bentonite can reduce this resistance and shorten the very long compaction time in situ. Additionally the permeability will be reduced. The objective is to obtain a convenient backfill material with a predictable behaviour used as a technical barrier in a repository. Several laboratory tests with mixtures of crushed salt and Ca-bentonite have been carried out in NF-PRO.

Key results/achievements

Basic results are achieved from strain controlled oedometer tests with a compaction rate of 6.9·10-10 s-1 which is relevant for in situ conditions. At room temperature (~30 °C), the backfill resistance (BGR oedometer stress definition) of the crushed salt can be reduced considerably by additives of Ca-bentonite with its natural moisture content of about 12%. At a void ratio of e = 0.1, for example, the backfill resistance of pure crushed salt is more than 25 MPa, with an addition of 10 to 20 % Ca-bentonite it can be reduced to values between 6 and 8 MPa. At higher temperatures the behaviour of crushed salt/bentonite mixtures is not congruent to that of pure crushed salt. At T = 200 °C The backfill resistance is much higher than that at 30, 70 and 100 °C, especially at small void ratios, but most of the values are smaller than those of the pure crushed salt at room temperature or even at 100 °C. The backfill resistance of an 85/15 mixture is smaller than that of a 90/10 mixture. It is to assume that the material behaviour of the crushed salt/bentonite mixture at higher temperature is influenced by the moisture content of the bentonite.
In contrast to the strain controlled oedometer tests, the triaxial compaction tests are performed stress controlled (quasi hydrostatic load). Subject to uncertainties at the determination of the volumetric strain rate by volume measurement during the test, the results indicate at void ratios less than about e = 0.15, that under triaxial load conditions the compaction rates are higher than applied in the oedometer tests at a comparable load. Hence, under in situ conditions which are closer to those simulated in a triaxial test, a lower backfill resistance can be expected than obtained from the results under oedometer conditions. The amount of time required to develop the barrier effect will be reduced.
The permeability tests with the material mixtures show that an addition of 10 % Ca-bentonite can reduce the permeability of crushed salt by about 2 orders of magnitude. About 2 orders of magnitude more can be obtained with an amount of 15 or 20 % Ca-bentonite. A different grain size distribution of the crushed salt used in a variant test showed no significant influence due to the permeability.
In a repository for radioactive waste in salt formations, crushed salt can be compacted well by the drift convergence at high temperatures (~ 150-200 °C) existing close to the waste canis-

ters. At lower temperatures with lower drift convergence, crushed salt with an addition of 15 % Ca-bentonite will be a sufficient backfill component, because the added material can reduce the backfill resistance as well as the permeability. However, the influence of the moisture content on the Ca-bentonite used as additive should be the subject of further investigations.

Publications

Stührenberg, D. (2007): Long-term laboratory investigation on backfill. – The Mechanical Behavior of Salt – Understanding of the THMC Processes in Salt, Proceedings of "Saltmech6" Hannover, Germany, Mai 2007: 223–229.
STÜHRENBERG, D. (2007): Compaction and Permeability of Crushed Salt/Ca-bentonite backfill. Poster presentation on NF-PRO's Fourth Workshop, Brussels, Belgium, October 2007.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D3.5.10

3.6 WP 3.6: RTDC 3 synthesis report

3.6.1 Overall objective of work package 3.6

The objectives of WP 3.6 are to elaborate a phenomenological analysis of the THM (C) behaviour of the buffer considered (salt and clay) explaining, on the physical bases, the evolution of its properties considering hydration rate and saturation, temperature and mechanical field imposed by the host rock.

3.6.2 Overview of work performed

4 RTDC 4: EDZ characterisation and evolution

4.1 WP4.1: EDZ state-of-the-art report

4.1.1 Overall objective of work package 4.1

The main objective of work package 4.1 is to provide a synthesis document summarising present knowledge acquired on EDZ during the past decades. The synthesis document will also provide information and data towards other NF-PRO components (notably components 2, 3 and 5).

4.2 WP4.2: EDZ state-of-the-art report

4.2.1 Overall objective of work package 4.2

The general objective of WP 4.2 was to characterise, to understand and to quantify the dominant phenomena during disturbances due to tunnel excavation (fracturing, fissuring, desaturation, deformation, mechanical-hydrological-thermal damage, hydraulic release, creep and relaxation, expansion…) in order to determine the specific EDZ input data to be provided for safety assessment analyses. The two most important parameters to be determined are the intrinsic transmissivity of the fractures induced by excavation as a function of the hydromechanical behaviour of the rock, and the hydraulic connectivity of the network of these fractures, which will govern the "bulk" permeability of the damaged zone.

4.2.2 Overview of work performed

4.2.2.1 EDZ state-of-the-art final report

Participants

ANDRA

4.2.2.2: In situ characterisation and EDZ modelling in the URL Meuse/Haute-Marne

Participants

ANDRA

Goals/objectives of the research

This work is part of the general programme of geological, hydrogeological, geochemical and geomechanical research undertaken by Andra to study the possibility of radioactive waste disposal in the Callovo-Oxfordian argillites.
In particular, the purpose of the geomechanical studies conducted during the sinking of the main laboratory shaft and the niche was to:

- Supplement knowledge on the geomechanical performance of argillites,
- Measure deformation of shaft and niche walls during excavation,
- Compare these measurements to deformation models,
- Assess the role of the support installed in the niche,
- Determine extent of the EDZ and characterise its permeability.

In order to fulfil these objectives, Andra carried out a special experimental programme known as "response to shaft excavation" ("REP" experiment) from the niche and the "Sections of Reinforced Geomechanical Measurements" ("SMGR").
The specific objectives of these experiments are to:

- Study and understand rock behaviour during and after shaft sinking. Geomechanical observations make it possible to estimate spatial variability of the massif in terms of rheological characteristics of the whole structure;
- Characterise the extent and size of hydro-mechanical disturbance (short term and delayed) caused by the shaft excavation, mainly by measuring spatial-temporal distribution of the EDZ, and deducing the relationship with changes in zone hydraulic properties;
- Test the capacity of rheological models and digital modelling to predict the hydro-mechanical behaviour of argillites. This exercise provides an initial adjustment of the laws describing the argillite behaviour.

Key results/achievements

The *in situ* experiments, together with the associated laboratory measurements on rock samples - leading to the acquisition of an extended data bank - are described in detail in the successive progress (Work Program [Deliverable.4.2.1], Site instrumentation and data acquisition [D.4.2.4, D4.2.7], Interpretation and modelling [D.4..2.11]), and this final synthesis report [D.4.2.12].

In situ measurements

The *in situ* measurements showed slight damage around the shaft (maximum extent ≈2 m) corresponding rather to a micro-fissured zone. This resulted in a slight variation in permeability, and in compression wave velocity (decrease less than 2% of initial velocity).

However, the existence of this zone of higher permeability results in greater shaft drainage, which could explain the differences observed between interstitial pressure distribution and the analytical poro-elastic model.
It was demonstrated that permeability & P wave velocity (measured 6 to 12 months after the shaft sinking) showed no significant changes in EDZ properties.

Modelling

The hydro-mechanical modelling of the main shaft sinking (REP experiment) has been performed in the framework of fully saturated porous medium with the 3-dimensional code, *FLAC3D*.
A predictive modelling of the shaft sinking has been performed in the framework of the European Modex-Rep project, using a poro-elastoplastic model based on a generalized Hoek and Brown criterion. Results of blind prediction emphasize that the model reproduces the *in situ* phenomena, but is not able to reproduce the amplitude of the drop in pore pressure during the shaft sinking. Further development of the model have been carried out in order to take into account additional characters of the EDZ such as permeability changes around the shaft which have been incorporated on the basis of the in situ measurements of permeability or as a function of damage (Souley et al 2007a, 2007b) . In situ measurement showed that permeability increases around the shaft but at maximum of 1.5 order of magnitude at the shaft wall.
For both approaches, results of hydro-mechanical modelling of REP experiment showed : (a) good agreement with in situ measurement for displacement, (b) a good agreement between the damaged calculated damaged zone extent and the measured one, (c) the peak of shear stress is not reached, just at the wall which is coherent with in situ observation where no fracture were observed.
In terms of pore pressure evolution during the shaft sinking:

- Compared to the previous "Blind predictions", taking into account evolution of the permeability in the EDZ (with regard to the average values of poroplastic parameters used), improves the predictions, but remains insufficient to simulate the observed drops of pore pressure, particularly in the direction of the major horizontal stress.
- Conversely, assuming an evolution of the permeability in the hydraulically disturbed zone established on the basis of the in situ measurements made it possible to improve the numerical predictions. This enables reproduction of the drops in pore pressure, independent of the orientation of the measuring chambers or their distances from the shaft wall. If, as a whole, the model made it possible to significantly improve the predictions of pressure in a near field, it has the disadvantage of using a relation based on a geometrical criterion (radial distance from the shaft wall) rather than an intrinsic character of material in the near field.

Further study is needed to identify and understand mechanisms responsible of permeability change in the hydraulic disturbed zone and determine a relationship with physical parameters and to better understand small discrepancy in term of pore pressure changes between models and measurements.

Publications

Publications

M. Souley, G. Armand, K. Su, Y. Wileveau (2007a). Modelling of the hydromechanical response of a shaft sinking in a deep claystone, tenth International Symposium on Numerical Models in Geomachanics NUMOG X, 25-27 April 2007, Rhode, Greece,

M. Souley, K. Su, G. Armand, M. Ghoreychi (2007b). Poromechanical behaviour of deep claystone and permeability changes around shaft, Int. Workshop on Constitutive Modelling - Development, Implementation, Evaluation, and Application; 12–13 Jan. 2007, Hong Kong, China

NF-PRO Deliverables

J.M. Krieguer, J. Delay, J.F. Aranyossy (2004). In situ experimental programme related to the Excavated Damaged Zone in the Callovo-Oxfordian argillite Andra Underground Research Laboratory in Bure. (D4.2.1)
G. Armand, J. Morel, J.M. Kreiguer, J.F. Aranyossy (2005). In situ EDZ Characterisation in the URL Meuse/Haute -Marne (D4.2.4, French version)
G. Armand, J. Morel, J.M. Kreiguer, J.F. Aranyossy (2006). In situ EDZ Characterisation in the URL Meuse/Haute -Marne (D4.2.7, English version)
G. Armand,J.F. Aranyossy (2007). Modelling of the Excavation Damaged Zone of the Callovo-Oxfordian argillites during shaft sinking in the Meuse / Haute-Marne URL (D.4.2.11)
G. Armand,J.F. Aranyossy (2008). In situ Characterisation and EDZ Modelling in the URL Meuse / Haute-Marne - Final report (Deliverable 4.2.12)

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D4.2.12

4.2.2.2: Spatio-temporal geophysical investigation of the excavation-damaged zone in the Mont Terri underground rock laboratory (Switzerland)

Participants

CUFRNIMES

Goals/objectives of the research

The present report summarizes the geophysical experiments performed in the Mont Terri Underground Laboratory by the FORPRO teams. These experiments are aimed at providing information concerning the development and the extent of the EDZ surrounding the galleries. These studies were conducted in the framework of the NF-PRO European Research Program through the Multidisciplinary Research Program of the FORPRO Research Group.

Key results/achievements

Geophysical studies undertaken include the following:

- *EDZ initiation* - The geophysical experiments performed by the FORPRO team benefitted of exceptional field opportunities with offered the possibility to define an experimental program to observe the evolution of the EDZ during the excavation of the new G04 gallery in the Mont Terri Underground Laboratory. Thanks to the facilities made at our disposal by the ANDRA, CNRS and Mont Terri staffs, we were able, during the first semester of 2004, to establish and implement a series of experiments dedicated to the monitoring of the EDZ during the excavation of the G04 gallery scheduled by the end of august 2004. The geophysical experiments performed in the Mont Terri URL mainly involve geo-electrical and seismic methods. In accordance with the basic research objectives of the FORPRO GdR, we designed as original as possible experiments with a reasonable probability of success. Accordingly, the experiments performed in the Mont Terri URL may be classified in the following way:
- *Electrical Resistance Tomography (ERT)* - These experiments consist in measuring the electrical resistivity with classical apparatus, and their originality relies in the field conditions which offered the possibility to make measurement very near the end face of the start niche of the future G04 gallery (see Figure 4 in the next section). By this way, we were able to observe the temporal evolution of the geo-electrical structure of the EDZ during the excavation of the gallery and, later, of the two nearby EZ-B and HG-A niches. Preliminary results of these experiments have already been published (Gibert et al., 2006) and are described in a full Section of the present report. The entire collection of ERT cross-section images is shown in Figure 2.
- *ERT in boreholes* - Four boreholes (BEZG1, BEZ-G2, BEZ-G3 and BEZ-G4) have been drilled to primarily perform seismic endoscopy experiments. Companion ERT measurement were also done to possess electrical resistivity data to be compared with the seismic data set. Measurements were done along the wall of each borehole at four orthogonal azimuths. Cross-hole measurements were also done.
- *Seismic endoscopy* - This experiment involves an original prototype of seismic probe designed and constructed at Geosciences Rennes (Conil, 2003). This probe operates in boreholes and is able to distinguish the different arrival directions of the seismic waves. The probe may be used either as a stand-alone tool (i.e. with its own seismic source) or as a direction antenna of 64 receivers. The frequency range of this probe

goes from 20 kHz to 120 kHz. Measurements were done in both configurations to obtain data in the vicinity of the walls of the boreholes (seismic endoscopy) and in the whole domain comprised between the boreholes (crosshole experiments).

