Reactive transport calculations to evaluate sulphide fluxes in the near-field of a SF/HLW repository

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Abstract. Radioactive waste is planned to be disposed in a deep geological repository in the Opalinus Clay (OPA) rock formation in Switzerland. Cu coating of the steel disposal canister is considered as potential a measure to ensure complete waste containment of spent nuclear fuel (SF) and vitrified high-level waste (HLW) or a period of 100,000 years. Sulphide is a potential corroding agent to Cu under reducing redox conditions. Background dissolved sulphide concentrations in pristine OPA are low, likely controlled by equilibrium with pyrite. At such concentrations, sulphide-assisted corrosion of Cu would be negligible. However, the possibility exists that sulphate reducing bacteria (SRB) might thrive at discrete locations of the repository's near-field. The activity of SRB might then lead to significantly higher dissolved sulphide concentrations. The objective of this work is to employ reactive transport calculations to evaluate sulphide fluxes in the near-field of the SF/HLW repository in the OPA. Cu canister corrosion due to sulphide fluxes is also simplistically evaluated.

1 Background and objectives

In Switzerland, SF and vitrified HLW are planned to be disposed in a repository constructed in the Opalinus Clay (OPA) at a depth of about 600-900 m. SF and HLW will be encased in canisters, emplaced into horizontal tunnels (drifts) excavated in the OPA, and backfilled with bentonite (Fig. 1, left). Nagra (the Swiss National Cooperative for the Disposal of Radioactive Waste) is considering candidate designs for Cu-coated steel canisters [1]. Sulphide has been recognised as a potential Cu corroding agent under anaerobic conditions, and its effect has been evaluated by various nuclear waste disposal organisations that have considered Cu for canister material [2-5].

Sulphide cycling under repository conditions would be affected by a complex system of biogeochemical reactions and transport processes. Reactive transport (RT) calculations offer a convenient framework within which such processes and their coupling can be represented. The objectives of this study were to: (1) conservatively assess the potential for

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SRB to generate elevated sulphide concentrations in the repository's near-field by considering specific geochemical constraints, (2) quantify main model uncertainties, and (3) to evaluate maximum sulphide fluxes towards the canister as well as, in a simplified manner, assess their potential to corrode the Cu canister coating.

Fig. 1. Schematic of the Swiss concept for disposal of spent fuel and high-level waste in the Opalinus Clay (left, courtesy of www.nagra.ch). Simplified 1D radial geometry of the disposal system with the orientation of the profile used in reactive transport calculations (right).

2 Conceptual model

The model assumes that sulphide can be generated in the repository's near-field due to metabolic activity of Sulphate Reducing Bacteria (SRB), according to the overall reaction (where $\text{CH}_2\text{O}_{(\text{aq})}$ is a simplistic formula representing dissolved organic matter – DOM):

SRB activity is considered exclusively within an “excavation disturbed zone” (EDZ) of the host rock (OPA). The calculations consider DOM as the electron donor to sulphate, while gypsum and celestite present in the backfill and OPA, respectively, are sources of sulphate. SRB activity is represented using a simplified Monod kinetic model:

$$R_{\text{SRB}} = k_{\text{SRB}} \cdot (C_{\text{DOM}} / (C_{\text{DOM}} + K_{\text{DOM}})) \cdot (C_{\text{SO}_4} / (C_{\text{SO}_4} + K_{\text{SO}_4})) \quad (2)$$

Where: R_{SRB} is the sulphate reduction rate, k_{SRB} is the SRB activity rate constant, C_{DOM} is the concentration of DOM, K_{DOM} is the half-saturation constant for DOM, C_{SO_4} is the concentration of dissolved sulphate, and K_{SO_4} is the half-saturation constant of sulphate. DOM concentration in the pore water of both the OPA and backfill is supplied by the dissolution of solid organic matter (SOM) according to the rate equation:

$$R_{\text{SOM}} = k_{\text{SOM}} \cdot (1 - C_{\text{DOM}} / C_{\text{DOM,max}}) \quad (3)$$

Where: R_{SOM} is the SOM dissolution rate and $C_{\text{DOM,max}}$ is the maximum DOM concentration. Generated sulphide can be precipitated as mackinawite (FeS), depending on chemical conditions in the pore water. Iron for mackinawite precipitation is provided by the dissolution of siderite and goethite. Sulphate reduction has an additional effect of depressing pH and elevating alkalinity, affecting sulphide solubility. The sole mass transport process is solute diffusion in fully water saturated pore space (single porosity) under isothermal conditions according to concentration gradients. At the canister surface,

sulphide undergoes a fast chemical reaction with Cu, and the model assumes canister corrosion rate to be proportional to the sulphide flux. A schematic representation of the main geochemical processes considered in the model is shown in Figure 2.

Fig. 2. Schematic illustration of main processes considered in the conceptual geochemical model.

3 Implementation and calculation cases

Reactive transport calculations are performed using the PFLOTTRAN code (www.pflotran.org) for a period of 100,000 years. Calculations consider a simplified 1D radial geometry (perpendicular to the main drift axis), which includes the canister, bentonite backfill, EDZ, and OPA (Fig.1, right). The chemical model includes 14 master and 41 secondary species, considers cation exchange and surface protonation reactions, as well as dissolution/precipitation reactions of 10 minerals. Chemical reactions are performed at 25 °C using the Thermochimie (<https://www.thermochimie-tdb.com/>) thermodynamic database v.9b with the extended Debye-Hückel aqueous activity model.

Main model uncertainties identified by scoping calculations include the rate of SRB activity, availability of DOM, the dissolution rate and extractability of SOM, the sulphide-solubility limiting mineral, and iron availability. Table 1 presents the calculation cases considered in this study.

