Chapter 1

Use of Alloy 22 as Long-Term Radioactive Waste Containment Material

Osvaldo Pensado, Roberto Pabalan, Darrell Dunn, and Kuang-Tsan Chiang

Center for Nuclear Waste Regulatory Analyses (CNWRA), 6220 Culebra Rd. San Antonio, TX, 78238-5166, USA, opensado@swri.org

An approach to estimate upper probability bounds for localized corrosion initiation in Alloy 22 as function of water chemistries relevant to a potential geologic repository for high-level radioactive waste is discussed. The approach is used to compare the effect of fabrication processes (e.g., welding) accounting for various chemical components that promote or inhibit localized corrosion.

1. Introduction

The waste package design for the potential geologic repository for high-level radioactive waste at Yucca Mountain in the United States includes an outer container made of Alloy 22 (Ni-22Cr-13.5Mo-3W-4Fe), for corrosion resistance, and an inner container made of Type 316 nuclear grade stainless steel, for structural support. The evaluation of Alloy 22 oxide stability in the repository setting is unique because of the long time frames involved (tens of thousands of years) and its dependence on changing environments. No natural processes, aside from the establishment of adverse environmental conditions, are envisioned capable of inducing passivity breakdown for extended periods. Therefore, Alloy 22 passivity is dependent on the quantity and chemistry of the waters that could contact waste packages. The repository design includes self supported titanium shields to protect waste packages from

seeping water. For reasons discussed elsewhere [1, 2], passivity breakdown (in the form of crevice corrosion) could only occur when (i) seeping water directly contacts waste packages and (ii) dynamic evaporation causes the development of concentrated brines. A simplified model to develop upper bounds for the probability of passivity breakdown, in the form of crevice corrosion, is discussed accounting for distributions of brine compositions after water evaporation, and for the different susceptibility of mill-annealed and weld zones.

2. Approach

A mechanistic equation for the computation of the corrosion potential, E_{corr}, as a function of pH, temperature, and the anodic current density associated with the passive dissolution of Alloy 22 has been developed elsewhere [2]. The equation is consistent with experimental values and trends (e.g., the corrosion potential decreases with increasing values of pH and temperature). Studies indicate that localized corrosion is initiated when the corrosion potential is above a critical potential; and that fabrication processes such as welding can cause Alloy 22 to become more susceptible to localized corrosion [3]. The crevice corrosion repassivation potential, E_{rcrev}, can define the critical potential. E_{rcrev} is a function of temperature and chloride concentration [3]. Oxyanions such as nitrate, carbonate, and sulfate are effective inhibitors of localized corrosion in Alloy 22 [4]. The effect of nitrate has been modeled as an increase in the repassivation potential as a function of the oxyanion to chloride concentration ratio [2]. This functional dependence has been extended to account for the possible simultaneous presence of multiple inhibiting oxyanions [5]. To estimate the probability of localized corrosion of Alloy 22 under the dynamic evaporation conditions stated in the introduction, values from distribution functions relevant to the repository setting of pH and anion concentrations (chloride, nitrate, carbonate, and sulfate) were randomly sampled to determine values of E_{corr} and E_{rcrev} (the latter for both mill-annealed and weld areas). The conditional probability of localized corrosion, P_c, was estimated by counting the fraction of times E_{corr} exceeds E_{rcrev}. Assuming that P_w is the probability of brine formation on the waste package, the localized corrosion probability can be estimated as $P_w \times P_c$.

