WP-2.1: Critical review and incorporation of information of EC, national and international programmes in RTD component 2

(D2.1.1)

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Date of issue of this report: **31 March 2005**

Start date of project: **01/01/2004**   Module duration: **48** Months

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(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   i/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

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(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   ii/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

TABLE OF CONTENTS

[**NF PRO**]

Dissemination level: PU

Date of issue of this report: **31 March 2005**

3.   NEAR-FIELD GEOCHEMICAL PROCESSES DURING THE HYDRATION/SATURATION STATES

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Dissemination level: PU

Date of issue of this report: **31 March 2005**

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1. INTRODUCTION

1.1. Report organisation

Chapter 1 gives a general view of the different conceptual designs of a Deep Geological Repository (DGR) in granite, clay and salt formations. It also provides information on the possibility of retrievability in the different disposal designs.

Chapter 2 is focused on the role and requirements of the different components of the Engineered Barrier System (EBS), giving special attention to the mineralogical, chemical and physico-chemical characteristics of the natural bentonitic clay (FEBEX and MX-80) and ordinary Portland cement.

It also presents a brief review of the mineralogical, chemical and physico-chemical characteristics of the C-steel and Cu/stainless steel containers, clay barrier and concrete, the latter being mainly used in clay repositories. The types of pore water, state, location and quantity of the FEBEX bentonite are reviewed. The chemical composition of the pore water in the clay barrier is discussed, as well as the techniques to collect the pore water and the difficulties posed by the small amounts of water collected. The thermo-hydro-mechanical properties of the clay barrier are also briefly mentioned.

The hydration stages of concrete are described together with the accompanying precipitation/dissolution processes of different minerals. The pore water chemistry of concrete is studied, and the degradation of concrete and its influence on the mobility of the radionuclides as well as the resulting high pH plume are briefly described.

Chapter 3 gives a general view of the processes that take place during the hydration/saturation states under thermal gradient. It is organized according to the chronological order in which the processes may occur. First, the groundwater will flow through a concrete plug in the case of clay and salt formations causing modifications in the concrete. The groundwater from the concrete or from the granite will interact with the bentonite generating a series of geochemical processes in the bentonite. Finally, the groundwater will reach the canister and corrosion processes will start. The geochemical processes that take place in a salt formation are also reviewed in this section.

Chapter 4 reviews the pro and cons of the chemical thermodynamic data bases relevant to nuclear systems. Kinetics is pointed out as being an important uncertainty in the data bases, since reaction kinetics depend on the environment conditions, making any extrapolation difficult. Anyway, the development of kinetic data base is in progress. The most used computer programs to model the near-field geochemical evolution are mentioned, as well as the main processes and reactions taken into account in the geochemical modelling. A brief review is given of the thermodynamic of the main reactions in the near field.

Chapter 5 describes the main chemical processes in each of the considered components of the EBS (conceptual model); furthermore, a review of the existing numerical models, and the uncertainties related to present-day models (identification of key chemical processes, critical concepts and missing parameters) are given.

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   1/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

Chapter 6 compiles the known and unknown facts and uncertainties in the host rock/ concrete/ bentonite/ canister interfaces and gives a list of those parameters that should be studied to broaden the knowledge and understanding of the geochemical processes in the near field.

1.2. Different near-field designs

The concept of the deep geological disposal (DGR) on land (depth of burial around 500 m) relies on a series of natural and engineered barriers to store the waste for thousands of years and to minimize the amount of radioactive material that will eventually be released from a repository and reach the human environment [1-1].

In this integrated project, the near-field concept comprises the key processes controlling dissolution of and release from the waste matrix, chemical processes taking place in the Engineered Barrier System (EBS), the thermo-hydromechanical (THM) evolution of the EBS and the characteristics and the evolution of the excavation disturbed zone (EDZ). With respect to the Research and Technology Development (RTD Component 2), it comprises fundamentally the geochemical processes that take place in the EBS.

The different conceptual designs of a DGR that will be described in this report are classified according to their host rocks. Thus, granites have been chosen by Sweden, Finland, Canada Spain, France, Switzerland; clays by Belgium, Switzerland, France, Spain; salts by Germany and volcanic tuffs by the United States.

1.2.1. Conceptual designs in granites

The **KBS-3V** concept, first designed by SKB (Sweden), is based on the storage of the spent fuel at a depth of approximately 500 m in crystalline rocks. The spent fuel will be placed inside copper canisters in vertical boreholes and a ring of bentonite will isolate the canisters from groundwater.

In Sweden, besides the KBS-V concept, which is still the reference design, a horizontal emplacement with several canisters one after the other in 300 m. long deposition holes (KBS-3 H) was studied [1-5] , [1 6] . The type and dimension of the canister remain the same in both concepts. However, the KBS-3H design requires great efforts to develop deposition technology as well as machines and other equipments. [1-5] [1-34].

The temperature at the surface of the container both in KBS-3V and 3H was established at 100°C. But, recently, a lower limit from 80 to 90°C is being considered as a safety factor in order to account for the uncertainties.

Finland and Canada have also chosen the KBS-3V as reference design for the storage of spent fuel. More information on the Finnish and Canadian site-specific layout adaptation can be found in [1-10] [1-16] .

The Swiss HLW repository design is foreseen for vitrified high-level waste from reprocessing, spent fuel and long-lived intermediate-level waste from the Swiss nuclear power plants. The repository conceptual design establishes a depth of 1200 m in granites located in Northern Switzerland. The steel container will be emplaced in 800 m-long horizontal deposition tunnels, and will be surrounded by bentonite blocks

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   2/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

situated underneath the container and by a mixture of bentonite pellets and powder bentonite (80/20) at the sides and on top. A temperature of 125°C is expected in the outer half of the buffer, in the inner half the temperatures can be higher [1-36] , [1-38] .

The **Spanish AGP** -ENRESA concept considers the storage of spent fuel (PWR and BWR type), fundamentally, a small amount of vitrified waste from fuel reprocessing and intermediate level waste from the dismantling of nuclear plants at a depth of 500 m [1-21] . The C steel containers will be emplaced in long horizontal deposition tunnels and are surrounded by compacted FEBEX bentonite blocks. Further information on the repository layout in [1-21] , [1-33].

The Czech Republic plans to store spent fuel and HLW in granitoid bodies within the Bohemian Massif. A preliminary conceptual disposal design considers a system of main and horizontal parallel disposal galleries, where stainless steel containers (titanium is also considered) will be surrounded by bentonite (and bentonite-based mixtures) as buffer and backfill material [1-32].

Backfilling and sealing materials

Once the emplacement of the spent fuel canisters is complete, all access routes from the surface to the disposal tunnels are backfilled and sealed, [1-3] , [1-4] , [1-5] , [1 6], [1-7] [1-8] , [1-10] , [1-33], [1-34]., [1-41] and.[1-45] .

Different materials and methods for backfilling and sealing of tunnels, rock caverns and shafts in the repository have been considered through the years, such as a 15-85% mixture of bentonite-crushed rock , bentonite and quartz , a mix of glacial rock clay and crushed granite aggregate or only crushed rock.

Experiences were performed in Äspö HRL (Backfill and Plug Test and Prototype Repository Test) to test these backfill and sealing materials and improve methods for compaction of the backfill of tunnels and determine their interaction with the host rock. Since 2003, special emphasis has been given to developing a low-pH cementitious (pH < 11) or non-cementitious materials for applications where the material cannot be removed before the closure of the repository like in grouting [1-5] [1-10] .

SKB plans to define in greater detail the function of the sealing, technical solutions will be then worked out and the location of plugs will most probably be determined by site-specific conditions, this being one of the design questions that is dealt with in the permit application for the deep repository.

1.2.3. Conceptual designs in clays

Many European countries have chosen suitable clay formations as probable sites for a DGR: Callovo-Oxfordian formation (France), Boom clay (Belgium), Opalinus clay (Switzerland) and a generic Lower Miocene Spanish argillaceous formation.

Callovo-Oxfordian formation

The construction of the Underground Research Laboratory (URL) facility, near the village of Bure, France started in September 2000. The potential host rock ([1-15]) is the **Callovo-Oxfordian horizontal clay formation** (150 My) of Eastern France (the

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   3/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

Meuse and Haute-Marne area), with a thickness is 130 m at the URL site and lies at an average depth of 500 m [1-14] [1-15] [1-40] .

Three types of high-level radioactive wastes are envisaged to be stored at the deep disposal: vitrified C waste, B waste and spent fuel.

In **Class C** wastes the use of concrete in significant amounts is excluded and the containers can be surrounded by a swelling clay buffer or not. On the contrary, , the inner walls of the excavated structures for **Class B** wastes are supported by concrete. More information on the lay out of the modules which will store class C and B wastes can be read in [1-15] .

With respect to the **spent fuel storage**, they will be emplaced in tunnels, and the material surrounding the container can be either concrete or clay A cellular lightweight concrete-type cementitious backfill (CLC) is being discussed as an alternative material [1-15] . Low and non-alloy steels for the metallic overpack is preferred, instead of nickel-chromium-based steels or copper and titanium [1-14] .

Boom Clay formation

The **Boom Clay formation** at Mol, Belgium is proposed to be the Belgian reference disposal concept to store vitrified wastes at a depth of approximately 240 m [1-2] [1-42] [1-43] .

The stainless steel drums will be introduced in a sort of "supercontainer", which will be buried in underground concrete galleries (Fig 4-1 and 4-2 in [1-43]). The repository will be entirely closed off with backfilling material (pre-compacted bentonite blocks of the FoCa type clay with added sand and graphite) and plugs (mixture of FoCa clay powder and pellets) [1-43] [1-12] . More information on the Belgian repository design in chapter 4 in [1-43] . Other materials such as concrete or cement are also being considered as sealing materials (RESEAL project)

Further research must be done to establish the minimum thickness of the overpack in relation to mechanical strength and to create full radiological protection; to determine the separation between the containers in the disposal tube; to decide what type of filling should fill the container-overpack gap; to study the type of weld and method of inspection of lids and to decide if Boom Clay can be used as backfilling material [1-43].

The concrete lining of the galleries is made from prefabricated concrete sections to ensure the stability of the galleries. Cements with no furnace slag and with low alkali level are the most suitable to be in contact with the backfill material and the Boom Clay [1-43]). Further information on the alteration of concrete and its effect on the Boom Clay in [1-42] . The possible use of other materials such as steel, cast iron or brick for the lining is not excluded but they need to be further tested to ensure that they have no negative effects on long-term safety assessment [1-43]

The disposal design for spent fuel (Fig 4-8 and 4-9 in [1-43]) in Belgium is based on the reference design for vitrified waste with several modifications regarding the repository layout (spacing between galleries, diameter of galleries, thickness of lining, etc [1-43])

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   4/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

Class B and C wastes will be separated from the vitrified waste and spent fuel, but their disposal design is not so advanced.

Future investigations will focus on the biodegradation of organic waste forms in repository conditions and their effect on the migration of radionuclides in clay [1-42] .

Opalinus Clay

Spent fuel and vitrified high-level waste will be buried in **Opalinus Clay** (Switzerland) at a depth between 400 and 1000 m [1-37] [1-46] .

The C-steel overpacks will be introduced in emplacement tunnels and will be surrounded by MX-80 bentonite blocks and pellets as buffer material; also, separate tunnels for long-lived intermediate-level waste are envisaged in the same disposal. After closure of the repository itself, the behaviour of the safety barriers can continue to be monitored in the pilot facility [1-13] .

More information on the description of the disposal in [1-37] [1-46] .

The repository layout is similar to the one described for the Swiss disposal in granites (Table 1). The main difference lies in the presence of concrete in the clay repository to give mechanical stability to the host rock.

Lower Miocene Spanish argillaceous formation

The concept adopted by ENRESA is very similar to the granite disposal as regards to types of wastes, repository design and backfilling and sealing materials. The host rock will be a **Lower Miocene Spanish argillaceous formation** (lacustrine lutites), but the site location is still unknown.

The HLW disposal will be situated at a depth of 260 m [1-22] , [1-23] . The main difference with the high level waste disposal in granites is the existence of concrete blocks, with different thickness depending if they line access or disposal galleries.

The backfill material for all the underground facilities, except for the disposal galleries, will be clay from the excavation. The disposal galleries will be backfilled with FEBEX compacted bentonite [1-23] .

1.2.4. Repository design in salts

The Gorleben district (Germany) has a salt dome at a depth of 250 to 3000 m where spent fuel and vitrified high-level waste will be emplaced.

The repository was planned to have a square gallery at a depth of 880 m. The use of steel and iron canisters is intended primarily to contain waste in the short-term [1-1].

Crushed salt will be used in Germany for backfilling and sealing of intermediate and high level waste repositories. A new salt backfill material on the basis of crushed salt with water free magnesium sulphate as an additive has been developed lately by GRS.

Backfill and sealing materials are partly based on cementitious materials and smectitic clays, the latter also relied upon as buffer material ([3-217] , [3-168]). The presence of

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   5/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

brine solutions in contact with cementitious materials and bentonite poses certain problems related to performance assessment due to changes in the properties of concrete and bentonite [1-44] and section 3.2.3 of this work.

1.2.5. Repository in volcanic tuff

The **Yucca Mountain** repository, located in the Nevada desert, is situated at a depth of 300 m in an unsaturated layer of volcanic tuff [1-2], [1-25] , [1-27] , [1-28] . The waste forms are spent fuel and high-level radioactive waste

The repository basic design includes fifty-eight 700 m-long horizontal emplacement tunnels [1-25] [1-28] .

By itself, the mountain would provide a high degree of protection to the public. The major engineered barriers include the following: **Solid waste forms** (section 3.3 in [1-25]); **Waste packages**; **Drip shields** and **Inverts**. More detailed information in [1-25] [1-26] , [1-28] **.**

Although the general corrosion rate in Yucca Mountain is extremely low, it is recommended that long-term corrosion tests using multiple specimens are carried out [1-26] , in order to build further confidence in the performance of the metal containers over thousands of years. More information on further tests on corrosion in [1-26] .

Confidence in the modelling of flow and radionuclide transport in the unsaturated zone should be increased through further experimentation.

2.   CHARACTERISTICS   OF   THE   NEAR   FIELD COMPONENTS

2.1.   Role and requirements of the different components:

2.1.1. Role of the EBS components

The EBS represents the man-made, engineered materials placed within a repository, including the waste canister, buffer materials, backfills- seals and concrete [2- 1]. Its main role is to provide physical, chemical, hydraulic and biological isolation of the waste and to minimize the radionuclide release to the geosphere over the long-term. The more robust the design of the EBS is, the less reliance can be placed on the performance of the geosphere.

Though waste form is one of the components of the EBS, it will not be included in this report, since it is comprehensively studied in RTD Component 1. The main functions of EBS components can be summarized as follows:

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   6/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

- The container/overpack facilitates waste handling, emplacement and retrievability and provides containment for up to 1000 years or longer depending on the waste type.

- The buffer/backfill is designed to stabilize the thermo-hydro-mechanical-chemical conditions, and to provide low permeabilities and/or diffusivities and/or long-term retardation.

- Concrete provides structural stability and works as a physical barrier to the release of radionuclides. Concrete components appear within the seal system at the very bottom, the very top, and several locations in between where they provide a massive plug that fills the opening and a tight interface between the plug and the host rock.

The repository is thus built up of several barriers (multi barrier concept) which support and complement each other. The safety of the repository must be adequate even if one barrier should be defective or fail to perform as intended [2-2].

2.1.2. Requirements of the EBS components

There are no standard requirements that can satisfactorily meet the needs of each component of the EBS in the different repository designs. The factors that must be taken into account when selecting the materials of the different components are: the heat that will be produced by the waste, the pH and Eh conditions that are expected, the expected groundwater flux, the local groundwater chemistry, possible interactions among different materials in the waste and EBS, the mechanical behaviour of the host rock after closure and the evolution of conditions over time. Anyway a general idea of the characteristics that the EBS components must exhibit to fulfil their function can be given as guidelines. These properties are briefly mentioned below:

Container:

- Good mechanical resistance to impacts and/or falls during its transportation or handling. Material deformation should occur without cracking. The container must withstand any stresses imposed by the repository.

- An adequate heat dissipation to keep the temperature at its surface approximately at 100°C (design criterion).

- Resistance to radiation.

- Resistance to corrosion. It is built with highly corrosion-resistant metals, such as C-steel, stainless steel , copper, and Ni and Ti alloys, as a way to delay as much as possible the contact of groundwater with the wastes [2- 6].

Bentonite buffer:

- Sufficient swelling pressures (approximately from 4 to 6 MPa) to guarantee self-sealing of the gaps between the different EBS components, as well as sealing the repository against any free water entrance. The swelling pressure depends on the water content and the dry density of the material.

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   7/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

- A low hydraulic conductivity ($\leq 10^{-12}$ m/s) so that solutes move primarily by diffusion, ensures a long transit time. As a consequence, the transport rates of corrodants to canisters prior to their failure are reduced and the transport of radionuclides into the surrounding rock after canister failure is retarded. Furthermore, the gas generated within the waste packages cannot reach an important gas pressure that may jeopardize the performance of the buffer. In addition, the small pore size of the bentonite assures that colloids generated in the waste package volume cannot migrate through the buffer.

- High surface area and cation exchange capacity to be able to incorporate radionuclides dissolved in the pore water.

- Adequate thermal conductivity when saturated to dissipate the heat and gas generated by the waste.

- From a chemical point of view, the clay minerals in bentonite have a very good chemical stability, which is favorable taking into account the long time scales involved. The carbonate content should not be excessively high ($\approx 0.4\%$) and the content of organic matter must not exceed the trace level to hinder bacteria growth.

- It is recommended that the grain size should not be smaller than 5 mm to prevent excessive dust that could difficult the handling activities.

The types of bentonite that are taken into account for the different repository designs are sodic or calcium-magnesium types, such as FEBEX, FoCa and MX-80, among others.

Bentonite-based backfill and seals ([2-4] [2- 7] [2-8])

- High thermal conductivity to ensure heat dissipation

- Low hydraulic conductivity (10^{-10} or lower) to prevent the formation of hydraulic circuits in the disposal system.

- Swelling pressures must not be larger than the in situ effective stress, though they must be sufficient to close the voids left after the backfilling work (about 100kPa).

- Low compressibility to prevent expansion of the buffer so that the density and other desired properties of the buffer remain unchanged.

- Contribute to the long-term mechanical stability of the cavities excavated in the host rock.

- The chemical composition should be such that no significant harmful effects can be detected on other barriers. Corrosive substances like sulphur must be limited, as well as organic matter. Illitization and cementation should be considered in further studies.

- Capacity to be compacted to sufficient density, also close to the roof to maintain the physical and chemical properties of the backfill, even in high salinity

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   8/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

environments. In case of pre-compacted blocks, materials with sufficient plasticity and cohesion are desirable.

- Materials easy to handle and compact to limit the risk of buffer dislocation before the backfill is installed.

The natural clay materials most used for backfilling purposes are: swelling clays (smectite), non-swelling clays (illite, kaolinite), additives such as crushed rocks and other potential soil types. In salt repositories, bentonite-based materials are not considered to be the preferred option.

In some repository designs, like in Sweden, a mixture of crushed rock and bentonite (70/30) is assumed to perform in groundwater salinity up to 1%. Pre-compacted bentonite blocks can perform well as backfill material, even in high saline groundwaters. AECL (Canada) is studying the use of pre-compacted bentonite pellets to enhance the density of both bulk material and bentonite itself. NAGRA has tested a groutable backfill material composed of bentonite pellets and bentonite powder (50/50). Although in this case the material was used as a buffer around a horizontal canister, the technique may be possibly applied elsewhere as backfilling material [2-8].

Concrete seals [2- 6][2- 9]

- Low permeability. Upon hydration, unfractured concrete is nearly impermeable (10^{-20} m^2).

- No gas generator.

- Radiation shield.

- Adequate structural compressive strength. The most important indicator of strength is the water used / amount of cement ratio. Basically, the lower this ratio is, the higher the final concrete strength will be. Superplasticizers are responsible for the recent development of very high strength concretes, some in excess of 15,000 psi because they greatly reduce the need for excess water for workability [2-10].

- Longevity. It will be reduced if large quantities of brine were available causing degradation of the major components of concrete.

- By addition of admixtures to concrete, there is a possibility to modify: its plasticity, the tendency of cement particles to bind together in flocs and thus escape complete hydration and the set time, which can be important when large masses must be placed in a repository [2-10].

- Availability, low cost and constructability.

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   9/106

2.2. Characteristics of the initial materials and industrial processing and manufacturing of the engineered barrier (EB).

