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## Thermodynamic modelling of "inside canister" conditions during UO<sub>2</sub> spent fuel dissolution in a failed steel container

Enzo Curti

(Laboratory for Waste Management, Paul Scherrer Institut)

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## **1** Introduction

A precise knowledge of the chemical conditions established at the interface between waste package and failed containment in a deep geological repository for spent fuel is of fundamental importance to determine the release rates of dose-relevant radionuclides into the surrounding buffer materials. This is because spent fuel dissolution rates and mobility of radionuclides are highly sensitive to chemical parameters such as pH, Eh and the type of solubility-limiting solids controlling dissolved radionuclide concentrations. These variables and their evolution in time largely determine the source-term functions for radionuclide release to the near-field and thus may affect directly calculated radiological doses in performance assessments.

Unfortunately, it is not easy to predict the aqueous and solid chemistry inside a failed containment canister flooded with water, particularly in the case of spent fuel waste. The system is complex, as it includes a large number of chemical elements distributed over a number of different materials in close vicinity to each other (spent fuel, Zircaloy, steel/copper canister and other structural materials). Radiation from the fuel induces water radiolysis, which may alter redox conditions and aqueous chemistry close to the fuel surface. Moreover, repository designs and expected canister failure times may vary considerably from country to country. Finally, the reactivity and fate of redox-relevant species such as sulphate and molecular hydrogen (mainly produced via degradation of metallic canisters) are still not completely understood.

In this report, the aqueous and solid chemistry inside a canister containing Cr-doped  $UO_2$  spent fuel canister will be assessed via *thermodynamic equilibrium calculations* using a setup and boundary conditions closely resembling the currently planned Swiss repository for high-level waste (Nagra 2002; Leupin et al. 2011). A scenario assuming instantaneous failure of a partially corroded steel canister after about 10'000 years and immediate contact of the intruding pore water with the materials inside the canister is considered. Two different models are developed and applied:

(i) A closed-system batch equilibrium model (BEM) simulating the reaction of *limited amounts* of spent fuel, Zircaloy, steel and other structural materials with bentonite pore water after its ingress into the open spaces inside a failed steel canister. This model focuses on comprehensive and carefully assessed chemical inventories (including Cr) of the aforementioned materials and takes into account their different corrosion rates. The determination of the reacting amounts of water and solid materials is an essential part of the model and will be discussed in detail in Section 3.

(ii) A more sophisticated reactive transport model (RTM) simulating the chemical evolution across a 1-dimensional fissure through a 4 cm thick failed steel canister separating a compacted bentonite buffer from  $UO_2$  spent fuel after flooding the fissure and open spaces in the spent fuel with bentonite pore water. This model conservatively assumes passivation of the fissure surfaces (i.e. transformation of metallic Fe to magnetite) and oxidative dissolution of spent fuel.

Both models were implemented using specific modules of GEM-Selektor (Kulik et al., 2013) and version 12/07 of Nagra-PSI/Nagra thermodynamic database (Thoenen et al., 2014),

complemented with recently reviewed thermodynamic data for the phosphate system (Hummel and Curti, 2020) Fe-bearing solids (Hummel and Thoenen, 2021) and mixing data for solid solutions (Section 2.3).

In the BEM calculations, spent fuel dissolution was considered to proceed reductively, which is considered to be realistic for a number of reasons. First, there is ample evidence that molecular hydrogen is activated on the SF surface, thereby protecting the spent fuel against oxidative dissolution by scavenging efficiently radiolytic oxidants (Broczkowski et al., 2005; Johnson et al., 2005; Carbol et al., 2009a,b; Trummer and Jonsson, 2010). Moreover, the effects of radiolysis will be reduced at the time of canister failure (> 1'000 years) since alpha and gamma radiolysis decrease with time (Johnson and Smith, 2000). Finally, also dissolved Fe<sup>2+</sup> released via steel corrosion has proven to be an efficient scavenger of radiolytic oxidants (Odorowski et al., 2017).

This report starts with a review of key complementary thermodynamic data used for the definition of the solid solution phases (Section 2) considered in the equilibrium calculations. This is followed by a concise presentation of the models, in which underlying assumptions and boundary conditions (Section 3) are specified, and by a detailed discussion with interpretation of the computational results (Section 4). Finally, essential conclusions arising from this modelling exercise are drawn in the perspective of safety assessment (Section 5). Details of the derivation of key parameters are given in Appenices.

## 2 Thermodynamic data selection and computational methods

## 2.1 PSI Nagra database and GEM-Selektor

As for the calculations previously carried out to determine in-pile oxygen potentials (Curti and Kulik, 2019), the GEM-Selektor code (v. 3.7.0) was used for this task, however coupled with a different thermodynamic database and applied to reactions in aqueous solutions. The in-house PSI-Nagra database v. 12/07 was used (Thoenen et al., 2014) in conjunction with the complementary data discussed in Section 2.2.

A complete list of the elements and potentially equilibrating phases included in the modelled system (BEM) is given in Table 2.1. Aqueous complexes are not reported, but a list is available in Thoenen et al. (2014) where the values of the constants are reported. All calculations were carried out at standard state conditions (25 °C, 1 bar). Calculations at higher temperature were not carried out, due to incomplete or missing temperature extrapolation parameters of some key solid phases.

## 2.2 Additional data (P, Fe, Cr)

The PSI-Nagra thermodynamic database v. 12/07 was not considered to be sufficient for the present modelling task. The database focuses on carefully reviewed data but excludes some important elements, species and solids for which thermodynamic data are available but not yet reviewed. For the present task, we could identify two such elements (P and Cr) and several solid phases susceptible to form in the system of interest, for which no or only partial data are available in the PSI-Nagra database. These phases (in italics in Table 2.1) are the Fe-alumosilicates berthierine, Fe<sup>III</sup>-berthierine, cronstedtite, the phosphate minerals Cl- and OH-apatite, the carbonates ankerite and chukanovite and various Cr solids that could conceivably form as secondary phases: metallic  $Cr(OH)_3$ ,  $Cr_2(SO_4)_3$  and chromiferous magnetite, Fe<sup>III</sup>, Cr<sup>III</sup>)\_2O\_4.

At first sight, phosphorus might not seem to be a critical element due to the low concentrations in the system of interest (it is present as minor element in steel). However, it forms sparingly soluble phosphate compounds both with major elements such as Ca and key actinides. Our calculations indicate that it could play a role in limiting the aqueous concentration of Ca and Pu in the failed canister environment, therefore inclusion of this element is compulsory.

Although version 12/07 of the PSI-Nagra database includes a few basic P data, potentially important complexes and solids are missing. Recently, P data have been critically reviewed (Hummel and Curti, 2020), leading to the selection of a large number of additional data, including the solubility products of OH- and Cl-Apatite. These new data, listed in Table 2.2, will be included in the next version of the PSI-Nagra database (Hummel and Thoenen, 2021). For the present calculations, these data were added manually in GEM-Selektor as supplemental data on top of version 12/07 of the database.

**Table 2.1-** Elements and phases considered for the BEM modelling task. Elements considered in the RTM model are given in bold. Solid phase names are as given in GEM-Selektor and marked with "s" (single component solids) or "ss" (solid solutions). Solids not included in the PSI-Nagra database v. 12/07 are shown in italics.

Elements Phase name		Composition	Phase name	Composition
	Aqueous solution:			
Al	aq_SIT	All elements listed	s NaNpO2CO3w3.5	NaNpO <sub>2</sub> CO <sub>3</sub> *3.5H <sub>2</sub> O
Am			s NpO2(am,hyd)	NpO <sub>2</sub>
Ba	Ideal gas:		s NpO2OH(am,ag)	NpO <sub>2</sub> OH
С	gas_gen	C, H, N, O, S, Se	s NpO2OH(am,fr)	NpO <sub>2</sub> OH
Ca			s NpO3(H2O)	NpO <sub>3</sub> *H2O
Cl	Solid phases:		s Palladium	Pd
Cs	ss Bar_Cel_RaSO_reg	$(Sr, Ba, Ra)SO_4$	s Pd-hydroxide	Pd(OH) <sub>2</sub>
Cr	ss Dol_Ank_reg	$Ca(Fe, Mg)CO_3$	s PuO2-carbonate	PuO <sub>2</sub> CO <sub>3</sub>
Eu	ss Mgs-Sid_reg	$(Fe, Mg)CO_3$	s PuO2(coll,hyd)	PuO <sub>2</sub>
Fe	ss Mag_Chr_reg	$Fe^{II}(Fe^{III},Cr^{III})_2O_4$	s PuO2(hyd,ag)	PuO <sub>2</sub>
Н	s Gibbsite	Al(OH) <sub>3</sub>	s Pu3-hydroxide	Pu(OH) <sub>3</sub>
K	s Berthierin_FeIII	$Fe^{II}_{2.34}Fe^{III}_{0.33}Al_{0.99}Si_{1.34}O_5(OH)_4$	s PuO2(OH)2w	PuO <sub>2</sub> (OH) <sub>2</sub> *H2O
Mg	s Berthierine	$Fe^{II}_{2}AlSiAlO_{5}(OH)_{4}$	s PuO2OH-amorph	PuO <sub>2</sub> (OH)
Mo	s Kaolinite	$Al_2Si_2O_5(OH)_4$	s Pu-phosphate	PuPO <sub>3</sub>
Na	s Am-carbonate	$Am(CO_3)_{1.5}$	s Pu-h-phosphate	$Pu(HPO_4)_2$
Ni	s AmOH-carbonate	AmCO <sub>3</sub> OH	s Ra-carbonate	RaCO <sub>3</sub>
Ν	s Am(OH)3am	Am(OH) <sub>3</sub>	s Selenium	Se
Np	s Am(OH)3cr	Am(OH) <sub>3</sub>	s BaSeO3(cr)	BaSeO <sub>3</sub>
0	s Witherite	BaCO <sub>3</sub>	s CaSeO3w1(cr)	CaSeO <sub>3</sub> *H <sub>2</sub> O
Р	s Aragonite	CaCO <sub>3</sub>	s MgSeO3w6(cr)	MgSeO <sub>3</sub> *6H <sub>2</sub> O
Pd	s Calcite	CaCO <sub>3</sub>	s NiSeO3w2(cr)	NiSeO <sub>3</sub> *2H <sub>2</sub> O
Pu	s Portlandite	Ca(OH) <sub>2</sub>	s SrSeO3(cr)	SrSeO <sub>3</sub>
Ra	s Apatite-Cl	$Ca_5(PO_4)_3Cl$	s BaSeO4(cr)	BaSeO <sub>4</sub>
S	s Apatite-OH	$Ca_5(PO_4)_3$	s Quartz	SiO <sub>2</sub>
Se	s Anhydrite	CaSO <sub>4</sub>	s Silica-amorph	SiO <sub>2</sub>
Si	s Goethite	FeO(OH)	s Tin	Sn
Sn	s Gypsum	$CaSO_4(H_2O)_2$	s CaSn(OH)6	CaSn(OH) <sub>6</sub>
Sr	s Eu-carbonate	$Eu_2(CO_3)_3$	s Cassiterite	$SnO_2$
Tc	s Eu-OH-carbonate	Eu(OH)CO <sub>3</sub>	s SnO2(am)	$SnO_2$
Th	s Eu(OH)3am	Eu(OH) <sub>3</sub>	s Tin-oxide	SnO
U	s Eu(OH)3cr	Eu(OH) <sub>3</sub>	s Strontianite	SrCO <sub>3</sub>
Zr	s Iron	Fe	s TcO2(H2O)1.6	$TcO_{2}(H_{2}O)_{1.6}$
	s Fe-carbonate	FeCO <sub>3</sub>	s Th-oxide	ThO <sub>2</sub>
	s Hematite	$Fe_2O_3$	s Th3(PO4)4(s)	$Th_3(PO_4)_4$
	s Magnetite	$Fe_3O_4$	s Rutherfordine	UO <sub>2</sub> CO <sub>3</sub>
	s Ferrihydrite-am	Fe(OH) <sub>3</sub>	s Uranophane	$Ca(H_3O)_2(UO_2)_2(SiO_4)_2*3H_2O$
	s Ferrihydrite-mc	Fe(OH) <sub>3</sub>	s Na-Weeksite	$Na_2(UO_2)_2(Si_2O_5)_3*4H_2O$
	s Melanterite	$FeSO_4(H_2O)_7$	s Na-Boltwoodite	$Na(H_3O)UO_2SiO_4*H_2O$
	s FeSe2(cr)	$FeSe_2$	s U4-oxide	UO <sub>2</sub>
	s Brucite	Mg(OH) <sub>2</sub>	s Schoepite	$UO_3^*(H_2O)_2$
	s Molybdenum	Mo	s Chernikovite	$UO_2HPO_4(H_2O)_4$
	s Molybdite	MoO <sub>3</sub>	s UL3ph2(H2O)4	$(UO_2)_3(PO_4)_2(H_2O)_4$
	s Tugarinovite	MoO <sub>2</sub>	s U(OH)2SO4(s)	$U(OH)_2SO_4$
	s N1CO <sub>3</sub> (cr)	NICO3	s Soddyite	$(UU_2)_2 S1U_4 * 2H_2 O$
	s Theophrastite	$N_1(OH)_2$	s US104(s)	$US1O_4$
	s NpO2-carbonate	$NpO_2CO_3$	s Zr(HPO4)2w1(cr)	$Zr(HPO_4)_2*H2O$
	s K3NpO2(CO3)2(s)	$K_3NpO_2(CO_3)_2$	s Baddeleyite	$ZrO_2$
	s K4NpL(CO3)3	$K_4NpO_2(CO_3)_3$	s Zr(OH)4(am,tr)	$Zr(OH)_4$
	s KNPU2CU3(s)	$\operatorname{KinpU}_2(\operatorname{CO}_3)$	s Chukanovite	$Fe_2(OH)_2CO_3$
	s Na3NpO2(CO3)2	$Na_3NpO2(CO_3)_2$	s $Cr(OH)_3(am)$	$Cr(OH)_3$
			s Cr2(504)5(cr)	$Cr_2(SO_4)_3$