The approach to estimate distributions of water compositions is described below. Thermodynamic simulations of the chemical evolution of in-drift waters resulting from evaporation of seepage waters were conducted. The simulations allowed determination of the types of brines that may form and the ranges of brine chemistry that may exist in emplacement drifts. The thermodynamic calculations were supplemented by an alternative approach based on the concept of chemical divide developed by Hardie and Eugster [6]. In the chemical divide concept, the chemical types of brines and salt minerals that form upon evaporation of natural waters are determined by early precipitation of insoluble minerals. Natural waters at Yucca Mountain are considered to evolve into three types of brines upon evaporation: (i) calcium-chloride, (ii) neutral, and (iii) alkaline. The evaporation simulations were conducted using thermodynamic equilibrium software [5]. Twenty-nine water compositions were used as input to the evaporation simulation, selected to represent the broad composition range of the more than 150 samples of Yucca Mountain unsaturated zone porewater reported by Yang et al. [7, 8, 9]. The evaporation simulations were done at 110 °C [230 °F] and at constant pressures of 0.85 or 1 bar [12.3 or 14.5 psi]. The likelihood of localized corrosion increases with increasing temperature. At temperatures higher than 110 °C [230 °F], water from seepage may not contact engineered barrier materials because of thermal mobilization of water away from drifts. Thus, consideration of this reference temperature is appropriate to estimate upper probability bounds for localized corrosion.

The thermodynamic simulation of seepage water evaporation used only a subset of the unsaturated zone porewater chemistry data reported by Yang et al. [7, 8, 9]. To provide a basis for estimating the frequency of occurrence of the three brine types and their respective chemical characteristics, the full set of Yang et al. [7, 8, 9] data on unsaturated zone porewater compositions was used with the chemical divide concept of Hardie and Eugster [6]. From 156 compositions, 8, 24, and 68 percent resulted into calcium chloride, neutral, and alkaline type brines, respectively. Distribution functions were numerically derived by interpolated sampling of empirical distribution functions for each brine type, and combining the three populations into a single population, preserving the brine type frequency (i.e., in a population with 10,000

stochastic vectors {pH, [Cl$^-$], [NO$_3^-$], [CO$_3^{2-}$]+[HCO$_3^-$], [SO$_4^{2-}$]}, 800 were calcium chloride; 2,400, neutral; and 6,800, alkaline brine type of vectors). The rank-correlation matrix of the 10,000 vector population was computed. A dominant correlation between pH and the carbonate concentration (equal to 0.9) indicated that highest carbonate concentrations were exhibited in alkaline brines. A negative correlation of -0.8 between chloride and pH mirrored the fact that acidic calcium chloride brines are highly concentrated in chloride.

3. Results and Discussion

Sampling from empirical distribution functions (10,000 samples) for the anions and pH while preserving the relevant rank correlations, and computing the corresponding values for the corrosion potential, E_{corr}, and critical potentials, E_{rcrev}, for each sample, the conditional distribution functions in Figure 1 were derived. Figure 1 (b) indicates that in 26 percent of the samples the corrosion potential exceeded the critical potential in thermally aged material (simulating welds), and only in 3 percent of the samples for mill-annealed material. It is therefore interpreted that P_c equals 0.26 along weld areas, and 0.03 on the rest of the body.
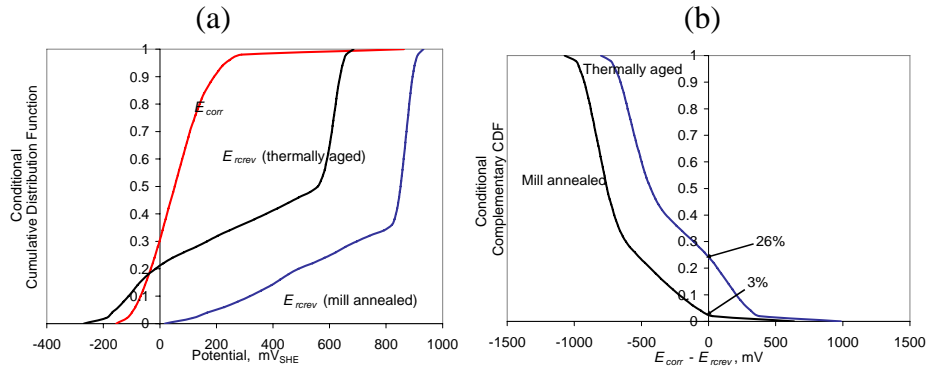
Figure 1. (a) Conditional distribution functions for the corrosion potential and critical potential for localized corrosion resulting from the adopted stochastic sampling approach. (b) Conditional complementary cumulative distribution function for the difference between the corrosion potential and repassivation potential.

