

DISSOLUTION OF HIGH-LEVEL WASTE GLASS AND SPENT NUCLEAR FUEL: AN INTERNATIONAL REVIEW

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ABSTRACT

Disposal of radioactive wastes in deep geologic repositories requires assessing the long-term performance of high-level waste (HLW) glass and spent nuclear fuel (SNF). Improved understanding of the degradation processes affecting dissolution and subsequent radionuclide release from HLW glass and SNF in the near field of a geologic repository would reduce uncertainty in the performance assessment calculations. This report presents information from a literature review of various international disposal programs with focus on three areas: (i) the current state of understanding of HLW glass and SNF dissolution processes in geologic repository environments, (ii) international collaboration projects on HLW glass and SNF dissolution, and (iii) assessment of HLW glass and SNF dissolution related parameters for use in NRC's performance assessment model for generic geologic repositories, titled Scoping of Options and Analyzing Risk (SOAR).

The HLW glass dissolution process typically shows three characteristic stages for glass alteration according to the rate-limiting mechanism, including the forward rate stage, the residual rate stage, and the potential resumption of alteration stage at an accelerated rate. The literature indicates that in certain combinations of glass composition and environment, precipitation of secondary silicate phases can trigger the resumption of glass alteration with an increase in the dissolution rate after a period of time at the low residual rate. The resumption of alteration is attributed to the loss of the passivating properties of the glass alteration layer (i.e., amorphous hydrogel layer) due to dissolution of aluminum from the alteration layer and the precipitation of zeolites at the expense of the alteration layer. Experimental results suggest that the resumption of alteration due to the precipitation of secondary silicate phases is unlikely in repository conditions below pH 10. The development of conceptual models for the resumption of alteration based on the chemistry of the hydrogel on the glass surface and interaction with leachate provides insights into mechanisms of the resumption of accelerated glass dissolution with respect to the precipitation of zeolites.

The SNF dissolution process governing SNF alteration includes three characteristic stages: (i) an "instant" release fraction stage, (ii) a radiolytic dissolution stage, and (iii) a solubility-controlled dissolution stage. The relatively rapid release of radionuclides on the free surfaces and grain boundaries of the fuel dominates the short-term release, while the release associated with fuel matrix dissolution corresponds to the long-term release of the radionuclides embedded in the fuel matrix. The literature indicates that the SNF dissolution rate increases with the alpha activity of the SNF, and there appears to be an activity threshold below which the rate becomes independent of the alpha activity. Additionally, the literature suggests that the presence of hydrogen formed upon waste container corrosion would strongly suppress SNF dissolution, but there is no consensus on the extent of the inhibiting effect. Experimental results with SIMFUEL specimens suggest that the presence of dissolved hydrogen is unlikely to completely suppress SNF dissolution.

Updates to the HLW glass and SNF dissolution rates input to SOAR were considered, and no updates are recommended at this time. Although the HLW glass dissolution rates input to SOAR do not account for the resumption of accelerated glass dissolution, Ebert (2017) concluded that accelerated glass dissolution rates (which were used to develop the input used in SOAR) were below upper rates from an HLW glass dissolution model developed by DOE in 2004. Based on the conclusion by Ebert (2017), no updates are recommended to the SOAR HLW glass dissolution inputs; however, the data presented by Ebert (2017) were not available for review. For the SNF dissolution rates, no new data have been published since the last

update (data documented in the SOAR user guide); therefore, no changes are recommended for the SNF fractional degradation rates in SOAR.

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ABBREVIATIONS/ACRONYMS

ALTGLASS	Accelerated Leach Testing of Glass (database)
CEA	Commissariat à l'Energie Atomique (France)
CNWRA®	Center for Nuclear Waste Regulatory Analyses
DOE	U.S. Department of Energy
HLW	high-level waste
IAEA	International Atomic Energy Agency
I-TEAM	International Technical Evaluation of Alteration Mechanisms (program)
NRC	U.S. Nuclear Regulatory Commission
PCT	product consistency tests
RTDC	research and technology development components
SIMFUEL	simulated fuel
SNF	spent nuclear fuel
SOAR	Scoping of Options and Analyzing Risk (model)
SUBATECH	Subatomic Physics and Associated Technologies (France)
S/V	glass surface to solution volume (ratio)

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QUALITY OF DATA, ANALYSES, AND CODE DEVELOPMENT

DATA: There are no original CNWRA-generated data in this report. Sources of other data should be consulted for determining the level of quality of those data.

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1 INTRODUCTION

Disposal of radioactive wastes in deep geologic repositories requires assessing the long-term performance of waste forms such as spent nuclear fuel (SNF) produced by the operation of nuclear reactors, and high-level waste (HLW) glass produced to immobilize waste from defense activities. HLW glass is a vitrified waste form produced by melting the waste with borosilicate glass and then pouring the molten material into stainless steel canisters, where it cools to form a glass. The major performance aspect of waste forms is their ability to prevent or reduce radionuclide releases due to slow degradation in a repository environment over geologic timescales. Improved understanding of the degradation processes affecting dissolution and subsequent radionuclide release from waste forms in the near field of a geologic repository would reduce associated uncertainties in repository system performance assessments.

The primary mechanism responsible for radionuclide release is reactions with water when a waste container fails and water contacts the waste forms. As the HLW glass and SNF matrix dissolves, radionuclides are initially released congruently. For high solubility radionuclides such as Tc-99 and I-129, the radionuclide release rate is primarily determined by the congruent dissolution rate of the waste matrix. For low-solubility radionuclides, such as Pu-239, the release rate is primarily determined by the solubility limit and the groundwater flow rate. Therefore, in performance assessments of repository systems, the dissolution rate of HLW glass and SNF is important for estimating both high- and low-solubility radionuclide release rates to the geosphere.

The HLW disposal programs in countries such as Canada, France, Japan, Korea, the United States, and other European Union countries have accumulated a large amount of data through laboratory experiments, in-situ tests, and modeling in an attempt to assess the long-term performance of HLW glass and SNF. This report presents information from a literature review on the current state of understanding of the HLW glass and SNF dissolution processes and controlling mechanisms in geologic repository environments, as well as the influence of the main physical and chemical parameters on the dissolution rates. Additionally, the review results are used to assess HLW glass and SNF dissolution rates obtained from various international disposal programs in an attempt to update the fractional degradation rates of waste forms as input to the Scoping of Options and Analyzing Risk (SOAR) model, NRC's performance assessment model for generic geologic repositories.

