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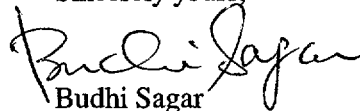Mail Stop T8 A23
Washington, DC 20555

Subject: Programmatic review of American Ceramic Society paper titled "Dissolution Kinetics of High-Level Waste Glasses and Performance of Glass in a Repository Environment"

Dear Mrs. DeMarco:

Enclosed please find the subject paper. This paper will be presented at the 103rd Annual American Ceramic Society meeting on April 24, 2001 and will be published in the Ceramic Transactions. The abstract of the paper was reviewed and approved by the NRC in November 2000. In the paper, dissolution kinetics of the simulated HLW glasses was investigated in a simulated internal WP environment containing steel corrosion products. Rate expressions for glass dissolution were developed taking account of the effects of corrosion products and compared with the DOE model used in TSPA. Performance assessment analyses indicate that during the regulatory period the mean dose rate is comparable to the dose rate from the spent fuel dissolution. However, the magnitude of the dose rate is small in both cases.

Please contact Yi-Ming Pan at (210) 522-6640 or Vijay Jain at (210) 522-5439 or Osvaldo Pensado at (210) 522-6084, if you have any questions regarding this paper.

Sincerely yours,

Budhi Sagar
Technical Director

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Enclosure

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DISSOLUTION KINETICS OF HIGH-LEVEL WASTE GLASSES AND PERFORMANCE OF GLASS IN A REPOSITORY ENVIRONMENT

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ABSTRACT

The chemistry of the water contacting the waste form after corroding the waste package may have a significant influence on waste form degradation. The dissolution kinetics of two simulated high-level waste (HLW) glasses (WVDP Ref. 6 and DWPF Blend 1), produced at the West Valley Demonstration Project and the Defense Waste Processing Facility, respectively, were measured in aqueous solutions of $FeCl_2$ and $FeCl_3$ at temperatures of 40, 70, and 90 °C using a modified product consistency test (PCT) method. These species simulate the presence of steel corrosion products. An empirical expression accounting for the intrinsic dissolution rate, pH dependence coefficient, and activation energy was obtained for modeling waste glass dissolution. Enhanced glass dissolution was observed in the presence of corrosion products. This expression was used to evaluate the impact of glass waste form on radionuclide release within the context of a performance assessment (PA) for the proposed HLW geologic repository at Yucca Mountain (YM), Nevada. Comparisons between the HLW glass cases and the spent fuel Base Case indicate that the enhanced glass dissolution by corrosion products results in a maximum dose contribution of about 30 percent of the Base Case dose at 52,000 yr, but the magnitude of the dose rates is small in all cases.

INTRODUCTION

The long-term dissolution behavior of waste glass immersed in aqueous solutions can be expressed by a general rate equation shown in Eq. 1 that was originally developed for silicate hydrolysis reactions.[1,2] A similar form of the rate expression has been adopted by the Department of Energy (DOE) to model waste glass degradation.

$$\text{Rate} = S\left\{ k \cdot \left[1 - \frac{Q}{K} \right] \right\} \tag{1}$$

where

S = surface area of glass immersed in solution
k = forward dissolution rate
Q = concentration of dissolved silica in the solution
K = a quasi-thermodynamic fitting parameter equal to the apparent silica saturation value for the glass

In a closed-system leaching test, glass dissolution follows a nonlinear behavior as a function of time. The glass components are initially released at a fast rate, but the rate decreases with time due to a combined effect of increased silica concentration in the contact solution and increased diffusion path due to development of a hydrated surface layer on the surface of the waste glass. The silica concentration effect can be quantified by the chemical affinity term $(1-Q/K)$. The forward dissolution rate, which represents the high initial rate in the absence of the build-up of dissolved silica and provides an upper bound to the dissolution rate, can be measured in experiments by maintaining the affinity term close to unity. The forward rate depends on glass composition, solution pH, and temperature, and can be expressed as

$$k = k_o \cdot 10^{\eta \cdot pH} \cdot \exp(-E_a / RT) \tag{2}$$

where

k_o = intrinsic dissolution rate, in unit of g/m^2-day
η = pH dependence coefficient
E_a = activation energy, in unit of kJ/mol
R = gas constant, which is 8.314 kJ/mol-K
T = temperature in Kelvin