Beside the experiments listed above, a number of theoretical and analysis studies were pursued:

- Wave propagation in random media - Interpretation of seismic data in terms of fracturation of the rock needs to understand the wave phenomena controlling wave propagation in random heterogeneous media. This is particularly critical for the data acquired with our seismic endoscopic probe which involves high frequencies, i.e. waves with wavelengths of the order of the size of the heterogeneities.
- Spatio-temporal inversion of ERT data - The data acquired during the experiments performed in the Mont Terri URL appeal for particular processing and analysis methods, many of them being yet to be developed (Figure 3). The main originality of these methods is the need to tackle with the temporal evolution of the auscultated medium during the period of geophysical observation. This time evolution makes most of the interest of the data acquired and several ways are currently explored to implement an inverse method able to account for the time-evolution of the electrical resistivity distribution under the eventual control of geomechanical constrains through modelling and data (e.g. deformation and stress measurements in the gallery).

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D4.2.13

4.4.2.3: Development of a tool for high-resolution velocity field imaging around a borehole

Participants

INDRIS

Goals/objectives of the research

The excavation of a deep underground structure induces a stress field redistribution that may create an Excavation Damaged Zone (EDZ). The study of the EDZ is essential in the framework of nuclear waste storage, where EDZ may constitute a preferential pathway of stored materials towards the biosphere. Analysis of ultrasonic wave propagation across the rock media around the excavation is generally used to characterise the EDZ.
In the framework of the NF-PRO European program, an inversion method and a specific probe have been developed to image the velocity field in the borehole vicinity, in order to characterize the EDZ.

Key results/achievements

The probe is composed by a couple of sensor able to sound the velocity in depth around the borehole wall. The original features of the probe rest on the automatic sensors displacement in rotation and in translation with a precision of 0.5° and 0.2 mm respectively allowing to building velocity images with a theoretical resolution of 2.16 megapixels per plan.
This method has been preliminary applied on a multi layer test bed to validate and optimise the experimental and numerical procedures. Based on those results, an in situ experiment has been run in the Meuse/Haute-Marne Underground Research Laboratory (URL) in France. Dedicated to the safety assessment of nuclear waste storage in the Callovo-Oxfordian argillaceous layer.
A specific tomographic inversion, based on the global matrix method and the bedding rays, has been used to process the experimental data. The method highlighted finely the velocity perturbation caused by a 86 mm diameter borehole. The damage zone extends until 0.175 diameter of depth with an anisotropic damage pattern oriented in the regional stress field. The measured velocity field around this borehole are well correlated with the one provided by numerical modelling. This approach, performed on several boreholes, allows estimating the EDZ and its variability at a tunnel or gallery scale.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D4.2.14

4.2.2.4 EDZ initial phase characterization and modelling - Influence of bedding planes (IfG)

Participants

IfG

Goals/objectives of the research

Argillaceous rocks are inherently anisotropic due to their sedimentary and tectonical history. Therefore, inelastic deformation and the relative dilatation are clearly a function of bedding plane properties, the spatial orientation and stress geometry resulting in a quasi-hexagonal anisotropy. In addition, such planar discontinuities can act as preferential flow paths and mechanical weakness planes. Both overlapping effects are particularly important during rock stress redistribution in the EDZ. The investigations performed by IfG were divided into three parts:

1. Detection of onset of dilatancy and quantification of coupled mechanical properties
2. Shear strength properties of bedding planes
3. Mechanical modelling the EDZ evolution

Key results/achievements

The main output of the experimental work can be summarized as follows:
(1) Initial sample state and transport properties: Both, seismic monitoring and permeability measurements clearly indicate pre-damage of the investigated core samples, and, in addition, only partial saturation due to sample disturbances during sample recovery and preparation whereby the relation to the bedding is apparent. Gas transport in Opalinus clay is affected by 2-phase flow (e.g. characterized by discontinuous gas transport) whereby capillary gas threshold pressure is a function of permeability. However, increase of confining pressures restores at least partially the initial sample integrity and saturation conditions as may be inferred e.g. by the observed permeability decrease respectively seismic velocity increase. The time and stress depending sealing was found most efficient perpendicular to the bedding.
(2) Determination of stress induced dilatancy and strength behaviour: In this context it has to be mentioned that detection of initial micro crack-opening in indurated clay under lab conditions depends mainly on the sensitivity of the measured physical parameter because during triaxial loading an overall matrix compaction of the clay rock occurs. Under deviatoric conditions local initial crack opening at 50 – 60% of the failure stress is only indicated by velocity decrease of radially measured p-waves or s-waves (oscillation direction perpendicular to crack planes). Primary at around 90% of the failure stress an increase of volumetric strain was observed associated with a permeability increase. In consequence, two pronounced stress boundaries have to be considered representing different stages of damage:
Sigma (initial damage) = 0.5 - 0.6 * Sigma (peak) , respectively Sigma (dilatancy) = 0.8 - 0.9 * Sigma (peak)
Therefore it follows, that the reliability of the term "dilatancy" regarding its importance for the EDZ in indurated clays has to be discussed. Nevertheless, the dilatancy concept for discriminating stress states regarding damage or sealing seems also to be valid in clay rocks; however, due to the rock anisotropy its application is much more complicated. In addition, because in the triaxial strength tests the damage is found to be concentrated on local shear zones, a simple coupling between mechanical (i.e. damage) and hydraulical properties seems to be unlikely.

Concerning the mechanical properties, it has been confirmed that the strength behaviour is strongly anisotropic and depends mainly on the orientation to the bedding (bedding = weakness plane) and on the minimal stress. In addition, simultaneous monitoring of stress induced changes of both, permeability and volumetric strains, clearly demonstrated that the corresponding relationships for mechanically induced sample compaction respectively damage are different, which implies that not a simple permeability/porosity relationship in Opalinus clay exists.
(3) Modelling EDZ: With respect of a prognosis of the EDZ a new modelling approach has been developed based on the obtained experimental results. It consists of two parts, i.e. of a (visco-)elasto-plastic constitutive model comprising the hardening/softening behaviour and dilatancy effects of the rock mass and a specific shear friction model, which describes displacement- and velocity-dependent shear strength softening for the bedding planes. For the modelling we applied the commercial UDEC (i.e. Universal Distinct Element Code of Itasca). Using the site-specific material parameters of matrix properties and bedding planes, the relevant EDZ phenomena for a local drift situation in the Mont Terri lab (e.g. tensile fractures at the wall respectively shear slip and tensile fractures in the roof, could be nicely simulated. Also the spatial extent of the EDZ corresponds fairly well to the in-situ observations.
Concluding the findings of our integrated study of experimental and modelling work, it has been confirmed that in bedded clay formations the evolution of the EDZ mainly depends on rock-mechanical properties of the indurated clay and the induced stress state. Only under consideration of the lowered bedding plane strength a reasonable simulation of the observed EDZ-phenomena (i.e. bedding plane slip respectively extensional failure) was obtained. The new developed modelling approach seems to be a powerful tool for quantifying mechanical EDZ phenomena.

Suggestions for future work:

It has to be mentioned, that in addition to rock mechanical conditions, the extent and order of rock disturbance is superimposed by weathering effects due to ventilation resulting in drying or wetting. In addition, literature results reveal a large scattering of mechanical properties of indurated clay, e.g. from the Mont Terri Site, which is attributed besides others mainly to the possible influence of pore pressures. From the experimental point of view the knowledge regarding coupling between mechanical (e.g. damage) and hydraulical properties is not sufficient, i.e. the effective Biot-coefficient is unknown. Preliminary lab tests with application of pore pressures demonstrate the difficulty ensuring stable conditions in short term tests due to the low rock permeability. This implies that more experimental work is necessary to quantify the respective parameters and processes for future THMC-modelling.

Publications

Deliverables (2005 - 2007)

D4.2.2 (IfG, 2005a): Interims Report 1: State of the art report / Test plan for shear testing (2005-01-15).
D4.2.6 (IfG, 2005b): Interims Report 2: First results of shear tests (laboratory tests) (2005-01-15).
D4.2.8 (IfG, 2006): Interims Report 3. Summary of results on shear tests / Triaxial compression tests (2006-02-10).
D4.2.15 (IfG, 2007): Final report (2007-10-01).

Contributions NF-PRO Workshops

POPP, T. & K. SALZER, 2006. Investigation of the influence of bedding planes to coupled HM properties of the damaged rock. 3th NFPRO-Workshop, El Escorial, Spain, Nov 14-16 2006. Poster.
POPP, T. 2006. Current understanding of the gas-frac scenario in salt. WP4.4 Long-term evolution/ RS 4 SF / steel canister / salt. Plenary Sessions on cross-cutting topics and issues. 3th NF-PRO-Workshop, El Escorial, Sapin, Nov. 14-16.2006. Talk.
POPP, T. & K. SALZER, 2007. Investigation of the influence of bedding planes to coupled HM properties of the damaged rock. 4th NFPRO-Workshop, Brussels, 15-17 October 2007. Poster.

Conferences and Conference Proceedings

POPP, T. & K. SALZER, 2005. Anisotropy of seismic and mechanical properties of Opalinus clay during traxial and shear deformation. 2nd International meeting “Clays in Natural & Engineered Barriers for Radioactive Waste Confinement”, Tours, 14-18 March 2005, P/THMN/03, Poster.
POPP, T. & K. SALZER, 2007. Anisotropy of seismic and mechanical properties of Opalinus clay during triaxial deformation in a multi-anvil apparatus. Physics and Chemistry of the Earth, 32, 879-888.
POPP, T., K. SALZER & MINKLEY, W., 2007. Influence of bedding planes to EDZ-evolution and the coupled HM properties of Opalinus clay. 3nd International meeting “Clays in Natural & Engineered Barriers for Radioactive Waste Confinement”, Lille, 17-20 September 2007, P/EDZ/01, Poster.
POPP, T., K. SALZER & MINKLEY, W., subm. Influence of bedding planes to EDZ-evolution and the coupled HM properties of Opalinus clay. Physics and Chemistry of the Earth (subm.).

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D4.2.15

4.2.2.5: Hydro-mechanical disturbances around the 2003 excavated gallery in the Tournemire site (WP 4.2) IRSN Final report

Participants

IRSN

Goals/objectives of the research

The main objective of the mine-by-test experiment carried out in the Tournemire site is to understand and to evaluate the various perturbations induced by the excavation and to assess the EDZ and its spatial and temporal evolution.

Key results/achievements

The analysis of the mine-by-test measurements, taking account of the excavation history, shows a good coherence between the mechanic and the hydraulic experimental results.
A linear poro-elastic model working in unsaturated conditions has been developed for the interpretation of these hydro-mechanical measurements. The analysis of the results comparison between measurements and calculations for the various probes shows that the model is able to reproduce some tendencies observed either on pressure or on displacements.

Publications

A. Rejeb (2005). *"Disturbances caused by the excavation of a gallery in the Tournemire site in 2003"*, IRSN Scientific and technical report 2005, pp. 6-15.
A. Millard, A. Rejeb (2008). *"Identification of the hydro-mechanical in-situ properties of Tournemire argillite from mine-by-test experiment".* Publication accepted in GeoProc 2008: 3rd International Conference on Coupled THMC Processes in Geosystems: Fundamentals, Modeling, Experiments and Applications, June 2- 6, 2008, Lille, France.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D4.2.16

4.3 WP4.3: Short-term evolution

4.3.1 Overall objective of work package 4.3

This work package studied the key processes taking place during the transient phase of the repository and includes the detailed investigation of effects in conjunction with the de- and re-saturation of the near field of the drift. Experimental work is conducted both in the Mont Terri Rock Laboratory (Switzerland), where a second phase of a ventilation test has been planned, and in the HADES facility at Mol (Belgium).

The primary objectives of the work to perform in WP4.3 were:

- To develop a common understanding of the effects of the required ventilation of the underground drifts during the construction and operational phases of the repository. This ventilation could give rise to a process of desaturation of the rock around the disposal drifts, changing its hydraulic and thermal properties which may have an impact on the design of the repositories (drift spacing and repository size). Following the ventilation phase, the reaction of the host rock during the re-saturation phase (after the waste emplacement and backfilling of the drifts) will be assessed. These investigations will help to gain insight in the development of the EDZ with time and the possible deformations and self-sealing effects associated with this process.
- to build up knowledge on geochemical processes taking place in the EDZ and their potential coupling to hydraulic and mechanical processes, due as well to drift ventilation. In particular, the oxidation of pyrite in the EDZ will be assessed in a quantitative way. Main emphasis will be on the formation and the migration pathway of the sulphate and its influence on the pore water chemistry.
- to evaluate the time-dependent changes of the physico-chemical properties in the EDZ. More specifically, the effect of fracturation (due to oxidation and dehydration) on these properties (e.g. gas permeability) will be investigated. The effects of a thermal imprint will be monitored and quantified based on mineralogical, geochemical and magnetic observations.

4.3.2 Overview of work performed

4.3.2.1 High-resolution seismic investigations within the VE experiment

Participants

BGR

Goals/objectives of the research

With the help of small scale high resolution seismic refraction measurements and borehole based interval velocity and cross hole measurements mainly the excavation damaged or disturbed zone (EDZ/EdZ) should be detected and characterised during the de- and resaturation phase of the experiment.