2 HIGH-LEVEL WASTE GLASS DISSOLUTION

2.1 Degradation of HLW Glass

Under conditions representative of geologic repository environments, the HLW glass dissolution process involves contact of a reactant (i.e., groundwater or water vapor) with the glass surface, chemical reaction between the reactants and glass surface, and transport of reaction products away from the reaction zone. The dissolution rate is controlled by the combination of these processes and depends on factors such as chemical composition of the glass and solubilities of the reaction products, exposed surface area, temperature, pH, and chemical composition and volume of the aqueous environment. The glass dissolution process is generally divided into three characteristic stages for glass alteration: (i) the forward rate stage, (ii) the residual rate stage, and (iii) the potential resumption of alteration stage at an accelerated rate (Gin et al., 2013; Vienna et al., 2013; Poinssot and Gin, 2012; Jantzen et al., 2010). As shown in

Figure 2-1, each of the glass alteration stages corresponds to different rate-limiting mechanisms.

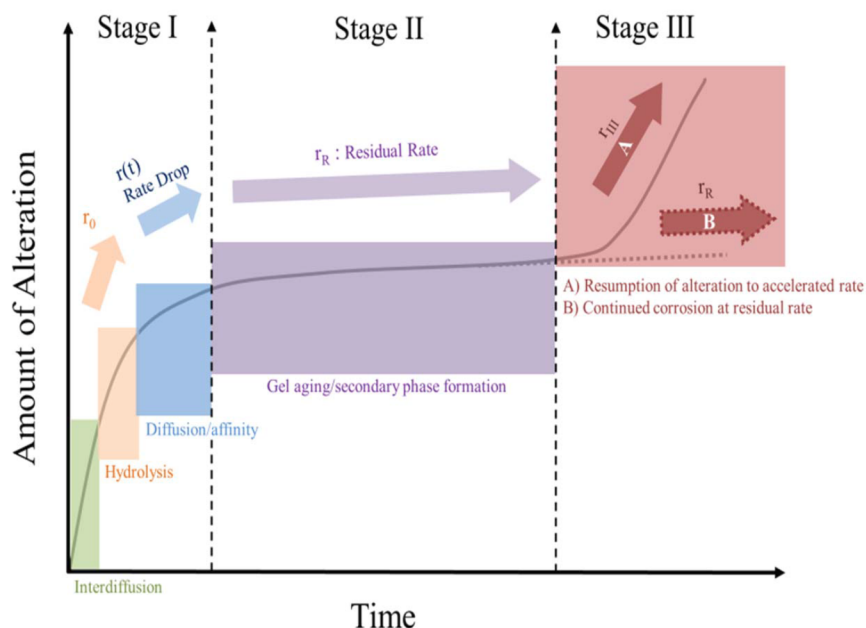


Figure 2-1. Schematic of glass dissolution processes (Trivelpiece et al., 2016). The resumption of alteration to an accelerated rate (Stage IIIA) occurs only under certain conditions (e.g., $\text{pH} > 10.5$).

The forward rate stage involves initial hydration and ion exchange of cations (or interdiffusion) followed by hydrolysis of the glass network. Interdiffusion results in release of glass network modifying cations (e.g., Na^+) into solution and an increase in the solution pH. Hydrolysis of the glass network results from nucleophilic attack on the bridging Si-O-Si bonds, which breaks the silicate structure and releases Si into solution as orthosilicic acid (H_4SiO_4). Both the interdiffusion and hydrolysis mechanisms are operative and competitive with each other during the forward rate stage. In practice it is difficult to distinguish the two mechanisms from dissolution experiments because of the short period of time for which the interdiffusion exceeds the glass network hydrolysis. The forward rate represents a high initial dissolution rate in the absence of concentration effects of dissolved silica and other aqueous species involved in the backward reaction, as well as reaction affinity limitations. The initial glass dissolution rate is dependent on the glass composition, solution composition, pH, temperature, surface area of the glass, and solution volume.

As the concentrations of the glass components in solution increase, particularly silica species for borosilicate glasses, the glass dissolution rate drops towards the residual rate stage with a slow dissolution rate that is generally several orders of magnitude lower than the initial rate. A typical long-term residual rate for borosilicate glasses is low enough to be expected to ensure immobilization of radioactivity for many thousands of years of HLW disposal {e.g., the long-term glass dissolution rate for the R7T7 HLW glass is about 5 nm [2.0×10^{-7} in] per year} (Chave et al., 2007). While dissolution at the initial rate is congruent for the major glass constituents (e.g., Si, B, Na, and Al), the residual rate is characterized by incongruent

dissolution due to the formation of an alteration layer (i.e., amorphous hydrogel layer) on the glass surface by silicon recondensation and the retention of some glass constituent elements, and by slow precipitation of secondary phases such as clay minerals. Several mechanisms limiting the residual rate seem to operate during this stage, including the slow transformation of amorphous phases into more stable products, changes in local solution concentration, water diffusion into the glass, and transport limitations in a passivating layer, but there is no consensus on the relative importance or relation between these mechanisms. There is general agreement that a transition from the forward rate stage to the residual rate stage is accompanied by the progressive saturation of the solution with respect to silica and the formation of protective alteration layers that act as a barrier for diffusion of glass components into solution (Van Iseghem et al., 2007; Frugier et al., 2006). Key parameters affecting the long-term glass dissolution behavior are temperature and pH, while other factors such as ionic strength and glass surface to solution volume (S/V) ratio play a minor role.

In certain combinations of glass composition and environmental conditions (e.g., $\text{pH} > 10.5$), precipitation of secondary silicate phases such as zeolites can trigger a sudden acceleration of the glass alteration rate after a period of time at the low residual rate, a phenomenon known as the resumption of alteration stage (Gin et al., 2004; 2011). Precipitation of secondary phases during this stage is expected to modify the chemical composition of the alteration layers. For example, the formation of a zeolite phase will remove Si and Al from the alteration layers, which may impact the stability of the alteration layers and lead to a resumption of glass alteration. A review of the mechanism and modeling for the resumption of alteration is provided in the next section.

