Assessment of the evolution of the redox conditions in a low and intermediate level nuclear waste repository (SFR1, Sweden)

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ABSTRACT

The evaluation of the redox conditions in an intermediate and low level radioactive waste repository such as SFR1 (Sweden) is of high relevance in the assessment of its future performance.

The SFR1 repository contains heterogeneous types of wastes, of different activity levels and with very different materials, both in the waste itself and as immobilisation matrices and packaging. The level of complexity also applies to the different reactivity of the materials, so that an assessment of the uncertainties in the study of how the redox conditions would evolve must consider different processes, materials and parameters.

This paper provides an assessment of the evolution of the redox conditions in the SFR1. The approach followed is based on the evaluation of the evolution of the redox conditions and the reducing capacity in 15 individual waste package types, selected as being representative of most of the different waste package types present or planned to be deposited in the SFR1. The model considers different geochemical processes of

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redox relevance in the system. The assessment of the redox evolution of the different vaults of the repository is obtained by combining the results of the modelled individual waste package types.

According to the model results, corrosion of the steel-based material present in the repository keeps the system under reducing conditions for long time periods. The simulations have considered both the presence and the absence of microbial activity. In the initial step after the repository closure, the microbial mediated oxidation of organic matter rapidly causes the depletion of oxygen in the system. The system is afterwards kept under reducing conditions, and hydrogen is generated due to the anoxic corrosion of steel. The times for exhaustion of the steel contained in the vaults vary from 5 ky to more than 60 ky in the different vaults, depending on the amount and the surface area of steel. After the complete corrosion of steel, the system still keeps a high reducing capacity, due to the magnetite formed as steel corrosion product.

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The redox potential in the vaults is calculated to evolve from oxidising at very short times, due the initial oxygen content, to very reducing at times shorter than 5 years after repository closure. The redox potential imposed by the anoxic corrosion of steel and hydrogen production is on the order of -0.75 V at pH 12.5. In case of assuming that the system responds to the Fe(III)/Magnetite system, and considering the uncertainty in the pH due to the degradation of the concrete barriers, the redox potential would be in the range -0.7 to -0.01V.

A Monte-Carlo probabilistic analysis on the rate of corrosion of steel shows that the reducing capacity of the system provided by magnetite is not exhausted at the end of the assessment period, even assuming the highest corrosion rates for steel.

Simulations assuming presence of oxic water due to glacial melting, intruding the system 60 ky after repository closure, indicate that magnetite is progressively oxidised, forming Fe(III) oxides. The time at which magnetite is completely oxidised varies depending on the amount of steel initially present in the waste package.

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The behaviour of Np, Pu, Tc and Se under the conditions foreseen for this repository is discussed.

KEYWORDS

Redox evolution
Nuclear waste repository
Radionuclide migration
Reductive capacity

1. INTRODUCTION

Redox conditions of a nuclear waste repository are of high relevance in the assessment of the future behaviour of the repository and the deposited wastes. The study of the evolution of the redox conditions presents a high level of complexity due, among other reasons, to the variety of the materials that can be present in the facility and react simultaneously. The assessment of redox conditions can only be approximated by adequately discussed assumptions (Wanner, 2007). Uncertainties concerning processes, parameters and materials must be also assessed and evaluated.

The most usual way to define the redox state of a system is based on the measure or determination of the redox potential (Eh), which can be related to the concentration of the redox active species in the system. Nevertheless, redox reactions are known to be slow and in many cases they need the action of catalysts to proceed, despite being thermodynamically favoured. Thermodynamic equilibrium among redox species can not be granted and this precludes the achievement of conclusions on the redox state of a system simply based on the determination of redox active species.

This implies that the simple monitoring and calculation of redox potentials is sometimes not a very good indicator of the redox state of all redox couples in the system, as it has been proven from many groundwater analyses that different redox potentials can be measured depending on the redox couple considered to be in equilibrium in the system (Lindberg and Runnells, 1984).

The redox potential is identified as one of the main chemical parameters affecting the chemical behaviour of radionuclides and consequently their mobility. The study of the

redox conditions of repositories requires an understanding on the processes affecting the existing materials and the rates at which the processes occur under the different conditions expected to prevail in the system.

Different attempts, normally site-specific studies, have been undertaken to determine the future evolution of the redox conditions in a low and intermediate level nuclear waste repository (Neall, 1994; Humpreys et al., 1997; Small et al., 2000&2008; Wersin et al., 2003; Grivé et al., 2011; Avis et al., 2012).

The objective of the work summarised here is to develop a methodology to calculate the evolution of the redox state of the SFR1 repository with deposition time. According to the Swedish regulations, the time frame for the assessment as must span over the maximum risk consequences with a maximum of 100 ky after repository closure (SSM, 2008). The model should be transferrable to a new configuration of the repository, possible extension, or changes in the type and/or composition of the waste packages deposited.

To this aim, a geochemical model has been developed that accounts for the inventory of the SFR1 facility and considers the most up to date scientific understanding of the redox and chemical processes likely to drive the redox evolution of the system. The model has been developed by individual waste packages and deposition vaults and has been applied to obtain the redox evolution of the complete repository system.

Due to the huge amounts of materials present in the system, such as metals and organic matter, in comparison with the amounts of redox sensitive radionuclides, it is very unlikely that the radionuclides can have any relevant effect on the redox evolution of the system. Nevertheless, the implications that chemical changes can have on the behaviour of redox sensitive nuclides, Np, Pu, Tc and Se, under the conditions developed in the repository are presented.

1.1. The system under study: the SFR1 Repository

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The SFR1 repository at Forsmark in Sweden is used for the final disposal of low- and intermediate-level radioactive waste (L/ILW) produced by the Swedish nuclear power program, industry, medicine and research. Waste disposed in SFR1 belongs to the short-lived waste category according to the IAEA definition (IAEA, 2009). This means that there is a limitation of long-lived α-activity of an average overall of 400 Bq/g per waste package, allowing a maximum per individual waste package of 4,000 Bq/g.

The repository system is placed in a shallow subsurface area of Forsmark under the Baltic Sea. It consists of four different vaults: the Silo and the BMA, BLA and 1&2BTF vaults. More details can be found in SKB (2008) and will not be repeated here. A sketch of the system showing the different vaults is shown in Figure 1.

