Current Efforts in Immobilized Low-Activity Waste Glass Testing to Support the Hanford Site Integrated Disposal Facility-17119

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ABSTRACT

Cleanup plans for Hanford site high-level radioactive mixed tank waste calls for separating the waste into high-level waste (HLW) and low-activity waste (LAW) fractions. The fractions will be vitrified separately at the Hanford Tank Waste Treatment and Immobilization Plant (WTP). The HLW glass will be sent to an offsite geological disposal facility while the immobilized low-activity waste (ILAW) glass will be disposed at the onsite Integrated Disposal Facility (IDF). In order to inform models used to predict the performance of ILAW glass at IDF, it is necessary to understand the corrosion behavior of the glass. In this paper, we discuss tests that account for the effects of 1) solution chemistry, 2) the ion exchange reaction, and 3) secondary phase formation on the glass dissolution rate. To quantify the effects of solution chemistry, specifically changes in pH, T, and Si concentration, the single-pass flow-through (SPFT) test method is applied. A designed set of these tests results in a set of kinetic rate law parameters that are used in a glass dissolution rate law based on transition-state theory. Furthermore, for SPFT tests with relatively high concentrations of Si, an ion exchange rate is provided. Additionally, through tests such as the pressurized unsaturated flow (PUF) test method, a suite of secondary phases can be compiled. The collection of kinetic rate law parameters, the ion exchange term, and the suite of secondary phases are provided to IDF performance assessment (PA) modelers. Lastly, we present a description of the efforts made to verify and validate the use of these parameters and secondary phases through the use of a field lysimeter present at the Hanford site.

INTRODUCTION

Approximately 50 million gallons of high-level radioactive mixed waste has accumulated in 177 buried single- and double-shell tanks at the Hanford Site in southeastern Washington State as a result of the past production of nuclear materials for the U.S. strategic defense arsenal. The United States Department of Energy (DOE) is proceeding with plans to permanently dispose of this waste. Plans call for separating the tank waste into high-level waste (HLW) and low-activity waste (LAW) fractions, which will be vitrified at the Hanford Waste Treatment and Immobilization Plant (WTP). The much larger volume of immobilized low-activity waste (ILAW) will be placed in the on-site, near-surface Integrated Disposal Facility

(IDF). Principal radionuclides of concern in LAW are ^{99}Tc, ^{129}I, and U, while non-radioactive contaminants of concern are Cr, and nitrate/nitrite [1,2].

Before the ILAW can be disposed of at the IDF, a performance assessment (PA) must be conducted. The PA is a document that describes the long-term impacts of the disposal facility on public health and environmental resources. One of the major inputs to the PA is the estimate of radionuclide release rates from the engineered portion of the disposal facility into the surrounding environment. The glass will corrode upon contact with ground water and radionuclides will be released into the near-filed environment. Once released, the transport of the radionuclides is based on chemical reactions that occur in the near- and far-field. Therefore, to provide credible estimates, a mechanistic understanding of the physical and geochemical processes that are occurring must be understood and incorporated into models used to predict radiation dose over the period of regulatory concern ($\sim$ 10,000 years).

In the IDF system, the glass matrix must dissolve for radionuclides to be released into the environment thus the main assumption to estimating the radionuclide source term is directly related to the glass dissolution rate. The major parameters known to control glass dissolution are glass composition, temperature, and solution composition of the fluid contacting the glass (including pH and concentration of key ions [e.g., H_4SiO_4]). The effect of these parameters on the glass dissolution rate is essential for developing credible PA models. Though the temperature of the IDF is expected to be roughly constant at 15 °C, the pH and fluid compositions are affected by flow rate (i.e., water infiltration), reactions with near-field engineered materials, gas-water equilibria, secondary phase formation, ion exchange of alkalis in the glass with cations in solution, and the dissolution of the glass matrix. Due to the various evolving conditions expected at the site, the glass dissolution rate may vary both as a function of time and the position of the glass in the disposal system. Therefore, a fixed glass dissolution rate and thereby radionuclide release is not credible during PA modeling.

