

Nuclear Waste Repository

T. Xu & S. Finsterle

Earth Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

R. Senger

INTERA Inc., 9111A Research Blvd., Austin, Texas 78758, USA

ABSTRACT: Corrosion of steel canisters, stored in a repository for spent fuel and high-level waste, leads to hydrogen gas generation in the backfilled emplacement tunnels, which may significantly affect long-term repository safety. Previous modeling studies used a constant H_2 generation rate. However, iron corrosion and H_2 generation rates vary with time, depending on factors such as water chemistry, water availability, and water contact area. To account for these factors and feedback mechanisms, we developed a chemistry model related to iron corrosion, coupled with two-phase (liquid and gas) flow phenomena that are driven by gas-pressure buildup and water consumption. Results indicate that if H_2 generation rates are dynamically calculated based on a chemistry model, the degree and extent of gas pressure buildup are much smaller compared to a simulation in which the coupling between flow and reactive transport mechanism is neglected.

1 INTRODUCTION

The reference design for the canisters, stored in a repository for spent fuel and high-level waste, involves a cast steel body with about 20 cm wall thickness (NAGRA, 2002). The canisters are about 1 m in diameter and are surrounded by a 0.75-m thick bentonite buffer in emplacement tunnels which are 2.5 m in diameter (Figure 1). The repository tunnel center is assumed to be located in the water-saturated zone at a depth of 650 m below the land surface and surrounded by Opalinus clay, which is the host formation.

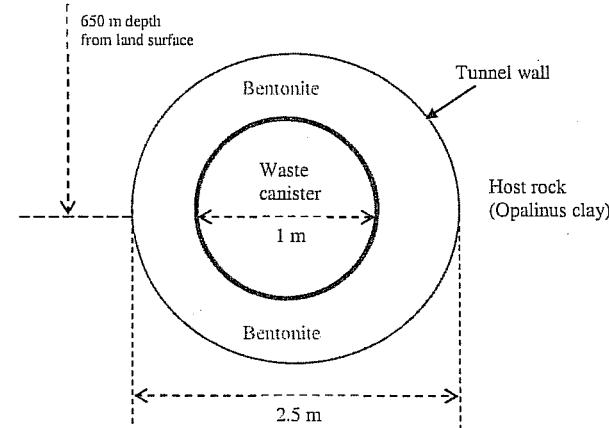


Figure 1. Schematic representation of a nuclear waste repository with single waste canister, bentonite backfill, and opalinus clay host rock (NAGRA, 2002).

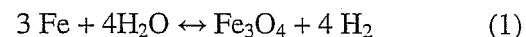
Corrosion of steel (iron) canisters leads to hydrogen gas generation in the backfilled emplacement tunnels. Gas generation may significantly affect long-term repository safety. Previous modeling studies used a constant H_2 generation rate (Senger, 2005; Poppei et al., 2002). However, iron corrosion and H_2

generation rates vary with time, depending on factors such as hydrological conditions, water chemistry, water availability, and water contact area. To account for these factors and feedback mechanisms, we developed a chemistry model related to iron corrosion, coupled with two-phase (liquid and gas) flow phenomena that are driven by gas-pressure buildup and water consumption. The purpose of this work is to apply the coupled chemistry and two-phase flow model to evaluate the impact of H_2 generation and migration on the system state in a nuclear waste repository.

2 PROCESS MODEL

2.1 Chemical reactions

The corrosion of the steel canisters under anaerobic conditions produces hydrogen gas and the solid corrosion product magnetite (Fe_3O_4) according to the following redox reaction (Neretnieks, 1985; Senger, 2005):



This chemical reaction indicates that each generated mole of H_2 consumes one mole of H_2O . In the current chemistry model, we consider the following species: (1) two minerals (iron (Fe) and magnetite (Fe_3O_4)), (2) two gases (H_2 and O_2), and (3) a number of aqueous species (H^+ , OH^- , H_2O , Fe^{2+} , Fe^{3+} , $H_2(aq)$, $O_2(aq)$, $Fe(OH)_2(aq)$, $Fe(OH)_2^+$, $Fe(OH)_3(aq)$, $Fe(OH)_3^-$, and $Fe(OH)_4^-$). The bentonite buffer and Opalinus clay are assumed non-reactive. Aqueous-aqueous and aqueous-gaseous reactions are assumed at local equilibrium. Mineral

dissolution and precipitation proceeds according to kinetic rate constraints.