Key results/achievements

Three high resolution seismic methods were applied in order to detect and to characterise the EDZ/EdZ around the test section in the Ventilation-Experiment. Emphasise was put on a repeated characterisation of the EDZ/EdZ during the de- and resaturation phase with the help of a non-invasive seismic refraction method. Between May 2005 and November 2007 measurements were repeated ten times. In October 2006 three 1 m long boreholes were drilled near the seismic refraction array. In and between these boreholes interval velocity and cross hole measurements were performed in October 2006 and July 2007.

At the beginning of the experiment the extent of the EDZ/EdZ was determined with the refraction method to be between 5 and 20 cm. Until October 2005 only a few seismic refraction data could be used due to the increasing wave attenuation. The assessed extent of the EDZ/EdZ stayed nearly constant. With ongoing time the wave attenuation became stronger. This effect can be attributed to a loosening of the rock within the first few centimetres of the tunnel wall. No extent of the EDZ/EdZ could be determined.

Only data from the last refraction measurement, during the resaturation phase in July and November 2007, show a slight increase in signal quality which can be explained with a regressive wave attenuation and consequently with a consolidation of the upper centimetres of the tunnel wall. But data are not good enough for a quantitative EDZ/EdZ extent estimation.

Results from the borehole-based methods (interval velocity and cross hole measurements) are pointing to an extent of the EDZ/EdZ between 10 and 25 cm what is in good accordance with results from the seismic refraction measurements.

This gives the range of a possible variation of the extent of the EDZ/EdZ at different spots along the profiles or the boreholes and gives at the same time a measure for the uncertainty of the extent estimation.

All results point to a pronounced seismic anisotropy of the Opalinus Clay which is caused mainly by the bedding.

The seismic parameters, mainly P-wave velocities, derived with the three methods, are partly different because the wave propagation paths were different, what is an important factor con-

sidering the anisotropic properties of the Opalinus Clay. Furthermore, local small scale inhomogeneities can be a reason.

The interval velocity methods gave hints for the existence of cracks in the ranges between 30 – 50 cm and 65 – 80 cm from the tunnel wall what partly could be confirmed with the borehole camera analyses.

Remarkable is that results from all three methods show similarities with results found during a geophysical investigation of the EB-Niche in 2001.

Publications

Schuster, K. (2007): EDZ/EdZ characterisation with seismic refraction and seismic borehole methods within the VE-Experiment. Poster presentation at the 4th NF-PRO Workshop, Brussels, October 15-17, 2007.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D4.3.17

4.3.2.2: The ventilation experiment phase II

Participants

ENRESA

Goals/objectives of the research

The ventilation of the underground drifts during the construction and operation of the radioactive waste repositories may produce the partial desaturation of the rock around the drifts, modifying its thermo-hydro-mechanical properties, specially in clayey rocks and in their Excavation Disturbed Zone (EDZ). This potential impact on the rock properties (if relevant and beyond some extent) might affect the design of the repositories (size and drift spacing), which depends on the thermal load that the engineering and the rock barriers can accept.
The Ventilation Experiment (VE), a demonstration test performed at relatively large-scale and of long duration, has allowed to evaluate "in situ" and better understand the desaturation process of a drift excavated in a hard clay (Opalinus Clay), when ventilated during several months with dry air. The experiment has been carried out at the Mont Terri underground laboratory (Switzerland), generating a flow of dry air (isothermal conditions, T » 15 -16oC) along a 10 m-long section of a non-lined microtunnel (diameter = 1.3 m).

Key results/achievements

The VE-II experimental phase has confirmed and complemented the findings of the previous VE-I phase. With the data and analyses of both phases, the understanding and evaluation of the desaturation-resaturation processes of hard clayey formations have been greatly improved. Specifically, the following main conclusions can be stated:

- Due to drift ventilation, the desaturation of clayey rocks of low hydraulic conductivity (K < 10-12 m/s) is very small. In both desaturation periods, the clayey rock around the 1.3 m diameter microtunnel remained practically fully saturated (except in a small ring of thickness about 30 cm); although a suction state developed up to a distance of approximately 2.0 – 2.5 m.
- The geochemical changes in the clayey rock near-field, around a microtunnel excavated more than eight years ago and after two extreme artificial ventilation periods, have a negligible effect upon the hydromechanical behaviour of this clayey rock.
- The extent of the EDZ stays practically constant along relatively long and extreme desaturation periods.
- Also, the mechanical effects on the rock of the ventilation (very small displacements registered) can be considered not relevant.

Then, as a final summary, it can be concluded that, under the real future repository conditions, the hydromechanical properties of clayey rocks similar to the Opalinus Clay will not be practically affected by the operational ventilation of the drifts.

Publications

Flow and reactive transport model of a ventilation experiment in Opalinus Clay. L. Zheng, J. Samper, L. Montenegro and J.C. Mayor . Lille international meeting in Clays, 2007

Structural organization of porosity in the Opalinus Clay under saturated and unsaturated conditions JM. Matray, JC. Parneix, E. Tinseau and JC. Mayor. Lille international meeting in Clays, 2007

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D4.3.18

4.3.2.3: Mineralogical, isotopic and magnetic behaviour of Mont Terri claystones subjected to a thermal imprint

Participants

CUFRNIMES

Goals/objectives of the research

This study aims to define the mineralogical, magnetic, chemical and isotopic transformations induced by a low thermal imprint in the Opalinus Clay formation of the Mont Terri Rock Laboratory. This approach is performed thanks to two heating experiments:

- an *in situ* heating experiment (HE-D) done in the Opalinus Clays of the Mont Terri Rock Laboratory during which thermal probes were subjected to a constant temperature of 100°C over 8 months;
- laboratory heating experiments performed at 95°C for tens of weeks under various atmospheric conditions, in which a monitoring of magnetic properties was specifically realized.

Key results/achievements

The laboratory experiments and particularly the monitoring of acquired remanence indicated that newly magnetic grains formed during moderate heating of Opalinus Clay at 100°C. The thermal demagnetization of laboratory-acquired CRM suggested that the newly formed magnetic grains are of magnetite type. A year experiment may produce no more than 0.1 ppmv of magnetite above the blocking volume, which is three to four orders of magnitude less than the content of initial magnetite in the Opalinus claystones (about 60 ppmv). This explains why it is almost impossible to detect the newly formed magnetite by means of XRD and SEM.
To the opposite, data obtained on samples collected after the in situ HE-D experiment show no substantial changes during this experiment. Demagnetization of NRM indicates that during the in situ experiment, no thermal stress was recorded at more than 3 meters from the probes and an upper temperature of 60-70°C was reached in their direct environment (0.5m). This conclusion is in agreement with temperature measurements performed during the HE-D experiment thanks to numerous sensors.
In these conditions, the temperature reached by the rock during the experiment was lower than the temperature recorded by the formation during its geological history (diagenesis). As a result, no significant mineralogical, chemical and magnetic changes were induced during HE-D experiment.

Publications

Aubourg, C., Pozzi, J.-P., Janots, D. and Sarahoui, L., submitted. Printing chemical remanent magnetization in claystones at 95°C. Earth and Planetary Science Letters.
Techer et Aubourg, 2005 Intermediate report on the physico-chemical characterization of the EDZ and the thermally damaged zone, NF-PRO (Contract Number: F16W-CT-2003-02389

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D1.5.18

4.3.2.4: Effects on ventilation on consolidated clay: Laboratory tests and in-situ monitoring of saturation changes (GRS Final report)

Participants

GRS

Goals/objectives of the research

The main objective of GRS' laboratory experiments is to investigate ventilation effects on EDZ evolution in indurated clay.
GRS' task in the frame of the Mont Terri Ventilation Test was the monitoring of saturation changes in the rock mass adjacent to the microtunnel by means of geoelectric tomography.

Key results/achievements

In order to investigate ventilation effects on argillaceous rocks, laboratory tests were performed by GRS on Opalinus clay samples drilled from the VE test field at the Mont Terri URL. The tests served to examine water retention capacity, swelling pressure, and swelling / shrinking strains induced by moisture changes and response of hollow clay samples to humidity changes of the air ventilating the central boreholes. Some typical laboratory tests were also numerically simulated by hydro-mechanically coupled calculations with CODE-BRIGHT.
Saturation changes due to ventilation with dry or humid air were monitored in situ in the VE microtunnel in the Mont Terri URL using geoelectric tomography. In several desaturation cycles, the evolution of a 30 to 40 cm wide desaturated zone with saturation down below 50% was detected.

Publications

Rothfuchs, T., Wieczorek, K. (2007): Monitoring of Solution Content by Geoelectric Tomography in the Mont Terri Ventilation Test. Poster presentation at the 4th NF-PRO Workshop, Brussels, October 15-17, 2007.
Zhang, C.-L., Rothfuchs, T. 2007: "Moisture Effects on Argillaceous Rocks", In: Proceedings 2nd International Conference of Mechanics of Unsaturated Soils (ed. T. Schanz), Springer Proceedings in Physics 112, p. 319-326.
Zhang, C.-L., Rothfuchs, T., 2007: Laboratory Investigations on Ventilation Effects on the Opalinus Clay. NFPRO Fourth Workshop, 15-17 Oct. 2007, Brussels, Belgium
Rothfuchs, T., Wieczorek, K., 2005: Monitoring Moisture Distribution in Engineered Barrier Systems and Host Rocks by Geoelectric Tomography. - WM '05 Conference, February 27 – March 3, Tucson, AZ, WM-5217.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D4.3.19

4.3.2.5: Ventilation test (phase II) at the Mont Terri rock Laboratory

Participants

IRSN

Goals/objectives of the research

This document represents the final contribution of IRSN to the study framed in the NF-PRO WP. 4.3 EC co-financed project and five partners (ENRESA coordinator, GRS, BRG, NAGRA and IRSN). This experiment, namely VEII, focused on chemical processes due to ventilation on hydro-mechanical properties in the host rock surrounding the VE test section developed in an horizontal micro-tunnel of 1,3m in diameter and 10m long sealed off by means of two double doors.
In this study IRSN aimed:

- To produce and maintain a pure dry air ventilation at 60Nm3/h in the VE test section for one-year. The evolution of the air flow rate and of the relative humidity in the test section shows that it was overall successful despite several unexplained phenomena and ruptures due to the material erosion. The three scale maintenance (preventive, functional and curative) set up all over the ventilation period was efficient enough to solve all the encountered problems.
- To visualize and quantify the structural organization of minerals and porosity**.** This report makes the synthesis of the characterization of rock mineralogy and structures around the microtunnel of the VEII experiment under assumed saturated (Borehole BVE-96, internal project deliverable D9 or NF-PRO deliverable D4.3.5a, IRSN Internal report 06-035) and unsaturated (Borehole BVE-103, internal deliverable D16 or NF-PRO deliverable D4.3.21, IRSN Internal report 07-031) conditions. Whatever the borehole, the drillcore mapping has shown the occurrence of unloading joints at distances of about 25 and 35cm and of dipping fault planes with some artificial discontinuities due to handling and removal of the drillcore. Large size gypsum spots were observed along the reactivated fault planes and the unloading joints.

Key results/achievements

The formation of gypsum could be either a consequence of pyrite oxidation due to the natural or artificial ventilation of these fissures but more likely to evaporation due to the removal of water molecules from the dry air ventilation. The increase of aqueous sulphates and chlorides in the vicinity of the microtunnel wall is in favour of this second hypothesis (see CIEMAT final report). Degree of saturation obtained from water content and volume determinations performed on pluri cm3 samples clearly indicate that the rock mass was not fully re-saturated prior BVE-96 sampling with values as low as 70%. Those measured on BVE-103 have decreased of about 20% with respect to BVE-96 for similar distances. To obtain true initial conditions it should be important in the future to drill and sample boreholes right after the gallery excavation. Surprisingly, total porosity does not show any clear trend with the distance from the borehole head with values of *ca* 18 +/-1%. Mineralogical studies including SEM observations, XRD and calcimetry did not enable us to detect obvious mineralogical variations along the two boreholes even though the presence of gypsum is confirmed. Whatever the boreholes and samples, SEM observations have shown the occurrence of fractures subnormal to the bedding, opened with a width greater or equal to10µm and partially filled with gypsum. These

fractures are likely attributed to unloading joints and/or to tectonic fissures. All samples also show an intense inframicrometric fracturation with fractures opened and parallel to the bedding. For BVE-96 samples, the density of these fractures decreases from the borehole head (~6 fractures/mm²) to the borehole end (~2 fractures/mm²). This fracturation is therefore assumed to be a consequence of the VE phase I ventilation. Compared to values of degree of saturation, it strongly suggests that these cracks are desaturation cracks. This hypothesis is confirmed by the 3D images obtained by low and high resolution Xray microtomography. Autoradiographs obtained after rock-fragments impregnation with a 14C-radioactive resin have confirmed the occurrence of numerous inframicrometric fractures roughly parallel to the bedding and enabled us to quantify the role of fracturation in total porosity by comparing the matrix porosity to mean total porosity. Results obtained on a surface of 5 cm2 including a thickness of 100 µm indicate that the clay matrix has increased of almost 4.5 % between BVE-96 and BVE-103 data.
Low resolution X-ray microtomography has enabled us to visualize and quantify porosity higher than the resolution of 30 µm. It demonstrated that this macroporosity composed of desaturation cracks, unloading joints and of tectonic features has essentially affected the samples in the vicinity of the microtunnel wall. High resolution X-ray microtomography analyses was performed with the aim of visualizing the organization of porosity in 3D at a micrometric scale and quantifying porosity and minerals. The proportions of minerals estimated by this method are consistent with the known mineralogy of the Opalinus clays. Macroporosity (>0.7µm) would be mainly composed of micrometric cracks mainly parallel to the bedding and is two to three times lower in the first sample in comparison to the 3 other and more distant samples. This result is inconsistent with that of autoradiographs and SEM observations indicating a decrease of inframicrometric fractures with the distance from the borehole head. Explanation is likely to be related to the sampling which has been performed in a poor fractured area for the first sample. To conclude, the combination of techniques applied in this study has revealed the occurrence of micrometric cracks parallel to the bedding and attributed to desaturation cracks. The increase of matrix porosities as well as of the fissure porosities (>0.7µm, > 30µm) between boreholes realized before and after the dry air ventilation strongly suggests that these cracks are the consequence of the ventilation test conditions. Samples located at the borehole end, i.e. at a normal distance from the microtunnel wall of about 60 cm, are all affected by desaturation cracks even though big cracks (> 30µm) only affect the very first 40 cm.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D4.3.21

4.3.2.6: Two phase flow and Hydromechanical modelling

Participants

NAGRA

Goals/objectives of the research

The main objectives of R&D regarding the investigation of two-phase flow and hydromechanical modelling were:

- Development of a numerical code (Mherlin) for the simulation of coupled thermo-hydro-mechanical processes in clay formations;
- Implementation and testing of an elastoplastic material law (modified CamClay);
- Insight calculations on the hydro-mechanical evolution of the EDZ around the VE tunnel of the Mt. Terri URL;
- Estimation of macropermeability and two-phase flow parameters of the Opalinus Clay using long-term monitoring data from the VE tunnel.