The model parameter values (k_o, η, E_a) in the rate expression in Eq. 2 have been determined by the DOE by regression of experimental data from single-pass flow-through tests for various waste glass compositions in buffer solutions prepared with deionized (DI) water.[3] However, the DOE model abstraction ignores the presence of corrosion products from the dissolution of waste package internal components such as FeOOH, $FeCl_2$, and $FeCl_3$ that could influence glass degradation. As previously reported in Pan et al.[4], the presence of aqueous solutions of $FeCl_2$ and $FeCl_3$ significantly enhances dissolution of

HLW glasses. Substantially high initial boron and alkali release rates, approximately 50 to 70 times greater than those in DI water, were measured in 0.25 M FeCl$_3$ solution at 90 °C.

This work describes experimental investigations into dissolution kinetics of two simulated waste glass samples from WVDP and DWPF. The glasses were subjected to leaching tests in the presence of FeCl$_2$ and FeCl$_3$ at temperatures of 40, 70, and 90 °C. While the test environment does not represent YM repository J-13 groundwater environment, the literature shows that dissolution behavior of glass observed in DI water is more aggressive than that in J-13 water.[5] The relatively high leach rates observed in DI water are attributed to the solution composition effects, as elemental concentrations increase in the leachate, elemental release rates decrease. Therefore, the DI water bounds the effect of J-13 environment. From the glass leaching results, model parameters, including the intrinsic dissolution rate, pH dependence coefficient, and activation energy, were determined. An empirical rate expression accounting for the effect of iron compounds on the glass dissolution behavior was used for PA calculations to evaluate the impact of glass waste form on radionuclide release for the proposed YM repository.

EXPERIMENTAL PROCEDURES

Two simulated HLW glasses, WVDP Ref. 6 glass frit and DWPF Blend 1 glass, were used for dissolution study. These glasses are referred hereafter as WVDP glass and DWPF glass, respectively, and their compositions are given in Table I. To simulate internal WP environment, DI water enriched with either ferrous or ferric chlorides of concentrations 0.0025 M and 0.25 M was used. All the tests were conducted using a modified product consistency test (PCT) method in accordance with ASTM Standard Test Method C1285-97.[6] The solutions were replaced at regular intervals. In these tests, 60-cm^3 perfluoroalkoxy (PFA) Teflon® vessels were used. Approximately 3 g of crushed glass specimen with a particle size distribution between -100 to +200 mesh was placed in each vessel. A 30 cm^3 test solution was added to the vessel. This gives a glass surface area to solution volume ratio (S/V) of 2,000 m^{-1}, as calculated in the ASTM standard. The test specimens were placed in an oven held at temperatures of 40, 70, and 90 °C. The solution was replaced entirely with an identical volume of fresh solution twice every week, at an interval of alternate three-day and four-day cycles, for a total test time of four weeks. At the end of each test period, the vessels were removed from the oven and allowed to cool. A small portion of leachate was used to measure pH. The leachate was then filtered with a 0.45 μm syringe filter for cation analysis using the inductively coupled plasma (ICP) atomic emission spectrometry technique.

The normalized concentration for element i, NC$_i$, and the normalized leach rate for element i, NLR$_i$, at the nth solution replacement can be calculated by the following

equations:

$$NC_i = \frac{C_i}{F_i} \tag{3}$$

$$NLR_i = \frac{(NC_i)_n - (NC_i)_{n-1}}{(S/V)(t_n - t_{n-1})} \tag{4}$$

where NC_i is in g/m^3, C_i is the concentration of element i in solution in g/m^3, F_i is the mass fraction of element i in glass, NLR_i is in g/m^2-day, t_n-t_{n-1} is the time in days between the n-1th and n[th] solution replacements, and S/V is the surface-to-volume ratio in m^{-1}.