4 Selected results and discussion

Considerable quantities of celestite (in the OPA) and gypsum (in the bentonite backfill) ensure continued sulphate availability during 100,000 years. Similarly, sufficient quantities of SOM result in a high availability of DOM. Consequently, the model predicts continuous sulphide production at a pessimistically high rate (especially for cases assuming fast dissolution rates of SOM). However, the results also indicate that sulphide concentrations in the repository near-field would be strongly limited by the precipitation of mackinawite. This process constitutes an effective sink for sulphide due to relative abundance of iron in the OPA (siderite). The solubility of mackinawite therefore controls sulphide release rates and significantly reduces the calculated corrosion depth of the canister. Figure 4 presents

the nominal Cu canister corrosion depths calculated for selected cases during a period of 100,000 years.

Table 1. Calculation cases. k_{SOM} – SOM dissolution rate constant [$\text{mol}/(\text{m}_{\text{bulk}}^3 \cdot \text{s})$], k_{SRB} – SRB activity rate constant [$\text{mol}/(\text{L}_{\text{water}} \cdot \text{yr})$], $C_{\text{DOM,max}}$ –maximum DOM concentration [$\text{mg}/\text{L}_{\text{water}}$], Ext. SOM – extractability of SOM [% total], S(-II) control – sulphide solubility controlling mineral, Fe control – iron solubility controlling mineral. Mack – mackinawite, Sid – siderite. 1A & 1B – defined based on [6]. 2A & 2B – defined based on [7]. 3A & 3B – defined based on [8]. 4 – arbitrary small value. 5 – siderite solubility reduced by a factor of ten.

Case code	k_{SOM}	k_{SRB}	$C_{\text{DOM,max}}$	Ext. SOM	S(-II) control	Fe control
REF1	10^{-11} (1A)	0.1	1 (3)	100	Mack	Sid
REF2	10^{-6} (1B)	0.1	1	100	Mack	Sid
SRB1a	10^{-11}	1 (2A)	1	100	Mack	Sid
SRB1b	10^{-11}	10^{-5} (2B)	1	100	Mack	Sid
SRB2a	10^{-6}	1	1	100	Mack	Sid
SRB2b	10^{-6}	10^{-5}	1	100	Mack	Sid
DOM1a	10^{-11}	0.1	0.1 (3A)	100	Mack	Sid
DOM1b	10^{-11}	0.1	10 (3B)	100	Mack	Sid
DOM2a	10^{-6}	0.1	0.1	100	Mack	Sid
DOM2b	10^{-6}	0.1	10	100	Mack	Sid
EXT1	10^{-11}	0.1	1	1 (4)	Mack	Sid
EXT2	10^{-6}	0.1	1	1	Mack	Sid
SSOL1	10^{-11}	0.1	1	100	FeS(am)	Sid
SSOL2	10^{-6}	0.1	1	100	FeS(am)	Sid
FESOL1	10^{-11}	0.1	1	100	Mack	Sid_10x (5)
FESOL2	10^{-6}	0.1	1	100	Mack	Sid_10x (5)
PES	10^{-6}	1	10	100	FeS(am)	Sid_10x (5)

Fig. 3. Nominal canister corrosion depths [m] calculated during 100’000 years for selected cases.

An important geochemical effect predicted by the model for all studied cases is localized acidification of the pore water associated with sulphate reduction (Reaction 1), the magnitude of which is proportional to the SRB activity rate. The decrease in pH constitutes an important factor increasing sulphide solubility under mackinawite equilibrium,

increasing sulphide fluxes to the canister. The calculations performed also highlight the role of dissolved Fe as a sink for sulphide. A further key factor is the solubility of the sulphide-controlling phase. Moreover, the kinetics of SOM dissolution and its solubility (DOM concentration), which are at present not well understood, are both relevant parameters affecting the calculated sulphide fluxes to the canister, and the nominal corrosion depths.

5 Conclusions

Realistic predictive modelling of SRB activity near the repository over long times (hundreds of thousands of years and longer) is at present not possible due to complexity and incomplete understanding of key processes. However, pessimistic estimates of sulphide concentrations and sulphide fluxes towards the canister can be derived from simplified models. In this study, we set out to develop a model with the aim to evaluate upper limits of sulphide fluxes towards the canister by considering geochemical constraints on sulphide generation and transport.

In the present model, uncertainties are bounded by a conservative choice of processes and parameter values. Consequently, the predicted geochemical evolution does not aim to represent quantitatively the “most likely” geochemical evolution of the system. Instead, the choice of processes and parameter values results in a prediction of a geochemical evolution that is pessimistic in terms of sulphide concentrations and sulphide fluxes due to potential SRB activity. An important conservatism of the model includes the assumption of a large and constant SRB population size, although many factors could lead to its significant reduction (e.g. availability of key nutrients). Another example is the assumption of fast dissolution kinetics of SOM and near-constant availability of DOM (while the quantity of leachable SOM and its dissolution rate could be much lower leading to a slowdown/termination of sulphide production). The assumption of mackinawite being the sulphide-controlling mineral is also conservative, as possible equilibrium with pyrite would greatly reduce sulphide concentrations. In addition, potential iron supply from other iron-bearing minerals (e.g. clay minerals) present both in the bentonite backfill and in the OPA is conservatively ignored. Similarly, enhanced pH buffering (decreased sulphide solubility under mackinawite equilibrium) due to Al-silicate minerals dissolution is not represented.

Despite the conservative nature of the model, our calculations suggest that canister corrosion over 100,000 years would be small (below 1 mm). Considering a Cu coating thickness of about 3–5 mm, the results of this study suggest that sulphide-assisted Cu corrosion is unlikely to compromise the Cu coating during hundreds of thousands of years.

References

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