2.2.1. Container

Steel

Steel is the common name for a large family of iron alloys which are easily malleable after the molten stage. Steels are commonly made from iron ore, coal, and limestone.

According to the chemical compositions, standard steels can be classified into three major groups: carbon steels, alloy steels, and stainless steels.

Carbon steels are steels whose alloying elements do not exceed the following limits : 1% C; 0.60% Cu; 1.65% Mn; 0.40% P; 0.60% Si and 0.05% S. General properties can be found in [2-16] .

Alloy steels exceed the element limits for carbon steels. Also includes steels that contain elements not found in carbon steels such as nickel, chromium (up to 3.99%), cobalt, etc. Alloy steels are generally more responsive to heat and mechanical treatments than carbon steels.

Stainless steel contains at least 10% chromium, with or without other elements (Ni, Mo, Ti, C). Stainless steel is renown for its resistance to corrosion and low maintenance requirements. Based on the structures, stainless steels can be grouped into three grades: Austenitic, ferritic and martensitic.

The most important type for repository purposes is included in the austenitic group and is known as AISI 316 with an extra 2-3% molybdenum and nickel to enhance corrosion resistance

The stainless steel corrosion resistance is attributable to the presence of a thin, durable film of passive, but stable chromium oxide . Should the film be damaged or removed, it will reform independently, provided that oxygen is present to allow the reaction to occur with the chromium content of the steel. In case no oxygen is available the passive film is destroyed [2-14] [2-15] .

Stainless steels have lower thermal conductivity than carbon steel and high toughness; they harden considerably, tend to be sticky and have poor chip-breaking characteristics.

The difference in the mechanical properties of different stainless steels is seen most clearly in stress-strain curves. Austenite steels have good creep resistance and can also be used in cryogenic applications and is in annealed condition the only non-magnetic steel [2-15] .

The welding of stainless steel is related to the microstructure. The steels of type ASTM 304, 316, 304L, and 316L have very good weldability. The old problem of intergranular corrosion after welding is very seldom encountered today [2-15] .

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   10/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

More information on other typical properties of steels at room temperature (25°C) and specifically on AISI 316 steel in [2-15] [2-16] .

Copper

Some countries favour the use of **copper** **containers** mainly because copper is naturally resistant to corrosion. Moreover because copper is a pure element and not an alloy, it is possible to calculate conditions under which the metal will remain stable indefinitely [2-11] [2-12] .

Copper is a very ductile metal even at low temperatures. It is easily worked into thin sheets and fine wires, and it can tolerate impact type loads without shattering [2-13]

2.2.2. Bentonitic clay

Bentonite is a clay composed essentially by minerals of the group of the smectites, independently of its genesis and way of appearance ([2-29]).

Commercial data on clay manufacturers, and export and import of bentonite materials can be found in Roskill ([2-37]: http://www.roskill.com/reports/bentonite).

MX-80 and FEBEX bentonites are planned to be used in the NF-PRO Project. Commercially available MX-80 bentonite is used in the repository concepts of Finland, Switzerland, France, Japan, Sweden; while FEBEX bentonite is used in Spain.

The bentonite occurrences in Almería (Spain) and Wyoming (USA) have been relatively well studied under laboratory conditions and as a natural analogue of the long-term behaviour of the bentonite barrier in the final nuclear waste repository.

Both bentonites are the result of the alteration of rhyolitic volcanic ash. The mineralogies of these two bentonite deposits are fairly similar. The most significant difference between them is the exchangeable cation. Wyoming bentonite mainly consists of Na-smectites, while Ca-smectites predominates in the Almería bentonite.

Mineralogical and chemical characteristics

Different authors have characterised the MX-80 and FEBEX bentonites ([2-35], [2-34], [2- 30], [2-25], [2- 23], [2- 24]). The following properties are the most important for exploiting a clay source to obtain buffer and backfill materials:

- Amount of smectite-rich material

- Smectite type

- Degree of homogeneity with respect to the smectite content

- Type and amount of accessory minerals

- Organic content

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   11/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

The reference MX-80 mineralogy was taken from [2-34]) and is reproduced in Table 2. The reference FEBEX mineralogy was taken from [2- 23]) and [2- 24]) and is reproduced in Table 3.

The major mineral phase of the MX-80 and FEBEX bentonites is montmorillonite. The content of montmorillonite in the former bentonite is more heterogeneous ($\approx$75 to 90 wt %) than in the FEBEX type (92 wt %). In spite of their high smectite content, these bentonites contain numerous accessory minerals, such as neoformed minerals, and unaltered remains of the original volcanic rock. In addition to the main minerals, carbonates, sulphates, sulphides, chlorides and organic matter are chemically important components. Phosphorous, nitrogen and the organic content of buffers may serve as nutrients to bacteria and produce organic colloids [2-36]. For MX-80, the organic content is 0.40%, while for Febex is 0.35%.

The typical chemical composition of the two bentonites is shown in Table 4. The chemical formula of the smectites is given in Table 5.

Based on XRD, the smectitic phases of the FEBEX bentonite are actually made up of a smectite-illite mixed layer with ~11 % of illite layers. 18 % of the charge comes from tetrahedral substitution, and 82 % from octahedral substitution. The *surface charge density* (σ), i.e., the excess charge per unit surface area of this smectite is 0.132 C/m^2.

In the case of MX-80 bentonite, 17% of the charge arised from tetrahedral substitution, and 83 % from octahedral substitution. The *surface charge density* (σ) is 0.120 C/m^2.

Physico-chemical characteristics

Most of the physical properties of smectites, such as swelling, adsorption, plasticity, permeability and shear strength are related to the electrical charge, the colloidal size and the interactions between electrically charged intelamellar surfaces and water molecules [2- 30]. Some of the main physico-chemical properties of the MX-80 and FEBEX bentonites are shown in Table 6. However, the bentonites also contain soluble salts which influence the chemical composition of the pore water. The chlorides and sulphate inventories of the two bentonites are shown in Table 7.

Cation exchange on clay minerals has been extensively studied and can contribute significantly to radionuclide sorption depending on the conditions ([2- 17]), [2- 20]). Furthermore, the type of adsorbed cations of smectite determines the degree of hydration and the reological properties. Maximum expandability is obtained for Li and Na as adsorbed cations, while it is minimum for Ca and polyvalent cations.

Cation exchange studies have shown that, under a given set of conditions, various cations are not equally replaceable and do not have the same replacing power. In principle, the following law of replacement power applies: Li < Na < K < Ca < Mg < NH$_4$. However, there is no single universal replaceability series. It varies depending on the experimental condition, the cations involved, the valence, the kind of smectite mineral, the ion concentration, the nature of anions in replacing solutions, etc.

Wyoming bentonite may have a significant fraction of the exchange sites occupied by magnesium and calcium although sodium dominates. In the case of the FEBEX

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   12/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

bentonite, calcium dominates although the amount of sodium and magnesium are similar (Table 8).

Cation exchange reactions are commonly described by selectivity coefficients defined over mass action equations ([2-26]). The selectiviy coefficients for MX-80 and FEBEX bentonites are shown in Table 9.

The H-Na selectivity coefficient for smectites is approximately unity ([2- 28]). Consequently, proton exchange on the permanent charge sites is not expected to be a significant process at the pH values relevant to the near field processes.

There is a second category of reactive sites associated with montmorillonite which are perceived as being surface hydroxyl groups ($\equiv$SOH) situated along the edges of the clay platelets, *edge or broken bond sites*. These sites have a capacity of ~10% of the CEC and can protonate and deprotonate so that the concentrations of neutral protonated and de-protonated edge sites ($\equiv$SOH, $\equiv$SOH$_2^+$, $\equiv$SO$^-$, respectively) change as a function of pH. Thus, the hydroxyl groups can potentially function as a powerful pH buffer ([2-19]). The $\equiv$SOH site types, capacities and protolysis constants for the FEBEX and MX-80 smectites are shown in Table 10 and Table 11.

2.2.3. Ordinary Portland Cement (OPC) + additives

Cementitious and clay materials are generally used for plugging and sealing deposition tunnels and galleries and are often found to be in contact in existing repository designs in granitic and argillaceous rocks.

A concrete mix with the proper thermal, mechanical and chemical characteristics for the repository design and its effect on the bentonite buffer has been the aim of several international programs (ECOCLAY I and II).

The standard concrete used in underground repositories is usually made with OPC, or formulations based on OPC. Among the Portland-based cements, the most suitable for repository purposes are a high alkali content cement (CEM I) and a sulphoresistant low alkali cement (CEM I–SR). Their average chemical and mineralogical composition are shown in Table 12 and Table 13.

It is common to add blending agents to cement, such as fly ashes (FA), blast furnace slags (BFS) or mixtures to control the amount of alkalies, Ca, Al and S (Table 14). Depending on the amount of blending agent, the global composition of the cement can vary widely. The principal effects on the composition are the increase in silica content and subsequent decrease formation of calcium hydroxide (CH) and decrease of the Ca/Si ratio of calcium silicate hydrates (CSH) [2-40].

Concerning concrete, numerous formulations based on Portland cement exist, but it is clear that the standard concrete for repository design is made with sulphoresistant ordinary Portland cement (CEM I-SR) with no organic additives and whose main characteristics are given in Table 15.

Experiments performed in ECOCLAY I and II have studied the stability of the bentonite in contact with different concrete pore solutions concluding that the initial pH of these

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   13/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

solutions is the main factor controlling the steady-state composition of the resulting solutions. This process was also confirmed by the modelling tasks. Also, experiments were carried out to study the dissolution-precipitation processes between the bentonite (VOLCLAY and FEBEX bentonites) and the concrete pore solution; the alteration of the VOLCLAY bentonite generates beidellite at pH >12.6, and FEBEX bentonite remains stable at pH =13.2, at higher pH zeolites and a Mg-type silicate (saponite) are formed. The kinetics studies of the cement-bentonite interface have concluded that there are chemical changes, as well as mineral fabric modifications, at this interface [2-41].

A methodology has been established to reproduce the process of degradation of the cement in contact with groundwaters in granitic media. The method allows to evaluate the evolution of the pore solution chemistry at different stages of the degradation process and to study the saturation state of such solutions by thermodynamic means.

The numerical approaches used to model the different experiments need to be refined, and the kinetic factors that condition the precipitation of beidellite or saponite must be better identified to incorporate them into the numerical codes using kinetic laws [2-41].

A vast infrastructure and experience on the study and behaviour of concretes is available [2- 6].

2.3. Characteristics of the EBS

2.3.1 Canister

<u>Steel canister</u>

The design lifetime of the steel canisters varies from 1000 to 3000 depending on the repository design, although a 10000 year lifetime might be more realistically expected ([2-83]).

The thickness and choice of material are determined on the basis of corrosion tests and the wall thickness may vary from 5 to 10 mm depending on the repository concept. The thickness must be enough to withstand drop tests from a height of 17 m onto shock absorbers [2-162] .

The small annulus of 1 to 2 cm between the primary containment and the overpack may be left unfilled or filled with glass frit, which would retard the corrosion of the glass matrix, and, hence, the release of radionuclides. If filling this annulus is decided, then the physicochemical interaction of the glass frit with the glass matrix would have to be studied and further corrosion tests would be necessary. Packing this void with a material of low compressibility would also affect the mechanical requirements of the overpack, possibly resulting in a reduction of its required thickness.

Most of the repository designs consider the presence of an overpack in stainless steel grade AISI 316L hMo with a thickness of 20 to 30 mm. This thickness is a rough estimate, and the extent to which this figure can satisfy a range of mechanical and physicochemical requirements is now being investigated. AISI 316 steel presents a low risk of pitting and generalised corrosion, however, further research is needed to be able

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   14/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

to demonstrate the suitability of this steel grade with greater certainty. Further reading on the steel overpack can be found in [2-162] .

Copper canister

Sweden and Finland favour the encapsulation of high level radioactive wastes in copper containers.

Based on tests over more than 15 years, copper is stable in the oxygen-free water that will exist in the Swedish repository [2-11] . Copper will eventually be corroded by the sulphides in the groundwater, but this will take place at a very low rate due to the extremely low concentration of sulphides.

The thickness of the canister walls must be approximately 50 mm, however recent studies carried out in Sweden with copper canisters have confirmed that thinner walls (10 mm) improve the mechanical strength and reduce the fabrication of the copper tubes using the pertinent methods, providing better control over the microstructure of the material. On the other hand, the reliability and quality of the weld is expected to be even higher with thinner walls, even though the welding techniques work well for 50mm copper. However, thinner walls lead to reduced mechanical stability of the copper cylinder. It has not been established whether this might complicate fabrication and handling [2- 3]. In order to meet the required mechanical strength, an inner structure made from nodular cast iron that supports the outer copper shell is provided.

Swedish scientists concluded that a copper canister of this type has a design lifetime of 100,000 years, although a corrosion evaluation suggests a lifetime in excess of 1 million years. In addition to the benefit of an increased canister lifetime, the choice of this canister design also essentially eliminates corrosion-induced H_2 production, except in the rare case of a prematurely breached canister [2-83] .

Most of the containers have been constructed using the roll-forming method but it must be optimised and scaled up to accommodate the large number of canisters that will be required in the future [2-11] . On the other hand, production of seamless tubes by extrusion and pierce-and-draw has yielded such promising results that these methods will become the focus of work in the immediate future. More information of manufacturing procedures for a seamless cylinder and a cast iron insert can be read in [1-10, section 2.4.2].

Experimental research and theoretical studies to quantify the rate of general corrosion of copper under the oxygen free and saline conditions prevailing at repository depth are expected to continue in the coming years.

If the elimination of gas production is deemed completely necessary, a chemically inert insert (ceramic or bronze) would be possible to design for a copper canister for spent fuel [2-83] .

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(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   15/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

2.3.2 Clay barrier

The bentonite used in nuclear waste disposal has been treated (excavated, air-dried and ground to powders and granulates) and is compacted under a pressure of 50-100 MPa to obtain compacted blocks. Nevertheless, predicting the behaviour of this kind of material requires mathematical models for material behaviour, which cannot be developed and justified without sufficient measurement data and knowledge about the mineralogy, chemistry, microstructure and other physico-chemical properties of the materials.

The physico-chemical properties of the compacted bentonite are closely related to the properties of the powdered material (section 2.2.2.), and mainly to the smectite component.

<u>Types of water in compacted bentonites</u>

Primary clay particles consist of a coherent stack of silicate layers, which often occur as aggregates. The cluster of the clay aggregates may generate a micro-structure (fabric) often with large pores between the clay aggregates. Thus, a clay may develop three kinds of pores: interlamellar pores within the primary particles, intraaggregate pores (0.01-0.2 μm size) delineated by the boundaries of primary particles within the aggregates, and interaggregate pores (0.2 to several micrometers size) within the microstructure ([2-58] ,[2-79]).

Three modes of clay hydration can be distinguished and may take place simultaneously with the increasing water activity or relative humidity ([2-58]): a) interlamellar hydration which involves the adsorption of limited amounts of water molecules on the internal surfaces of primary clay particles, named *interlamellar water*; b) continuous (osmotic) hydration which is related to an unlimited adsorption of the water on the internal and external surfaces of primary particles, named *intraparticle water*; and c) capillary condensation of free water in micropores within the clay fabric (i.e., in the interaggregate and intraaggregate pores), named *interparticle water*.

The swelling pressure is due to interlamellar hydration of expandable minerals and to osmosis related to interparticle forces. The hydration of expandable minerals depends on the type of adsorbed interlamellar cation, which determines the maximum number of hydrates and hence the maximum c-dimension of the stacks of lamellae ([2-76] , [2-77]). The second stage of swelling is due to double-layer repulsion, also known as osmotic swelling, which was found to be inversely proportional to the square-root of the salt concentration in the solution ([2-74]).

The sorption of water into interlamellar space is governed by the hydration energy of the interlayer cations and their polarization degree (charge/size relationship), the location of the layer charge of the adjacent silicate sheets, the relative vapour pressure, the water content and the salinity of the solutions surrounding the clay particles ([2-74] [2-80] [2-78] [2-73] [2-65] [2-46]).

Usually a continuous variation of d(001) with water content has been experimentally found. Some authors ([2-59]) theoretically showed that the c-axis dimension spacing varies continuously but not uniformly with water content. Others showed that the apparently continuous change in the c dimension results from an alternation of

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   16/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

successive discrete hydrates ([2-56] [2-66]). This phenomenon has been observed in the FEBEX bentonite as a function of the water content ([2-49] [2-50] . Based on wetting experiments, the FEBEX montmorillonite expands or swells in the c-dimension to an extent equivalent to a maximum of three monolayers of water in the interlayer space. In the case of the sodium smectites, like MX-80 bentonite, the expansion is unlimited in powdered material.

As summary, the different types of waters in the FEBEX bentonite powder, their state, location and quantity are shown in Table 16.

In the case of MX-80 bentonite, the results of water vapour adsorption as a function of the water activity can be observed in Table 17.

However, in compacted bentonite, the amount of adsorbed water depends on the dry density. As it was shown, the compaction of the bentonite originates an intergranular porosity which is a function of the compaction degree (dry density) and the amount and size of the accessory minerals. In a compacted material, the total volumetric water content is equivalent to the total pore volume. The distribution and physico-chemical characteristics of the water in the system depend on the types of pores and the pore size distribution.

Different techniques were used to determine the amount of internal and external water for the MX-80 ([2-76] [2-77]) and FEBEX bentonite ([2-50]). In the case of FEBEX bentonite, a statistical model has been used to distinguish between internal porosity (interlayer water) and external porosity (external water) in compacted material. The internal porosity for the MX-80 bentonite is shown for comparison. However, the saline content of the infiltrating solutions must be taken into account (Table 18). The external water also allows to model the pore water chemistry of the FEBEX compacted bentonite, both as a powder and as a compacted material (see the *pore water chemistry* section below).

Thus, rehydration of the interlayer cations is the main mechanism responsible for the generation of swelling pressures in highly compacted bentonite systems. The swelling accompanying the re-saturation of the compacted bentonite tends to fill most of the initially present macroporosity and turns it into predominantly interlayer porosity.

Chemical composition of the pore water

The pore water composition in the clay barrier is essential for performance assessment, since it influences the release and transport of the radionuclides, canister corrosion, dissolution of the waste matrix, sorption on mineral surfaces, solubility of radionuclides, etc.

However, obtaining reliable data on the pore water chemistry of compacted bentonite (dry density around 1650 kg/m^3) under initial and saturated conditions where the water contents (w.c.) are so low (8-14 wt.% and 24 wt.% of the dry mass, respectively), is very difficult. Many of the different laboratory techniques employed so far to obtain pore water compositions tend to perturb the system and introduce sampling artefacts into the measured data ([2-54]). For example, squeezing at high pressures may produce

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   17/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

oxidation and dissolution of the accessory minerals present in the bentonite, the outgassing of CO_2 and chemical fractionation ([2-75]). Furthermore, squeezing techniques cannot extract pore water from bentonites with water contents below 20 wt.% ([2-48]).

Also, pore water chemistries for compacted bentonite cannot be obtained directly from aqueous extraction experiments. They are generally carried out at unrealistically low solid to liquid (S:L) ratios and the unconstrained dissolution of highly soluble salts and sparingly soluble minerals, together with cation exchange reactions on the montmorillonite, leads to water compositions and cation occupancies which are very dependent on the experimental conditions ([2-42] ; [2-48] ; [2-69]).

Rather, indirect methods based on geochemical modelling must be applied to deduce the chemical composition of the pore water. There are numerous papers concerning the modelling of the pore water in compacted bentonite and the argillaceous rocks ([2-42] ; [2-43] , [2-44] ; [2-48] , [2-81] , [2-71] ; [2-77] , [2-45] , [2-82] , [2-47]).

The pore water chemistry in bentonites is the result of different interactions occurring in the clay/water system: interactions between water, solutes and clay. For this reason, it is necessary to know the mineralogical and chemical components of the clay system; their physico-chemical characteristics, the hydration mechanisms, as well as the types of waters, porosity, microstructure, and the ion diffusion pathways of compacted bentonites ([2-52]).

Usually, Bradbury & Baeyens´s procedure ([2-43]) is used in order to model the pore water chemical composition. This procedure is based on physico-chemical characterisation and geochemical modelling.

Besides knowing the physico-chemical characterisation of the bentonite material, two quantities need to be fixed in order to calculate a unique aqueous chemistry and to fully define the bentonite-water system: the pH (or pCO_2) and the chloride concentration.

A bentonite-water system must be defined, among other parameters, by a water/rock ratio, which can be conveniently described by a quantity analogous to the porosity. In compacted bentonite, the total porosity (physical porosity) can be divided in: i) internal porosity (interlayer water) and, ii) external porosity (external water) which corresponds to free water plus double diffusion layer (DDL) water. The external porosity is called effective porosity or geochemical porosity. The amount of water involved in the geochemical processes in the engineered barrier corresponds to the free water or inter-particle water (the external water), taking into account that the amount of this water depends on the modifications of the dry density and the saline concentration in the system.

