BNWL- 2051

1-1

8003110039



RADIATION EFFECTS IN SOLIDIFIED HIGH-LEVEL WASTES PART 2 - HELIUM BEHAVIOR

Non-report was proposed as an estimate of social promoved in the time of basics surveyment. Vertices, the Extend States rule that survey the social former of social basics and social basis, a survey the emphasizes, non-say, of these reserves of the emphasizes, non-say, of these reserves of the emphasizes, non-say, or these reserves and subscription of impled, or assures as legal bactures express of impled, or assures as legal bactures of any entermolecular production of unclusters of any entermolecular production process, table and, or represents that he would not unline provession and or products.

by

R. P. Turcotte Ceramics and Graphite Section Materials Department

21

May 1976

Battelle Pacific Northwest Laboratories Richland, Washington 99352

ABSTRACT

An experimental investigation of helium diffusion in a simulated zinc borosilicate nuclear waste glass is described. The helium inventory was generated by 244 Cm doping and the influence of a damage demonstrated. Diffusion at short times and low fractional release values follows Arrehnius behavior and the diffusion coefficient is given as $D_U = 2.1 \times 10^{-3} \exp(-15,000/RT)$. At longer times and higher fractional release values, trapping effects are observed, causing an apparent decrease in diffusivity by about one order of magnitude. Some estimates are presented with respect to a ster pressurization as a function of storage time, temperature, and glass geometry.

POOR ORIGINAL

TABLE OF CONTENTS

Dago

																		rage
LIST	OF F	IGURES .							•								÷	ii
1.0	INTR	ODUCTION	ù.															1
2.0	EXPE	RIMENTAL	•															4
	2.1	GLASS P	REP.	ARA	rio:	:.												4
	2.2	GAS ANA	LYS	IS					•					•				6
	2.3	DIFFUSI	0:1	THE	ORY.	•				•					•			8
3.0	RESU	LTS AND	DIS	cus	SIO	:.												11
	3.1	ISOTHER	MAL	EXI	PERI	ME	T	5.										13
	3.2	CONSTAN	тн	EAT	ING	RA	ΓE	E	(PE	RI	ÍME	ENT	rs					16
	3.3	DISCUSS	ION															19
	3.4	CANISTE	R P	RES	SURI	ZA	I°I (011										22
	3.5	OTHER H	ELI	UM I	Eŀ i ł	ECT	s.											28
4.0	CONC	LUSIONS.	•					•										31
ACKU	OWLED	GEMENT .			•													32
REFE	RENCE	s																33

i



LIST OF FIGURES

1.	Thermal power output and cumulative helium generation in fuel waste(21)	3
2.	Mass spectrometer system for helium release measurements	6
3.	Typical isothermal release curve (426°C) plotted as release rate versus time	8
4.	Calculated release curves for the slab geometry plotted as fractional release versus time for various D values	0
5.	Helium diffusivity and solubility at 200°C in common glass systems compared to the present glass 1	2
6.	Consecutive isothermal He release on the capacitance manometer system	4
7.	Isothermal helium release comparing release at 350°C, with and .ithout radiation damage 1	4
8.	Isotherms at 250, 300, and 350°C plotted as fractional He release versus \sqrt{t}	5
9.	Isotherms at 400 and 450°C plotted as fractional He release versus /E	5
10.	Short time diffusion coefficients plotted as log D versus 1/T	6
11.	Release rates versus 1/T(°K) for different samples (1-4) and inventories as indicated, obtained in constant heat-	
12.	Release rates plotted as lnR vs 1/T (°K) for a single	7
	sample with different helium inventories	8
13.	Activation energy values plotted as a function relative He inventory (F_S)	8
14.	Helium release from powdered glass (<40 μm) plotted versus comperature and showing only a broad release peak 2	0
15.	Schematic representation of diffusion process with transport controlled by rate constants k_2 (normal	
16	Maximum belium pressures in conjetere with the last	0
	plenum plotted as a function of time for UO2 and UO2- 3.3% FuO2 fuel wastes	

17.	Fractional helium release plotted versus time for $D = 2.5 \times 10^{-14} \text{cm}^2/\text{sec}$ and sphere radii as indicated			24
10	Fractional release curves plotted versus time for monolithic and fractured class at 25°C	į	1	25
19.	rractional release curves plotted versus time for monolithic and fractured glass at 300°C			25
20.	Estimated canister pressurization for UO2 fuel waste glass at 25 and 300°C, plotted versus time		1	26
21.	Estimated canister pressurization for UO2-3.3% PuO2 fuel waste glass at 25 and 300°C, plotted versus time			27
22.	Schematic of four point load cell used for glass button fracture tests.			30



POOR ORIGINAL

1.0 INTRODUCTION

The incorporation of fission product wastes in a glass matrix or in some other solid state form requires a consideration of the various aspects of radiation damage to the host matrix, if optimum confinement is to be achieved. In reactor fuel wastes, the transuranium elements will be the major source of solid state damage, through decay to more stable isotopes by emission of high energy a particles (~5.5 MeV per event). In slowing to rest, the a particles capture two electrons to become stable helium atoms which must somehow be physically incorporated in the solid, or diffuse out to the surrounding atmosphere. It is the purpose of this report to discuss an experimental study of helium diffusion, in a simulated zinc borosilicate nuclear waste glass containing the fission product elements in their expected proportions. The influence of radiation damage on diffusion and possible implications with respect to long term waste storage are considered. In this section, early literature and the vitrification process are briefly reviewed.