Because understanding the behavior of glass in the IDF disposal environment is a key to a defensible PA, several ILAW testing strategies and data packages have been produced [3-5]. These strategies have outlined various test methods used to study the glass corrosion process and the data packages have provided parameter values for a number of ILAW glasses. This paper summarizes the rate law equation based on transition state theory that is presently used in PA modeling efforts, the laboratory testing strategy that provides input parameters to the rate law equation, and briefly discusses areas where improved understanding of the glass dissolution process would lead to a stronger technical underpinning of the PA modeling efforts.

Overview of the Glass Dissolution Process

Before discussion of the testing strategy for ILAW glass, we provide an overview of the glass dissolution process. A large amount of data on the glass-water interaction has been collected and summarized in recent review articles [6,7]. Based on these

reviews, the glass dissolution reaction can be divided into three regimes or stages (Figure 1) that occur as the reaction proceeds (e.g., Stage I, II, and III).

- Stage I—Initial rate,
- Stage II—Residual rate, and
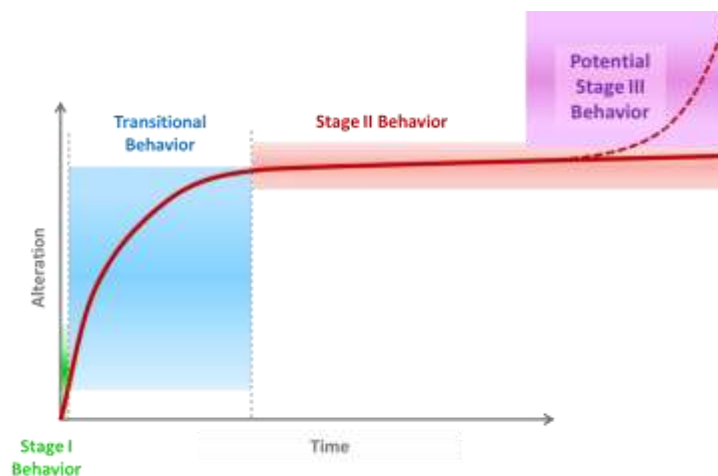- Stage III—Possible alteration rate renewal,

Figure 1. General Schematic of the Stages of Glass-Water Reaction

The initial stage (Stage I) of the glass-water reaction consists of a set of coupled reactions and processes that include interdiffusion and hydrolysis. The interdiffusion process includes interfacial ion exchange between alkali metals located at solid (i.e. glass) network terminal sites and protons in the solution followed by their interdiffusion in the glass network. Hydrolysis of the glass network involves a nucleophilic attack on the Si atom by water species, which directly disrupts the connectivity of the silica network. If the hydrolysis reaction occurs at a terminal silanol group it leads to the dissolution of the glass network and the release of orthosilicic acid (H_4SiO_4) into the leachate.

The following stage (Stage II), which is defined as the residual rate. In Stage II, the solution is saturated with respect a silica polymorph and the lowest rate of dissolution is observed. The rate is up to four orders of magnitude slower than the rate observed in Stage I. It is important to note that in the case of glass, the dissolution rate cannot become zero because silicate glasses are thermodynamically unstable in water. It is under these conditions that the process of ion exchange continues. For ILAW glass, ion exchange is modeled as a constant flux of Na out of the glass, which is defined as the ion exchange rate (r_{IEX}). In simple terms, the ion exchange rate is simply the difference in Na release, used as an indicator of ion exchange, and B release, used as an indicator of matrix dissolution. However, ion exchange is not the only process occurring at this stage of glass corrosion. This solution, and more importantly, the activity of H_4SiO_4(aq), is also affected by the formation of alteration phases on the glass surface or in the near field. Secondary phases may also form on the altered glass surface during this stage but do not appear to affect the overall dissolution rate.

