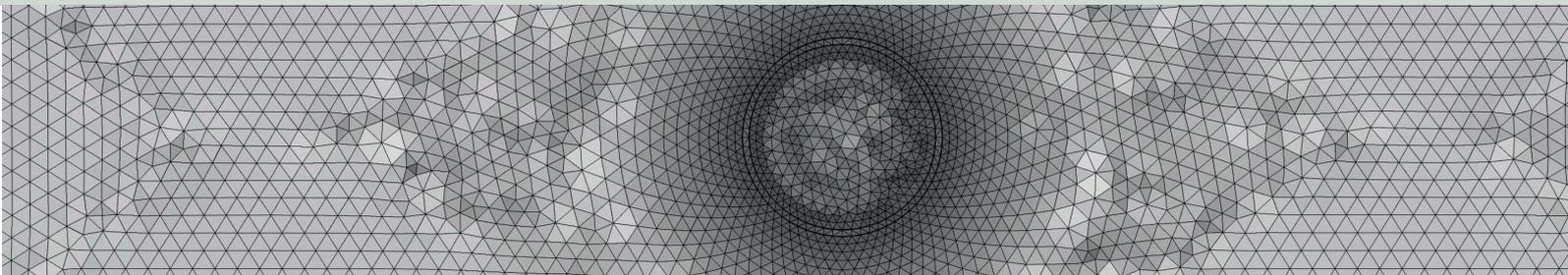




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Swiss Federal Nuclear Safety Inspectorate ENSI



Expert review of Waste and Near-field topics

Expertenbericht

im Rahmen der Beurteilung des Vorschlags von mindestens zwei geologischen Standortgebieten pro Lagertyp, Etappe 2, Sachplan geologische Tiefenlager

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Disclaimer:

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Expert review of Waste and Near-field topics

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1. Background and Objectives

Amphos 21 has received a *Task description for ENSI experts* to review part of the documents delivered by NAGRA to ENSI, focused on waste form and near-field issues.

This document contains the draft final report of the expert review, in line with the indications received from ENSI.

The general objective of ENSI within this work is quoted below:

The derivation of representative model parameters for the provisional safety analyses in stage 2 (a complete safety analysis will be required for the general license application in stage 3) is an important step in the assessment of the safety of a deep geological repository. The evaluation of the parameters involved in the geochemical processes of the near field of spent fuel and high-level waste (technical barriers and their interactions with the host rock) are part of this preliminary study. A careful review is necessary to verify if all safety relevant geochemical processes and their consequences on the near field are considered.

The focus should be on processes with possible negative influences on the near field behaviour like the reduction of the sorption capacity of barrier materials or the acceleration of metal corrosion, spent fuel dissolution and glass dissolution.

The specific objective of this work is to provide an expert review on the work conducted by NAGRA regarding the following issues:

- High level waste glass dissolution
- Spent fuel dissolution
- Interaction of bentonite with concrete and iron, focused on reduction of the sorption capacity and swelling capacity, clogging of porosity for gas and water flow.

ENSI is specifically interested in obtaining answers to the following questions:

-
1. Whether the information and data presented by NAGRA on this topics is sufficient and in accordance with the current state-of-the-art and whether the assumptions followed by NAGRA are well balanced in terms of conservatism
 2. Whether the appraisal made by NAGRA on these processes for the long term near field evolution is comprehensive and correct in the light of the current state-of-the-art

An additional question that ENSI would like to have answered is:

3. Whether NAGRA has considered all relevant processes for the long-term evolution of the HLW/SF near field with respect to radionuclide release.

The answer to these questions is provided along the report.

2. Methodology

As per the request of ENSI, the main report to review is:

- NTB 12-01: The Long Term Geochemical Evolution of the Nearfield of the HLW Repository, Nationale Genossenschaft für die Lagerung radioaktiver Abfälle, Nagra Technischer Bericht, Wettingen, 2014.

And other NAGRA reports of relevance are:

- NTB 13-02: An Assessment of the Impact of the Long Term Evolution of Engineered Structures on the Safety-Relevant Functions of the Bentonite Buffer in a HLW Repository, Nagra Technischer Bericht, Wettingen, 2014
- NAB 13-37: A model for radionuclide release from spent UO₂ and MOX fuel, Nationale Genossenschaft für die Lagerung radioaktiver Abfälle, Nagra Arbeitsbericht, Wettingen, 2013.

Our team has considered all those relevant information to provide the best answers to ENSI's request, including reports of other waste management organisations such as SKB, ANDRA, NIRAS/ONDRAF and POSIVA among others, as well as scientific and technical literature of relevance. The close participation of Amphos 21 with other national programmes has facilitated the access to the information and the understanding of the level of discussion required by ENSI.

A preliminary review of the NTB 12-01 report was submitted to ENSI by Amphos 21 on June the 25th. On June 27th, a meeting was held between ENSI and Amphos 21, with participation of:

- ENSI: B. Graupner and A.K. Leuz
- Amphos 21: L. Duro, J. Bruno and D. Arcos

During the meeting, the main comments to the NTB 12-01 report were presented and discussed. The preliminary review consisted on a deep understanding of the report and Amphos 21 highlighted the weaker points of the above mentioned document.

ENSI indicated that focus must be on identifying whether all the relevant processes had been considered for each one of the subsystems of the near field and whether the approaches followed by NAGRA and the values used for the relevant parameters were up-to-date and according to the state-of-the-art.

With the aim to provide a clear answer to the questions put by ENSI besides facilitating the identification of the relevant points raised during the review, the structure of this expert review report mimics that of the original NTB 12-01.

3. General overview of the evolution processes in a SF/HLW nearfield

No comments are necessary on this section, although we keep it as a separate chapter for the sake of maintaining the structure of the main report under review.

4. "Initial states"

In the "initial states" chapter of the NTB 12-01 report, the initial composition of the various components of the system is described.

It is somewhat concerning that the mineralogy of the MX 80 is taken from a primitive reference by Müller-Vonmoos and Kahr (1983), while more exhaustive characterizations have been performed lately. Even if MX-80 is only a reference bentonite the characterization used in the analysis of its evolution in the near field should be more complete and up to date.

