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GLASS CONSISTENCY AND GLASS PERFORMANCE

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ABSTRACT

Glass produced by the Defense Waste Processing Facility (DWPF) will have to consistently be more durable than a benchmark glass (evaluated using a short-term leach test), with high confidence. The DWPF has developed a Glass Product Control Program to comply with this specification. However, it is not clear what relevance product consistency has on long-term glass performance. In this report, we show that DWPF glass, produced in compliance with this specification, can be expected to effectively limit the release of soluble radionuclides to natural environments. However, the release of insoluble radionuclides to the environment will be limited by their solubility, and not glass durability.

WASTE ACCEPTANCE PRODUCT SPECIFICATIONS

Currently, the Savannah River Site (SRS) is storing 130 million liters of liquid high-level waste (HLW) in large carbon steel waste tanks. The Defense Waste Processing Facility (DWPF) at the Savannah River Site (SRS) will immobilize the radionuclides contained in SRS HLW in a durable borosilicate glass. This glass in its sealed stainless steel canister, the DWPF product, eventually must be sent to a federal repository for final disposal. In order to ensure that the DWPF product is suitable for acceptance by the U.S. Department of Energy's Civilian Radioactive Waste Management System, the Department has established the Waste Acceptance Product Specifications for Vitrified High Level Waste Forms (WAPS).[1]

The Product Consistency Specification requires that DWPF glass be more durable than the glass whose properties were the basis for the approval to start construction of the DWPF. The durability of the glass is evaluated in terms of the results of the Product Consistency Test (PCT) - a seven day test of the interaction between crushed glass and deionized water at 90°C. The specification further requires high confidence that the glass product is more durable than the benchmark glass.

The DWPF has established a program to ensure that it complies with these specifications.[2] The DWPF will comply with the Product Consistency Specification by using its Glass Product Control Program.[3] This program is based on the premise that the best way to control the durability of the glass is to control the composition of the feed to the glass melter. The composition of the feed in the last feed preparation vessel prior to glass melting will be carefully measured, and then used to evaluate glass acceptance. If, based on the composition, it is predicted that an acceptable glass will be produced, the feed is passed forward to the melter. However, if it is predicted that an unacceptable glass will be produced, the feed will be held and adjusted until the DWPF is sure that an acceptable glass will be produced.

A correlation between feed composition and glass durability (as measured by the PCT) has been developed which will be used to make these predictions.[4] This correlation is based on the interaction between glass components and water. Using a basis set of glass components, the free energy of reaction between a given glass and water (free energy of hydration) is calculated as the sum of the free energy of hydration of each component in the basis set, weighted by the amount of that component in the glass. This free energy of hydration has been correlated with the results of the PCT, to obtain an equation relating composition and leach test results.

RELATION TO GLASS PERFORMANCE

The purpose of the product consistency specification is to ensure that a consistent glass product is produced, in terms of its reactivity with water. However, this leads to several questions:

- How useful is it to limit glass reactivity to the benchmark glass, in terms of long-term glass performance?

- Why require high confidence that this limit is not exceeded?

- Will the DWPF's program for compliance with this specification help limit release of radionuclides in natural environments?

- How relevant is short-term testing to long-term glass performance in natural environments?

These questions cannot be definitively answered until a repository is finally chosen. However, this study was conducted in order to develop general guidance based on laboratory testing and a simple glass performance model.

DETERMINATION OF LONG-TERM LEACH RATE

In this study, thirty model glasses were prepared. These compositions contained representatives of each of the major elements in DWPF waste glasses, varied over a range which included that expected for DWPF glass compositions. All major components of DWPF waste glasses — silica, the most abundant component of DWPF glasses, alumina, ferric and ferrous oxides, and B_2O_3 — were each included in the model glasses. Sodium oxide was used to represent all of the alkali metals, and calcium oxide represented the alkaline earth and other +2 cations. The compositions were varied over the ranges 46-61 mol% silica, 0-16 mol% alumina, 4-15 mol% B_2O_3, 13-27 mol% Na_2O, and 0-10 mol% CaO. The free energy of hydration correlation referred to above was applied to the compositions, and led to the prediction that their PCT results would span the range of PCT results of expected DWPF glass compositions and the benchmark glass. The glasses were tested using the PCT, and the results confirmed the prediction, i.e., the PCT results of these glasses spanned the range of PCT results of DWPF glasses and the benchmark glass.