A great deal of information on waste fixition R&D prior to 1972 is contained in the Proceedings of the Symposium on Management of Radioactive Wastes, Paris, 1972.⁽¹⁾ Until recently, work has continued at a relatively low level both in Europe and in the United States, with near universal agreement that a silicatebased matrix is the lost promising near term solid form. In the United States, the major and continuing effort on waste vitrification has been at Battelle's Pacific Northwest Laboratories, as reported on a quarterly basis.⁽²⁾ The major features of the Battelle glass process have recently been summarized by McElroy⁽³⁾ and a comprehensive program for glass characterization has recently been presented by Mendel.⁽⁴⁾ The work presented here is part of a continuing characterization effort and is the second

BLANK PAGE

of a series of documents dealing with high-level waste fixation. The first report, by Roberts, Jenks, and Bopp, ⁽⁵⁾ dealt with stored energy from radiation damage in the same glass system as investigated in the present work.

The impact which most of the physical and chemical properties of the waste glass might have with respect to long term stability is in part determined by the processing and early storage conditions. In its simplest form, the vitrification process will involve in-canister-melting of a blend of fission product oxides and an appropriate glass frit. Due to self-heating, the ~30 cm diameter by 2 meter long canister will have an initial centerline temperature (in air) of v800°C and a wall temperature v400°C. If the canisters are water cooled, centerline temperatures will be ~403°C. The thermal power output for UO2 fuel waste reprocessed 150 days out of reactor is shown in Figure 1, plotted as watts/ metric ton of fuel versus time. Helium generation is also shown as relacive concentration versus time. Although a linear relation is not strictly true, if the centerline temperature is 800°C at the time of vitrification, it will have fallen to < 200°C after 10 years and to near ambient after 100 years. Clearly, the helium ingrowth and associated radiation damage will for the major part occur after the wa te is at ambient temperatures.

The thermal conditions experienced by the glass during the first years of storage are important with respect to devitrification phenomena resulting in possible actinide concentration regions and cracking. Storage with water cooling will also result in cracking from thermal shock. It follows that helium release will be directly affected and both monolithic and highly fractured geometries will therefore be considered in later discussion. Even if maintained vitreous, the glass will probably not be homogeneous on the microscale with Pd metal, RuO_2 , and CeO_2 being expected second phases in the present glass. In addition, viscosity will probably not be low enough to allow complete removal of H_2O/O_2 gas bubbles. These macro-defects, in

2

POOR ORIGINAL

St. 10

addition to radiation damage at the atomic level, can all be expected to have a significant influence on helium release behavior, generally in the direction of lower diffusivity. A review of thermal and radiation damage effects in the present glass system by Mendel and co-workers has been recently presented. ^(f)



FIGURE 1. Thermal power output and cumulative helium generation in fuel waste. (21)

POOR ORIGINAL

2.0 EXPERIMENTAL

2.1 GLASS PREPAR TION

The borosilicate glass composition (excluding actinides) is given in Table I. One wt.8 244 Cm₂O₂ was added in powder form with an isotopic composition 244 Cm(82.18), 245 Cm(0.88), 246 Cm(4.38), 247 Cm(0.18), 240 Pu(11.28), 243 Am(1.28). The frit-calcine mixture was melted at 1200°C in platinum for 3 hours, with stirring. Small buttons (53 grams) were formed by pouring the melt onto a stainless steel plate. The buttons were then pressed to disce 2.80 cm in diameter and 0.165 cm thick in a graphite mold contained in quartz, according to the following steps:

- 1. 10⁻³ Torr vacuum while heating to 550°C,
- 2. 550-730°C 100 Torr N2,
- 3. 15 minutes 730°C in 100 Torr N2.
- 4. 15 minutes 730°C in 600 Torr No.
- 5. Cool to 400°C in 600 Torr N2 and remove from furnace,
- 6. Surface polise discs with 400 grit silicon carbide paper,
- Wash with EtOH and outgas one-half hour at 10⁻³ Torr, 500°C.

Following preparation, the discs were stored at v25°C, to undergo a decay. Twelve discs were prepared from five different melts, with some fine pubbles present. By microprobe examination, Cm was found to be uniformly distributed but RuO₂ powder and 'mall Pd metal spheres were present as discrete phases, not nomogeneously distributed. Some SrMoO4 was also present as a devicrification product. The discs transmitted light through 5-50. of their surface area depending on the RuO₂ distribution. Since these inhomogeneities (1.7 wt.% RuO₂, 0.8 wt.% Pd) do not appear to have masked the general trends to be discussed, we will not further consider this deviation from ideality. Actual

4

POOR ORIGINAL

waste glisses will almost certainly not be any more defect free than those studied here. That the results obtained are reasonably coherent, suggests that the system complexity (35 elements) does not preclude obtaining systematic, average properties. We will nevertheless restrict the theoretical treatment to the simple diffusion case, and the discussion to empirical understanding, rather than, for example, attempt determination of defect trapping constants in a more sophisticated diffusion analysis.