Because of the presence of large amounts of iron in the system of interest, mainly due to the interaction with a massive steel canister, a careful selection of data for potentially forming secondary Fe solids is essential. The PSI-Nagra database includes reviewed data for metallic Fe and the most common *pure* Fe(II/III) oxides (magnetite, hematite), hydrous oxides (goethite, ferrihydrite), sulphides (pyrite, troilite), sulphates (melanterite) and carbonates (siderite). However, it does not include data on Fe-silicates and mixed Fe-carbonates.

A number of low-temperature clay-like Fe-silicates is expected to form in reducing Fe-rich environments upon sufficient supply of silica, e.g. at the interface between a steel canister and a buffer material consisting of bentonite or sand-bentonite mixtures (see chapter 7 in Bradbury et al., 2014 and references therein). At the internal side of a failed steel canister, silicon may be supplied not only via diffusion of aqueous silica species from the pore water in contact with the buffer material, but also from the steel itself (Si being is used as strengthening element in steel alloys). There is scarce but significant experimental evidence that phases like berthierine and cronstedtite could form as stable end-products in such environments (see Johnson et al. 2008 and references therein). We defined equilibrium constants for these minerals in GEM-Selektor based on the calorimetric data of the ThermoChimie database (Blanc et al., 2015a,b). These data (Table 2.2) will also be included as supplemental data in the next update of the PSI-Nagra database (Hummel and Thoenen, 2021).

Reaction	log <sub>10</sub> K°	ΔrHm°	$\Delta r C_{n,m}^{\circ}$
	(298.15 K)	$[kJ \cdot mol^{-1}]$	$[\mathbf{J} \cdot \mathbf{K}^{-1} \cdot \mathbf{mol}^{-1}]$
$Na^+ + PO4^{3-} \rightleftharpoons NaPO4^{2-}$	$1.56\pm0.17$	$7\pm8$	-
$Na^+ + HPO_4^{2-} \rightleftharpoons NaHPO_4^-$	$1.03\pm0.07$	$23 \pm 15$	-
$Na^+ + H_2PO_4^- \rightleftharpoons NaH_2PO_4(aq)$	$0.30\pm0.17$	$17\pm8$	-
$K^+ + PO_4^{3-} \rightleftharpoons KPO_4^{2-}$	$1.46\pm0.16$	$6\pm8$	-
$K^+ + HPO_4^{2-} \rightleftharpoons KHPO_4^{-}$	$0.88\pm0.07$	$18 \pm 15$	-
$K^+ + H_2PO_4 \rightleftharpoons KH_2PO_4(aq)$	$0.29\pm0.16$	$5\pm 8$	-
$Mg^{2+} + PO_4^{3-} \rightleftharpoons MgPO_4^{-}$	$4.9\pm0.50$	-	-
$Mg^{2+} + HPO_4^{2-} \rightleftharpoons MgHPO_4(aq)$	$2.73\pm0.06$	$13.3\pm7.4$	-
$Mg^{2+} + H_2PO_4^- \rightleftharpoons MgH_2PO_4^+$	$1.11\pm0.20$	-	-
$Ca^{2+} + PO_4^{3-} \rightleftharpoons CaPO_4^{-}$	$6.46\pm0.11$	$-1 \pm 18$	-
$Ca^{2+} + HPO_4^{2-} \rightleftharpoons CaHPO_4(aq)$	$2.58\pm0.05$	$13.1\pm6.3$	-
$Ca^{2+} + H_2PO_4^- \rightleftharpoons CaH_2PO_4^+$	$0.99\pm0.09$	3 ± 13	-
$Sr^{2+} + H_2PO_4^- \rightleftharpoons SrH_2PO_4^+$	$5.62\pm0.20$	-	-
$Sr^{2+} + HPO_4^{2-} \rightleftharpoons SrHPO_4(aq)$	$2.35\pm0.12$	$9\pm15$	-
$Sr^{2+} + H_2PO_4^- \rightleftharpoons SrH_2PO_4^+$	$0.69\pm0.20$	-	-
$Ca_5(PO_4)_3OH(cr) \rightleftharpoons 5 Ca^{2+} + 3 PO_4^{3-} + OH^{-}$	$-58.29\pm0.15$	$-68 \pm 15$	$-1938 \pm 50$
$Ca_5(PO_4)_3Cl(cr) \rightleftharpoons 5 Ca^{2+} + 3 PO_4^{3-} + Cl^{-}$	$-46 \pm 5.00$	$-120 \pm 41$	$-1920\pm100$
Berthierine(FeIII) + 8.64 $H^+ \rightleftharpoons 2.34 \text{ Fe}^{2+} + 0.33$			
$Fe^{3+} + 0.99 Al^{3+} + 1.34 Si(OH)_4(aq) + 3.64 H_2O$	28.76	-302.91	297.41
Berthierine(FeII) + 10 H <sup>+</sup> $\rightleftharpoons$ 2 Fe <sup>2+</sup> + 2 Al <sup>3+</sup> +			
$Si(OH)_4(aq) + 5 H_2O$	34.45	-379.80	283.50
Cronstedtite + 10 $H^+ \rightleftharpoons 2 Fe^{2+} + 2 Fe^{3+} +$			
$Si(OH)4(aq) + 5 H_2O$	16.11	-257.03	257.02
Fe-Ankerite $\Rightarrow$ Ca <sup>2+</sup> + Fe <sup>2+</sup> + 2 CO <sub>3</sub> <sup>2-</sup>	-20.87	1335.32	-221.08

**Table 2.2** - Selected equilibrium constants, enthalpies and heat capacities for complex formation and dissolution reactions involving phosphate complexes, apatites and Fe-silicates.

Fe- carbonates are also potentially important secondary phases that could form at the interface between spent fuel and steel canister. In nature, even more widespread than siderite is the ferroan carbonate ankerite, a solid solution with generic formula Ca(Fe, Mg, Mn)(CO<sub>3</sub>)<sub>2</sub> isostructural with dolomite, which means that Ca and Fe are ordered in alternating lattice planes. Ankerite is ubiquitous in alpine hydrothermal veins within Fe-bearing crystalline rocks, together with calcite and/or quartz (Fig. 2.1), as well as in late diagenetic cements of Fe-bearing sandstones (Zhang et al., 2020). Recently, a large-scale experiment to test the feasibility of geological CO<sub>2</sub> storage showed unequivocally ankerite formation in basaltic rocks at depths of 827-887 m (McGrail et al., 2017). These depths are comparable to those of planned radioactive waste repositories, indicating that ankerite may form also under low temperature-pressure conditions typical of repository sites. These results are confirmed by laboratory CO<sub>2</sub>-basalt interaction experiments showing ankerite formation at 75 °C (Gysi and Stefansson, 2012) and by the experimental characterization of iron rods corroded at 90 °C in Cox clay saturated with pore water during 2 years (Schlegel et al., 2014), showing massive precipitation of ankerite at the clay/iron interface.



Figure 2.1 – Alpine hydrothermal vein with ankerite (brown) and quartz (white).

In spite of its widespread occurrence, the thermodynamic properties of the Fe-ankerite endmember, CaFe(CO<sub>3</sub>)<sub>2</sub>, are poorly known. To obviate this situation, calorimetric data in conjunction with extrapolation techniques have been used in the literature to determine its formation properties. The selected solubility product of pure Fe-ankerite selected for the present calculations (log  $K_{sp}^0$ = -20.87, see Table 2.2) is based on the formation properties reported by Holland and Powell (1998), which are similar to those given by Wood and Garrels (1992).

Another Fe-carbonate considered is chukanovite, a metastable corrosion product of carbon steel, which was detected as secondary solid in the MOX leach experiments in presence of iron carried out at CEA and modelled in the framework of DisCo WP5 by ARMINES. The thermodynamic data of Azoulay et al. (2012) were implemented in GEM-Selektor to describe this phase.

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Finally, we decided to use updated thermodynamic data for pyrite, goethite and magnetite (Thoenen, 2017) which are based on the recent NEA review on Fe and also include an estimated constant for the complex FeS(aq). Omission of Fe-sulfide complexes would result in unrealistically low Fe concentrations at high pH.

Concerning the Cr phases, data for amorphous  $Cr(OH)_3$  and  $Cr_2(SO_4)_3$  were taken from the THERMODDEM database, whereas for the chromite end-member used for defining the magnetite-chromite solid solution, the data of Klemme et al. (2000) were taken. It should be noted that the reliability of the results involving Cr-phases is however severely limited by the lack and incompleteness of aqueous complexes in the database, particularly Cr-sulphate complexes. The results pertaining to Cr-speciation are therefore to be taken with caution.

#### 2.3 Solid solutions

Carbonate and sulphate minerals generally form solid solutions rather than pure stoichiometric phases. In order to carry out realistic calculations, solid solutions were defined for these two classes of minerals, taking into account compositional restrictions derived from geological observations.