There are two aspects that deserve some attention:

1. In the reference from Müller-Vonmoos & Kahr (1983) the analytical techniques used do not have the precision of present-day techniques, especially for the quantification of accessory minerals.
2. As MX-80 bentonite is a natural material, its composition is heterogeneous and, therefore the compositional range of this material deserves some discussion, especially if some of the key accessory minerals can be absent in some parts of the rock formation.

As an example of the previous comment, the mineral composition analysed by different authors is presented in Table 1.

Table 1. Different analyses of bentonites in the literature. Data in %wt.

Phase	Müller-Vonmoos & Kahr (1983)	Madsen (1998)	Karnland (2010)	Kumpulainen & Kiviranta (2011)		
				ABM MX80	WyMX80	Volclay
Montmorillonite	75.0	75.5	81.4	81.3	77.5	79.1
Illite			0.8	0.5	0.6	0.6
Kaolinite	<1					
Calcite	0.7	1.4	0.2	0.5	0.7	3.1
Gypsum			0.9	0.7	1.2	1.3
Muscovite		<1	3.4	5.3	8.3	8.3

K-Feldspar	5-8	5-8				
Plagioclase			3.5	1.5	2.3	1.7
Pyrite	0.3	0.3	0.6	0.7	0.8	0.6
Siderite	0.7					
Quartz	15.2	15	3.0	3.8	4.8	4.4
Cristobalite (SiO ₂ (am,c))			0.9	1.9	0.4	0.5
Tridymite (SiO ₂ (am, t))			3.8	2.6	1.6	1.9
Hematite					0.4	0.1
Magnetite				1.2	1.4	1.1
Anatase				0.1		0.2
Zircon					0.1	0.1

According to this table, differences between the content of some accessory minerals can result in very relevant differences on the expected geochemical evolution of the system (i.e. the large variability of calcite or the presence/absence of gypsum or siderite).

Therefore, we recommend to perform the calculations on geochemical evolution by considering this range of mineral content, which can result in a sensitivity analysis on the geochemical behaviour of the system based on possible mineral heterogeneities of the bentonite.

A similar reasoning should be taken into account when considering the cation exchange capacity. There are several values in the literature, depending on different authors and publications, most of the differences can be attributed to the heterogeneity of the material (i.e. montmorillonite content, variability in cation distribution, etc.). This variability must be considered and, as in the case of the mineralogy, the impact on the geochemical evolution must be evaluated.

The consideration of porosity (total vs. anionic) has not been discussed in detail in the report, only a brief discussion is found in Appendix C. It is stated that anion porosity is the only porosity available for reactions, indicating that this assumption is “consistent with the current understanding on the behaviour of water in compacted bentonite”. However, far from being the “current understanding”, it is a matter of controversy, and there are different views of the transport pathways in compacted bentonite (Bourg et

al., 2007; Holmboe et al., 2012; Holmboe & Bourg, 2014) depending on whether all porosity is considered as equivalent for diffusive transport or whether two types of porosity are considered: one accessible for both, anions and cations, and another only accessible to cations. This last assumption implies there are two different types of pore water. In our understanding, it is necessary to highlight this controversy and indicate why NAGRA selected this assumption.

There is no discussion in this point about the degree of water saturation and the expected saturation times, which are discussed in later parts of the report but without an explicit statement on the definition of the initial state of saturation at the onset of the calculations. In this respect, NAGRA should provide an explicit statement on the saturation state of bentonite at disposal, so that the evolution can be assessed accordingly.

The composition of the Opalinus Clay is well represented by the selected reference mineralogy of Traber and Blaser (2013), although some discussion on the heterogeneity of the mineral composition of such a rock formation could be of interest, especially considering that some accessory minerals can play a role on the geochemical evolution of the system, as already pointed out above.

The chemical composition of the Opalinus pore water is discussed and the reference compositions as calculated by Mader (2009) appear to be reasonable.

The composition of the ESDRED shotcrete and the equilibrium pore solution are taken from Berner et al. (2013). We have traced the derivation of the so-called ESDRED “low pH” shotcrete to Berner et al, 2013. The details of the cement composition are given as supplementary material of the publication. When looking at the details of the composition there a few points that deserve discussion.

The composition of the low alkalinity cement arises from the work by Lottenbach and Winnefeld (2009), published as an EMPA Technical Note. A few changes are introduced by Berner et al. (2013) on the composition established by EMPA. The most relevant to our discussion are the ones concerning the substitution of Glenium 51 and

Sigunit L53 by chloride and inert quartz in the proposed composition. Glenium 51 is a polycarboxilate superplasticiser used in the cement formulation to improve workability. Sigunit L53 is an alkali-free accelerator for shotcrete applications. Both materials contain organic compounds in their composition and degrade into different organic compounds with temperature, radiation and pH changes. Glenium 51 contains sodium, sulphate and organic carbon in the form of more or less complex carboxylates (Lottenbach and Winnefeld, 2009). The nature of the organic fraction of the carboxylate is not known. In their simulation of the chemical evolution of cement, Berner et al. (2013) incorporated sodium and sulphate from Glenium 51 and, instead of using an organic polycarboxilate of unknown nature, decided to use chloride to compensate for charge imbalance. This approach can serve the purposes of charge balancing, although it neglects the influence that the degradation of the carboxylate compounds can have on the complexation of radionuclides. Carboxylates are normally species prone to complex metal ions, so that an increase of radionuclide mobility would be expected in the presence of this type of organic compounds. Sigunit L53 contains, besides aluminium sulphate and formiate. As in the case of Glenium 51, Berner et al. (2013) decided to represent aluminium formate as aluminium hydroxichloride to preserve charge. Formiate also has the tendency to form complexes with some radionuclides, so that this substitution would also neglect the potential mobilization effect of the organic compounds in the cement composition. NAGRA should explain how these substitutions could affect the proposed chemical evolution of the near field and the potential radionuclide mobility.

5. Interaction of a low pH concrete tunnel liner with Opalinus Clay and bentonite

General comments on the different sections of issues related with the interaction between low pH concrete and Opalinus Clay and bentonite are presented below.