In order to develop long-term leach rates, PCT-type tests were performed for 27 of the glasses for 14, 28, and 168 days. The other three were only leached for 14 days, because they had completely dissolved after that time. For each of the glasses, the leach results were plotted as the logarithm of the normalized boron concentration as a function of the logarithm of time. In all cases, linear plots resulted. The resulting slopes (G) were then used to calculate the leach rate at one week, which corresponds to the PCT test conditions. One week was selected as the time of interest for subsequent modeling because it is more conservative (higher) than the leach rates calculated for 24 weeks by one to two orders of magnitude. The one week rate may also be more representative of the rate which would be associated with slow-moving ground water. Leach rate values determined as above varied from $1 \cdot 10^{-4}$ to 0.4 g glass/$m^2 \cdot$d.

The correlation between these experimentally determined long-term leach rates and the calculated free energies of hydration of the model glasses is shown in Figure 1. As can be seen from the Figure, there is a reasonably good correlation between the free energy of hydration and the long-term leach rate. Thus, the results of this testing indicates that limiting release on a short-term leach test such as the PCT can limit longer-term leach rates. However, it is clear that the long-term leach rate will vary with composition (since the free energy of hydration is a function of composition).

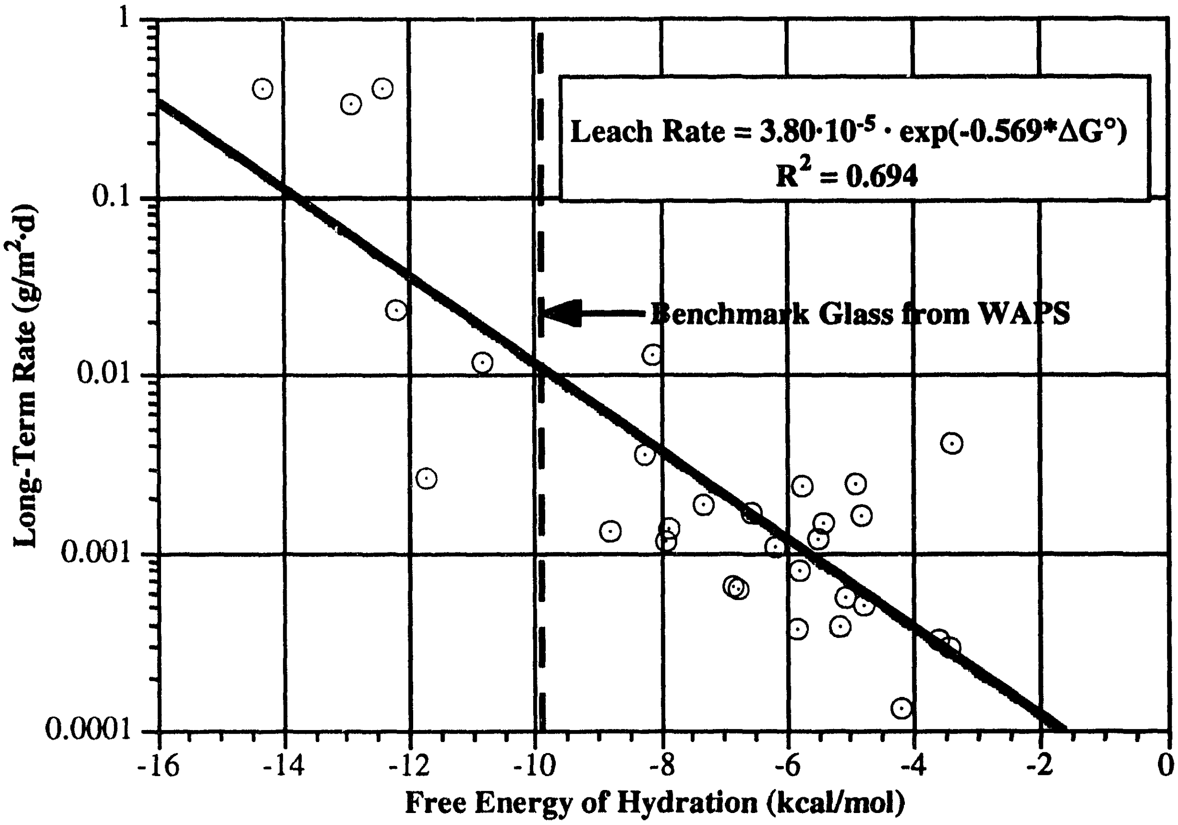
The free energy of hydration of the benchmark glass is also indicated on Figure 1 (-9.97 kcal/mol). Application of the equation given in Figure 1 indicates a leach rate of 0.0111 g glass/$m^2 \cdot$d for the benchmark glass. The scatter around the best fit line indicates that there would be significant uncertainty if this predicted value for the long-term leach rate was used, for example in performance modeling. However, because the Product Consistency Specification requires high confidence that production glass is more durable than the benchmark glass, the free energies of hydration of glasses produced in the DWPF will be significantly better than that of the benchmark glass (from -4.8 to -7.2 kcal/mol). In practice, this means that the long-term leach rates of production glasses will be less than 0.01 g glass/$m^2 \cdot$d. Thus, by bounding the short-term leach rate of production glasses, and requiring high confidence that this condition is met, the Product Consistency Specification provides high confidence that the long-term leach rate of production glass is bounded by that of the benchmark glass.

