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Review

Multiple lines of evidence for performance of the canister and waste form in long-term nuclear waste disposal: Reviews

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ABSTRACT

The time scales required for nuclear waste disposal are very large compared with those for other engineering endeavors. Because of this, there are many uncertainties associated with the quantitative performance assessment of canisters containing high-level radioactive waste in a waste form. Multiple lines of evidence can be helpful in building confidence in the long-term behavior (corrosion and dissolution) of the canister and waste form. These lines of evidence are derived from long-term supports and probabilistic models and developed based on shorter term tests, bounding and conservative approaches, and available observations on natural analogs. This paper presents the progress made for important lines of evidence considered in quantitatively assessing radionuclide release behavior from canisters and waste forms. This paper considers risk-significant issues for canisters and waste forms (i.e., risk informed approach) in the probabilistic performance assessment of the disposal system which has also other components such as geology and hydrology.

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1. Introduction

High-level radioactive waste (HLW) contains some very long-lived radionuclides (i.e., half-lives longer than 10,000 to 1,000,000 years). These radionuclides are embedded in the uranium dioxide (UO_2) (pellet) matrix of spent nuclear fuel (SNF) or silica-based HLW glass (i.e., waste forms). The waste forms are contained in robust metallic canisters destined for disposal in deep geologic disposal facilities. When the canisters are breached (for example, by corrosion caused by ground water), the waste forms would begin to degrade by dissolution. The dissolved radionuclides would migrate into host rock and then farther into the biosphere. However, the release of radionuclides may be limited by the use of intact canisters, small openings on those failed canisters, slow waste form dissolution, and slow dispersion of radionuclides out of the canister.

Because of the long time period associated with geologic disposal, the following supporting bases (i.e., multiple lines of evidence) are important for addressing uncertainties in estimating the performance of canister and waste form:

- shorter term tests, and mechanistic understanding and modeling
- probabilistic performance assessment (PA) of the disposal system, including various components such as canister, waste form, geology, and hydrology
- natural (e.g., archaeological) observations
- assessment of long-term supports for the component performance

Probabilistic PAs sometimes use a bounding or conservative approach. The bounding approach uses a worst case value from a range of uncertain values. The conservative approach is not worse case and adopts conservative values rather than using realistic values that may be very uncertain. Both approaches can be incorporated in the uncertainty distribution, if necessary. These two approaches are used as long as the safety objectives of the disposal system continue to be met. The use of these two approaches also depends on how robust design feature is in the disposal system. Quantitative representations for these degradation processes are generally of simple forms, which rely, in part, on bounding and conservative approaches to help address uncertainty.

In 1992, the author of this paper organized a session addressing this topic at the annual meeting of the Materials Research Society, and the journal *Science* (Amato, 1992) highlighted the session. Since then, the author has periodically reported on the progress made for

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peer reviews (Ahn, 2003a; 2013b; Ahn et al., 2008, 2013; U.S. Nuclear Regulatory Commission, 2008; U.S. Nuclear Regulatory Commission, 1996; Ahn, 1994). Each report focuses on selected new or updated issues and then reviews, interprets, and analyzes the issues as appropriate. The reports build on the work of the U.S. Nuclear Regulatory Commission (NRC) and work it has sponsored. This paper presents more recent progress on important (i.e., risk-significant) lines of evidence considered in assessing long-term radionuclide release behavior from canisters and waste forms. It independently analyzes appropriate but shorter term data and understanding in the literature on risk-significant topics, including probabilistic system PAs. The analog information presented herein is qualitative in nature, as the materials and environments are not the same as modern engineering products in diverse candidate natural environments.

2. Canister corrosion

2.1. Corrosion allowance canister

The first type of canister considered is made of metal that would corrode slowly without forming a protective oxide passive film on the metal surface. Such metals include copper (Cu) or carbon steel in a reducing environment with very limited oxygen (e.g., less than 1 part per billion (ppb)). Fig. 1 (KAIST, 2008) is a calculated electrochemical equilibrium diagram for copper in contact with water (H_2O). The reaction of copper with water results in product phases of various chemical forms, depending on the electrochemical potential of copper and the pH of the water. The figure shows boundary lines for the electrochemical potentials between two phases. For each boundary, log activities (i.e., concentration) of dissolved species are drawn in multiple lines. Line (a) is the H^+/H_2 (hydrogen) equilibrium and line (b) is for the water breakdown. The figure also shows the immune domain of copper in water. The H^+/H_2 equilibrium potential represented by line (a) is always lower than the Cu^{+2}/Cu equilibrium potential in the nonoxidizing environment. The H^+ ions are then in contact with immune copper metal that cannot corrode.