The probability for Alloy 22 to exhibit localized corrosion equals $P_w \times P_c$, where P_w is the probability of brine formation on the waste package. If (i) drip shields perform their water-diverting function, or (ii) fail at later

times when development of brines is not longer possible (i.e., when the seepage rate exceeds the evaporation rate), or (iii) there is no water seepage during the thermal pulse, P_w would equal zero. In any of these three cases, localized corrosion would not be exhibited and passive dissolution would be the dominant corrosion mode (sustained by moisture in the environment or condensed water). A more detailed assessment is needed to estimate the probability P_w.

In addition to the dependence on P_w, other caveats to this simplified analysis are offered. There exists evidence that localized corrosion propagation could stifle, even in strongly oxidizing conditions [5]. Stifling may limit the extent of crevice attack. Localized corrosion experiments are performed in bulk solutions. If concentrated brines develop in the repository, localized corrosion may be activated under a limited supply of water. The stifling mechanism is likely to be more effective in solutions of limited volume due to local saturation with corrosion products. A second caveat is that the kind of localized corrosion that could affect Alloy 22 is crevice corrosion. Formation of crevices on waste packages may be limited to the contact area with the waste package support system. Additional crevice sites could form from direct contact between the waste package and drip shield caused by drift degradation and rockfall. Therefore, the probability for waste packages to be affected by localized corrosion is also conditional on the probability of formation of crevice sites. If crevice corrosion affects a waste package, the corroded area will be limited and the degraded waste package could still offer protection against radionuclide release.

4. Conclusions

The passive dissolution can only be affected by processes inducing compositional changes to the alloy at some significant depth. No processes are currently envisioned that could accomplish such a change. The persistence of Alloy 22 passivity in the repository setting is mainly dependent on the quantity and chemistry of water that could contact this alloy. An approach to estimate the probability for waste packages to be affected by localized corrosion was discussed accounting for possible brine chemistries developed after water evaporation. The approach did not consider protection from additional engineered and natural barriers,

localized corrosion stifling, nor crevice site requirements. The analysis accounted for the effect of various chemical components that promote (chloride) or inhibit (nitrate, carbonate, and sulfate) localized corrosion in Alloy 22, and for fabrication processes.

5. Acknowledgments

References

[1] L. Browning, R. Fedors, L. Yang, O. Pensado, R. Pabalan, C. Manepally, and B. Leslie, *Mat. Res. Soc. Symp. Proc*. 824 (2004) 417-424.

[2] D.S. Dunn, O. Pensado, and G.A. Cragnolino, "Performance Assessment of Alloy 22 as a Waste Package Outer Barrier" in Proceedings of the CORROSION 2005 Conference, paper 588. NACE International, Houston, Texas (2005).

[3] D.S. Dunn, L. Yang, Y.M. Pan, and G.A. Cragnolino, "Localized Corrosion Susceptibility of Alloy 22" in Proceedings of the CORROSION 2003 Conference, paper 697. NACE International, Houston, Texas (2003).

[4] D.S. Dunn, L. Yang, C. Wu, and G.A. Cragnolino, *Mat. Res. Soc. Symp. Proc.* 824 (2004) 33-38.

[5] D.S. Dunn, O. Pensado, Y.-M. Pan, R.T. Pabalan, L. Yang, X. He, and K.T. Chiang. "Passive and Localized Corrosion of Alloy 22—Modeling and Experiments." CNWRA 2005-02, San Antonio, Texas (2005).

[6] L.A. Hardie and H.P. Eugster, *Mineralogical Society of America*, Special Paper No. 3 (1970) 273-290.

[7] I.C. Yang, Z.E. Peterman, and K.M. Scofield, *Journal of Contaminant Hydrology*, 1878 (2003) 1-20.

[8] I.C. Yang, P. Yu, G.W. Rattray, J.S. Ferarese, and J.N. Ryan, "U.S. Geological Survey Water-Resources Investigations Report 98-4132," Denver, Colorado (1998).

[9] I.C. Yang, G.W. Rattray, and Y. Pei, "U.S. Geological Survey Water-Resources Investigations Report 96-4058," Denver, Colorado (1996).