In iron-rich environments, pure magnesite, siderite, Fe-ankerite and calcite can be regarded as end-members of solid solutions involving Ca<sup>2+</sup>, Fe<sup>2+</sup> and Mg<sup>2+</sup> mixing on a single cationic site. However, observations indicate compositional restrictions in natural systems. Woods and Garrels (1992) found that in unmetamorphosed precambrian banded iron formations (BIF) ankerites are in equilibrium with almost pure calcites that contain only trace amounts of Fe and Mg ( $x_{Fe} \approx x_{Mg} < 2\%$ ). The compositional diagram in their Fig. 1 indicates for the higher members of the studied BIF coexistence between these almost pure calcites with ankerite-dolomite solid solutions having  $x_{Fe} \approx 0.26$ -0.71 and  $x_{Ca} < 0.05$ . Significant siderite or magnesite components do not appear in calcite, suggesting that it is not necessary (and probably inappropriate) to describe these carbonates as ternary magnesite-siderite-calcite solid solutions. In the lower, more reduced part of the BIF, ankerites coexist with almost pure magnesite-siderite solid solutions, but calcites are absent (Fig. 2 in Woods and Garrels, 1992). These observations suggest that carbonates in the Ca-Fe-Mg-CO<sub>3</sub> system can be treated in a simplified manner as combination of three phases:

CaCO <sub>3</sub>	(pure calcite)
Ca(Mg,Fe)(CO <sub>3</sub> ) <sub>2</sub>	(binary dolomite-ankerite solid solution)
(Fe,Mg)CO <sub>3</sub>	(binary siderite-magnesite solid solution)

whereby calcite and siderite-magnesite are mutually exclusive. For the present modelling of chemical equilibria inside a breached canister, we used this simplified representation with pure calcite and the two binary carbonates (magnesite-siderite and dolomite-ankerite). The thermodynamic data selected for the two binary solid solutions are listed in Table 2.3. We selected a regular symmetric model based on the interaction coefficients estimated by Woods and Garrels (1992).

Phase name (GEMS)	end-members	log K <sup>o</sup> sp	<b>a</b> <sub>0</sub> (-)	W <sub>G</sub> (J mol <sup>-1</sup> )	Reference (a <sub>0</sub> ,W <sub>G</sub> )
Dol_Ank_reg	CaMg(CO <sub>3</sub> ) <sub>2</sub> CaFe(CO <sub>3</sub> ) <sub>2</sub>	-17.09 -20.87	2.84	7040	Woods and Garrels (1992)
Mgs-Sid_reg	MgCO <sub>3</sub> FeCO <sub>3</sub>	-8.29 -10.89	2.00	4958	Woods and Garrels (1992)

**Table 2.3** – Standard state (25  $^{\circ}C$ , 1 bar) end-member solubility products and interaction coefficients used to describe symmetric regular solid solutions in the system Fe-Ca-Mg-CO<sub>3</sub>.

In addition, we defined a ternary, non-symmetric (Sr, Ba, Ra)SO<sub>4</sub> solid solution (Table 2.4) based on the recent non-ideality data of Vinograd et al. (2018). This allows a realistic determination of the solubility limit of  $^{226}$ Ra, which was found to strongly depend on the Sr/Ba proportion in the solid solution.

**Table 2.4** – Standard state (25 °C, 1 bar) end-member solubility products and interaction coefficients used to describe solid solutions in the system Sr-Ba-Ra-SO<sub>4</sub>.

Phase name (GEMS)	end-members	log K <sup>o</sup> sp	<b>a</b> <sub>1</sub> , <b>a</b> <sub>2</sub> , <b>a</b> <sub>3</sub> ( - )	W <sub>12</sub> ,W <sub>13</sub> ,W <sub>23</sub> (J mol <sup>-1</sup> )	Reference (a0,WG)
	Ba(SO <sub>4</sub> )	-9.97	2.00	4950	
Bar_Cel_RaSO_reg	Sr(SO <sub>4</sub> )	-6.63	1.00	2470	Vinograd et al. (2018)
	$Ra(SO_4)$	-10.26	7.06	17500	

In order to model Cr speciation in the secondary solids, one cannot ignore that the main corrosion product of anaerobic Fe corrosion is likely to be magnetite. This is an inverse spinel that can host a number of cations occurring in the system of interest, including  $AI^{3+}$ ,  $Cr^{3+}$  and  $Ni^{2+}$ . Cation mixing in spinels is very complex and complicated by the fact that specific cations, such as Fe<sup>3+</sup>, may enter both tetrahedral and octahedral sites depending on the "degree of inversion".

Here, we limit the description to a binary magnetite-chromite solid solution with ideal mixing, which is justified by the findings of Kurepin (2005) who found that at low temperatures Cr(III)-Fe(III) mixing is almost ideal. Because Cr(III) has a strong affinity for octahedral coordination, one can assume that Cr(III) will substitute only for octahedral Fe(III), which greatly simplifies the thermodynamic description of the binary magnetite-chromite solid solution.

To conclude this section we note that for this modelling task, we decided to treat secondary U, Pu solids as pure stoichiometric phases rather than solid solutions, due to the lack of pertinent mixing data. Under the assumed reducing conditions, aqueous concentrations of U and Pu at equilibrium will be very low (<  $10^{-8}$  M) and therefore have anyway no impact on the bulk water composition and characteristics.

## **3** Model setup and assumptions

#### 3.1 Basic scenario of damaged canister in a deep geological repository

The present model relies on the repository design for spent fuel disposal developed in Switzerland (Nagra, 2002; Leupin et al., 2011), which foresees encapsulation of the spent fuel assemblies in massive steel canisters and horizontal emplacement in cylindrical tunnels excavated at a depth of 600-900 m in the Jurassic Opalinus Clay formation. The tunnels will be backfilled with a 70 cm thick annulus of compacted sodium bentonite (1450 kg m<sup>-3</sup> dry bulk density), ensuring a strictly diffusive solute transport regime. According to the reference scenario, canister breaching will occur 10'000 years after repository closure, at which time bentonite pore water will intrude "instantaneously" and flood the cavities between waste package and canister. Fully water-saturated conditions and a failed Zircaloy cladding are assumed, implying that the intruded water will then interact with all exposed materials (spent fuel, Zircaloy, steel and its corrosion products, other structural materials).

## 3.2 Composition and amount of intruding Bentonite Pore Water (BPW)

The composition of the pore water flooding the canister cavities used for the present modelling is shown in Table 3.1. It is a moderately saline, sulphate-rich water derived from the simulated reaction between pore water from the Opalinus Clay host-rock and MX-80 compacted sodium bentonite with dry bulk density 1450 kg m<sup>-3</sup> (Curti, 2021).

IS (m) pH	0.616 7.41	pe Eh (V)	-3.04 -0.179				
Element o	concentrations (	(mol/kgw)					
Al	1.69E-08	K	2.46E-03				
Ba	1.47E-07	Mg	1.87E-02				
C(IV)	1.10E-03	Na	4.83E-01				
Ca	2.77E-02	S(VI)	5.79E-02				
Cl	4.62E-01	Si	1.78E-04				
Fe	1.24E-05	Sr	2.41E-04				
Saturated solids							

**Table 3.1** – Input composition and characteristics of bentonite pore water reacting with the exposed materials inside the failed canister.

calcite, gypsum, magnetite, pyrite, celestine

The void volume inside an intact canister was estimated to 700 L based on geometrical data on the spent fuel assemblies (Nagra 2002, p. 110). This open space is assumed in the model to

remain constant, although it could be conceivably reduced by canister collapse and formation of Fe corrosion products, and to be completely flooded by bentonite pore water. The water volume of 700 L must therefore be regarded as a maximum value, implying that calculations are carried out at the upper limit of possible water/solid ratios.

## **3.3** Composition and scaling of reacting solids

One of the aims of the present task was to carry out calculations reflecting as much as possible both the chemical complexity of the materials inside the canister and the different reactivity of the materials owing to their different corrosion resistances. This required to set up realistic chemical inventories of canister, spent fuel, Zircaloy and other structural materials present in the assemblies (Ni alloys, Al<sub>2</sub>O<sub>3</sub>), and also to evaluate the rates at which these materials corrode. Clearly, it was not possible, in the framework of this task, to take into account the diversity of conceptual designs and materials foreseen in the different repository sites planned in European countries. We limited our modelling to data and concepts pertaining to the planned Swiss SF/HLW repository, which has nevertheless a near-field environment similar to that of other countries (e.g. France, Sweden, Finland).

Table 3.2 shows the chemical inventories used for the present calculations. They are based on averaged data for UO<sub>2</sub> spent fuel, Zircaloy and other structural materials given in Table 5.5 of McGinnes (2002) and for a potential canister material (stainless steel ASTM A516, Grade 70, see Pike et al., 2010). The Table includes three different columns. The first one specifies the mole amounts of elements in the aforementioned materials normalized to 1 L of solution inside the water-filled canister cavity ("normalized inventory"). This means that multiplying these amounts by the volume of water (700 L) yields the total amounts per spent fuel assembly.

The second column ("scaled inventory") takes into account that spent fuel, Zircaloy and structural materials corrode at much slower rates than the canister. Accordingly, the inventory of each material is reduced by a factor equal to the ratio of its corrosion rate to steel corrosion rate. A rate of  $4.6 \times 10^{-9}$  mol m<sup>-2</sup> s<sup>-1</sup> was assumed for canister corrosion, a value derived from a penetration rate of 1 µm a<sup>-1</sup>. The latter value is about the upper limit assumed by Nagra for homogeneous stainless steel corrosion and is close to the assumed reference corrosion rate for carbon steel (Diomidis et al. 2016, p. 18). Although carbon steel is the preferred container material, chemically more complex alloys are still on the list as potential candidates in many countries (King, 2013). This choice introduces additional elements such as Cr, Ni, Si and S in significant quantities. Corrosion rates of  $6.5 \times 10^{-12}$  mol m<sup>-2</sup> s<sup>-1</sup> and  $2.2 \times 10^{-11}$  mol m<sup>-2</sup> s<sup>-1</sup> were assumed for spent fuel and Zircaloy, respectively, leading to scaling factors of 0.0014 and 0.0049, respectively. Details and procedures used to select these values are given in Appendix 1. For the remaining structural materials (e.g. end pieces and springs in the fuel assemblies), for which no such data are available, the same corrosion rate as for Zircaloy was assumed, as such materials are usually made of resistant metal alloys.

The third column in Table 3.2 ("reactive inventory") specifies the actual amount of "scaled inventory" that is effectively allowed to react with 1 L of solution in the "base case" calculations discussed in Section 4.1. This is a second normalization step which takes into account the

corrosion rates of the materials in combination with the estimated water flux into the cavities inside the canister. Explanations on how the reactive inventories are determined are given in Section 3.4.2 and Appendix 2.

Material	Element	normalized inventorv <sup>1</sup>	scaled inventory <sup>2</sup>	reactive inventorv <sup>3</sup>
		(mol/L)	(mol/L)	(mol/L)
Steel canister	С	3.09	3.09	2.30E-04
	Р	0.36	0.36	2.68E-05
	S	0.35	0.35	2.59E-05
	Si	7.93	7.93	5.90E-04
	Cr	2.14	2.14	1.59E-04
	Ni	1.90	1.90	1.41E-04
	Fe	653.11	653.11	4.86E-02
Zircaloy	Zr	10.39	5.05E-02	3.76E-06
	Sn	0.12	5.94E-04	4.42E-08
Structural materials	Са	3.21E-03	1.56E-05	1.16E-09
	Se	1.83E-03	8.91E-06	6.63E-10
	Sr	1.18E-02	5.72E-05	4.25E-09
	Pd	3.36E-02	1.63E-04	1.22E-08
	Eu	2.44E-03	1.19E-05	8.84E-10
Spent fuel	U	9.40	1.33E-02	9.86E-07
I I I I I I I I I I I I I I I I I I I	Pu	2.41	3.39E-03	2.53E-07
	Ba	6.93E-02	9.77E-05	7.27E-09
	Тс	2.50E-02	3.52E-05	2.62E-09
	Pd	6.54E-03	9.22E-06	6.86E-10
	I	3.64E-03	5.13E-06	3.81E-10
	Cs	6.58E-03	9.28E-06	6.90E-10
	Np	5.34E-03	7.53E-06	5.60E-10
	Am	1.78E-03	2.51E-06	1.87E-10
Balancing oxygen <sup>4</sup>	0	459.16	435.44	3.24E-02

Table 3.2 – Element inventory of solid materials inside the canister. See text for explanations.

