



Modeling of oxygen gas diffusion and consumption during the oxic transient in a disposal cell of radioactive waste



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ARTICLE INFO

Article history:

Received 12 July 2013

Accepted 7 December 2013

Available online 14 December 2013

Editorial handling by M. Kersten

ABSTRACT

The oxic transient in geological radioactive waste disposals is a key issue for the performance of metallic components that may undergo high corrosion rates under such conditions. A previous study carried out in situ in the argillite formation of Tournemire (France) has suggested that oxic conditions could have lasted several years. In this study, a multiphase reactive transport model is performed with the code HYTEC to analyze the balance between the kinetics of pyrite oxidative dissolution, the kinetics of carbon steel corrosion and oxygen gas diffusion when carbon steel components are emplaced in the geological medium. Two cases were modeled: firstly, the observations made in situ have been reproduced, and the model established was then applied to a disposal cell for high-level waste (HLW) in an argillaceous formation, taking into account carbon steel components and excavated damaged zones (EDZ).

In a closed system, modeling leads to a complete and fast consumption of oxygen in both cases. Modeling results are more consistent with the in situ test while considering residual voids between materials and/or a water unsaturated state allowing for oxygen gas diffusion (open conditions). Under similar open conditions and considering ventilation of the handling drifts, a redox contrast occurs between reducing conditions at the back of the disposal cell (with anoxic corrosion of steel and H₂ production) and oxidizing conditions at the front of the cell (with oxic corrosion of steel). The extent of the oxidizing/reducing front in the disposal cell is strongly dependent on the gas diffusion coefficient in partially saturated zones.

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1. Introduction

The environment in a deep geological disposal of high-level radioactive waste (HLW) will be initially aerated, due to the air introduced into the disposal cell during its excavation and waste emplacement. The project developed in France by Andra involves carbon steel materials and horizontal disposal cells in Callovo-Oxfordian argillite, containing significant amounts of pyrite. The oxygen is considered initially entrapped in the porosity of materials and in the residual voids between components. In addition, it is assumed that the ventilation of handling drifts will renew oxygen at the front of the disposal cell over a period from a few years to many decades. So far, the reducing conditions generally prevailing in deep geological environments are supposed to be quickly restored after the closure of such facilities because of the consumption of the oxygen by corrosion of the carbon steel (C-steel) of waste overpacks, oxidation of pyrite of the host rock and, to a probably lesser extent, microbial activities (e.g. Wersin et al., 2003; Yang et al., 2007; Bennett and Gens, 2008; Johnson and King, 2008). However, the duration of this oxic stage is of first

importance since corrosion rates under oxic conditions are known to be particularly high (Féron et al., 2008; Johnson and King, 2008) and may thus lead to a premature loss of the watertightness of metallic components, as well as an alteration of their mechanical integrity.

A previous study of the in situ corrosion of carbon steel samples was carried out in boreholes drilled horizontally in the Tournemire experimental site (France), a century-old tunnel crossing a 250 m thick formation of Toarcian argillite (a fine-grained sedimentary rock composed predominantly of indurated clay particles). The steel samples were representative of carbon steel overpacks that may be selected for radioactive waste geological disposal. The tunnel was naturally ventilated. The experimental concept, the materials and the results have been detailed by Foct et al. (2004) and Gaudin et al. (2009). C-steel samples (A42 type) were placed in a 10 m long borehole filled in by re-compacted argillite, during 6 years, at 8 m from the wall of the tunnel. The re-compacted argillite materials used for this experiment indicated a near isotropic texture. The analytical characterization of the sample interface showed a Fe-rich enrichment of the altered argillite, concomitant with the crystallization of significant amounts of goethite/lepidocrocite and some traces of magnetite near the C-steel contact. The crystallization of few amounts of gypsum and melanterite, probably due to pyrite

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oxidation, was also noted. Dissolution of primary calcite minerals and calcium leaching was also revealed, probably related to a slight decrease of pH due to pyrite oxidation. Eventually, localized corrosion patterns were highlighted on the C-steel coupons. Although oxygen partial pressure was not monitored during the 6 years of interaction, these observations led to the conclusion that oxidizing conditions had lasted a significant period of time, even though the presence of magnetite tends to show that reducing conditions were recovered before the end of this period. This indicates that usual assumptions, such as fast oxygen consumption by pyrite, have to be partly reconsidered in the case of open conditions such as an open ventilated tunnel scenario.

From a modeling point of view, to the authors' knowledge, there are only a few studies devoted to the consumption of oxygen entrapped in the voids of the near-field components and to the short-term geochemical evolution during this oxic stage in a HLW repository (Kolar and King, 1996; Yang et al., 2007; the technical reports of Wersin et al., 1994, 2003). These previous studies have considered, neither the reactive transport of oxygen in the gas phase, nor the extension of the oxidizing perturbation inside the whole disposal cell in case of ventilation.

In a preliminary step, this study aims at deciphering the physico-chemical processes involved in the oxygen consumption in the Tournemire in situ experiment. For this purpose, a reactive transport model was developed, which included gas diffusion, aqueous chemistry, cation exchange and dissolution/precipitation processes. Kinetic formulations were introduced for C-steel corrosion and pyrite dissolution under both oxic and anoxic conditions, as well as an empirical relationship between the gas diffusion coefficient and the water saturation.