RESULTS AND DISCUSSION
Glass Leaching Results

As generally observed in closed-system leaching tests, the release rates for glass components decreased continuously with time for all test conditions used in this study, even though the decrease in release rate varied with the test conditions. Leach rates calculated after the first solution replacement were used as initial leach rates to provide a conservative account of the effect of glass dissolution and are plotted as a function of leachate pH in Figure 1. The initial leach rates for all major components were pH dependent. While the leach rates for B and alkali decreased with an increase in pH, the Si release rate remained relatively constant. Al leach rate showed a minimum for both the 70 and 90 °C tests. The pH value at which the minimum rate occurred varied with both the glass composition and test temperature. For the 40 °C tests, however, the leach rates for all elements decreased continuously with increasing leachate pH. Figure 2 shows the log NLR_B as a function of leachate pH at each temperature for both the WVDP and DWPF glasses, based on the initial release of boron. A linear regression between log NLR_B and leachate pH was performed, and the regression equations are also given in Figure 2. A good correlation between leach rate and pH is found for all test temperatures, as indicated by the high correlation coefficients (R^2).

In contrast to a linear pH dependence with a negative slope observed for B release in this study, Knauss et al.[7] and Abraitis et al.[8] conducted experiments in controlled pH environments and reported V-shaped dissolution rate versus pH curves with minima at near-neutral pH for both B and Si release. McGrail et al.[9] also studied glass dissolution kinetics at pH values between 6 and 12 and showed that glass dissolution increases with increasing pH. These observations suggest that the effect of pH on glass dissolution depends on the glass compositions and test conditions. Note that the initial leach rates for

B and most alkali elements are much higher in comparison with the Si release rate in the low pH ranges. In addition, the measured amount of Si in the solution is limited because of a low silica solubility limit. HLW glass dissolution rates could be significantly underestimated if based on measured Si release rates. The use of B release rates provides a conservative upper bound to the release rate of radionuclides.

Determination of Model Parameters

From Figure 2 the slopes of the linear regression equations provide the pH dependence coefficients (η). It is apparent that η does not significantly change with the test temperature and glass composition. Activation energy (E_a) can be regressed from the experimental data in a plot of ln NLR_B versus $1/T$ based on the rate equation in Eq. (2), and the intrinsic dissolution rate (k_o) can then be determined using the values of η and E_a. The model parameters are summarized in Table II. The E_a values for both waste glasses are consistent with the values reported in the literature for borosilicate waste glasses.[7-10] The mean and standard deviation values calculated for a combined case are listed in Table III and compared to other parameter values published elsewhere.[3] Then model parameters in Table III were used in PA calculations and discussed later in this paper.

The rate expression for dissolution of waste glasses has been evaluated by the DOE,[3] primarily based on the experimental results by Knauss et al.[7] Because the glass dissolution rates were found to have a V-shaped pH dependence, with minima at near-neutral pH, separate rate expressions were obtained for dissolution under acidic or basic conditions, as reflected in Table III. In addition, the release of B occurred faster than that of Si under some test conditions. The model parameter values based on B release rates were determined to bound the range of HLW glass compositions and environmental conditions. Figure 3 compares the calculated dissolution rates on the basis of Equation (2) and various model parameters in Table III. It is seen that the model parameters supported by experimental data in this paper are associated with higher dissolution rates than those reported elsewhere, in the near-neutral pH range. The higher dissolution rates are consistent with the observations of enhanced glass dissolution in the presence of iron-containing corrosion products.[4]