According to Bradbury & Baeyens ([2-43]), the free water volume, i.e., the pore water volume in compacted bentonite, is supposed to be equivalent to the accessible porosity to chloride in *through-diffusion* experiments (Table 19). The results of the chemical composition calculated for the MX-80 bentonite are shown in Table 20.

In the context of the FEBEX project ([2-60]), the chemical composition of the pore waterin the FEBEX bentonite was determined ([2-54] ; [2-53] , [2-50] , [2-51]). A combination of methodologies was applied based on different pore water extraction

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   18/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

methods, physico-chemical and mineralogical characterisation and geochemical modelling.

A distribution of the external and internal porosity as a function of dry density was obtained for FEBEX bentonite ([2-50]), based on the types of water and their distribution in the FEBEX smectite and on the statistical distribution of the water in the compacted material (external/internal water) as a function of the total porosity. The external porosities calculated have been found to be similar to the accessible porosities determined in through-diffusion tests (Table 21). Most of the water is situated in interlayer space, but there is always a small fraction of external water in the compacted saturated bentonite-system.

In order to calculate the chemical composition of the FEBEX bentonite pore water, Bradbury & Baeyens´s procedure was followed. However, the external porosity has been considered as the accessible porosity or free water volume ([2-54]). The pore water chemistry of the FEBEX bentonite is shown in Table 22 and Table 23 as a function of the total porosity and as a function of the effective or geochemical porosity.

The thermodynamic formulation is a powerful tool to calculate the properties of the bentonite-water system and all the possible interactions among water, clay and solutes. Macroscopic properties, such as accessible porosities to chloride and swelling pressure, can be determined by improving the knowledge of the chemical composition of the pore water, which reflects the thermodynamic equilibrium of the microscopic system. The swelling pressures can be explained by osmotic pressures in the bentonite-water system. Because the DDL thickness at dry densities higher than 1400 kg/m^3 is lower than 3 Å, the application of the DDL models could be not valid in these systems ([2-50] , [2-53]).

Other works about these issues can be found in [2-72] , [2-61] , [2-62] .

Thermal-hydro-mechanical characteristics

Thermal properties

The main thermal property of the bentonite affecting the barrier behaviour is the thermal conductivity. Its dependence on dry density and water content of the bentonite and on temperature is well known (FEBEX, [2-115] , the MX-80 [2-109]   and the FoCa bentonites [2-84]).

More information about the relation between specific heat and temeperature can be found in [2-88] , and on the thermal properties of high density pellets in [2-110] ..

Mechanical properties

The mechanical property of the bentonite that mostly conditions its behaviour is its volume change capacity. The swelling capacity and the swelling pressure of a bentonite strongly depend on the content of smectite , the type of adsorbed cations, the density and the microstructure, the brine composition and the applied hydrostatic pressure [3-184]).

The relation between swelling pressure / swelling strain and dry density of the bentonite can be defined by well established empirical equations . The dependence of these properties on the initial water content of the clay has also been studied. The

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   19/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

repercussion of salinity on swelling has been experimentally analysed and modelled, although it is not completely understood (MX-80 bentonite ([2-92]), Kunigel V1 bentonite ([2-110]), FEBEX). The effect of temperature on the volume change of bentonite has been scarcely analysed, although it does not seem to be crucial. The aspects less studied –due to the experimental difficulties involved– are the variation of swelling properties with suction and the kinetics of swelling development; the latter seems to depend on the structure of the material (compacted blocks, pellets/powder mixtures).

More on the swelling pressure of precompacted samples and pellets/ powder samples in [2-120] , [2-114] . More information on how salinity affects the swelling pressure in [2-92]] Information on the behaviour of the swelling pressure as a function of suction can be read in [2-115] , [2-100] , [2-94] , [2-95]] for FEBEX bentonite, and in [2-87] for a silt/bentonite mixture.

Papers referring to thermal effects on saturated expansive soils are [2-113] , [2-111] , [2-86] and on unsaturated soils [2-93] , [2-106] , [2-108] , [2-117] , [2-121] . Results on the effect of heating on the swelling pressure as a function of the adsorbed cations in the exchange complex can be found in [2-104]] The results of heating on the swelling capacity in terms of the confining stress can be found in Lloret *et al*. ([2-96] , 2004), Villar & Lloret ([2-117] , 2003) and Karnland *et al.* ([2-91] , 1994).

Other aspects of the mechanical behaviour of bentonite regarding temperature, such as the effect on the apparent preconsolidation pressure, the stiffness upon loading and the compressibility, have been scarcely studied ([2-117] , 2003; Lloret *et al*., [2-96] , 2004,).

Swelling pressure in contact with brines

Since none of the existing predictive models can describe the complex processes involved in the swelling of bentonites in high saline solutions ([3-182]), GRS suggested a pragmatic approach to the problem.

In order to obtain the needed data, a set of experiments was carried out in which MX-80 bentonite reacted with high molar saline model solutions with varying proportions of Na and Mg and constant concentrations of K and Ca [3-184] . The swelling pressures of bentonites in contact with high saline brines is considerably lower than those with pure water. The brine composition influences the resulting swelling pressure. Experiments with synthetic brines have demonstrated that the swelling pressures increase with increasing Mg in solution, and decrease with K. Because of these opposite effects of K and Mg, the swelling pressures obtained with naturally occurring brines with varying K and Mg contents do not differ as much as expected.

Interlayer spacing and total water content of MX-80 in contact with the model solutions increases as the Na/Mg-ratio in solution decreases. For a precise differentiation between pore water and interlayer water of MX-80 being in contact with a high molar salinar solution, an independent method could be applied for the determination of the density of hydrated clay minerals.

At the time being the existing knowledge on swelling pressures in contact with brines is neither complete nor consistent enough for a successful modelling. Factors like dry

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(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   20/106

density, microstructure, flooding regime, sample dimensions seem to have a much bigger influence on the swelling pressure than brine composition. The flooding regime has a decisive influence on the resulting permeability and thus on the sealing capacity of the bentonites. With the same solution a very similar swelling pressure can be obtained under different brine inflow rates. Under certain conditions the build-up of a pore pressure is faster than the closure of the pores by the swelling and a relative high permeability is maintained despite a high swelling pressure. Therefore in order to obtain data which can be used for the practical purposes future swelling pressure experiments must be performed under boundary conditions as close as possible to the expected in-situ conditions.

Hydraulic properties

The most important hydraulic properties of the bentonite barrier are the hydraulic conductivity and the retention capacity.

The hydraulic conductivity is considered to be independent of the hydraulic gradient applied to measure it ([2-102] , [2-115]). However, it has not been established whether the hydraulic gradient threshold pointed out by several authors exists or not, below which the relation between flow and gradient in clays deviates from linearity ([2-99] , [2-115] , [2-119] , [2-123]). Other authors also find this threshold in their tests performed with mixtures of expansive clay and crushed granite For larger hydraulic gradients, they observe a linear relation between flow and hydraulic gradient.

The variation of hydraulic conductivity with dry density is well defined (dry or saturated clay), and its variation with water content (or suction) is conceptually understood and can be approximated by equations derived from modelling of experimental data. Temperature affects slightly the hydraulic conductivity (kaolinite and bentonite [2-113] , [2-107]]; saponite and montmorillonite [2-118]).

The influence of salinity on permeability is different depending on the type of bentonite and its density and it is not completely explained (FEBEX bentonite, MX-80 bentonite), while the effect on the unsaturated permeability of less expansive granite/bentonite mixtures is more significant. Probably, the hydraulic gradient and the existence of a water vapour phase have an effect on permeability but it is currently not known.

More reading of the relation between effective porosity and permeability in [2-115] , and on hydrated clay in confined conditions in [2-116] , [2-112] . Information on the method generally used to determine permeability to water in the unsaturated state of highly expansive materials in ([2-98] , [2-101] , [2-94]).

With respect to the retention capacity, the confinement state of the bentonite is the key factor (unconfined samples and in confined samples) and consequently its dry density ([2-122] , [2-105] , [2-115] , [2-118]). The effect of temperature has started to be studied, but the experimental data are scarce [2-96] . The influence of salinity on the retention capacity is practically unknown. The results for a crushed granite / Na

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   21/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

bentonite mixture (70/30 wt %) show that the influence of salinity on hydraulic parameters is more important than that of temperature [2-89] .

The investigated reactions not only caused mineralogical changes but also considerable changes of the water uptake capacity. The MX-80 montmorillonites in salt solutions lost about half of their water uptake capacity compared with pure water. The reduction was found to be dependent on the reaction time and temperature. Smectites in salt solutions with cement lost their water uptake capacity almost completely. They revealed a water uptake behaviour similar to that of non swelling materials [3-185] .

2.3.3 Concrete

The design for underground disposal of nuclear wastes in geological formations includes the use of concrete and bentonite as engineered barriers, seals or supporting structures. Bentonite and concrete will be directly in contact with each other, leading to chemical interaction between them. Furthermore, cementitious materials can potentially degrade because of their instability when they are in contact with water from the host rock. This gradual degradation creates a high-pH plume which can affect the swelling and transport properties of the bentonite, as well as the properties of the adjacent host rock and groundwater flowing through. An overview of the alteration processes is given in [3-163] , [3-193] , [3-218] , [3-220] , [3-223] , [3-187] , [3-195] .

For safety purposes, it is necessary to identify the magnitude of the water-rock reaction processes and physical changes in the host rock (granite, clay or salt), bentonite and in the concrete.

Physico-chemical characteristics and pore water

The cement widely used in the investigations related to the repositories to produce concrete is Portland cement, which is a combination of 60-70% CaO, 17-25% SiO_2, 3-8% Al_2O_3, 0.5-6% Fe_2O_3, 0.1-4% MgO, 1-3% SO_3, 0.5-1.3% Na_2O+K_2O ([2-132]).

The addition of water to cement causes exothermic reactions and leads to the formation of a plastic paste that sets and eventually hardens to a hard, rock-like mass ([2-167] , [2-151]). Hardening is associated with the formation of a cohesive mass of hydration products: the major hydration product is calcium-silica hydrated gel (CSH-gel), ([2-147] , [2-148]). This gel occupies approximately 60% of the total volume of the hydration products and acts as a binding agent in the hardened cement, 20-25% of the total volume is occupied by portlandite ($Ca(OH)_2$), 10-20% by ettringite (AF_t), monosulphate (AF_m) and ferric phases, 10-20% by pore solution and 0-5% by minor components ($NaOH$, KOH, $Mg(OH)_2$), which gradually replace the water between the cement grains and finally bind the composite cement mass together. Berner ([2-124] , 1992) and Bourbon ([2-126] , 2003) present a thermodynamic description of the main constituents of hydrated Portland cement, such as CSH-gels.

The development of the microstructure and mechanism of hydration of cement has been studied extensively. The processes are complex but in general it is accepted that in contact with water, the cement grains are rapidly surrounded by thin layers of colloidal gelatinous hydrates which are tipically 0.1-1.0 μm thick. After several hours, CSH gel

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(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   22/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

grows in a variety of forms (fibrils, sheets, hollow tubes) ([2-131] , [2-134]). The basic structure of the gel is, however, composed of an agglomeration of colloidal particles of ≈ 50 nm in size which is in agreement with the high specific surface area and microporosity of cement pastes ([2-127]).

In a cement paste as described above, under normal conditions, the hydration reaction does not usually go to completion, leaving residual grains of unreacted cement embedded in a matrix of CSH gel ([2-135]). The physical characteristics of the developed hardened cement product, such as permeability and strength, partially depend on the degree of hydration, temperatures reached during the hydration reactions, and the degree to which the CSH phases efficiently fill the space. These factors will also affect the chemical stability of the hardened product and the permeability of the hardened material, which is a function of the macro/microporosity of the material and the degree of macrocracking/thermal strain induced during curing.

Lastly, the concrete consists of a mixture of the above described paste formed during the hydration of Portland cement and crushed rock aggregates[1]. The water/cement ratio is of paramount importance to the final set strength of the concrete, and the cement/aggregate ratio and aggregate size distribution are also important. The resultant solid phases are in equilibrium with a pore water solution.

For the NF-PRO studies, a sulphate resistant Portland cement, as described in subchapter 2.2.3., has been selected.

Distribution of porosity

Concrete has a 20-50% porosity, with sizes significantly smaller than soil materials ([2-143]).

It has been generally accepted that the water/cement ratio determines the initial porosity. The hydration process results in the formation of two classes of pores: gel and capillary. Gel pores are characteristic of the main hydration product (CSH) and constitute 28% of the total gel volume. Their sizes vary from 0.5 to 4 nm, being only an order of magnitude greater than the size of the water molecules, to which they have a great affinity. The capillary pores range in size from 10 nm to 10 μm and are associated with most of the mechanical and durability aspects in concrete ([2-140]). The two pore systems are interrelated, not only in the fact that both are a function of the hydration process, but also on their interdependence of the moisture content. ([2-167]).

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[1] To ensure strength and durability of the finished product, concrete aggregates, found in natural sand and gravel deposits from igneous, sedimentary and metamorphic rocks, must generally satisfy a number of specifications relating to: mechanical performance (resistance to fragmentation, abrasion and polishing), durability (resistance to environmental conditions, particularly freezing/thawing cycles), chemical stability (resistance to any deleterious reaction, e.g. dissolution, sulfatation), alkali-aggregate reactivity (with the highly basic and alkaline concrete pore solution), harmful substances (soft and friable particles, organic matter, low density matter), particle shape and surface texture (sphericity and angularity, toughness and alteration), particle size distribution (gradation and amount of fines, % < 80 μm), other useful (for concrete proportioning) or specified properties (for special uses) (surface moisture, water content, absorptivity, specific gravity, bulk density, and percentage of voids).

[NF PRO]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   23/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

Based on its influence on the mechanical properties with changing moisture state, the pore system of concrete is described as active and non-active ([2-140]). The former has an effect on the mechanical properties, while the influence of non-active porosity on the mechanical properties is invariant of the moisture state. The active pore volume is controlled by the water/cement ratio, extent of hydration and moisture conditions, all of which affect the total porosity and pore size distribution during the life of the cementitious matrix. Non-active porosity is the volume of entrained (1-50µm) or entrapped air (1000-3000 µm) introduced at the time of mixing, and remains constant throughout the life of the cementitious matrix.. Active porosity or capillary porosity can be described as long continuous channnels as compared to the circular or nearly circular shape and discontinuous nature of non-active pores.

Yaman et al. ([2-140]) mention that porosity can be kept constant with large variations in the water/cement ratio (w/c) and viceversa (Table 24). For example, the use of low w/c ratio will maximize density and consequently, minimize porosity, and favour autogeneous sealing. Therefore, the porosity properties of the concrete are related to the density, homogeneity and distribution of the cement paste, which in turn may be due to aggregate properties and mixing procedures.

Diffusion coefficient

One of the critical properties controlling the service life of concrete structures is the resistance that concrete provides to the diffusion ingress of deleterious species such as chloride and sulphate ions ([2-128]).

Tang and Nilsson ([2-139] , 1992) do provide a set of measured chloride diffusion coefficients for concretes determined with w/c ratios of 0.32 and 0.7 at several different curing ages and with different volumes of aggregates. The diffusivities vary from $4.5 \cdot 10^{-11}$ to $1.74 \cdot 10^{-12}$ m^2/s. Bentz et al. ([2-125] , 1998) predicted chloride diffusivity values using a multi-scale microstructural model. The diffusivities vary within two orders of magnitude, from $2.1 \cdot 10^{-13}$ to $8.18 \cdot 10^{-11}$ m^2/s. For simulated seawater tidal condition, a chloride diffusion coefficient was obtained using open-circuit potential measurements, ranging from $6.4 \cdot 10^{-8}$ to $1.24 \cdot 10^{-7}$ cm^2/s ([2-129]).

Johnston and Wilmot ([2-133] , 1992) measured effective diffusive coefficient for tritiated water and ^{36}Cl in sulphate resistant Portland cement. The measured effective diffusive coefficient varied from $1.12 \cdot 10^{-11}$ to $4.81 \cdot 10^{-12}$ m^2/s for tritium and from $7.46 \cdot 10^{-12}$ to $1.41 \cdot 10^{-12}$ m^2/s for ^{36}Cl. The same authors calculated the effective diffusive coefficient for ^{137}Cs and ^{85}Sr, which vary from $1.1 \cdot 10^{-12}$ to $2.6 \cdot 10^{-13}$ m^2/s for ^{137}Cs and from $4.0 \cdot 10^{-13}$ to $1.7 \cdot 10^{-13}$ m^2/s for ^{85}Sr.

Diffusion in cement is far from being well understood. It seems that the chemistry of the radionuclides in the cement is the key issue for understanding their migration in cement or concret.

Other alternative method that provides important information was studied by Jakob et al. ([2-180], 1999) and Tits et al ([2-181], 2003). The former measured effective diffusion coefficients for ^{36}Cl$^-$, ^{125}I$^-$, ^{134}Cs$^+$ and ^{63}Ni^{2+} in sulphate resistant Portland cement at a w/c ratio of 1.3.

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(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   24/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

Tits et al. (2003) measured the diffusion of HTO and $^{22}Na^+$ in sulphate resistant Portland cement at a w/c ratio of 1.3 using a through- and an out-diffusion method. The measured effective diffusion coefficient varied from $2.7 \cdot 10^{-11}$ to $3.0 \cdot 10^{-11}$ m^2/s for HTO and $1.0 \cdot 10^{-11}$ to $1.6 \cdot 10^{-11}$ m^2/s for $^{22}Na^+$.

Water adsorption by concrete

The structure of concrete and the chemical conditions of the cement paste will change over time. In the young concrete, the paste is not in chemical equilibrium. CSH precipitate and grow on the surface of the clinker grain, while others like calcium hydroxide and ettringite can precipitate in the water phase.

The first step of the hydration reaction is the dissolution of sulphate and alkali constituents, together with protonolysis of the very reactive C_3A. This will form ettringites (Aft). Later, when the sulphates are used up, the Aft will transform into monosulphates (Afm) that contain relatively less sulphate. Also, simultaneously the major calcium silicate minerals of the cement starts to react. Hydroxyl and silicate ions are generated, and the simultaneously liberated Ca-ions will precipitate the silicate ions as CSH at the surface. The first stage product will act as a barrier, which slows down the migration of water to the clinker surface and the release of calcium and hydroxyl ions to the pore water. After a couple of hours, this first product seems to undergo changes that makes it more permeable and the major phase of hydration can start. The composition of the pore fluid follows a reverse picture with high Ca and sulphate contents to start with but low when portlandite and ettringite start to precipitate. The different types of early formed phases and compounds will reequilibrate slowly, and it will take some time before a proper equilibrium is reached.

The later stages of hydration are also complex and there are several models to explain the phenomena observed in the cement paste ([2-134] , [2-168]). As the hydration is a fast process, the system is not in equilibrium. Therefore, one can assume that it will change over time, to lower its energy and reach a more proper equilibrium. The system will thus change chemistry and texture, which in turn will change the porosity and leaching conditions. This must be taken into account when long-time performance is considered.

During leaching, the concrete will be constantly in contact with an excess of water for a very long time. The hydration will slow down with time but, given the long-term perspective of the leaching, prolonged hydration and re-equilibration will become important. Theoretically, with a w/c ratio of around 0.4 or lower, all the water will be consumed and no capillary space will remain. In this case the gel porosity will dominate and will influence the leaching [2-167] .

The diffusion in cementitious materials mainly occurs in the connected porosity of the cement paste. The connected porosity, in turn, depends both on the structure and the unevenness of the cement paste. A critical element for the diffusion is the interfacial zone between the aggregates and the cement paste, which is more porous and contains more calcium hydroxide and ettringite than the rest of the cement paste.

Hygroscopic water uptake in cemented waste containing various amounts of salts has been demonstrated experimentally [2-160] . At humidities below 80%, the infiltrating

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   25/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

solution is accommodated inside the available pore space. However, at humidities above 95%, the pore water solution is leached from the cemented samples. The process is relatively slow. However, in the case of concrete, the transport (by a condensation-evaporation mechanism) of water vapour through the pore system takes place relatively easily.

Even at low humidities, some capillary condensation of water occurs in cement pores and of course, an aqueous phase is always an important constituent of the cement systems. The pore structure of a well mature paste extends over a very wide range of pore sizes. The diffusion and permeability properties are dominated by the larger pores, whereas sorption is dominated by the smaller pores and chemical surface potential of the hydrates.