The model performed to evaluate the geochemical evolution of the system has certain conceptual aspects that need some discussion and justification.

One of these aspects is the consideration of montmorillonite (and other clay minerals) to dissolve or precipitate under thermodynamic equilibrium considerations. The thermodynamic equilibrium approach is not appropriate for clay minerals, as they are metastable under a wide range of conditions. Moreover, the mechanism of clay mineral formation has been widely discussed over decades. Some authors claim that, at low temperatures, clay minerals can only form due to alteration of other silicates, and they cannot precipitate directly from a solution.

Despite these considerations, clay minerals can be considered into models using three different approaches:

1. Thermodynamic equilibrium, considering them as single phases or different degrees of solid solutions (modifications only for cations in the interlayer space, modifications also in the octahedral sites, or modifications in all positions, including tetrahedral sites).
2. Dissolution – precipitation following a kinetic approach, although precipitation has to be considered with care. This approach can also consider cation exchange reactions by associating surface sites to the amount of clay mineral available at each time step.
3. Considering that clay minerals do not dissolve and only cation exchange reactions occur. This could be valid for models simulating relatively short time periods, or under relatively stable chemical conditions for which clay minerals can be considered under near-equilibrium conditions.

Experimental laboratory data, as well as information gathered from natural analogues, indicate that the effect of very alkaline solutions on the mineral composition of bentonite is mainly the precipitation of CSH phases and hydroxides (brucite) in the

vicinity of the contact and the precipitation of zeolites further into the clay barrier (NF-PRO, 2008a, b; Savage et al., 2011; Savage, 2013). Also some clay transformations can occur, with changes in the octahedral sites. It is worth noting that for low-pH concrete, the leachates do not show the first two typical stages of OPC degradation (alkalis leachate and portlandite dissolution). Instead, the CSH degradation stage occurs from the beginning, which results in a much less aggressive solution, leading to less pronounced changes than in experiments and natural analogues.

The consideration of thermodynamic equilibrium of clay minerals can lead to an unrealistic increase of the clay mineral content as well as produce different pore water compositions (a net clay content increase can be observed in Figs. 5.5 to 5.8 of NTB 12-01, mainly due to excess of montmorillonite precipitation). This precipitation of montmorillonite inhibited the possible precipitation of Mg-hydroxides, CSH phases and zeolites, as montmorillonite acts as a sink for Ca, Mg, Al, Si. Therefore, the results from the model will be unrealistic as their effects on the bentonite are not the same as those observed in experiments or natural analogues, so the conclusions extracted could be erroneous, although the clogging of the porosity also observed in experiments can be reproduced, but as a result of different geochemical processes.

Also considering the third option, non-reactive clay minerals except for cation exchange, will lead to erroneous results. If clay minerals are not allowed to dissolve, their potential source of Al and Si and other elements will not occur, inhibiting the precipitation of CSH, hydroxides and zeolites.

It is therefore necessary to consider clay mineral dissolution – precipitation following a kinetic behaviour, whereas cation exchange can be considered in different ways, as a fixed CEC value or associated to the clay content.

Finally, the consideration of “low pH-cement” implies that the initial states of degradation of OPC are not occurring, thus less pronounced changes in the surrounding environment are expected. The initial conditions of the OPC degradation include an OH concentration of 0.1 M compared to the millimolar level of “low-pH

cement". Likewise, the concentrations of alkali cations (K + Na) are much lower, which is bound to give a different (smaller) degree of alteration.

6. The elevated temperature period

In this chapter, the effects of the heat induced by the waste on the near field are discussed. The geochemical processes are based on those described in Wersin et al. (2007). However, in Wersin et al. (2007) the focus is on irreversible temperature-induced effects on mineralogical and macroscopic physical properties. Among the processes reviewed are illitisation and chloritisation of smectite and cementation. Wersin et al. (2007) indicate that illitisation and the associated cementation is not likely to occur at temperatures below 150°C. Also the chloritisation process in the near field is discarded. The only relevant process to occur, based on natural analogues and experimental data, is the transformation of smectites into beidellite, saponite or dehydrated smectite in the vicinity of the canister, although some of these transformations are associated to the availability of iron (i.e. canister corrosion).

Long-term experiments for the thermal period have been performed at small scale (Villar et al., 2008, 2010; Gens et al., 2009; Villar & Gómez-Espina, 2015) and under large-scale underground laboratories (Karnland et al. 2009a & b; Sena et al, 2010; Svensson et al., 2011, Salas et al., 2014). From these experiments, run in some cases for up to 8 years, it was shown that some very relevant changes occurred on both the macroscopic physical properties of the bentonite and the geochemical evolution of the system, something that had not been clearly indicated in Wersin et al. (2007). The most relevant changes affect the water content, dry density and the geochemistry of the bentonite. Geochemical changes are related to dissolution and re-precipitation of highly soluble minerals, loss of exchangeable positions in the smectite and fast changes in the cation occupancy in the CEC. It is worth noting that replacement of Ca by Na in the CEC of the smectite have some consequences on the swelling capacity of the bentonite, as well as on the capacity to sorb radionuclides in the cation exchange sites. These changes, although reversible, modify substantially the geochemical evolution of the system, and therefore must be considered in the long-term evolution of the near field and assessed by means of thermo-hydro-geochemical models, not included in the main report reviewed.

7. Interaction between iron and bentonite in the HLW repository

General comments on the different sections of issues related with the interaction between iron and bentonite are presented below.

This chapter draws from previous work by Johnson et al (2005) and Wersin et al (2007). There is a comprehensive discussion on the occurrence and characteristics of Fe-rich clays and Fe-phylosilicates. The information collected is quite large and includes the main Fe-rich clay minerals found in nature, most of them in conditions, which are far from the ones expected to occur in the near field of the SF and HLW repository. However, a few findings are relevant for the disposal situation including the abundance of berthierine a Fe-rich 1:1 phyllosilicate and its relation to chamosite an iron-chlorite which is formed in organic rich sediments, this phase has been proposed by Savage et al (2010) as the final result of the interaction of iron with bentonite. Berthierine is basically a non-swelling clay and therefore the swelling capacity of the bentonite is reduced by the extent of substitution of the initial montmorillonite by the Fe-containing berthierine. In any case, the analysis of the experimental data is more complex. This is because the iron-bentonite interactions are relatively slow at the conditions expected in the near field of a HLW repository. From the analysis of the experimental evidences, the authors of NTB 12-01 draw some conclusions. The main one being that the alteration zone enriches in iron which is even visible by the color. The actual morphology of the phases formed is more difficult to ascertain but the experiments performed under 100 °C (relevant for the repository situation) have given indications of the formation of berthierine and chlorites, depending on the temperature range.