2.2 Resumption of Accelerated HLW Glass Dissolution

2.2.1 Mechanism for the Resumption of Alteration

The resumption of rapid glass alteration causes the long-term dissolution rate to reaccelerate to the initial dissolution rate, which is controlled by hydrolysis of the glass network. The acceleration of the glass dissolution rate after the residual rate stage during leaching experiments was first demonstrated in the mid-1980s (Fournier et al., 2014). The resumption of more rapid alteration has been shown to be related to the formation of secondary phases on the glass surface during aqueous alteration. Van Iseghem and Grambow (1987) investigated leaching of two simulated HLW borosilicate glasses (SAN60 with 18.1 wt% Al_2O_3 and 0.3 wt% Fe_2O_3 ; SM58 with 1.2 wt% Al_2O_3 and 1.2 wt% Fe_2O_3) and found that the formation of Al^{3+} -rich zeolite [i.e., analcime $\text{Na}(\text{AlSi}_2\text{O}_6) \cdot \text{H}_2\text{O}$] in leaching of the SAN60 glass accelerated the glass dissolution by consuming H_4SiO_4 from the leachate solution. The high aluminum content of the SAN60 glass induced the analcime precipitation that was reported to be responsible for accelerating dissolution. While analcime is the mineral most frequently identified in the event of a resumption of alteration, precipitation of Fe^{3+} -rich zeolites and smectite clays does not appear to accelerate glass dissolution. Additional studies of the resumption of accelerated dissolution have shown that the resumption of alteration is observed at high pH, temperature, and S/V ratio during laboratory experiments, and the incubation period before the resumption of alteration and its intensity is strongly dependent on the composition of the glass and the leaching solution (Fournier et al., 2014; Jantzen et al., 2010).

Gin and Mestre (2001) conducted static experiments to investigate the effect of pH on the mechanisms of SON68 HLW glass alteration under saturation conditions. Results of the experiments over 600 days between pH 7 and pH 11.5 showed that a protective hydrogel forms in all the test solutions, and the stability of the hydrogel is pH-dependent. A resumption of glass

alteration was observed only at pH 11.5 (after 50 days) and pH 11 (after 250 days) (Figure 2-2). In both cases, the precipitation of a potassium and sodium aluminosilicate caused degradation of the alteration layer, which resulted in a resumption of glass alteration and led to rapid

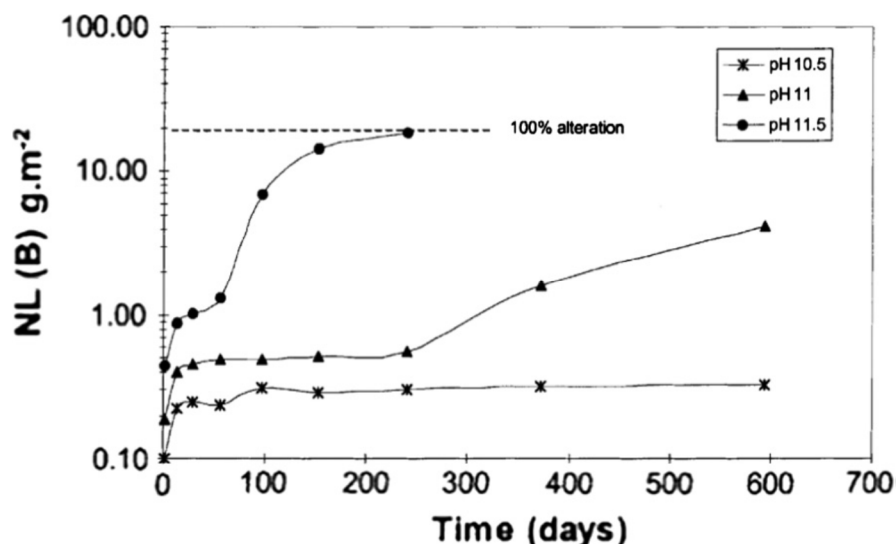


Figure 2-2. Normalized boron mass losses during leaching of SON68 glass at 90 °C [194 °F] and at controlled pH values of 10.5, 11, and 11.5 (Gin and Mestre., 2001)

dissolution of the glass into alteration products. It was also observed that the aluminosilicate phase is unlikely to precipitate below pH 10, and aqueous alteration of the glass results in the formation of a protective hydrogel with long-term stability at pH 7-10. The resumption of alteration was attributed to the loss of the passivating properties of the alteration layer due to dissolution of aluminum from the alteration layer and the precipitation of secondary phases in the form of zeolites. Ribet and Gin (2004) also observed that the resumption of SON68 glass alteration is accompanied by a reduction in the pH, resulting in a drop in the zeolite crystal growth rate and thereby diminishing the glass alteration rate. When a high solution pH during the renewed alteration stage is artificially lowered to 9.5, the zeolites gradually dissolve and glass dissolution ceases. This phenomenon was attributed to the instability of the secondary phases at low alkaline pH. These results suggest that the occurrence of a resumption of alteration due to the precipitation of secondary silicate phases is unlikely in repository conditions between pH 7 and pH 10.

2.2.2 Modeling the Resumption of Alteration

A glass dissolution model based on transition state theory was developed and applied to describe the dissolution of HLW glass (Grambow, 1985). Since the resumption of glass alteration is associated with the precipitation of secondary phases, modeling efforts have been devoted to the effects of glass composition and environmental conditions on zeolite formation in triggering the resumption of accelerated dissolution. Van Iseghem and Grambow (1987) first modeled a resumption of glass alteration using the PHREEQE and GLASSOL codes for borosilicate glasses. The thermodynamic stability conditions of secondary phases were predicted with respect to the glass alteration reaction progress and the aluminum and silicon content. More recently, Ebert (2013) developed a conceptual coupled rate model for the resumption of alteration by coupling the glass dissolution and secondary phase precipitation

kinetics. The model identifies the conditions that trigger the increased glass dissolution rate based on the relative kinetics of glass dissolution and secondary phase precipitation. Secondary phases that precipitate slower than the glass dissolves will establish a low steady-state rate referred to as the residual rate, whereas secondary phases that precipitate faster than the glass dissolves will lead to the resumption of accelerated dissolution.