Key results/achievements

As part of work performed by NF-PRo on two-phase flow and hydromechanical modelling, the following results are reported:

- The modified CamClay model was successfully implemented in Mherlin. Code verifications were performed with analytical solutions along two complementary stress paths and by comparison of simulation results with code Aster;
- Hydro-mechanical insight simulations with the elastoplastic constitutive law indicate that the deformation due to the tunnel ventilation is restricted to a narrow zone around the tunnel, ranging between a few mm and 15 cm;
- The large scale permeability of the Opalinus Clay formation can be bracketed by the analysis of the VE desaturation and resaturation events. The estimated intrinsic permeability ranges between 1.5 10-20 and 3 10-20 m2;
- Inconsistencies between the analyses of different test phases indicate a temporal change in permeability in the immediate vicinity of the VE tunnel. Such changes could be attributed either to precipitation of solutes or to capillary hysteresis effects.

Publications

Mayer et al.(2007): Modelling of an in-situ ventilation experiment in the Opalinus Clay. Clay in Natural and Engineered Barriers. pp629. Elsevier Publishers.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D4.3.22

4.3.2.7 Modelling and interpretation of the ventilation experiment: HM-C mechanisms in Opalinus Clay

Participants

CIMNE

Goals/objectives of the research

The principle objectives of the contribution by CIMNE to NF-PRO's RTDC 4 were twofold. First, it was planned to develop the numerical formulation to incorporate new variables and processes in order to consider:

- **redistribution of stresses due to the excavation of the drift:** it can modify the porosity and permeability of the EDZ, which is the zone that controls the entry of vapour into the rock;
- **modifications of the hydromechanical properties of the rock due to the prescription of a relative humidity:** the hydraulic conductivity for the liquid water and the vapour diffusivity will depend on the state of hydration (suction and degree of saturation) at every point of the rock. Significant suction changes can also alter the mechanical properties of the rock and cause deformations;
- **modification of the hydro-mechanical properties of the rock due to changes in the pore water chemistry:** the experimental programme includes the evaluation of the retention curve of the rock as a function of pore water salinity.
- **osmotic flow due to the high concentration gradients in the microtunnel wall:** the relatively low porosity, the existence of an osmotic efficiency, as experimentally observed, and the increase of salinity on the wall of the microtunnel due to evaporation are factors that support the possibility of an osmotic flow from the inside of the rock (low saline concentration zone) towards the microtunnel wall (high saline concentration zone).

Second, work undertaken aimed to assess the performance of coupled numerical modelling of the two phases of the VE (ventilation) test carried out in the Mont Terri laboratory in Opalinus clay.

Key results/achievements

The coupled numerical modelling based on the extended formulation has achieved a close quantitative agreement with the experiment in many instances and has shown its ability to explain qualitatively most observations.
The results of the numerical modelling has allowed an enhanced understanding of the processes involved through the identification of a number of relevant phenomena:

- Water transport occurs mainly through water pressure gradients and is thus determined by the permeability of the porous medium.
- In the unsaturated zone, vapour diffusion has a non negligible influence.
- An accurate representation of the retention curve is necessary, because of its importance in the determination of the permeability of the unsaturated zone.
- Stress redistribution is suspected to have a possible influence on the permeability in the first meter near the microtunnel.

- Water content distribution was found to depend on permeability anisotropy and on mechanical-hydraulic coupling.
- Osmotic flow was shown to have little significance

The numerical analysis of the VE analysis clearly indicates the effects of permeability anisotropy, with a lower value in vertical direction, in accordance with the local orientation of the bedding planes.
The numerical analyses results also suggest strongly the presence of an Excavation Damage Zone, due to excavation and possibly intensified during the ventilation cycles.

Publications

Garitte, B., Gens, A.., Vaunat, J. 2006. A constituive model that incorporates the effect of suction in cemented geological material. 4th Int. Conf. on Unsaturated Soils. ASCE Geo-Institute: 2488-2499.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D4.3.23

4.3.2.8 Overview of oxidation around galleries in Boom Clay

Participants

SCK-CEN

Goals/objectives of the research

Workpackage 3 within RTDC4 is focussed on the short term evolution of the EDZ. Within this frame, SCK•CEN is mainly focussing on the geochemical processes that take place in the EdZ during excavation and ventilation of the galleries within a clayey host rock. The major geochemical disturbance taking place is oxidation. This oxidation might have an effect on the mineralogy of the host rock and on the pore water geochemistry. As the host rock is the major barrier to radionuclide release in many concepts, it is important to evaluate the perturbation caused by oxidation of this host rock.
With this respect, SCK•CEN developed two *in-situ* experiments within the HADES underground research laboratory in Mol, Belgium.
The first in-situ experiment aims at evaluating the oxidation that occurred around the HADES URF and to define the extent of oxidation around two parts of the HADES URF: the old 'Test Drift' which was manually excavated and where ventilation during 20 years has taken place already, and the new 'Connecting Gallery' which was industrially excavated and where ventilation is limited to 3 years. In addition to the geochemical analyses, near field scoping calculations are performed regarding the extent of oxidising conditions in the host formation for a deep vitrified high level waste repository in Boom Clay .
The second in-situ experiment aims at following the influence of oxidation on the pore water chemistry during and shortly after the excavation of a new gallery: the PRACLAY gallery, perpendicular to the existing HADES URF.
The objective is to evaluate if the oxidation caused by the excavation and exploitation of a repository is acceptable in terms of its extent and impact on the performance of a clay host rock and its favourable properties to retain radionuclides. Therefore, the effects of the oxidation on the mineralogy and pore water chemistry are evaluated. Moreover, the spatial and temporal extent of oxidation around the underground research laboratory is studied. This information will be used as input for the performance assessment evaluation of geological disposal in clay layers.

Key results/achievements

The extent of oxidation as a result of excavation and ventilation of galleries in the Boom Clay (HADES URL, Mol, Belgium) was studied by experimental and modelling assessments.
The first in-situ experiment aimed at comparing the oxidation around the Test Drift (excavated in 1987) and around the Connecting Gallery (excavated in 2002). Two identical piezometers with filters at different distances from the gallery lining, were installed in an old and a new gallery of the HADES URF. The pore water was sampled and analysed in order to study the effect of oxidation. The most striking result of this in-situ experiment is definitely the similarity between the Test Drift and the Connecting Gallery. For both parts of the HADES URF, undisturbed conditions prevail in the Boom Clay pore water up to a distance of about 1 m away from the gallery. Within the first metre of clay, increasing sulphate concentrations were measured in the pore water.
The trend of increasing sulphate concentrations towards the gallery, as observed in the piezometer-waters, is further continued in the pore waters obtained from the leaching of the clay cores. Very close to the gallery lining, the effect of oxidation is the most pronounced and sul-

phate concentrations up to 20000 mg/l are reached. The high concentrations of sulphate are associated with high concentrations of most cations. This can be explained by mineral precipitation/dissolution reactions and cation exchange.
The effect of oxidation on the mineralogy of the Boom Clay is less pronounced. Pyrite and calcite are still present in the clay close to the gallery lining, but the presence of gypsum, and occasionally jarosite, suggests that oxidation processes indeed affected the mineralogy of the Boom Clay. The extent of change in mineralogical composition is much smaller than the extent of change in pore water composition. Changes in mineralogy have been observed within the first 4.5 cm of clay ahead of the concrete/clay interface, both in the old and the new gallery.
Based on the experimental data and underbuild with scoping calculations performed in RTDC5, it was possible to set-up a first conceptual model. During excavation, fractures are created up to about 1 m. Immediate oxidation occurs along the fractures. Due to the fast sealing of Boom Clay, the oxidation products are trapped within these fractures. The redistribution of the oxidation products during the operational phase occurs mainly within the first meter around the galleries. Due to the large hydraulic gradient, most of the sulphates are dragged towards the open gallery. During ventilation, additional oxidation is possible as oxygen can dissolve into the pore water and diffuse into the Boom Clay. However, experiments and scoping calculations (only considering diffusive transport and no reactive transport) show that the in-diffusion is limited to maximum about 1 metre, even after about 20 years.
Extended scoping calculations on the in-diffusion of oxygen from the ventilated galleries into the clay were performed which took into account reactive transport. These calculations have shown that dissolved oxygen in-diffusing into the clay is very rapidly consumed and cannot account for the high sulphate levels measured in the in-situ experiment. This is another argument in favour of the above proposed conceptual model, suggesting that oxidation of the Boom Clay is mainly related to the instantaneous oxidation due to the presence of oxygen in open fractures, rather than in-diffusion of oxygen during ventilation of the galleries.
The proposed conceptual model was finally tested during the second in-situ experiment, which aimed at following-up the pore water composition before, during and after the excavation of the PRACLAY gallery. In the frame of NF-PRO, two piezometers were foreseen for the geochemical follow-up of the pore water composition close to the PRACLAY Gallery. The different filters are present at an extent between 0.6 m and 2.0 m from the PRACLAY Gallery. Before excavation, all pore waters are indicative of undisturbed conditions. During excavation of the PRACLAY Gallery, no change in pore water composition is observed. This is probably because no fractures reached the considered filters for pore water sampling, and hence no oxygen could enter the system. This experiment shows that the proposed conceptual model, suggesting that the extent of the oxidised zone is determined by the extent of the fractured zone, can be valid.
Especially towards Performance Assessment studies, the proposed conceptual model may be a valuable input.
Another important input towards Performance Assessment studies is also related to the extent of oxidation around galleries in Boom Clay. The extent of the oxidised zone is rather limited: about 1 m around the HADES galleries, and probably less that 0.6 m around the PRACLAY gallery. Note that the latter is a preliminary estimation based on the above results, and needs to be confirmed by the HM-studies. The effect of oxidation will probably remain limited in time, as suggested by our experimental and modelling assessments (time frame 20 years).

Publications

Van Geet M., De Craen M., Weetjens E. & Sillen X. (2006) Extent of oxidising conditions in the host formation: Experimental data and scoping calculations. External SCK•CEN report: SCK•CEN-ER-05.

De Craen M., Van Geet M., Weetjens E., Sillen X. (2006) Extent of oxidation around the HADES URF (Mol, Belgium) - experimental data versus scoping calculations. NF-PRO 3th workshop and general project meeting, San Lorenzo de El Escorial, Spain, 2006/11/14-16.

De Craen M., Van Geet M., Honty M., Weetjens E., and Sillen X. (2007) Extent of Oxidation in Boom Clay as a result of excavation and ventilation of the HADES URF: experimental and modelling assessments. Oral presentation at the International Meeting "Clays in Natural and Engineered Barriers for Radioactive Waste Confinement", Lille, France, September 17-20, 2007.

De Craen M., Van Geet M., Honty M., Weetjens E., and Sillen X. (submitted) Extent of Oxidation in Boom Clay as a result of excavation and ventilation of the HADES URF: experimental and modelling assessments. Paper submitted to Physics and Chemistry of the Earth.

De Craen M., Van Geet M., Honty M., Weetjens E., and Sillen X. (2007) Extent of Oxidation in Boom Clay as a result of excavation and ventilation of the HADES URF: experimental and modelling assessments. Poster presentation at the 4th NF-PRO workshop, Brussels, Belgium, October 15-17, 2007.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D4.3.24

4.3.2.9: Ventilation test phase II: Geochemical characterisation of the rock samples for the VE-test before and after a second cycle of drying

Participants

CIEMAT

Goals/objectives of the research

The ventilation in the tunnel produces an evaporation process close to the tunnel wall, which may involve changes in the water and the pore water composition of the argillaceous material. As a consequence of evaporation and/or resaturation processes, a salinity gradient will be generated from the rock to the microtunnel wall surface. Possible geochemical changes in the rock can generate alterations in the pore water composition, mineralogy, microfabric (such as oxidation processes and precipitation of readily soluble sulphate and chloride salts), and other rock physical properties of the argillaceous rock, which could affect the hydromechanical properties.