TABLE I

COMPOSITION OF BOF DELICATE GLASS 72-68

Constituent	We.s.	Constituent	Wt.8
sio ₂	28,21	Ag20	0.05
B203	11.51	CdO	0.06
250	22.04	TeO2	0.42
Na20	4.19	Cs ₂ 0	1.68
к20	4.19	La203	1.87
C10	1.53	CeO2	3.75
Mạo	1.53	Pr6011	0.37
SrO	2.15	Nd203	1.34
BaC	2.44	Sm203	0.23
Rb_0	3.21	Eu ₂ 03	0.08
¥203	0.02	Ga203	0.16
aro ₂	2.88	Fe ₂ 03	0.88
мооз	3,71	Cr 203	0.20
Rud	1.73	Sio	0.03
Rh_03	0.28	Pro - 3	0.30
r.io			



2.2 GAS ANALYSIS

Some qualitative gas release measurements were made using a capacitance manometer apparatus described previously.⁽⁷⁾ The quantitative measurements were made using a quadrupole mass spectrometer (Finnigan Corporation Model 400)-furnace system shown schematically in Figure 2. A calibrated helium leak (6.6 x 10^{-8} std cc/sec ±10%) was used as reference, response being checked throughout the course of every run. By use of the leak valve and capacitance manometer (See Figure 2), helium leak tates were systematically varied to establish a linear response to helium concentration over the full experimental range. Temperatures were measured with Pt-Pt10%Rh thermocouples to ±3°C. Furnace tomperatures were maintained to ±2°C using a proportional band controller. The furnace tube was quartz and the glass samples were suspended with platinum wire.



FIGURE 2. Mass spectrometer system for helium release measurements.

6

POOR ORGIN

A typical release curve is given in Figure 3, plotted as release rate versus time. Because of the need to conduct the experiment in a glove box facility, the mass spectrometer was separated from the sample by v20 ft of 1/4 inch tubing. The subsequent release-detection lag was about 2 minutes, although pumping inefficiency for a rapid change (sample out of furnace, Figure 3) had some effect for >10 minutes. Areas under release rate versus time curves were obtained by weighing segmented graphs, giving cumulative cm³ He(STP) as a function of time in isothermal runs. In order to obtain fracticaal release values, either the calculated inventory was assumed, or the measured total content was used, whichever was the largest value (see Table II). Although errors should not be more than ±5%, the experiments were long term and there was no easy way to establish overall accuracy for samples known to be somewhat variable in true composition. Moreover, in order to maintain the disc geometry, the samples were not heated above 525°C (i.e., they were kept below the glass transition temperature), meaning that the entire helium inventory could not be safely assumed to have been released. Nevertheless, the isothermal runs did give total release values in fair agreement with the calculated inventories. as shown in Table II, for the three samples for which a total value was obtained. If the standard leak uncertainty of ±10% and an experimental error of "3% are accepted, the deviations from calculated inventories are not unreasonable.

171 %	75	÷.	274 ····	-	-
1 PA	D	L	E	1	1

	HELIUM CONCENTRATIONS	IN	ISOTHERMAL PUNS	
--	-----------------------	----	-----------------	--

Storage Time (Days)	Isotherm (°C)	Calculated [He] (cm ³ @ STP)	Measured [He] (cm ³ 3 STP)	a/cm ³ Glass x 10-18
188 249 264 330 351	350 250 450 300 400	0.0381 0.0515 0.0535 0.0669 0.0705	0.046 ~0.042 ~0.087	1.1 1.5 1.6 2.0 2.1





FIGURE 3. Typical isothermal release curve (426°C) plotted as release rate versus time.

2.3 DIFFUSION THEORY

16

3

The diffusion controlled release of inert gas from solid slabs, cylinders, or spheres, with an initial uniform concentration of gas, is well described in standard texts. $(^{(8,9)})$ The Fick's law solution for the slab is given in terms of fractional release (F) as

$$F_{slab} = 1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \exp\left[-D(2m+1)^2 \pi^2 t/t^2\right]$$

where D has the units m^2/sec , t is time (seconds) and l is the slab thickness (centimeters). The expression in the case of a sphere (which we will use in later analysis) is

3

POOR ORIGINAL

Sec. 16

 $F_{\text{sphere}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\pi} \frac{1}{n^2} \exp\left[-Dt \pi^2 n^2 / A^2\right]$

where A is the sphere radius (centimeters). Computer programs were written to generate calculated release fractions by direct summation as a function of time, for selected values of D and l (or A). Although it may be noted that the summations are infinite, the series actually converge very rapidly in both cases because the summation indices m (for the slab) and n (for the sphere) are squared and in the divisor. Consequently, even 4 or 5 terms given reasonable values in some cases (high D) and most of the experimental results could be treated with a 100 term expansion. In order to handle small D values (or large geometries), the programs were written to automatically terminate when the exponential terms became smaller than 10^{-110} or exceeded a predetermined number of terms. For D = 10^{-13} cm²/sec and sphere radii in the centimeter range, several thousand terms were needed for accurate values at low F values.

In Figure 4, some calculated curves are shown for the slab geometry used, as a function of D. These curves were used to estimate D for a given isothermal experiment by comparison to the form of the plotted data. By a series of iterative computer runs, a calculated curve could be fit to experiment, with D estimated to three significant figures. As will be shown, the experimental release curves do not correspond to simple diffusion theory, but can be reasonably fit, assuming two release mechanims with single apparent diffusion coefficients predominating at short or long times.