Other conceptual models for the resumption of alteration account for the effects of glass composition on the precipitation of secondary phases, particularly the silicon and aluminum content of HLW glasses. These models are based on thermodynamic approaches to identifying the conditions under which secondary phases form and cause the glass dissolution rate to increase. Jantzen et al. (2017a,b) used glass leaching data from the Accelerated Leach Testing of GLASS (ALTGLASS) database to develop conceptual models for the triggering of the zeolite precipitation that causes resumption of glass alteration. The glass leaching data from the short-term and long-term product consistency tests (i.e., PCT-A and PCT-B) were first compiled into the ALTGLASS database in 2013. The current version of the database, ALTGLASS Version 3.0, contains leachate and glass composition data for 490 different glasses, of which 113 are HLW glasses (Trivelpiece et al., 2016). A subset of HLW glasses from the database was analyzed by Jantzen et al. (2017a,b) to understand the relationship between glass composition and leaching behavior, coupled with hydrated amorphous surface layer formation and precipitation from solution. HLW glass surfaces form a hydrogel layer when in contact with water as a result of ion-exchange and diffusion processes. Jantzen et al. (2017a) indicates that the hydrogel layer ages in response to changes in the solution chemistry and forms secondary phases (i.e., clays or zeolites) by Ostwald ripening. For Fe^{3+} -rich glasses, ripening of the hydrogel layer into clay mineral assemblages occurs at lower pH ($\text{pH} < 10$), which will not cause acceleration of glass dissolution because there is little interaction between the hydrogel layer and the leachate species. In contrast, ripening of the hydrogel layer on Al^{3+} -rich glasses leads to precipitation of zeolites from strong interaction with leachate species at higher pH ($\text{pH} > 10$), causing a resumption of accelerated dissolution.

The chemical interactions between the hydrogels and the leachates were also modeled by Jantzen et al. (2017b), particularly focusing on the role of excess strong base in the leachate. During static leaching of a glass in deionized water, the glass chemistry drives solution acid-base equilibria that are expressed as $[\text{SB}]_{\text{ex}} \equiv [\text{SB}] - [\text{WA}]$, where $[\text{SB}]$ is strong bases and $[\text{WA}]$ is weak acids in the leachate. The excess strong base, $[\text{SB}]_{\text{ex}}$, in the leachate solution, which interacts with alteration products formed during the glass dissolution process, is shown to be the activation parameter for zeolite precipitation. The authors analyzed the $[\text{SB}] - [\text{WA}]$ for both the nonresumption and resumption glasses. A plot of $[\text{SB}] - [\text{WA}]$ versus measured pH (Figure 2-3) indicates that leachates become enriched in weak acids for the nonresumption glasses (i.e., SON68 glass) whereas leachates become enriched in strong base for the resumption glasses (i.e., AFCI glass). For resumption glasses, the leachates are buffered at a neutral $[\text{SB}] - [\text{WA}]$ of ~ 0 until experiencing a sharp break in the pH versus $[\text{SB}] - [\text{WA}]$ curve at pH of ~ 10.8 . As shown in Figure 2-3, the transition to a steep rise in pH is manifested in the pH dependency of the hydrogel layer and the phases that form. Depending on the molar concentration of Si in a solution, stable polymeric silica forms within the pH 10.5–11 range, whereas monomeric silica species exist at lower pH values. Stabilization of polymeric silica species can help stabilize polymeric anions and condensation of the silica in the hydrogel through the hydrogel-leachate interactions.

On the other hand, the potential resumption of alteration appears to be correlated with Al/Si ratio attained in the surface hydrogel layer, rather than the Al/Si ratio in the glass. Jantzen et al.

(2017a) analyzed the hydrogel composition data of HLW glasses at various percentages of reaction progress. The aluminum and silicon elemental concentrations retained in the hydrogel layer (symbolized as Al* and Si*) are plotted in Figure 2-4. Different evolutionary pathways are

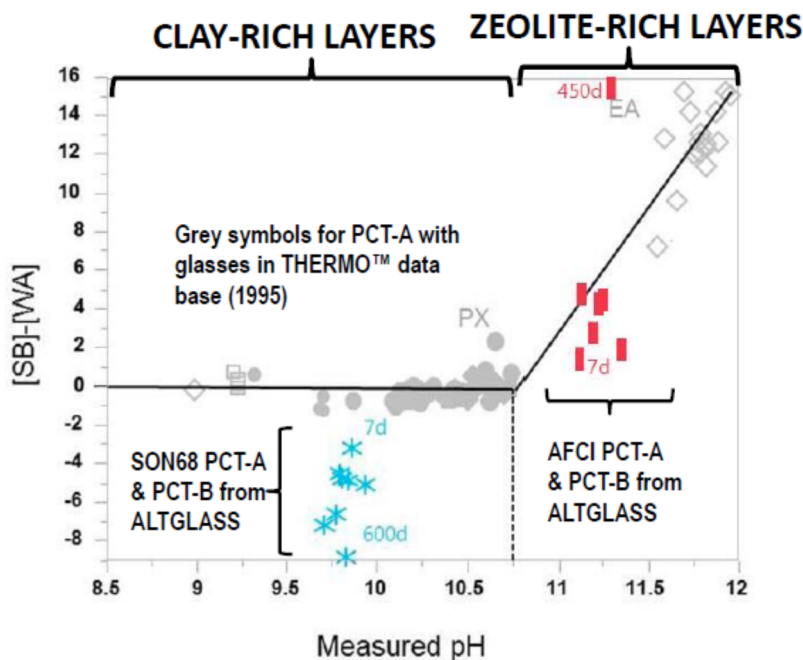


Figure 2-3. Graphical representation of the effects of excess leachate weak acid on the measured pH of the long-term leachates from nonresumption and resumption glasses (Jantzen et al., 2017c)