As indicated above, the range of leach rates of DWPF glasses can be inferred from Figure 1. They range from 0.0007 to 0.003 g glass/$m^2 \cdot$d. These long-term leach rates agree reasonably well with other values reported in the literature. For example, Cunnane, et al., quoted a value of 0.0025 g glass/$m^2 \cdot$d as typical for DWPF waste glasses, based on an extensive review of the literature.[5] Rechard, et al., came to a similar conclusion on the leach rates to be used for performance assessment modeling of defense waste glasses.[6]

GLASS CORROSION MODEL

To determine the relationship between this long-term leach rate and retention of radionuclides by the glass, a simple model of glass performance was developed. In order for

Figure 1. Correlation between free energy of hydration of model glasses, and long-term leach rate.



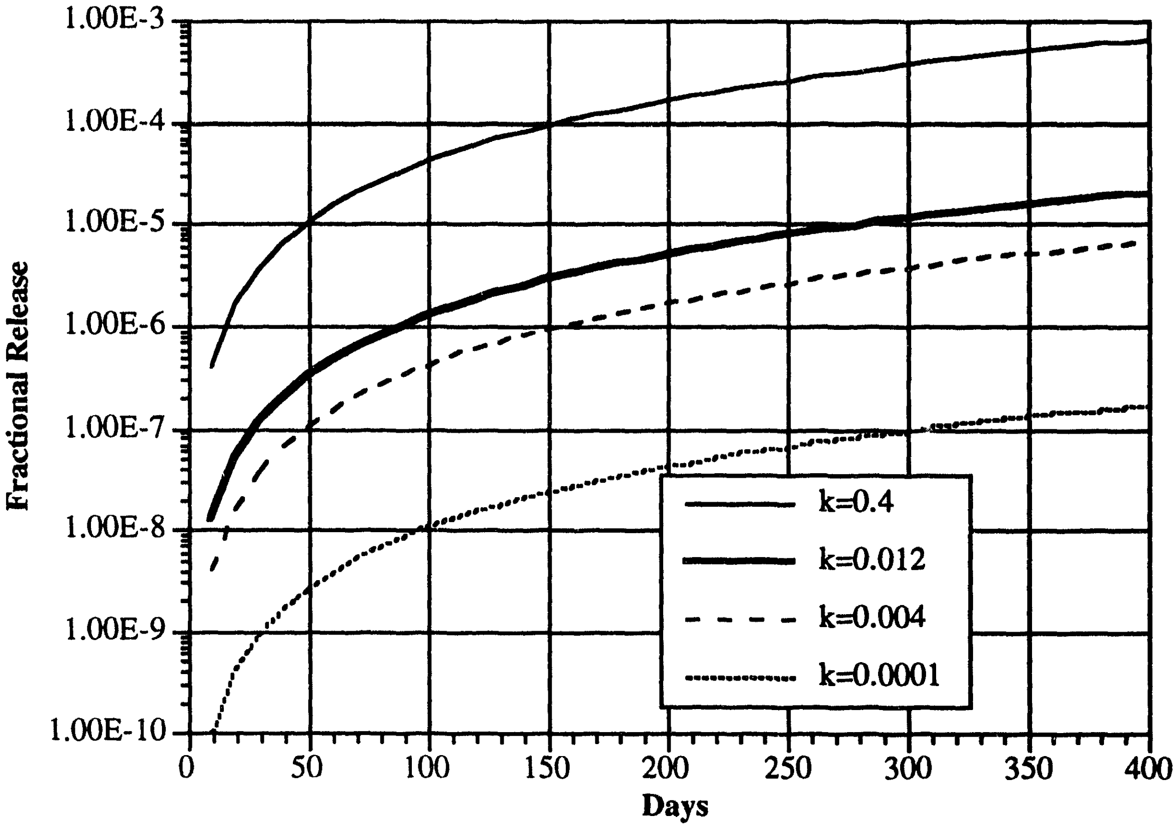
radionuclides to be released from waste glass, glass must react with water. In a natural environment (such as a repository), water will most likely enter the canister containing the glass through cracks in the canister. The water will then collect in the head space of the canister, react with the glass, and then flow out when displaced by fresh unreacted water. In the model, the amount of reaction of the glass with incoming water was assumed to be the product of the leach rate times the surface area of the glass, integrated over time. The surface area used was 5 m^2 - the surface area of the glass monolith. Glass cracking was ignored, based on large-scale leach tests which showed that cracking of the glass in the canister did not contribute to the amount of reaction observed.[7]

