

Corrosion of Spent Nuclear Fuel and High-Level Waste Glass in Anoxic Clay Disposal Environment

Tae M. Ahn^{a,b}, Jack Gwo^a,
Office of Nuclear Material Safety and Safeguards
U.S. Nuclear Regulatory Commission (NRC), Washington, DC 20555-0001, USA

1. Introduction

Many countries are pursuing deep geologic disposal of spent nuclear fuel (SNF) and/or high-level waste (HLW) glass in carbon steel containers in anoxic clay (and/or bentonite backfill) environments. If water contacts the nuclear material due to container failure by corrosion, corrosion (i.e., traditional dissolution) of SNF and/or HLW glass will occur potentially resulting in radionuclide release to the geosphere. Studies, generally independent of each other, have been conducted on corrosion of containers, corrosion of SNF and HLW glass, and radionuclide transport in the geological disposal setting. The output of these efforts is abstracted into integrated system performance assessments (PAs) in order to analyze generic deep geologic disposal systems of SNF and/or HLW glass (together called HLW).

This technical note considers the application of laboratory experiment results from multiple research programs in the United States, Canada, Japan, and the European community on corrosion of SNF and/or HLW glass and mass transport in the clay/bentonite medium of a repository system. This includes studies by staff at the U.S. Nuclear Regulatory Commission (NRC) and the Center for Nuclear Waste Regulatory Analyses (CNWRA). Specific consideration is given to the diffusional corrosion of SNF and HLW glass as the chemical corrosion is reaching solubility (or steady state) limit.

2. Corrosion of Spent Nuclear Fuel

The long-term test results for SNF corrosion from Carbol et al. (2005) and Poinssot et al. (2005a) are of particular interest for consideration here. Context for the present evaluation is provided by on-going NRC/CNWRA efforts in corrosion testing of SIMFUEL (simulated unirradiated SNF) along with related literature analyses. The evaluation has led to three points to consider: (1) the meaning of corrosion rates based on laboratory (static) immersion tests; (2) the effect of hydrogen on corrosion rates; and (3) the effect of coupling corrosion to the conditions of repository near-field barriers and migration into the surrounding geological material.

Corrosion Rates Based on Immersion Tests

Immersion tests with coupons/wafers in closed cells entail (i) solutions of varying chemical conditions, (ii) high water volume/sample surface area ratios, and (iii) periodic sampling of solution for chemical analysis. Carbol et al. (2005; Table 2-6) report results for three different isotope-doped coupons of UO₂ fuels used to simulate SNF with substantial radioactivity decay during the containment time. The test samples were composed of (1) UO₂(²³³U-1%) [SNF 1], (2) UO₂(²³³U-10%) [SNF 2], and (3) UO₂ [SNF 3]. These samples were immersed in anoxic solutions under (99.98%) Ar/(0.02%) CO₂ at ambient temperature. An aliquot of ~ 10 ml [17.5 m-pints] was taken from each on 0.042, 0.084, 0.68, 4.69, and 46.88 days. The concentration of ²³⁸U (mole/liter) in these samples was nearly constant over the time of solution sampling.

This resulted in a calculated corrosion rate that appeared to decrease over time, from dividing the near-constant ^{238}U concentration by increasing values of time. An alternative interpretation is that the solubility limit (or steady-state concentration) arrived quickly, and further corrosion was limited. It is therefore unclear what the true corrosion rate is for the closed system of the laboratory test and how relevant such rates are to deep geological disposal conditions.

Separately, related tests were performed with SNF under immersion conditions up to 1095 days in anoxic deionized water (RON/COB, Rondinella et al., 2001, and 2003). In these experiments, actinides and fission products were all saturated in the solution before 100 days. The saturated values in terms of Cs and Sr concentrations were $\sim 10,000$ times higher than U in terms of fractions of radionuclide inventories in the aqueous phase (fractions). This suggests that oxidative corrosion occurred with radiolysis in anoxic water and uranium was deposited back to the solid fuel phase (as stated in the report) until Cs and Sr reached saturation. Independent studies of SNF dissolution in oxidizing environments showed similar behaviors (Wilson, 1990). Therefore, the corrosion rate needs to be determined based on the release of fission products not uranium. After the fission product saturation, the SNF corrosion is considered to stop or to continue with precipitation of uranium, unless some additional mechanism transports the dissolved species away from the SNF (by diffusion or advection of groundwater in a repository setting). The transport question is considered in the following sections.