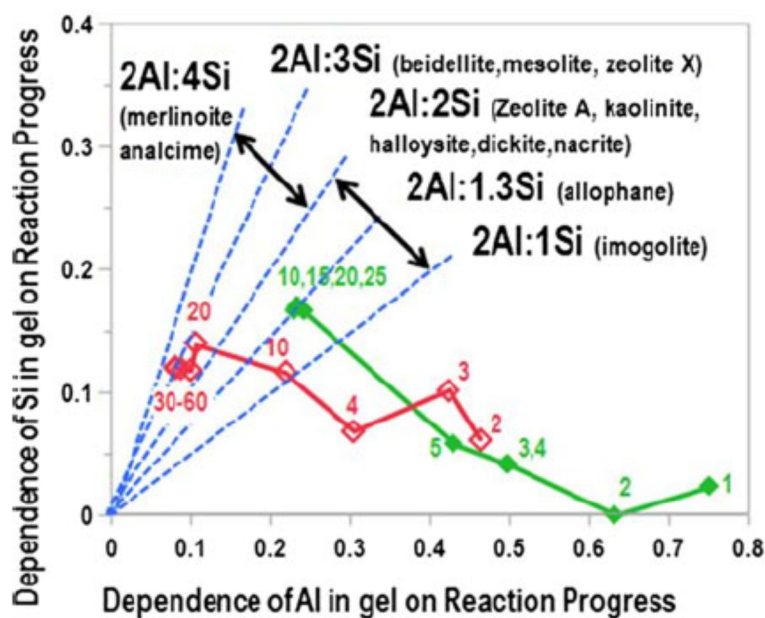


Figure 2-4. Comparison of elements retained in the hydrogel layer with reaction time for glasses that do not undergo resumption of alteration (green) vs glasses that undergo resumption of alteration (red) (Jantzen et al., 2017a)

evident in Figure 2-4 for the nonresumption and resumption glasses. The hydrogel composition data demonstrated that for the nonresumption glasses, hydrogel compositions with Si^*/Al^* ratios less than one generate clay minerals (e.g., allophane) and maintain low dissolution rates. Glasses that form hydrogel compositions with Si^*/Al^* ratios greater than one generate various types of zeolites (e.g., zeolite X and analcime) accompanied by a resumption of the faster glass dissolution rate. At an Si^*/Al^* ratio that is approximately equal to one, both zeolites and clays can readily form, implying that some additional driver is active in triggering the resumption of glass alteration. Jantzen et al. (2017a) demonstrated that the emerging conditions that indicate a potential resumption of accelerated dissolution need to be determined on the basis of the activated Si^* and Al^* complexes coupled with the [SB]-[WA] approach to leachate acid-base equilibrium. Dissolution of resumption glass compositions generates leachates enriched in strong base, high alkali containing glasses, which give Al/Si ratios consistent with zeolite X (2Al:3Si) and analcime (2Al:4Si). Therefore, the role of the hydrogel Si^*/Al^* ratio, as well as the interactions with the leachate, would provide a mechanistic understanding enabling prediction of the resumption of accelerated HLW glass dissolution with respect to the precipitation of zeolites.

2.3 International Collaborative Projects on HLW Glass Dissolution

The development, testing, and production of vitrified HLW in the form of borosilicate glasses has been performed or is planned under several national radioactive waste management programs. In addition, a number of international collaborative projects have been undertaken to coordinate research and improve understanding on the long-term degradation of HLW glass. A brief summary of these international collaborative projects is provided below in terms of the project title, time period, objectives, and pertinent findings.

NF-PRO: Understanding and Physical and Numerical Modelling of the Key Processes in the Near Field and their Coupling for Different Host Rocks and Repository Strategies (2002-2006)

- The project was established by the European Commission within the sixth framework program (NF-PRO, 2008). The overall goal of the project was to coordinate European research on the safe management and disposal of HLW. The project was divided into five research and technology development components, with component 1 (RTDC-1) concentrating on dissolution of and release from the waste matrix. The objective of RTDC-1 was to resolve a number of outstanding issues with respect to the key processes affecting matrix dissolution and radionuclide release from HLW glass and SNF, which included processes related to the release of radionuclides from the glass matrix to the geologic environment.
- Experiments were conducted to study the dissolution of vitrified waste in the presence of various compacted near-field media. These experiments have allowed measuring the diffusion of radionuclides through different near-field media. The simultaneous measurement of several critical coupled processes has made it possible to calibrate and improve glass dissolution models. As a result, more accurate glass source term data

have been established, and the data have been produced and interpreted for input to performance assessments.

IAEA CRP 1813: Processing Technologies for High Level Waste, Formulation of Matrices and Characterization of Waste Forms (2012-2016)

- There has been an informal international collaboration on glass dissolution undertaken by six countries including Belgium, France, Germany, Japan, the United Kingdom, and the United States (Gin et al., 2013; Vienna et al., 2013; Ferrand et al., 2015). The aim was to obtain consensus on mechanisms controlling the long-term dissolution rate of glass. Some participating countries were working with the International Atomic Energy Agency (IAEA), and their contributions were reported for IAEA CRP1813. Several workshops have been organized since 2009 in conjunction with the American Ceramic Society.
- As part of its involvement, the U.S. Department of Energy (DOE) developed a plan in 2011 for the International Technical Evaluation of Alteration Mechanisms (I-TEAM) program, which delineated the need for an improved mechanistic understanding of glass dissolution processes, identified key information gaps or uncertainties that limit modeling the long-term behavior of glass waste forms, and described the current and planned efforts to fill those gaps and develop a mechanistically-based glass degradation model to fulfill the objective of safe, technically defensible long-term disposal of nuclear waste (Ryan, 2015). Experimental and modeling work conducted under I-TEAM has led to new insights regarding processes occurring at the interface of glass and surface alteration layers, within the layers, and when secondary phases precipitate. These efforts resulted in significant improvements to the suite of analytical algorithms used to model long-term glass dissolution.