Pore water chemistry

The chemistry of the pore solution is of prime importance to understand the mobility of trace element and migration processes in cement. Ionic strength, pH, Eh and the ion composition are important parameters of the chemistry of the pore solution in cements.

The most important parameter to study in the cement pore water is the hydroxyl ion concentration, from a safety assessment point of view in a repository. Cementitious materials are fundamentally unstable in water and their properties will change with time. Moreover, the degradation reaction will contaminate the groundwater, which must be taken into account with respect to the safety system as a whole. When the cement paste is formed, it is in equilibrium with a pore solution with a pH of 13 to 14. Due to leaching, the pore solution of concrete equilibrates with the surrounding water of pH around 6-8. This will result in a change of chemistry of the pore solution, which in turn leads to chemical changes and dissolution of the cement paste.

If water can flow through the concrete, the pore water will be continuously renewed and the leaching will be fast. Moreover, the flowing water will dissolve components, which, in turn, will increase the porosity and the degree of penetration. This, however, requires a water pressure or some other force to drive the water through the concrete. When the concrete is saturated, no water will penetrate the concrete and dissolution will then be controlled by diffusion through the surface of the concrete. The driving force for diffusion controlled leaching will be the difference of concentrations between the pore solution and the external water ([2-167]).

Due to the slow hydration process of cementitious material, there are problems in quantifying the chemical composition of cement pore water with predictive equilibria models. Indeed, the reactions and equilibria in cement are complicated and not well defined. Firstly, many of the hydrated reaction products are complex solid solutions, not pure mineral phases; and secondly, a cement/water system is always in a transient state. Many different solid phases are formed during the hydration of cement and these phases are changing with time. The kinetics of the mineral dissolution/precipitation reaction does not determine this transient state because both the original anhydrous material and the hydrated alteration products are very reactive in water even at low temperatures. Rather, the transient state is determined by the slow diffusion of elements to the pore water from unreacted cores of the original minerals of the cement and by

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   26/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

their hydrated alteration layers. Consequently, the solution/mineral equilibrium is closely attained soon after the contact of water with cementitious material, even though the composition of the solution and solid phases may be dynamically evolving. Some equilibrium models have been applied to obtain the composition of the pore water in cement/water systems ([2-154] and [2-156]).

Within 12 months, 95-98% of a typical modern Portland cement will have hydrated at ~15-25ºC, assuming that the moisture content of the system is preserved. This may be taken as the reference state and almost no further changes occur at least for the next 100-200 years. After 12 months, a typical hydrated Portland cement comprises an aqueous phase, which is largely confined to filling pores <1µm in radius and a paste matrix, which is itself heterogeneous. The solid phase contains crystalline phases (as ettringite, Monosulphate, hydrogarnet, Portlandite), and an amorphous or a gel-like phase designated as C-S-H because it contains Ca, Si and water. This gel constitutes the principal binding phase. The aqueous phase concentrates much of the alkali present with OH^- as the counter ion. Hence the pH is high (normally >12.5). [2-153] .

The pore fluids are in quasi-equilibrium with the solid hydrated phases of the matrix. The Ca solubility is principally controlled by $Ca(OH)_2$. Sulphate solubility is limited by ettringite. The Mg contents are controlled by $Mg(OH)_2$ and Al solubility by C_3AH_6. Si concentrations are determined by the solubility of alkali-containing C-S-H gels.

The redox potential of Portland cement lies in the range +0 to +100 mV, but this value depends on the type of cement. Slag cements give a redox potential of –305 mV, due to the presence of reduced S species [2-153] .

Extraction techniques of pore solution

The pore water of the cement pastes is usually obtained by the squeezing technique [2-166] . High pressures are applied to cylindrical samples, up to 483Mpa, to obtain 4 to 10mL of pore solution, which are chemically analyzed. Some typical pore water solutions as a function of the cement type are shown in Table 25

Thermo-Hydraulic-Mechanical Characteristics of concrete

Although cement has several unfavorable characteristics as a solidifying material, i.e. low volume reduction and relatively high leachability, it possesses many practical advantages: good mechanical characteristics and thermal stability.

International programs (e.g. ECOCLAY) are focused, among other studies, on the development of concrete mixtures with certain requirements related to chemical, strength, durability and plastic properties, and on the performance of tests on thermal, mechanical and creep properties to characterize the candidate concrete mixture. These properties are inherently controlled by the original formulations of concrete and its microscopic structure. A short review of the characteristics of concrete and their relation with thermo-hydraulic-mechanical properties is made in [2-166] . Reliable conceptual models to predict the combined hydro-mechanical behaviour of concrete seals with compacted bentonites however are not yet available [3-183] .

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   27/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

Some laboratory studies have been made to assess the factors affecting the long-term properties of concrete ([2-136]).

The pore structure of hydrated cement systems influences significantly the physico-mechanical and chemical behaviour of concrete. Several experimental techniques have been employed to evaluate the microstructure of the cement paste. The relationship between pore structure and strength/permeability is broadly included in Ramachandran and Beaudoin ([2-137] , 2001).

Thermal properties

Thermal behaviour can have an impact on strength and mechanical properties.

During heating, concrete is subjected to many changes in its inner structure, mainly the porous structure, which result in strong alterations of the properties of the material. This degradation causes both mechanical damage and thermally induced deterioration of the material. This kind of damage has been called thermo-chemical damage ([2-130]).

Chemical degradation of the cement paste (eg. Dehydration) results in the introduction of free liquid water in concrete pores and modifies the microstructure geometry and transport properties. During the dehydration process, considerable amounts of heat are consumed. The sorption isotherms of concrete are strongly temperature dependent, influencing the hydrothermal behaviour of concrete. Permeability has a sharp increase when dehydration starts. Moreover, the physical properties of fluids saturating the medium (e.g. liquid water and air) are also strongly temperature dependent. As far as the solid phase is concerned, isotropic damage effects, together with thermo-chemical damage, are taken into account.

Mechanical properties

Strength and microstructure development of cementitious materials are crucial factors that control the various parameters defining the durability of concrete. The main mechanical properties of concrete are concerned with the effects of the constituent materials: water, cement and aggregates.

In general, the mechanical characteristics of concrete are based on:

Micropore structure of concrete expressed as pore size distribution

There is experimental evidence on the influence of concrete porosity (active and non-active pores) and the amount of moisture within the permeable pore structure on the mechanical properties under saturated and dry conditions ([2-138]). In Yaman et al ([2-140] , 2002) relationships between porosity and key mechanical indexes of concrete such as strength and modulus of elasticity are shown.

Degree of hydration of cement in concrete

Probably the most important property of concrete is the water/cement ratio. The concrete hardens by uptake of water through a process called hydration, described in the section on water absorption by concrete. A certain proportion of water (water/cement

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   28/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

ratio about 0.25 by weight) is required to achieve complete hydration. Additional water is necessary to make the concrete workable during placement, but too much additional water will weaken the concrete resulting in shrinkage when the moisture dries. The properties above (strength and durability) decrease with increasing water content. Lower water-cement ratios generally produce stronger and more durable concrete.

Pore water content

There is a strong dependence of shrinkage and swelling of cementitious systems with the presence of water in the pores. It should be pointed out that once the interlayer water is removed from the in-between gel layers, the gel layers collapse together, which results in the opening up of the capillary porosity. This collapse and opening of the pore structure have been demonstrated by permeability tests showing variations of orders of magnitude in flow through capillary channels depending on the state of the gel [2-140] .

Mechanical properties are also affected by the moisture content of the pore structure. Dry concrete can be as much as 10-15% stronger than in a saturated state [2-140] . The decrease or increase of strength is due to the shrinkage and swelling of the microstructure as the water is removed or added from the pore structure. The strength decrease with increasing moisture content is related to the swelling pressure as given by the Kelvin equation:

$$\Delta P = A \ln(P/Ps)$$

where, A=constant; P=equilibrium water pressure; Ps=saturation water pressure

The moisture movement in and out of the cementitious system results in the redistribution of the gel/capillary porosity (active porosity), with the removal of the interlayer water. Consequently, a collapse of the gel layers and opening of the capillary porosity occur, while swelling of the gel upon the re-entry of water results in volume decrease of the large capillary pores. The shape factor of the pores is likely to change between dry and saturated states.

In contrast to the active porosity, entrained and entrapped air (non-active porosity) is not affected by the continuous hydration and presence or absence of water. Yaman et al. ([2-140] , 2002) conclude that not all the pores are created equal. Even though the pore size of entrained air is ten times that of the largest capillary, capillary porosity has a much greater effect on the overall properties. Moreover, the changes in the capillary porosity under various moisture conditions are responsible for the changes in the mechanical properties. The influence of air pores on mechanical properties is invariant with moisture content.

Hydraulic properties

Permeability

Concrete is a very low permeable material (K < 10^{-12} m/s, [2-143]), but mature cement-based materials have permeability of K < 10^{-13} or lower if supplementary cementing materials are added ([2-142]). The maximun continuous pore radius is related to permeability, since it is representative of the size of pores in which water

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   29/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

flows. Christiansen et al. ([2-142] , 1996) measured and calculated the permeability as a function of time.

The presence of capillary pores and air voids influences the permeability of concrete to a large extent. Various factors, such as water to cementitious material ratio, degree of hydration, air content, consolidation, mineral admixtures, aggregates, reaction between aggregates and cement paste, pozzolanic admixture, etc. affect the concrete porosity. Previous investigations relating concrete porosity to permeability, and other durability-related properties are intensively investigated by several authors.

The permeability of a cement paste or concrete can be decreased by three primary methods ([2-142]): by decreasing the initial water/cement ratio of the mix, by increasing the degree of hydration, and by adding pozzolanic material, such as fly-ash, blastfurnace slag or silica fume.

2.3.4. EBS materials in salt formations

Crushed salt

Stress and creep-induced room closure (convergence) ultimately leads to consolidation of crushed-salt backfill and to the complete encapsulation of waste containers. The backfill material in drifts will consist of crushed salt as received by drift excavation. It is a coarsely grained material with a maximum grain size of 60 mm. The initial porosity of crushed salt backfill will be about 35 %. Due to the creep of the surrounding salt host rock, the initial permeability of the crushed salt backfill will be reduced continuously until it finally reaches permeability values of the undisturbed rock salt ($<10^{-21}$ m^2). From a mineralogical and geochemical point of view, crushed salt is an ideal barrier material as it is in perfect equilibrium with the host formation and potentially occurring brines. The geochemical [3-180] , [3-181] , [3-182] , [3-201] and thermo mechanical behaviour is well understood and can be predicted with accuracy [3-162] , [3-205] , [3-172] , [3-200] , [3-173] , [3-208] , [3-209] , [3-210] , [3-230] .

Salt mixtures

Crushed salt minimizes and stabilizes the open voids and reduces the total permeability. This material however does not act as a barrier against intruding brines. The addition of self-sealing materials (dehydrated $MgCl_2$ and/or KCl, NaCl) to this backfill, can render it into a reactive mixture that, upon contact with brine, increases its volume, thus leading to a substantial reduction of the pore space. The water consumption due to the formation of new hydrated minerals leads to an over-saturation of the remaining solution and consequently to the precipitation of new solid phases. A tight seal free of pore water that prevents the intrusion of further brine is the result of the reaction. Laboratory experiments have been performed to study the reactions of different self-sealing mixtures. The investigated reactions were most effective. They led to the precipitation of large amounts of hydrated minerals. For certain initial compositions the volume increase of the solid phases upon completion of the reaction was almost two-fold. The reaction backfill-brine set in immediately after the first brine intrusion and resulted in a sharp reduction of permeability. The brine flow decreased continuously

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   30/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

and eventually ceased completely. After 12 days a maximum crystallisation pressure of 10 MPa was reached. The permeability had decreased to $<10^{-20}$ m^2. The Young's-module determined on cylindrical samples of the reacted material was in the range of 1 to 2.2 GPa. In further experiments the behaviour of these mixtures were investigated on a larger scale. Tubes with a diameter of 20- and 40-cm and 200- and 400-cm length were filled loosely with mixtures of dehydrated magnesium and/or potassium chloride and sodium chloride and than flooded with brine. Brine tight seals were obtained which resisted a brine pressure of 3 MPa. However scale effects with respect to time and backfilled length needed for the expected sealing have been observed and need further investigation. While on lab-scale the sealing started within a few days, on larger scale it takes weeks and months until a remarkable increase of the injection pressure (which indicate the reduction of the intrinsic permeability) appeared. From the experiments performed so far, it is concluded that special salt mixtures added to crushed rock salt backfill open new possibilities to prevent brine intrusion into disposal sections of repositories in salt formations. Detailed description of these materials may be found in [3-211] , [3-213] , [3-214] .

Salt cements

Salt cements are used as backfill and sealing materials in low and intermediate level radioactive waste repositories as well as in repositories for hazardous chemical wastes in former potash mines. These materials consist mainly of cement, crushed salt, fly ash and water. The additive crushed salt instead of sand is typical for salt cements, which are used only in a salt environment. In the closure concept of the repository at Morsleben, different salt cements are foreseen as backfill and sealing materials.Drifts and open voids will be filled with salt cement to prevent brine intrusion into the disposal areas. In the case of brine intrusion in the repository, the cement matrix of the cemented wastes, the seals of salt concrete and the salt concrete backfill will be affected by significant changes regarding the mineralogy, the chemical composition as well as the hydraulic and mechanical properties. The changes are due to dissolution and precipitation reactions, inducing variations in the solution composition and in the pH of the brines.

Mechanisms of salt cement degradation in salt formations

In contact with NaCl rich or Mg-rich solutions, the following degradation processes have to be taken into account. During **acid attack**, the CSH phases, which are responsible for the mechanical properties of concrete, will be dissolved by the slightly acid salt solutions. $Ca(OH)_2$ will be dissolved as well as CSH, [3-157] , [3-178] , [3-195] , [3-179] . The reaction of salt solutions with high chloride contents with cementitious materials (**chloride attack**) lead to the formation of Friedel's salt $(C_3A.CaCl_2.10H_2O)$. In case of salt cements or cements hydrated with a saturated NaCl solution, certain quantities of Friedel' salt have already been precipitated during the curing process [3-198] . The degradation of the cement structure in the **magnesium sulphate attack** is based on four single processes: precipitation of brucite on the cements surface [3-165] , [3-166] , sulphate diffusion into the cement body and conversion of calciumhydroxide in calciumsulphate (gypsum), conversion of calcium aluminates C_3A in monosulphates into ettringite [3-197] and dissolution of the CSH

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   31/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

network into MSH gel. More information on the degradation of cementitious materials in contact with $MgSO_4$-rich solutions can be found in [3-163] , [3-221] .

In LLW repositories significant amounts of CO_2 can possibly arise from chemical or biological conversion of organic matter. In contact with CO_2, the CSH phases will be degraded due to the drop of pH (**CO_2 corrosion**) [3-221] .

3. NEAR-FIELD GEOCHEMICAL PROCESSES DURING THE HYDRATION/SATURATION STATES

The long term geochemical stability and the understanding of the chemical and thermomechanical interactions of the EBS and the rock is a precondition for safety assessments for deep geological repositories in any host formation.

This chapter tries to explain how the geochemical processes take place in a somewhat chronological order. In repositories in clays and salts, the first component of the EBS that the groundwater will be in contact with is the concrete plug. The concrete-groundwater interaction will generate modifications both in the concrete and in the groundwater (section 3.1). As the groundwater leaves the concrete and starts moving through the bentonite, a series of geochemical processes will take place in the bentonite (section 3.2). In the case of a repository in a granitic formation, the groundwater will interact directly with the bentonite (section 3.3.). Finally, the groundwater reaches the canister and given time, the container will undergo corrosion (section 3.4). After canister failure, the transport of radionuclides by diffusion in the clay barrier begins (section 3.5).

3.1. Hydration/saturation of the concrete support with saline and high saline water (clay and salt formation) or fresh water (granitic formation) under thermal gradient

During the hydration stage, leaching will be a dominant process in the system, and the pore solution of concrete equilibrates with the surrounding saline or fresh water. The result is the change of the chemistry of the pore solution with subsequent dissolution/precipitation of different mineral phases.

Different Projects such as ECOCLAY I and II have dealt with these subjects, mainly on how the concrete changes both its chemical and physical properties over time and how it interacts with groundwater. This project comprised batch leaching tests with bentonite mixed with four synthetic solutions of cement pore water and determination of chemical and microstructural changes at the cement/bentonite interface.

In the Underground Reasearch Laboratory at Manitoba, Canada, geochemical monitoring was made after injecting a sulphate resistant concrete in fractures in a granitic rock.

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   32/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

3.1.1. Reaction of the solid phases of the concrete with saline and fresh water

As already mentioned., it is important to consider that the saturation of concrete with groundwater produces a hyperalkaline pore fluid with a pH in the range of 10-13.5 due to solubilization of sodium and potassium hydroxides ([3-8]). The resultant fluids react with the bentonite, likely affecting its physical and chemical properties. This fluid could also enter the host formation, and react with it. The main reactions described in the literature consist of ion exchange and mineral dissolution/precipitation, which affect the sorption and transport properties of the whole system.

In 1997, an experiment (Cement Water experiment – CW) started in Mt Terri with the objective of the detection of long-term interaction (1-3 years) of high-pH water (cement water) with Opalinus Clay under in situ conditions relevant for a repository scenario.

The initial results ([3-7]) showed that buffering to pH 10 took place after 6 months, but that subsequent buffering is less efficient. Mass loss to the rock is about 2g/day, and no significant decrease of the mass transfer rate was observed.

Baker et al. ([3-3] , 2002) stated that groundwater that has reacted with cement within a cementitious repository will subsequently react with the surrounding rock and groundwater to form an 'alkaline disturbed zone' (ADZ). Hence, the main reactions that are expected to occur within the ADZ in a repository built in a silicate-rich host rock are dissolution of rock-forming silicates, and precipitation of hydrated calcium silicates (CSH phases), aluminium-substituted CSH phases, and possibly zeolites. It is likely that the hydrogeological and chemical retardation properties of the ADZ will be different to those of the unaltered rock. In this report, an overview is provided of the research work performed by Nirex Safety Assessment Research Programme (NSARP) on the ADZ. The results of this research are used to describe the evolution of the ADZ. Residual uncertainties and possible ways of resolving them are discussed.

3.1.2. Leachability of concrete and/or neoformation of solid phases

The rate of dissolution in leaching varies as a function of the phase chemistry and this dissolution exposes or enlarges pores; thus, the leaching behaviour must be related to the pore structure and to the composition of the pore solution.

The leachability of concrete depends on different flow regimes in the system and/or on variations in the composition of the concrete pore solution and the external water (saline or fresh water). Hence, different cases of leaching have been described in the literature ([3-4] and [3-5]). For example, after the repository is closed and the groundwater level restored, the water pressure will be adjusted and the leaching will be controlled by diffusion. Then, different cement hydrate phases will dissolve or change their composition according to the pH and contents of calcium in the local pore water.

Leaching is basically an acid/base reaction where the basic pore solution is neutralised by the more acid water. The hydroxide ions and specially the protons can move more easily than all the other ions. The major component of cement paste is calcium and loss of Ca is the main leaching process. As calcium ions move more slowly than protons, the former ions will govern the dissolution and the alteration rate. As a consequence, the pH of the groundwater is of minor importance as long as it does not dissolve silica or other

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   33/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

restite products. Decalcification leaves behind a shell of silica and metalhydroxides. This will result in a zonal pattern in the concrete with progressively more Ca-depleted paste towards the alteration front.

The outward movement of hydroxide anions will be counter-balanced by an inward movement of anions from the external water. These anions may be chloride, carbonate and sulphate. The carbonate or bicarbonate ions will precipitate as calcite, while the sulphate ions will react with aluminates and form ettringite. The chloride ions can sorb on the surfaces or form Friedel's salt, but most of it will remain in the pore solution and penetrate deeper into the concrete.

More detailed aspects of these processes and a scheme are presented in [3-5] (pags 35-36).

Calcium hydroxide (portlandite) is the most soluble compound in concrete, and controls the solubility of CSH. This will remain stable as long as the pore solution is controlled by the buffering effect of calcium hydroxide.

The leaching rate is highly dependent on the stability of restite products and precipitates at the surface.

Leaching experiments with salt cements

In salt formations, NaCl-rich and a $MgCl_2/MgSO_4$-rich.type solutions may occur. At GRS, leaching cascade experiments (Batch experiments in several steps) were carried out with these typical fluids using a cemented fly ash, salt cement and an oxychloride cement [3-198] .

The experimental and calculated development of the elements in solution for the leaching process of cemented coal fly ash (SFA) has been performed, resulting in a strong decrease of Mg^{2+} in solution due to the precipitation of brucite ($Mg(OH)_2$).