Performance Assessment Analyses

The Nuclear Regulatory Commission (NRC) and Center for Nuclear Waste Regulatory Analyses (CNWRA) have been developing a tool, the Total-system Performance Assessment (TPA) code,[11] intended to support review activities for a potential license application, by the DOE, for construction of a HLW repository at YM. Based on a Monte Carlo scheme, the TPA code is used to compute the expected annual dose to an individual of a critical group in the event of failure of the waste packages to

isolate radionuclides. A Base Case (defined as a particular set of models and model parameters describing likely behaviors of the YM repository system) is generally selected to perform sensitivity and uncertainty analyses and to study the performance of the system, as simulated by the TPA code. In the Base Case model or description, it is assumed that 70,040 metric tons of spent nuclear fuel is packaged in 7,176 waste packages and emplaced in the proposed repository. Each waste package contains, on average, 9.8 metric tons of spent nuclear fuel. The Base Case description does not account for the presence of HLW in glass form. Equation (2) was incorporated into the TPA code to account for glass leaching in the event glass is contacted by water. Computations presented in this section are aimed at evaluating the relative importance of glass dissolution with respect to spent nuclear fuel dissolution, in units of dose-risk.

In the computer simulations, the model parameters obtained from this work (Case A) and from the DOE(Case B) in Table III were considered. The current TPA model version 4.1e does not allow for the simultaneous inclusion of two waste forms in the estimation of the dose risk. To circumvent that problem, it was assumed that glass was the only kind of waste form in the system and that a total of 4,667 metric tons of HLW glass[12] contained in 3,910 waste packages[13] was emplaced in the proposed repository. The initial radionuclide inventory was selected from available data.[13] In order to obtain appropriate comparison of the dose deriving from glass dissolution to the Base Case dose, a temperature versus time curve for the latter case was employed. The justification is that in the mixed system, spent fuel—glass form, the temperature of the repository is dictated by the thermal activity of the spent fuel. The total surface area of the exposed glass form per waste package was set equal to 99 m^2, as suggested by other studies.[14] In the Monte Carlo analysis, the pH was uniformly sampled in the range 4.8 to 10, consistent with predictions of the chemistry inside the waste package.[15] Results of the computations are summarized in Figure 4.

The mean dose rates reported in Figure 4 were computed from 200 Monte Carlo realizations for each case. As shown in Figure 4, the mean dose rates for Case A are higher than those computed for Case B (Cases A and B refer to the notation in Table III), which are a direct consequence of the higher dissolution rates in the near-neutral pH associated to Case A that accounts for the effect of corrosion products (see Figure 3). The impact of glass dissolution on the mean dose rate in Case A could be up to 30 percent of the base case at times of the order of 52,000 yrs. Within the first 10,000 yr, the dose deriving from glass dissolution is of the same order of magnitude as the Base Case dose. Nevertheless, the magnitude of the dose rates is less than 10^{-3} rem/yr at times t < 60,000 yr in Figure 4. The doses at earlier times are a consequence of the assumption that initial defects could be present in waste containers. At times greater than 40,000 yr, a significant number of waste packages fail due to general corrosion; thus, additional

sources of radionuclide release are available in the system, causing the increase in the dose. The most important radionuclides contributing to the mean dose rate are ^{237}Np at all times, and ^{99}Tc and ^{129}I at early times (< 15,000 yr).

CONCLUSIONS

Rate expressions for glass dissolution were developed taking account of the effect of corrosion products. The model parameters including the intrinsic dissolution rate, pH dependence coefficient, and activation energy, were determined based on the initial release of boron from leaching of two simulated waste glass compositions in aqueous solution of $FeCl_2$ and $FeCl_3$. Dissolution rates calculated on the basis of Equation (2) and model parameters derived in this paper (Case A in Table III) are higher, in the near-neutral pH range, than those computed with parameter values suggested by other studies. Performance assessment analyses of the proposed HLW repository at YM, indicate that the mean dose rate deriving from glass dissolution could be as high as 30 percent of the dose rate caused by leaching of the spent nuclear fuel. The presence of corrosion products enhances glass dissolution and subsequent release of radionuclides to the environment.