There is one specific piece of work that the authors of NTB 12-01 have not fully considered in their analysis of the experimental data. This is the work performed by Carlsson et al (2006) and Smart et al (2006) investigating the anaerobic corrosion of cast iron and carbon steel coupons as well as carbon steel wires in compacted Wyoming bentonite (MX 80). The tests were run at 30 and 50°C in a saline and alkaline carbonate solution, 0.54 mole/dm³ + 0.01 mole/dm³ at pH=10.4. The contact

time was up to 3 years and the authors run a post-mortem spectroscopic analysis of the metal and bentonite surfaces as regular analyses on the chemical composition and the cation exchange capacity of the resulting products. The main outcome of their work was that the metal corrosion layer was much less than expected in the absence of bentonite and it was a mixture of magnetite, hematite and goethite. The analyses of the reacted bentonite indicated that iron had been incorporated in the clay in larger amounts in the most reactive samples, the iron wires. The incorporation of iron had induced a loss of cation exchange capacity as well as an increase on the hydraulic conductivity at similar swelling pressures. Experimental data from Carlson et al (2007) would indicate that the replacement of some 10-15% of bentonite by a rich Fe clay decrease the initial CEC from 75 mol/kg to 58 mol/kg which corresponds roughly to a 30% decrease. Moreover, the Fe(II)/Fe(III) ratio had doubled compared to the one in fresh bentonite, indicating a Fe(II) sorption and that some of the octahedral iron had been reduced to Fe(II), as suggested by the FTIR measurements and the greenish color of the reacted samples. The authors could not identify any newly formed iron-rich clay phase.

The findings from this work would indicate that, given the sufficient reactivity or time, extensive interaction between iron and bentonite is possible, even at the temperatures expected under repository conditions. The only limiting aspect is the alkalinity of the contacting fluids, which is higher than the one expected in the absence of cement.

Nevertheless, this would confirm that Fe(II) sorption and ion-exchange processes are relevant when assessing the interactions between the corroding iron and the bentonite. This is confirmed in the experiments performed within the NF-PRO project. In NF-PRO, several tests were performed to obtain information about the corrosion products at the bentonite/steel interface, both with and without a temperature gradient (NF-PRO, 2008a & b; Arcos et al. 2008; and references therein). The results from these experiments showed there was no evidence for the presence of any iron oxide or oxyhydroxide phases in the bentonite matrix, despite the fact that a local concentration of iron in some parts of bentonite increased up to 20 %. No discrete iron-rich clay phases were observed. This can be explained by a very high tendency of iron (II) ions to sorb on clay edges or by the formation of meta-stable amorphous 'gel' precursors, which are not easy to detect by conventional analyses. These experiments were modelled (Arcos et al. 2008; NF-PRO, 2008b) and the results indicate that the most

relevant iron retention process in bentonite is sorption on montmorillonite edge sites, which limits the extent of iron penetration into the bentonite to less than 5 mm. Cation exchange is also an important retention mechanism, although retained iron by this process is half that retained by surface sorption. Other modelling studies carried out within NF-PRO (Savage et al., 2010) have emphasized the need to address reaction kinetics to estimate the long-term degree of bentonite alteration due to interaction with iron.

Results obtained during NF-PRO have thus challenged the previous acceptance that iron corrosion would lead to the development of thick corrosion product layers and accumulation of iron in situ. It is clear from experiments with compacted bentonite conducted under NF-PRO that this is not the case over experimental timescales, in which only thin corrosion product layers develop, with iron diffusing and sorbing readily through the bentonite, driven by the concentration gradient between the internal and external boundary of the bentonite.

The authors of NTB 12-01 also analyze some of the modelling attempts performed by various investigators (equilibrium models by Wilson et al, 2006; reaction-path thermodynamics by De Combarieu et al, 2007 and a number of reactive transport models by Montes-Hernández (2005a and 2005b), Bildstein et al, 2006, Samper et al, 2008, Marty et al 2010 and finally Savage et al 2010).

The main issue with all these modelling studies is that their outcome depends highly of the thermodynamic and kinetic data used in the models. These data are fraught with uncertainties, which make these models at most informative about the potential alteration pathways and the extent of these alterations, but no quantitative conclusion can be drawn from them.

The final outcome of the analysis performed by the authors of NTB 12-01 is to apply a mass balance approach in order to ascertain the maximum extent of alteration that could be expected in the near field of the Nagra disposal concept. This is done following the approach suggested by Wersin et al (2007) in their calculations for the KBS-3H disposal concept.

The calculations performed by NAGRA are made assuming that the reference corrosion rate for iron was 1 $\mu\text{m}/\text{year}$, while the revised reference value by NAGRA is 2 $\mu\text{m}/\text{year}$. In addition, a maximum corrosion rate of 5 $\mu\text{m}/\text{year}$ has been explored.

We have checked the mass balance calculations performed by the authors of NTB 12-01 and we have extended the calculations to cover the higher corrosion rates of 2 and 5 $\mu\text{m}/\text{year}$.

The outcome of this check indicates that there is a minor inconsistency, although this does not compromise the general results presented by the authors of NTB 12-01. The radius of the canister as presented in Tab. B1 (50.025 cm) does not correspond to the radius used in mass balance calculations using total iron inventory (52.5 cm). The actual radius used in the rate calculations reported appears to be the correct one (52.5 cm) implying a typing error in the table.

The outcome of the additional mass balance calculations is presented in Table 2.