Hydrogen Effect

Results of immersion tests for analog SNF performed with and without the presence of hydrogen were reported in Carbol et al. (2005). Impedance measurements with 10% ^{233}U doped UO_2 [SNF 2, Table 2-12 in Carbol et al., 2005] show estimated corrosion rates of 35 $\text{mg}/(\text{m}^2 \text{ day})$ [2.3×10^{-5} m-ounce/inch²] at 162 days with no hydrogen, and $\sim 36 \text{ mg}/(\text{m}^2 \text{ day})$ at 186 days with 8% hydrogen, both in 10 mM NaCl solution. The corrosion rate is alternatively presented too, as fractional release rate. The rate of 35 $\text{mg}/(\text{m}^2 \text{ day})$ is $\sim 10^{-5}/\text{year}$, which depends on time and fragment size. The reported data are with 1% ^{233}U doped UO_2 [SNF 1, Table 2-13], 8.1 $\text{mg}/(\text{m}^2 \text{ day})$ at 600 days with no hydrogen and 8.6 $\text{mg}/(\text{m}^2 \text{ day})$ at 837 days with 8% hydrogen both in 10 mM NaCl solution. The 10 mM NaCl solutions with inert N_2 was purged without and with 8% H_2 .

For up to 2082 hours (Carbol et al., 2005, Table 2-12 and Table 2-13), the impedance gradually increases, the corrosion potential increases, and the redox potential fluctuates and eventually increases. This indicates that the solution may have become more oxidative or a deposit may have occurred on the surface of sample or test vessel. Similar observations were also made for SNF 1. In the immersion tests of SNF 2 at 340 days, there was little change in the ^{238}U concentration in each aliquot. These observations imply that hydrogen effects are not significant. Even in the presence of hydrogen, oxidation seems to occur by radiolysis and the steady state arrives very rapidly. Data from NRC/CNWRA indicate that the hydrogen effect does not seem to be significant in suppressing the SNF corrosion (Shukla and Ahn, 2015). The NRC/CNWRA data used 1-3 mM (less than 8%) dissolved hydrogen.

In separate leaching tests for spent fuel conducted in 5 M NaCl under 40 Bar (92%) $\text{Ar}/(8\%) \text{H}_2$ overpressure (Carbol et al., 2005) with and without the presence of iron, the effect of hydrogen was monitored. The corrosion rate is reported to decrease linearly with hydrogen pressure (data plotted in log-log scale, Figure 3-11, though it is unclear whether the decrease is due to

time increase (with constant solubility limit) or hydrogen pressure increase. As stated earlier, the saturation of both actinides and fission products occurred very rapidly.

Coupling of SNF Corrosion to the Radionuclide Transport in Clay/Bentonite

When SNF corrosion and radionuclide groundwater transport in clay/bentonite medium are considered together, the overall release rate, R , of radionuclides from the fuel surface without considering sorption (such as fission products), with the SNF corrosion rate, SR , and transport rate, TR , can be expressed in series as

$$R^{-1} = SR^{-1} + TR^{-1}$$

This relation is very simplified to understand the chemical/physical processes (Ahn, 2017) associated with the corrosion rate and the diffusional transport rate. The test domain is after container failure with well network in clay (Mallants et al., 2001). Ahn (2017) further presented analytical formula for illustration of several other processes. In the series relation, the slowest process will control the overall kinetics. When SNF dissolves quickly and solution concentrations become steady state, the release of radionuclides is controlled by the radionuclide transport rate in surrounding clay/bentonite. The SNF corrosion rate has been claimed as $10^{-6} - 10^{-5}$ /year fractional release rate (Johnson, 2005). In reality, the rate is faster because the initial release is greater due to the geometric effect (Poinssot et al., 2005b). Regardless, as discussed above the solubility limits will occur very quickly. The transport rate of fission products (e.g., Tc-99), calculated by PA is $10^{-4} - 10^{-3}$ /year fractional release rate in clay with very low sorption coefficient (Mallants et al., 2001). Therefore, the transport in clay/bentonite is rate-limiting, compared to the SNF corrosion rate.