This kind of behavior is common to radiation damaged materials. Important contributions to basic understanding of the phenomena have been made by Elleman and co-workers ⁽¹⁰⁻¹³⁾ and by Kelly and co-workers. ^(14,15) It is generally believed that gas is trapped at defect sites either 'permanently' or reversibly. Elleman has developed formalism in which the diffusion equation includes several trapping constants in addition to D, assuming that only one kind of defect trap is involved. Stored energy measurements by

Roberts,⁽⁵⁾ however, show that defects in the present system are annealed over a broad temperature range, suggesting a distribution of gas traps exist. A diffusion theory to handle this situation does not yet exist. We will therefore treat isothermal release curves empirically, as $\pm \pm$ to release from untrapped gas (D_U), and trapped gas (D_m), as shown later.



FIGURE 4. Calculated release curves for the slab geometry plotted as fractional release versus time for various D values.

10

e

3.0 RESULTS AND DISCUSSION

There have not yet been any reports of helium solubility or diffusivity in very complex glass systems. There are, however, several studies from which a range of probable behavior can be defined. As a matter of convenience, we plot in Figure 5 the logarithm of diffusivity versus solubility for helium at 200°C in a number of glass systems in which D and S changes are due to incorporation of alkali elements. (16-13) Solubility was determined for the present glass by equilibrating a glass disc (no Cm doping) in 730 Torr helium at 400°C for four days. The sample was then cooled in the helium atmosphere before reheating in the mass spectrometer vacuum system. The isotherm (350°C) was continued until the helium release rate fell below the detection limit of the instrument, which occurred after three days of observation. By graphical integration of the release rate versus time curve, a solubility value of $S = 1.5 \times 10^{16}$ atoms/cm³ was obtained. As suggested in Figure 5, this result for the present glass may suggest a very steep dependence for log D/log S in borosilicate systems. Since both properties will be affected by "openness" of the glass structure, some correlation between D and S seems reasonable. The other glasses do show 'regular' trends with changing alkali content but with greati; differing slopes. As expected, the changes are in the direction of lower D and S values as the interstitial positions are filled. The borosilicate glass system⁽¹⁸⁾ had an activation energy for He diffusion increasing from 6.3 kcal/mole at 1.94 moles Na₂O to 10 kcal/mole at 13.4 mole% Na20. For a highly substituted nuclear waste glass, E_D . 10 kcal/mole might be expected. (We show later that $F_{0} = 15$ kcal/mole in the present waste glass system.)

The temperature dependence for solubility is much smaller and for (Na_20, SiO_2) , a trend with increasing Na_20 is not evident. ⁽¹⁶⁾ An energy value $E_S \sim 1$ kcal/mole is expected [S = $S_0 \exp(-E_S/RT)$]. More important to the waste problem is a recognition that Henry's law is obeyed for rare gas solution in lasses to quite high pressures. ^(19,20) Accordingly, S = kC_q where S is the gas con-



centration in the solid and C_g is the concentration in the gas phase. Using the measured solubility value in the present glass, the Henry's law constant is $k = 6 \times 10^{-4}$. This constant, although high by comparison to ionic crystals or metals, nevertheless establishes that under equilibrium conditions in the closed system described earlier, only 0.06% of helium generated will remain in solid solution. The other 99.94% of the gas must collect as internal gas bubbles or diffuse to the plenum. Consequences with respect to possible canister pressurization will be considered later.



FIGURE 5. Helium diffusivity and solubility at 200°C in common glass systems compared to the present glass.

Some preliminary measurements were made in constant heating rate experiments to establish the general features of the diffusion process. Six individual isotherms were also obtained at 200, 250, 300, 350, 400, and 450°C.

3.1 ISOTHERMAL EXPERIMENTS

The results of a series of consecutive isothermal experiments are shown in Figure 6, using the capacitance manometer to measure total gas pressure. Based on the calculated helium inventory and the system volume, full release would have given $\Delta P = 2.5 \times 10^{-2}$ Torr. If the form of any one of these curves 's compared to the theoretical release curves given in Figure 4, it is immediately clear that while the initial release rates are quite high, there is no single diffusion coefficient which can describe both the high initial rate and rapidly decreasing rate at longer times. Other experiments using the manometer technique gat much more gas than calculated, which we found to be primarily oxygen and water. For this reasen, the mass spectrometer was used to measure He concentrations directly, confirming this qualitative demonstration of trapping effects in more detail.

The quantitative isothermal results are given in Figures 7, 8, and 9 plotted as fractional release versus . At low release fractions, a linear dependence is expected (and observed), but as bas already been suggested, the long time data are less (in fractional release) than predicted by theory, given a constant D value. In Figure 7, the sample containing dissolved helium (equilibrated in 730 Torr He at 400°C for 4 days), can be fit reasonably well to a single diffusion coefficient (1.5 x 10⁻⁸ cm²/sec) over all release fractions. The curium doped sample (i.e., with radiction damage) requires a much smaller D value to fit long time data but gives good agreement with the damage-free sample up to F = 0.5. In Figure 8, good agreement for two runs (different samples) is shown at 350°C and a reasonable trend to more rapid release at higher temperatures is demonstrated for short time release. At the higher temperatures, neither the respective positions of the long time curves, nor their slopes (compare $\sqrt{t} = 60$, Figure 9), follow a regular trend. It can be concluded that the trap characteristics change with temperature, sir : Arrehnius behavior is not followed. The short time release in other radiation damaged systems (10,13) is often independent of





FIGURE 6. Consecutive isothermal He release on the capacitance manometer system.