In relation to the dissolution of salt cement, the reaction with the Mg-rich IP21 solution leads to dramatic changes of the cement mineralogy and the solution chemistry, whereas the reaction of the same salt cement in contact with a NaCl-rich solution showed only slight changes in the solution chemistry. The results show that salt cement have a much higher resistivity against NaCl-rich solutions than against Mg-rich salt solutions. On the other hand, oxychloride cement is dissolved much faster in NaCl-rich solutions than in Mg-rich solutions. Mg-oxychloride phases, which are responsible for the mechanical strength of this type of cement, are easily dissolved in NaCl-solutions, as indicated by the sharp increase of Mg in solution during the experiments. A mineral phase transformation was observed into a thermodynamically more stable Mg-oxychloride phase.

The facts mentioned above were further confirmed by the experiments performed by the technical University of Freiberg using a blast furnace cement with 80% of slag and NaCl saturated solution with a water/cement ratio of 0.4. The contact with $NaCl/CaSO_4$ saturated solution, nevertheless, did not lead to any visible alteration. Under the same conditions, but in contact with Mg-rich solution, an alteration depth of 1.5 mm within 70 days could be determined.

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(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   34/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

In the Asse salt mine, 200 liter barrels of cemented waste were leached with a Mg-rich IP21 solution over a period of more than 10 years [3-192] . The concentrations observed in the leaching solution after 10 years in the Asse experiment correspond to the concentrations found in the leaching experiments at laboratory scale. By the increase of Ca in solution, the time dependant degree of degradation of the material could be approximated for in-situ conditions.

Experiments at the WIPP Site were performed using a Class H Oilwell cement. The cement is mixed with distilled water and NaCl saturated solution ([3-203] , [3-202] . Evidences of alteration (Gypsum, Friedel's salt, halite Mg-oxychloride, brucite) were found up to 45 mm in depth.. After 90 days, calcium had disappeared from the samples, resulting in a drop of the mechanical strength.

In the course of the WIPP SSSPT program ("Small-Scale seal performance tests"), 12 drill holes (4 m deep) were filled with special salt cement BCT 1 F ("saltwater grout", drilling diameter 2 inches) and Escs ("expansionist salt-saturated concrete", drilling diameter 2 inches). The investigations aimed at the long-term behaviour of cement based materials under disposal conditions. The experiments lasted for 8 years. Both on the surface and in cracks brucite and Mg-oxychloride were found. Furthermore, dolomite, calcite, quartz, ettringite, Friedel's salt, halite, gypsum and anhydrite could be identified [3-228] .

At the Institut für Nukleare Entsorgung (INE) in Karlsruhe, Portland and blast furnace cements (CEM III, HOZ) served as cement matrix with and without addition of bentonite at 40 to 90 C [3-225] , [3-222] , [3-226] , [3-227] . Micro probe examinations of the concentration profiles of several elements were measured in the cross-section area of the sample. The depth of the alteration front was derived from the chloride penetration depth. The penetration depth after 48 weeks at 40°C and at a pressure of 130 bar was approx. 9 mm.

3.2. Hydration/saturation of the clay barrier through the concrete support under thermal gradient (clay and salt formation)

The geochemical processes in relation to the degradation of cements, and in particular to the interaction of an alkaline plume with geological materials are highly complex. The work within the ECOCLAY II project simulates the results of experiments on such systems and gives confidence in current capabilities to identify the main processes contributing to the behaviour of the system and to predict the long-term behaviour of these systems.

3.2.1. Geochemical processes due to concrete/bentonite interaction

Formation of a hyperalkaline plume

Once the concrete plug is saturated, a hyperalkaline fluid starts moving towards the bentonite.

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(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   35/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

The evolution of the microstructure of cementitious materials in contact with groundwaters will vary depending on the type of cement used to produce concrete. CSH gel, together with $Ca(OH)_2$ and alkalies, dominate the observed chemical properties of the aqueous phase in Portland cement pastes, and account for its high pH and calcium solubility. The leaching of alkalies (NaOH and KOH) present in fresh cement originates a highly alkaline water with a hydroxide concentration of 0.3-0.4 mol/L which corresponds to a pH about 13-13.5. However, this leaching process is fast and after all the alkalis have been leached and transported away, the hydroxide concentration drops to approximately 0.03-0.04 mol/L (pH ~ 12-12.5) determined by the solubility of portlandite ($Ca(OH)_2$) ([2-155]). Finally, the pore water composition is governed by calcium silicate hydrate (CSH) phases (pH 9-10). This gradual degradation of cementitious materials can create a high pH plume in the adjacent groundwater, and thus, cause severe physicochemical transformations that can modify the confinement properties of the disposal components [2-161] . Consequently, in order to determine the water chemistry, it is, therefore, important to study the time scale for which portlandite is the key mineral controlling the system. Pore water evolution has been studied experimentally and/or by modelling by several authors ([2-156] , [2-157] ,[2-158] ,[2-159]).

Reactions of montmorillonite-bearing clays with hyperalkaline fluids have been investigated from a very wide perspective, including radioactive waste disposal, cement aggregate reactions, leaching and modelling ([2-169] , [2-170] ,[3-29] ; [3-33] ; [3-21] ; [3-22] ; [3-50] ; [3-1] ; [3-10] ;[3-11] ; [3-49] ; [3-31]). Interactions of clays with hyperalkaline fluids have usually been investigated by batch experiments at laboratory scale. All these studies have in common that they have been performed in a relative short time, initially dominated in several cases by cation exchange processes. The rise of temperature and the increase of time, solution pH and the solution to solid ratio tend to favour mineral dissolution-precipitation reactions that become relatively more important in controlling mass transfer ([2-166] , [2-167] , [2-134]], [2-168] , [2-169] , [2-170] , [2-171] , [2-172] , [2-173] , [2-174] , [2-175] , [2-176] , [2-177] , [2-178] , [2-179] , [3-50]).

Reported solid products of clay-alkaline pore fluid interactions in laboratory experiments or natural systems include Ca (Al) silicate hydrate gels and minerals ([3-16] ; [3-32] ; [3-31]), framework silicates or zeolites ([3-18] ; [3-46] ; [3-41] ; [3-21] ; [3-22] ; [3-11] ; [3-31]), brucite ([3-40]), and sheet silicates such as illite or mixed-layer clays ([3-21] ; [3-22] ; [3-55] ; [3-24] ; [3-11]).

In salt formations, despite the formation of a CSH-layer (tobermorite) at the interface, the precipitation of zeolites follows irregular patterns associated with the circulation of fluids. Diffusion of Ca^{2+} from the Portland cement produced progressively Ca-exchange [3-177] . The interaction with host clay formation will imply that CSH-gels are washed away into the surrounding water ([3-36]), and that formation of hydroxides ([3-52]) and carbonates ([3-33] , [3-52]) will take place.

The nature of the products is strongly affected by the cation content of the reactant fluid, pH, temperature and the duration of the reaction both in clay and salt formations (e.g. [3-21] ; [3-22]).

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(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   36/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

3.2.2. Geochemical processes due to the influence of salt solutions

The most often described process which may reduce in the long run the swelling and sealing capacity of smectites is illitisation [3-170] , [3-156] . Thus, the transformation of smectite must be influenced by the composition of the reacting fluid. From over 140 reviewed papers dealing with experimental studies only a few address the influence of high saline solutions [3-176] , [3-164] , [3-206] , [3-169] , [3-194] , [3-158] , [3-167] , [3-159] , [3-175] , [3-161] , [3-186] . The transition from smectites to illites is also dependent on temperature [3-189] , [3-174] , [3-224] , [3-159] , [3-170] , [3-207] . However, most experimental studies were conducted at temperatures > 120 °C or even > 250 °C, which is above the temperatures expected in a high level waste repository. Many papers also stress the influence of pH on the smectite alteration process [3-174] , [3-188] , [3-160] .

Another important factor which may influence the illitisation process is the solid-liquid ratio. A high ratio may inhibit the illitisation [3-190] , [3-229] . Lippman (1974, [3-196]) showed the influence of K and Si content as well as the influence of pH on the direction of the smectite transformation path.

The objective of the GRS experiments reported in [3-186] was to investigate the mineralogical and chemical changes of bentonites (MX-80) in a saline environment under the boundary conditions of a repository in salt formations (brines with a specific chemical composition, wide range of pH, high solid:liquid ratio, high temperature).

The fraction < 2 µm of the MX-80 bentonite was reacted with two high saline solutions, a NaCl and a MgCl$_2$ rich brine at 25°, 90° and 150 °C, at three different pH, 1, 6.5 and 13. After 580 days, montmorillonite was the predominant phase regardless of the temperature and pH of the experiments, with full ethylene-glycol expandibility to 17 Å. However significant changes could be detected by looking at parameters like morphology, crystallinity, particle height, particle surface, interlayer charge and chemistry of octahedral layers. The experimental results suggest that under repository conditions the MX-80 montmorillonites will be transformed into kaolinites and pyrophyllites rather than into illites.

The existing knowledge of the long term behaviour of bentonites in saline environments is not yet sufficient for a reliable safety assessment.

3.2.3. Modification of bentonite due to the concrete/bentonite interaction

Different short-term laboratory scale experiments (batch experiments, percolation tests) have provided data on the transformations of the bentonite by the bentonite/concrete interaction. The outstanding compilation of results from these studies include the following reactions:

- o Cation exchange processes with cement pore water ions. The cation exchange reactions are favoured by rising temperature ([3-39]) and increasing time.

- o Minor or none modification in the cation exchange capacity ([3-36] , [3-39]).

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(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   37/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

- Specific surface decrease, as well as pore-size increase due to agglomerate formation

- Dissolution of smectite and montmorillonite [3-177]

- Dissolution of cristobalite and increase in quartz content ([3-36]).

- Formation of Ca/Mg (aluminium) silicate hydrates (C/M(A)SH) ([3-36] , [3-52] [3-45]).

- Formation of zeolites. Several authors ([3-35] ; [3-54] ; [3-44] ; [3-54]) describe the formation of phyllipsite as the main zeolite.

- Minor formation of sheet silicates such as illite or mixed-layer clays ([3-35] ; [3-24] ; [3-36] ; [3-12] ; [3-44]).

- Minor formation of chlorite ([3-36]).

3.2.4. Modification of hydro-mechanical properties of bentonite due to the concrete/bentonite interaction

Saturation of cementitious materials with groundwater from a clay formation produces a hyperalkaline pore fluid with a pH in the range 10-13.5 ([3-9] ; [3-13]). The reaction of these pore fluids with bentonite may affect its physical and chemical properties. Potential reactions include the loss of swelling capacity, and changes in porosity, mineralogical composition or sorption capacity ([3-48]).

In salt formations, the presence of high saline brines tend to reduce the swelling capacity of the bentonite and no swelling pressure will develop if the swelling capacity is reduced to an extent where the void volume is not filled by the swollen clay. For very high salt contents, the existing models are not able to predict or reproduce the experimental results. For the use of cements in radioactive waste repositories in salt formations, a release of high alkaline and saline solutions has to be taken into account due to the cement degradation in time in contact with geological water. This will induce transformations that will modify the properties of the engineered barriers.

In experiments performed by Karnland ([3-36] , 1997), a large decrease in swelling pressure was recorded for compacted MX-80 bentonite samples percolated for 16 months at 40ºC with artificial cement water with a high content of potassium and a pH of 13.7. Experiments with a less alkaline solution (pH =12.8) did not show such decrease.

GRS performed swelling pressure measurements of MX-80 in contact with high saline and high alkaline solutions, simulating young cement pore solutions [3-184] .

The performed experiments indicate that bentonites develop swelling pressures not only in contact with water, but also in contact with high saline brines and alkaline solutions. The swelling pressures in contact with brines or cement reaction solutions, however, are considerably lower than those with pure water. The brine composition influences the resulting swelling pressure. A lower swelling pressure was somewhat expected from earlier investigations that showed that the water uptake of MX-80 bentonite in contact with cement solutions was reduced.

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(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   38/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

The few results obtained so far cannot be extrapolated to other boundary conditions. GRS experimentalists think that this is true not only for their own experiments. The knowledge on swelling pressures in contact with brines is neither complete nor consistent enough for a successful modelling. Factors like dry density, microstructure, flooding regime, sample dimensions seem to have a much bigger influence on the swelling pressure than brine composition [3-177] , [3-199] .

3.3. Hydration/saturation of the clay barrier with fresh water (granitic formation) under thermal gradient

3.3.1. *Modification of bentonite due to the granite/bentonite interaction*

The information on the modifications affecting the bentonite as a consequence of the interaction between thermal and hydraulic flows comes, apart from theoretical considerations ([3-70]), from the experience gained from laboratory and *in situ* tests. The laboratory tests basically consist in subjecting blocks of compacted clay, confined in hermetically sealed and non-deformable cells, to simultaneous heating and/or hydration on opposing fronts ([3-75] , [3-68] , [3-70] , [3-78]). Among the *in situ* tests, several of them –performed according to different disposal concepts– have been dismantled and analysed: the Buffer Mass Test (BMT, [3-73]), the Buffer Container Experiment (BCE) and the Isothermal Test (ITT) ([3-69]), the "Long term tests of buffer material" (LOT, [3-72]) and the FEBEX *in situ* test at the Grimsel Test Site ([3-70] [3-67]). However, it must be also taken into account that the results available up to now refer only to periods of thermo-hydraulic treatment smaller than five years and that the effect of radiation has not been evaluated in these *in situ* tests.

Theoretical and experimental considerations

Hydration of the EBS: The bentonite will initially have a high degree of suction, which is a characteristic that fundamentally conditions the performance of the barrier. This high initial suction favours and conditions the saturation of the blocks.

However, the low permeability of the bentonite, which is even lower when not saturated, and the decrease of the intrinsic permeability as saturation progresses will make the saturation process very gradual.

The hydration of the clay barrier can be influenced by the effect of the EDZ and an inhomogeneous host rock permeability as was observed in Stripa underground laboratory and at the *in situ* test at the Grimsel underground laboratory for the FEBEX Project ([3-69] , [3-73] , [3-70] , [3-77] .).

The hydraulic pressure gradient established in the disposal facility is not important until the suction of the bentonite becomes small, that is, towards the end of the process. At this moment, if a hydraulic threshold exists, the full saturation of the barrier could be

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   39/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

significantly delayed, although this aspect has not been confirmed. On the other hand, the air initially contained in the bentonite pores will become compressed as hydration advances, and the studies performed suggest that this air will be completely dissolved in the ingressing water, thus allowing for the complete saturation of the barrier ([3-73]). However, it is still unclear whether the high temperatures around the canister would hinder the full saturation of the inner part of the barrier or just delay it.

Volume changes of the EBS: During the transient phase of the disposal facility, as the material in the clay barrier becomes hydrated, expansion occurs. The swelling of the bentonite will seal gaps and joints, which will locally reduce the dry density and will prevent the formation of preferential pathways.

Since the overall barrier is confined, radial stresses in the barrier tend to increase. These stresses cause the internal dry parts of the barrier to compress, thus increasing their density. In this way, a density gradient is established in the system, with lower densities in the outermost areas affected by water, where the bentonite will have expanded, and higher in the innermost dry areas which are "pushed" by neighbouring zones. Consequently, an inverse relationship is established in the barrier between dry density and water content ([3-69]). These density modifications affect increasingly larger areas as hydration progresses and are enhanced by the effect of heating.

Establishment of a thermal gradient: The thermal conductivity of the bentonite increases with the water content of the clay and, consequently, during the transient stage would be higher for the external part of the buffer and lower in the desiccated area near the canister. This has been verified in samples retrieved from the FEBEX *in situ* test. The evaporation of the water causes desiccation and shrinkage of the bentonite, which contributes to the decrease in porosity of the blocks in the internal areas of the barrier. However, the swelling tests performed with sealing materials retrieved from *in situ* tests have shown that the swelling capacity of the clay is not irreversibly affected after thermo-hydraulic treatment.

The vapour generated spreads towards more external and colder regions of the system, where it condenses. The water that condenses in the colder areas may move once more towards the canister. In this way, the process of evaporation/condensation is repeated and small "convection cells" are established, the most evident effect of which is an increase in salinity in the hotter areas ([3-76]). This movement of vapour is, therefore, an important mechanism for the transfer of water content and heat.

Processes in the final stages: Finally, once saturation is reached in the whole barrier, there could be a certain homogeneisation of the dry density and the water content The hydraulic conductivity measurements performed in samples retrieved from *in situ* tests have not shown any important variation after the bentonite has been subjected to repository conditions.

Long after the closure of the disposal facility, there might be an important generation of gases in the inner part of the barrier. These gases are most probably produced by corrosion of the steel of the canister, bacterial degradation of organic matter and radiolytic decomposition of water. Diffusion is the dominating gas transport mechanism during the initial stages of saturation of the barrier. If there are large volumes of gases, they could escape via instantaneous "fractures" in the barrier, a

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   40/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

process known as break-through that basically consists in transport via preferential paths ([3-79] , [3-74]).

A summary scheme of the sequence of processes mentioned above is given in SR 97 [3-57]

3.3.2. Geochemical processes due to the granite/bentonite interaction

The chemical evolution of the buffer and backfill is determined by a number of transport and reaction processes. In the buffer, advection occurs almost exclusively during the water saturation process. After saturation, diffusion is the main transport mechanism. By means of ion exchange/sorption, the original ions on the surfaces of the clay particles in the buffer may be replaced by other ionic species. The chemical degradation of smectite may occur, for example in the form of illitization. On swelling, the buffer penetrates into the fractures in the surrounding rock, where it may form colloids which may be carried away by the groundwater, leading to gradual erosion of the buffer. The clay may be transformed by radiation effects and the pore water may be decomposed by radiolysis. Finally, microbial processes may occur in the buffer/backfill system.

Over time, the pore water chemistry will evolve reflecting interactions between the species present at the time of closure, and ions entering with the groundwater during saturation ([3-58]). Migration of salts and bentonite accessory minerals will result due to the thermohydraulic field ([3-59] , [3-60] , [3-61]). Thus, the main processes affecting the chemical evolution of the buffer will be the dissolution/precipitation of accessory minerals, mainly calcite, gypsum, quartz and pyrite, ion-exchange processes, surface complexation processes and the long-term dissolution and alteration of montmorillonite to illite ([3-62] , [3-63] , [3-64] , [3-65] , [3-66]).

3.4   Corrosion at the bentonite/canister interface under thermal gradient

3.4.1. Corrosion of canister

C-steel, stainless steel

A number of Community-supported Framework Programme and national projects ([3-121] , [3-123] , [3-122] , [3-141] , [3-142] , [3-93] , [3-117] , [3-118] , [3-154]) have been devoted to the experimental investigation of corrosion resistance of metals in relation to deep geological repository. The research was focussed both on corrosion allowance and corrosion resistance materials such as, carbon steels, stainless steels, the alloy of Ti99.8-Pd and nickel base alloy Hastelloy C4. It was found that both corrosion resistance and corrosion allowance materials can be utilized as spent fuel or high level waste canister materials. All of them can corrode under certain conditions by general (uniform) or localized corrosion. The tendency of metals to corrode by localized corrosion, usually by orders of magnitude higher than general corrosion rate, is one of

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   41/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

the most important factors for selection of spent fuel canister materials. One of the advantages of corrosion allowance materials such as carbon steels is their low tendency to localized corrosion in a repository environment. The danger is that the passive state might occur under certain conditions depending on the pH, composition of groundwater, and the amount of oxygen diffusing to the surface of metal canisters ([3-122] , [3-123] , [3-121] , [3-96])

Corrosion mechanisms of metals under repository conditions will depend primarily on the content of oxygen and the content of aggressive and/or passivating ions in a groundwater contacting the canisters. During the operation phase of a repository and some time after its closure, oxygen (~8 ppm of O_2) is trapped in the buffer and backfill materials allowing the overall aerobic corrosion reactions to occur. The mechanism of corrosion depends [3-97] in this phase mainly on the level of humidity around the canister. The time of aerobic/anaerobic[*] phase will depend primarily on the value of the diffusion coefficient of oxygen in compacted bentonite [3-123] , [3-120] . It is evident that under reducing conditions, all available oxygen will be consumed and iron will corrode with water in an anoxic environment under hydrogen generation. After canister failure, the groundwater will get in contact with spent fuel and inner parts of the canister. The properties of the groundwater and, consequently, of the corrosion products can be, from this moment, affected by the waste package inner materials including spent fuel matrix and by radiation. Results of some experiments showed that in the presence of radiation the corrosion of metals can be significantly increased [3-121] , [3-125] .