2.2 Kinetic rate expression

A simple rate law, similar to the transition state law (Lasaga et al., 1994), was used:

$$r = kA \left[1 - \left(\frac{Q}{K} \right) \right]. \quad (2)$$

Here, r is the kinetic rate (positive values indicate dissolution, negative values precipitation), k is the rate constant (moles per unit mineral surface area and unit time), A is the total reactive surface area for the grid block representing a steel canister, K is the equilibrium constant for the mineral-water reaction written for the destruction of one mole of mineral, and Q is the reaction quotient. For iron dissolution, the rate can be expressed as

$$r_{iron} = kA \left[1 - \left(\frac{[Fe^{2+}][H_2(aq)]^{0.5}}{[H^+]^2} \right) \right]. \quad (3)$$

The surface area can be calculated from

$$A = A_0 \frac{V}{V_0} f(S_w), \quad (4)$$

where A_0 is the initial surface area, and V_0 and V are mineral (iron) volume fractions at initial and current times, respectively. The factor f , ranging from 0 to 1, accounts for the area contacted by water, divided by the total surface area. Here, we assume that f depends on the water saturation (S_w). At water-saturated conditions, $f = 1$. At under-saturated conditions, $f < 1$. The following relation of f depending on S_w is used in the present work:

$$f(S_w) = (S_w)^n. \quad (5)$$

By substituting Eqs. (4) and (5) into Eq. (3), the overall rate can be obtained from

$$r_{iron} = k \cdot \left[A_0 \frac{V}{V_0} S_w^n \right] \cdot \left[1 - \left(\frac{[Fe^{2+}][H_2(aq)]^{0.5}}{[H^+]^2} \right) \right]. \quad (6)$$

The initial total surface area can be calculated from

$$A_0(m^2) = V_E(m^3)(1 - \phi) f_v \rho(g/m^3) A_s(m^2/g), \quad (7)$$

where V_E is the canister grid block volume, ϕ is the porosity, f_v is the initial volume fraction of the mineral in the solid phase, ρ is the density of the mineral, and A_s is specific surface per unit mineral mass.

2.3 Two-phase flow

Two-phase flow phenomena arising from the corrosion of the steel canister and gas generation includes initial dissolution of H_2 gas in the pore water in the canister and in the surrounding buffer and host rock. As pore water becomes fully gas saturated and no more gas can be dissolved, a free gas phase develops, causing a significant increase in the gas pressure. Driven by the pressure buildup, gas starts to migrate into the surrounding bentonite buffer and further into the Opalinus clay. The buffer and surrounding host rock become partially saturated. There is a potential for some displacement of pore water as the gas front migrates from the canister through the buffer into the surrounding host rock. The water involved in the corrosion reaction is taken from the water in the waste canister or adjacent bentonite, and water and vapor transport toward the canister.

2.4 Numerical implementation

The previous modeling of processes associated with a constant H_2 gas generation with corrosion of the waste canister and the potential impact of H_2O consumption is implemented in iTough2 (Finsterle, 2004), which is an inverse code for the non-isothermal, two-phase fluid and heat flow code TOUGH2 (Pruess, 1991). In order to consider water withdrawal under two-phase conditions, Senger (2005) changed the iTough2 code to allow only the liquid phase to be extracted.

In the present work, H_2 gas generation rates due to iron corrosion is dynamically calculated from the chemistry model. The geochemical transport part of TOUGHREACT (Xu et al., 2006) was linked to iTough2. TOUGHREACT is a non-isothermal reactive geochemical transport program that was developed by introducing reactive geochemistry into TOUGH2. It can deal with a wide range of subsurface coupled thermal-physical-chemical processes under various thermal-hydrological and geochemical conditions (Xu et al., 2006). It can accommodate any number of chemical species present in aqueous, gaseous, and solid phases.

3 PROBLEM SETUP

3.1 Thermo-physical conditions and parameters

The simplified, radially symmetric model previously used by Senger (2005) (which ignores the lateral flow boundary and gravity effects) was employed here for the coupled modeling. The system is initially fully water saturated with a background pressure of 65 bar. A radial distance of 75 m was

modeled with a constant pressure of 65 bar specified at the outer boundary. Heat generation from the waste package was not considered in the current study; a constant temperature of 40°C was used. The thermo-physical properties for the different materials (waste canister, bentonite buffer and Opalinus clay) were taken from Senger (2005).

3.2 Chemical conditions and parameters

The initial water is dilute water with very low ion concentrations. Constant aqueous concentrations (dilute water) are specified at the outer boundary. Initially, a volume fraction of iron of 0.8 was assumed available for the corrosive reactions.