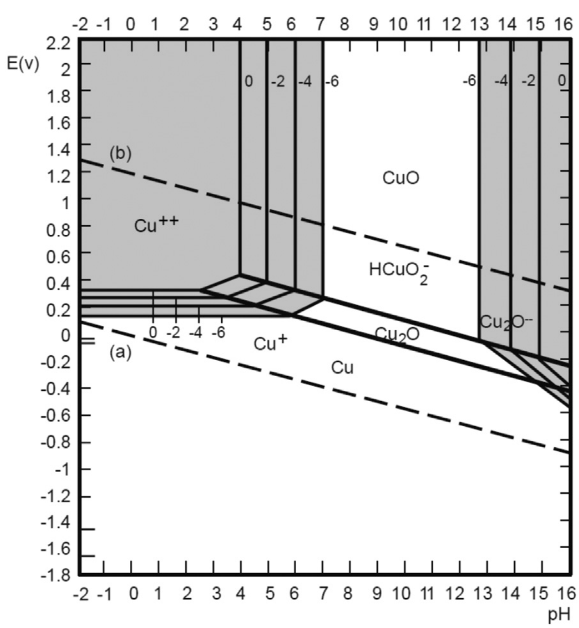

Fig. 1. Electrochemical equilibrium diagram for copper ((KAIST, 2008), permission by Korea Advanced Institute of Science and Technology). Lines are drawn for the chemical potentials for equilibrium between two phases. For each boundary, log activities of dissolved species are drawn in multiple lines. Line (a) is the H^+/H_2 equilibrium and line (b) is the water breakdown.

In Fig. 1, the amount of copper dissolved in water is indicated by multiple lines of the boundary. Varying the dissolved activity of copper ions over a reasonable range representative of a longer time does not significantly change the area and position of the immune domain. The dissolved copper ions may have limited diffusion out but insignificant copper corrosion. Therefore, one can postulate that copper will not corrode in the absence of oxygen, as shown in natural copper. Nevertheless, there have been arguments about the validity of this thermodynamic approach. A more fundamental approach using molecular dynamics showed that the copper corrosion could be significant in water in the absence of oxygen (Huktquist et al., 2009). However, the picking of a copper-oxygen-hydrogen molecule in the model was arbitrary, and the environmental conditions of the analog site cited are likely to have varied.

Very low corrosion rates were also reported in pure water as a monolayer of copper oxide (Cu_2O) after 6 months at 50 °C (C) (Boman et al., 2014).

$$2Cu + H_2O \Leftrightarrow Cu_2O + H_2$$

Tests at the NRC-supported Center for Nuclear Waste Regulatory Analyses (CNWRA), using simulated granitic ground water of a disposal repository with less than 10 ppb oxygen (i.e., reducing) and approximately 0.1 M (Molar, mol/m^3) chlorides at 80° C for 3 months, showed black corrosion products (He et al., 2015). There is general consensus that copper corrosion could occur in the presence of chlorides or sulfides. The issue is how much or how fast these species could affect the corrosion in a disposal system. The NRC and CNWRA assessed probabilistic corrosion rates including sulfides and potential enhancement by localized corrosion (Jung et al., 2011). This study (Jung et al., 2011) presents that 5-centimeter (cm) copper will not fail in 1,000,000 years; conservatively, 5 cm will be safe for 100,000 years (as quoted from (Huktquist et al., 2009)).

As mentioned above, another type of metal that corrodes slowly in the near-neutral pH and reducing environment of a disposal repository is carbon steel. Corrosion rates for (iron-based) carbon steel are in general agreement within the uncertainty range among various studies. The corrosion rates in this environment range from 0.1 to 10 micrometers per year, which include data from testing and analog studies (Jung et al., 2011; Dillmann et al., 2014; Yoshikawa et al., 2008; Taniguchi et al., 2005; Wersin et al., 1994), as shown in Table 1 (Jung et al., 2011).

The distribution of corrosion rates is log-normal. As previously mentioned, analog data may not exactly fit in a mathematical description; the analog materials in diverse candidate natural environments are not the same as modern engineering test materials under controlled conditions. Confirmatory testing by CNWRA also shows this range of values of Table 1 (He and Ahn, 2015). Roman ingots immersed for approximately 2000 years at a depth of 12 m in reducing conditions maintained by mineral concretions and a biofilm that entirely covered the ingots appear very well preserved.

Table 1
Corrosion rates reported in the literature in micrometers per year of carbon steel in an oxidizing and reducing environment.

Environment	Corrosion rate
Oxidizing	10–100
Reducing	0.1–10

Maximum and Minimum Values, Log-Normal Distribution. Source: (summary (Jung et al., 2011)).