An important role in corrosion of metals can be played by salts dissolved in groundwater. Chloride is the most aggressive anion in the context of localized corrosion of stainless steels. Both pitting and protection potentials of stainless steels are a function of the chloride concentration [3-93] . The role of sulphates in corrosion of metals is not unambiguous. Sulphates are known as being aggressive ions enhancing localized corrosion [3-123] , but it was also shown [3-93] that an increasing amount of sulphates in oxidised clay water is beneficial towards the corrosion protection of the stainless steels. Carbonates/bicarbonates can significantly contribute to passivation of steels [3-121] , [3-122] , [3-123] .

Under certain conditions, corrosion of steels could be influenced by microbial corrosion. [3-114] . It is now widely recognized that the microbial activity is possible within a deep geological repository [3-114] , [3-129]]. The presence of anaerobic bacteria, such as the sulphate reducing bacteria (SRB), can be explained in sites under aerobic conditions, because aerobic bacteria colonies form a film on the surface of the metal, which allows the SRB to thrive underneath, where little or no oxygen is present [3-111] . However, the results of the investigations of survival and of activity of

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[*] The anaerobic environment is here understood as the environment with limited flux of oxygen (0.03 – 8 ppm) and anoxic environment as the environment that does not contain measurable amounts of dissolved oxygen ($\leq 10^{-6}$ M or 0.03 ppm)

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(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   42/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

microbes in bentonite [3-129] suggest that the number of viable microbes will rapidly decrease during swelling of compacted bentonite.

A study of the corrosion that affected different components, after 7 years, of the in situ test of the FEBEX project was carried out by INASMET Foundation in Grimsel (Switzerland) [3-111] . The steel or C steel components consisted of the heater, liner, coupons within the bentonite and sensors, which were protected by an austenitic alloy tube or sheath to measure displacement of the heaters and temperature.

The heater (a C steel cylinder, wall thickness 100 mm) underwent a very slight generalised corrosion, due to the absence of humidity around it which prevented or slowed down the advance of generalised and/or localised corrosion. The liner (a steel perforated guide tube, 15 mm thick) presented a stronger generalised corrosion than the heater; its contact with the bentonite and the presence of a higher degree of humidity can account for the corrosion processes undergone by this component. The C steel coupons showed very slight generalised corrosion with corrosion rates of 0.10 μm/year, probably because they were embedded in bentonite with very low humidity. Finally, the sensors were, by far, the components that underwent the greatest corrosion damage due to the presence sulphides generated by SRB. Transgranular cracking and localised pitting are the corrosion phenomena identified in the sensors [3-111] .

Copper

Metallic copper is planned to be used as the outer canister material in some repository designs. Assessments of the long-term behaviour of copper canisters have been made in four countries; Sweden, Finland; Canada and Japan.

A comprehensive overview of the four assessments has recently been published by King et al (2001, [3-115]). Although the various assessments vary in detail, they provide a consistent picture of the copper canister and the chemical reactions that might damage it under repository conditions.

The Swedish and Finnish studies included general corrosion under oxic and anoxic conditions, localized corrosion pitting, microbially influenced corrosion, and stress corrosion cracking.

During the aerobic period ($\approx$ first 1,000 yrs), the combined general corrosion was caused by trapped O_2 and radiolytic oxidants. According to steady-state mass transport modelling, the copper corrosion rate is determined by the diffusion of Cu(II) away from the canister surface [3-152] .

During the long anaerobic period, corrosion is supported by HS^- from the groundwater, from the MX-80 bentonite itself and from microbial reduction of SO_4^{2-} in the deposition hole and tunnel and in the groundwater. The corrosion is also further assumed to be supported by reduction of Fe(III) or of H_2O/H^+ in the presence of HS^-.

The Canadian and Japanese assessments differed somewhat from the Swedish and Finnish ones, but all the results point in the same direction: the planned type of copper canisters will not be seriously corroded under the expected repository conditions. The Japanese assessment was similar to that used in Sweden and Finland, although

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(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   43/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

significant more conservative assumptions were used like the very high HS$^-$ concentrations in groundwater used in the assessment. The overall extent of general corrosion and pitting after 1,000 yrs was predicted to be 27-39 from a pitting factor approach and 10-15 mm based on the extreme value pitting analysis. The Japanese study did not contain any estimate of the canister life time. In the Swedish, Finnish and Canadian cases, such estimates were made, which indicated that the copper canister life-time exceeds 10^6 yrs. Details concerning the referred assessments are found in King et al. (2001, [3-115]) and in references therein.

The Cu-ETP and the Cu-30Ni alloy coupons studied in Grimsel Test Site underwent similar generalised corrosion after 7 years. These types of coupons presented a generalised corrosion rate of 0.71 μm/year, with a measured corrosion rate of 0.5 μm/year [3-111] .

Generated corrosion products

The generation of corrosion products in the repository is not clear enough to know exactly the corrosion products that will be formed at the canister/bentonite interface. The nature of the corrosion products will depend on the disposal concept, repository conditions and time after repository closure.

Iron corrosion products

In a system with low concentration of carbonate species and negligible concentration of sulphides, the major corrosion products under low Eh environment, pH > 8.5 and temperature below ~ 85 ^{o}C will be ferrous hydroxide. Otherwise, at low Eh values in the repository, environmental magnetite will be formed [3-86] . In sulphide-bearing groundwaters, all Fe^{2+} will be precipitated by sulphide anions until their depletion [3-83] . In carbonate-rich (~1 mol/l) and sulphide-poor groundwaters, siderite ($FeCO_3$) can be formed [3-83]]. At lower concentrations of carbonates, carbonate green rusts ($GR(CO_3^{2-})$) are formed ([3-92] , [3-90] , [3-91] , [3-138]). The stability of these species is not, however, clear. Their abundance mainly depends on the ratios of Fe^{2+}/OH^- or CO_3^{2-}/SO_4^{2-} groups and the concentration of oxygen in the groundwater. At high concentration of sulphates or chlorides, sulphate or chloride green rusts could be also formed [3-134] , [3-128] . In the long term, at the canister/bentonite interface, iron silicates will be formed. Due to the very slow kinetic of the reactions of iron with silicate species, it is difficult to experimentally determine their nature [3-80] , [3-81] , [3-82] , [3-99] , [3-85] , [3-147] , [3-154] .

The microbiological corrosion of steel sensors at Grimsel produced black iron sulphides, and also a chrome enrichment was detected in the bentonite surrounding the sensors, thus the presence of green amorphous hydrated chrome oxides ($Cr_2O_3xH_2O$) is not discarded. Likewise, chlorine and nickel-rich yellow corrosion products are also generated. Consequently, the corrosion of the sensors indicates that the damage was done by bacteria activity, as well as by the effect of chlorides in the environment [3-111] .

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   44/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

Copper corrosion products

The types of products that will form during canister corrosion depend to a high degree on the chemical conditions under which the corrosion takes place. A summary of the ranges of groundwater and bentonite pore-water for the Olkiluoto case is found in Table 26 and Table 27.

The recent review by King et al. (2000, [3-115]) distinguishes between 1) corrosion prior to water saturation, 2) corrosion during water saturation, and 3) corrosion after water saturation. The division into different times is based on the different wetting stages of the bentonite.

The **corrosion of copper prior to water saturation** is due to the corroding effect of the atmosphere to which the copper canister is exposed before getting in contact with the groundwater.

The copper corrosion products are mainly copper oxides like cuprous oxide and above it copper hydroxides containing other anions. In the open atmosphere and sheltered from the rain, the sulphates like posnjakite, brochantite and antlerite, as well as the chlorides nantokite and atacamite have been found on the copper surface after an 8-year exposure period [3-148] , [3-154] .

There are only a few studies concerning atmospheric corrosion of copper at elevated temperatures, and some of them give quite different models for kinetics. Anyhow, the total oxide thickness predicted is 0,03-0,07 µm at 100 °C after a few years of exposure. The atmospheric pollutants accelerate the oxidation rate by a factor of 3-8 [3-115] .

In a granitic repository, after the disposal, when the canister has been installed into the bedrock and the free space filled with bentonite, the conditions are not controlled any more, but atmospheric corrosion is possible in these conditions.

During the period of the unsaturated phase, the corrosion will most probably be uniform and the corrosion product layer will consist of a compact layer of Cu_2O covered by basic Cu(II) salts. No pitting corrosion is expected to occur [3-115] .

The **corrosion of copper during water saturation** includes the wetting of the compacted bentonite and of the backfill mixture of bentonite and crushed rock. Reactions between copper and bentonite pore water are expected only in fully saturated bentonite.

During the wetting process, the buffer will probably not swell homogeneously, and there will be local contact places between the canister and the bentonite, which can function as preferential points to start pitting corrosion, especially when there is oxygen available. During the swelling of the bentonite, the gaps will close so that the contact points will move and the corrosion shows an uneven nature with corrosion pits.

Depending on the groundwater composition, several corrosion products may form, for example Cu_2O and $Cu_2CO_3(OH)_2$ (malachite), and basic cupric chloride ($CuCl_2 \cdot 3Cu(OH)_2$) [3-115] . The conditions have been interpreted to be oxidising during the formation of the products mentioned above. The corrosion products formed by the corrosion of the copper coupons studied at Grimsel after 7 years under repository

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   45/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

conditions, are cuprite and $CuCl_2$, chlorides being provided by the FEBEX bentonite itself [3-111] , [3-154] .

Survival conditions for the SRB at the canister surface are very difficult (low availability of water), but without a careful investigation, the microbiological influences cannot be excluded.

As a result of the **water saturation** and the evolution of the environment, the corrosion behaviour of copper will evolve from an initial period of relatively fast uniform corrosion accompanied by possible localized corrosion to a long-term steady-state condition of a low rate of uniform corrosion with little or no localized attack [3-154] .

The canister surface will upon saturation be covered by a double layer consisting of an inner layer of Cu_2O and an outer layer of basic Cu(II) salts, such as $Cu_2CO_3(OH)_2$ (malachite) and $CuCl_2 \cdot 3 Cu(OH)_2$ (atacamite), depending on the relative concentrations of CO_3^{2-} and Cl^- ions in the pore water. When the bicarbonate content of the groundwater exceeds 600 ppm, $Cu_2CO_3(OH)_2$ can be assumed to dominate over $CuCl_2 \cdot 3 Cu(OH)_2$. Based on the review by King et al. (2001, [3-115]), no significant changes in the composition of the corrosion film take place even after the change of the conditions to anoxic. In the presence of sulphide ions, the formation of Cu_2O/Cu_2S films in reducing conditions is also possible.

3.4.2. *Geochemical processes induced in the bentonite due to corrosion*

The hydrogen generation, due to corrosion of a C steel canister, will lead to possible overpressure and aperture of preferential pathways [3-127] . A number of papers ([3-112] , [3-101] , [3-139] , [3-104] , [3-143] , [3-149]) and reviews ([3-130] , [3-153] , [3-154]) have been therefore devoted to this issue.

The following facts can be drawn from the review of these papers: Hydrogen evolution rate is very high until a protective layer is formed on the surface of iron. It increases with ionic strength of the groundwater and temperature ([3-143] , [3-86] , [3-149]) until about 85 ^{o}C, above which ferrous hydroxides will decompose directly to magnetite and iron without hydrogen evolution. Hydrogen evolution is higher in the environment containing remnant oxygen, probably due to localized corrosion ([3-104] , [3-95]).

Hydrogen may escape by diffusion through the backfill and if this transport is not sufficient, flow will eventually take place [3-127] . If the escape by these mechanisms is not sufficient to keep the pressure below the lithostatic pressure (325 atm –[3-126]), the rock will expand and the repository may be disrupted ([3-131] , [3-132] , [3-108] , [3-105] , [3-146] , [3-135] , [3-136] , [3-137] , [3-150]). No evidence was found that the development of pressure-induced gas pathways in any way compromises the sealing capacity of the bentonite barrier. Some of the researchers [3-105] , however, admit that only small-scale experiments have been performed and will have to be verified at larger scale.

The corrosion of canisters and the near-field environment will be also affected by the rate of release of ferrous iron from metal surfaces [3-113] . This will be hindered by mass transport constraints due to the formation of secondary precipitates and compacted

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   46/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

bentonite. A number of papers addresses the measurements of diffusion coefficients of iron in bentonite ([3-119] , [3-109] , [3-110] , [3-116] . The diffusion coefficients of iron in bentonite were in the range from 10^{-14} to 10^{-11} m^2/s.

The presence of iron species and products of iron reactions with bentonite could change the properties of bentonite affecting transport of radionuclides to the geosphere. Swelling pressure could be influenced by the formation of chlorites and bentonite cementation. According to a number of papers ([3-133] , [3-100] , [3-99] , [3-102] , [3-154]), this effect will not be significant. Sorption capacity of bentonite could be also affected by a high content of ferrous ions released from the canisters [3-84] . Corrosion products can also have a direct effect on the transport of radionuclides through bentonite to flowing water by facilitating their transport in gas bubbles [3-126] and/or in the form of pseudocolloids formed by ironhydroxides [3-140] .

Corrosion products tend to be greater in volume than the original metal. Molar volumes for iron corrosion products are increased more than 2 times [3-151] . Corrosion layers can thus act on the canister and the bentonite and could contribute to the premature failure of the canisters [3-87] . A program of experimental work was undertaken to investigate the effect of corrosion product expansion on the generation of stress in a canister [3-145] . No expansion was observed in two years exposure, suggesting that the corrosion product is too soft and deformable to cause jacking of the canister walls. Bentonite will also act as an efficient buffer for the stresses induced by corrosion of the canister [3-87] .

3.5. Migration

3.5.1. Diffusion in bentonite

The retention properties of the bentonite backfill play a very important role in the safety analyses of high-level radioactive waste repository facilities ([3-252]). In this respect the key parameter in the transport calculations is the apparent diffusion coefficient, D_a. Even in moderately compacted bentonite, for moderately sorbing species, diffusion rates are very low, $< 10^{-12}$ m^2 s^{-1}. D_a values can be either directly determined from diffusion measurements, or they can be calculated from separately determined parameters, usually K_d and the effective diffusion coefficient for HTO. According to the literature ([3-242], [3-248], [3-244]) these two approaches often result in different values: the directly measured D_a values are generally (significantly) higher than the corresponding calculated ones.

This apparent lack of compatibility may lead to a high degree of uncertainty in the PA calculations since predominantly batch sorption data, whether simple K_d values or mechanistic model calculations, are used in conjunction with an effective diffusion coefficient, usually that of HTO, to calculate D_a values. The question of compatibility between measured and calculated D_a values is a key issue, which requires urgent clarification.

This uncertainty is a symptom of a much larger problem, which is that the transport processes through highly compacted bentonite are not very well understood. In

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   47/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

particular, there are at least three broad types of porosity in compacted bentonite and it is critical to know which porosity types are associated with the diffusion of which radionuclides and the corresponding diffusion mechanism. Attempts to clarify the diffusion mechanism (or diffusion pathway for different ionic species) have already started ([3-243], [3-240], [3-233], [3-241], [3-249], [3-239]). Although for some elements the observed phenomena can be qualitatively explained, no real models exist. As an example, it has been observed that the diffusion of anions in bentonite depends on the ionic strength of the porewater which can be explained by the so called Donnan effect. A mechanistic model, however, does not so far exist.

One of the major factors contributing to the uncertainties is the porewater chemistry in highly compacted bentonite ([3-237]). In some recent work focused on the reference Japanese bentonite Kunigel V1, it was shown that the porewater chemistry is a critical component in assessing the correspondence between measured and calculated D_a values. In fact, in this study for Cs(I), Ni(II), Sm(III), Am(III), Zr(IV) and Np(V), Bradbury & Baeyens ([3-238], 2003) found good agreement over a wide range of initial dry densities when the porewater chemistry was calculated with their model ([3-237]). Because the porewater chemistry plays such a vital role in understanding the retardation processes of elements diffusing through compacted bentonite, key parameters and assumptions in the porewater chemistry model have to be checked as a function of initial dry density. One of these is the chloride accessible porosity ([3-237]). This is essentially the pore volume occupied by the porewater and is equivalent to the porosity determined in through diffusion experiments using chloride. Other approaches have also been proposed ([3-245], [3-247], [3-246]). The discussion on the "right" model is still ongoing and there is an urgent need to agree on a common approach for estimating the composition of a bentonite porewater.

3.5.2. Retention in bentonite

The uptake of radionuclides by mineral surfaces is one of the main pillars upon which the safety of radioactive waste repositories rests. Sorption processes mainly consist in ion exchange and surface complexation. The former has long been known as a control of the chemistry of water in clay formations and as a means to retard the transport of radionuclides, and it provides support and justification for the sorption data bases used in PA.

Sorption in most natural bentonite systems is inherently too complex and multi-faceted to be directly understood in terms of mechanisms and their associated parameters. One of the approaches chosen has been to investigate a simplified system first, and then, using this understanding as a basis, increase the complexity in a stepwise systematic manner until the natural system is reached, the "bottom up" approach. Since MX-80 consists of more that 75% montmorillonite, its properties, in particular sorption, are essentially determined by this clay mineral.

A 2 site protolysis non electrostatic surface complexation model was developed, and, together with cation exchange, was incorporated into the chemical equilibrium code MINEQL ([3-250]). The resulting code, MINSORB, has been used successfully to model titration measurements for Na-montmorillonite and sorption edge / isotherm data

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   48/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

for Ni, Zn, Eu and U(VI) in simple 1:1 and 2:1 background electrolytes in the absence of carbonate, ([3-231], [3-234], [3-235], [3-236], [3-238], unpublished U data, EU 5th Framework Programme, Febex II).

Carbonate is omnipresent in almost all geochemical systems and the influence of radionuclide speciation with carbonate on sorption needs to be investigated and modelled before predictions for real systems can be made. The same is true for organic ligands. Depending on the type of host rock, organic molecules such as humic acids (HA) can effect the sorption and the migration of nuclides through the near-field. A prerequisite for this is that such molecules can migrate from the host rock into the bentonite. The first results available indicate that the sorption of Eu(III) on bentonite is decreased by the presence of HA leading to an enhanced diffusion ([3-251]).

There still remains the important open question as to whether sorption values measured in dispersed systems (batch sorption measurements) are similar to sorption measurements in compacted systems (diffusion measurements). Some attempts to clarify this problem have led to diverging results. Because all sorption databases for PA are based on batch sorption data obtained in dilute systems, there is an urgent need to obtain clarification here.

4. THERMODYNAMIC OF THE NEAR-FIELD PROCESSES INVOLVED IN THE GEOCHEMICAL EVOLUTION OF A DEEP GEOLOGICAL REPOSITORY. DATA BASES

4.1. Data bases

The eventual migration of radionuclides into the environment should be predicted in order to assess the safety of a radioactive waste repository. Numerical simulation and/or modelling of processes affecting the behaviour of radionuclides in natural and man-made systems is an integral part of a radiological assessment methodology. Some of the basic information is provided by speciation calculations using general, non-site-specific, chemical thermodynamic data. The value of the results of geochemical modelling as a predictive tool is strongly dependent on the quality of the thermodynamic data used to calculate the chemical speciation [4-1] .

To be useful in performance assessment work, a data base must:

- contain data for all the elements of interest in radioactive waste disposal systems
- document why and how the data were selected
- document the sources of experimental data used
- be internally consistent
- treat all solids and aqueous species of the elements of interest

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   49/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

It is difficult that a data base can fulfill all of these criteria. It is frequent that the how and why of a certain datum is omitted, or specialized thermochemical databases intended for quite different purposes are common. For this reason, PA groups often use their own databases for modelling purposes. However, these individual data bases often lack internal consistency and differ significantly from each other, specifically in the data of the actinides [4-1] .

These shortcomings were taken into account by some countries that undertook the task of developing a comprehensive, internally consistent and internationally recognized thermodynamic database for the inorganic, aqueous and solid chemistry of U, Am, Tc, Np and Pu (NEA TDB project).

Selection of parameters

The selection of the parameters to include in the NEA data base was based on the needs of existing chemical models, the generality of applications and the availability of data. The data set collected in the TDB project includes standard molar Gibbs energy ($\mathit{1}_fG_m$) and enthalpy ($\mathit{1}_fH_m$) of formation, standard molar entropy (S_m) and heat capacity at constant pressure ($C_{p,m}$). The equilibrium constants needed can then be derived from these parameters for the aqueous species and solid phases of interest. This approach also makes it easier to check the internal consistency of the selected thermodynamic parameters.

As the parameters in this data set vary as a function of temperature, the compilation of the coefficients of empirical temperature functions for these thermodynamic data was included, as well as the temperature ranges over which they are valid. Only temperature dependencies for $C_{p,m}$ have been selected in the TDB data base so far. As a rule, selected data are presented for a temperature of 298.15 K and a pressure of 1 bar (1_10_5 Pa).

