Application of EQ3/6 to Modeling of Nuclear Waste Glass
Behavior in a Tuff Repository

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INTRODUCTION

The Nevada Nuclear Waste Storage Investigations project, NNWSI is evaluating the tuffaceous rocks of Yucca Mt., Nevada, for suitability as a site for a high level nuclear waste repository. As part of that project Lawrence Livermore National Laboratory is responsible for the design of the waste package and assessment of its performance in the repository. One form in which high level waste will be stored is borosilicate glass poured in stainless steel containers; waste of this form will be produced by the Defense Waste Processing Facility at the Savannah River Plant, and by the West Valley Demonstration Project at West Valley, New York. Further information concerning these waste forms may be found in Oversby (1984) and references in that report. This report describes preliminary development of glass degradation modeling capabilities for repository performance assessment modeling using the geochemical modeling code EQ3/6. Included are summaries of the principles behind the glass modeling effort and of the additions to EQ3/6 and its database that must be made in order to undertake this work.

The behavior of nuclear waste glass under repository conditions is currently being investigated by NNWSI and numerous other projects and investigators. Laboratory experiments are yielding data on time scales of up to several years. These data may be used to interpret models of glass leaching and degradation as well as provide direct numerical values for the release of elements of interest at those time scales. A number of empirical and semi-empirical models have been proposed which yield release rates that match the observed data. Glass degradation and radionuclide release is always observed to slow with time, so these models and data from short-term experiments can provide upper limits to the long term release of radionuclides from glass. This type of data may easily be plugged into performance assessment codes as a "source term" if the experiments from which the data are obtained are sufficiently similar to the repository conditions at the time of interest.

The extension of these semi-empirical relationships based on several years of testing to time spans of hundreds to thousands of years cannot be done without understanding the mechanisms involved and assessing the effects of factors such as the build-up of layers of crystalline material. In order to obtain a detailed understanding of the behavior of glass in the repository at long times, glass degradation and radionuclide release must be accounted for with a geochemically sound model that accounts for the perturbations expected in the repository, and is consistent with existing data. Current models for glass degradation are unable to meet all these criteria. The desired model for long term behavior must be based upon the mechanisms for glass degradation which are the origin of the observed rate laws. Current understanding of glass leaching mechanisms and the interaction of glass with an aqueous environment has advanced to the point

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where it is now feasible to begin designing this type of comprehensive model. A comprehensive model will have its foundation in both the experimentally observed rates of glass degradation and established geochemical principles already in use in the geochemical modeling code EQ3/6 (Wolery, 1983, 1986).

Although the various components of nuclear waste glasses are released into solution at widely varying rates, the use of a glass degradation model based on a unified mechanism is supported by the current understanding of the degradation mechanisms of nuclear waste glasses. This work has been summarized by the Defense High-Level Waste Leaching Mechanisms Program (Mendel et al., 1984). They showed that current formulations of borosilicate waste glasses are sufficiently resistant to selective leaching processes that their behavior over the long time spans of interest in repository performance assessment is determined by the overall breakdown of the glass framework (called matrix dissolution). The release of glass components would be congruent, that is all components would be released at the same rate, except that many of the glass components are re-precipitated onto the surface of the glass. The resultant layers do not offer any physical barrier to release, such as a diffusional barrier to the motion of ions, because they are low density, cracked, and separate easily from the glass. These layers are the result of the chemical precipitation processes that will control the long term behavior of the glass. Any model of glass behavior must adequately model the formation and behavior of the precipitated phases. These phases can permanently or temporarily sequester elements released from the glass and they also control solution chemistry by this precipitation. This control of solution chemistry allows the precipitated phases to affect the rate of glass degradation.