The SFR1 system presents a high capacity to buffer an oxidant intrusion, given the amount of materials prone to oxidise. The most relevant characteristics of the repository for the purpose of the redox assessment presented here are that (1) the wastes are predominantly conditioned in concrete matrices; (2) bitumen is also used as matrix for some wastes; (3) the waste packages are made of concrete or steel, and (4) the wastes, although very varied in composition, contain important amounts of metals and organic materials, including cellulose.

About fifty different type of waste categories are foreseen to be deposited in the SFR1 until its closure (approx. at year 2050). They can be represented by 15 generic waste packages (see Table 1) differing in the type and materials of the container, type and amount of immobilising matrix and type and amount of waste.

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The amount of the different materials to be deposited in each one of the vaults of the SFR1 repository at the time of its closure (at year 2050) is shown in Figure 2 (data from Almkvist and Gordon, 2007).

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In the light of the amount of materials present in the repository, many redox processes can be identified as being of relevance in the SFR system: metal corrosion, degradation of organic matter, radiolysis, sulphate reduction, gas generation and fermentation,... The level of radiation that may cause generation of oxidants in the repository is very low and previous assessments on the influence that radiolysis can have on the oxidant

balance of the repository, such as the one in Moreno et al. (2001) have shown that this effect is expected to be minimal.

Therefore, processes that a priori can have a larger influence in the short and long-term redox evolution of the repository are:

- Metal corrosion
- Organic matter degradation (bitumen, non-classified organic matter and cellulose)
- Microbial activity

An important feature of the repository is the ubiquity of concrete and cement, what conditions the system to high pH values.

Just after repository closure, there will be oxidants in the system due to repository construction and operation periods, and under non-disturbed conditions it is foreseen that these oxidants will be rapidly consumed and the system will reach anoxia and later develop reducing conditions. Groundwaters reaching the repository at long-term are not expected to contain appreciable concentrations of oxidising species, due to their prior interaction with soils and minerals that will cause oxidant consumption. According to the expected evolution of the SFR1 environment (SKB, 2008), the only possibility of oxidising conditions to reach repository depths arises from an inflow of glacial oxygen-rich and diluted water. This situation would, if at all, happen during ice melting events. According to the foreseen climatic evolution of the system, the earliest time at which melting water would reach the repository is 60 ky after its closure. This means that, once the system has reached reducing conditions, its capability to buffer an oxidising intrusion will basically remain the same until 60 ky and that after this time, it will be jeopardised only in the case of melting ice water inflowing the system.

Suprimit: Table 1. Representative waste packages in each one of the vaults of the SFR1 repository (SILO, BMA, 1 and & 2 BTF and BLA), amounts of the different materials contained and porosity of the wastes. Data from Almkvist and Gordon (2007) and updated inventory. Φ: porosity; BIT: bitumen; GOM: non classified organic matter. CELL: cellulose.¶ ...

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Metallic corrosion and organic matter degradation (either biotically-mediated or chemical) will provide most of the capacity of the system to buffer any potential oxidant intrusion. However, although the reducing capacity of the repository can be far larger than the one needed to account for total consumption of the oxygen initially trapped, the kinetics of the electron-transfer processes must be considered to assess the redox evolution of the system with time.

A qualitative sketch of the expected evolution of the redox conditions in the repository is shown in Figure 3. The sketch shows the time scale, the different redox processes occurring, microbes involved, and a redox scale in the right, with the different redox potential achieved in the system if equilibrium with the main redox pairs is calculated at pH = 12.5, which corresponds to equilibrium with portlandite, $Ca(OH)_2(s)$, as a proxy for concrete.

2. MODELLING METHODOLOGY

When assessing the behaviour of this type of systems it is important to consider not only the theoretical capacity that the system has to accept oxidants (ReDucing Capacity or RDC, Scott and Morgan (1990)), but also the relative rate of reduction versus the rate at which the oxidant intrusion occurs. Therefore, the conceptual and numerical models developed include:

-the assessment of the time evolution of the system, i.e., the rate at which reducing conditions are attained and how fast it reacts towards an oxidant intrusion; and,
-the assessment of the remaining buffer capacity of the system in the case of any future oxidising disturbance, that is, the RDC.

The different vaults of the repository have been considered as a combination of generic waste package types. In this way, the combination of the evolution of the redox conditions in each generic waste package type is used to assess the evolution of the redox conditions in the vaults and this, in turn, in the complete repository system.

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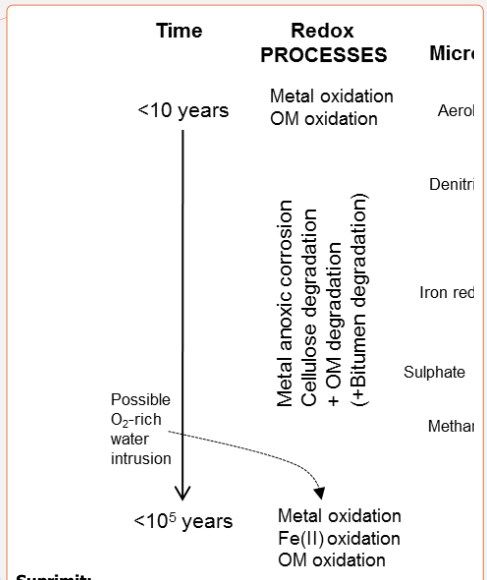

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Figure 2. **Sketch showing the evolution of the redox potential in SFR1 under non disturbed conditions, depending on the redox couple governing the Eh, at a pH 12.5 (portlandite equilibrium).**¶

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The following approach has been implemented in the model.

a. Calculation of the chemical evolution of each one of the 15 different types of waste packages presented in Table 1 by implementing the relevant redox processes into a conceptual and numerical model.

b. From the results in a., calculation of the temporal evolution of the RDC of each one of the 15 types of waste packages.

c. Combination of the results from b. to obtain the RDC at each time for each one of the vaults Silo, BMA, BLA and 1&2BTF.

d. Combination of the results from c. to calculate the RDC of the complete SFR1.

With the aim of monitoring the role of the different processes responsible for the redox evolution of the system, three temporal scales have been implemented in the model: a very short term (up to 30 days), short term (up to 5 years) and long term (from 5 years to 100 ky).

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3. CONCEPTUAL AND NUMERICAL MODEL

The rate and extent of the different redox processes occurring in the system is discussed in the light of the available data in the literature. Several assumptions are made for the sake of the modelling procedure, as presented below.