Poppei et al. (2002) and Senger (2005) used a constant H₂ generation rate at the canister grid block of 1.049×10⁻¹⁰ kg/s. For a water solution far from equilibrium, the dissolution rate expression of Eq. (3) can be reduced to $r_{iron} = kA$, which is the case for the conditions at early times. By applying Eq. (7) and using a canister grid block volume of 0.2827 m³ and a specific surface area of 121.8 cm²/g, this H₂ generation rate corresponds to an iron dissolution rate constant of 2.0×10⁻¹² mol/m²/s. The specific surface area and rate constant above are used for the input of TOUGHREACT in the current study. The reaction rate may decrease over time because of (1) reduction of iron volume, (2) approaching chemical equilibrium, and (3) reduction of water contact areas, which is dynamically calculated according to Eq. (6).

The water-contact-area factor f depends on water saturation according to Eq. (5). Three values of the exponent n were used, 0.5, 1 and 2. For $n = 1$, f is equal to the water saturation S_w ; for $n < 1$, f is greater than S_w ; and for $n > 1$, f is less than S_w . To provide a basis for comparison with the variable generation rates calculated with the fully coupled flow and reactive transport model, an additional simulation without modeling of geochemical reactions ("flow-only" simulation) was carried out using the constant H₂ generation rate of 1.049×10⁻¹⁰ kg/s.

4 RESULTS

For the flow-only simulation using constant H₂ generation rates, pressures at the canister grid block continuously increase to about 82 bar after 5,000 yr. If the chemical model is coupled to the two-phase flow model, the magnitude and spatial extent of the gas pressure buildup are much smaller than in the flow-only case (Figure 2). Pressures increase initially and reach a peak at 600 yr. Later, gas pressures decrease because of (1) migration to the surrounding bentonite buffer and (2) decreases in the reaction

rate (Figure 3) caused by water consumption and decreases in water saturation. The rate factor f (Eq. 5) decreases according to $f(S_w) = (S_w)^n$. For $n = 0.5$, f is greater than S_w but less than 1, yielding the largest reaction rate, which produces a peak pressure of about 70 bar and a final stabilized pressure of 65.5 bar, a pressure slightly greater than the background pressure of 65 bar. At this stabilized state, only a small water saturation remains to maintain iron corrosion. Near steady state, the amount of gas generation is equal to its migration to the bentonite buffer, and the amount of water consumption is equal to the supply from the surrounding bentonite. For $n = 1$, f equals S_w . This produces a peak of 67.5 bar and pressures decrease slowly. The H₂ generation and gas pressure buildup ($p > 65$ bar, the background pressure) extends to a radial distance of approximately 4 m. For $n = 2$, no peak pressure is formed, but a stabilized pressure of 65.6 bar is eventually obtained. The amount of iron dissolution is presented in Figure 4. Magnetite precipitates due to the iron dissolution with a volume increase by a factor of 2.1. Iron corrosive dissolution consumes H⁺ and generates Fe²⁺. Initially, the pH increases from the background value of 7 to 9.5 (Figure 5), and then stabilizes at about 9. Dissolved Fe²⁺ increases to 7×10⁻⁵ mol/l, and then stabilizes at about 1×10⁻⁵ mol/l. Values of dissolved ion concentrations from all coupled simulations are similar because of strong, diffusive exchange with the surrounding materials.

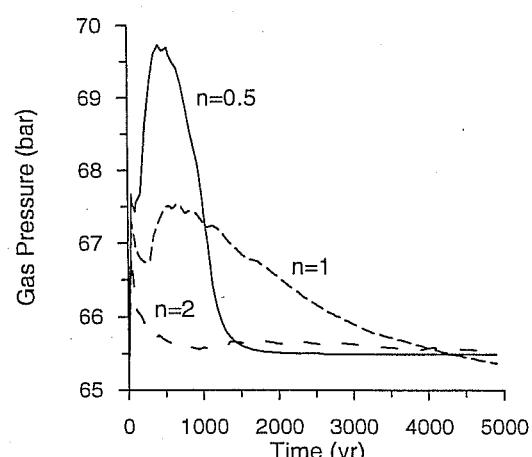


Figure 2. Pressure as a function of time at the canister surface for different n values relating water contact area to liquid saturation.

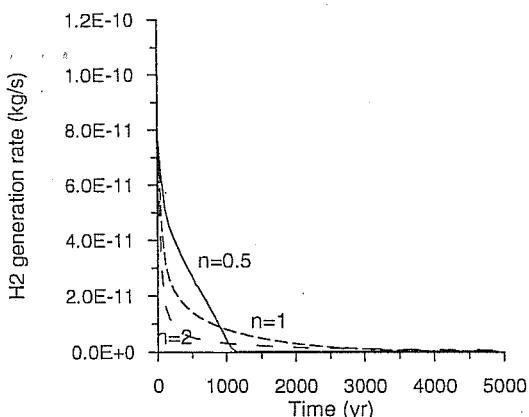


Figure 3. H_2 generation rate as a function of time at the canister surface.