It is also apparent that for extremely resistant glasses, like the current DWPF 165 frit formulation, the time period required to establish matrix-dissolution controlled behavior can be substantial on a laboratory scale (as much as one year). Even though an extremely small amount of the glass is removed by selective leaching before matrix dissolution becomes dominant, it may be necessary to model the behavior in this time period in order to interpret some laboratory experiments such as the NNWSI Unsaturated Test (Bates and Gerding, 1985). Glass degradation in the incipient stages of breakdown is controlled by the diffusional exchange of hydrogen in the leachate for very soluble alkalis in the glass, Na, Li, and Cs for instance. Other glass components are not released in this incipient stage. The significance of this hydration-diffusion controlled release in a repository may be in the initial release of radionuclides when water contacts the glass. At long times the rate of hydration-diffusion slows to less than that of matrix dissolution and no further material is released by that mechanism.

GOALS

Derivation of a complete, repository relevant model based on the stated principles will require staged development over a period of years. This staged development may be tailored to accomplish important goals along the way. Accordingly the goals of glass modeling listed here are progressively more complex. At each stage the modeling effort would be verified with experimental work, and additional experimental work required for data acquisition would be identified. The goals are:

- 1) To calculate solution compositions that would be in equilibrium with the solid phases precipitated on a waste glass, independent of the continuing breakdown of the glass, at ambient temperatures expected in the repository (up to 95°C).
- 2) To model the breakdown of glass in the absence of precipitated phases. This would involve applying kinetic rate laws for dissolution. Rate constants would be determined from experimental data. Both matrix dissolution and diffusional release of alkalis must be considered for short terms, but diffusion is unimportant for long terms. One simplified case of this type would be the reaction of glass with distilled water over short time periods.
- 3) To model the long-term formation of surface layers and precipitated phases in conjunction with solution compositions. This would correspond to modeling of laboratory experiments. Determination of the extent to which radionuclides are expected to be incorporated in surface layers would be an important aspect of this work.
- 4) To combine the results of (3) with flow of solution at rates anticipated in the repository to determine release of elements of interest from the vicinity of the glass. The composition of fluids leaving the waste package would be modeled as a function of flow rate.
- 5) To add repository interactions to the model, including those of canister materials and tuff. Other repository materials may be treated separately if they are not in the immediate vicinity of the waste package.
- 6) To arrive at a complete model by adding thermal changes with time as the waste package cools, and changes in the surface area and geometry of the glass as degradation progresses.

MODELING APPROACH

Glass is not thermodynamically stable, and will eventually convert to more stable, crystalline forms over time. In a repository at Yucca Mt., this process would be expected to occur as a result of water contacting the glass. EQ3/6 currently contains kinetic rate laws designed to model the dissolution of a crystalline phase where the kinetics are controlled by the concentrations of the product species and the surface area of the reactant. If appropriate thermodynamic data were available, and the rate-limiting steps of the dissolution mechanism could be determined, then this method could be applied to the dissolution of glass. The thermodynamics of glass dissolution have been addressed by several groups (Paul, 1977; Plodinec et al. 1984). The most detailed assessment of the kinetics of glass dissolution has been done by Bernd Grambow of the Hahn-Meitner Institute (Grambow, 1984, 1985). He has given an example of how transition state theory may be applied to glass dissolution. His work demonstrates that the dissolution of glass may be modeled using fundamental geochemical principles.

In the work done by Paul and Grambow, the dissolution of silica is the rate limiting step in glass dissolution. There is considerable evidence to support this. However, even if other species or mechanisms are found to be important, the same modeling principles could still apply. The concentration of silica in solution is considered as the controlling factor in the removal of hydrated silica from the surface of the glass. This is the rate-limiting irreversible step in the transition state formulation. The concentration of silica in solution is calculated by straightforward means involving identifying precipitated phases. However, the free energy change upon hydration and subsequent dissolution of a glass is not an easily definable thermodynamic quantity. This value is calculated based on the summed values for the hydration and dissolution of the oxide components in the glass. The species considered by Grambow are shown in Table 1. This is clearly an approximate method, but appears to give reasonable results. Improvement in Grambow's results may be obtained by more accurate model of the hydration thermodynamics of the glass, which will be evaluated during the course of the work. Again, however, this does not significantly affect the modeling method. Observed degradation rates are used to calculate the rate constant for the transition state kinetic formulation. In this model formulation the rate constant is independent of the condition of the glass (that is fresh, strongly degraded, etc.) and as such laboratory measurements may be applied to calculate long-term results.