FIGURE 7. Isothermal helium release comparing release at 350°C, with and without radiation damage.



10. 71





R ORIGIN



FIGURE 9.

9. Isotherms at 400 and 450°C plotted as fractional He release versus it trapping phenomena and reflects damage free, 'normal' diffusion. The experimental data for short times are plotted as log D versus 1/T in Figure 10 and do follow a linear relation. In agreement with constant heating rate results discussed later, a line with slope yielding E = 15 kcal/mole is obtained.



FIGURE 10. Short time diffusion coefficients plotted as log D versus 1/T.

3.2 CONSTANT HEATING RATE EXPERIMENTS

If we consider the instantaneous release rate for the diffusing helium as a function of temperature but at constant helium concentration, then $R = R_0 \exp(-E/RT)$ where E is the activation energy for diffusion, provided the release rate (R) is diffusion controlled. Experimentally, a \sim constant helium concentration was obtained by cooling the samples from the highest desired temperature at 100°C/hr, having first allowed an isothermal soak at the maximum temperature, to attain the desired helium inventory (F_S). Most of the data to be presented were obtained by cooling from within the release region where gas trapping is involved. In this case, the time required for a change in F_S of 0.01 was on the order of 6 hours, about the time involved for a complete cooling-heating cycle.

In Figure 11, results are shown (with cooling only) for four different samples with different fractional inventories and different absolute concentrations as well, both affecting position with respect to the release rate axis. Plotted as In R versus 1/T, the slopes of the lines should give E/R. The difference from sample to sample (compare 3 and 4) is greater than any apparent trend as a function of Fs. In order to observe a dependence with F_{g} , a single sample (1) was examined more carefully with complete cooling-heating cycles, as shown for $F_S = 0.70(1)$. A hysteresis effect of 10°C is seen at the 100°C/hr heating rate which we did not explore further but simply took the average value [(R_c + $R_{\rm H}$]/2] as representing the true steady-state value. These data are shown in Figure 12, giving excellent straight lines. The activation energy is plotted in Figure 13 as a function of Fs, showing only a small trend, especially since we place a low reliability on the high temperature point. Considering the sample to sample variations (Figure 11), the average of al! the constant heating rate runs is taken as the 'best' value, being E = 15 : 1kcal/mole.



FIGURE 11. Release rates versus 1/T(°K) for different samples (1-4) and inventories as indicated, obtained in constant heating rate experiments (100°C (hr).



FIGURE 12. Kelease rates plotted as lnR vs 1/T (°K) for a single sample with different helium inventories.



FIGURE 13. Activation energy values plotted as a function relative He inventory (Fg).



To examine the possibility of the variety of helium-defect complexes likely present, a release measurement was made on part of a disc first ground to fine powder (<40 um). A rapid heating rate (9°C/min) was used with the objective being as in a differential thermal analysis experiment--to resolve specific annealing/ release stages. As shown in Figure 14, with release rate plotted versus temperature, only a broad release peak was observed, compatible with the near featureless Differential Scanning Calorimetry (DSC) curves given by Roberts⁽⁵⁾ on the same glass, also curium doped at the 1 wt.% level. The DSC curves in the latter work do have a much less peaked form and fall to zero only near 600°C.

3.3 DISCUSSION

The major features of the diffusion process include a short time release (high Fc) not affected by trapping and following Arrehnius behavior, a long time release (lower Fc) in which trapping occurs, giving apparent low D values, and an apparent corunon activation energy for diffusion of 15 ±1 kcal/mole. This last point can be understood by reference to Figure 15. A radiation damaged sample is shown with trapped gas being released to the undamaged matrix with some rate constant k,. We interpret the isothermal release measurements given earlier as resulting from release of untrapped gas (k,) at short times, until the matrix is depleted of all but trapped gas. As this condition is approached, the constant k, becomes rate controlling with respect to absolute release rates from the surface. If, however, a relative experiment is conducted by which concentrations do not significantly change during the measurement, as in the present constant rate of heating experiments, then the temperature dependence will relate mainly to free gas diffusion as controlled by k2.

The release of trapped gas on an absolute scale should proceed with rate constants (i.e., activation energy and preexponential terms) which relate to annealing of defects. Since we did not obtain Arrehnius behavior in this release region, there



FIGURE 14. Helium release from powdered glass (<40 µm) plotted versus temperature and showing only a broad release peak.



FIGURE 15.

Schematic representative of diffusion process with transport controlled by rate constants k_2 (normal diffusion) and k_1 (release from traps).

is no way to estimate these constants, nor is it strictly valid to assume the 15 kcal/mole activation energy, since, as discussed above, this value relates to free gas diffusion. For the purpose of establishing order of magnitude, apparent diffusion coefficients, we have nevertheless assumed the 15 kcal/mole energy value for both untrapped (D_U) and trapped (D_T) gas diffusion to arrive at Arrehnius expressions

$$D_U = 2.1 \times 10^{-3} \exp(-15000/RT) cm^2/sec$$

and

 $D_{T} = 1.7 \times 10^{-4} \exp(-15000/RT) cm^2/sec.$

Calculated values based on these expressions are compared to the curve fitted isothermal values in Table III. The agreement for D_U is good in comparison to agreement for D_T , as expected.