The TDB project does not cover non-thermodynamic data such as diffusion and kinetic data and only takes into account primary experimental data.

Kinetics is one of the critical points in the database. The lack of kinetic constraints in the geochemical equilibrium calculations was considered to be an important source of uncertainty. One of the major problems associated with developing a kinetics database is the dependence of the reaction kinetics on the environmental conditions. It is, therefore, difficult to apply a standard and then extrapolate from this. Also for complex systems, the number of possible interdependent reactions increases as a power series and therefore obtaining experimental rate data or estimating rate constants for a multicomponent multiphase problem can be very onerous. To overcome this lack of kinetic data, a commonly used approach in assessment studies is to perform thermodynamic calculations with chemical reactions, which are unlikely to form due to kinetic constraints. For example, in geochemical modelling, most codes consider local equilibria only. Few kinetic data are available for geochemical systems and, in most cases, meta-stable phases are hardly considered, even when they are stable for relatively long periods of time.

As revealed in the survey conducted by NEA, there are very few kinetic databases which are readily available for widespread applications. However, NIST has two

[NF PRO]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   50/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

chemical kinetics databases (NIST Chemical Kinetics Database, NDRL/NIST Solution Kinetics database). The HARKIN database is currently being developed by AEA Technology from critically assessed or calculated rate constants for thousands of chemical reaction steps [4-2] .

The geochemical calculations used in the ECOCLAY II project depend on thermodynamic databases as well as in some cases on reaction rate data (including reactive surface area values). However, it appears to be the case that it is possible to generate a thermodynamic data base for most studies that includes sufficient representative phases (and solution species) that allow the overall behaviour of the system to be reasonably represented. An important conclusion, from the studies so far, is that the distance the plume will penetrate into the clay is very small and no severe impact of the geological clay barrier has to be feared. But technical barriers can still be affected in contact with alkaline and/or saline solutions. In case of alkaline high saline solutions the modelling attempts indicate that the processes are manifold and more complex than in case of solution with low salinity. More work has to be invested in the reaction path prediction of clay material in contact with high saline and alkaline solutions.

4.2. Extrapolation to zero ionic strength

The standard state in the NEA database for dissolved species is the hypothetical ideal solution at unit activity. Thus the data which are evaluated from experimental measurements need to be corrected for activity coefficients. The specific ion interaction method (SIT) is used in the NEA database [4-1] .

The SIT method has several advantages that make it more suitable for the TDB project:
- it is simpler (fewer parameters are needed)
- missing parameters can easily be estimated from values for ions of similar charge and size
- the extraction of relevant parameters requires fewer experimental data,
- changing from the SIT would require a large amount of recalculation work for already selected data, and
- although there are cases (e. g. brines) where the SIT method is clearly not applicable, its accuracy and range of usefulness is adequate for geochemical modelling of a majority of the environments encountered in radioactive waste disposal sites.

4.3. Computer programs

Different computer programmes are being applied in the scientific literature in order to model the near-field geochemical evolution. The programs can be classified as: a) thermodinamic equilibrium programs and b) reactive transport programs:

The following are among the most usual programs :

- PHREEQC2 (Parkhurst & Appelo, 1999[4-3])

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   51/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

- EQ3/6 (Wolery, 1992 [4-5])

- CORE^{2D} (Samper et al., 2000[4-4])

In the ECOCLAY II project, namely PHREEQC, CRUNCH, EQ3/6, PRECIP, Hydrogeochem, MINTEQ and Medusa have been used to predict the chemical reaction processes of alkaline solutions in contact with clay. Also CHESS/Hytec has been developed for these kinds of reactions. The variety of programs used to obtain rather similar conclusions gives confidence in the performance (verification) of these tools, although the facilities offered by them may suggest that one is more appropriate than other for a particular application [3-171] , [3-215] , [3-177] .

The main processes and reactions taken into account in the geochemical modelling are shown in Table 28.

4.4. Thermodynamics of the main reactions in the near field

Thermodynamic data are available from various studies, in order to assess the long term chemical behaviour of the different materials in the context of radioactive waste repository. Discrepancies are generally noticed and it is then difficult to perform calculations with "well known uncertainties" on data.

The selected reactions and minerals described in Table 29 (a, b, c, d) take into account the main processes that will take place in the near field. The aim of this review is to give a list of major minerals and secondary phases formed under various geological chemical conditions.

The thermodynamical data set for cement-based materials has been studied by many authors [4-6] , [4-7] , [4-8] [4-9] ,[4-10] ,[4-11] ,[4-12] ,[4-13] ,[4-14] ,[4-15] and [4-16] . In the case of cement-based materials, the portlandite, CSH and sulpho-aluminates are sufficient to describe the majority of the hydrated cements. To complete the species, alkali oxides (Na_2O and K_2O) are also considered [4-7] .

The redox control in a cement-based environment is focussed on the identification of compounds likely to control this parameter. Traditionally, this parameter is associated with the iron or sulphur present in cement-based materials. Iron is found in variable quantities in the clinker, whereas sulphur is generally introduced (at least in the form of sulphide) by compounds like blast furnace slag. In some cases, aggregates can be a source of pyrites whose dissolution can make a significant contribution to control the potential redox in solution. Its oxidation play an important role on the modification of these conditions, in particular with the oxygen consumption all the more rapid since the pH is high and a lowering of pH together with a production of sulphate. The aluminates (type C_4AH_{13} or C_3AH_6 hydrates or sulpho-aluminates) can be responsible for the control of iron in solution. The portlandite phase controls the pH and calcium content in solution. CSH gels (according to temperature) control the silica content in solution and pH in absence of portlandite. Calcium sulpho-aluminates (or ettringite) control the sulphate and aluminium contents in absence of other aluminates in the system. C_4AH_{13} and/or C_3AH_6 control the content of aluminium in solution (in the absence of these compounds, the aluminium in solution will come from the sulpho-aluminates).

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   52/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

The main geochemical processes of the bentonite-water system to be considered in the modelling are determined from experimental results obtained in experiments performed at high (squeezing tests) and low (aqueous extracts solutions) solid to liquid ratios ([4-18] ,[4-19] ,[4-20] ,[4-21] ,[4-22] ,[4-23] ,[4-24]):

- Equilibrium with respect to calcite

- Equilibrium with respect to gypsum and celestite

- Equilibrium with respect to chalcedony

- Dilution of chlorides

- Ionic exchange reactions

- Surface complexation reactions

- Thermodynamic stability of the clay fraction (smectite) at the expected pH conditions (7<pH<11).

5.   NEAR-FIELD SYSTEM BEHAVIOUR MODELLING

The chemical buffer capacity of the bentonite is a direct consequence of the bentonite/groundwater chemical interactions. This buffer capacity mainly resides in the montmorillonite clay component and the bentonite accessory minerals. However, the presence of other components of the EBS, as concrete and the canister material could also affect the chemical buffer capacity of the bentonite.

As different EBS concepts are considered in different countries (see section 1.2), the geochemical behaviour of the EBS could differ substantially among these different designs. This is related to compositional differences of a specific material, the consideration of additional components in the EBS or the type of host rock.

In the following sections, the main chemical processes in each of the considered components of the EBS (conceptual model) will be described, as well as a review of the existing numerical models.

5.1.   Conceptual model (relevant processes for the NF component behaviour and for PA)

In this section, the main processes involved in the geochemical evolution of the near-field of a nuclear waste underground repository will be described. These processes will be divided according to the EBS component where they take place (host rock, concrete, bentonite, and canister) according to the different designs as described in section 1.2.

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   53/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

5.1.1. Bentonite

The main geochemical processes occurring in the bentonite barrier are almost the same than in the case of the clay host rock. However, the relative importance of the different reactions could differ from the clay rock. In addition, there are different bentonite types considered by different agencies (see section 1.2).

The main geochemical processes affecting the evolution of the bentonite component of the near-field are the following:

Dissolution-precipitation of carbonates. Although the carbonate content in bentonite tends to be relatively small, the dissolution-precipitation reactions are of paramount importance to buffer the alkalinity of bentonite pore waters.

Cation exchange reactions. The control exerted by this process on the calcium and magnesium concentrations in pore water directly affects the dissolution-precipitation of carbonate accessory minerals in the bentonite.

Protonation-deprotonation surface reactions. This process could contribute to the pH buffering due to the surface related reactions on smectite.

Sulphate dissolution-precipitation. Precipitation or dissolution of gypsum (and/or anhydrite) is another process which can control the calcium availability in the system, leading to an indirect buffering, due to its effect on the carbonate dissolution-precipitation reactions.

Equilibrium with pCO_2 in an open system. In the construction of blocks with compacted bentonite, the presence of atmospheric CO_2 can exert a significant control on the alkalinity. This process is especially relevant in the pre-operational stage of the repository, as in this stage the system will behave as an open system (constant pCO_2). However, during the operational stage, pCO_2 will varye depending on carbonate-involved reactions and CO_2 diffusion from or to the surrounding barriers.

Oxidation-reduction processes in the bentonite. In the bentonite, the redox capacity is an essential parameter for the repository stability. The redox in the bentonite barrier will be controlled by:

Pyrite oxidation. This process depends on the presence or absence of pyrite in the bentonite (depending on the type of bentonite selected in each near-field design). If pyrite is present, the oxidation will take place through the following reaction:

$$FeS_2(s) + 3.75O_2(g) + 3.5H_2O \; ? \quad Fe(OH)_3(s) + 2SO_4^{2-} + 4H^+$$
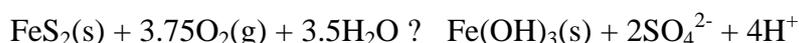
If there is no pyrite in the bentonite, then the oxidation of sulphide to sulphate will not occur and the redox of the system will be buffered by the redox pair Fe(II)/Fe(III).

Siderite dissolution / amorphous Fe(III) oxy-hydroxide precipitation. This is likely the most relevant redox process in the bentonite (if pyrite is not present as accessory mineral). If a significant fraction of carbonates in bentonite contains Fe(II), the equilibrium between Fe(II) carbonates and Fe(III) oxy-hydroxides can readily buffer the redox capacity of the bentonite.

Other processes. Finally, other processes that can be considered to play a role in the barrier are the dissolution-precipitation of silica phases (quartz, cristobalite and

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   54/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

amorphous SiO_2) and chlorides, especially in the presence a thermal gradient ([5-1]], [5-1]).

Also the aluminosilicate dissolution is a process which can be potentially considered. This process is related to the dissolution of smectite or its replacement by other clay minerals (saponite) resulting in a decrease of the swelling capacity of bentonite. However, the evaluation of the relevance of this process is difficult. There are some kinetic expressions for the dissolution of smectite, but there is no reliable thermodynamic data. As a consequence, it is not possible to calculate the saturation dependence of the dissolution rate.

5.1.2. Host rock

The host rock (clay rock or granite) will influence the hydraulic behaviour and consequently the chemical buffering. The difference is mainly related to the relative importance of the water transport mechanism (diffusion or channelled advective flow). The chemical processes expected to occur in the host rock of a repository are basically the same, for both granite and clay rock, although differences are related to their relative importance and the solute transport mechanism.

The host rock should contribute to buffer the alkalinity of the near-field and supply the necessary reduced conditions to maintain the stability of the EBS. The main processes buffering the alkalinity and redox capacity in the host rock are the following:

Carbonate dissolution-precipitation. It is clear that carbonate dissolution-precipitation reactions, specially those reactions involving calcite, will be important to maintain the alkalinity at optimum levels.

Cation exchange reactions. The control exerted by this process on the calcium and magnesium concentrations in groundwater directly affects carbonate dissolution-precipitation reactions, especially in clay formations, where clay minerals with exchangeable cations are the dominant minerals. However, clay minerals could also be important fracture-filling minerals in granitic rocks.

Protonation-deprotonation surface reactions. This process could contribute to the pH buffering due to the surface related reactions on clay minerals. It is clear that the relevance of these reactions will be more important in clayey host rocks, where higher clay mineral content is expected. However, their relevance in granitic rocks should not be discarded as in some cases the clay fraction in fracture-fillings could be significant.

Dissolution-precipitation of sulphates. As in the case of the bentonite barrier, this is another process that can affect the availability of calcium in the system, exerting an indirect control on the precipitation-dissolution of carbonates.

Aluminosilicate dissolution. This is a process related to the dissolution of the host rock-forming minerals, such as plagioclase or K-feldspar. This is a kinetically driven process. However, this process is of secondary importance due to the very slow dissolution rates.

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   55/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

Equilibrium with pCO₂ in an open system. It is expected that during the repository construction and the pre-operational stage, atmospheric CO_2 can exert a significant control on the alkalinity.

Before repository closure, there could be a CO_2 gradient from the walls of the deposition hole (atmospheric pCO_2) into the host rock formation (host rock formation pCO_2). However, this process should not be discarded in the operational stage of the repository, as degradation of organic matter through bacterial activity (especially in fracture open spaces from granitic host rocks) could produce significant amounts of $CO_2(g)$.

Main redox processes in the host rock formation. Redox reactions in the host rock can affect the properties of the near-field. The redox capacity of the host rock formation will be controlled by the processes described below following the energetic yield as described in natural systems ([5-17]).

Oxidation of the host rock formation organic matter. This process is represented by the following reaction:

$$CH_2O + O_2(aq) ?\quad CO_2(g) + H_2O$$
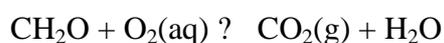
The CO_2 generated in this process is involved in the carbonate (calcite) dissolution-precipitation reactions and thus, affecting the pH buffering capacity of the system.

In addition, groundwaters from host rock formations with a high concentration of sulphate can gather the activity of sulphate-reducing bacteria (SRB) oxidising organic matter. This process can lead to the formation of sulphide minerals (mainly pyrite) and will contribute to the acidity and alkalinity of the system.

Pyrite oxidation. The next electron donor in the host rock formation is the sulphide content, mainly pyrite. Most clay rocks and fracture-fillings in granitic rocks have certain amounts of pyrite. This oxidative process has some limitations from the kinetic point of view and, consequently, it is necessary to discuss which are the main factors affecting the oxidation rate in order to assess whether it could be treated as an equilibrium process at the repository conditions.

Dissolution-precipitation of siderite and amorphous Fe(III) oxy-hydroxide. The third reducing process is the oxidation of Fe(II) from carbonates. The oxidation of Fe(II) carbonates to form Fe(III) oxy-hydroxides can exert a certain control on the redox of the system.

It is also possible, especially in the case of granite fracture-fillings, that hematite or other iron oxides with different Fe(II)/Fe(III) ratios (e.g. magnetite) could be present. Then the redox buffering could be exerted by the equilibrium between these phases.

5.1.3. Concrete

The most relevant process associated with the presence of a concrete lining is related to the microstructural changes due to its interaction with groundwaters. These alteration processes exert a relevant control on the alkalinity of the system, whose extent is a

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   56/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

function of the transport parameters associated with the concrete microstructure and with the alkalinity neutralising processes.

In the groundwater-concrete interaction, some dissolution-precipitation processes take place, resulting in the concrete alteration. In the alteration of a Portland-based concrete, the following processes can be identified.

Alteration due to leaching of dissolved phases in the pore space. In the leaching process of concrete, some phases initially present in the concrete will be dissolved. This process will exert an effect on the pH of the pore water. The first phases to dissolve will be Na and K hydroxides, leading to an increase in the alkalinity of pore waters (pH > 13).

Dissolution of portlandite (and brucite). Once the Na and K hydroxides have been dissolved, the dissolution of portlandite will begin. This process also produces an effect on the pH, which can reach values around 12.5.

Precipitation-dissolution of CSH gels. After the complete dissolution of portlandite, the alteration of CSH phases will start. These gels, with initially high Ca/Si ratios (= 1.8) will be altered to other phases with lower Ca/Si ratios (< 1). There are some experimental evidences ([5-18]) pointing to a mean Ca/Si ratio equivalent to that of tobermorite (Ca/Si = 0.8) and or jennite (Ca/Si = 1.5).

Precipitation of new solid phases. Together with all these concrete degradation reactions, other parallel reactions can occur, as precipitation of carbonates and sulphates. The precipitation of some silica phases is also possible because of the increase of SiO_2 in solution due to the dissolution of CSH gels.

In addition, since some pyrite exists in the concrete matrix, the pyrite oxidation cannot be discarded. This would be the main process responsible for the redox control in the concrete barrier.

Finally, the precipitation of other minerals, such as zeolites (analcite and/or phillipsite), CASH gels (together with the CSH gels) or magnesian silicates (talc and hydrotalcite) has also been described during concrete degradation experiments. The formation of these phases could modify the porosity, leading to substantial changes in the transport parameters of the system (e.g. changes in diffusion coefficient).

5.1.4. Steel canister/cast iron insert

Much has been written on the corrosion of iron and the overall process is quite well understood, particularly that which refers to iron corrosion in the presence of oxygen. The anaerobic corrosion of iron has been less studied, although in recent years SKB has undergone some research works on the anoxic long term corrosion of carbon steel ([5-12], [5-5]; [5-3], [5-4]) and the comparative effects with iron ([5-16]). According to the present state of the art, the main chemical processes that will take place under the anoxic (anaerobic) corrosion of the iron insert are the following.

1. Oxidation of metallic iron by water, precipitation of solid Fe(II) hydroxide and the subsequent generation of hydrogen gas.

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   57/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

2. The oxidative alteration of $Fe(OH)_2(s)/FeCO_3(s)$ to build a $Fe_{3-x}O_4$ passive layer with the spinel structure.

However, the groundwater presents other species thermodynamically able to oxidise iron, mainly SO_4^{2-} and CO_3^{2-}. This is thermodynamically favoured under all chemical conditions expected in natural groundwaters. Sulphate and/or carbonate reduction has not been observed in the absence of organic matter and bacteria. However, the reduction of sulphate and the production of methane is common in sediments because of the existence of organic matter and sulphate reducing and methanogenic bacteria. These microorganisms can use organic matter and H_2 as electron donor and either sulphate and/or CO_2 as electron acceptor. However, according to Pedersen and Karlsson (1995, [5-11]), the bentonite buffer constitutes a hostile environment for most microbes.

5.1.5. *Copper canister*

The use of copper canisters is envisaged in the SKB and POSIVA designs for the near field of a HLRW underground repository. The copper canister is expected to provide protection against corrosion in the repository. However, the presence of oxygen near the canister can lead to general corrosion or pitting of copper ([5-15]). The copper corrosion will be enhanced by the presence of sulphide, oxygen, or high concentrations of chloride in waters ([5-13]). However, these processes will lead to the formation of a protective layer, so the corrosion rate of the copper canister will decrease with time, despite the high temperature expected on the copper surface. In addition, it is expected that the extent of the corrosion attack will have a negligible effect on the canister lifetime ([5-10]). In any case, it is important to take into account that an increase in both temperature and chloride concentration will increase the corrosion potential of copper.

Once the oxygen initially present in the near field has been exhausted, anaerobic corrosion is the dominant process affecting the stability of the copper canister. The presence of aqueous sulphide in pore waters will form copper sulphides and generation of hydrogen gas. The source of this aqueous sulphide could be the dissolution of sulphide minerals initially present in the bentonite or, even, sulphide produced by sulphate reducing bacteria; provided they were active in the near field. Then, the rate of copper sulphide generation will be limited by the diffusion of sulphide to the canister surface, which will be very slow ([5-15]).

5.2. Existing numerical models

A small number of references can be found in the scientific literature dealing with numerical models of the geochemical evolution of the near field. Two different approaches are considered among the published models: a) mixing-tank models ([5-19]; [5-21]; [5-6]), and b) reactive transport models ([5-1], [5-1]; [5-14]; [5-20]; [5-8]). Mixing tank models consist in successive pore water replacements in the modelled domain, where this pore water is allowed to react with the phases defined in the system

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   58/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

(precipitation-dissolution of minerals, either in thermodynamic equilibrium or according to a kinetic rate law; cation exchange, protonation-deprotonation surface reactions, etc.). On the other hand, reactive transport models simulate a more realistic domain, where advection and/or diffusion (depending on the properties of the simulated medium) are the processes considered for water and solute transport. In addition, in reactive transport models, chemical reactions are calculated once the transport equations are solved. A more detailed description of these models dealing with near-field geochemical evolution can be found in Arcos et al. (2004, [5-2]).

5.3. Predictive model

The use of models is essential for the assessment of the geochemical evolution of the near field of a repository. However, although most of the processes considered are based on experimental data (mainly laboratory experiments), there is a need to validate these models through data obtained from long-term experiments under repository conditions and/or natural analogues. Unfortunately, long-term experiments devoted to geochemical behaviour of the near field have not been specifically conducted. There are only two experiments, initially considered for the study of thermo-hydro-mechanical behaviour of bentonite, which have been later adapted to obtain some geochemical information on the near field behaviour, the FEBEX project ([5-7]) and the LOT experiment ([5-9]).