Grambow describes the mathematics of his approach as follows. The general rate equation for glass corrosion is derived from the work of Aargaard and Helgeson (1982) on the weathering of minerals. It is assumed that the activated complex of interest is a hydrated silanol group in the process of being released into solution. The concentration of this activated complex is controlled by the number of hydrolyzed and non-hydrolyzed bonds in the reaction zone which is in turn related to the Gibbs free energy of reaction of glass and solution. This free energy of reaction is a summation of the standard Gibbs free energies of hydration of oxide and silicate components of the glass (Paul, 1977). For the reaction of ξ moles of glass in 1 kg of solution the general rate equation is given as:

$$r_m(t) = X \cdot \exp(-\Delta G_R(\xi)/RT) \cdot \exp(-E_A/RT) \cdot (1 - \exp(-A_{SiO_2}(\xi)/RT)) \quad (1)$$

where X is a proportionality constant

$\Delta G_R(\xi)$ is the free energy as a function of reaction progress (ξ)

$A_{SiO_2}(\xi)$ is the affinity of the rate limiting reaction.

E_A is the activation energy.

R is the gas constant

T is the absolute temperature.

When the affinity is large (silica far from saturation in solution) the logarithm of the reaction rate will be proportional to the Gibbs free energy, as confirmed experimentally by Plodinec, et al. (1983). The constant of proportionality is the product $X \cdot \exp(-E_A/RT)$. Close to silica saturation (approximately $A < RT/3$) the reaction rate is directly proportional to the affinity. These relationships allow the required constants to be determined from experimental work. Grambow's and Plodinec et al.'s work suggest that an activation energy of 75 kJ/mol and a proportionality constant (X) of 3400 mol m⁻²sec⁻¹ are appropriate for waste glasses.

Table 1. Species and hydration reactions of the hypothetical oxide and silicate components of glass (Grambow, 1984).

SPECIES	HYDRATION REACTION
Amorphous Silica	$\text{SiO}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_4\text{SiO}_4$
Mullite	$1/6(3\text{Al}_2\text{O}_3 + 2\text{SiO}_2 + 18\text{H}^+ \rightarrow 2\text{H}_4\text{SiO}_4 + 6\text{Al}^{3+} + 5\text{H}_2\text{O})$
Willemite	$1/2(\text{Zn}_2\text{SiO}_4 + 4\text{H}^+ \rightarrow 2\text{Zn}^{2+} + \text{H}_4\text{SiO}_4)$
Mg-metasilicate	$\text{MgSiO}_3 + 2\text{H}^+ + \text{H}_2\text{O} \rightarrow \text{Mg}^{2+} + \text{H}_4\text{SiO}_4$
Ca-metasilicate	$\text{CaSiO}_3 + 2\text{H}^+ + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + \text{H}_4\text{SiO}_4$
Ba-metasilicate	$\text{BaSiO}_3 + 2\text{H}^+ + \text{H}_2\text{O} \rightarrow \text{Ba}^{2+} + \text{H}_4\text{SiO}_4$
Li-metasilicate	$1/2(\text{Li}_2\text{SiO}_3 + 2\text{H}^+ + \text{H}_2\text{O} \rightarrow 2\text{Li}^+ + \text{H}_4\text{SiO}_4)$
Na-metasilicate	$1/2(\text{Na}_2\text{SiO}_3 + 2\text{H}^+ + \text{H}_2\text{O} \rightarrow 2\text{Na}^+ + \text{H}_4\text{SiO}_4)$
K-metasilicate	$1/2(\text{K}_2\text{SiO}_3 + 2\text{H}^+ + \text{H}_2\text{O} \rightarrow 2\text{K}^+ + \text{H}_4\text{SiO}_4)$
MoO ₃	$\text{MoO}_3 + \text{H}_2\text{O} \rightarrow \text{MoO}_4^{2-} + 2\text{H}^+$
Nd ₂ O ₃	$1/2(\text{Nd}_2\text{O}_3 + 6\text{H}^+ \rightarrow 2\text{Nd}^{3+} + 3\text{H}_2\text{O})$
B ₂ O ₃	$1/2(\text{B}_2\text{O}_3 + 3\text{H}_2\text{O} \rightarrow 2\text{H}_3\text{BO}_3)$
Hematite	$1/2(\text{Fe}_2\text{O}_3 + 6\text{H}^+ \rightarrow 2\text{Fe}^{3+} + 3\text{H}_2\text{O})$