	DIFFU	SION COEFFICIE	NTS (cm ² /sec)	
	D	U	D	
T(°C)	Calc	Exp	Calc	Exp
200	2.74×10^{-10}	2.7×10^{-10}	2.20×10^{-11}	
250	1.25×10^{-9}	1.4×10^{-9}	1.00×10^{-10}	1.6×10^{-10}
300	4.36 x 10^{-9}	6.0 x 10 ⁻⁹	3.49×10^{-10}	
350	1.25×10^{-8}	1.4×10^{-8}	1.00×10^{-9}	0.75 x 10 ⁻⁹
400	3.05×10^{-8}	1.5×10^{-8}	2.44×10^{-9}	1.5×10^{-10}
450	6.59×10^{-8}	3.5×10^{-8}	5.28 x 10 ⁻⁹	1.9×10^{-9}

TABLE III

For purposes of canister pressurization analysis, this work clearly demonstrates that use of D_U values will be conservative, since D_U/D_T is v10. Trapping at radiation induced defects will only serve to increase the margin of 'safety' if helium generation does even theoretically (i.e., assuming full release) become a potential problem. This question is considered in more detail in the following section.

3.4 CANISTER PRESSURIZATION

The results discussed in the preceding sections can be applied to conditions relevant to actual waste storage. If we assume a glass waste form with 30 wt.% fission products and providing a 10 vol.% plenum, then the maximum possible pressures arising from helium generation (assuming complete release) are given in Figure 16. The curves represent fuel waste processed 150 days out of reactor after a burnup of 33000 MWd/MT, considering both UO_2 and UO_2 -3.3%PuO_2 fuels. The curves are based on Origen Code⁽²¹⁾ runs provided by F. Roberts and in part reported in reference 5 as Figure 1a. For UO_2 wastes, several hundred years' storage will be required after 15 psi He pressures become theoretically possible, while $C = PuO_2$ enriched fuel waste reaches this level in a few years.

In solid forms, the rate of pressure buildup will generally be less than the theoretical maximum, depending on the waste form geometry and the diffusion coefficient. Using the expression given previously for untrapped gas diffusion, we will consider long time release ($T = 25^{\circ}C$, $D = 2.5 \times 10^{-14} \text{ cm}^2/\text{sec}$) and conditions representing short times (or a long time accident condition)--($T = 300^{\circ}C$, $D = 4.4 \times 10^{-9} \text{ cm}^2/\text{sec}$). For simplicity, we assume spherical geometry and that a monolithic form is a sphere of 15 cm radius (the cylindric form has a few large cracks). It seems likely however that waste glass will be thermally shocked. As a severe example we assume after Ross⁽²²⁾ a thermal shocked glass with a particle distribution as follows: 95.9%

22

radius = 1.25 cm, 4% r = 0.125 cm, 0.1% r = 0.0125 cm. In Figure 17 fractional release values are given for these particle sizes plotted as a furction of time for D = 2.5×10^{-14} cm²/sec (25°C). If we consider the expression given earlier for release from a sphere, it can be shown that the time required to reach some constant release fraction is directly proportional to the square of the radius. As shown in this figure, for example, spheres with radii 0.0125, 0.125, 1.25 cm require 10, 10^3 , 10^5 years respectively to reach F = 0.6.



FIGURE 16. Maximum helium pressures in canisters with a 10 vol.% plenum plotted as a function of time for UO2 and UO2-3.3%PuO2 fuel wastes.

In Figures 18 and 19 we show fractional release curves for monolithic and fractured glass at 25 and 300°C, respectively. The curves at 25°C are shown shaded in the direction of longer times to indicate the influence of t apping by radiation induced

defects. At 25°C, where most of the helium will be generated, more than 10³ years are needed to reach 10% release even for a badly fractured glass. In monolithic form, and considering lower D values arising from radiation damage trapping, 10⁶ years could be required to reach this release fraction. At 300°C (Figure 19), times are relatively short even for a monolithic waste, which yields 25% release in 10 years.



FIGURE 17. Fractional helium release plotted versus time for D = 2.5 x 10^{-14} cm²/sec and sphere radii as indicated.

It should be pointed out that all of these curves (Figures 17-19) consider only the times required for fractional release of some given constant concentration of helium. In real waste, the time dependence for He production must be considered. As a simplification in the conservative direction, we have calculated expected pressures assuming the helium inventory at a given time is constant at that level from time = 0. As an example, in UO₂ waste, the maximum He pressure possible at 10^6 years is 300 psi

24





Fractional release curves plotted versus time for monolithic and fractured glass at 25°C.



FIGURE 19. Fractional release curves plotted versus time for monolithic and fractured glass at 300°C.

POOR ORIGINAL

(Figure 16). For a monolith at 25°C and diffusion occurring without trapping, a fractional release of 20% will occur in 10^6 years (Figure 18). Hence a conservative estimate of pressurization is 0.2 x 300 = 60 psi. The curves given in Figures 20 and 21 were obtained in the same fashion and are conservative estimates for UO₂ and UO₂-3.3%PuO₂ waste glass canisters, respectively.



FIGURE 20. Estimated canister pressurization for UO2 fuel waste glass at 25 and 300°C, plotted versus time.