In this report, the results of the geochemical characterization of the rock inside the VE-Test after the second cycle of drying are presented. The objective is to define the geochemical conditions and processes taking place in the host rock after the changes resulting from a second long-term desaturation, i.e.:

- To assess the impact of the ventilation cycle on pore water composition and content by means of squeezing of unaltered core samples and aqueous extraction tests.
- To analyse possible alterations in the mineralogy (oxidation processes and precipitation of readily soluble sulphate and chloride salts) by means of XRD and SEM analysis.
- To analyse the micro and macrostructure by means of water vapour adsorption/desorption isotherms.
- To assess the impact of chemical processes due to ventilation on hydromechanical rock properties (HM-C coupling).

Key results/achievements

The main results can be summarised as follows:

- In the ventilated area, solutes from the pore water of the rock are transported by advection towards the gallery surface, increasing the salinity at 0.2-0.6 m. In this zone, the water flow due to the hydraulic gradient is enhanced by the desaturation process, being the salinity gradients higher than in the non ventilated area.
- The increase of salinity by advective transport, apart from evaporation, provokes the neoformation of mineral phases (gypsum, calcite) and a dissolution of other ones (dolomite) modifying the exchange cation population at the first 0.2-0.6 m of the rock.
- The successive hydration/dehydration cycles or the natural ventilation of the open gallery would tend to accumulate solutes taking place different precipitation/dissolution processes. Gypsum and other salts will concentrate at the surface of the gallery walls over time. A self-sealing (gypsum and calcite) may be produced in the long-term, modifying the porosity and the permeability of the rock. However, this process is limited to the EDZ zone.
- The increase of salinity in the first centimetres of the rock (by evaporation and water

flow) implies an increase of the osmotic pressure and a decrease of the water activity. A possible hydraulically and osmotically driven water flow towards the gallery can also take place.

- A pyrite oxidation may simultaneously occur due to the diffusion of oxygen from the gallery to the rock through the fractures or dissolved in the pore water. However, the extent of this process is limited to 0.02-0.1 m.

Publications

Abstracts sent to conferences:
Evaluation of the geochemical processes occurred in the Opalinus clay formation subjected to a ventilation test. A. M. Fernández, A.M. Melón, M.V. Villar, M.J. Turrero, B. Garitte, L. do. N. Guimaraes, A. Gens, J. C. Mayor. Clays in natural & Engineered barriers for radioactive waste confinement. ANDRA. Lille, 17-20 Sept. 2007.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D4.3.26

4.3.2.10 EDZ short term evaluation: Ventilation test phase II

Participants

AITEMIN

Goals/objectives of the research

A Ventilation Experiment (VE) was performed at Mont Terri Underground Rock Laboratory between December 2001 and May 2004 under EC Project Contract No. FIKW-CT-2001-00126. This experiment is continued, as phase 2, within RTDC 4.3 of the integrated project NF-PRO. The main objective of the VE phase 1 was to evaluate the desaturation process of consolidated clay formations as produced by drift ventilation "in situ".
The second phase of the VE project concentrates on the characterisation and short-term evolution of the excavation damaged or disturbed zone (EDZ), including the study of chemical processes and their potential coupling to hydraulic and mechanical processes, taking place during the operational phase due to normal ventilation of the repository galleries.
Specifically, the following objectives have been identified:

- Assessment of the impact of chemical changes due to ventilation on hydromechanical properties.
- Determination of solute transport properties of the EDZ and comparison to known values in both sound and naturally fractured ('main-fault') rock.

To achieve these objectives, a second desaturation-saturation cycle is performed in the test section, under climatically controlled air conditions, along with a sampling and an extensive subsequent laboratory programme.
Within the in-situ measuring programme AITEMIN was in charge of the development of the Test Plan of the phase 2 of the test, of the installation of new instrumentation and of the supervision of some aspects of the test evolution, which are described below in more detail.

Key results/achievements

A document, identified as Test Plan, was developed by AITEMIN thanks to the inputs received from WP4.3 partners. Such document is the general design of the experimental arrangement of VE phase 2 and it includes the pursued objective, the laboratory tests and the required sampling campaigns. It also contains the description of the existing instrumentation and the new one planned to be installed, as well as the testing to be performed. Besides, it covers the basis of the second operational phase and the related activities, as the maintenance and operation of the ventilation and the data acquisition systems. Finally, it describes the planned modelling and interpretation works, the project organisation and the time schedule.
As the general performance of the sensors already installed was adequate and almost all the sensors were working properly by the end of the phase 1, only four additional capacitive hygrometers were installed by AITEMIN in the phase 2. As it was expected that during the planned ventilation, rock desaturation will only occur in a relatively small ring, the four additional capacitive hygrometers were installed at different depths from surface to a maximum depth of 25 cm (7 cm, 12 cm, 17 cm and 22 cm), in the cross-section SB2.
The data registered by the existing Data Acquisition System (DAS) were periodically analysed and synthesised for the monitoring of the main aspects of the test. Weekly tables, containing relevant information from the test, were elaborated until September 2006.
Main results of the test are as follows:

- At the end of the new desaturation phase the relative humidity was less than 95% only in a small ring around the wall (thickness » 25 cm), afterwards the progress of resaturation of this ring was clearly observed.
- As expected, the ventilation of the test section has induced again very small mechanical effects in the rock: at the end of the resaturation period a very small enlargement was registered with a mean value about 1.5 mm, during the new desaturation phase the trend changed and again a shrinkage of the rock was detected but smaller than 2.0 mm, finally from the start of the new resaturation phase an enlargement is being registered. As during phase 1 of the test, displacement trends were similar in both cross-sections but slightly higher movements were recorded in cross-section SD2, maybe due to its proximity to the inflow pipe.
- Then, again the mechanical effects of the ventilation may be considered as almost negligible. Besides, most of the installed sensors (to monitor the rock behaviour and the air of the test section) worked properly, demonstrating their adequate selection and installation (done in difficult conditions due to the small space available).

Publications

José Luis García-Siñeriz, María Rey Mazón, Ana María Fernández, Antonio Gens, Paul Marschall, Jean-Michel Matray, Juan Carlos Mayor, Jean-Claude Parneix, Kristoff Schuster, Manuel Velasco (2005). Test Plan D 4.3.2.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D4.3.27

4.4 WP4.4: Long-term evolution

4.4.1 Overall objective of work package 4.4

Work package 4.4 investigated the long-term evolution of the EDZ and its relevant properties with respect to the transport of radionuclides. The development of the EDZ will be investigated for (plastic and indurated) clays as well as for salt. The main objectives are to develop a common understanding of gas transport processes, in particular to assess the role of the EDZ as an important gas path as well as of the self-sealing or self-healing capacities of salt and clay in laboratory and *in situ* tests; and finally to investigate time dependent processes at different temperatures and during transport of water.

4.4.2 Overview of work performed

4.4.2.1 Self healing of clay at elevated temperature

Participants

BUTEC

Goals/objectives of the research

The objective of the here described work is to investigate in laboratory experiments the self sealing of clay stone in the EDZ at elevated temperatures. Therefore investigations with clay samples from the underground laboratory Mont Terri were conducted. To get a basis to compare the initial configuration of the samples, the intrinsic permeability was measured using nitrogen as measuring fluid. To investigate the effect of using an immiscible fluid without any chemical reaction isooctane was used as measuring fluid. The main tests were performed using formation water from Mont Terri at room temperature and at 90 °C. The essential difference between isooctane and formation water is that isooctane doesn't suspend clay and no chemical reactions occur to clay.

Key results/achievements

In summary the investigations show that using dried samples and nitrogen as measuring fluid a decrease of permeability only occurs if the confining pressure increases. Using isooctane as measuring fluid, the permeability decreases continuously and the decrease is reversible. After removing the isooctane out of the sample, the intrinsic permeability was nearly the same as measured before the test with isooctane. The use of formation water as measuring fluid results in a severe decrease of permeability. Within a few minutes no more flow is detectable. But depending on the initial permeability a water flow can be detected within a time period of several hundred hours. The now measured permeability is about 2 to 3 decades lower than the initial permeability. Independent on temperature only a very low decrease of permeability could be detected if the confining pressure was not changed. Not until the confining pressure increases the permeability decreases also. A confining pressure of 3 MPa leads to a total blockade of flow within 500 h. Due to self-sealing effects no principle difference between the behaviour at room temperature and at 90 °C could be detected.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D4.4.11

4.4.2.2: Investigations on damage and healing of rock salt

Participants

BGR

Goals/objectives of the research

In a rock salt formation, the excavation of underground openings will cause deformation by creep. In the dilatant stress domain this ductile deformation is coupled with the evolution of damage and the formation of an EDZ. After back-filling and closure of a repository the convergence will cause the reduction of the deviatoric stress. When the non-dilatant stress domain is obtained again, rock salt starts to compact. As a consequence, the EDZ and the permeability in this zone are reduced. BGR has investigated the self sealing / self healing of rock salt.

Key results/achievements

The prerequisite for the prediction of damage and healing of rock salt is the knowledge of the dilatancy boundary which yields the criterion whether dilatation or compaction is dominating. The processes, which are active in the dilatant stress domain and which produce damage, are described by the CDM-system used by BGR.
The investigation on the compaction and healing behaviour of pre-damaged dry rock salt shows that the decrease of the porosity and the permeability is primarily time dependent. The amount of the isostatic pressure has a minor influence.
The relation between permeability and porosity can be described by a power law $k \sim \Phi^n$. The sensitivity (i.e. the exponent n) during compaction in the non-dilatant stress domain is much greater than in case of progressing damage during loading in the dilatant stress domain.
The principal challenges remaining for the understanding of the coupled processes of damage and compaction respectively healing in rock salt are:

- Further long-term compaction tests at moderate stresses are needed with the consecutive measurement of permeability and porosity. The testing duration has to be much longer than several month, otherwise the empirical equations for the extrapolation of the compaction behaviour cannot be checked with respect to stresses of in-situ relevance.
- Development of generally agreed constitutive models for the compaction of dilated rock salt.
- Implementation in numerical codes, which facilitate reliably extrapolations to in-situ conditions.
- Understanding of physical processes which control the efficiency of healing in dilated rock salt with respect to humidity effects.
- The impact of a pore-pressure (gas respectively salt solutions), i.e. chemical and hydraulic interaction.

Publications

Schulze, O. (2007): Investigations on damage and healing of rock salt.- In: M. Wallner, K.-H. Lux, W. Minkley, & H.R. Hardy, Jr. (eds.), The Mechanical Behavior of Salt. Understanding of THMC Processes in Salt. Hannover 2007: 33-43. London: Taylor & Francis (Balkema).

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D4.4.14

4.4.2.3: Numerical modelling of the long-term evolution of EDZ

Participants

FZK-INE

Goals/objectives of the research

The objective of numerical modelling was to predict the development and long-term evolution of the EDZ in rock salt under different conditions.

Key results/achievements

The work includes the following key results:

- Improvement of the constitutive model to describe the damage (dilatancy) of the rock salt in the near field of excavations;
- Calibration of the model parameters on new laboratory tests;
- Simulation of the long-term evolution of the EDZ around a 37 years old gallery and comparison of numerical results with in situ measurements (i.e. model validation);
- Predictive modelling of thermo-hydro- mechanical behaviour of rock salt in the vicinity of a disposal drift for heat-generating waste in a conceptual repository.

Publications

Pudewills, A.: Numerical Modelling of the long-term Evolution of EDZ: Development of material models, implementation in finite-element codes, and validation, FZKA-7185, 2005.
Pudewills, A.: Modelling of the hydro-mechanical processes around excavations in rock salt, Van Cotthem, A. [Ed.], Eurock 2006: Multiphysics Coupling and Long-term Behaviour in Rock Mechanics; Proc. of the Internat. Symp. of the Internat. Soc. for Rock Mechanics, Liege, B, May 9-12, 2006, pp. 527-530
Pudewills, A.: Modeling of hydro-mechanical behvior of rock salt in the near field of repository excavations, The Mechanical Behavior of Salt : Understanding of THMC Processes in Salt, Proc. of the 6th Conf., Hannover, May 22-25, 2007, pp.195-200.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D4.4.15

4.4.2.4: Modelling of Dilatancy Around an Open Drift in Rock Salt and investigations on Self-Sealing of Indurated Clay

Participants

GRS

Goals/objectives of the research

The GRS work consisted of laboratory and modelling tasks. The main objective of GRS' laboratory experiments was to investigate the self-sealing potential of indurated clay under relevant repository conditions. Modelling of an open drift in rock salt was performed to test the constitutive laws implemented in Code_Bright regarding their potential for modelling EDZ evolution.
Besides this work, GRS also contributed the chapters dealing with rock salt to the state-of-the-art report on "Gas Migration in the Near Field" (Deliverable 4.4.1).