In order to use this type of model as a source term for performance assessment modeling, real-time kinetics will have to be applied. The controlling rate constant will probably be found to be that of the initial

dissolution of the glass, as suggested by Grambow, but it is also possible that the precipitation of a secondary phase could control the reaction rate. Both experimental and calculational results will be considered in evaluating the appropriate constants for long-term modeling.

REQUIRED ADDITIONS TO EQ3/6

Much of the work described here can be done with the existing EQ3/6 codes. Items (1) and (2) of the goals do not require any changes. However, the following additions must be made to the geochemical modeling code in order to accomplish all the outlined goals.

- * A solid-solution model for the thermodynamics of glasses must be added. This will be similar to the current mineral solid solution capability, which is being designed to handle large numbers of components in ideal solution.
- * Data for the phases known or predicted to form on nuclear waste glass must be upgraded in the data base. A list of minerals currently thought to be important is shown in Tables 2 and 3.
- * A flow model for successive packets of fluid moving past a single, stationary, reacting material must be added.
- * Changes in surface area of glass during reaction must be accounted for. This may be done by programming changes in the surface area as a function of reaction progress. This is essential for accurate modeling because of the initially cracked and pulverized glass at the surface of the can.
- * Redox disequilibrium capabilities must be added to deal with the effects of the canister steel.
- * Sorption must be added so as to accurately calculate the release of radionuclides from the vicinity of the waste package.
- * A method must be derived for a diffusion type kinetic rate law to operate in parallel with the matrix dissolution rate law to model short term results. The appropriate rate constants must be determined from experimental work.

The addition of new mineral data, redox disequilibrium, and sorption will all require supporting experimental work. The phases and systems in question are not currently well enough understood to accurately model them; good thermodynamic data are required. The ways in which the code is applied to the overall glass breakdown will require further studies of glass reaction mechanisms. The following areas will require further research before the final goals of the glass modeling effort can be achieved.

- * Phases that form on glass. The phases in Table 2 have been reported to precipitate on nuclear waste glass. Their importance must be evaluated and thermodynamic parameters added to the data base if necessary. Phases with a "+" are represented in the current data base. Phases with a "?" have been reported but their identification is questionable. Formulas given are from Fleischer, 1983. Unidentified phases of the chemistries and structural types shown in Table 3 have also been reported.