<sup>1</sup>The inventories were normalized to 1 L of solution in the cavities inside the canister.

<sup>2</sup>The inventory of each material is reduced proportionally to the ratio of material corrosion rate to canister corrosion rate. <sup>3</sup>Effective amounts of element equilibrated assuming a FCR (Fraction of Canister Reacted) of 7.44 x 10<sup>-5</sup>

<sup>4</sup>Assumes contributions of half Fe in the canister as magnetite, in addition to UO<sub>2</sub> and PuO<sub>2</sub>.

#### 3.4 Simulation of interaction between intruded pore water and materials

#### 3.4.1 Models outline (BEM, RTM)

As previously mentioned, the model adopts the geometry and reference scenario of the Swiss disposal concept. Accordingly, after canister failure the open space inside the canister is filled with pore water pre-equilibrated with the surrounding MX-80 Na-bentonite. Owing to its large thickness, the canister is assumed to breach no earlier than 10'000 years after repository closure, putting important constraints on the intensity of water radiolysis processes.

Two types of model are applied, both relying on GEM-Selektor calculations:

(a) A batch equilibration model (BEM) in which the corroding solid materials react with intruded bentonite pore water filling the open spaces in the canister. In this model, the chemical environment inside the canister is treated as a "closed" system, i.e. the continuous in- and outdiffusion of solutes is neglected. In the "base case" calculations, the intruded water (see composition in Table 2.2) is allowed to equilibrate only with *limited amounts* of the surrounding solid materials, the so-called "reactive inventory" (Table 3.2), determined based on the balance between the assumed materials corrosion rates and an estimated incoming water flux. The "reactive inventory" is defined as the amount of materials that have been irreversibly corroded during the time required for a full exchange of the water volume inside the canister (see Section 3.4.2). Although the model does not allow for explicit reactive transport simulations, it allows calculating the chemical evolution inside the canister as a function of corrosion rates, simply by assuming increasing amounts of irreversibly corroded spent fuel, Zircaloy, steel and other structural materials in the proportion of their relative corrosion rates.

(b) A 1-dimensional purely diffusive reactive transport model (RTM) in which bentonite pore water (BPW) first floods the pore space inside a thin fracture across a partially corroded iron canister in contact with spent fuel. After a first equilibration step inside the fracture, in which metallic iron is converted anaerobically to corrosion products (magnetite) counter diffusion of BPW on one side and of a constant source of dissolved uranium on the other side is simulated and fully coupled to chemical equilibria for the elements highlighted in bold in Table 2.1. The initial state of the canister is treated here simplistically as a mixture of metallic Fe and magnetite (partially corroded canister)

#### 3.4.2 Determination of water exchange time and "reactive inventory" (BEM)

Assuming an appropriate water self-diffusion coefficient through compacted bentonite (5.97 x  $10^{-11}$  m<sup>2</sup> s<sup>-1</sup>) and the geometrical parameters of the Swiss disposal concept, a water diffusion flux of 1.1 x  $10^{-4}$  mol s<sup>-1</sup> was calculated to be maintained across the bentonite/waste package interface at steady state. This implies that the bulk water volume inside the canister (0.7 m<sup>3</sup>) would be renewed every 11.158 years. The fraction of steel canister material corroded at a rate of 1 µm/a during this time is calculated to be 7.44 x  $10^{-5}$ , which leads to the "reactive inventories" in Table 3.2. Details of these calculations are given in Appendix 2.

#### 3.4.3 Treatment of redox reactions (S, C, Fe)

Three different sets of calculations have been carried out for the BEM model. In the first one (*case 1*), considered to be the most realistic, reduction of both C(IV) and S(VI) was suppressed. This choice represents the case, supported by experimental evidence, that these multi-electron reduction reactions are usually inhibited in the absence of microbial activity (Miao et al., 2012) and that conditions in repository near-field are hostile to microbial life. Stroes-Gascoyne (2011) reviewed the literature relevant for assessing whether microbial activity is possible in compacted bentonite. He concluded that above dry densities exceeding 1300 kg/m<sup>3</sup> microbial activity in saturated bentonite is strongly reduced or suppressed. The reduction is sufficient to prevent significant sulphide-mediated copper corrosion in bentonite with 1450 kg/m<sup>3</sup> dry density. Experimental work by Karri et al. (2005) showed that both sulphate reduction and methanogenesis are strongly inhibited in the absence of sulphate-reducing bacteria in the presence of iron powder. Moreover, it seems unlikely that significant microbial life could be subject.

In spite of this evidence, alternative calculations were carried out in which H<sub>2</sub> is reactive and sulphate reduction (*case 2*) and additionally carbonate reduction (*case 3*) are allowed. Indeed, it is difficult to exclude such processes in the long term, particularly in the light of experimental evidence for sulphide formation in field experiments mimicking repository conditions in underground laboratories (Fernández et al., 2018) and considering the ample evidence for H<sub>2</sub> activation by noble metal particles on spent fuel surfaces. As will be shown in Section 4, the results of these calculations largely differ from those of *case 1*, implying that the reactivity of H<sub>2</sub> and the redox behaviour of the sulphur and (to a lesser extent) carbon systems critically affect the chemistry inside the canister.

In contrast to C and S, Fe(II/III) redox reactions were always allowed to proceed in both directions, as this single-electron redox process usually proceeds rapidly even in the absence of microbial mediation. As outlined in Section 2.2 a number of Fe-bearing solids (including solid solutions) were selected as potential equilibrium phases in the simulations (Table 2.1).

A final important note concerns the simplifications made in the treatment of carbon system. There is ample evidence that a large variety of aqueous organic carbon species (reduced and oxygenated hydrocarbons) may form as metastable species during the anaerobic corrosion of steel or iron powders under neutral to hyperalkaline pHs (Wieland and Hummel, 2015). Although thermodynamic data for simple low molecular weight organics are available, the variety of these compounds and the large uncertainties on their long-term stability make it impossible to make reliable predictions on their concentrations using partial equilibrium models. For this reason they are excluded in the present model, except for methane, the most stable organic species, which is included in the *case 3* calculations to simulate complete thermodynamic equilibrium for the BEM.

## 4 Results and Discussion

#### 4.1 "Base case" calculations (BEM)

In the "base case" calculations for the BEM, 1 L of bentonite pore water is equilibrated with the "reactive inventory" defined in Table 3.2 for the three different cases defined in Section 3.4.3 with distinct treatments of the C and S redox systems. The results, summarized in Table 4.1, show almost identical concentrations for many elements in the three cases. However, important differences emerge in terms of pH, Eh and a few elemental concentrations between the results obtained assuming inhibition of S(VI) and C(IV) reduction (*case 1*) and those in which reduction reactions are allowed for one or both species (*case 2* and *case 3*, respectively).

Compared to *case 1*, the nearly identical results of *case 2* and *case 3* are characterised by more alkaline pH (9.79 vs. 8.25), a higher though still reducing Eh (-381 mV vs. -487 mV), and much lower aqueous Fe concentrations (about 0.1  $\mu$ M vs 0.2 mM). In *case 1*, the gas composition is dominated by H<sub>2</sub> produced via anaerobic Fe oxidation, whereas N<sub>2</sub> is the major component in the other two calculations, with H<sub>2</sub> at trace levels (a consequence of treating hydrogen as a reactive species in *case 2* and *case 3*). Large differences are predicted for Pu equilibrium concentrations (nanomolar in *case 1*, picomolar in *case 2* and *case 3*), while equally low U concentrations close to 1 nM are calculated in all three calculations.

The discrepant Pu concentrations are related to the lower oxidation potential calculated in *case 1* (Eh = -487 mV) which stabilizes the Pu(III) state in aqueous solution, whereby  $Pu^{III}HSiO_3^{2+}$  is the dominant complex (90% of total Pu). In this case the solubility is limited by Pu(III) phosphate. In the *case 2* and *case 3* the oxidation potential is higher (Eh = -381 mV) and Pu(III) destabilized. Pu(IV) dominates the speciation in this case and the solubility of Pu is limited by the less soluble hydrous Pu(IV) oxide.

Besides the aforementioned Pu solids, other secondary phases are predicted to form in amounts varying from less than 1  $\mu$ mol/L (FeIII-berthierine, barite-celestine-RaSO<sub>4</sub> solid solution, Pu phosphate and oxide, uraninite) up to 16 mmol/L for magnetite-chromite solid solution. The latter is the major secondary solid. It precipitates as almost pure magnetite with 0.5 % chromite component. The main end-member of the ternary (Ba,Sr,Ra)SO<sub>4</sub> solid solution is celestine (83%-96%) followed by barite (2.2-12%) and RaSO<sub>4</sub> (1.5-4.8%). Ankerite, Ca (Fe, Mg) (CO<sub>3</sub>)<sub>2</sub> forms only in *case 1* as almost pure Fe end-member with 99.9 % CaFe(CO<sub>3</sub>)<sub>2</sub>. Noteworthy are also the precipitation of other Fe-bearing phases such as the alumosilicate FeIII-berthierine (only in *case 1* and very small amounts) and pyrite (obviously not stable in *case 1* since sulphate reduction is purposely suppressed) as well as brucite and baddeleyite, which limit the aqueous concentrations of Mg and Zr, respectively.

Compared to the composition of the initial bentonite pore water, the equilibrated "inside canister" waters are all more alkaline (the pH increases from 7.41 to 8.25 or 9.79), more reducing (Eh decreases from -180 mV to -381 or -487 mV), depleted in carbonate (decreases from about 1 mM to about 0.02 mM) and are either enriched (*case 1*) or depleted in Fe (*case 2* and *case 3*).