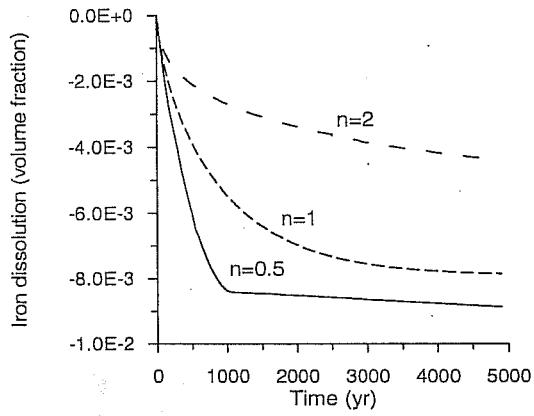


Figure 4. Iron dissolution as a function of time at the canister surface for different n values relating water contact area to liquid saturation.

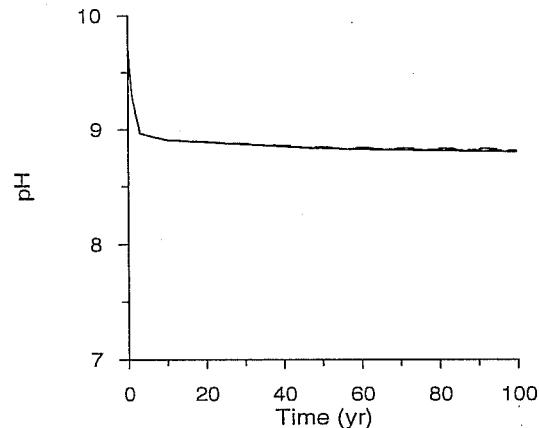


Figure 5. pH evolution as a function of time at the canister surface.

5 CONCLUSIONS

A chemistry model describing iron corrosion and H_2 generation has been coupled with two-phase flow and reactive transport to study gas buildup in a nuclear waste repository. Results indicate that if H_2 generation rates are dynamically calculated based on an model of corrosion chemistry, the degree and extent of gas pressure buildup are much smaller than when neglecting the coupling between flow and

reactive transport mechanisms. Assuming a constant H_2 generation rate thus provides an upper bound and a conservative estimate of pressure buildup. These corrosion processes are limited by water supply, which depends on hydrogeological conditions and parameters. Alteration of minerals in bentonite buffer, the Opalinus clay host rock and waste materials will influence iron corrosion and gas generation. All of these processes need to be addressed in a coupled manner.

ACKNOWLEDGMENT. This work was supported by National Co-operative for the Disposal of Radioactive Waste (NAGRA) of Switzerland, and, in part, by the U.S. Dept. of Energy under Contract No. DE-AC02-05CH11231

REFERENCE

Finsterle, S., 2004. Multiphase inverse modeling: Review and iTOUGH2 applications, *Vadose Zone J.*, 3: 747-762.

Lasaga, A.C., J.M. Soler, J. Ganor, T.E. Burch, K.L. Nagy, 1994. Chemical weathering rate laws and global geochemical cycles. *Geochimica et Cosmochimica Acta*, 58, 2361-2386.

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

Neretnieks, I., 1985. Some aspects of the use of iron canisters in deep lying repositories for nuclear waste. Nagra Technical Report NTB 85-35, Nagra, Wettingen, Switzerland.

Poppei, J., G. Mayer, and J. Croise., 2002. *OPA/Hydrogeology: Scoping Calculations on Gas Transport Processes in the Vicinity of a HLW/SF/ILW Repository in Opalinus Clay*. NAGRA Internal Report NIB 02-34.

Pruess, K., 1991. TOUGH2: A General-Purpose Numerical Simulator for Multiphase Fluid and Heat Flow. Lawrence Berkeley Laboratory, Report LBL-29400, Berkeley, California, USA.

Senger, R., 2005. Investigation of Two-Phase Flow Phenomena Associated with Corrosion in an SF/HLW Repository in Opalinus Clay, Project Report, INTERA Inc., Austin, Texas, USA.

Xu, T., E.L. Sonnenthal, N. Spycher, and K. Pruess, 2006. TOUGHREACT: A simulation program for non-isothermal multiphase reactive geochemical transport in variably saturated geologic media, *Computer & Geoscience*, 32(2), 145-165.