Key results/achievements

The self-sealing potential of the Callovo-Oxfordian argillite (COX) and the Opalinus clay (OPA) was investigated on strongly damaged samples by measuring the gas permeability as a function of the confining stress before and after water re-saturation. The experiments were carried out on four normally-sized COX samples, one hollow cylindrical COX sample and one large OPA sample. The durations of the tests are long in a range of 5 to 16 months. The main experimental findings are:

- The permeability of the pre-damaged samples decreases significantly with increasing the confining stress which induces fracture closure. The permeability measured in radial direction on a hollow sample (D/d/L=80/20/103mm) decreases exponentially from 10-15 m2 at 1 MPa to 10-21 m2 at 28 MPa along the isotropic loading path. The compression resulted in plastic closure of the pre-existing fractures, indicated by the much lower permeability values measured along the unloading path. Similar permeability reduction with increasing confining stress was also observed in axial direction parallel to the bedding plane. But at low stresses below 10 MPa, axial permeability parallel to the bedding is about one to two orders of magnitude higher than the radial one perpendicular to the bedding. The hydraulic anisotropy runs off with increasing the confining stress.
- The permeability of fractured clay rocks is more dominated by the confining stress normal to the fracture plane. This is validated by gas permeability measurements on a large sample (D/L=260/600mm) with fractures oriented more parallel to the sample axis. The increase of lateral stress from 3 to 18 MPa at 19 MPa axial stress led to a decrease in axial permeability of five orders of magnitude from 10-13 to 10-19 m2. As the radial stress was reduced again to the initial level of 3 MPa, the permeability increased to 10-16 m2 which is still two orders of magnitude lower than the initial value. This clearly indicates the strong plastic closure behaviour of the fractures.
- The permeability of damaged clay rocks under stress decreases also with time due to the time-dependent compaction of the pores and fractures. On the pre-damaged samples, significant permeability reduction by a factor of 4 to 8 was observed over two months under a confining stress of 1.5 MPa.
- Due to the high capacity of water adsorption and thus the high swelling capacity of the studied clay rocks, the volume of unsaturated fractures tends to be reduced by re-

hydration. This is confirmed by measuring the gas permeability before and after water re-saturation. A very low gas permeability of 10-21 m2 was observed after water re-saturation, being about five orders of magnitude lower than before which is the same as that of intact rock.

- On strongly-damaged samples (D/L=86/80mm) with relatively high gas permeability of 10-17 - 10-16 m2, which was measured in time intervals of several days, no water outflow was observed during a long time period of five months when synthetic formation water was injected at a pressure of 1 MPa and a confining stress of 2 MPa. This clearly indicates that water conductivity of the clay rocks is lower than the gas conductivity due to the reduction of the effective pathways to water by clay swelling.
- After water re-saturation, a gas breakthrough pressure was recorded in a range between 0.5 and 1.0 MPa under confining stresses of 2 to 3 MPa, at which a gas permeability of 10-18 m2 was determined.

All these experimental results provide strong evidence of the high self-sealing capacity of the studied clay rocks under the combined impact of re-consolidation and re-hydration.
EDZ evolution in an open drift in rock salt was modelled using CODE_BRIGHT with the existing material laws developed by UPC and compared to the measurement results obtained for the AHE drift in the Asse mine in the frame of the BAMBUS II project. The comparison showed that the dilatant behaviour of the EDZ can in principle be modelled using this formulation. The degree of dilatancy (i. e., the porosity increase) is, however, modelled to small. The parameters and perhaps also the formulation itself need a careful calibration which is done by UPC and GRS in cooperation in the frame of the ongoing project THERESA.

Publications

Zhang, C.-L., Wieczorek, K., Rothfuchs, T., 2006: Experimental Study on Damage and Self-Sealing of Indurated Clays. NF-PRO Third Workshop, 14 – 16 Nov. 2006, Spain
Zhang, C.-L. Rothfuchs, T., 2007: Damage and Sealing of Clay Rocks Detected by Permeability Measurements. Proc. 3rd International clay Meeting, Lille, Sept. 17-20, 2007 (to be printed)

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D4.4.16

4.4.2.5 Gas Transport in the EDZ. EDZ Long-Term Evolution

Participants

NAGRA

Goals/objectives of the research

The task “Gas migration in the EDZ” as part of WP 4.4 was aimed at compiling the existing knowledge on the role of the EDZ as a preferential gas path. The task activities concentrated on a survey of relevant literature with emphasis on the following topics:

- Treatment of the gas issue in the context of repository safety assessment (sources of gas production, typical gas production rates for the different types of waste, geological aspects and role of the repository layout, examples for the treatment of the gas issue in different national disposal programmes).
- Gas transfer in rock salt and argillaceous formations (basic gas transport mechanisms, coupled hydro-mechanical process, representative gas transport parameters in rock salt and clay).
- Survey of recent experimental programmes, related to the gas release from HLW/ILW disposal systems

Key results/achievements

The following key achievements are discussed in the report:

- Survey of relevant gas transport mechanisms in the EDZ; assessed formations are rock salt and clays
- Phenomenology of basic self-sealing mechanisms
- Conceptual models of mechanical self-sealing in fractures
- Compilation of case studies on gas transport in rock salt, Opalinus Clay, Boom Clay

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D4.4.17

4.4.2.6: EDZ Long-Term Evolution

Participants

TUC

Goals/objectives of the research

This Final Activity Report gives a short summary of the main results that have been carried out within the performed research work on the material behaviour of indurated clay. *Section no. 3* and *no. 4* refer to the principle enlargement of the *Hou/Lux-T* constitutive model, the verification and validation process as well as on site confirmation via back-analysis of in situ data, taking into account strength anisotropy. *Section no. 5* describes hydro-mechanical interactions in laboratory testing experience and in numerical simulations. Finally *Section no. 6* gives some conclusions and outlook for the scientific work that has to be done in the future.

Key results/achievements

Based on common experience and the investigations of *Lux et al.* it seems necessary to take into account the following mechanical and hydraulic characteristics of argillaceous rock mass for reliable physical modelling as well as numerical simulation with site specific specification:

- usage of 3D simulation models including gradual excavation processes,
- physical models including the following properties that might have significant influence on the load bearing system and the development of damaged zones (isothermal conditions):
    - elastic, plastic and viscous deformation (isotropic, anisotropic)
    - raising deformability and reduced strength on bedding planes,
    - bedding plane orientation,
    - pore water and pore water pressure related effects,
    - primary stress field (anisotropic),
    - permeability and it's changes due to destrengthening or compaction,
    - validation of physical models via on site confirmation.

Furthermore, considering high level waste disposal with heat generation, the effect of temperature changes (heating, cooling) on the mechanical and hydraulic properties and processes has to be studied and taken into account in physical models and numerical simulation as well as validated with help of field measurements.
Concluding it may be stated that the mechanical behaviour of claystone in the minimum is as complex as the mechanical behaviour of rock salt, but there are also some important properties more based on the rock mass structure and genesis that together cause the necessity for much more scientific work to finally get qualified instruments for reliable prognosis.
One important task in the future will be the classification of certain observed degrees of damage of the rock mass in relation to calculated values of the damage parameter D which amounts to $0 < D < 1$. Therefore the most important experience for further laboratory investigations is online pore water pressure measurement as precondition for further development of material parameters of indurated clays.

Publications

Method for Ageing Resistant Storage of Argillaceous Rock Samples to achieve Reproducible Experimental Results even after Long Intermediate Storage and further Experiences, Czai-

kowski, O.; Düsterloh, U.; Lux, K.-H., Clausthal University of Technology - Professorship for Waste Disposal and Geomechanics, NF-PRO 4rd Workshop, 15th-17th October 2007, Brussels, Belgium

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D4.4.19

4.5 WP4.5: Integration of results

4.5.1 Overall objective of work package 4.5

In work packages WP4.2, WP4.3, WP4.4, experimental data were produced and detailed models addressing various aspects of EDZ development and evolution were used and developed. The main objective of work package 4.5 was to integrate results these work packages in view of providing concise EDZ conceptual models and parameters as input to Performance Assessment of the Near-field (RTD component 5).

The integration of models and parameter values generated within previous WPs enables to provide a global description of the EDZ (in time and space). To establish this (or theses) "global model(s)" an "output function" calculated by each individual model corresponding to the specific time and space scale concerned (initial, transient, long-term phases) will be taken into account. These "output functions" will take account of the main processes and corresponding parameters of each model, but also the boundary conditions of the preceding state (and model). Sequencing calculations coming from the different WPs will lead to an integrated conceptual and phenomenological EDZ model.

4.5.2 Overview of work performed

4.5.2.1: EDZ Development and evolution. Final Synthesis report

Participants

ANDRA

Goals/objectives of the research

The objectives of the component 4 of the NF-PRO project (RTDC4) have consisted in:

- Providing a comprehensive synthesis based on available knowledge in order to better define main pending issues and identify uncertainties;
- Improving and quantifying mechanical, hydrological, thermal, chemical processes (individual and coupled) taking place in the EDZ and developing and corresponding models;
- Providing PA with updated assessment of the main processes during the EDZ creation and evolution, and with estimates of main parameters to be taken into account in PA exercises.

Key results/achievements

Considering that no specific works on EDZ in crystalline rocks was carried out in the framework of the NF-PRO, the conclusive chapter of the Final Synthesis report only concerns the remaining issues and recommendations for future works related to clay and salt rocks.

1 Remaining uncertainties and recommendations for studies on Clay rocks

Even if the individual activities of the RTDC4 were generally did not directly cover all aspects of EDZ for the clay “reference systems" , the information, data and conclusions acquired from:

- various experiments (in situ in URLs & on rock samples),
- various representative clay rocks features (soft clay, indurated clay, isotropic samples, anisotropic samples, undisturbed rock, fractured rock…), and
- various types of underground works (depth, geometry…), excavation methods (tunnelling, blasting…), and lining techniques,

can be usefully put together and used to assess the specific reference system issues related to initial EDZ development.
This improvement in the global understanding of the main processes taking part in the EDZ creation, together with the knowledge of the role of the different initial rock features and intrinsic mechanical parameters, have permitted an acceptable description and modelling of the initial EDZ development.
Full understanding of coupled hydro-mechanical processes and their effect on the EDZ development still, however, remains to be improved, together with the corresponding modelling.
The same applies to the chemical processes coupled with the hydraulic and hydro-mechanical evolution of the EDZ. However, a major contribution of NF-PRO is the consensus which emerges on the effectiveness of self-sealing of the EDZ for all types of clay rock, over the

long-term, but also most probably in the short term. This consensus covers today only hydraulic aspects, and not work related to solute transfer and retention.
Nonetheless, PA/SA studies undertaken to date included a broad range of sensitivity analysis calculations of radionuclide transport, including even extreme "what if ?" values . These studies illustrated that radionuclide transport through the EDZ would not make a significant contribution to dose, even if very little or no self-sealing occurred. The hydraulic self-sealing that is consistently observed further strengthens these findings and opens prospects for more realistic representation of the EDZ in PA.
The major processes that must be investigated are:

- Modelling of hydro-mechanical behaviour of clay rock (incl. EDZ) around the repository structures;
- Thermal effects on HMC properties of EDZ (RS2 and RS3)
- Chemical interactions between the EBS (waste form, metallic components, cementitious components) and the EDZ : iron / clay interaction (RS2), alkaline plume (RS3), waste form interaction (RS2 and RS3);
- Gas migration and its effects on others EDZ properties;
- Solute transfer properties of EDZ with time, taking into account THMC processes involved.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D4.5.3

5. RTDC 5: Process couplings and integration in performance assessment

The objective is to ensure that synthesis of information is achieved for the NF-PRO Project. While the main detailed scientific synthesis (new information, data, models) was done in Components 1 to 4, the intention in Component 5 synthesis reports is to evaluate this information and take it further, considering the broad safety case perspective (i.e. not limited merely to assessment models and the underlying process models),in particular addressing the questions:

- Has confidence in the science in various areas increased?
- Are the new developments significant/marginal (better data that reduces uncertainty a lot/a little)?
- Are there major new developments (new findings with significant improvements, improved process models)?
- Has conceptual model uncertainty been reduced?
- If the models/data were used, how might they be applied in PA and would they make a difference (based on our experience: a semi-quantitative or qualitative judgement)?
- How are the processes treated now in assessment and how might this change as a result of NF-PRO work?
- Have new issues/processes been raised? If so, how should they be resolved?
- What future research work needs to be done?

5.1 WP5.1: Integrated analyses

5.1.1 Overall objective of work package 5.1

WP5.1 is focusing on development of overall NF system understanding. There are diverse NF concepts, with widely varying designs and boundary conditions. In order to provide a framework, Component 5 specialists have focused on producing five reports for the various different reference systems. These provide a basic definition of the various different NF design approaches as well as an outline and discussion of the processes in the NF for each of these systems. The reports and responsibilities are: SF/iron/bentonite/granite (ENRESA), SF/HLW/iron/bentonite/clay (ANDRA), HLW/concrete/steel/clay (SCK), SF/steel/salt (GRS), SF/Cu/bentonite/granite (VTT). In addition, each of these organisations has also documented the present understanding of processes through calculations examining chemical, hydraulic and mechanical interactions among the various NF components.

Members of Component 5 have experience in performance assessment, including evaluation of detailed process models, model abstraction and development of integrated assessment models. The various reference system reports produced in Component 5, when combined with the state-of-the-art reports produced in RTD Components 1 to 4, provide a baseline for evaluating the subsequent progress in research achieved in each of the RTD Components over the period 2004-2007. Component 5 has a particular role to play in several areas that are dealt with more in isolation in other RTD Components. For example, the relative significance of processes such as waste form dissolution rates, radionuclide solubilities, radionuclide sorption and diffusion rates in bentonite in controlling radionuclide release from the near field is being examined in a report planned to be completed in June 2006. In addition a report on hydrogen

production and dissipation rates for various near-field disposal concepts is also being prepared.