#### DisCo

	BPW	case 1	case 2	case 3	
IS(m)	0.616	0.615	0.592	0.592	
рН	7.41	8.25	9.79	9.79	
Eh	-0.180	-0.487	-0.381	-0.381	
Molalities					
Al	1.69E-08	4.04E-09	1.69E-08	1.69E-08	
Ва	1.47E-07	1.96E-08	6.68E-08	6.54E-08	
С	1.10E-03	2.29E-05	2.17E-05	2.17E-05	
Са	2.77E-02	2.70E-02	2.64E-02	2.64E-02	
Cl	4.62E-01	4.62E-01	4.62E-01	4.62E-01	
Fe	1.24E-05	2.08E-04	1.27E-07	1.27E-07	
К	2.46E-03	2.46E-03	2.46E-03	2.46E-03	
Mg	1.87E-02	1.87E-02	1.03E-02	1.03E-02	
Na	4.83E-01	4.83E-01	4.83E-01	4.83E-01	
Р	1.01E-12	5.10E-09	1.91E-10	1.91E-10	
Pu	1.01E-12	3.37E-08	3.90E-12	3.90E-12	
S	5.79E-02	5.80E-02	4.84E-02	4.84E-02	
Si	1.78E-04	2.00E-04	5.30E-04	5.30E-04	
Sr	2.41E-04	2.35E-04	2.40E-04	2.40E-04	
U	1.01E-12	9.82E-10	9.83E-10	9.83E-10	
Zr	1.01E-12	6.12E-10	6.12E-10	6.12E-10	
Gas phase (partial press	sures, bar)				
CO <sub>2</sub>		4.21E-06	2.60E-08	2.60E-08	
CH <sub>4</sub>		-	-	4.03E-12	
H <sub>2</sub>		0.982	2.10E-07	2.10E-07	
N <sub>2</sub>		1.81E-02	0.983	0.997	
O <sub>2</sub>		0	0	0	
H <sub>2</sub> S		-	1.32E-07	1.32E-07	
Stable solids (mol/L)					Formulae
barite-celestine-RaSO <sub>4</sub>		6.09E-06	7.06E-07	7.82E-07	(Ba,Sr,Ra)SO₄
ankerite-dolomite		6.50E-04	0.00E+00	0.00E+00	Ca (Fe, Mg) (CO <sub>3</sub> ) <sub>2</sub>
magnetite-chromite		1.60E-02	1.47E-02	1.47E-02	Fe <sup>2+</sup> (Fe <sup>3+</sup> ,Cr <sup>3+</sup> ) <sub>2</sub> O <sub>4</sub>
Fe(III)-berthierine		1.28E-08	0.00E+00	0.00E+00	Fe <sup>2+</sup> <sub>2,34</sub> Fe <sup>3+</sup> <sub>0,33</sub> Al <sub>0,99</sub> Si <sub>1,34</sub> O <sub>5</sub> (OH) <sub>4</sub>
calcite		0.00E+00	1.30E-03	1.30E-03	CaCO <sub>3</sub>
hydroxy-apatite		8.85E-06	8.93E-06	8.93E-06	Ca₅(PO₄)₃(OH)
pyrite		-	4.70E-03	4.70E-03	FeS <sub>2</sub>
brucite		0.00E+00	8.26E-03	8.26E-03	Mg(OH)
hydrous Pu(IV) oxide		0.00E+00	2.52E-07	2.52E-07	PuO <sub>2</sub>
Pu(III) phosphate		2.19E-07	0.00E+00	0.00E+00	PuPOa
quartz		5.68E-04	2.42E-04	2.42E-04	SiO <sub>2</sub>
uraninite		9.89E-07	9.89E-07	9.89E-07	UO <sub>2</sub>
baddeleyite		3.76E-06	3.76E-06	3.76E-06	ZrO <sub>2</sub>
calcite hydroxy-apatite pyrite brucite hydrous Pu(IV) oxide Pu(III) phosphate quartz uraninite baddeleyite		0.00E+00 8.85E-06 - 0.00E+00 0.00E+00 2.19E-07 5.68E-04 9.89E-07 3.76E-06	1.30E-03 8.93E-06 4.70E-03 8.26E-03 2.52E-07 0.00E+00 2.42E-04 9.89E-07 3.76E-06	1.30E-03 8.93E-06 4.70E-03 8.26E-03 2.52E-07 0.00E+00 2.42E-04 9.89E-07 3.76E-06	CaCO <sub>3</sub> CaCO <sub>3</sub> Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> (OH) FeS <sub>2</sub> Mg(OH) PuO <sub>2</sub> PuPO <sub>3</sub> SiO <sub>2</sub> ZrO <sub>2</sub>

Table 4.1 – Selected results of "base ca	use" calculations.
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#### 4.2 Dependence on reaction progress (BEM)

In order to understand the key reactions affecting pH, Eh and speciation in this system, systematic calculations were carried out in which the bentonite pore water filling the canister's open space reacts with progressively increasing amounts of materials. This is equivalent to increase proportionally the corrosion rates of the solids or decrease the flux of incoming pore water from bentonite. To this aim, the fraction of "scaled inventory" (Table 3.2) to be equilibrated with bentonite water was varied systematically from 0.0001 % to a maximum of 0.1 % in a sequence of GEM-Selektor calculations. Because the scaling factor for the canister is unity by definition, this quantity is equal to the Fraction of Canister Reacted irreversibly through corrosion (shortly named "FCR" in the following).

Figure 4.1 shows the resulting Eh and pH evolution for the three cases as a function of FCR. In *case 1* rather uniform conditions are predicted. The pH always remains in the mildly alkaline region (pH = 7.6 - 8.5) and the Eh is always negative in the strongly reducing range (Eh = -500 to -450 mV). The almost identical pH and Eh curves for *case 2* (S reduction allowed) and *case 3* (S and C reduction allowed) differ largely from *case 1* and are characterised by two stepwise pH increases (from 7.8 to 9.7 and from 10 to 12.3). Only at very high reaction progress the curves for *case 2* and *case 3* differ, indicating that it is the sulphur system, rather than carbon, which plays the major role in determining the differences to *case 1* calculations.



**Fig.** 4.1 – Eh and pH evolution as a function of reaction progress for the three cases discussed in the text: (1) C(IV) and S(VI) reduction suppressed; (2) only C(IV) reduction suppressed; (3) all redox equilibria allowed. The position of the "base case" calculations is indicated by the vertical dotted line.

In order to decipher the chemical reactions responsible for the two pH steps in the calculations with allowance of S(VI) and C(IV) reduction, selected results of *case 3* were analyzed and plotted as a function of FCR. Fig. 4.2 reveals that aqueous sulphate is progressively reduced to pyrite with increasing reaction progress. Indeed, the 1 mmole decrease in aqueous sulphate is matched by a corresponding amount of 0.5 mmoles of pyrite precipitated (the molar amount of pyrite, which carries two S atoms, is exactly half of the molar amount of sulphate disappeared). In addition to pyrite, ankerite and magnetite precipitate, with the latter mineral being the main sink of Fe. The sum of the iron stored in these three minerals exactly matches the amount of Fe delivered by canister corrosion. These mass balance relations therefore point to the following basic reaction, which explains the first pH increase from 7.5 to 9.6:

 $5.5 \text{ Fe}(\text{cr}) + 2 \text{ H}_2\text{O} + 2 \text{ SO}_4^{2-} = 1.5 \text{ Fe}_3\text{O}_4(\text{cr}) + \text{FeS}_2(\text{cr}) + 4 \text{ OH}^-$ (1)

This does not does explain why the pH stops increasing at FCR  $\approx 6 \times 10^{-6}$  (plateau at pH=9.6) as reaction (1) continues to produce hydroxyl ions at larger FCR. The plateau is however readily explained by the onset of Mg hydroxide (brucite) precipitation, which starts exactly at FCR =  $6 \times 10^{-6}$ . This reaction withdraws the excess OH<sup>-</sup> produced by the sulphate-reducing reactions, so that the pH remains well buffered at a value of about 9.6.



**Fig. 4.2** – Plot showing the correlation between pH and amounts of corroded Fe, pyrite, brucite, magnetite and aqueous sulphate decrease as a function of the Fraction of Canister Reacted (FCR) for case 3. The black dotted line shows that practically all Fe corroded from the canister precipitates as Fe-bearing minerals.

Fig. 4.3 and Fig. 4.4 show the complete evolution up to  $FCR = 10^{-3}$ . Fig. 4.3 reveals that the pH buffering via brucite precipitation is maintained until all available aqueous Mg is consumed (cf. brucite and aqueous Mg curve going to zero). From this point onward, the hydroxyl ions produced via sulphate to pyrite reduction are no longer consumed and remain in solution, causing the second stepwise pH increase (up to pH 12.6). Once all aqueous sulphate ions have been reduced, pyrite dissolves and the pH decreases slightly while methane is formed.



Fig. 4.3 – Plot showing the correlation between pH and aqueous sulphate, Mg, methane (aqueous + gas), sulphide (aqueous + gas), brucite and pyrite as a function of the Fraction of Canister Reacted (FCR) for case 3. The FCR value of the "base case" calculations is indicated by the vertical dotted line.

The final decrease in pH after pyrite dissolution is best understood by examining Fig. 4.4, which illustrates the mass transfers of carbon species. Up to the maximum pH, all carbon is stabilized as aqueous or solid carbonate. Calcite precipitates until the first pH step; then its amount remains stable and increases again after most of the bicarbonate has been consumed. At FCR =  $5 \times 10^{-4} \text{ C(IV)}$  is no longer stable. The calcite dissolves abruptly and all carbonate is reduced to aqueous and gaseous methane, according to the acidic reaction:

$$CaCO_3 + 4 H_2(g) = CH_4(g,aq) + Ca^{2+} + 4 H^+$$
 (2)

Note that the increase in aqueous Ca induced by calcite dissolution is only barely visible in Fig. 4.4 due to the logarithmic scale. Fig. 4.5 shows an analogous plot, in which the correlation between Eh and the Fe/sulphide system is displayed.



**Fig.** 4.4 – Plot showing the correlation between pH and the carbon system (bicarbonate, carbonate, calcite and methane) as a function of the Fraction of Canister Reacted (FCR). The FCR value of the "base case" calculations is indicated by the vertical dotted line.



**Fig. 4.5** – Plot showing the correlation between Eh and redox controlling species (sulphate, sulphide, pyrite, ankerite, calcite) as a function of the Fraction of Canister Reacted (FCR). The FCR value of the "base case" calculations is indicated by the vertical dotted line.

DisCo

This plot shows clearly that Fe-bearing solids and the  $SO_4^{2-}/HS^{-}$  couple control the Eh up to the destabilization of carbonate. Initially, the Eh is fixed to constant values by the coexistence of ankerite, pyrite and magnetite (not shown, but present throughout the entire evolution). This ternary system acts as buffer for the Eh. The first decrease in Eh corresponds to the destabilization of ankerite. The final step coincides with the carbonate to methane transformation.

#### 4.3 Reactive transport calculations (RTM)

As anticipated in Section 3.4.1, a reactive transport model (RTM) was set up in order to simulate the chemical evolution a thin fissure across a corroded steel canister separating a spent  $UO_2$  fuel domain on one side from saturated compacted bentonite on the opposite side. The model also predicts the chemical evolution at both interfaces. A sketch of the model setup is shown in Fig. 4.8 below.



**Fig.** 4.8 – Sketch showing the model setup for the RTM calculations. Note that the fissure is assumed to be filled with grains of corroded canister materials and bentonite, leading to a small effective diffusion coefficient for solutes ( $D_e = 1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ).

The canister is assumed to fail via formation of a tubular 1-dimensional fissure of 40 mm length, half-filled with fine-grained canister material. The remaining pore space in the fissure is filled with injected saturated bentonite from the engineered barrier, providing considerable diffusion resistance. An effective diffusion coefficient typical for cation diffusion in compacted bentonite was therefore assumed ( $D_e=1 \times 10^{-10} \text{ m}^2/\text{s}$ ). When the canister fails, the open spaces inside the spent fuel (cracks and accessible grain boundaries) are assumed to be immediately flooded with bentonite pore water (BPW) through a perforation of the cladding.

Contrary to the BEM, spent fuel dissolution is conservatively postulated to be oxidative. This condition is simulated by imposing a high constant U(VI) concentration of 1 mM (on "top" of

the BPW composition) at the left boundary. When diffusion starts, the surfaces of the fissure and canister fragments inside the fissure are assumed to be coated with Fe corrosion products, meaning that all metallic Fe inside the fissure (grains and walls) is considered to have reacted and converted to magnetite. This process is simulated in the very first time step of the RTM simulation by calculating instantaneous equilibration between the BPW and 1% of the canister material inside the fissure. Afterwards, no further reaction with metallic Fe can take place, which is (as the postulated oxidative  $UO_2$  dissolution) a conservative assumption, since redox conditions are no longer buffered by the highly reactive metallic Fe.