As expected, the time required for a full transformation of the montmorillonite to berthierine is diminished by a factor of 5 when the corrosion rate is increased by a factor of five. In the case of the SF canisters the full transformation of the smectite to berthierine is achieved after some 14,500 years with the obvious implications for the performance of the near field. Key safety functions of the bentonite buffer barrier, such as decrease of swelling capacity, increase in hydraulic conductivity and decrease of CEC an increase in the corrosion rate of iron means a decrease in the bentonite performance.

Table 2. Mass balance calculations of the time needed to corrode the canister and involved mineral transformations, depending on the rate of steel corrosion considered.

Steel corrosion rate = 1µm/year			
		SF BWR	HLW
Canister	Time needed for complete corrosion of canister	155,000 yr	127,000 yr
Berthierine	Time needed for transformation of montmorillonite	72,600 yr	127,000 yr
	Amount of montmorillonite transformed	100 %	78 %
	Amount of iron corroded	52 %	100 %
Chamosite	Time needed for transformation of montmorillonite	155,000 yr	127,000 yr
	Amount of montmorillonite transformed	72 %	29 %
	Amount of iron corroded	100 %	100 %
Steel corrosion rate = 2µm/year			
		SF BWR	HLW
Canister	Time needed for complete corrosion of canister	78,000 yr	64,000 yr
Berthierine	Time needed for transformation of montmorillonite	36,000 yr	64,000 yr
	Amount of montmorillonite transformed	100 %	78 %
	Amount of iron corroded	100 %	100 %
Chamosite	Time needed for transformation of montmorillonite	78,000 yr	64,000 yr
	Amount of montmorillonite transformed	72 %	29 %
	Amount of iron corroded	100 %	100 %
Steel corrosion rate = 5µm/year			
		SF BWR	HLW
Canister	Time needed for complete corrosion of canister	31,000 yr	26,000 yr
Berthierine	Time needed for transformation of montmorillonite	14,500 yr	26,000 yr
	Amount of montmorillonite transformed	100 %	78 %
	Amount of iron corroded	52 %	100 %
Chamosite	Time needed for transformation of montmorillonite	31,000 yr	26,000 yr
	Amount of montmorillonite transformed	72 %	29 %
	Amount of iron corroded	100 %	100 %

These are of course bounding mass balance calculations that give an indication of the extent of potential transformation of the montmorillonite as a result of the anaerobic corrosion of iron. However, it is important to consider that the mechanism for the Fe(II) montmorillonite interactions are not fully understood and that possibly sorption and ion-exchange processes will occur earlier than the full phase transformation impacting the performance of the bentonite buffer material. This is an area where NAGRA must put more effort in order to ascertain the mechanisms and rates of such critical processes

in order to bring some clarity. No modelling effort will be useful at this stage if the processes to be modeled are not understood and quantified.

8. Vitrified High Level Waste

General comments on the different sections of issues related with Vitrified Level Waste are presented below.

The introduction describes the amounts of HLW that are going to be disposed vitrified in borosilicate glass and the sources of information used to gather the necessary data. However, no information is provided about the composition and radionuclide inventory in the vitrified waste. For future works, including a summary of the radionuclide inventory of the wastes is advised.

Glass corrosion kinetics

NTB 12-01 discusses the merits and limitations of the silica affinity empiric rate law which has been largely used to explain glass (leaching) dissolution data. Furthermore, they elaborate on the influence of the diffusive layer composition on the kinetics of radionuclide release from the glass. This discussion is very relevant and reinforces the need to characterize and quantify the radionuclide inventory in the HLW glass to be disposed by NAGRA, as the radionuclide inventory may influence the kinetic behaviour of the diffusive glass layer.

The dissolution of the glass is apparently considered congruent, however, the possibility of incongruence, i.e., preferential release of some elements, is not assessed. Grambow (2006) in his review paper on glass-dissolution, states that congruent release of radionuclides is not observed, unless very acidic conditions or fast flow rates are imposed. Either precipitation of radionuclides as solid phases and sorption onto the available surfaces are very likely to occur, thus preventing congruent dissolution. In addition, the preferential dissolution of aluminium and boron with respect to silicon is also a source for incongruence. In the above-mentioned reference, Grambow shows crystals of uranyl silicates formed from glass leaching, indicating non-congruency of the process. The effect of incongruent dissolution should be assessed.

Jordan et al. (2009) observed that sorption of Si onto the surface of iron corrosion products largely affect the retention of Se through competition for the available surface

sites. The relevance of the effect that Si sorption on iron corrosion products can have on radionuclide mobility must be discussed.

The effect of near field materials on glass corrosion kinetics

This is an area of substantial controversy and concern. The authors put together most of the experimental evidence regarding the effect of bentonite on the kinetics of dissolution of borosilicate glass.

The facts as exposed by the authors of the NTB 12-01 report are the following:

Long-term (up to 7.5 years) in situ dissolution tests of glass chips immersed into Boom clay give dissolution rates which are up to 1000 times faster (Kursten et al 1997) than the ones measured with the same glass composition in pure water and at the same temperatures (90°C) (Curti, 2003).

The findings are rationalized in terms of the effect of the clay as a silica sink from the glass, in this context the initial silica content of the clay as well as the ratio between the glass and the contacting clay would play an important role. This is supported by the experiments performed by Gin et al. (2001), Walcke et al. (2007) and Godon et al. (2008), where addition of silica to the system slows the glass dissolution.

Hence, the critical issues to ascertain the pertinent glass dissolution rates in the near field are:

1. The initial content of silica in the contacting bentonite
2. The expected bentonite/glass ratio in the event of a container breach

In addition, a dedicated experimental program to determine the key parameters controlling the glass dissolution in contact with MX-80 bentonite is needed to ascertain how the expected near-field conditions would contribute to accelerating or slowing the dissolution of glass.

The report shows non-conclusive results on the effect of Fe alteration products on the kinetics of glass dissolution, although the experimental evidences provided by the authors indicate an important acceleration of this process in the presence of magnetite. As in the case of the effect of clay, the so far observed effect of iron deserves consideration, thus our recommendation is in line with the selection made by NAGRA. data.