JOPRAD: Towards a Joint Program on Radioactive Waste Disposal (2015-2017)

- The project was established by the European Commission in June 2015 with the objective of assessing the feasibility and initiating a process to set up a joint program in the field of radioactive waste management and disposal. The joint program would coordinate European research and development activities on geologic disposal for high-activity, long-lived radioactive waste.
- A strategic research agenda was developed in the JOPRAD project (JOPRAD, 2018; Grambow, 2017). It is anticipated that a new European joint program will be initiated in 2019. The scope of activities considered for the joint program includes radioactive waste management and disposal of SNF, HLW, and intermediate level waste, along with related predisposal activities. The key research items associated with HLW glass include the impact of fracturing, hydration under unsaturated conditions, interaction with surrounding materials (e.g., corrosion products, concrete, and clay), resumption of alteration, the influence of irradiation on the residual rate, the mechanisms governing the residual rate, the influence of composition congruency between glass alteration and radionuclide release, and improved understanding of coupled interaction between reactive transport and dissolution of glass in the near-field environment.

2.4 Assessment of HLW Glass Dissolution and Fractional Degradation Rates in SOAR

A rate expression in a form of the transition state rate law was used in the glass degradation model for the proposed repository in the United States (Bechtel SAIC Company, LLC, 2004). The rate equation used to predict HLW glass dissolution contained two main factors. The first

factor was the forward rate, defined as a function of pH and temperature. The forward rate represents the dissolution rate in the absence of concentration effects of dissolved silica and other aqueous species. The other factor was the reaction affinity term, which quantifies the feedback effect of solute species on glass dissolution. Currently, the SOAR performance assessment model incorporates a range of fractional release rates (from 1.5×10^{-6} 1/year to 2×10^{-4} 1/year) intending to enclose a range of reported HLW glass dissolution rates. In deriving the range of HLW fractional release rates input to SOAR, there was no consideration of the resumption of alteration that could lead to accelerated dissolution rates.

Ebert (2017) analyzed the glass leaching data in the ALTGLASS database. Based on the test results for resumption glasses, the measured dissolution rates during the renewed alteration stage are essentially constant until glass is completely dissolved. Ebert (2017) concluded that the higher glass dissolution rates were bounded by the upper rates of the glass degradation model implemented by DOE in 2004 (Bechtel SAIC Company, LLC, 2004). Based on the conclusion by Ebert, no changes are recommended for the HLW glass fractional degradation rates inputs to SOAR, but it is recognized that Ebert (2017) did not disclose detailed data to support the conclusion that renewed alteration rates are within rates previously reported and considered in the 2004 DOE analyses. If the data by Ebert (2017) were available, it would be recommended to compare renewed alteration stage glass dissolution rates to the glass fractional release rates input to SOAR. Ebert (2017) also considered HLW containment, glass dissolution, groundwater flow, and radionuclide behavior in radionuclide transport modeling. In system level assessments, it can be shown that a steady-state in-container radionuclide concentration below solubility limit could exist (Iwalewa and Farnan, 2019; Carbol et al., 2005).

DOE-funded researchers developed a conceptual model of precipitation of secondary phases such as zeolites that drives enhanced dissolution of glass during the resumption of alteration stage (Ebert, 2017). This model updates the understanding of the conditions required to trigger the resumption of accelerated dissolution and supports the conclusion that the residual rates persist if those resumption conditions do not occur. Technical uncertainties associated with the causation mechanisms and timing of the resumption of glass alteration under disposal conditions are being addressed by modeling and focused laboratory tests to measure kinetic parameters at the DOE laboratories.

3 SPENT NUCLEAR FUEL DISSOLUTION

3.1 Degradation of SNF

Radionuclide release from SNF in contact with water after waste container breach in a geologic repository can be broken down into two main fractions: (i) the “instant” release fraction from the gap and grain boundary inventories and (ii) the long-term release fraction through fuel matrix dissolution, often referred to as the matrix contribution (Poinssot and Gin, 2012; Shoesmith, 2007; De Windt et al., 2006). The short-term radionuclide releases are dominated by the rapidly released radionuclide inventory on the free surfaces of the fuel and the grain-boundary inventory (typically over a period of several months to several years). The matrix contribution corresponds to the slow release of the radionuclides that are embedded within the fuel matrix, which may last several thousands of years or longer depending on the repository setting. Radiolytic-enhanced dissolution and solubility-controlled dissolution affect the release of the fuel matrix inventory. In a failed waste container, SNF could dissolve in the groundwater that contacts the SNF. During the first few hundred years, if water were to contact waste forms, water radiolysis from beta and gamma radiation could produce high levels of dissolved oxidizing species such as oxygen and hydrogen peroxide (MICADO, 2010;

Poinssot et al., 2005a). Radiolytic-enhanced dissolution of the SNF surface may be the rate limiting process controlling SNF dissolution. After the first few hundred years radiation becomes dominated by alpha decay (from longer lived radionuclides), which is weakly oxidizing. When the radiation field falls below a certain threshold, the radiolysis rate of the water may be too low to sustain radiolytic-enhanced dissolution. Solubility-controlled dissolution would be the rate limiting process if and when oxidants became scarce. Based on a review of literature information, the overall SNF dissolution process governing SNF alteration includes three characteristic stages in a deep anoxic repository setting: (i) the instant release fraction stage, (ii) the radiolytic dissolution stage, and (iii) the solubility-controlled dissolution stage (Figure 3-1).

Poinssot et al. (2005b) conducted leaching experiments with α -doped material (U-233 or Pu-238) in deionized water. They found that the fuel dissolution rate increases with the alpha activity in the fuel specimen, and there appears to be an activity threshold below which the dissolution is independent of the alpha activity. Poinssot's team claimed that fuel dissolution is radiolytically controlled above this threshold, while a solubility-controlled process becomes predominant below this threshold, as illustrated in Figure 3-2. This alpha activity threshold was observed to be located between 3.5 and 33 MBq/g(UO_2) for deionized water (vertical lines in Figure 3-2). This threshold was also demonstrated to be environment dependent, strongly depending on the solution characteristics. Poinssot et al. (2005b) reported that in strongly reducing media like the Boom Clay porewater, the threshold is much higher than 245 MBq/g(UO_2) due to the strong reducing capacity of the clay medium.