For CO₂ waste glass the importance of temperature is demonstrated in Figure 20. At 300°C, there is only a small difference between monolithic and fractured glass because the helium generation rate is limiting, and the curve for fractured glass is identical to the theoretical maximum pressurization curve given in Figure 16. At 25°C, the particle size is considerably

· ...

more important, with the times required to reach a given pressure differing by a factor of -50 for the fractured and monolithic forms. The influence or radiation damage will be to cause a further shift to longer times by a factor of 10 or more as shown by the shaded areas. There will be a smaller damage influence at elevated temperatures where only part of the release will be affected by trapping, as shown earlier. For UO_2 fuel wastes, assuming a fractured glass geometry, times on the order of 10^4 years will be required before the canister becomes helium pressurized.



FIGURE 21. Estimated canister pressurization for UO₂-3.3% PuO₂ fuel waste glass at 25 and 300°C, plotted versus time.

For the UO_2 -3.33PuO_2 wastes, the trends are similar as shown in Figure 21, but the much nigher a activity shifts the pressurization curves to lower times. Even if monolithic, 15 psi pressures will likely be exceeded in less than ten years, considering the

high storage temperatures during the first decade. If the canisters were vented after reaching the ambient temperature range (10^2 years), even fractured glass would not build back up to significant pressures until 10^3 years had elapsed.

From a technical viewpoint, the maximum pressurization curves given in Figure 16 might be compared in magnitude to everyday usage of compressed gas cylinders at >2000 psi, and water pressure 50-80 psi contained by thin walled copper tubing in every home. In this frame of reference, it is clear that helium pressurization will not be a serious technical concern for typical fuel wastes. The information in this document can be utilized for consideration of other storage needs which might arise if for example the actinides were partitioned from the waste stream for separate disposal or to calculate pressures in microencapsulated waste forms, etc. It is suggested that Henry's law be assumed (i.e., virtually no gas will remain in solution) and that 'normal' diffusion coefficients be utilized to generate conservative pressurization-time estimates in other glass systems.

3.5 OTHER HELIUM EFFECTS

The objective of the present work has been to experimentally establish the nature of helium diffusion in nuclear waste glass and to make some estimates concerning canister pressurization. A potential effect of helium ingrowth has not been examined; namely, whether or not helium bubbles are formed and whether or not stresses induced by ingrowing helium might result in extensive cracking. This question has been considered briefly by Newman and Quimby $^{(23)}$ and by Ross and Newman. $^{(24)}$ Their analysis assumes Henry's law holds and that the maximum internal stress generated in the glass is equivalent to the helium gas pressure which would be required to achieve the equivalent r-ingrown concentration. Depending on internal porosity concentration, stresses from a few hundred to several thousand lbs/in^2 were suggested as possible. The diffusion coefficients and Henry's law constant used in their analysis $^{(23,24)}$ were of the correct order of magnitude and the

actual values obtained in the present work would not significantly change conclusions arrived at by these authors. It is not clear, however, that the basic assumption made (that external equilibrium pressure is directly related to internal stress) is entirely valid.

POOR ORIGINAL

The use of kilobar pressures to dissolve large quantities of inert das by Faille and Roy (19) does not appear to produce an unstable, highly stressed glass. When heated, gas bubbles are nucleated (presumably containing high pressure das) but stress induced cracking was not reported. Work by A. K. De et al. (25) involving He⁺ bombardment of nuclear waste glass-ceramics also demonstrated bubble formation even at room temperature after 1016 ions/cm2 (50 keV He1). Because of the high implantation rate, the latter result may be a reflection of a thermal component in the bombardment process. In actual waste glass it is still possible that microbubbles may form since the helium is deposited as a high energy particle and localized thermal spikes will affect the entire glass volume many times over, even during the first 100 years. The present work, in demonstrating that only part of -ingrown helium is released via a simple atomic mechanism, could be interpreted as due to the influence of gas-bubble traps. Since the release measurements required thermal treatment however, they do not relate well to the real situation which will mainly consist of storage at ambient temperatures (see Figure 1). We conclude that there is not yet sufficient information to know whethe, or not helium microbubbles will form in nuclear waste glass.

Recardless of whether or not bubbles form, there is no experimental evider of that serious internal stresses arise in das containing classes obtained either by high pressure equilibration or through oparticle deneration by actinide decay. The curium doped discs used in the present work and a large number of surium doped glass buttons remain visibly unchanged after storage times equivalent to -500 years for actual waste. A preliminary mechanical strength test also supports the nonexistance of any internal stress buildup due to ordecay. Glass buttons approximately

3 cm diameter by 0.5 cm thick were fractured in a four point load cell, shown schematically in Figure 22. Ten nonradioactive buttons gave an average load-to-fracture value of 129 kg. Two curium doped buttons with an α dose equivalent to 500 years storage (1.17 x $10^{18} \alpha/\text{gram}$) fractured at loads of 143 kg and 119 kg. Although a more detailed examination of mechanical strength is just beginning, it is clear that a large effect due to a damage is not expected.



FIGURE 22. Schematic of four point load cell used for glass button fracture tests.