After this first pre-equilibration, counter-diffusion of solutes from the opposite compacted bentonite and SF sides starts. The diffusion is fully coupled with the chemical equilibria by using GEM\_Selektor's random-walk "GEM2MT" module, allowing to compute the chemical evolution inside and at the boundaries of the fissure. The composition of the BPW is the same used for the BEM calculations (Table 3.1). In order to keep the system reasonably simple some elements listed in Table 2.1 were not considered (Am, Cs, Eu, Mo, Ni, Np, P, Pd, Pu, Ra, Se, Sn, Tc, Th, Zr). This means that all calculations were carried out in the simplified chemical system Al-Ba-C-Ca-Cl-Fe-H-K-Mg-Na-N-O-S-Si-U, however with all gaseous species and solids (including solid solutions) involving these elements or combination thereof.

The main purpose of these calculations was to assess whether an oxidizing front from an oxidatively corroding SF could still propagate through a fissure devoid of metallic Fe, or if such a fissure could still provide sufficient resistance to the propagation into the near-field of a radiolysis-induced oxidizing front. The calculations were carried out only for the *case 2* scenario, in which both sulphur and iron redox systems are considered to be active. A summary of results is presented in Fig. 4.9 and Fig. 4.10. The former shows the evolution of pH, Eh, ionic strength, aqueous element concentrations and major solids immediately after the first equilibration in the fissure (t = 0) and for 5.5 days and 11 days diffusion time, while Fig. 4.10 shows the complete solid inventories for the same times (in logarithmic scale, to allow also minor solids to be visible).

After the first pre-equilibration event shortly after formation of the fissure and flooding (t=0), the pH inside the fissure is uniform and alkaline (pH  $\approx$  12) and the Eh strongly reducing (Eh  $\approx$  -0.7 V), see Fig. 4.9 Ia). These values are consistent with the findings of the BEM model at high FCR (see *case 2* curves in Fig. 4.1). The main mechanism responsible for the high pH and low Eh is the anaerobic corrosion of metallic Fe, which is an alkaline reaction and thus induces precipitation of brucite from the Mg-rich BPW (see Fig. 4.9 Ic). The process can be described by the following key reactions:

 $3 \text{ Fe}(cr) + 4 \text{ H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 4 \text{ H}_2(g)$   $\text{Fe}(cr) + \text{Mg}^{2+} + 2 \text{ H}_2\text{O} \rightarrow \text{Mg}(\text{OH})_2(cr) + \text{Fe}^{2+} + \text{H}_2(g)$  $\text{SO}_4^{2-} + 4 \text{ H}_2(g) + \text{H}^+ \rightarrow 4 \text{ H}_2\text{O} + \text{HS}^-$ 

The first reaction is the classical anaerobic Fe oxidation producing magnetite as a corrosion product and hydrogen. This reaction consumes water but it does not affect pH nor Eh. The

second reaction (anaerobic Fe oxidation combined with brucite precipitation) buffers Eh to low potentials via  $Fe(0)/Fe^{2+}$  equilibrium, but does not affect pH. This reaction also produces aqueous Fe(II) which reaches sub-millimolar concentrations across the entire fissure due to formation of the strong FeS(aq) complex (pyrite is still undersaturated at this stage). It is however the third reaction (proton consuming reduction of sulphate to sulphide by activated hydrogen) which is responsible for the high pH.

At both boundaries (SF and compacted bentonite) near-neutral pHs and more oxidizing conditions are maintained. As the counter diffusion proceeds, nearly symmetrical pH depressions and increased Eh fronts propagate from both sides (Fig. 4.9 IIa and IIIa). After 11 days the pH has decreased on both sides under 10 in regions a few mm-thick adjacent to the boundaries. An analogous effect is observed for the Eh which slightly increases in two steps over a wider region, however remaining well in the reducing region. Fig. 4.9 IIc and Fig. IIIc show that the pH decrease correlates with precipitation of pyrite and brucite at the expense of magnetite. Moreover, the formerly produced  $H_2$  has been totally consumed (not shown). This allows us to derive the following reaction to explain the observed mass transfers:

 $Fe_{3}O_{4}(cr) + 22 H_{2}(g) + 6 MgSO_{4}(aq) \rightarrow 3 FeS_{2}(cr) + 16 H_{2}O + 6 Mg(OH)_{2}(cr)$ 

In other words, hydrogen (treated as reactive species in the *case 2* model) reduces  $Fe^{3+}$  from magnetite and sulphate diffusing from the bentonite, releasing alkalinity which is neutralized via further brucite precipitation. These changes are reflected by the elemental aqueous concentration profiles, particularly of Fe, S, Mg and C. The Fe concentrations are close to 0.1 mM in the central regions and drop below 1  $\mu$ M in the peripheral regions affected by the pyritization front.

Fig. 4.10 shows the amounts of solids as a function of diffusion time across the fissure. Each bar in the graph represents the contents in each of the 41 one-mm model cells, whereby cells 1 and 41 represents the assemblages at the boundaries of the SF and bentonite "reservoirs". All minerals except the dominating magnetite are shown. In the first equilibration step (t=0), calcite and brucite precipitate in the fissure and metallic Fe is converted to magnetite via anaerobic corrosion. At the SF boundary, a number of phases precipitate: dolomite-ankerite solid solution, goethite, the calcium uranyl silicate uranophane, calcite,  $UO_2$  and the hydrous uranyl oxide schoepite (in order of increasing amounts). At the bentonite boundary, goethite and a nanomolar amount of kaolinite are formed. As diffusion progresses, the aforementioned pyrite-brucite fronts migrate towards the center of the fissure. The assemblage at the SF boundary remains the same. Moreover, uranyl diffusing from the SF precipitates as  $UO_2$  in the adjacent cell within the fissure, limiting the U concentration to the usual low levels expected under reducing conditions (about 10<sup>-9</sup> M, see Fig. 4.9 IIb and IIIb). In other words, our calculations predict that after 11 days, assuming the Fe, S redox systems and H<sub>2</sub> to be chemically active, no oxidation front would migrate into the fissure in spite of strongly oxidizing conditions assumed within the SF.







*Fig.* 4.9 – *Selected results from RTM model for three diffusion times:* t=0 (*left*), 5.5 (*middle*) and 11 days (*right*).







**Fig.** 4.10 – Solids inventories calculated from RTM model: first equilibration at t=0 (a), 5.5 days (b) and 11 days diffusion time (c). Small amounts of kaolinite formed in the rightmost cell are not visible since they are less than  $10^{-6}$  mol/kgw. For the sake of clarity, magnetite (dominating solid) was excluded from the graphs.

In order to investigate long-term effects, further calculations on the same chemical system and setup were carried out to simulate longer diffusion times (up to 165 days). Selected results are presented in Fig. 4.11, which shows the progressive evolution of pH, Eh, ionic strength and dissolved U concentration using the outputs obtained for 16.5, 77 and 165 days diffusion time. Fig. 4.12 shows the distribution of solids for the same times. Fig. 4.11 reveals that the high pH region (pH> 10) disappears after 16.5 days and levels off to pH = 9.7 across the fissure. Later, at both boundaries lower pH regions start to slowly propagate inwards towards the center of the fissure. This effect correlates well with the propagation of increased Eh regions on both sides and with a sharp front of dissolved U propagating from the SF side. After 165 days, the oxidized U front has moved about 3 mm into the fissure.



**Fig. 4.11** – Selected results of RTM calculations: (a) Evolution of pH, ionic strength and Eh across the fissure (16.5, 77 and 165 days in order of increasing colour saturation); (b) evolution of aqueous U concentration between 16.5 and 165 days.

The moving oxidation front is visible also in Fig. 4.12, as  $UO_2$  and goethite precipitation regions start to move into the fissure with increasing time. After 165 days, their fronts have reached (as the pH and Eh fronts) x=3 mm. Moreover, the central calcite region disappears after 16.5 days and is replaced by ankerite-dolomite solid solution.

It should be noted that with increasing time such calculations become more and more unrealistic, since effects due to changes in porosity are neglected in the calculations. Specifically, the accumulation of secondary solids in the fissure would eventually lead to clogging phenomena. In this perspective, the omission of porosity effects can be regarded as an additional degree of conservatism, as transport resistance is minimized in this way.



**Fig. 4.12** – Solids inventories calculated from RTM model: t=16.5 days (a), 77 days (b) and 165 days diffusion time (c). Small amounts of kaolinite formed in the rightmost cell are not visible since they are less than  $10^{-6}$  mol/kgw. For the sake of clarity, magnetite (dominating solid) was excluded from the graphs.

## 5 Summary and Conclusions

Thermodynamic equilibrium calculations were carried out to model chemical conditions at the spent fuel / canister interface after breaching of the latter and intrusion of pore water from the surrounding bentonite buffer material, based on the disposal concept currently foreseen in Switzerland. Two types of calculations were carried out: (i) a batch equilibration model (BEM) in which corrosion-limited amounts of the materials involved (UO<sub>2</sub> spent fuel, Zircaloy, steel canister and other structural materials) react with the intruded bentonite pore water filling the open spaces in the canister; (ii) a reactive transport model (RTM) simulating thermodynamic equilibrium during counter-diffusion of solutes from saturated bentonite on one side and oxidatively corroding spent fuel on the opposite side (  $[U]_{tot} = 1 \text{ mM}$  ) across a 1-dimensional 4 cm long fissure in a failed iron canister, assuming that all surface-exposed metallic Fe in the fissure has been previously converted to magnetite.

The BEM calculations assume realistic reductive SF dissolution rates and take into account detailed material inventories as well as possible limitations of redox reactions. Specifically, three cases were distinguished in which both C(IV) and S(VI) reduction are suppressed (*case 1*), S(VI) reduction allowed but not C(IV) reduction (*case 2*) and both S(VI) and C(IV) reduction are permitted (*case 3*, full thermodynamic equilibrium). The results indicate large differences in terms of pH and Eh between *case 1* and *case 2/3*, which yielded similar results. Most differences could be explained by the large impact of sulphate reduction reactions on pH and Eh. Such reactions were permitted in *case 2* and *case 3* but were intentionally suppressed in *case 1* calculations to simulate conditions in which H<sub>2</sub> is chemically inert and sulphate reduction cannot take place due to lacking microbial activity. In all three cases the equilibrated solutions were predicted to be more alkaline and more reducing than the initial input bentonite pore water.

It is important to realize that, contrary to case 1, both case 2 and case 3 models assume  $H_2$  to be a chemically reactive species. This is normally considered to be unrealistic at the low temperatures established during the evolution of geological repositories, unless appropriate microbial activity or else abiotic activation mechanisms are operating. For the system considered here, molecular hydrogen activation mediated by noble metal inclusions has been proven to be an effective mechanism for consuming radiolytic oxidants produced in a narrow region near the UO<sub>2</sub> surface (Johnson et al., 2005; Broczkowski et al., 2005; Trummer et al., 2010). The sulphate and carbonate reducing reactions proceeding in case 2 and case 3calculations (which require H<sub>2</sub> as reactant) would however not be confined to such thin water region in contact the fuel surface. They would mostly proceed at some distance from the fuel surface, where analogous abiotic activation mechanism cannot be assumed (Truche et al., 2009). Reduction of sulfate and carbonate at low temperatures in the bulk solution according to the overall reactions (1) and (2) would thus probably require microbial mediation, which is unlikely in a  $\gamma$ -radiation field. Moreover, it has been shown that microbial activity in compacted bentonite rapidly decreases as the degree of bentonite compaction increases (Stroes-Gascoyne, 2011). These circumstances make microbial mediation of redox processes unlikely, prompting us to consider *case 1* model to be the most realistic of the three examined.