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Table I. Chemical compositions of test glasses (in weight percent)

Oxide	WVDP Ref. 6[a]	DWPF Blend 1[b]	Oxide	WVDP Ref. 6[a]	DWPF Blend 1[b]
Al_2O_3	6.67	4.16	MnO	0.51	—
B_2O_3	11.48	8.05	MnO_2	—	2.05
BaO	—	0.18	MoO_3	—	0.15
CaO	0.66	1.03	Na_2O	11.94	9.13
Cr_2O_3	—	0.13	Nd_2O_3	—	0.22
Cs_2O	—	0.08	NiO	—	0.89
CuO	—	0.44	P_2O_5	2.01	—
FeO	—	—	RuO_2	—	0.03
Fe_2O_3	11.95	10.91	SO_3	0.25	—
K_2O	5.15	3.68	SiO_2	42.28	51.9
La_2O_3	—	—	TiO_2	1.04	0.89
Li_2O	4.84	4.44	ZnO	—	—
MgO	0.18	1.41	ZrO_2	1.28	0.14
	—	—	Total	100.24	99.91

[a]Composition provided by West Valley Nuclear Services Co., Inc.
[b]Composition provided by Westinghouse Savannah River Company.

Table II. Glass dissolution model parameters summary

Galss	Temperature (°C)	$\log_{10} k_o$ (g/m^2-day)	η	E_a (kJ/mol)
WVDP Ref. 6	40	8.53	−0.2345	49.2±7.4
WVDP Ref. 6	70	8.57	−0.2260	49.2±7.4
WVDP Ref. 6	90	8.22	−0.1789	49.2±7.4
DWPF Blend 1	40	8.49	−0.1894	52.8±2.5
DWPF Blend 1	70	8.60	−0.2026	52.8±2.5
DWPF Blend 1	90	8.37	−0.1780	52.8±2.5