The dominant factors affecting SNF dissolution inside a failed waste container are the redox condition at the fuel surface, temperature, and the chemical composition of the contacting aqueous solution (Shukla et al., 2016). The redox conditions partly depend on the dissolved oxidizing species as well as reducing species such as dissolved hydrogen. The oxidizing species concentrations are affected by the radiolytic reactions with the solution, whereas dissolved hydrogen concentrations are predominantly dependent on the anaerobic corrosion of iron-based waste containers. Shukla et al. (2016) reviewed a large body of literature on the effect of dissolved hydrogen on SNF dissolution and found that literature information varies widely on the dissolution rate of SNF under reducing conditions. Some studies reported that the presence of small amounts of dissolved hydrogen (ranging from 0.1 μM to 1 mM) is sufficient to completely suppress SNF dissolution, while other studies suggested that the effect is more limited. Suppression of SNF dissolution is probably due to the scavenging of radiolytic oxidants by hydrogen. Experimental work conducted by NRC (Shukla et al, 2016; Pan and Ahn, 2018) indicates that dissolution of simulated fuel (SIMFUEL) is dependent on the dissolved oxidizing species concentration along with the hydrogen concentration in the solution. The experimental results showed that the SIMFUEL dissolution rates are lower under reducing conditions compared to oxidizing conditions, and that the presence of dissolved hydrogen is unlikely to completely suppress SNF dissolution.

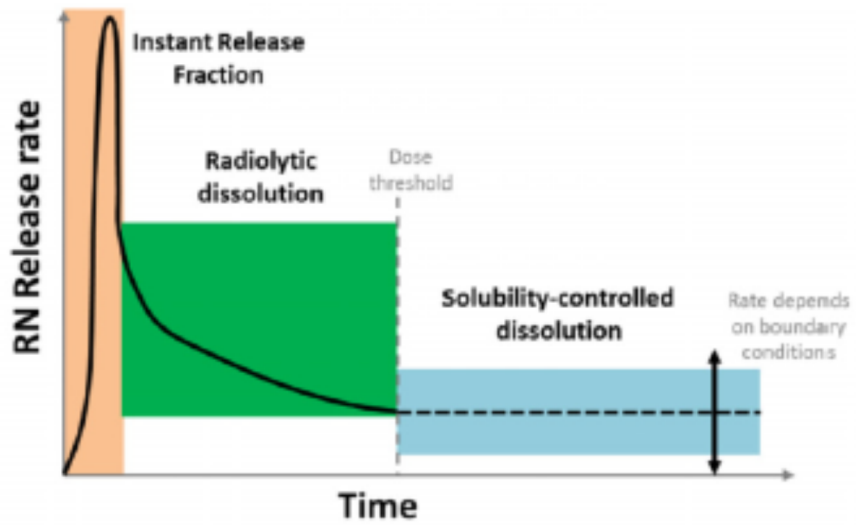


Figure 3-1. Schematic of spent nuclear fuel dissolution processes (Poinssot and Gin, 2012)

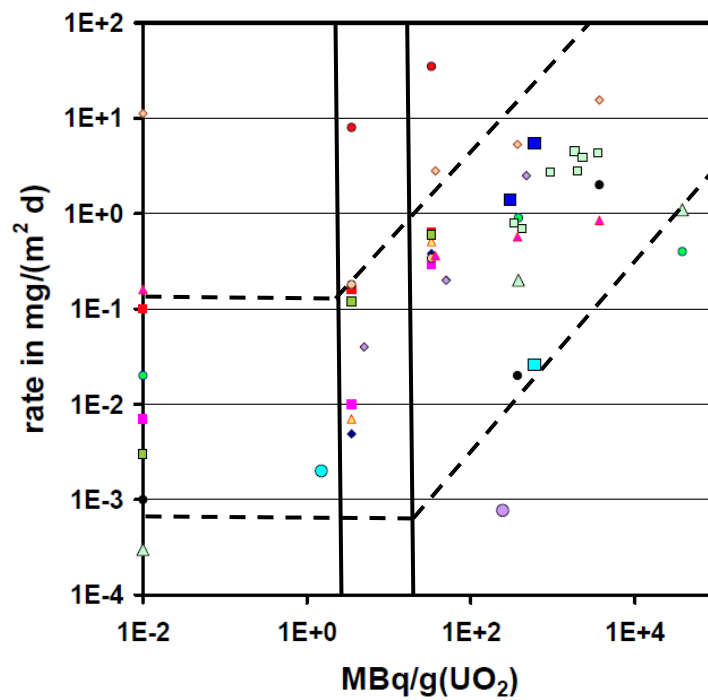


Figure 3-2. Dissolution rates as a function of alpha activity on alpha-doped and undoped UO₂, and spent fuel (Data from Figure 25 in Poinssot et al., 2005b)

3.2 International Collaborative Projects on SNF Dissolution

A number of international collaborative projects have been undertaken to improve scientific bases and predictive capabilities on the evolution of SNF in repository environments. A brief summary of these international collaborative projects is provided as follows.

NF-PRO: Understanding and Physical and Numerical Modelling of the Key Processes in the Near Field and their Coupling for Different Host Rocks and Repository Strategies (2002-2006)

- As summarized in Section 2.3, the NF-PRO project was established by the European Commission with the goal in part of resolving outstanding issues with respect to the key processes affecting matrix dissolution and radionuclide release from SNF.
- Experimental studies were conducted on the evolution of spent fuel prior to water ingress for the normal evolution scenario and during the transient period of the early failure scenario. These studies have expanded knowledge on grain-boundary characteristics and inventories, as well as grain-boundary stability in SNF. Evaluation of the effect of helium diffusion and accumulation on the spent fuel microstructure has also decreased the uncertainties in instant release fractions of key radionuclides for SNF.
- The project has yielded insights in quantification of key processes affecting the spent fuel source term under geologic repository conditions. The electrochemical radiolysis model developed in this project has been incorporated into a radiolytic transport code to describe the effect of oxidizing and reducing species formed by water radiolysis on SNF dissolution. The inhibiting effect of hydrogen on SNF dissolution against the oxidative effect of alpha radiolysis was represented in the model by the action of hydrogen on the corrosion potential at the fuel surface. The model also assessed the radiation threshold below which there is no effect of alpha radiolysis on the long-term dissolution rate of SNF. Additionally, experiments were conducted to investigate the retention of radionuclides in compacted bentonite contacting SNF in NaCl brine. It was observed that a trace of bromide present in groundwater may reduce significantly the inhibiting effect of hydrogen with respect to the release of radionuclides and the yield of radiolytic products.