Table 2. Phases Reported to Form on Nuclear Waste Glass

<u>Acmite</u> $\text{NaFeSi}_2\text{O}_6$	Jantzen and Bickford, 1985
+ <u>Analcime</u> $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$	e.g. Bates et al., 1984
<u>Augite</u> $(\text{Ca}, \text{Na})(\text{Mg}, \text{Fe}, \text{Al}, \text{Ti})(\text{Si}, \text{Al})_2\text{O}_6$	Bates et al., 1984
+ <u>Eucryptite</u> LiAlSiO_4	Van Iseghem et al., 1985
<u>Ferrihydrite</u> $5\text{Fe}_2^{3+}\text{O}_3 \cdot 9\text{H}_2\text{O}$	Strachan et al., 1984
<u>Gyrolite</u> $\text{Ca}_2\text{Si}_3\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$	Bates et al., 1984
?+ <u>Magnetite</u> Fe_3O_4	Mendel (compiler), 1984
?+ <u>Montmorillonite</u> $(\text{Na}, \text{Ca})_{0.33}(\text{Al}, \text{Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$	Mendel (compiler), 1984
?+ <u>Sepiolite</u> $\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$	Strachan et al., 1984
<u>Sauconite</u> $\text{Na}_{0.33}\text{Zn}_3(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$	Strachan et al., 1984
? <u>Searlesite</u> NaBSi_2O_5	Mendel (compiler), 1984
+ <u>Spinel</u> NiFe_2O_4	Jantzen and Bickford, 1985
?+ <u>Talc</u> $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	Strachan et al., 1984
<u>Tobermorite</u> $\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$	Bates et al., 1984
<u>Truscottite</u> $(\text{Ca}, \text{Mn})_{14}\text{Si}_{24}\text{O}_{58}(\text{OH})_5 \cdot 2\text{H}_2\text{O}$	Mendel (compiler), 1984
+ <u>Weeksite</u> $\text{K}_2(\text{UO}_2)_2\text{Si}_6\text{O}_{15} \cdot 4\text{H}_2\text{O}$	Bates et al., 1984

Table 3. Additional Precipitates on Nuclear Waste Glass

"Amorphous" clays	Mendel (compiler), 1984
Aluminum Hydroxide	Mendel, 1984
Calcium-Tin-Potassium Borosilicate	Sheetz et al., 1985
Calcium Arsenate	Haaker et al., 1985
Calcium-Barium Molybdate	Haaker et al., 1985
Calcium-Phosphorus Silicate	Bates et al., 1984
Calcium Silicates	Mendel (compiler), 1984
Calcium Uranyl Silicate	Haaker et al., 1985
Calcium Sulphate	Mendel (compiler), 1984
Lanthanum Hydroxide	Mendel (compiler), 1984
Magnesium Oxychloride	Mendel (compiler), 1984
Nickel-Iron Silicates	Mendel (compiler), 1984
Silica	Mendel (compiler), 1984
Vermiculite	Haaker et al., 1985
Zeolites	Van Iseghem, et al., 1985
Zinc Silicates	Haaker et al., 1985

- * Phases present in the Repository. These include tuff minerals, air, groundwater, possible added materials, canister and liner materials. The breakdown products of metals such as the canister must be determined. The tuff mineralogy is fairly well known and represented in the data base; possible problems are secondary phases, for example manganese oxides and zeolites.
- * Solution-Reprecipitation Kinetics. EQ3/6 is currently capable of handling several rate laws. The appropriate laws and rate constants must be determined for important minerals in order to achieve the more advanced (non steady-state) goals of this modeling effort.
- * Glass Breakdown Rates. The current theory must be verified and modified as required. Other factors than silica concentration in solution (the only factor considered by Grambow) will certainly have some importance.

- * Relationship Between Glass Breakdown and Layer Formation. The formation of thick layers may change reaction mechanisms. One possibility is that EQ3/6 may have to be modified to model partial box systems, where the reaction zones are partially isolated from each other. An example of this is a thick layer with trapped fluid which can only exchange by diffusion with the surrounding leachate.

CONCLUSION

Modeling of glass degradation based on sound geochemical principles appears to be possible with revisions to EQ3/6. Realistic source terms for several repository scenarios may be generated with such a model. One scenario which appears very likely and which is also amenable to modeling using EQ3/6 is that in which an intact but perforated canister holds water in contact with waste glass. The water overflows continuously or periodically, allowing radionuclides to come in contact with repository rock. This isolated-type scenario will be the first realistic modeling effort because it limits complex interactions between rock and glass. However, EQ3/6 modeling should be possible even for very complicated scenarios if sufficient experimental data are available on rates and thermodynamics. This will be the limiting factor in progress toward modeling the complete system.

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