This is especially important in the light of the publication of a more recent paper, Burger et al. (2013) reporting the results of an integrated experiment with glass, iron and clay kept under anoxic conditions for 2 years. The authors characterized the solid phases with Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy, Transmission Electron Microscopy, Raman microspectroscopy and Scanning Transmission X-Ray Microscopy at the SLS Synchrotron, providing very good quality data to support their conclusions. The experimental setup aimed at reproducing the conditions expected in a deep geological repository: anoxic to reducing conditions, low flow rates, fractured glass represented by powdered material. The results indicated an important effect of the contact of Fe with the glass which resulted in an increase of the glass corrosion rate (0,02 g/m²d) up to 400 times higher than the values reported in pure water and 40 times higher than in groundwater in the absence of near-field materials. According to the observations, this acceleration is due to the precipitation of iron silicates, which act as a pump in the system, delaying the effect of silica saturation. Nevertheless, as the same authors highlight, this enhancement is only visible in those areas close to the iron, given that the proximity with silica is needed for the formation of these phases, therefore, those grains of glass located far from iron do not experiment an increase in their corrosion rate (4e-4 g/m²d).

These observations reinforce our recommendation of continuing an experimental programme aimed at providing firmer roots to predictive models.

The role of the glass (silicate or borosilicate) on the release of radionuclides has not been assessed. In the surroundings of the glass, the concentration of silicate will probably affect the solubility of the radionuclides in a different way than in the surroundings of the spent fuel. Although there is a solubility assessment on the SF section, there is no reference to solubility control in the vicinity of the glass. We recommend a discussion, supported by specific calculations, about the effect that silicate concentrations can have on the solubility of radionuclides.

9. Spent fuel dissolution and related effects

General comments on the different sections of issues related with Spent Fuel dissolution are presented below.

Long term ageing of SF in the absence of water

The authors describe the main physicochemical characteristics of spent fuel prior to disposal in order to give an indication of the initial conditions of spent fuel as a contributor to the source term. The information contained is up to date and builds on the work by Ferry et al (2004), (2005), (2008) and Johnson (2005).

While most of the process discussion and description is correct, it appears that the discussion on the initial state of the fuel on disposal should be better explained by NAGRA, particularly what concerns the design and operational measures to prevent spent fuel oxidation during storage. A personal communication is not sufficient. This is particularly critical when assessing the potential effects of residual moist on the radiolytic oxidation of the spent fuel surface under “dry” storage conditions. At present stage initial oxidation of the fuel during “dry” storage cannot be discarded.

Aqueous corrosion of canister and Zircaloy cladding

According to the NTB-12-01, the effect of hydrogen on the mechanical stability of the engineered barriers is out of the scope of the current report. In this context it would be important to understand how NAGRA is going to integrate the mechanical and hydrochemical effects of hydrogen generation by anaerobic corrosion of iron into the near field evolution models.

The probability of failure of cladding of spent fuel elements should be substantiated beyond personal communications. At present it appears to be just an educated guess from NAGRA. This is important when trying to assess the time of groundwater contact with the spent fuel after canister corrosion.

Aqueous corrosion of the spent fuel

By and large, the operational definition of the various source terms in the spent fuel follows the accumulated knowledge in the field and the differentiation between the various components of the Instant Release Fraction (IRF) is appropriated, and follows the scheme proposed by Johnson (2014) in which the IRF is correlated to operational parameters like Fission Gas Release (FGR) and Linear Power Rating (LPR).

The authors give best current IRF (total) estimates for UO₂/MOX fuel from Swiss nuclear power plants ranging 2 – 16 % (FGR) , 5 – 48 % for ³⁶Cl, 6 – 20 % for ¹²⁹I, 6 – 13 % for ¹³⁵Cs, 10 % for ¹⁴C, 1 % for ⁹⁰Sr, ¹⁰⁷Pd and ⁹⁹Tc, 0.2 % for ⁷⁹Se and 0.1 % for ¹²⁶Sn (as proposed in Johnson 2014). They indicate that among the listed IRFs, only the values for ¹²⁹I and ¹³⁵Cs are correlated to FGR.

The upper range for ³⁶Cl is due to the extreme behaviour of spent fuel from Gösgen that apparently has operated at much higher linear power ratings. It is not clear from the report how these large ³⁶Cl contributions are going to be handled in the source term calculations.

We recommend to use the IRF database compiled within the FIRST-Nuclides project for future IRF evaluations (www.first-nuclides.eu).

We also recommend to provide the range of burnups of the fuel expected to be disposed by NAGRA. This information will help in the selection of IRF values.

The authors discuss the fact that the spent fuel matrix is a dynamic redox system in the presence of water. They argue, based in a substantial body of evidence that radiolytic oxidation of the spent fuel surface will be balanced by the H₂ generated by the anaerobic corrosion of iron as a result of the catalytic effect of the metallic particles present in the fuel. Hence, the system will evolve towards reducing conditions and the UO₂/PuO₂ matrix will be thermodynamically stable.

However, they propose that even under these circumstances recrystallization of the matrix will continue to release radionuclides. This is mainly based on investigations

performed by Ollila (2007) and (2008) by using the isotopic dilution technique with spiked ^{233}U solutions. The interpretation of isotopic disequilibrium in phase transitions is a subject of intense debate within the geochemical community and therefore conclusions driven from these investigations have to be taken with extreme care.

The authors conclude that recrystallization rates calculated from the experiments by Ollila (2008) are in the range of 10^{-5} to 10^{-7} g m² d⁻¹. These are comparatively lower than the rates obtained from oxidative dissolution of the spent fuel matrix. In any case, they would imply radionuclide release rates larger than the ones assuming thermodynamic equilibrium of the matrix under reducing conditions.

In this case, NAGRA should explain how are they going to introduce recrystallization effects in their source term model, in order to account for the dissolution of minor radionuclides not subjected to recrystallization of the matrix.

The range of values presented in table 9-1 on UO₂ and SF matrix dissolution rates cover all data published in the literature, although the works referenced do not consider all relevant data. A reference rate of 10^{-7} y⁻¹ is given in Johnson (2014), based on selection from SKB. Given the proven influence of parameters such as carbonate, pH or molecular oxidants on the rate of SF matrix dissolution, we strongly recommend to provide an uncertainty to this value, as well as an upper limit for the dissolution rate considering variation of the abovementioned parameters.