POUR ORIGIN

4.0 CONCLUSIONS

The major conclusions concerning helium effects in the present waste glass system are as follows:

- At short times and low fractional helium inventory, diff.sion follows Arrehnius behavior typical of undamaged, 'normal' glass as given by the equation $D_U = 2.1 \times 10^{-3} \exp(-15,000/RT)$ cm²/sec.
- At long times and higher fractional helium inventory, an Arrehnius temperature dependence is not observed due to the effects of trapping at radiation induced defects. The apparent diffusion coefficient is lower than at short times by about one order of magnitude and is approximated as $D_T =$ 1.7 x 10⁻⁴ exp(-15,000/RT)cm²/sec.
- A helium solubility value (730 Torr He, 400°C) was measured as S = 1.5 x 10¹⁶ atoms/cm³. As the temperature dependence for rare gas solubility in glasses is small and Henry's law is followed, it can be expected that 99⁴% of the helium generated in nuclear waste glass will not remain in solid solution but will diffuse to internal pores or to the manister plenum at rates depending on the diffusion coeffic:
- Assuming a canister with a 10 vol.% plenum, the mallerum possible helium pressures after 10^6 years fall in the range of common experience, being less than 1200 lbs/in² for $(UO_2-3.38PuO_2)$ fuel wastes. For UO_2 fuel wastes, even if the glass is not monolithic, pressures exceeding 15 lbs/in² will not likely be reached until times on the order of 10^4 years are reached.
- There is insufficient experimental evidence to ascertain whether or not helium bubbles will form at ambient temperatures. It does not appear likely however that helium generated through actinide decay will significantly affect the strength of waste glasses.

ACKNOWLEDGEMENT

J. E. Mendel provided the fracture data and Figure 22, and suggested a number of improvements in the manuscript, as also did Dr. T. D. Chikalla. R. W. Stephens provided careful technical assistance throughout the course of the work.

2 2

REFERENCES

- Proceedings of ENEA/IAEA Symposium on Management of Radioactive Waste From Fuel Reprocessing, Paris, December 1972.
- J. L. McElroy, (compiler) Quarterly Progress Reports, Research and Development Activities, Waste Fixation Program, Battelle, Pacific Northwest Laboratories, Richland, Washington 1973 and continuing.
- J. L. McElroy, The Expected Behavior of HLW Glass in Storage BNWL-SA-5581 (1975).
- J. E. Mendel, A Program Plan for Comprehensive Characterization of Solidified High-Level Wastes, BNWL-1940 (December 1975).
- R. P. Roberts, G.H. Jenks, and C. D. Bopp, <u>Radiation Effects</u> <u>In Solidified Hich-Level Waste</u>, Part I, Stored Energy, <u>BNWL-1944</u> (January 1976).
- 6. J. E. Merdel, W. A. Ross, F. P. Roberts, R. P. Turcotte, Y. B. Katayama, and J. H. Westsik, "Thermal and Radiation Effects on Borosilicate Waste Glasses," <u>Proceedings IAEA</u> Conference on the Management of Radioactive Wastes From The Nuclear Fuel Cycle, Vienna, March 1976.
- R. P. Turcotte, T. D. Chikalla, and L. Eyring, <u>Analyt. Chem.</u>, 43, 958 (1971)
- W. Jost, Diffusion in Solids, Liquids, Gases, Academic Press (1952)
- J. Crank, The Mathematics of Diffusion, Oxford University Press (1964).
- D. L. Morrison, T. S. Elleman, and D. N. Sunderman, J. Appl. Phys., 35, 1616 (1964).
- 11. T. S. Elleman, C. H. Fox, and L. D. Mears, <u>J. Nucl. Mat.</u>, <u>30</u>, 89 (1969).
- A. S. Ong and T. S. Elleman, Nucl. Inst. and Methods, 86, 117 (1970).
- 13: A. S. Ong and T. S. Elleman, J. Nucl. Matls, 42, 191 (1972).
- 14. R. Kelly and H. Matzke, J. Nucl. Matls., 20, 171 (1966).
- 15. R. Kelly and C. Jech, J. Nucl. Matls., 30, 122 (1969).
- 16. J. E. Shelby, J. Appl. Phys., 43, 3068 (1972).

- J. E. Shelby, <u>Gas Migration in Glass</u>, Sandia Laboratory Report SLL-75-5210 (March 1974).
- 18. V. C. Altemose, J. Amer. Cer. Soc., 56, 1 (1973).
- 19. S. P. Faille and D. M. Roy, J. Amer. Cer. Soc., 49, 638 (1966).
- 20. S. P. Faille and D. M. Roy, J. Amer. Cer. Soc., 56, 12 (1973).
- M. J. Bell, Origen--The ORNL Isotope Generation and Depletion Code, USAEC Report ORNL-4628 (May 1973).
- 22. W. A. Ross, Quarterly Progress Report, Research and Develop-Ment Activities, Waste Fixation Program, BNWL-1893, p. 35 (February 1975).
- D. F. Newman and D. C. Quimby, Quarterly Progress Report, Research and Development Activities, Waste Fixation Program, BNWL-1788, p. 35 (October 1973).
- 24. W. A. Ross and D. F. Newman, <u>Quarterly Progress Report</u>, <u>Research</u> <u>And Development Activities</u>, <u>Waste Fixation Program</u>, <u>BNWL-1809</u>, p. 48 (January 1974).
- 25. A. K. Dé, B. Luckscheiter, W. Lutze, G. Malow, and E. Schiewer, "Development of Glass Ceramics for the Incorporation of Fission Products," Paper presented at the 77th American Ceramic Society Meeting, May 1975.