The releases of both an insoluble radionuclide (plutonium), and a more soluble species (technetium) were modeled. For both, release from the canister was assumed to be by displacement of reacted water by unreacted water. The maximum void space in the DWPF canister - 70 L - was assumed. A displacement rate of 0.5 L per year was used (This is probably a bounding value for a tuff repository). A solubility of $7 \cdot 10^{-5}$ g/L was used for plutonium.[8] Technetium was assumed to be soluble. This is consistent with experimental observations of Hall, Hough, and Marples, who found that release of plutonium was solubility limited, while technetium release apparently was not limited by solubility.[9] For both technetium and plutonium, it was assumed that the radionuclide made up 0.1 wt% of the glass (For DWPF glasses, this is a very conservative assumption - generally the concentrations of these radionuclides will be 5 - 10 times less than this.). The model was developed using simulation software which facilitates rapid model development and modification (iThink, by High Performance Systems, version 3.0.4). The progress of release was followed over a 400 day time period, using a Runge-Kutta numerical integration technique included in the software. The results are presented as cumulative fractions of the radionuclide released.

MODELING RESULTS

The leach rate was varied around the bounding value for the benchmark glass to determine whether the Product Consistency Specification affected release of radionuclides (A

Figure 2. **Fractional release of technetium from waste glass as a function of leach rate.** Technetium assumed to be soluble; bold line denotes rate for benchmark glass (0.012 g glass/m^2·d), at 90°C.



value of 0.012 g glass/m2·d was used for the benchmark glass, because points on either side of the position of the benchmark glass had this rate). The values used were both above and below that of the benchmark glass, and were based on those experimentally determined (Figure 1).

The results of the model calculations for technetium are shown in Figure 2, while those for plutonium are shown in Figure 3. As Figure 2 shows, limiting the glass leach rate to less than the benchmark glass clearly limits the release of soluble species such as technetium. For DWPF production glasses, this translates into fractional releases from 3 to 10 times less than that of the benchmark glass. However, as can be seen in Figure 3, the fractional release of plutonium is relatively insensitive to variation in the leach rate in the range of values for DWPF waste glasses. Thus, the DWPF Glass Product Control Program will play only a small role in limiting the release of highly insoluble species such as plutonium.