Table III..Comparison of glass dissolution model parameters

Parameter	Case A (CNWRA Rate Expression)	Case B (DOE Rate Expression)[3]
k_o (g/m^2-day)	$10^{8.46 \pm 0.14}$	$10^{14.0 \pm 0.5}$ if pH < 7.1
		$10^{6.9 \pm 0.5}$ if pH $\geq$ 7.1
η	-0.20 ± 0.02	-0.6 ± 0.1 if pH < 7.1
		0.4 ± 0.1 if pH $\geq$ 7.1
E_a (kJ/mol)	51.0 ± 5.6	80 ± 10 if pH < 7.1
		80 ± 10 if pH $\geq$ 7.1
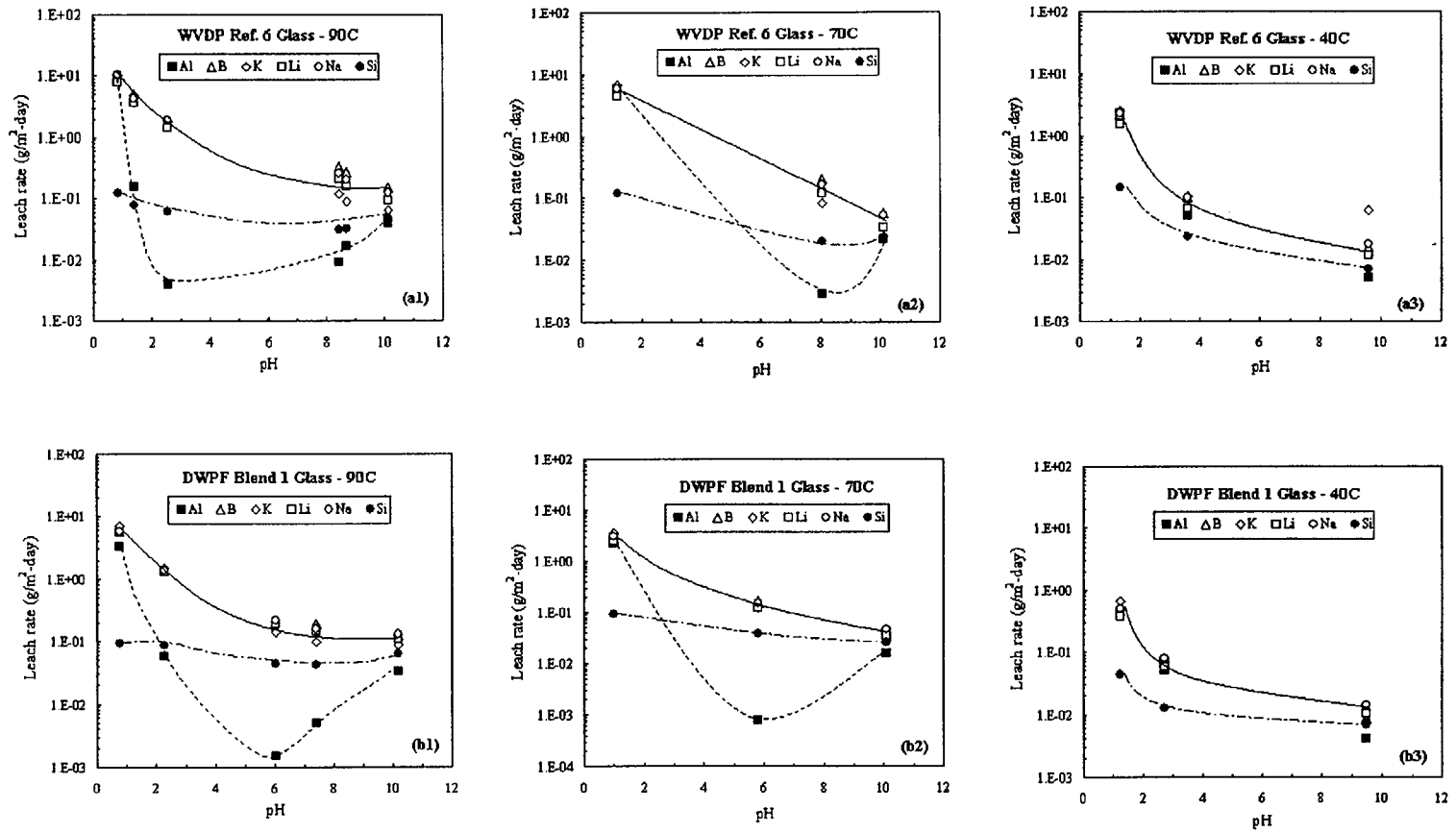
Figure 1. Normalized leach rate for various elements versus leachate pH after first solution replacement for (a) WVDP and (b) DWPF glasses at various temperatures
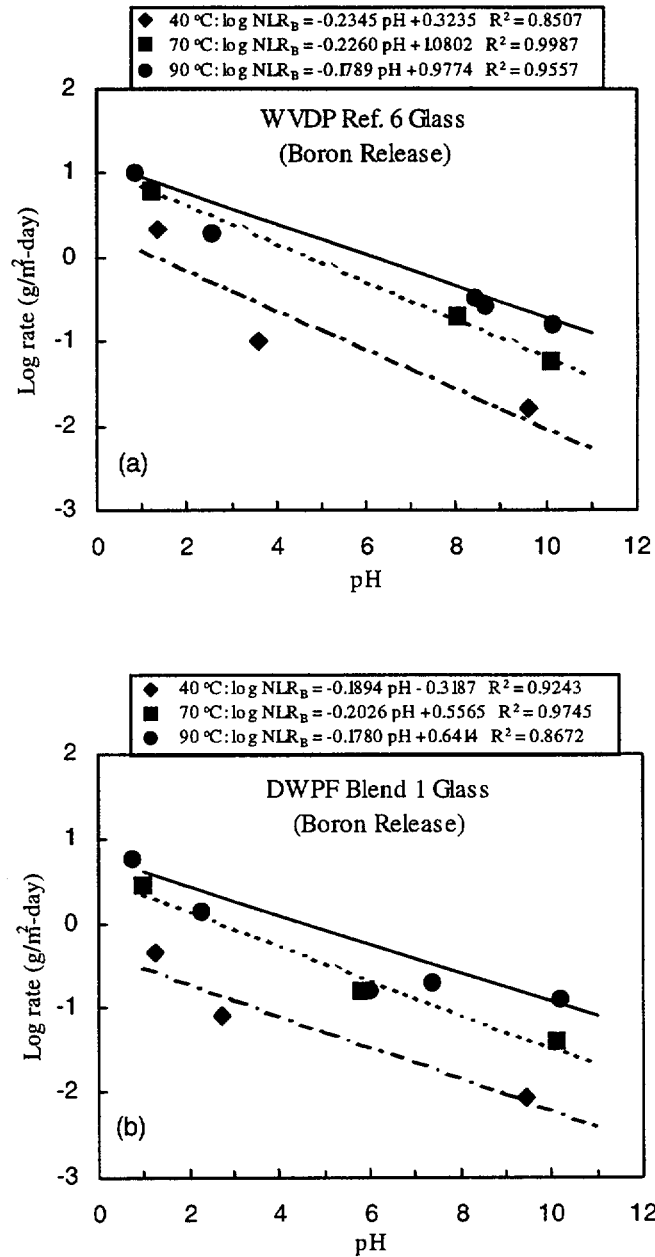