3.1. Redox processes and implementation

3.1.1. Metal corrosion

In the presence of oxygen, iron corrosion produces Fe(III) oxides and hydroxides. Hematite is the thermodynamically stable Fe(III) oxide in the stability field of water followed by goethite and ferrihydrite or hydrous ferric oxides. However, despite their lower stability with respect to hematite, goethite and hydrous ferric oxides can prevail

as metastable solid phases for long time periods and they have faster formation kinetics when metallic iron oxidises in the presence of oxygen than hematite.

In the absence of oxygen, iron can corrode through water reduction given that Fe(s) is thermodynamically unstable in water. As for the corrosion of other metals also present in the system, such as aluminium and zinc, $H_2(g)$ is generated (eq.1). $Fe(OH)_2(s)$ is metastable and with time evolves towards magnetite, according to the Schikorr reaction (eq.2). The composition of the magnetite formed on the surface of iron is not exactly known, although it has been suggested that it consists of an oxide $Fe_{3-x}O_4$ with a spinel-like structure varying in composition from Fe_3O_4 (magnetite), in oxygen-free solutions, to $Fe_{2.67}O_4$ under the presence of oxygen (Stumm and Morgan, 1996).

$$Fe(s) + 2\ H_2O \rightarrow Fe(OH)_2(s) + H_2(g) \qquad \text{eq.1}$$

$$3\ Fe(OH)_2(s) \rightarrow Fe_3O_4 + H_2\ (g) + 2\ H_2O \qquad \text{eq.2}$$

In the presence of carbonate, sulphide or chloride, iron corrosion can lead to the formation of other corrosion products different from magnetite, such as iron sulphides, carbonates or green rusts.

Eq.3 shows the global redox reaction for the transformation of iron into magnetite under anoxic conditions.

$$3\ Fe(s) + 4\ H_2O \rightarrow Fe_3O_4(s) + 4\ H_2(g) \qquad \text{eq.3}$$

Iron corrosion under both oxic and anoxic conditions is a process kinetically controlled. Corrosion rates are influenced by different parameters such as composition of the material, temperature, groundwater composition, presence and composition of gases, evolution of the surface (whether it has been previously corroded or not), etc. Corrosion products may form a protective layer on the steel surface, and cause a decrease of the corrosion rate with time, as observed from experimental data (Smart et al. 2010 and references therein). Steel corrosion rates used in this work are presented in Table 2 and have been selected after an extensive literature review.

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It is relevant to point out that fast corrosion of Al and Zn has been pessimistically neglected in the model approach. These metals are present only in very specific locations, not in all the waste packages, as Fe-bearing metals, and are therefore not considered to provide an important reducing capacity to the system in comparison with iron and steel.

3.1.2. Degradation of Organic Matter: bitumen, generic organic matter and cellulose.

Under highly alkaline conditions, bitumen can be subjected to microbially-mediated degradation (Zobell and Molecke, 1978; Roffey and Norqvist, 1991).

Biodegradation of bitumen is a complex process given that each of its components can degrade at different rates (Petersson and Elert, 2001; Pedersen, 2001). There is increasing evidence for the generation of soluble organic compounds from natural organic matter under hyperalkaline conditions (Claret et al., 2003; Elie et al., 2004). The constituents of the industrial bitumen such as that used in SFR1 repository (Petersson and Elert, 2001) are the same than those identified in natural bitumen and petroleum although they may differ in their proportions (Faure et al., 1999).

The conceptual model assumes that generic organic matter and bitumen are degraded under alkaline and near neutral conditions. Degradation is microbially mediated under biotic conditions and organic matter and bitumen are chemically degraded once abiotic conditions are achieved. Acetate is assumed as the main representative product of both microbial and chemical degradation.

Bitumen has been represented by the stoichiometry $C_{7.33}H_{10.91}O_{0.06}$ (Petersson and Elert, 2001) while the non-classified or generic organic matter reported in the waste packages has been attributed a generic composition of CH_2O. The same mechanism is considered for both "generic organic matter" and bitumen degradation (eq.4).

$$C_{7.33}H_{10.91}O_{0.06} + 7.28\ H_2O \rightarrow 3.67\ CH_3COO^- + 10.8\ e^- + 14.47\ H^+ \qquad \text{eq.4}$$

The three different generic microbial communities considered to be present in the repository (O_2- consumers (aerobes); iron reducing bacteria (IRB) and sulphate reducing

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bacteria (SRB)) contribute to the degradation of bitumen, generic organic matter, acetate and/or cellulose and also depend on these substrates to survive.

The biological activity of each microbial group is modelled according to the extended Monod growth model (Rittmann and Van Briesen, 1996; Sena, 2009) as shown in Table 2. Electron acceptors in the process are oxygen, ferric iron and sulphate. In order to implement the bacterial activity and growth in the system, a threshold concentration of 10^{-6}M for each one of these three electron acceptors has been defined, so that inactivity of aerobes is considered for oxygen concentrations below 10^{-6}M, inactivity of IRB is assumed for ferric iron concentrations below 10^{-6}M and inactivity of SRB for sulphate content below 10^{-6}M. These thresholds are in the order of values reported in the literature (McMahon and Chapelle, 2008; Small et al., 2008; Appelo and Postma, 2005; and references therein).

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Under abiotic conditions, that is, when electron acceptor concentrations are too low to keep microbes active, generic organic matter and bitumen are assumed to chemically degrade at a constant rate, equal to 10^{-12} mol dm^{-3} s^{-1}, two orders of magnitude below the biotic rate. Table 2 and Table 3 show the values of the parameters for these equations.

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In the model it is assumed that acetate generated during organic matter degradation microbially degrades to carbonate according to eq.5. As in the case of bitumen and generic organic matter, the acetate biotic degradation rate is controlled by the growth rate of aerobes, IRB and SRB and the availability of O_2, Fe(III) or S(VI) in solution. In agreement with the available information in the literature, it is assumed that acetate cannot further degrade abiotically. Thus, once abiotic conditions are achieved, acetate accumulates in solution and can precipitate in the form of $Ca(CH_3COO)_2$ (s) if oversaturated.

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$$CH_3COO^- + 4\ H_2O \rightarrow 2\ HCO_3^- + 9\ H^+ + 8\ e^- \qquad \text{eq.5}$$

Degrading cellulose is considered from a monomer of cellulose already hydrolysed ($C_6H_{12}O_6$ in eq.6).