Mathematically with aqueous diffusivity and clay/bentonite thickness,

$$TR = D \times [\text{saturated concentration}] / \text{transport distance, } L$$

where D is diffusivity of radionuclides (mainly fission products) with minimum sorption in clay/bentonite and L is the diffusional transport distance in clay/bentonite. Detailed geometry is not considered. Simply, a one-dimensional approximation is made as

$$\text{Time} = L^2 / D$$

Using the data (Poinssot et al., 2005a) of

$$D = 10^{-6} \text{ cm}^2/\text{second (clay and bentonite), } L \text{ (effective clay/bentonite thickness) = 100 cm,}$$

the saturated concentration of fission product = 10^{-4} mole/liter (M), and SNF density of 10 g/cm^3 .

Because the radionuclide concentration in solution (primarily fission products) has reached equilibrium (or saturation), the rate of radionuclide transport away from the fuel surface will dictate the corrosion rate of SNF. Alternatively, a steady state may be reached (Iwalewa and Farnan, 2019), if SNF dissolves irreversibly (e.g., electrochemically with oxidants resulting in precipitates, Shoosmith and Sunder, 1991).

If the diffusion time ($= L^2/D$, above) is greater than ~ 300 years (Mazurek, 2017; Mallants et al., 2001) and, then, the SNF of 3 mm will last $> 10^5$ years. The solution volume is assumed to be 1 cm^2 (unit area of SNF package) $\times 100 \text{ cm}$ (conservative L value). Mallants et al. (2001) reported calculated total dose rates due to activation (e.g., C-14) and fission products (e.g., Tc-99) for the

well pathway in clay. The release started as early as ~1000 years. If $L = 300$ cm, the release may start at ~10,000 years ($\text{Time} = L(300 \text{ cm})^2 / D$). On the other hand, transport geometry and sorption will delay radionuclide transport. For actinides, the efficiency of sorption will be very high. In PA exercises, this range of transport time and total SNF loss time were reported (Mazurek, 2017, Mallants et al., 2001).

3. Corrosion of HLW Glass

As is the case for SNF corrosion (Section 2), the glass corrosion rate is also related to the transport rate of radionuclides in series. Typical glass corrosion rates used in PA (e.g., Mallants et al., 2001), are on the order of $10^{-4} - 10^{-3}$ fractional release per year (note: the size of glass piece is bigger than the spent nuclear fuel). Therefore, it is likely that the concentration and transport will be controlled by either or both rates of glass corrosion and transport in clay/bentonite, as shown in the PA calculated transport rate above for SNF). Recently, there has been a new phenomenon recognized on glass corrosion which is also assessed below.

HLW glass corrosion has shown an abnormal behavior after ~ 10 years in immersion tests. Following the initial period of rapid corrosion (stage 1), and a subsequent period of very slow corrosion (stage 2), corrosion appears to once again resume at a fast rate. This behavior after the slow rate of stage 2 has been referred to as stage 3 corrosion, or resumption of HLW glass corrosion (Gin et al., 2013). While this phenomenon has not been reported in analogue studies (e.g., Cary, 2017; Jantzen et al., 2008), it is of sufficient interest that the U.S. Nuclear Waste Technical Review Board (NWTRB) has summarized various issues related to this apparent resumption of corrosion (NWTRB, 2017).