During Stage III (alteration rate renewal), the solution becomes saturated with respect to secondary minerals that form that have the ability to significantly alter the composition of the fluid in contact with the glass. These phases, specifically zeolites, are believed to precipitate and consume key elements from solution (e.g., Al and Si) that remove the system further from the quasi-equilibrium conditions established during Stage II [8-10]. Stage III is most commonly observed in static conditions at elevated temperature and high-pH.

ILAW Kinetic Rate Equation

A mathematical model that describes glass reactivity is needed to predict the long-term fate of glass in the subsurface over the period of regulatory concern. For ILAW glass disposal at the IDF, the equation is based upon the TST of chemical kinetics, in which the overall reaction rate is governed by the slowest elementary reaction. The slowest overall reaction for glass has been theorized to be the hydrolysis of the glass matrix, which can be simplified through the following equation describing the dissolution of a silica polymorph to form silicic acid:

(1)
$$SiO_2(s) + 2H_2O \leftrightarrow SiO_2 \cdot 2H_2O^{\ddagger} \rightarrow H_4SiO_4(aq)$$
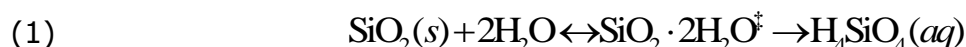
where $SiO_2 \bullet 2H_2O^{\ddagger}$ represents an activated complex. Note that a double-headed arrow, symbolizing a reversible reaction, links the reactants and the activated complex in Equation (1). Equation (1) also illustrates that the TST formulation assumes that the decay of the activated complex is an irreversible reaction. The use of Equation (1) was developed because experimental observations showed that the buildup of Si in solution in glass dissolution experiments led to slower glass corrosion rates as the contacting solution becomes more concentrated. Waste glasses represent a significantly more complex system, but the assumption is that a similar process defines their degradation.

The transition state theory rate law that appears to best describe this overall dissolution behavior applied to glass by Grambow [11], is presented as follows:

(2)
$$r_i = \vec{k}_o v_i a_{H^+}^{\eta} \exp\left(\frac{E_a}{RT}\right)\left[1 - \left(\frac{Q}{K_g}\right)^{\sigma}\right]\prod_j a_j$$

where r_i =   dissolution rate, g m-2 d-1
  $\bar{k}_0$ =   intrinsic rate constant, g m-2 d-1
  v_i =   mass fraction of component i, unitless
  a_{H^+} =   hydrogen ion activity
  E_a =   apparent activation energy, kJ/mol
  R =   gas constant, kJ/(mol·K)
  T =   temperature, K (assumed constant at 15°C or 288 K)
  Q =   ion activity product for glass
  K_g =   pseudo-equilibrium constant

η =   pH power law coefficient
σ =   Temkin coefficient (σ = 1 assumed).

When the rate-controlling reaction from Equation (1) is used to describe Equation (2), Equation (2) can be parameterized with the assumption that the only variables controlling the glass dissolution rate are solution pH, temperature, and the activity of orthosilicic acid (H_4SiO_4) in solution.

In addition, test results with ILAW glasses show that these high-sodium containing glasses are particularly susceptible to a secondary reaction mechanism, alkali-ion exchange. This reaction results in the selective extraction of Na via the reaction:

(3) $$\text{Matrix-Na} + H^+ \rightarrow \text{Matrix-H} + Na^+$$

where Matrix-Na represents the unreacted glass containing Na, and Matrix H represents a hydrated glass where the Na^+ has been replaced with an equimolar amount of a hydrogen-containing monovalent ion (H^+ or $H3O^+$). The rate of this ion-exchange reaction is referred to as r_{IEX}. For the ILAW rate model, the value of r_{IEX} is assumed to be a constant. The assumption from the ion exchange term is that there is a continuous release of alkali from the glass into the near-field. This changes the local pH and an equilibrium, which would occur in Equation (2) when Q=K, cannot be reached.