5.1.2 Overview of work performed

5.1.2.1 Engineered barrier system coupled process modelling

Participants

VTT, ENRESA, ANDRA

Goals/objectives of the research

Key results/achievements

Publications

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D5.1.5

5.1.2.2: Final report on H2 production and transport for various disposal systems

Participants

NAGRA

Goals/objectives of the research

Key results/achievements

Publications

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D5.1.6

5.1.2.3: Final report on RN sensitivity analysis for various disposal systems

Participants

ENRESA

Goals/objectives of the research

Key results/achievements

Publications

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D5.1.7

5.1.2.4: Final Activity Report Quintessa

Participants

Quintessa

Goals/objectives of the research

One of the principal objectives of NF-PRO's WP5.1 was to develop a description of the evolution of the conditions in the near field of a High-level Waste (HLW) or Spent Fuel (SF) repository. The description needs to include the transient evolution of the system and its response to the expected evolution of the boundary conditions provided by the host rock. The goal of this work was to develop a methodology for coupled system evolution modelling of relevant near-field processes.
The objective was to model the Engineered Barrier System (EBS) evolution due to coupled Thermal (T), Hydraulic (H), Mechanical (M) and Chemical (C) processes to a level of abstraction and approximation that is appropriate to performance assessment, such that the general features of its evolution can be understood. The primary purpose in carrying out such modelling is to build sufficient confidence in the long-term Safety Case for disposal. In addition, such modelling has the potential to facilitate interactions with the scientific and engineering communities.

Key results/achievements

The approach adopted in this work is to make use of a compartmental approximation to the system geometry and to simulate the key processes, and their couplings, which determine the evolution of the EBS. In principle, the approach proposed here can be applied to transport in the aqueous and gaseous phases, to inward and outward energy flows and to the alteration of solid materials. However, the primary application within NF-PRO has been restricted to the evolution of a bentonite buffer.
The methodology has been implemented using QPAC-EBS, which is a flexible software tool that is being developed outside the NF-PRO project. Key features of the code are as follows. The system is discretised into compartments, which are not necessarily space filling, reflecting its intended use for system-level rather than research-level calculations. While some processes are built into the code, these can be changed and others can be added using a powerful input language. For example, this facilitates the use of simplified equations for processes and interactions of relevance to system-level modelling. Unlike other compartmental modelling tools, the system can be strongly coupled, for example all properties can depend on all other properties, and all properties (including the compartmental volumes) can be time dependent. Simple examples of the application of QPAC-EBS to a contaminant transport problem and a thermal evolution problem are presented to illustrate the types of situations that can be modelled and to demonstrate verification of the code.
The presence of both iron canisters and bentonitic clay in some EBS designs for the geological disposal of HLW creates the potential for chemical interactions which may impact upon the long-term performance of the clay as a barrier to radionuclide migration. Flooding of potential radionuclide sorption sites on the clay by ferrous ions and conversion of clay to a non-swelling sheet silicate such as berthierine are two possible outcomes that would be deleterious to long-term performance. The state of knowledge of iron-bentonite interactions at the start and end of the NF-PRO project is reviewed from a performance assessment perspective. Specifically, impacts on the following processes are considered: canister corrosion; alteration of bentonite transport and physical properties; glass corrosion; sorption on canister corrosion

products; redox and pore chemistry; mechanical integrity of the canister; consumption of oxidants; and the physical and chemical effects of hydrogen gas. Natural systems evidence suggests that the sequence of alteration of clay by Fe-rich fluids will proceed via an Ostwald step sequence. The processes of nucleation, growth, precursor cannibalisation, and Ostwald ripening have been incorporated in the QPAC-EBS code to address the issues of the slow growth of bentonite alteration products. This, together with inclusion of processes of iron corrosion and diffusion, has enabled investigation of a representative model of the alteration of bentonite in a typical EBS environment. This approach thereby facilitates the extrapolation of short-term experimental results to PA timescales. Simulations with fixed mineral surface areas show that berthierine dominates the solid product assemblage, with siderite replacing it at simulation times greater than 10 000 years. Simulations with time-dependent mineral surface areas show a sequence of solid alteration products, described by: magnetite -> cronstedtite -> berthierine -> chlorite. Using plausible estimates of mineral-fluid interfacial free energies, chlorite growth is not achieved until 5 000 years of simulation time. The results of this modelling work suggest that greater effort should be placed upon providing key data for iron silicates (e.g. kinetic data, solubilities, and mineral-fluid interfacial free energies), through a dedicated programme of laboratory experimental and natural analogue research.
Overall, this work illustrates the power of the methodology and modelling tool for treating strongly coupled THMC processes at a systems level and provides a basis for applications to a wider range of Safety Case issues in the future. It is important to stress that the value of participating in NF-PRO was not confined to the scientific developments described in this report. Active participation in a large number of meetings and workshops proved to be an extremely worthwhile experience for sharing knowledge and insights of relevance to the safety of geological disposal.

Publications

Savage, D., Watson, C., Benbow, S. and Wilson, J. (2007) Modelling iron-bentonite interactions. Workshop on Long-Term Performance of Smectitic Clays Embedding Canisters with Highly Radioactive Waste, (ed. R. Pusch), Lund, Sweden, 356-365.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D5.1.15

5.1.2.6: Final Activity Report IRSN

Participants

IRSN

Goals/objectives of the research

Work by IRSN as part of NF-PRO's RTDC-5 was devoted to:

- modelling studies dealing with the chemical evolution of clays due to the presence of cement, the development of a free gas phase (H_2 due to corrosion process) within the near-field and the migration of radionuclides within both the near-field and a whole repository system. These studies are in particular carried out in the framework of the performance assessment methodology developed by IRSN to review applications files.
- reviewing the experimental and modelling works related to the chemical evolution of the EBS performed under the NF-PRO's RTDC2 and RTDC5 components

Sensitivity calculations were performed with the view to address the influence of uncertainties linked to some processes, parameters or events on the characteristics of either major components of the repository (being the plugs/seals in this particular case) or on the confinement capabilities of the repository as a whole.

Key results/achievements

The main outcomes of the IRSN contribution to RTDC5 concern numerical modelling results of:

- the chemical evolution of clays due to the presence of cement, with a specific emphasis on the sensitivity of cement/clay interaction modelling to mineralogical and transport hypotheses;
- the free gas phase within the near-field, assessed in terms of potential extent and pressure for various modelling assumptions;
- the migration of radionuclides within both the near-field and a whole repository system including drifts and a shaft, with a focus on the influence of UO_2 degradation mechanisms, radionuclide transport properties and seal performances on the overall confinement capabilities of the repository.

Reviewing activity of the experimental and modelling works related to the chemical evolution of the EBS performed under the RTDC2 and RTDC5 components has also been performed with the view to put the scientific results in perspective with the global performance assessment of the whole geological repository. The corresponding chapter n°5 of the RTDC5 Synthesis Report has thus been produced for review by other RTDC5 partners. In addition, IRSN commented on the draft versions of the other chapters of RTDC5 Synthesis

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D5.1.16

5.1.2.7: Modelling of corrosion-induced processes in emplacement boreholes and drifts

Participants

GRS

Goals/objectives of the research

There are a number of physical and chemical effects occurring in the near field of an underground repository with steel containers. Such containers tend to corrode under the influence of humidity, both in the presence and the absence of gaseous oxygen. While in clay the resaturation of the host rock with liquid water is the normal evolution, a repository in salt is expected to remain dry, but a brine intrusion can never be completely ruled out. Moreover, there is always some residual humidity in the salt backfill. Therefore, it should be assumed, that in all cases there is enough water available for corrosion.
There are two kinds of iron corrosion. The aerobic iron corrosion process in the presence of elementary oxygen requires the presence of water without consuming it. The anaerobic iron corrosion process consumes water and produces hydrogen gas, transforming iron to magnetite. Corrosion processes may exert a mechanical impact to the surrounding environment since the volumes of the corrosion products are different from those of the original substances and a considerable amount of gas is produced. This can lead to a high pressure in the pore space around the containers. The gas can also displace liquids from the near-field and finally escape itself. In salt host rock, there is additionally the effect of convergence by creep which leads to a reduction of the pore space within the backfill and further brine displacement. It is possible that the corrosion stops because the available water is exhausted and cannot be replaced due to lack of void space near the canisters. In this case the canisters are totally included and isolated. The following interacting corrosion-induced effects, which can have an essential influence on the further evolution of the system, are considered in this report:

- *Gas production*: Hydrogen gas is generated by iron corrosion. It can displace water or brine from void volumes inside the canister or from pores in the backfill. The gas pressure can reach considerable values and influence the mechanical evolution of the system.
- *Water consumption*: As opposed to the aerobic corrosion, the anaerobic corrosion does not only require the presence of water but also consumes it. This may lead to the possibility of water being replenished.
- *Salt precipitation*: If the water contains solutes, these are precipitated when water is consumed by corrosion. A consequence of this may be the reduction of backfill porosity. This effect is of specific interest in the case of a repository in rock salt, where the fluid is normally expected to be saturated NaCl solution.
- *Solid volume increase*: During anaerobic corrosion, iron is transformed to magnetite which has a lower density and occupies a higher volume than the original iron. This can lead to a reduction of pore space, which has an effect on the fluid pressure inside the borehole or drift.

The mentioned near field effects are coupled. In the work described here, they have been investigated by means of model calculations in three steps. In the first step, total mass and volume balances are considered without taking account of the time dependence of the processes and their various couplings. Two simplified disposal concepts are considered, borehole and drift disposal of Spent Fuel canisters. Both rock salt and clay formations are taken into ac-

count. In the second step a numerical model is described that allows one to calculate the time-development of a disposal borehole or drift in rock salt under consideration of all of the mentioned processes. The model is implemented in the LOPOS code, which is part of the EMOS package for integrated performance assessment, and applied to the same simplified model structures that have been investigated in the first step. The results are compared with those of the first step in order to verify both approaches against each other. In the third step the model applied to a more complex generic repository structure in rock salt.
The work described in this report was performed in the context of the European research project NF-PRO and funded by the European Commission as well as by the German Federal Ministry for Economics and Technology.

Key results/achievements

The present study shows that the modifications of the models of disposal segments work correctly. Brine consumption yields a time delay with respect to filling up the disposal segments and thus a later release of brine and radionuclides from disposal locations. Additionally, there is a reduction of maximum amount of brine which the disposal locations can take. This is, on one hand, related to the pore volume reduction due to volume increase of solid material, on the other hand by the ongoing faster convergence due to time delay of the fill-up phase of the mine and, hence, a somewhat later pressure increase. This smaller volume of brine may also have influence on the radionuclide concentration in the disposal locations, if there is low solubility of the respective radionuclide. This effect is expected to take place in boreholes where one has a rather small pore volume from the beginning. The effect time delay is more pronounced in disposal drifts where one has a larger amount of metal, but also more pore volume. Thus, the volume increase of solid material and the large amount of brine consumed during corrosion have a stronger delay in brine and radionuclide release. Therefore, radionuclide with a high inventory in disposal drift show a more pronounced effect on release. In general, taking into account the volume increase of solid material and the brine consumption during corrosion has a benefit on the isolation potential of the repository. However, not the increase of solid material but rather the brine consumption is responsible for this effect.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D5.1.17

5.1.2.8: Final Activity Report by ENRESA

Participants

ENRESA

Goals/objectives of the research

RTDC 5 had two objectives:

- To provide useful inputs to the scientific components of NF-PRO through the identification of key processes and remaining uncertainties in the near field, and
- To analyze the outcomes of the whole project from the point of view of the global system and the performance assessment, and integrate them in a synthesis report with conclusions and recommendations in terms of influence of key processes on the performance of the near field components.

Key results/achievements

The first objective has been fulfilled through:

- The phenomenological description of one of the 5 Reference Concepts adopted in RTDC5 to cover the spectrum of reference concepts and host rocks.
- Several calculations that analyse different aspects of the near field evolution of repositories in granite and clay. Most calculations deal with mass and energy fluxes into or from the near field.
- A report with the sensitivity analyses for radionuclide releases from the near field performed by 6 organisations involved in RTDC5 (Enresa, VTT, Nirex, IRSN, NRI and NAGRA). This report was edited by Enresa and provided to NF-PRO Components 1 to 4 to help them focus their efforts on the radionuclides and processes more important for safety.

The second objective has been fulfilled through the RTDC5 Synthesis Report that has been prepared by all the organisations envolved in RTDC5. Enresa contribution has been mainly focused on reviewing the experiments and modelling related to the Thermo-Hydro-Mechanical evolution of bentonite barriers performed in NF-PRO WP3.2 and 3.3 in order to analyse the usefulness of the scientific results for the Safety Case.

Publications

Enresa has provided its contributions to several project deliverables:
D5.1.4 “Description of the five reference concepts”.
D5.1.5 “Mass balance and energy flows calculations”.
D5.1.7 “Sensitivity analyses for radionuclide releases from the near field”. (Enresa acted as editor of D5.1.7).
RTDC5 Synthesis Report.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D5.1.18

5.2 WP5.2: Synthesis

5.2.1 Overall objective of work package 5.2

In WP 5.2, a synthesis reports was produced at the end of the project, addressing each reference system. The objective is to ensure that synthesis of information is achieved for the NF-PRO Project. While the main detailed scientific synthesis (new information, data, models) is done in Components 1 to 4, the intention in Component 5 synthesis reports is to evaluate this information and take it further, considering the broad safety case perspective (i.e. not limited merely to assessment models and the underlying process models), in particular addressing the questions:

- Has confidence in the science in various areas increased?
- Are the new developments significant/marginal (better data that reduces uncertainty a lot/a little)?
- Are there major new developments (new findings with significant improvements, improved process models)?
- Has conceptual model uncertainty been reduced?
- If the models/data were used, how might they be applied in PA and would they make a difference (based on our experience: a semi-quantitative or qualitative judgement)?
- How are the processes treated now in assessment and how might this change as a result of NF-PRO work?
- Have new issues/processes been raised? If so, how should they be resolved?
- What future research work needs to be done?