System evolution in a realistic scenario

The report presents a solubility assessment for radionuclides under different groundwater compositions, as shown in Table 9-3.

The calculations simulate the reaction between bentonite porewater infiltrated into the canister hull and the surrounding solid materials and compare the calculated solubilities with those obtained with bentonite porewaters.

The complete process of solubility assessment is shown in two reports, different from the one reviewed and that have also been included in our review: Berner (2014) and Curti (2011).

As explained in the text, Curti simulated an early stage of the chemical evolution after failure of the steel containment by assuming that only a small fraction of the canister (1%) had reacted with the initial bentonite-equilibrated porewater.

The concentrations were calculated by assuming that the solubility control in the evolved groundwater was given by different solid phases. The selection of the solid phases was done after preliminary calculations presented in Berner (2014) following the usual procedure of adding a given concentration of all radionuclides of interest to the groundwater and computing the most stable solid phase to form (the one presenting the highest saturation index). The final selection of the solid phase was done by expert judgement in order to account for unrealistically low solubilities obtained when assuming a control exerted by very crystalline solids, not expected to precipitate from solution due to kinetic constraints, among others.

The previous calculations rendered values for solubilities comparable to the ones used in other PA exercises, and a comparison between the approach named “SFZC (this work)” and the later solubility assessment made by Berner (2014) and other experimental data from the German programme is shown in Table 9-4 of the report:

The report, however, does not provide data for all relevant radionuclides, so that the more recent report from Berner(2014) has been considered to judge the adequacy of the concentration limits by NAGRA. In the following table, only those values that seem to be inconsistent are commented:

	Berner 2014		NTB 12-01 SFZC (from Curti 2011)
	ref	upper	ref
Mo	2,00E-05	5,00E-05	<1e-12
Pd	6,00E-08	2,00E-07	<1e-12
Th	4,00E-09	7,00E-07	?
U	2,00E-07	2,00E-04	3,50E-09
Np	1,00E-08	4,00E-08	4,00E-10
Pu	7,00E-10	1,00E-08	<1e-12
Am	3,00E-06	5,00E-05	3,00E-08

Selected solubility value for Mo in NTB 12-01 is very low, calculated by assuming control by $\text{MoO}_2(\text{s})$, as in most previous solubility assessments. Although it is said that Berner (2014) selects the same solid phase, the original report (Berner, 2014) selects $\text{CaMoO}_4(\text{s})$ as solubility controlling solid phase. This apparent inconsistency must be explained.

No value for Th is selected in the report. The value given in Berner (2014) is in line with values in the literature. NAGRA should consider the adequacy of including the values for all radionuclides of interest in future stages.

The solubility for U in Berner (2014) is very high, probably due to the consideration of the mixed U-Ca- CO_3 aqueous complexes, recently included in the thermodynamic database selections. The consideration of these very stable complexes, has important consequences for uranium concentration limits, not only for solubility but also for sorption. How uncertain is the calculated solubility and, how do the stability of these mixed U-Ca- CO_3 complexes affect sorption of uranium onto EBS materials is an important issue that NAGRA should comment on.

Np solubility estimated under SFZC conditions is very low in comparison with the value in Berner (2014), and this is not expected to be explained the lower Eh of the SFZC groundwater.

The value reported for Pu solubility in SFZC is extremely low, apparently given by equilibrium with $\text{PuPO}_4(\text{s})$. The concentration of phosphate in the groundwater composition is very high ($5.85\text{e-}3\text{M}$ according to Tab 9-3) what could explain the very low Pu concentration. What is not clear for the reviewers is the reason for this very high phosphate concentration in solution, which would cause precipitation of Apatite (occurring around $1\text{e-}5\text{M}$ of phosphate). NAGRA should state the reason for this high phosphate concentration and how the uncertainty on this value would impact the Pu concentration limit.

Also the activity correction approach should be indicated.

Including a comparison with solubility limits used by similar organisations, not only from previous Nagra assessments, is strongly advised.

The role of hydrogen in the system is a question of interest and concern, both due to chemical as well as stability issues. In the absence of hydrogen, oxidising conditions could develop without being counteracted. In fact, the possibility of oxidizing conditions around the spent fuel matrix cannot be ruled out, although they would occur under variant scenarios. Oxidising conditions could develop, for example, if diluted oxidizing waters reached the repository. Local oxidising conditions can developed due to radiolysis of water with low activation of hydrogen. This would also imply considerations for secondary solid phases forming on the surface of the corroding spent fuel. There is a complete body of literature on this regard:

- Amme M. (2002). "Contrary effects of the water radiolysis product H₂O₂ upon the dissolution of nuclear fuel in natural groundwater and deionized water." *Radiochimica Acta* 90:399.
- Hanson B., McNamara B., Buck E., Friese J., Jenson E., Krupka K., Arey B. (2004). "Corrosion of commercial spent nuclear fuel. 1. Formation of studtite and metastudtite." *Radiochimica Acta* 93:159.
- McNamara B., Hanson B., Buck E., Soderquist C. (2005). "Corrosion of commercial spent nuclear fuel. 2. Radiochemical analyses of metastudtite and leachates." *Radiochimica Acta* 93:169.
- M. Amme a*, B. Renker b, B. Schmid c, M.P. Feth c, H. Bertagnolli c, W. Dobelin € d Raman microspectrometric identification of corrosion products formed on UO₂ nuclear fuel during leaching experiments. *Journal of Nuclear Materials* 306 (2002) 202–212
- M. Amme a*, T. Wiss a, H. Thiele a, P. Boulet a, H. Lang b Uranium secondary phase formation during anoxic hydrothermal leaching processes of UO₂ nuclear fuel. *Journal of Nuclear Materials* 341 (2005) 209–223
- C. Jégou a*, R. Caraballo a, J. De Bonfils a, V. Broudic a, S. Peugeot a, T. Vercoüter b, D. Roudil Oxidizing dissolution of spent MOX47 fuel subjected to water radiolysis: Solution chemistry and surface characterization by Raman spectroscopy *Journal of Nuclear Materials* 399 (2010) 68–80
- F. Clarens a, J. de Pablo a, I. Casas a, J. Giménez a*, M. Rovira a, J. Merino b, E. Cera b, J. Bruno b, J. Quinones c, A. Martínez-Esparza The oxidative dissolution of unirradiated UO₂ by hydrogen peroxide as a function of pH *Journal of Nuclear Materials* 345 (2005) 225–231.