Under oxic conditions, ($[O_2] > 10^{-6}$ mol dm^{-3}), these previously hydrolysed cellulose monomers degrade to carbonate, although this reaction is often not complete leading to acetate and carbon dioxide according to eq.7.

Under anoxic conditions, approximately 80% of the products generated in the degradation process of cellulose are isosaccharinic acid compounds (ISA) (Van Loon and Glaus,1994). For the sake of simplicity, eq.8 is used for cellulose degradation under alkaline anoxic conditions and has been defined after assuming that 80% of cellulose degrades to ISA and 20% to acetate.

Given the high aqueous concentration of Ca under cementitious conditions and the increase of aqueous concentration of ISA foreseen because of cellulose degradation, $Ca(HISA)_2$ (cr) can precipitate if oversaturated.

As in the case of bitumen and acetate, cellulose degradation under biotic conditions is controlled by the growth of O_2-, Fe(III)- and S(VI)-reducing bacteria and the availabity of O_2, Fe(III) or S(VI) in solution.

$$(C_6H_{10}O_5)_n + nH_2O \rightarrow n(C_6H_{12}O_6) \quad \text{eq.6}$$

$$C_6H_{12}O_6 + 2\ H_2O \rightarrow 2\ CH_3COO^- + 2\ CO_2\ (g) + 10\ H^+ + 8\ e^- \quad \text{eq.7}$$

$$C_6H_{12}O_6 + 0.40\ H_2O \rightarrow 0.8\ ISA + 0.4\ CH_3COOH + 0.4\ CO_2(g) + 1.6\ H^+ + 1.6\ e^- \quad \text{eq.8}$$

Glaus et al. (1999), Van Loon et al. (1999) and Glaus and Van Loon (2008) studied the abiotic degradation of cellulose under alkaline conditions and proposed that the peeling-off reaction is responsible for an initial fast reaction phase (between 2 and 3 years depending on the cellulose type), while a later slower phase depends on the amount of cellulose available for reaction (Glaus and Van Loon, 2008, Knill and Kennedy, 2003).

Based on the results of their experiment, Glaus and Van Loon (2008) proposed the kinetic law shown in eq.9, where celdeg is the fraction of cellulose degraded as a

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function of time, k_i different reaction constants and G_t the reciprocal of the starting degree of polymerization. This rate has been used in the present model.

$$celdeg_{cellulose} = 1+e^{-k_h t}\left[\frac{k_1}{k_h}(G_t)_o\left(1-e^{-k_h t}\right)-1\right] \quad \text{eq.9}$$

3.2. Flow, boundary and initial conditions

During the operational period, the repository is open to air, thus it is not water saturated. This study has been done assuming that the re-saturation is very fast after repository closure. According to Holmen and Stigsson (2001) the time needed for complete saturation of the repository is very short in comparison with the 100 ky considered in this study. It has been also considered that water is always available and accessible for chemical reactions.

Gases generated from corrosion of steel and chemical or microbial degradation of cellulose, bitumen and other organic materials such as H_2, CH_4 and CO_2(g) in case of non-alkaline conditions can dissolve in the contacting water. Gases will be able to form an individual gas phase and leave the system only in case an overpressure is created. The hydrostatic pressure at 70 m depth is 6.87 atm.

The numerical model neither considers the transport or diffusion of gases through the container wall nor the mechanical effects on the system that the presence of these gases can produce.

Initial porewater of the different waste package types is considered to be in equilibrium with atmospheric O_2, at P_{O2} of 0.21 atm, due to the construction and operational periods; and in equilibrium with portlandite in those cases where concrete has been used as waste matrix and/or groundwater has interacting with the repository structures (made of concrete) before reaching the waste. This occurs in all cases except for waste package

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Suprimit: **Table 2.** Kinetic rRates used in the calculations. Rates in mol dm^{-3} s^{-1}, except when indicated. Values for parameters listed in **Table 3.**¶
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O.12, for which initial waste porewater is considered to be a granitic porewater. Groundwater compositions are listed in Table 4.

The studied radionuclides are Se, Tc, Np and Pu which, besides U, are the main redox sensitive radionuclides present in SFR1. The analysis presented here has been conducted by assuming that the initial concentration of the radionuclides in the system is given by the dissolution of the complete inventory in the total void volume of the vaults (void volume is completely water saturated) (Figure 4).

3.3. Code and Thermodynamic Data Base

The model has been run with the code PHREEQC (Parkhust and Appelo, 1999) and the thermodynamic database SKB_TDB_2009. This thermodynamic database is based on the selection by Hummel et al. (2002) with modifications reported in Duro et al. (2006, 2010, 2012) for the sulphur, iron and carbonate systems"

3.4. Calculation of the Reducing capacity (RDC) of the system

Scott and Morgan (1990) proposed the concepts of OXidising and ReDucing Capacities (OXC and RDC) in analogy to quantities such as total acidity or alkalinity in the case of acid/base systems. They defined the reductive capacity as the sum of all reductants that can be oxidised by strong oxidants (e.g., O_2) to a preselected equivalence point, which is the Electron Reference Level (ERL). The RDC of a system gives, thereof, an estimation of its capacity to accept oxidants, i.e., is a chemical sum of the maximum amount of oxidants that the system is able to buffer.

The generic definition of RDC is shown in eq.10, where [Red] and [Ox] are, respectively, the concentration of reducing and oxidising species present in the system, and n_i and n_j are the number of electrons involved in the redox reactions.

$$RDC = \sum_i n_i \times [Red] - \sum_j n_j \times [Ox] \qquad \text{eq.10}$$

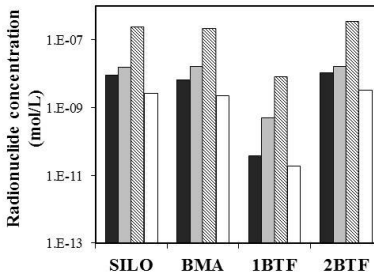

Figure 3. **Calculated concentrations of Np, Pu, Tc and Se resulting from dissolving the complete inventory in the saturated void volume.** ¶

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Suprimit: Table 4**.** Composition of the cementitious and granitic porewater used in the calculations. *From SKB (2008). &From Salas et al. (2010).¶