Two main conclusions, however, arise from the comparison of the results of the different model variants:

I. Assessment of C/S redox kinetics and  $H_2$  chemical reactivity under *faithful* repository conditions (realistic temperature, radiation field, clay compaction) is critical as these reactions can profoundly affect the water chemistry inside a breached steel canister in contact with  $UO_2$  spent fuel assemblies. It is recommended to carry out dedicated experiments in future in order to clear up under which conditions  $H_2$  and S(VI) reduction are activated under repository-realistic conditions.

II. Although the mechanism of SF matrix dissolution (reductive vs. oxidative dissolution) profoundly affects the solubility of U and radionuclide release rates, it has only a minor effect on the bulk aqueous and solid chemistry inside the breached canister. This is simply due to the fact that the chemical environment will be dominated and buffered by a few reactive major elements, even in the case of oxidative  $UO_2$  dissolution. The pH, Eh and major element concentrations will be largely controlled by the redox-sensitive Fe, C and S systems.

The latter conclusion is supported by our reactive transport simulations (RTM). Indeed, the results presented in Section 4.3 indicate that if sulphate reduction takes place and  $H_2$  is chemically reactive (*case 2*), a radiolytic oxidation front from oxidatively corroding UO<sub>2</sub> would move only very slowly through a fissured canister, even if metallic Fe is no longer available for reaction.

## References

Azoulay I., Rémazeilles C. and Refait Ph. (2012) Determination of standard Gibbs free energy of formation of chukanovite and Pourbaix diagrams of iron in carbonated media. Corrosion Science 58, 229–236.

Bestel M., Glaus M.A., Frick S., Gimmi Th., Jurany F., Van Loon L.R., Diamond L.W. (2018) Combined tracer through-diffusion of HTO and <sup>22</sup>Na through Na-montmorillonite with different bulk dry densities. Appl. Geochem 93, 158-166.

Blanc, P., Vieillard, P., Gailhanou, H., Gaboreau, S., Gaucher, E., Fialipsd, C.I., Madé, B. and Giffaut, E. (2015a). A generalized model for predicting the thermodynamic properties of clay minerals. American Journal of Science 315, 734-780.

Blanc, P., Vieillard, P., Gailhanou, H., Gaboreau, S., Marty, N., Claret, F., Madé, B. and Giffaut, E. (2015b). ThermoChimie database developments in the framework of cement/clay interactions. Applied Geochemistry 55, 95-107.

Bradbury M.H., Berner U., Curti E., Hummel W., Kosakowski G. and Thoenen T. (2014) The Long Term Geochemical Evolution of the Nearfield of the HLW Repository. Technical Report NTB 12-01, National Cooperative for the Disposal of Radioactive Waste (Nagra), Wettingen, Switzerland.

Broczkowski M.E., Noël J.J. and Shoesmith D.W. (2005) The inhibiting effects of hydrogen on the corrosion of uranium dioxide under nuclear waste disposal conditions. J. Nucl. Mat. 346, 16–23.

Carbol, P., J. Cobos-Sabate, J-P. Glatz, B. Grambow, B. Kienzler, A. Loida, A. Martinez Esparza, V. Metz, J. Quiñones, C. Ronchi, V. Rondinella, K. Spahiu, D. H. Wegen, T. Wiss (2009a): The effect of dissolved hydrogen on the dissolution of <sup>233</sup>U doped UO<sub>2</sub>(s), high burnup spent fuel and MOX fuel, European Commission SFS Project Report, Contract No. FIKW-CT-2001-20192-SFS, SKB Technical Report TR-05-09, SKB, Stockholm.

Carbol P., Fors P., Gouder Th. and Spahiu K. (2009b) Hydrogen suppresses UO<sub>2</sub> corrosion. Geochim. Cosmochim. Acta 73, 4366–4375.

Curti E. and Kulik D. (2019) Defect chemistry and thermodynamics of Cr-doped UO<sub>2</sub> fuels: Model development and applications (Mid-term report). Deliverable D5.2, DisCo project (Grant Agreement 755443), Euratom Research and Training Programme on Nuclear Energy, Horizon 2020 Framework Programme, European Commission.

Curti E. (2021) Bentonite Pore Waters (BPW) for the Sectoral Plan, phase SGT-3: model development and testing. Technical Note TM-44-21-02, Paul Scherrer Institut, Villigen, Switzerland.

Diomidis N., Cloet V., Leupin O.X., Marschall P., Poller A. and Stein M. (2016) Production, consumption and transport of gases in deep geological repositories according to the Swiss disposal concept. Nagra Technical Report NTB 16-03, Nagra, Wettingen, Switzerland.

Fernández A.M., Kaufhold S., Sánchez-Ledesma D.M., Rey J.J., Melón A., Robredo L.M., Fernández S., Labajo M.A. and Clavero M.A. (2018) Evolution of the THC conditions in the FEBEX in situ test after 18 years of experiment: Smectite crystallochemical modifications after interactions of the bentonite with a C-steel heater at 100 °C. Applied Geochemistry, 98, 152–171.

Gysi A.P. and Stefàsnsson A. (2012) Experiments and geochemical modeling of CO<sub>2</sub> sequestration during hydrothermal basalt alteration. Chemical Geology 306–307, 10–28.

Holland T.J.B. and Powell R. (1998) An internally consistent thermodynamic data set for phases of petrological interest. J. metamorphic Geol.16, 309–343.

Hummel W. and Curti E. (2020) The PSI Chemical Thermodynamic Database 2020: Data Selection for Phosphorus and Application to HLW near-field pore water modelling. Technical Communication TM-44-20-06, Paul Scherrer Institut, Villigen, Switzerland.

Hummel W. and Thoenen T. (2021) The PSI Chemical Thermodynamic Database, Nagra Technical Report NTB 21-03, Nagra, Wettingen (in review).

Ilton E.S., Liu Ch., Yantasee W., Wang Z., Moore D.A., Felmy A.R. and Zachara J.M. (2006) The dissolution of synthetic Na-boltwoodite in sodium carbonate solutions. Geochim. Cosmochim. Acta 70, 4836–4849.

Johnson L.W. and Smith P.A. (2000) The Interaction of Radiolysis Products and Canister Corrosion Products and the Implications for Spent Fuel Dissolution and Radionuclide Transport in a Repository for Spent Fuel. Technical Report NTB 00-04. Nagra, Wettingen, Switzerland.

Johnson L.H. (ed.) et al. (2005) Spent Fuel Evolution under Disposal Conditions. Synthesis of Results from the EU Spent Fuel Stability (SFS) Project. Technical Report NTB 04-09. Nagra, Wettingen, Switzerland.

Johnson L., Marschall P., Wersin P. and Gribi P. (2008) HMCBG processes related to the steel components in the KBS-3H disposal concept. Report R-08-25, Svensk Kärnbränslehantering AB Swedish Nuclear Fuel and Waste Management Co (SKB), Stockholm, Sweden.

Karri S, Sierra-Alvarez R, Field JA. Zerovalent iron as an electron-donor for methanogenesis and sulfate reduction in anaerobic sludge. Biotechnology and Bioengineering. 2005; 92(7):810–819.

King F. (2013) Container Materials for the Storage and Disposal of Nuclear Waste. Corrosion 69(10), 986-1011.

Klemme S., O'Neill H.S.C., Schnelle W. and Gmelin E. (2000) The heat capacity of  $MgCr_2O_4$ , FeCr<sub>2</sub>O<sub>4</sub>, and Cr<sub>2</sub>O<sub>3</sub> at low temperatures and derived thermodynamic properties. American Mineralogist 85, 1686–1693.

Kulik D.A., Wagner T., Dmytrieva S.V., Kosakowski G., Hingerl F.F., Chudnenko K.V., Berner U. (2013): GEM-Selektor geochemical modeling package: revised algorithm and GEMS3K numerical kernel for coupled simulation codes. Computational Geosciences 17, 1-24.

Kurashige, T., Fujisawa, R., Inagaki, Y. & Senoo, M. (1999): Gas generation behavior of Zircaloy-4 under waste disposal conditions. In: Proceedings of the 7th International Conference on Radioactive Waste Management and Environmental Remediation, September 26 – 30, 1999 Nagoya, Japan, ASME.

Kurepin V.A. (2005) A thermodynamic model of Fe–Cr spinels. Contrib. Mineral. Petrol. 149, 591–599.

McGinnes D.F. (2002) Model Radioactive Waste Inventory for Reprocessing Waste and Spent Fuel. Nagra Technical Report NTB 01-01, Nagra, Wettingen, Switzerland.

McGrail B.P., Schaef H. T., Spane F. A., Horner J. A., Owen A.T., Cliff J. B., Qafoku O., Thompson C. J., and Sullivan E.C. (2017) Wallula Basalt Pilot Demonstration Project: Post-Injection Results and Conclusions. Energy Procedia 114, 5783 – 5790.

Nagra (2002) Project Opalinus Clay: Safety Report. Demonstration of disposal feasibility for spent fuel, vitrified high-level waste and long-lived intermediate-level waste (Entsorgungsnachweis). Nagra Technical Report NTB 02-05. Nagra, Wettingen, Switzerland.

Leupin O.X., Smith P., Marschall P., Johnson L., Savage D., Cloet V., Schneider J and Senger R. (2011) High-level waste repository-induced effects. Nagra Technical Report 14-13. Nagra, Wettingen, Switzerland.

Miao Z., Brusseau M.L., Carroll K.C., Carreón-Diazconti C. and Johnson B. (2012) Sulfate reduction in groundwater: characterization and applications for remediation. Environ. Geochem. Health. 34(4), 539–550.

Odorowski M., Jégou Ch., De Windt L., Broudic V., Jouan G., Peuget S. and Martin Ch. (2017) Effect of metallic iron on the oxidative dissolution of  $UO_2$  doped with a radioactive alpha emitter in synthetic Callovian-Oxfordian groundwater. Geochim. Cosmochim. Acta 219, 1–21.

Pike S., Allen C., Punshon C., Threadgill P., Gallegillo M., Holmes B. andf Nicholas J. (2010) Critical Review of Welding Technology for Canisters for Disposal of Spent Fuel and High Level Waste. Nagra Technical Report NTB 09-05, Nagra, Wettingen, Switzerland.

Prikryl J..D. (2008) Uranophane dissolution and growth in  $CaCl_2$ -SiO<sub>2</sub>(aq) test solutions. Geochim. Cosmochim. Acta 72, 4508–4520.

Schlegel M.L., Bataillon Ch., Brucker F., Blanc C., Prêt D., Foy E. and Chorro M. (2014) Corrosion of metal iron in contact with anoxic clay at 90 °C: Characterization of the corrosion products after two years of interaction. Applied Geochemistry, 5, 1–14.

Stroes-Gascoyne, S. (2011) Microbiological characteristics of compacted bentonite for a dry density of 1'450 kg/m<sup>3</sup>: A literature review. Nagra Arbeitsbericht NAB 11-05.

Thoenen T., Hummel W., Berner U. and Curti E. (2014) The PSI/Nagra Chemical Thermodynamic Database 12/07. PSI Bericht Nr. 14-04, ISSN 1019-0643, Paul Scherrer Institut, Villigen, Switzerland.

Thoenen T. (2017) The PSI Chemical Thermodynamic Database 2020. Data Selection for Iron. Technical Note TM-44-17-07, Paul Scherrer Institut, Villigen, Switzerland.

Truche L., Berger G., Destrigneville C., Pages A., Guillaume D., Giffaut E. and Jacquot E. (2009) Experimental reduction of aqueous sulphate by hydrogen under hydrothermal conditions: Implication for the nuclear waste storage. Geochim. Cosmochim. Acta 73, 4824–4835.