5.2.2 Overview of work performed

5.2.2.1 RTDC 5 Synthesis Report

Participants

Goals/objectives of the research

Key results/achievements

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D5.2.3

5.2.2.2: Near Field Sensitivity Studies of a Reference Repository Concept for UK High-level Waste/Spent Fuel

Participants

NDA/NIREX

Goals/objectives of the research

This study reports a series of sensitivity calculations focussed on the near field and in particular on the role of the bentonite buffer, to determine the sensitivity of flux from the near-field to changes in input parameters. The work aims to identify key processes and key parameters affecting near-field performance, and will assist in the development of understanding of how near-field processes can affect movement of radionuclides in the near field for this concept.

Key results/achievements

NDA (Nirex) has previously reported a preliminary post-closure assessment of a Reference Repository Concept for UK High-level Waste/Spent Fuel. The current study reports a series of sensitivity calculations focussed on the near field and in particular on the role of the bentonite buffer, to determine the sensitivity of flux from the near-field to changes in input parameters. The work aims to identify key processes and key parameters affecting near-field performance, and will assist in the development of understanding of how near-field processes can affect movement of radionuclides in the near field for this concept.
The methodology developed by Nirex for scenario and conceptual model development (using a structured FEP-based approach) was used to support the development of scenarios for sensitivity studies on the performance of the bentonite buffer. Scenarios identified were:

- Base Scenario
- SKB's SR-97 Scenario
- Bentonite Degradation + SR-97 Scenario
- Canister Corrosion + Bentonite Degradation + SR-97 Scenario
- Saline Water Scenario
- External Events Scenario
- Inside Out Effects Scenario

The descriptions of these scenarios guided the choice of sensitivity calculations to be performed. In many cases there is a lack of data which would be required to parameterise these scenarios precisely. Therefore the approach that has been taken has been to define some bounding sensitivity calculations which encompass the key aspects of the scenarios.
In the sensitivity calculations reported in this Technical Note three sets of calculations were carried out; a set of calculations based on the reference case assumptions, a set with a single canister failure at 10,000 years, and a set with 10 canisters failing at 1,000 years. For each of these sets, the following sensitivity calculations were carried out:

- The effective diffusivities in bentonite for all radionuclides were set to 10-9 m2/s, the free water value;
- All radionuclides were given unlimited solubility in bentonite water;
- The sorption coefficients to bentonite for all radionuclides were set to zero;
- For radionuclides with instant release fractions (IRFs), all IRFs were set to 1;

- Bentonite density was lowered;
- A combined case, whereby the effective diffusivities in bentonite for all radionuclides were set to 10-9 m2/s, the sorption coefficients to bentonite for all radionuclides were set to zero, and the bentonite density was lowered, to scope the combination of potential effects of the saline water scenario.

Additionally, for the case with the packages failing at 1,000 years, a calculation was carried out in which the hole grows linearly from zero to 1m2 area over the period 1,000 to 108 years.
The study has focussed on flux from the near-field as the main performance indicator. Lead-210 and radium-226 are key contributors to the total flux in all three sets of calculations. These radionuclides are ingrown as part of the uranium-238 decay chain series. The peak fluxes of these radionuclides are not significantly affected in any of the sensitivity cases. This does not imply that they are not important in terms of radiological risk, only that their peak flux is insensitive to the parameter variations considered in the sensitivity calculations.
The identification of radium-226 and lead-210 as key radionuclides is a key conclusion – these radionuclides are daughters of long-lived parents. The half life of uranium-238 is 4.5 billion years and this means that it won't have significantly decayed over the timescales for which it can realistically be claimed that any engineered barrier system might be capable of isolating it. However, the risk from such radionuclides can be mitigated by substantial retardation and dispersion in the geosphere (i.e. other aspects of the multi-barrier system). Because of these timescales, for uranium-238 a highly-engineered near-field (e.g. with copper canisters) is not expected to significantly reduce the peak dose in the biosphere.
Chlorine-36, nickel-59, iodine-129 and caesium-135 are also key contributors in all three sets of calculations. Shorter-lived radionuclides that are not ingrown by longer-lived parents, for example carbon-14 and niobium-94, are key radionuclides in the 10,000 year failure calculations and 1,000 year failure calculations, but are not prominent in the reference case calculations.
From the sensitivity calculations undertaken, it is observed that not taking credit for sorption to bentonite or assuming that instant release fractions are 100% (for applicable radionuclides) tends to have a greater impact on peak fluxes than increasing the diffusivities in bentonite, increasing solubility in bentonite water, or decreasing bentonite density. Linking back to the previously-identified scenarios, no bentonite sorption is considered within the Saline Water Scenario.
In the work reported in [1], the peak value of the mean annual individual risk (over 5000 realisations) was found to be 10-11 , which is substantially below the regulatory risk target (which is applicable to the disposal of ILW and LLW) of 10-6. The peak was calculated to occur at about 1 million years post-closure and was primarily due to iodine-129. This low calculated risk is a result of the combination of a long groundwater travel time and a robust engineered physical barrier (the copper canister) in which considerable confidence can be placed. The calculated risk is so far below the risk target that, for the given assumptions about the generic geology (it has been assumed in [1] that a groundwater travel time of 100,000 years is achievable), it is difficult to envisage scenarios that would give rise to an unacceptable risk from the groundwater pathway for the Reference Repository Concept for UK High-level Waste/Spent Fuel.
In the 1,000 year failure case and 10,000 year failure case considered in this study, the near-field peak flux of iodine-129 is increased by a factor of 30 in the All IRFs = 1 case. However, this would not translate to a 30-fold increase in risk for these cases with early failure of a canister(s), because processes affecting radionuclide transport in the geosphere, e.g. dispersion, would act to spread out in time the release of this radionuclide to the biosphere.

Publications

S Norris & MJ Poole, "Near Field Sensitivity Studies of a Reference Repository Concept for UK High-level Waste/Spent Fuel" (delivery to NF PRO, and published on NDA bibliography)

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D5.2.5

5.2.2.3: Integrated modelling of the glass-iron-clay system evolution: impact for RN migration

Participants

CEA

Goals/objectives of the research

This report summarizes the results of integrated calculations on the near-field evolution in the VHLW/steel/bentonite/clay system. The calculations of the near-field evolution include different components: the vitrified waste packages, the steel container, the bentonite-based EBS (optional), the EDZ and the geological medium. Coupled reaction-transport is used to simulate the corrosion of the steel canister and the glass alteration phase in presence of corrosion products, looking at mass transfer for chemical elements, especially iron and silica, pH, and porosity change.
Calculations as performed give actual parameters for PA calculations: rate of glass alteration (through the calculated pH) as a function of time, extension of altered zone for iron-clay interactions with their own transport parameters, nature of CPs, effect on porosity distribution.

Key results/achievements

According to the operational model currently used at the CEA and the calculations performed on the glass-iron-clay system, the alteration rate of glass and the evolution of the system strongly depend on the timing of CPs saturation with respect to silica sorption. The fate of silica which can be sorbed or precipitate is crucial to the lifetime of glass and to the overall evolution of the system.
The other process that might influence the glass is the porosity decrease due to the precipitation of CPs and silica rich phases. However, it is difficult to assign a safety functions to clogging. It is scarcely observed in experiments, either because the conditions are not met for clogging or because the timescale of experiments does not allow for observable clogging. Moreover, the effect of mechanical stress in the NF has to be accounted for in the assessment of the effect of porosity changes.

Publications

Bildstein O., Trotignon L., Pozo C. and Jullien M. (2007) Modelling glass alteration in an altered argillaceous environment, J. Nucl. Mat. 362, 493-501.
Bildstein O., Trotignon L., Lartigue J.-E., Piault E., Deville E.(2008). Modeling the long-term behaviour of glass in deep geological repositories, 3rd International ATALANTE Conference on Nuclear Fuel Cycle for a Sustainable Future - 19/05/2008 - 23/05/2008, Montpellier , France
Bildstein O. (2007) Integrated modelling of the glass-iron-clay system, CEA Technical Report CEA/SMTM/LMTE-2006-23, 47 p.
Hairapetian T., Trotignon L., Bildstein O. (2006) Simulation des interactions fer-argillite : étude de sensibilité en système fermé 0-D (contribution au Projet NFPRO). CEA Technical Report CEA/SMTM/LMTE-2006-14, 51 p.
Trotignon L., Bildstein O., Lartigue J.-E. et de Combarieu G. (2005) Modélisation géochimique des argilites du Callovo-Oxfordien : élaboration et application d'un modèle utilisable dans des scénarios de champ proche simplifié (contribution au Projet NFPRO). CEA Technical Report CEA/SMTM/LMTE-2005-26, 45 p.

Trotignon L., Lartigue J.E., Bildstein O., de Combarieu G. (2005). Modélisation géochimique des interactions entre fer et argilites du Callovo-Oxfordien. Analyse de scénarios à partir de simulations en mode statique (contribution au Projet NFPRO), CEA Technical Report DEN/SMTM/LMTE-2006-26, 81 p.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D5.2.6

6 RTDC 6: Training and knowledge management

6.1 WP6.1: Portal development/KM

6.1.1 Overall objective of work package 6.1

The principal objective of RTD Component 6 is to provide both training within the consortium (internal training) and training of scientists and engineers outside the consortium (external training). Also in RTD Component 6, a Knowledge Management (KM) Portal is developed to facilitate and to support the internal and external transfer and dissemination of results of the whole IP NF-PRO.

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6.1.2 Overview of work performed

6.1.2.1 Final activity report for UWC and SCK-CEN, WP6.1

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium as deliverable D6.1.14

6.1.2.2 Final activity report for GSL, WP6.1

Participants

GSL

Goals/objectives of the research

Work carried out by Galson Sciences Limited (GSL) as part of the NF-PRO project has fallen within Component RTD6 of the Work Plan (Knowledge Management and Training), in which it was stated that '*a Knowledge Management (KM) Portal will be developed to facilitate and to support the internal and external transfer and dissemination of results of the whole IP NF-PRO'*.

Key results/achievements

Development of a KM system into which relevant contents of the state-of-the-art reports from the other work areas has been uploaded.

Detailed report

A detailed report on the execution of this part of NF-PRO's "Programme of Work" is available on the NF-PRO consortium website as deliverable D6.1.15

6.2 WP6.2 and WP6.3: Internal and external training

6.2.1 Overall objective of work package 6.2 and 6.3

The main objective of this work package is to organise annual thematic workshops. This is in order to ensure that the experts working in different fields correctly interpret each others results and "languages". These workshops are open for participation by members of the NF-PRO consortium and are the main instrument for internal training. The KM system is used to support the workshops, from announcements to the storage and dissemination of the workshop results. This includes also the programme, abstracts, papers, workshop presentations and reports on discussions.

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6.2.2 Overview of work performed

6.2.2.1 Final activity report WP6.2 and WP 6.3

Participants

UWC and SCK-CEN

Goals/objectives of this activity

The principal objective of RTD Component 6 was to provide both training within the consortium (internal training) and training of scientists and engineers outside the consortium (external training). External training was intended to focus mainly on requirements in new and applicant EU States at the initial stage of the development of a geological repository for the disposal of high-level and long-lived radioactive waste and spent fuel.
Also in RTD Component 6, a Knowledge Management (KM) Portal was planned to facilitate and to support the internal and external transfer and dissemination of results of the whole IP NF-PRO. This knowledge management tool was to be developed and implemented as part of WP6.1 at the initial stage of the integrated project and subsequently be populated with the results of the various activities of the project.
In order to ensure that the experts working in different fields correctly interpret each other's results and "languages", **annual thematic workshops** were planned (WP6.2). These workshops were intended to be open for participation to all members of the NF-PRO consortium and be the main instrument for internal training. In addition to internal training, and to ensure the dissemination of the IP results outside the consortium, two training workshops open to experts outside the consortium were planned (WP6.3).
As part of this component, UWC was involved in all three work packages and in particular had responsibility for the organisation and coordination of both the internal and external training activities.

Key results/achievements

After some discussion a programme of four workshops was agreed to address the objectives of WP6.2 and WP6.3.
The first workshop was organised and held in Madrid, Spain in November 2004. In total 53 individuals were registered for and attended the workshop. All of the presentations and minutes of the discussions have been published on the portal.
The second workshop was organised and held in Cardiff, UK, in October 2005. In total 87 individuals were registered for the workshop, with six being offered financial assistance. All of the presentations and a number of written supporting papers have been published on the portal.
The third workshop was organised and held in El Escorial, Spain in November 2006. In total 96 delegates attended the workshop, with all of the presentations published on the portal.
The fourth workshop was organised and held in Brussels, Belgium in October 2007. In total 108 delegates (both internal and external) attended the workshop, with all of the presentations and posters published on the portal.
UWC, with assistance from Partners local to the workshop venue, coordinated and organised each workshop. The assistance provided by the local partners, in particular ENRESA and SCK.CEN, is gratefully acknowledged.

UWC contributed to WP6.1 via the supplying of information related to RTDC6 activities to the portal, for example provision of e-versions of workshop announcements, joining instructions, presentations, and reports.

Detailed report

A detailed report on the execution of this part of NF-PRO's programme of work is available on the NF-PRO consortium website as Deliverable D6.2.7.