In any case, the results from the geochemical models dealing with the near field show that a few processes will buffer relevant parameters of the system, such as pH, Eh and alkalinity, independently of the near field design, with the only exception of the specific effects of adding a concrete liner. In the following sections, these processes will be discussed, as well as the main gaps related to their knowledge.

6. KNOWN AND UNKNOWN FACTS AND UNCERTAINTIES

This chapter will deal with the geochemical processes that take place in each of the EBS component. It will also point out which are the aspects less studied highlighting the key parameters

6.1. Near-field geochemical processes

For safety purposes, it is necessary to identify the magnitude of the water-rock reaction processes and physical changes in the host rock (granite, clay or salt), bentonite and in

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   59/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

the concrete. The present section tries to summarize the most relevant known geochemical processes, and poses a series of uncertainties as well as the key parameters to be studied to be able to clarify the least understood or studied fields.

6.1.1. Known facts

In concrete

The saturation of concrete with fresh, saline and high saline groundwaters produces a hyperalkaline pore solution that reacts with the bentonite and the host rock affecting the sorption and transport properties of the whole system.

Reactions of bentonite in hyperalkaline conditions: The leaching of concrete causes:

- Dissolution of Na, K hydroxides and portlandite

- Precipitation-dissolution of CSH gels

- Precipitation of carbonates, sulphates, quartz, CASH gels, zeolites (analcime, phillipsite), talc and hydrotalcite

- Oxidation of pyrite present in the concrete matrix

The main leaching process is loss of Ca. Decalcification leaves behind a shell of silica and metalhydroxides. In the CW-Experiment at Mont Terri (Opalinus Clay) the initial results showed that buffering to pH 10 took more than 6 months and that mass loss to the rock is ~ 2g/day. Concrete-Boom Clay interactions studied by in situ experiments indicated that the alteration zone both in the clay and in the concrete was about 100 to 150 μm [3-155].

Leaching experiments in salt formations show that salt cements have a higher resistivity against NaCl-rich solutions than against Mg-rich solutions. No visible alteration was observed with NaCl saturated solutions, while an alteration depth of 1.5 mm occurred with Mg-rich solutions.

In compacted bentonite

Modifications of bentonite due to concrete/bentonite interaction

Previous studies dealing with cement/clay interactions are very few and focused mainly on the subjects of composition of cement pore solutions, degradation products of cement (silicate) degradation and interactions between granite and cement. During the last decade the ECOCLAY project (part one and two) financed by the European Commission had been conducted with the main objective to characterise the comprehension of the physicochemical behaviour of the release of a hyperalkaline plume by cement degradation for different host rocks. A series of laboratory and in-situ tests had been performed to build a knowledge base on the hyperalkaline plume, and to analyse the geochemical processes.

The main reactions of the hyperalkaline pore fluid (pH 10-13.5) and the bentonite are:

- Cation exchange processes with cement pore water ions. The cation exchange reactions are favoured by rising temperature and increasing time. Short-term interactions are dominated by ion exchange processes.

[NF PRO]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   60/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

- Minor or none modification in the cation exchange capacity.

- Specific surface decrease, as well as pore-size increase due to agglomerate formation.

- Experimentally calculated thickness of bentonite affected by alkaline solutions: in the order of microns/mm (reaction time: 1 year, ECOCLAY Project)

and for longer-term interactions and/or at higher temperatures, the following mineral dissolution-precipitation processes become relatively more important in controlling mass transfer.

- Dissolution of smectite and montmorillonite.

- Dissolution of cristobalite and increase in quartz content.

- Formation of Ca/Mg (aluminium) silicate hydrates. In salt formations:tobermorite.

- Formation of zeolites, mainly phillipsite.

- Minor formation of sheet silicates such as illite or mixed-layer clays Minor formation of chlorite.

Modifications of THM properties of bentonite due to concrete/bentonite interaction

- Loss of swelling capacity, changes in porosity and sorption capacity

- In salt formations, experiments have confirmed the reduction of swelling pressure in the presence of brines and/or hyperalkaline solutions. The few results obtained so far cannot be extrapolated to other boundary conditions.

Geochemical/physico-chemical modifications of bentonite due to granite/bentonite interaction

- Main geochemical/physico-chemical processes: Dissolution-precipitation of carbonates, sulphates, quartz, chlorides; cation exchange reactions; oxidation-reduction processes; alteration of montmorillonite to illite)

- Modelling of the chemical composition of pore water under different assumptions (equilibrium with atmospheric pCO_2 , and carbonates/$\equiv$ SOH groups) at initial and saturated conditions for different dry densities.

- A first approach to know the distribution of water in the bentonite (structural, interlamellar, external) in a steady state.

- After a 5-year period, the FEBEX bentonite has not undergone significant mineralogical and physico-chemical changes (FEBEX project).

- Colloids are generated in favourable geochemical conditions (low ionic strength, alkaline groundwaters)

THM modifications of bentonite due to granite / bentonite interaction

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(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   61/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

The results available up to now refer only to periods of thermo-hydraulic treatment smaller than five years and that the effect of radiation has not been evaluated in the *in situ* tests (BMT, BCE, ITT, LOT and FEBEX).

- High initial suction which favours the saturation of the blocks. The hydraulic pressure gradient established is not important until the suction of the bentonite becomes small, towards the end of the process.

- Complete dissolution of air, initially contained in the bentonite pores, allows for the complete saturation of the barrier.

- Swelling of the bentonite. Establishment of a density gradient (lower at the outermost part and higher at the innermost part of the bentonite). These density modifications affect increasingly larger areas as hydration progresses and are enhanced by the heating effect.

- Establishment of a thermal gradient. The thermal conductivity increases with water content, thus it is higher in the external part of the buffer and lower in the desiccated area near the canister. Desiccation and shrinkage of the bentonite contributes to the decrease in porosity of the blocks in the internal zones of the barrier.

- Increase in salinity in the hotter areas due to evaporation/condensation processes.

- The hydraulic conductivity measurements performed in samples retrieved from *in situ* tests have not shown any important variation after the bentonite has been subjected to repository conditions.

Corrosion at the bentonite/canister interface

- Processes and types of corrosion. Chloride, sulphide, sulphates and oxygen ions are very aggressive enhancing pitting and localized corrosion, respectively, but also increase the corrosion protection of the metals, resulting in the decrease of the corrosion rate.

- Types of products produced by corrosion (hematites, magnetite, oxyhydroxides, siderite pyrrhotite

- Corrosion rates. Experimental corrosion results within the FEBEX project estimated a corrosion rate of 0.10 µm/year of C steel coupons after 7 years.

- Corrosion is a function of time and temperature. Experimental results showed that in the presence of radiation the corrosion of metals can be significantly increased.

- Corrosion products tend to be greater in volume than the original metal and stress can develop causing premature failure of the canisters.

- Microbial corrosion can be present. Clear evidences of this process are frequently found in spite of the adverse conditions in a repository for the survival of bacteria.

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   62/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

- Hydrogen generation as a result of corrosion. No evidence was found that the development of pressure-induced gas pathways compromises in any way the sealing capacity of the bentonite barrier.

Modification of transport properties due to corrosion:

- Swelling pressure can be affected by the formation of chlorites and bentonite cementation, though not in a significant way.

- Sorption capacity could be affected by the presence of ferrous ions. Corrosion products can favour sorption. For example, magnetite can reduce the redox sensible elements resulting in their immobilization.

- Transport of radionuclides can be easier as pseudocolloids formed by iron hydroxides.

Migration of radionuclides

- Ion exchange and surface complexation are the main mechanisms of sorption. Ion exchange provides support and justification for the sorption data bases in PA. The processes involved in surface complexation are well understood and can be adequately modelled for the non-clay mineral phases.

- Ion exclusion is well known in principle. The extent to which ions are excluded increases with compaction and decreases with salinity. Ion exclusion results in differences in the porosity accessible for transport of solutes (geochemical or free water porosity) of various charges and sizes.

- Colloidal transport of radionuclides has been measured and it is negligible.

6.1.2. Uncertainties:

This section tries to compile all the uncertainties that have arisen in the different chapters of this paper and is focussed on those processes known to be the most relevant in the near field evolution, though they need a more detailed knowledge, especially under repository conditions.

Bentonite related processes.

- As outlined by experimental data and geochemical models, cation exchange is one of the main processes controlling the geochemical evolution of the system. However, the different initial cation occupancy in the exchanger will lead to very different buffering capacity. In addition, most of the experiments have been performed at density conditions far from those expected in the repository (e.g. low density and relatively high water/bentonite ratios). For this reason, one may expect to have a good knowledge on the density dependency of cation exchange coefficients, as well as temperature effects on these reactions.

- It has been demonstrated that the pH buffering capacity of bentonite is controlled by calcite dissolution-precipitation. Moreover, this process is linked to cation exchange reactions as they will control the calcium availability in solution. On the other hand, the redox buffering capacity of bentonite is somewhat controversial, as some authors argue that this buffering will be

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   63/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

exerted by pyrite oxidation, whereas others think that the control is made by siderite/Fe(III) oxy-hydroxides. Obviously, this will depend on the initial inventory of accessory minerals in the selected bentonite. A detailed experimental work is needed to determine which of these processes is responsible for the redox buffering in the bentonite barrier.

- The stability of clay minerals is another issue that needs a better understanding. There is a large amount of data concerning the kinetic dissolution of smectite. Although it has been demonstrated that, under repository conditions, montmorillonite dissolution will occur at a very low rate, the partial transformation of smectite to other clay minerals (illite, kaolinite) could affect the isolating properties of the bentonite. In addition, during the high temperature transient phase in the near field, montmorillonite could be transformed into other non-swelling sheet silicates as chlorite, especially in the case of high iron concentrations in pore water due to canister corrosion. How relevant is the illitization process of montmorillonite?

- How do the Eh, pH and electric conductivity of the bentonite change during the hydration/heating process?

Bentonite saturation

- The influence of the thermal gradient on saturation specially for high temperatures needs to be better understood. Will full saturation be hindered until dissipation of the thermal gradient? Will the high temperatures around the canister hinder the full saturation of the inner part of the barrier or just delay it?

- Will the possible existence of a threshold hydraulic gradient prevent the movement of water in the final stages of the repository, when suction is low and the only driving force is the hydraulic pressure?

- It has not been possible to experimentally check if the density gradients observed in the EBS are recovered when the final water content of the barrier is homogeneous and if the volume changes induced during saturation are irreversible.

- There are not enough experimental evidences regarding the modification of HM properties of bentonite by the effect of temperature. Are the modifications induced by temperature reversible or not?

Migration of radionuclides

Diffusion mechanisms

- The problems of deriving sorption parameters (D_a) from laboratory Kd measurements that are consistent with those from diffusion measurements have been studied for compacted bentonite but have not yet been solved. The question of compatibility between measured and calculated D_a values requires urgent clarification.

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   64/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

- The diffusion process for retarded solutes is not well understood. Knowledge provided by laboratory experiments and field tests is only enough for an extrapolation in space and time related to the experimental constraints.

- There are three broad types of porosities in compacted bentonite and it is critical to know which porosity is associated with the diffusion of a certain radionuclide and its corresponding diffusion mechanism. In spite of the attempts to clarify the diffusion mechanisms, no mechanistic model exists so far.

- The pore water chemistry plays a vital role in understanding the retardation processes of elements diffusing through compacted bentonite. For this reason, key parameters and assumptions in the pore water chemistry model have to be checked as a function of the initial dry density. The discussion on the right model is still ongoing.

- The mechanistic understanding of cation and anion diffusion is very important to explain certain phenomena, such as ionic exclusion and surface diffusion, but it is still not well known. For example, salinity affects the diffusion of anions, but this effect has not been quantified yet. On the other hand, surface diffusion is controversial, and there are doubts about the existence of interlayer diffusion.

Retention mechanisms

- For a reliable interpretation of the sorption results, the identity of the sorbing aqueous species and sorbed species must be known. However, the aqueous speciation of the actinides is not well known, which can lead to uncertainties in the extension of laboratory measurements to field conditions..

- The processes involved in surface complexation are not so well understood for clay minerals and complex media containing carbonates or organics.

- Also, the role of protonation-deprotonation of surface reactions must be clarified. Some authors indicate that these processes control the pH besides the calcite equilibrium (something which is against the Gibbs phase rule). Anyway, it is clear that these reactions will have a clear control on the sorption capacity of bentonite for some of the radionuclides of interest. Thus, a good characterisation of these reactions and the associated constants must be carried out.

Brine-bentonite processes

- In salt formations, the knowledge on swelling pressure in contact with brines is incomplete. What is the influence of the brine composition in the swelling pressure of the bentonite? What other factors can be involved (dry density, microstructure, flooding regime, sample size)?

Concrete related processes

- Concrete degradation will produce a hyperalkaline plume into the components surrounding the concrete (e.g. bentonite and host rock). Although the degradation sequence is relatively well-known, CASH gels, zeolites and other alumino-silicates are usually difficult to include in the geochemical models due

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   65/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

to the lack of thermodynamic data. Data bases on highly alkaline groundwaters are needed.

- The porosity variation during concrete degradation seems to be one of the most relevant processes in this component as it could retard or speed up groundwater flow velocity to the bentonite barrier.

- The physico-chemical retention capacity of concrete must be clearly established and the chemical perturbations induced by the concrete on the clay should be quantified, since the current studies only state that the mineralogical transformations originated are very limited .

- What is the effect of concrete degradation on the evolution of the pore water composition and the hydration dynamics of the bentonite (both in clay and salt formations)?

- The chemistry of cementitious materials in the clay barrier is not well known.

- Although the distance of penetration of the high alkaline plume in the bentonite is very small (in the order of mm at the most), there are still some doubts on how technical barriers can be affected when alkaline and/or high saline solutions are in contact with them. More work is required concerning the reaction path prediction of clay material in contact with these solutions.

Influence of brines on the cement processes

- How can the brine-cement interactions affect the pH, stability of cement phases and cement leaching?

Canister corrosion related processes

- Although the corrosion of the copper canister has been demonstrated, it is not an important process for the long-term evolution of a repository, it will be interesting to implement the overall process in a near field model, in order to check the consequences of the copper corrosion on the bentonite, especially for the redox of the system.

- The iron corrosion is a more complicated process. One of the main problems is the difficulty to implement it in a near field model by adding a kinetic rate which can decrease with time, as the passivation layer grows on the canister surface. Moreover, the hydrogen evolution (maximum pressure, out-diffusion from the near field) is one of the problems not really understood, so there is a need for further investigation.

- There is uncertainty on the volume of gas and corrosion products generated. Some available data suggest that the volume of corrosion products could be huge, and its implications on the stress state of the barrier (break-through process) is of major importance. The same could be said if the gas generation rate were large.

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   66/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

<u>Host rock related processes</u>

- The groundwater composition in the host rock is essential for any near field model. Although this could be part of the far field characterisation, some reactions will take place in the host rock portion of the near field (including the EDZ). One of the key points is related to the presence of atmospheric oxygen and $CO_2(g)$ in the EDZ, which can lead to substantial modifications of the alkalinity, pH and Eh. The interaction of the modified groundwater with the host rock minerals (or the fracture filling minerals in the case of a granitic host rock) will result in reactions like sulphide oxidation (mainly pyrite), precipitation of Fe(III) oxy-hydroxides, and dissolution-precipitation of carbonate minerals. However, the understanding of these processes in the EDZ of the host rock must be evaluated by experimental studies. In addition, the effect of bacterial activity on these processes must also be assessed and characterised.

6.1.3. *Critical concepts to be developed*

There are several concepts related to the near field evolution that require further conceptual and numerical development. The following is a list of the most relevant issues:

- Implementation of the thermal gradient in near field models

- Water saturation of bentonite

- Implementation of bentonite swelling in near field models

- Porosity evolution in bentonite, concrete and host rock

- Atmospheric gases

- Bacterial activity in the near field

- Implementation of processes related to canister corrosion

6.1.4. *Missing parameters to be determined*

One of the main uncertainties in geochemical models is the composition of the bentonite pore water. Due to the difficulties in obtaining reliable pore water samples from compacted bentonite, the most suitable way to obtain the chemical composition of this pore water is by means of geochemical calculations. For this reason, a good characterisation of the mineralogical composition, as well as the cation occupancies in the exchanger and their associated exchange coefficients must be carefully determined for bentonite densities relevant to repository conditions. In addition, there is a need to clarify the volume fraction of pore water which is involved in chemical reactions.

Quantitative information related to iron and copper corrosion kinetics under repository conditions is also needed, as well as the characterisation of the corrosion products and the maximum depth of corrosion penetration.

6.1.5. *Key parameters to be studied*:

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   67/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

- Short and long-term chemical behaviour of the EBS materials

- Rate of volume expansion or reduction of the EBS materials in contact with brines and hyperalkaline fluids.

- Volume rate of room closure.

- Modifications of the EBS properties as a function of brine chemistry, temperature, rock stress and time.

- Density dependence of cation exchange coefficients and temperature effects on these reactions.

- Good characterization of protonation-deprotonation of surface reactions and the associated constants.

- A better understanding of the stability of the clay minerals. There are some kinetic expressions for the dissolution of smectite, but there is no reliable thermodynamic data. As a consequence, it is not possible to calculate the saturation dependence of the dissolution rate.

- Evolution of the pH, Eh and electric conductivity of the bentonite during the hydration/heating process.

- Further investigation on the chemical and mineralogical irreversible reactions (mobilization/precipitation of SiO_2).

- Characterization of the porosity variation during the concrete degradation.

- Study of the advance of the hyperalkaline plume and the magnitude of the transformations during hydration/saturation of the bentonite.

- Implementation of the overall corrosion process in a near field model

- Understanding the hydrogen evolution (maximum pressure, out-diffusion from the near field).

- Swelling pressures in contact with brines. Determination of the effect of dry density, microstructure, flooding regime, sample dimensions on swelling.

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   68/106

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CHAPTER 2

Role and requirements of the different components of the EBS

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Dissemination level: PU

Date of issue of this report: **31 March 2005**

ACRONYMS

ADZ: Alteration Damaged Zone

AECL: Atomic Energy of Canada Limited

Afm: monosulphate

Aft: ettringite

AGP: Almacenamiento Geológico Profundo (Deep Geological Disposal)

ANDRA: Agence Nationale pour la Gestion des Déchets Radioactifs

BCE: Buffer Container Experiment

BFS: Blast Furnace Slag

BMT: Buffer Mass Test

BWR: Boiling Water Reactor

CEC: Cation Exchange Capacity

CH: Calcium Hydroxide

CLC: Cellular Lightweight Concrete

CSH: Calcium Silicate Hydrates

DDL: Double Diffusive Layer

DGR: Deep Geological Repository

EBS: Engineered Barrier System

EDZ: Excavated Damage Zone

ENRESA: Empresa Nacional de Residuos Radiactivos, S.A. (Spain)

FA: fly ashes

FEBEX: **F**ull-Scale **E**ngineered **B**arriers **Ex**periment

GRS: Gessellschaft für Anlagen und Reaktorsicherheit

HA: humic acid

HLW: High Level Waste

HRL: Hard Rock Laboratory

INE: Institut für Nukleare Entsorgung (Germany)

ITT: Isothermal Tests

LLW: Low Level Waste

LOT: Long Term test of buffer material

NAGRA: Nationale Genossenschaft für die Lagerung Radioaktiver Abfälle (Switzerland)

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   100/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**

NSARP: Nirex Safety Assessment Research program

ONDRAF/NIRAS: Belgian Agency for Radioactive Waste and enriched Fisssile Materials

OPC: Ordinary Portland Cement

PWR: Pressure Water Reactor

RAWRA: Radioactive Waste Repository Authority (Czech Republic)

RESEAL project: A large in situ demonstration test for Repository SEALing in an argillaceous host rock

RTD: Research and Technology Development

S:L: Solid:Liquid ratio

SCK-CEN: Studiecentrum voor Kernenergie-Centre D´Etude de l´Energie

SFA: fly ash

SKB: Svensk Kärnbränslehantering AB

SR: sulphoresistant

SRB: Sulphoresistant Bacteria

THM: Thermo-Hydro-Mechanical

THMCB: Thermo-Hydro-Mechanical Chemical and Bacteria

URL: Underground Research laboratory

w/c: water/cement ratio

[**NF PRO**]

(D2.1.1) – State of the art report. Final version [CIEMAT/DIAE/54511/07/04]   101/106

Dissemination level: PU

Date of issue of this report: **31 March 2005**