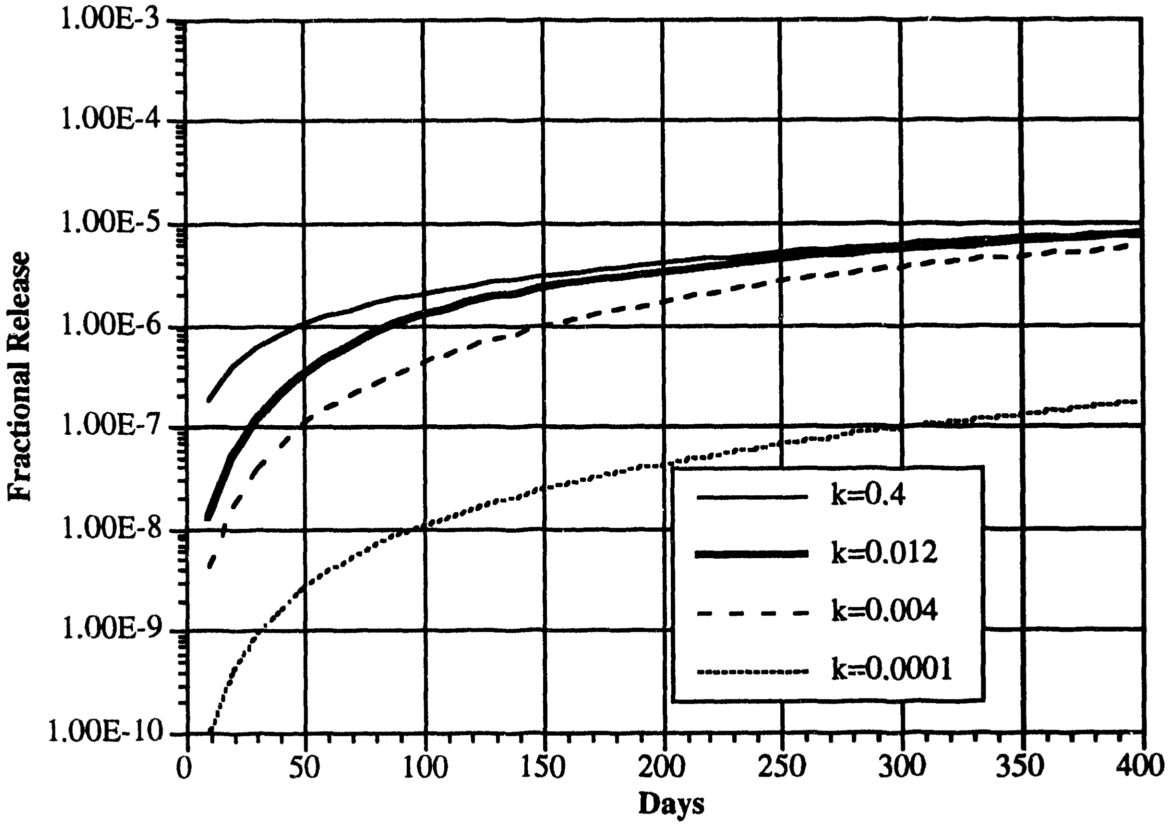
MODEL LIMITATIONS

The modeling results reported here are intended to show the sensitivity of glass performance to the parameters varied. The results should not be construed as a definitive determination of glass performance. The model used contains several conservative assumptions. The rate constants used correspond to conditions at 90°C. Even initial glass/ground water interactions are more likely to occur at lower temperatures. The rate constants are derived from relatively short-term data. As noted above, longer-term rates are one to two orders of magnitude lower. No credit was taken for saturation of the leachate by glass components such as silica. There is a rich body of data which indicates that the presence of silica in the leachant greatly reduces the rate of glass attack.

DISCUSSION AND CONCLUSIONS

The results from both the experimental and modeling efforts described in this paper provide tentative answers to the questions posed above. The DWPF will use a leach rate cor-

Figure 3. Fractional release of plutonium from waste glass as a function of leach rate. A solubility of $7 \cdot 10^{-5}$ g/l assumed for plutonium; bold line denotes rate for benchmark glass (0.012 g glass/m^2·d), at 90°C.



relation based on hydration thermodynamics to limit the short-term leaching behavior of waste glasses, as measured by the PCT. There is also a reasonable correlation between the free energy of hydration calculated from the composition of the glass and the long-term leach rate. Thus, by providing high confidence that production glasses will be more durable than the benchmark glass, the DWPF's Glass Product Control Program will ensure that the long-term leach rate of DWPF glasses will also be limited by the rate for the benchmark glass. This is also supported by the results of in-situ testing.[10,11] Tests in brine, granitic ground water, and a carbonate ground water all show that the long-term rate of glass alteration of DWPF glasses is less than that of the benchmark glass. However, limiting the long-term leach rate to the value for the benchmark glass will only limit release of soluble radionuclides. For radionuclides which are insoluble (e.g., plutonium), limiting the leach rate is relatively ineffective at limiting radionuclide release.

Requiring high confidence that production glass is more durable than the benchmark glass is useful because it minimizes the effects of uncertainties in leach rates used to assess long-term glass performance. In effect, it allows use of the long-term leach rate of the benchmark glass without any associated uncertainty, since this value is used as a bounding value.

It is clearly not yet possible to demonstrate the truth of these conclusions for any specific repository (since there is none in existence). However, these answers do provide confidence that DWPF glass, produced in compliance with the WAPS, can be expected to effectively limit the release of radionuclides in natural environments.

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