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554 Given the relevance that the iron system has in this environment, we have defined as
555 electron reference level the most oxidised form of iron, Fe(III). By considering this,
556 eq.11 and eq.12 are used to calculate both terms of eq.10.
557
558 $\sum n_i \times [Red] = [Fe(0)] \times 2 + [Fe(II)(aq)] \times 1 + [magnetite] \times 1 + [HS^-] \times 8 + [bitumen] \times$
559 $11 + [organic\ matter] \times 11 + [cellulose] \times 3.2 + [acetate] \times 8 + [H_2] \times 2$ eq.11
560
561 $\sum n_j \times [Ox] = [O_2] \times 4$ eq.12
562 Given the uncertainty existing on the reactivity of $H_2(g)$ and on the role of bitumen as
563 reducing agent fast enough to occur in the timeframe and under the conditions of the
564 assessment, the contribution of $H_2(g)$ to the RDC of the system has not been included in
565 the calculation of RDC and in some cases the RDC has been calculated with and
566 without considering bitumen in the formulae.
567
568 ## 4. RESULTS AND DISCUSSION
569
570 According to the redox processes considered in the model, different groups of waste
571 package types can be identified:
572 - waste package types in which only steel corrosion is considered (R.16, R.15 and
573 S.13);
574 - waste packages where both corrosion of steel and degradation of generic organic
575 matter are considered (O.02, R.01 and B.07/O.07);
576 - waste package types where both corrosion of steel and degradation of bitumen
577 are considered (B.06, F.18, F.05 and F.17);
578 - waste package types where besides the previous processes, cellulose degradation
579 has also been included (O.23, F.23, B.05 and O.12).
580
581 Initial concentrations differ among the waste packages types as shown in .
582 In all package types except O.12 in vault BLA pH is buffered to 12.5 due to the
583 equilibrium with portlandite, which also controls Ca^{2+} aqueous concentration.
584
585 A comparison of the time evolution towards reducing conditions depending on the
586 different redox processes considered is shown in Figure 5. As can be seen, low redox

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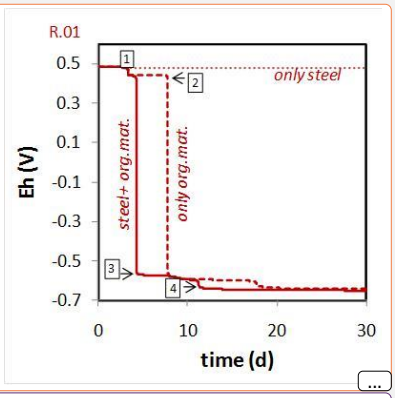
potentials are reached much faster when considering the processes of degradation of organic matter than when only steel accounts for oxidant consumption. This is a consequence of the different kinetics of the reactions responsible for oxidant depletion. In all those waste package types containing organic matter, the oxic period is very short (about 3.3 days). In its absence, the period exceeds 30 days, because O_2 consumption by steel corrosion is slower. In the case of O.12, where neutral pH conditions prevail, the higher steel corrosion rates shorten the oxic period to less than one day.

Figure 6 shows the evolution of the redox potential in a waste package in which steel corrosion is responsible for oxidant depletion. Three different stages can be appreciated: oxygen consumption, sulphate consumption and anoxic corrosion of steel. Initially, the corrosion of steel under oxidising conditions generates goethite. Further steel corrosion causes goethite consumption and formation of magnetite and hydrogen.

The time at which all the steel initially present in the waste package is corroded depends mainly on two factors: the initial amount of steel and its reactive area. Figure 7 shows the time period needed to corrode all the steel present in the packages. In two of the modeled cases steel is not predicted to corrode completely, even after the 100 ky of the assessment. That implies that the RDC of the system provided by steel will remain for long periods of time.

The degradation of organic matter in the system has several consequences of interest for the assessment, such as the production of organic compounds that may have implications in the behaviour of radionuclides due to their ability to form complexes. Once O_2 concentration is depleted, the degradation of generic organic matter, bitumen and acetate occurs mediated by SO_4^{2-} reducing bacteria (SRB). The biotic period is considered to finish when sulphate concentration falls below 10^{-6}M. Once SRB are no longer active, the degradation of generic organic matter or bitumen to acetate occurs following an abiotic rate, which is considered constant with time ().

In the absence of microorganisms, acetate is not allowed to degrade to CO_2 in the model, thus accumulates in solution. The same applies to ISA produced by the degradation of cellulose under abiotic conditions. The consequence is that acetate and



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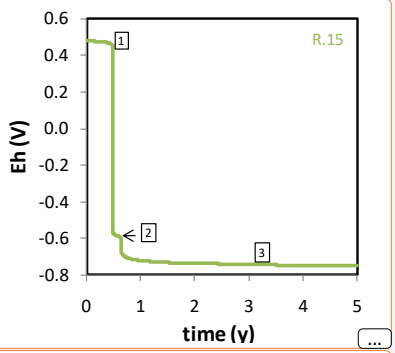

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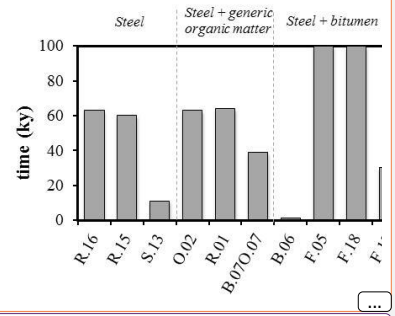

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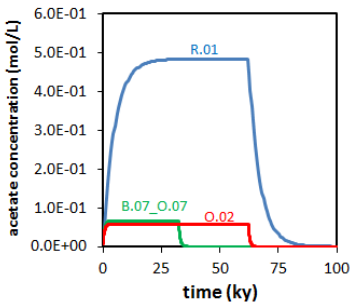
ISA accumulate in solution until precipitation of Ca-acetate and/or Ca-isosaccharinate occurs. After 5 years, the maximum calculated concentrations of acetate and ISA achieved are $6 \cdot 10^{-4}$M and 5×10^{-3}M respectively. In the long-term, higher concentrations are calculated. Acetate reaches a maximum of 0.5M. Due to the high solubility of acetate solids, no acetate is predicted to precipitate and the maximum concentration of this compound in the system is given by the steady state reached between its generation and the flow rate at which it is being transported out of the system. An example of the evolution of the concentration of acetate in solution is shown in Figure 8 or different waste packages. In contrast, in Figure 8a the organic matter is completely degraded thus acetate is no longer generated and it is being transported out of the system while in Figure 8b the organic matter generating acetate (bitumen in this case) is never completely degraded and the concentration of acetate reaches a steady state.