Figure 2. Linear regression of normalized leach rate for boron versus leachate pH after first solution replacement for (a) WVDP and (b) DWPF glasses at various temperatures
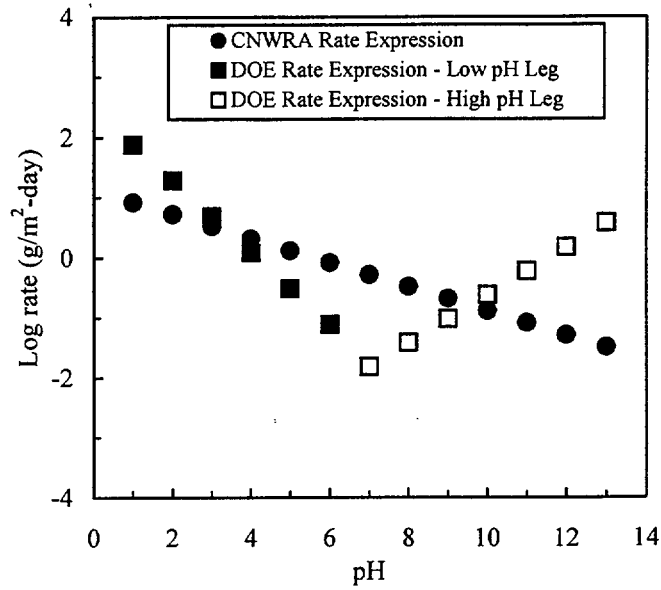
Figure 3. Comparison of calculated glass dissolution rates using different rate expressions
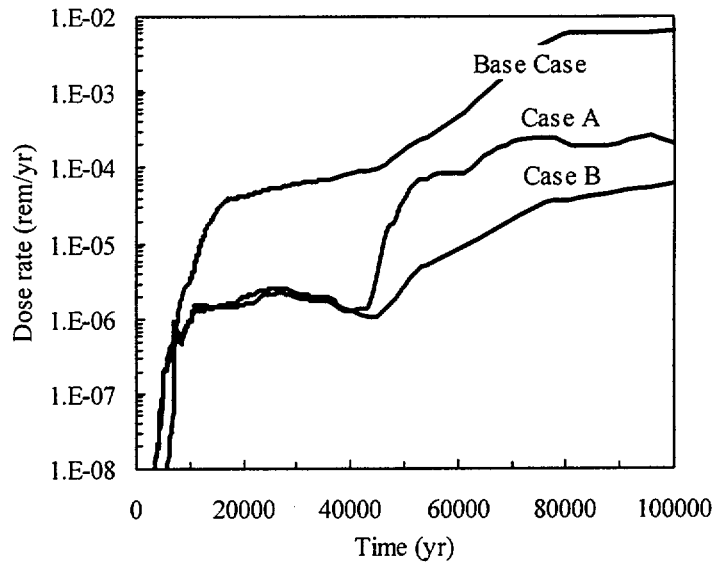

Figure 4. Estimated mean dose rates for three cases. The Cases A and B refer to the parameters in Table III. The Base Case is the nominal case of the TPA Code model, in which it is considered that 70,040 metric tons of spent nuclear fuel are buried in the system.