We recommend NAGRA to assess the likelihood of development of local oxidising conditions that could affect the system.

Hydrogen consumption may happen due to different processes, such as: 1) sorption of Hydrogen on clay surfaces, 2) Reduction of Fe(II)/Fe(III) by H₂; 3) reduction of pyrite by hydrogen and 4) reduction of sulfate by hydrogen. All previous processes can be catalyzed by microbes. Given the relevance of hydrogen in keeping the system under reducing conditions, and also its relevance in suppressing spent fuel dissolution, addressing the actual ability of hydrogen as a redox active species as well as ensuring that hydrogen will be present in sufficiently high concentrations as to play these roles is important. Recent simulations reported in Roman-Ross et al (2015) have shown that the presence of microbes could be sufficiently important in reducing hydrogen

concentrations only if sufficiently high biomass is present. A plot of the calculated concentration of hydrogen in the opalinus clay obtained by considering hydrogen generated by anoxic corrosion of steel and consumption due to sulphate reduction in the presence of SRB is shown in Figure 1.

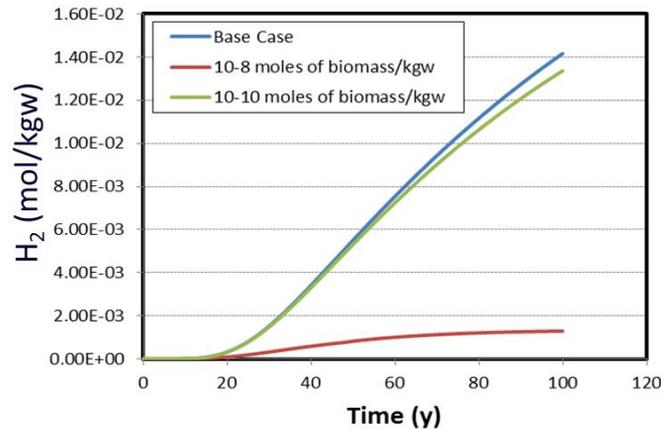


Figure 1. Comparison of the evolution of the hydrogen concentration with time in the System depending whether consumption by microbe-mediated sulphate reduction is considered. Two different, biomass concentration are tested (for explanations see text).

According to the previous results, with biomass concentration of 1e-10 moles/kg no important effect on hydrogen effect suppression would be expected. Nevertheless, for microbial populations two orders of magnitude higher, hydrogen concentration would be importantly decreased. We recommend NAGRA to conduct a careful evaluation of the expected biomass in the system, in order to assess the likelihood of biomass mediated hydrogen consumption.

10. Conclusions

The main conclusions from the review conducted are reported along this report. A summary of the answers to the main three questions of concern for ENSI is shown below, although for details on individual systems the reader is strongly advised to go through the precedent sections of the report.

1. Is the information and data presented by NAGRA on these topics sufficient and in accordance with the current state-of-the-art, and are the assumptions followed by NAGRA well balanced in terms of conservatism?

The information and data seem to be in accordance with the current state-of-the-art, as far as these reviewers have been able to find. Many selections are in line with selections made by other radioactive waste management organisations. Most assumptions are conservative.

2. Is the appraisal made by NAGRA on these processes for the long term near field evolution comprehensive and correct in the light of the current state-of-the-art?

The appraisal made by NAGRA is comprehensive, although several issues do not appear correct:

- Approach implemented for the simulation of clay mineral dissolution. As described in Section 5, thermodynamic equilibrium is not a valid approach to simulate clay processes, neither it is neglecting dissolution of clays. Dissolution/ precipitation of clay minerals should follow a kinetic behaviour, whereas cation exchange can be considered in different ways, as a fixed CEC value or associated to the content of clays.
- The rate of glass dissolution is a best estimate although it does not consider the influence of other near field components in the reference rate value. This approach, although accepted by other agencies, presents rather large uncertainties and therefore, we recommend to obtain additional experimental evidences in order to

reduce the uncertainties associated to the selection of the current values for the reference rate.

- Apparent incongruence in the selected solubilities and solid phases selected between the different reports of NAGRA. This has a direct relation also with the derivation of some parameters for the composition of the groundwater, such as the concentration of phosphate, which is not justified by the approach followed, as explained in the text.
- The influence that organics present in the cement, such as superplasticizers and other additives may have on the behaviour of radionuclides is not well represented by the models presented.
- The rate of spent fuel dissolution must clarify how minor radionuclides will be released and how the lack of impact of crystallization on the release of these radionuclides is going to be implemented, as considered in the assessment.
- The role of microorganisms should be better assessed.

The later is only a list of the main issues that deserve further attention, although for a more detailed explanation of concerns, the reader is advised to read the precedent sections of the report.

3. Has NAGRA considered all relevant processes for the long-term evolution of the HLW/SF near field with respect to radionuclide release?

This question is complex to answer in the light of the reporting procedures followed by NAGRA. There is no process report or document where all the processes for radionuclide release and retardation are compiled and discussed. As an example, there is no much information in the reference report on sorption parameters used and the selected reduction factor of sorption parameters due to the presence of organic materials/compounds. In general, there is no clear indication on where the data, the models and the assumptions can be found in the reporting system of NAGRA. In this way, it is not easy to confirm if the assumptions are sufficiently well supported by data, models and evidences. For this reason, we strongly recommend to follow a clear reporting procedure for future SA exercises, clearly identifying: Data report; Process

report; System description report, as well as SA reports for each subsystem of the repository system. This will provide a much more robust position of NAGRA for presenting and defending the case in front of stakeholders review and subsequent consultation processes.

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