MICADO: Model Uncertainty for the Mechanism of Dissolution of Spent Fuel in Nuclear Waste Repository (2007-2010)

- The project was established by the European Commission to assess the uncertainties in models describing the dissolution processes of SNF in a repository for different stages in the temporal evolution of the disposal system (MICADO, 2010). Modeling exercises were performed to evaluate the influence of uncertainties associated with about 20 parameters that included 5 data inputs to source term models (i.e., instant release fraction, SNF dissolution rate, uranium solubility, specific surface area, and corrosion rate of zircaloy) and 15 parameters associated with the properties of the repository components such as sorption coefficients and diffusion and advection rates.
- Six models were assessed in the project, including one instant release fraction model and 5 matrix dissolution models. The matrix dissolution models included: (i) the matrix alteration model developed as part of the European Union Spent Fuel Stability project that accounts for water radiolysis, solution chemistry, and surface complexation kinetics;

- (ii) a model developed by KTH Royal Institute of Technology, Sweden that accounts for water radiolysis, diffusion, and homogeneous kinetics at the spent fuel surface;
 - (iii) a model developed by the Laboratory of Subatomic Physics and Associated Technologies (SUBATECH), Ecole des Mines de Nantes, France that also accounts for water radiolysis and diffusion, but deals with interfacial reactions using electrochemistry rather than surface complexation; (iv) a model developed by the Commissariat à l'Energie Atomique (CEA), France that accounts for oxidizing radiolytic species produced near the fuel surface, but neglects reducing species and the recombination of radicals; and (v) another CEA model consisting of a complete radiolytic model, which accounts for radiation field gradients and diffusion similar to the SUBATECH model.
- The assessment carried out under the MICADO project indicated that SNF dissolution and radionuclide release rates are key parameters in assessing repository performance, while the characteristics of the disposal components (e.g., sorption, diffusion, and advective flows) also strongly influence the transfer of radionuclides to the biosphere. The results showed that SNF is an effective barrier to prevent radionuclide releases for tens of thousands to millions of years, and the instant release fraction is the dominant dose contributor if the matrix dissolution rate is small and the resulting lifetime of the spent fuel is significantly longer than 10^6 years.
 - For fuel matrix dissolution, the dissolution inhibition effect in the presence of hydrogen from waste container corrosion was confirmed. Although uncertainties in the surface area of SNF exposed to solutions are very large (up to 5 orders of magnitude for a given specific surface area), the effect of surface area uncertainties on dissolution rate and subsequent radionuclide release was observed to be much smaller. Additionally, agreement was reached on ranges for the value of the dissolution rate during the first hundreds of thousands of years in the presence of hydrogen and the period beyond hundreds of thousands of years without hydrogen. The dissolution rates in the two periods are between 0.02 and 5 $\mu\text{g}/\text{m}^2/\text{day}$, depending on the value chosen for the total accessible specific surface area (ranging between 0.001 and 0.0072 m^2/g).

JOPRAD: Towards a Joint Program on Radioactive Waste Disposal (2015-2017)

- As summarized in Section 2.3, the JOPRAD project was established by the European Commission with the objective of establishing a new joint program in the field of radioactive waste management and disposal.
- A strategic research agenda was developed for the joint program, including radioactive waste management and disposal of SNF, HLW, and intermediate level waste, along with related predisposal activities (JOPRAD, 2018; Grambow, 2017). The key research items associated with SNF include the development of (i) an improved mechanistic understanding of the release of fission products from the different types of SNF to better predict the radionuclide source term in post-closure safety studies and (ii) an understanding of the behavior of SNF contained in waste containers in a range of fire and impact scenarios.

3.3 Assessment of SNF Degradation Rate Parameters in SOAR

The SNF fractional degradation rates in SOAR were updated in 2015. There have been no new SNF dissolution rates reported since then. As a result, no changes are recommended for the

SNF fractional degradation rates in SOAR. Current values are documented in the SOAR user guide.

4 SUMMARY

Long-term performance of HLW glass and SNF is important to preventing or reducing the release of radionuclides from the waste forms. Literature information from various international disposal programs was reviewed to gain insights into the HLW glass and SNF dissolution processes and controlling mechanisms under deep geologic repository environments, as well as the influence of key physical and chemical parameters on the dissolution rates. Available data on HLW glass and SNF dissolution rates were also assessed with respect to the fractional degradation rates of waste forms in the SOAR model.

The literature review of the HLW glass dissolution process indicates that there are three characteristic stages for glass alteration, including the forward rate stage, the residual rate stage, and the potential resumption of alteration stage at an accelerated rate. Precipitation of secondary silicate phases was observed at high pH, temperature, and glass surface to solution volume ratio during laboratory experiments, which triggers the resumption of alteration that could lead to an increase in the glass dissolution rate. Technical uncertainties associated with the mechanisms and timing of the resumption of glass alteration under disposal conditions should be addressed in assessing the long-term performance of HLW glass. Ebert (2017) concluded that resumed accelerated rates are below HLW glass dissolution rates from a model DOE developed in 2004 (Bechtel SAIC Company, LLC, 2004). Based on the conclusion by Ebert, no updates to HLW glass dissolution rate inputs to SOAR are recommended. It is noted, however, that the data presented by Ebert (2017) were not available for detailed scrutiny and comparison to SOAR inputs.

The three characteristic stages of the SNF dissolution process identified in the literature are the instant release fraction stage, the radiolytic dissolution stage, and the solubility-controlled dissolution stage. Radionuclide release from SNF, if in contact with water after waste container breaching in a geologic repository setting, is described as the combination of the instantaneous release from the free surfaces and grain boundaries of the fuel, and the long-term release associated with fuel matrix dissolution by both radiolytic-enhanced dissolution and solubility-controlled dissolution. The inhibiting effect of hydrogen on SNF dissolution has been reported in the literature without reaching a consensus on quantification of the effect. Given no new SNF dissolution rates have been reported since the last SOAR update in 2015, no changes are recommended for the SNF fractional degradation rates.

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