Cellulose is completely degraded before 7 ky after repository closure in three out of the four waste packages containing cellulose. The concentration of ISA in all cases is limited to 1.6×10^{-2} mol/L due to the precipitation of $Ca(HISA)_2(cr)$ in the presence of calcium concentrations given by equilibrium with portlandite.

In the case of O.12, where granitic groundwater instead of hyperalkaline groundwater is contacting the waste, the Eh is kept at a less reducing value than in the other cases (-0.34 V). Due to the carbonate content of the contacting water, the main corrosion product of steel is in this case siderite.

The anoxic corrosion of steel has, as a consequence, the production of $H_2(g)$ at expenses of water reduction. $H_2(g)$ is the most abundant gas generated in the system. According to the model constraints, hydrogen dissolves and accumulates in solution until the total gas pressure exceeds the hydrostatic pressure of the repository (6.87 atm). Then H_2 aqueous concentration is kept constant and in equilibrium with $H_2(g)$. Figure 9 shows the calculated volume of gas generated in the system. The production of $CO_2(g)$ is only relevant in the case of the O.12 waste package (10% vol.) due to the lower pH of the contacting water.



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Neither concrete degradation, nor the formation of other corrosion products other than goethite and magnetite are considered in the calculations. Both processes can, however, have an important control on the pH or the Eh finally achieved in the repository. Table 5 shows the Eh/pH field framed by the different redox couples more likely to exert the redox control in the repository at the different pH values that porewater can reach due to concrete degradation. In all cases reducing redox potentials are developed. Only in the case of considering ferrihydrite (HFO) as the oxidation product of magnetite (extreme case considering the modeling time), mildly reducing potentials could be attained.

4.1. Evolution of the Reducing Capacity (RDC) of the waste package types.

The initial RDC in the system is given by steel and the different type of organic matter considered (generic organic matter, bitumen and cellulose).

Steel is considered to corrode mainly to magnetite (except under the conditions of O.12 where siderite is formed) that, due to its Fe(II) content, still presents RDC. The length of the period during which steel is the main contributor to the RDC (Figure 10) depends on the rate of steel corrosion, which is in turn dependent on the reactive surface of the steel, as well as on the initial amount of steel in a given waste package type.

In spite of the potential role that organic matter or bitumen can have in the reductive capacity of the system, the uncertainties on their degradation kinetics might decrease their effective role down to insignificant values. For this reason, the RDC of the waste package types containing organic matter or bitumen besides steel has been calculated with and without considering the contribution of organic matter or bitumen remaining in the waste. Therefore, main contributors to the RDC are also in this case steel and magnetite. As already mentioned, observed differences between the RDC of the different waste package types depend on the amount of steel and its reactive surface.

Cellulose is totally degraded before 7 ky except in one of the waste packages (F.23), where the contribution of cellulose to the RDC of the package is relevant in the time period assessed (Figure 10).

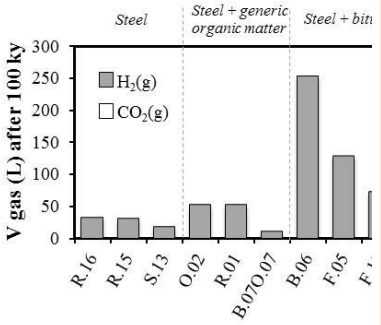

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Figure 8. **Gas volume generated after 100,000 ky years in each one of the waste package types.**¶

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Suprimit: **Table 5.Table 5.** Range of redox potential calculated depending on the active couple considered to control the system and the pH marked by the degradation of cementitious materials. A specific calculation is indicated for O.12, with no cementitious materials present. Fe_2O_3: hematite; FeOOH: goethite; Fe_3O_4: magnetite; HFO: ferrihydrite.¶
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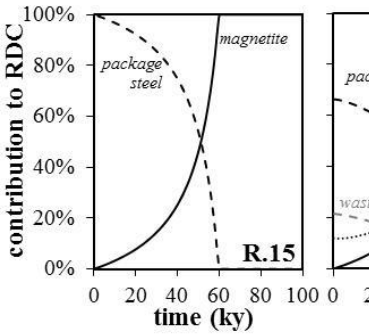
4.2. Evolution of the Reducing Capacity (RDC) of the repository.

The evolution of the overall RDC of the different vaults of the SFR repository has been estimated by considering the number of each type of waste packages in each vault.

Figure 11 shows the temporal evolution of the RDC for the four vaults and for the Silo of the SFR repository. In the early times of evolution, BLA presents the highest RDC of the repository, BMA is the vault most contributing to the RDC of the repository at intermediate and long-term, and 1&2BTF and BLA are the vaults with the lowest RDC values in the long-term, therefore the most susceptible of losing the reducing conditions under the event of an oxidant intrusion). In none of the cases the RDC goes to zero, showing that after 100 ky, under non-disturbing conditions, the system is sufficiently robust as to keep the reducing conditions imposed by the process of steel corrosion.

Steel corrosion rates available in literature span over more than 4 orders of magnitude depending on the type of material studied, the conditions imposed and the methods used in the steel corrosion rate determination (measurement of the hydrogen evolution, current intensity, and metal loss or gain).

Data in Smart et al. (2004) have been used to define the Probability Distribution Function (PDF) for steel corrosion rate under alkaline conditions. In the light of the existing corrosion rates, a PDF of the natural logarithm of the rate (in µm/y) with an average of -2.61 and a standard deviation of 0.60 has been determined. Sensitivity calculations have been conducted with the waste package type S.13, and the software MC-PHREEQC (de Vries et al., 2012) which provides a way to conduct Monte-Carlo simulations automatically. The results can be seen in Figure 12 for 4 different times. The RDC of S.13 waste package type after 100 ky is not very affected by the uncertainty in the corrosion rate, given that steel has been already completely corroded and the remaining RDC is provided by magnetite. For a corrosion rate of 2×10^{-10}



Suprimit: Figure 9. **Contribution of magnetite, steel, cellulose and siderite to the calculated RDC (in %) in the waste package types R.15, F.23 and O.12.**¶