EXPERIMENTAL METHODS

Single-Pass Flow-Through (SPFT) Test

The purpose of the Single-Pass Flow-Through (SPFT) test method is to determine the kinetic rate model parameters needed to calculate the glass dissolution rate over long time periods. This is achieved by placing a solid material in a reactor and continuously flowing a chemically-controlled solution through the reactor in an oven of fixed temperature. A schematic apparatus of the SPFT system is presented in Figure 2. The system functions through the use of syringe or peristaltic (not shown) pumps that draw the chemically controlled solution (i.e. pH, [H_4SiO_4]) from the input reservoirs and transfers it to the reactor vessels through Teflon tubing. No recirculation of solution occurs. The oven is maintained at a desired temperature for the entire test duration. The reactors contain one influent and one effluent port with the solid sample dispersed at the bottom of the reactor. Effluent solutions are analyzed for elements that can trace the extent of glass dissolution. The steady-state of reaction is assumed when effluent concentrations of the analyte of interest differed by less than 15%.
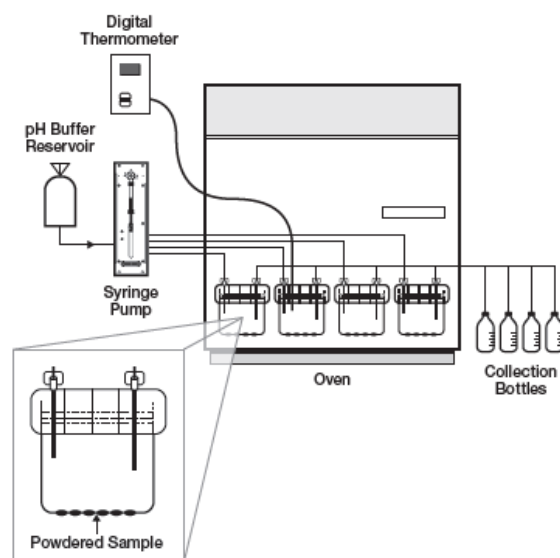
Figure 2   Schematic of the Single-Pass Flow-Through (SPFT) Apparatus for Determining Reaction Rates in Continuous Flow Solution.

Tests must be performed as a function of the quotient of the flow rate, q, and the sample surface area, S, to ensure that the glass is corroding at forward rate conditions (i.e. when Q from Equation (1) is zero). SPFT experiments are commonly conducted at room temperature, 40, 70, and 90 °C. The pH of the inlet solution is held at values from 7-12 with the use of various chemical buffers. The value of the K_g and r_{IEX} parameters can be calculated by performing experiments where Si has been added to the inlet solution. The elemental concentration of various elements is measured using inductively coupled plasma optical emission spectroscopy (ICP-OES).

The goal of the tests is to measure the steady-state release concentration. The average steady-state concentration is then used to calculate the corresponding dissolution rate, r (Equation 1).

$$r = \frac{C_i \times \frac{q}{S}}{f_i} \qquad \text{(Eq. 1)}$$

Where C_i is the steady-state concentration of element i in the outlet solution in g/m^3, q is the solution flow rate in m^3/d, S is the surface area of the material available for corrosion in m^2 and f_i is the mass fraction of element i in the original FBSR material. Typical 2σ uncertainties for releases are on the order of $\pm40\%$.

Pressurized Unsaturated Flow (PUF) Test

The PUF apparatus is used to mimic hydraulically unsaturated flow in vadose zone environments, such as the IDF, while allowing the corroding waste form to achieve

a final reaction state in a shorter time period compared to the PCT-B method. More details of the system and test procedure have been described previously [12].The PUF column operates under a hydraulically unsaturated condition by creating a constant-pressure, steady-state vertical water flow, while maintaining uniform water content throughout the column using gravity to induce flow. Hydraulically unsaturated porous media are characterized by the presence of a continuous air phase along with a continuous water phase. A constant pressure is achieved with monitored gas pressure and a porous stainless steel plate (0.2-μm pores) at the effluent end of the column wicks water from the material which then transports to the sample vial.