Trummer M. and Jonsson M. (2010) Resolving the H<sub>2</sub> effect on radiation induced dissolution of UO<sub>2</sub>-based spent nuclear fuel. J. Nucl. Mat. 396, 163–169.

Vinograd V.L., Kulik D.A., Brandt F., Klinkenberg M., Weber J., Winkler B. and Bosbach D. (2018) Thermodynamics of the solid solution - Aqueous solution system  $(Ba,Sr,Ra)SO_4 + H_2O$ : I. The effect of strontium content on radium uptake by barite. Appl. Geochem. 89, 59-74.

Wang Z., Zachara J.M., Gassman P.L., Liu Ch., Qafoku O., Wassana Y. and Catalano J.G. (2005) Fluorescence spectroscopy of U(VI)-silicates and U(VI)-contaminated Hanford sediment. Geochim. Cosmochim. Acta 69, 1391–1403.

Wieland E. and Hummel W. (2015) Formation and stability of 14C-containing organic compounds in alkaline iron-water systems: preliminary assessment based on a literature survey and thermodynamic modelling. Mineralogical Magazine, 79(6), 1275–1286.

Woods T.L. and Garrels R.M. (1992) Calculated aqueous-solution-solid-solution relations in the low temperature system CaO-MgO-FeO-CO<sub>2</sub>-H<sub>2</sub>O. Geochim. Cosmochim. Acta 56, 3031-3043.

Zhang K., Fanf X., Xie Y., Guo S., Liu Z. and Wang L. (2020) Diagenesis and Origination of Carbonate Cements in Deeply Buried Sandstones of the Eocene Es3 Member, Raoyang Sag, Bohai Bay Basin, China, Geofluids, Volume 2020, Article ID 8728432, 18 pages.

## **Appendix 1 – Determination of scaling factors for reactive inventories**

In order to determine the factors to scale the inventories of spent fuel and Zircaloy proportionally to the corrosion rates, we proceeded as follows:

#### (a) Spent fuel

We started from an average value of 6.5 x  $10^{-13}$  mol m<sup>-2</sup> s<sup>-1</sup> based on the range between 0.3-1.0 x  $10^{-12}$  mol m<sup>-2</sup> s<sup>-1</sup> proposed in Section 6.4 of Johnson et al. (2005). Because these values are normalized to the geometric surface areas of the pellets, we decided to multiply by a factor of ten to account for the fracturing of spent fuel pellets, resulting in a selected dissolution rate of  $R_S = 6.5 \times 10^{-12}$  mol m<sup>-2</sup> s<sup>-1</sup>.

#### (b) Zircaloy

Zircaloy corrodes very slowly due to surface passivation (formation of a protective ZrO<sub>2</sub> film). Based on the scarce available corrosion data (Kurashige et al., 1999), a linear corrosion rate  $R_L$  [m/a] of 10<sup>-8</sup> m/a was selected, which is about the maximum expected (Nagra 2002, p. 141). This rate was transformed to the surface normalized corrosion rate  $R_S = 2.24 \times 10^{-11} \text{ mol m}^{-2} \text{ s}^{-1}$  using the following formula:

$$R_s = R_L \frac{\rho}{WF} \tag{A1}$$

where  $\rho = 6440 \text{ kg m}^{-3}$  is the density of Zircaloy,  $W=0.09122 \text{ kg mol}^{-1}$  is the molar weight (taken for simplicity to be equal to the atomic weight of Zr) and  $F = 3.1536 \text{ x} 10^7 \text{ s} \text{ a}^{-1}$  is a time conversion factor.

#### (c) Canister (stainless steel)

Depending on the type of steel, homogeneous corrosion rates may vary by orders of magnitude. For the stainless steel composition considered in this report, we selected a value of  $10^{-6}$  m a<sup>-1</sup>, about the upper limit assumed by Nagra for homogeneous stainless steel corrosion and close to the assumed reference corrosion rate for carbon steel (Diomidis et al., 2013, p. 18). By applying eq. (A1) with  $\rho = 8000$  kg m<sup>-3</sup> for the density of steel, and W= 0.055 kg mol<sup>-1</sup> we obtain  $R_S = 4.6 \times 10^{-9}$  mol m<sup>-2</sup> s<sup>-1</sup>.

#### (d) Scaling factors

In order to scale the mole amounts of Zircaloy and spent fuel dissolved for a given amount of canister corroded, one simply divides the corrosion rates of Zircaloy and spent fuel to the corrosion rate of the canister. Therefore, the scaling factor  $f_s$  for the spent fuel inventory assuming reductive dissolution is calculated as follows:

$$f_s = R_{mat}/R_{can} = 6.5 \text{ x } 10^{-12} \text{ mol m}^{-2} \text{ s}^{-1}/4.6 \text{ x } 10^{-9} \text{ mol m}^{-2} \text{ s}^{-1} = 1.41 \text{ x } 10^{-3}$$

Applying the same procedure we obtain the scaling factors specified in Table A1. Note that the amount of SF dissolved in the (hypothetical and unrealistic) case of maximal oxidative dissolution is nearly equal to the mole amount of canister corroded and almost three order of magnitude larger than for reductive spent fuel dissolution. For the structural materials, the same scaling factor as for Zircaloy was assumed in the absence of data.

Material to scale	$R_{mat} \ (mol \ m^{-2} \ s^{-1})$	$R_{can} \pmod{\mathrm{m}^{-2} \mathrm{s}^{-1}}$	$f_s(-)$
Canister	4.6 x 10 <sup>-9</sup>	4.6 x 10 <sup>-9</sup>	1
Spent fuel (reductive dissolution)	6.5 x 10 <sup>-12</sup>	4.6 x 10 <sup>-9</sup>	0.0014
Zircaloy	2.2 x 10 <sup>-11</sup>	4.6 x 10 <sup>-9</sup>	0.0049

 Table A1 - Calculation of scaling factors for chemical inventories dissolved.

## Appendix 2 – Determination of water exchange rate

The model set up in the present report calculates thermodynamic equilibrium between a fixed volume of "bentonite pore water" (corresponding to the flooded cavities inside the canister) and fixed amounts of irreversibly corroded material. The amounts of corroded spent fuel, Zircaloy and other structural components with inventories are scaled to the amounts of corroded steel container using the respective corrosion rates. An intrinsic problem of such a batch-type model is that in reality the system to be modelled is not closed but open to water exchange. A realistic model should thus take into account that the equilibrated water is dynamically replaced by fresh bentonite pore water via diffusion through the surrounding compacted bentonite.

Because full reactive transport calculations were not possible within the resources allotted to this project, an alternative approach was taken to simulate the dynamic nature of the processes involved. In practice, we calculated the time required for a full water exchange cycle. From this water exchange time and the selected canister corrosion rate the amount of steel that reacts per water exchange cycle (and consequently the scaled amounts of spent fuel, Zircaloy and structural materials) can be readily computed.

The rate of diffusive water exchange was determined by calculated from the diffusive flux of  $H_2O$  through the (cylindrical) outer canister surface. Owing to the much larger porosity of the corroded container, is implied that diffusion through the canister is much faster than through the compacted bentonite, i.e. we assume that the effective diffusion coefficient of water through the canister  $D_e(H_2O, canister)$  is much larger than  $D_e(H_2O, bentonite)$  and can thus be disregarded.

For the calculation,  $D_e(H_2O, bentonite) \equiv D_e$  is set to an appropriate value of the self-diffusion coefficient of water in compacted bentonite using recent experimental data by Ref. Bestel et al (2018). These authors measured the diffusion of tritiated water (HTO) through compacted Namontmorillonite with dry bulk densities between 1340 and 1678 kg m<sup>-3</sup>. At 25 °C, effective diffusion coefficients in the range 3.6 - 9.1 x 10<sup>-11</sup> m<sup>2</sup> s<sup>-1</sup> were found (see data in their supplemental materials), from which we selected the average value ( $D_e = 5.97 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ ), which is representative for MX-80 Na-bentonite compacted to 1450 kg m<sup>-3</sup> dry bulk density. This is the reference compaction currently assumed in Swiss safety assessment calculations.

The flux of water diffusing through compacted bentonite across the external canister boundary (i.e. the inner bentonite boundary) was then calculated for steady state conditions, assuming a cylindrical geometry corresponding to the setup of the planned HLW repository in Switzerland. The following steady state flux equation was derived and applied:

$$J = \frac{C_i - C_o}{\ln(r_i/r_o)} \tag{A2-1}$$

where *J* is the water flux across the bentonite/canister interface [mol m<sup>-2</sup> s<sup>-1</sup>];  $r_i$  and  $r_o$  [m] are the radial distance at ther inner (bentonite/canister interface) and outer (bentonite/host rock) bentonite boundary, respectively;  $C_i$  and  $C_o$  [mol m<sup>-3</sup>] are the concentration of water molecules originating from the inside canister volume at the inner and outer bentonite boundaries,

respectively. Inside the canister a constant concentration condition of  $C(H_2O^*)^1 = 55.5 \text{ M}$  (pure water) was set, while at the external bentonite boundary, we arbitrarily choose  $C(H_2O^*) = 0$ , implicitly assuming fast advection. This choice maximises gradient and water flux across the bentonite/canister interface, leading to the shortest possible water exchange time. Table A2 shows the numerical parameter used, taken from Ref. Nagra 2002.

**Table A2:** Parameters used for the application of the steady state flux equation.

inner and outer bentonite radius	$H_2O^\ast$ concentrations at $r_i$ and $r_o$
[m]	[mol / L]
<i>r</i> <sub><i>i</i></sub> =0.525	<i>C</i> <sub><i>i</i></sub> =55.5
$r_{o} = 1.25$	$C_o = 0$

Applying eq. A2-1 with the parameters listed in Table A2, the exchange flux of water is  $7.27 \times 10^{-6}$  mol m<sup>-2</sup> s<sup>-1</sup>. The bentonite/canister interface area corresponding to a single assembly of 4.6 m length is given by

 $2 \ \pi \ r_i \ L = 2 \ \pi \ x \ 0.525 \ \text{x} \ 4.6 = 15.17 \ m^2$ 

from which one derives the following radial diffusive flux:

15.17 m<sup>2</sup> x 7.267 x 10<sup>-6</sup> mol m<sup>-2</sup> s<sup>-1</sup> = 1.1 x 10<sup>-4</sup> mol H<sub>2</sub>O\*/s

Considering that the open space inside the canister assembly has a volume of 0.7 m<sup>3</sup> and that it contains in total 38856 moles of water when it is completely flooded, the water exchange time  $t_{ex}$  is:

 $t_{ex} = 38856 \text{ mol} / 1.1\text{e-4 mol s}^{-1} = 3.521 \text{ x} 10^8 \text{ s} = 11.158 \text{ years is needed}$ 

This means that at the assumed canister corrosion rate of 1  $\mu$ m/a (i.e. a fractional canister corrosion rate of 6.67 x 10<sup>-6</sup> a<sup>-1</sup> for a 15 cm thick canister) the fraction of canister reacted (FCR) per water exchange cycle is:

FCR =6.67 x  $10^{-6}$  a<sup>-1</sup> x 11.158 a = 7.44 x  $10^{-5}$ 

The above FCR value is the multiplication factor to be used as input in GEM-Selektor calculations to transform the "scaled inventory" into the "reactive inventory" (see Table 3.2).

<sup>&</sup>lt;sup>1</sup> The asterisk in  $C(H_2O^*)$  indicates that one is considering only "marked" water molecules, i.e. those molecules originating from inside the canister.  $C(H_2O^*)$  inside the canister is by definition constant and equal to the concentration of water molecules in pure water, i.e. 55.5 mol/L.