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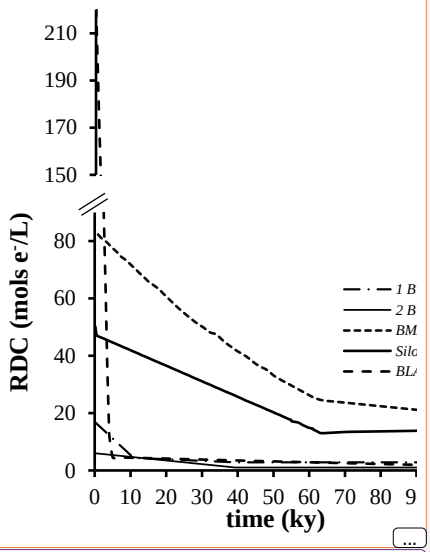

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mole/m^2/s (0.05 μm/y) after 5ky the RDC remaining only relies on magnetite, while when the rate is 1×10^{-10} mole/m^2/s (0.025 μm/y) steel is still present in the system after 5ky and provides additional RDC to the system. As expected, for short time periods, higher RDC are obtained for lower corrosion rates.

The effect of a glacial event in the RDC of a waste package type has been tested with the S.13 waste package type. As seen in Figure 7, steel contained in S.13 is completely corroded around 11 ky after the closure of the repository. From this moment onwards, most of the RDC of the system is provided by magnetite. In SKB (2008) it was considered that the earliest melt water flow will occur at 60ky after the closure of the repository. Glacial groundwater (composition in Table 4) has been assumed to flow through the S.13 from the moment of the glacial event (after 60ky of the deposition of the wastes) to the end of the period of interest (100 ky), that is for a period of 40 ky.

The results of the calculation indicate that at the end of the assessment period of interest (100 ky) the system has not been depleted of its RDC, which is equivalent in this simulation to say that not all magnetite has been transformed into goethite and, therefore, the system is still able to buffer an oxidant intrusion (Figure 13). After 40ky of infiltration of meltwater, the amount of magnetite oxidised into goethite is 95%, and 5% of the magnetite remains unoxidised.

The amount of magnetite in the system provides enough RDC as to counteract an O_2 intrusion for more than 50 ky. After this period Eh increases.

4.3. Assessment of the behaviour of Se, Tc, Np and Pu

4.3.1. Selenium

Se speciation is dominated by Se(-II) species, mainly HSe^- in the reducing period of time. Neither the presence of acetate nor ISA in solution affects the Se aqueous speciation. The most favoured solid phase to be formed under the conditions of the assessment is Se(cr), if the concentrations of Se are high enough. Depending on the

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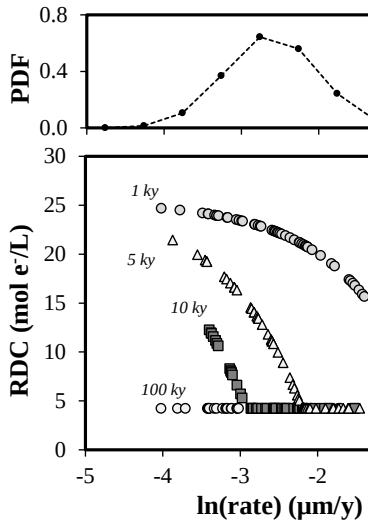

Suprimit: Figure 11. **Variation of the RDC due to changes in steel corrosion rate accordingly to the PDF function calculated for S.13 waste package type at different times.** ¶

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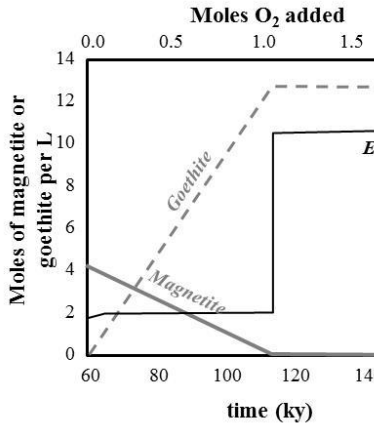

Suprimit: Figure 12. **Evolution of the molesamounts of magnetite and goethite in S.13 waste package type and the value of the redox** ...

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concentration of Fe present in the system, Fe(II) selenides can form, reducing the mobility of Se. According to the available thermodynamic data, the precipitation of these phases will require concentrations of Fe in solution higher than the ones calculated to be present in the system.

As shown in Figure 14, vaults inventories are lower than calculated solubilities except for the BLA, where the formation of metallic Se could account for a more effective retardation mechanism than for the other vaults. Therefore, the most likely retention mechanism for Se is not expected to be precipitation, but interaction with solid surfaces of the system.

4.3.2. Technetium

As in the case of Se, no influence of ISA or acetate on the chemical behaviour of Tc under the conditions of interest is expected. Under reducing conditions Tc can precipitate as $TcO \cdot 1.63H_2O(s)$, while under oxidising conditions Tc is mainly soluble as Tc(VII), forming the oxyanion pertechnetate (TcO_4^-). Under reducing conditions the main aqueous species are $TcO(OH)_2(aq)$ and $TcO(OH)_3^-$.

In the BLA vault, the Tc inventory is below the calculated solubility limit in all cases, implying that Tc will not be solubility limited in this vault (Figure 14). In the case of 1BTF, the inventory is either below of very close to the solubility limit (6.7×10^{-9}M), indicating that solubility will neither be an important retardation process for Tc in this vault.

Regarding the SILO, BMA and 2BTF vaults, the calculated solubility is below the inventory only in the case of pH = 10.5, that is when concrete has been degraded to CSH. This would also point towards other retardation processes, such as sorption on the surface of cement degradation phases or iron corrosion products, as mainly contributing to the retention of Tc in the system.