In the core of the present work, the resulting model was then applied to the 2D-configuration of a HLW disposal cell in a deep argillaceous formation representative of the design developed in France by Andra (Andra, 2005). The main point was to assess the extent of the oxic perturbation inside the cell when the ventilation is maintained in the handling drift, and to model the redox contrast between the back and the front of the disposal cell. Simulations were performed over a 100 y timescale, which is the estimated period of the operation phase for a HLW disposal before its closure. Temperature was set to 25 °C, which underestimates the temperature of the environment of HLW disposal cells during this period, estimated between 50 and 90 °C (Andra, 2005). However, modeling of interdependent and coupling effects of heat transfer, gas phase physics, vapor evaporation/condensation, water resaturation of the porous components, C-steel corrosion and chemical reactions is a highly complex task that cannot be handled by the code. This paper considers a subset of those processes, i.e. gas diffusion and reactivity (for both H₂ and O₂), C-steel corrosion, redox chemistry and pH-buffering.

2. Modeling approach and parameters

2.1. HYTEC reactive transport code

The reactive transport code HYTEC is based on a finite element discretization in a representative elementary volume (REV) approach and a sequential iterative operator-splitting method for coupling between chemistry and transport (van der Lee et al., 2003). A simplified two phase dynamics of mass transfer can be simulated, namely a reactive transport modeling in the water phase linked to diffusion in the gas phase.

Under water unsaturated conditions, the general HYTEC formulation of the reactive transport of solute writes as follows:

$$\frac{\partial(\theta^w T_i^w)}{\partial t} = \nabla \cdot (D_e^w(\theta^w) \nabla T_i^w) + Q_i^w \quad (1)$$

where θ^w is the volumetric content of the water phase, T_i^w is the total aqueous concentration of an element or basis component i per unit volume of solution (mol L⁻¹), D_e^w is the effective diffusion coefficient in the aqueous phase common to all elements (m² s⁻¹) and Q_i^w is the source-sink term of the element i (mol L⁻¹ s⁻¹) driven by the chemical reactions with the gas and solid phases. D_e^w is itself a function of the water content according to the relation:

$$D_e^w(\theta^w) = \frac{\theta^w}{\omega} D_{e,sat}^w = S^w D_{e,sat}^w \quad (2)$$

where ω is the total porosity of the porous media, S^w is the water saturation degree and $D_{e,sat}^w$ is the effective diffusion coefficients (m² s⁻¹) at water fully saturated conditions.

The reactive transport equation for the gaseous phase writes as

$$\frac{\partial(\theta^g C_j)}{\partial t} = \nabla \cdot (D_e^g(\theta^g) \nabla C_j) + Q_j^g \quad (3)$$

where θ^g is the volumetric content of the gas phase, C_j is the concentration of a gas species j regarding the gas phase volume (mol L⁻¹), D_e^g is the effective diffusion coefficient in the gas phase common to all gas molecules (m² s⁻¹) and Q_j^g is linked to the variation of the partial pressure of the gas species j [(mol L⁻¹)(sec⁻¹)] driven by the dissolution of the gas in the aqueous phase according to the Henry's law.

In this study, the empirical relationship of Aachib et al. (2004) was selected to estimate the dependency of D_e^g on θ^g (i.e. indirectly with the water saturation state since $\theta^g = \omega - \theta^w$). That writes as:

$$D_e^g(\theta^g) = \frac{(\theta^g)^{3.3}}{\omega^2} D_0^g, \quad (4)$$

where D_0^g is the gas diffusion coefficient in air. This law has been calibrated for oxygen gas diffusion in unsaturated media with applications to soil cover. It has recently been applied to numerical simulations of pyrite oxidation in unsaturated waste rock piles (Molson et al., 2005).

The concentration of each gas species is related to its partial pressure according to the perfect gas law, which was a good approximation under the pressure (~1 bar) and temperature (25 °C) of the present study. That is to say

$$C_j = \frac{P_j}{RT} \quad (5)$$

where n is the number of mole, T is the absolute temperature [K] and R is the perfect gas constant (L bar K⁻¹ mol⁻¹). The Dalton's law is, therefore, applicable:

$$P = \sum_j x_j p_j \quad (6)$$

where P is the total pressure of the gas phase [bar] and x_j is the mole fraction of the species j .

The mass balance is made over the aqueous (dissolved) phase, the solid phases (including the mineral and fixed fractions) and eventually the gas phase:

$$T_i^{tot} = T_i^w + T_i^s + T_i^g. \quad (7)$$

The corresponding sum of the subtotal concentrations is expressed in terms of mole per kg of water, of which the gas contribution is calculated according to the following expression:

$$T_i^g = \left(\frac{p_i \theta^g}{RT} \right) \left(\frac{1}{\theta^w \rho_{H_2O}} \right) \quad (8)$$

where ρ_{H_2O} is the water density (kg L⁻¹) at the given temperature (25 °C in this study).

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