The columns are constructed from polyether ether ketone (PEEK) materials and are 7.62-cm long and 1.91-cm wide with a porous plate placed at the bottom between the material and the effluent port. The porous plate is water saturated before packing and stays saturated throughout the experiment to maintain water flow. Gravity transports water from the influent port to the plate and the positive gas (air) pressure applied keeps the material uniformly water unsaturated at the constant flow rate supplied by programmable syringe pumps (2.0 mL day-1). All system parameters including temperature, pressure, system mass, effluent pH, and electrical conductivity are continuously monitored. The mass was used along with measurements at the start and end of the experiment to calculate the relative hydraulic saturation (% saturation).

Columns are dry packed with the glass. After packing, the column is mounted on the apparatus and a heating coil with thermocouples is attached to the column. The column is then vacuum-saturated with 18.2 MΩ DI H_2O at ambient temperature. The column initially is allowed to desaturate by gravity drainage with the gas pressure being brought up to the desired level. The influent valve is opened and influent is set to a low flow rate of (~2 mL/d). Effluent samples are collected and acidified for elemental analysis with ICP-OES or mass spectrometry (ICP-MS). After termination of the experiment the solid samples can be collected from the column at individual, incremental step depths of 0.5 cm to characterize the evolution of phases along the height of the column.

DISCUSSION

The combined effort of SPFT and PUF tests have allowed for a compilation of a data package for ILAW glasses [5]. The data package consists of rate law parameters that can be used in Equation (2), where the glass dissolution rate can be described as a function of pH and the activity of orthosilicic acid in solution. In addition, the pseudo-equilibrium constant, K_g, and the ion exchange term, r_{IEX}, can be measured at multiple temperatures and extrapolated to 15 °C, the assumed constant temperature at IDF. The rate law parameters are described are obtained from a designed set of SPFT tests.

In addition to the rate law parameters, the secondary phase reaction network is an important input to the PA model. One test that can provide a suite of secondary phases is the PUF test. We also note that the long-term Product Consistency Test

(PCT-B) may also be used to identify secondary phases that form on glass. Many PCT-B tests have been run on a wide range of ILAW glass compositions [13]. The PCT-B tests [14], which are conducted in saturated conditions, the PUF test is also capable of obtaining a secondary phase reaction network in representative, unsaturated conditions. The PUF test also has the advantage that Stage III dissolution behavior occurs in shorter time periods occurs in shorter time periods compared to the PCT-B. In addition, because of the inline monitoring system of the PUF system, Stage III dissolution can also be identified in real-time conditions compared to the PCT-B.

Although laboratory work provides valuable information to the PA on waste form degradation, field-scale experiments can provide a description of near-field release rates, interactions of the waste forms with the backfill and near-field sediments, as well as the far-field fate and transport behavior of the contaminants. Early PA efforts recognized the need to obtain field data, and set up the Field Lysimeter Test Facility (FLTF) at the Hanford Site. These types of tests are invaluable and will strengthen the technical foundation of the PA calculations. The tests should be run for an appreciable duration (several years or longer) and the lysimeter tests should focus on new ILAW glass formulations as well as the interaction with any near-field material that may also be present at the site. Pore water percolating from the lysimeter should be sampled and key hydrologic parameters, such as drainage rate, moisture content, and soil water potential should be monitored.

To conclude, an overall laboratory testing strategy for evaluating the long-term performance of ILAW glasses being considered for treatment of Hanford LAW has been presented. Various testing to be performed include SPFT, PCT-B, and PUF tests. Additional tests that can efficiently provide relevant data that can be used in PA efforts should also be considered. We also emphasize a more concerted effort to understand the effect of ion exchange and secondary phase formation (including propensity for Stage III dissolution behavior) on the long-term performance of glass in the IDF due to the new, high-Na compositional space. The tests will also allow an understanding of the chemical reaction network that can then be used to constrain the calculations that will be used in a chemical transport models used in PA efforts. The data gathered from laboratory experiments, and the models that are developed from them, should be use to predict and verify glass behavior in a representative environment such as the field lysimeter.

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