4.3.3. Neptunium

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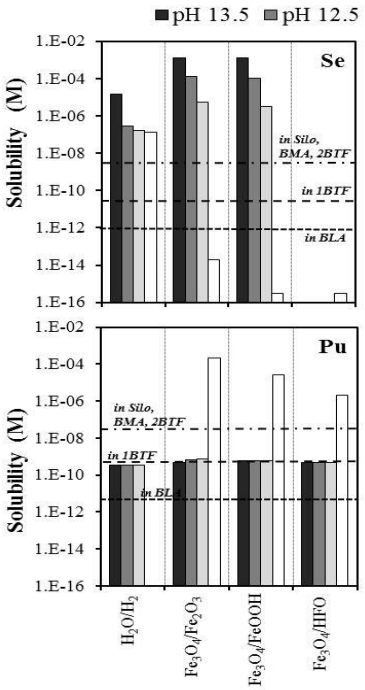

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Figure 13. **Comparison between dissolved inventory of Se, Tc, Np and Pu in the different vaults (dashed lines) with the solubility of these radionuclides assuming the formation of the most stable phase under the geochemical conditions expected in the vaults.**¶

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The most likely solid phase that can be formed under the conditions of the assessment is the tetravalent $NpO_2 \cdot 2H_2O(am)$ whose precipitation occurs at concentrations above 10^{-9} M in the absence of organic ligands. The effect of acetate on the Np solubility is negligible at the acetate concentrations calculated in the SFR. At pH 12.5 and reducing Eh value, an increase of the concentration of ISA produces the predominance of aqueous complexes of Neptunium with ISA and causes an important increase in the solubility of this solid (see Figure 15 and Figure 16a). The high concentration of Ca imposed by the equilibrium portlandite, favours the precipitation of calcium isosacharinate and limits the concentration of ISA available for Np complexation, as shown in Figure 16a. The inventory of Np in 1BTF and in BLA is below the solubility limit of Np under all the conditions of the assessment, what means that the most relevant retention processes in these cases will not be precipitation of secondary phases but sorption onto the surface of the major solid phases present in the system, presumably cement and its degradation products as well as iron oxides (Figure 14).

In the case of the SILO, BMA and 2BTF, the inventory of Np is slightly above the calculated solubility of Np, thus setting the control of the Np concentration to values about 10^{-9} moles/L given by the solubility of Np(IV) oxides.

4.3.4. Plutonium

Pu(IV) and Pu(III) species dominate the speciation of Pu and the precipitation of $PuO_2 \cdot 2H_2O(am)$ is favoured under the conditions of the assessment. Acetate complexes are only relevant for pH below 9.5 and in the absence of calcium. As in the case of Np, the concentration of Ca in equilibrium with portlandite produces the precipitation of calcium isosaccharinate and limits the concentration of ISA available for the complexation with Pu (Figure 16.b).

The inventory of Pu in the wastes is definitively over the calculated solubility limits for the SILO, BMA and 2BTF vaults. If neglecting the effect of organics in the vaults, the maximum concentration of Pu in the SILO, BMA and 2BTF can be limited to values around 10^{-9} M due to the precipitation of Pu(IV) oxides under the conditions of pH and Eh covered by this assessment. Nevertheless, the solubility of Pu in the presence of ISA would be increased to values around 10^{-6} M, thus the concentration of Pu in solution

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will be controlled either by the inventory or by sorption processes also in the case of the SILO, BMA and 2BTF vaults (Figure 14).

5. CONCLUSIONS

The main purpose of the work presented here has been the development of a methodology to assess the evolution of the redox state and the RDC of a complex system containing different redox active materials over long time periods. The case used for the development of the model has been the SFR1 intermediate and low level waste repository of SKB (Sweden).

The modular configuration applied in the model, by evaluating the individual evolution of the waste packages and combining them to obtain the evolution of the vaults and the complete repository can be transferred to a different geometrical and compositional set-up of the system. This transferability becomes especially relevant in the case of changes in the actual composition of the waste inventory at the time of closure of the repository, or to possible extensions of the SFR1 disposal facility.

The RDC of the system is mainly provided by steel and organic matter but even under the assumption of redox inertness of bitumen, the assessment shows that the metal content of the waste packages is enough as to provide RDC for the complete time of the assessment (100 ky). Corrosion of steel keeps the system under reducing conditions for long time periods. The role of organic matter is important, especially at the initial stages after repository closure, when microbial activity contributes to a fast oxidant consumption through degradation.

The redox potential in the vaults is calculated to evolve from oxidising at very short times, due the initial oxygen content, to very reducing at times shorter than 5 years after repository closure. The redox potential imposed by the anoxic corrosion of steel and hydrogen production is on the order of -0.75 V at pH 12.5 in case of assuming that the system responds to the Fe(III)/Magnetite equilibrium. The uncertainty in the response of

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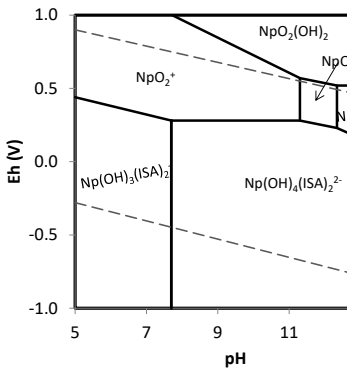

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Figure 14. Predominance diagram of aqueous species of neptunium in equilibrium with $NpO_2 \cdot 2H_2O$ (am) in the presence of 0.016 mol/L of ISA.

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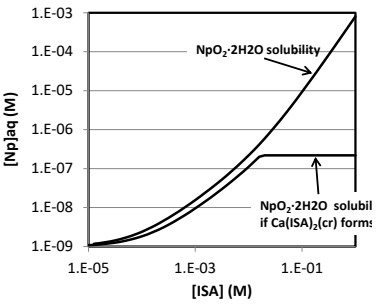

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the system to a given redox pair combined with the uncertainty regarding the pH evolution due to concrete degradation brackets the redox potential in values where the redox sensitive radionuclides are it their most immobile form.

The production of acetate from the degradation of organic matter is not calculated to affect the mobility of radionuclides, while that of ISA from cellulose degradation can increase the solubility of plutonium and neptunium up to two logarithmic units.

Most of the gas volume produced is hydrogen, caused by the anoxic corrosion of steel-related materials, while carbon dioxide only accounts for a maximum of a 10% of the total volume produced in the waste packages kept at non hyperalkaline values.

Simulations assuming presence of oxic water due to glacial melting, intruding the system 60 ky after repository closure, indicate that magnetite is progressively oxidised, forming Fe(III) oxides and that the system is effectively able to buffer a continuous inflow of oxygen for long periods of time.

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6. ACKNOWLEDGEMENTS

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This work has been financially supported by SKB (Sweden). I.Puigdomènech, K. Spahiu, P. Wersin and J. Carlsson are greatly acknowledged for their helpful comments that contributed to improve the quality of the model. J. Molinero, A. Nardi, L.M de Vries and P. Trinchero from Amphos 21 have collaborated in the sensitivity analyses of steel corrosion rate and in the 3D representation.

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