Pegg (NWTRB, 2017) summarized two long-term tests over 36 years at various temperature and glass surface area to solution volume ratio, with water replenishment. One of the tests used 25% water replenishment over a maximum of one year. No glass corrosion resumption was observed. This is effectively equivalent to a period of 144 years ($36 \text{ years} \times 4 [= 1/0.25] = 144 \text{ years}$), assuming the same stage 2 corrosion over different times. As discussed in Section 2, complete effective water replenishment will occur in approximately ~ 300 years or more. Over such period, the solution pH may never reach ~ 11 under replenishment conditions, considering that the experiments (Pegg, in NWTRB, 2017) did not show resumption beyond 36 years. A solution pH of ~ 11 has been considered as a threshold for the resumption to occur. The time for resumption could be longer given the variabilities/uncertainties associated with compositions of glass and corrosive solution including groundwater. Under conditions of dripping ground water or vapor, the dripped water after glass corrosion rarely reached pH 11 (Bechtel SAIC Company, 2002; Ebert, 1995).

The stage 3 glass corrosion rate is ~ 0.13 g/(m² day) (Ebert and Jantzen, NWTRB, 2017) which is ~ 1.7×10^{-3} cm/year. The stage 2 rate is ~ 5×10^{-4} g/(m² day). In assessing glass durability, PA models use glass corrosion rates up to 1 – 2 g/m²-day at alkaline and acidic pHs (Bechtel SAIC Company, 2002). The coupling effects with other components are also treated in conjunction with the statistical nature of container failure (Ahn, 2017) which reduces effective glass corrosion. If 120 mg/L (2×10^{-3} M) (Pradeep et al., 2016) is taken as the silica solubility limit, the glass corrosion rate following the analysis in Section 2 is ~ 10^{-6} cm/year.

This suggests that no silica release occurs once the solution reaches the silica solubility limit, even under resumption conditions. The resumption (stage 3) conditions may primarily represent by boron release rather than bulk corrosion of the HLW glass. While high

solubility boron continues to dissolve, dissolved silica is at its solubility limit, and silica-bearing precipitates may potentially form on the glass. Therefore, the increase in boron concentration in the solution in stage 3 is a poor surrogate for release of fission products (such as Tc-99), and a corrosion rate based on boron release would lead to an overestimate of the fission product release rate. Rates consistent with the solubility limits of fission products, on the order of 10^{-4} M (Section 2) in silica-rich environments, may be more representative for use in PA models.

4. Summary

1. SNF corrosion occurs very rapidly under anoxic repository conditions, reaching steady state relatively rapidly. The effects of hydrogen on SNF corrosion may not be significant in anoxic repository conditions. The release of actinides or fission products (e.g., Cs or Sr) is likely to be dictated by a steady-state concentration (or solubility) of radionuclides at the waste form boundary and their much slower diffusive transport in a repository with a clay/bentonite medium.
2. Consideration of the coupling of corrosion effects to reactions and transport processes in the clay/bentonite medium suggests that resumption of HLW glass corrosion may not be as significant as previously considered. The solubility limits of radionuclides will control the radionuclide releases coupled with the clay/bentonite medium. Other engineering components such as the container may also mitigate the fast resumption of HLW glass corrosion, considering a statistical treatment of container failure in performance assessment.

^a Disclaimer

The NRC staff views expressed herein are preliminary and do not constitute a final judgment or determination of the matters addressed or of the acceptability of any licensing action that may be under consideration at the NRC.

^b Contact: Tae M. Ahn, tae.ahn@nrc.gov, +1-301-415-5972

References

T. Ahn, Risk-informed Assessment of Radionuclide Release from Corrosion of Spent Nuclear Fuel and High-level Waste Glass, Nuclear Engineering and Design, 317 (2017) 242-250.

Bechtel SAIC Company, Defense HLW Glass Degradation Model, ANL-EBS-MD-000016, REV 2, 2004.

P. Carbol, J. Cobos-Sabate, J.-P. Glatz, and Others, The Effect of Dissolved Hydrogen on the Corrosion of ²³³U Doped UO₂(s), High Burnup-Up Spent Fuel and MOX Fuel. Technical Report, TR-05-09, Swedish Nuclear Fuel and Waste Management Co., Stockholm, Sweden, 2005.

A. Cary, Glass from Ancient Swedish Fort Provides Knowledge for Hanford Cleanup, Tri-City Herald, January 22, 2017.

- W. Ebert, The Effects of the Glass Surface Area/Solution Volume Ratio on Glass Corrosion: A Critical Review, Argonne National Laboratory, ANL-94/34, 1995.
- S. Gin, A. Abdelouas, L. J. Criscenti, et al., An International Initiative on Long-term Behavior of High-Level Nuclear Waste Glass, *Materials Today*, Vol. 16, No. 6, (2013) 243-248.
- T. M. Iwalewa and I. Farnan, Coupling Radioactive Waste Glass Dissolution Measurements in Generic Groundwaters with Reactive Transport Modeling of Repository Scenarios, *Water Resources Research*, 2019.
- C. M. Jantzen, D.I. Kaplan, N.E. Bibler, D.K. Peeler, and M.J. Plodinec. Performance of a Buried Radioactive High-Level Waste (HLW) Glass after 24 Years, *Journal of Nuclear Materials*. 378 (2008) 244–256.
- L. Johnson Ed., 2005, Spent Fuel Evolution under Disposal Conditions – Synthesis of Results from the EU Spent Fuel Stability (SFS) Projects, NAGRA Technical Report NTB 04-09, Nagra Wetingen, Switzerland.
- D. Mallants, J. Marivot and X. Sillen, Performance Assessment of the Disposal of Vitrified High-Level Waste in a Clay Layer, *J. of Nuclear Materials*, 298 (2001) 125-135.
- M. Mazurek, Far-Field Process Analysis and Radionuclide Transport Modeling for Saturated Media, in *Geological Repository Systems for Safe Disposal of Spent Nuclear Fuels and Radioactive Waste*, ed. By M. Afted and J. Ahn, Woodhead Publishing, 2017.
- U.S. Nuclear Waste Technical Review Board (NWTRB), U.S. Department of Energy (DOE) Research Activities Related to Corrosion and Long-term Performance of Borosilicate High-Level Radioactive Waste (HLW) Glass, Board Meeting, June 21, 2017, NWTRB (in *Google*)– Past Public Meetings - Summer 2017 Board Meeting, High-Level Radioactive Waste Glass Corrosion.
- C Poinssot, C. Ferry, M. Kelm, and others, Spent Fuel Stability under Repository Conditions – Final Report of the European Project, European Commission, 2005a.
- C. Poinssot, C. Ferry, P. Lovera et al., Spent Fuel Radionuclide Source Term Model for Assessing Spent Fuel Performance in Geological Disposal, Part II: Matrix Alteration Model and Global Performance, *J. Nucl. Mater.*, A346 (2005b) pp. 66-77.
- K. Pradeep, M. Nepolian, P. Anandhan, and others, A Study on Variation in Dissolved Silica Concentration in Groundwater of Hard Rock Aquifer in Southeast Coast of India, *Mater. Sci. Eng.* 121, 2016, IOP Publishing.
- [RON/COB 2001] Rondinella V V, Cobos J, Matzke Hj, Wiss T, Carbol P, Solatie D. Leaching behaviour and α -decay damage accumulation of UO₂ containing short-lived actinides, *Mat. Res. Soc. Symp. Proc.*, 663 pp 392–399, 2001.
- [RON/COB 2003] Rondinella V V, Cobos J, Wiss T, Hiernaut J-P. Studies on Spent Fuel Alterations during Storage and Radiolysis Effects on Corrosion Behavior using α -doped UO₂, *proc. ICEM ' 03*, Oxford, UK, Sept 21–25, 2003, ASME 2003, (CD-ROM).
- D. W. Shoesmith and S. Sunder, An Electrochemically-Based Model for the Atomic Dissolution of UO₂, AECL-10488, Atomic Energy of Canada Limited, Pinawa, Canada, 1991.

P. Shukla and T. Ahn, Hydrogen Effects on Corrosion of Spent Nuclear Fuel under Reducing Repository Conditions, International High-Level Radioactive Waste Management Conference (IHLRWC), 2015, pp. 660-670.

C. Wilson, Results from NNWSI Series 3 Spent Fuel Corrosion Tests, Pacific Northwest Laboratory, Richland, Washington, 1990.