AIM

Association for Information and Image Management

1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910
301/587-8202

Centimeter

Inches

MANUFACTURED TO AIM STANDARDS
BY APPLIED IMAGE, INC.

1 of 1

Off-Gassing Induced Tracer Release from Molten Basalt Pools

**August W. Cronenberg^a
Richard A. Callow**

Published January 1994

**Idaho National Engineering Laboratory
EG&G Idaho, Inc.
Idaho Falls, Idaho 83415**

**Prepared for the
U.S. Department of Energy
Office of Environmental Restoration and Waste Management
Under DOE Idaho Operations Office
Contract DE-AC07-76ID01570**

a. Engineering Science and Analysis, 8015 Mountain Rd Place/#212, NE, Albuquerque, New Mexico, 87110.

MASTER
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED *875*

Off-Gassing Induced Tracer Release from Molten Basalt Pools

EGG-WTD-10942

Prepared by

A. W. Cronenberg, Consultant
Engineering Science & Analysis

Date

R. A. Callow, S&E Project Manager
Demonstration, Testing, and Evaluation

Date

Reviewed by

R. K. Farnsworth, Project Manager
Demonstration, Testing, and Evaluation

Date

Approved by

K. M. Kostelnik, Coordinator
Buried Waste Integrated Demonstration

Date

ABSTRACT

Two in situ vitrification (ISV) field tests were conducted at the Idaho National Engineering Laboratory (INEL) during the summer of 1990 to assess ISV suitability for long-term stabilization of buried waste that contains transuranic and other radionuclide contaminants. The ISV process uses electrical resistance heating to melt buried waste and soil in place, which upon cooldown and resolidification fixes the waste into a vitrified (glass-like) form. In these two ISV field tests, small quantities of rare-earth oxides (tracers Dy_2O_3 , Yb_2O_3 , and Tb_4O_7) were placed in the test pits to simulate the presence of plutonium oxides and assess plutonium retention/release behavior.

In the first intermediate field test (IFT-1), release of tracer material (ranging from about 1.2 wt% for Dy_2O_3 to ≈ 3.9 wt% for Tb_4O_7) occurred during soil melting and gas generation associated with the pyrolysis of buried organic waste components (e.g., wood, paper, and cloth and carbon monoxide gas) and steam release caused by dryout of the sludge. Little release, however, was noted in the second test (IFT-2) for which the off-gassing was greatly reduced.

The analysis presented in this report indicates that dissolution of tracer oxides into basaltic melts can be expected with subsequent tracer molecular or microparticle carry-off by escaping gas bubbles, which is similar to adsorptive bubble separation and ion flotation processes employed in the chemical industry to separate dilute heavy species from liquids under gas sparging conditions. Gaseous bubble escape from the melt surface and associated aerosolization is believed to be responsible for small quantities of tracer ejection from the melt surface to the cover hood and off-gas collection system. Methods of controlling off-gassing during ISV would be expected to improve the overall retention of such heavy oxide contaminants during melting/vitrification of buried waste.

SUMMARY

An in situ vitrification (ISV) testing program is being conducted at the Idaho National Engineering Laboratory (INEL) to assess ISV suitability for long-term stabilization of buried radioactive waste and contaminated soil. The process uses electrical resistance heating to melt contaminated soil or buried waste in place, which upon resolidification fixes the waste into a glass-like form. To assess process suitability and overall technical issues, two intermediate field tests (IFT 1 and 2) were conducted at the Idaho National Engineering Laboratory (INEL) during the summer of 1990. Both tests contained rare-earth oxides (tracers Dy_2O_3 , Yb_2O_3 , and Tb_4O_7) to simulate the presence of plutonium oxide contaminants. In IFT-1, release of tracer material (ranging from about 1.2 wt% for Dy_2O_3 to ≈ 3.9 wt% for Tb_4O_7) occurred during soil melting and associated off-gassing. Essentially no release was observed in the second experiment (IFT-2) for which off-gassing was greatly reduced. This report assesses gas generation and bubble rise phenomena that could explain differences in tracer release behavior.

The analysis presented indicates that dissolution of tracer oxides into basaltic melts can be expected. Subsequent tracer molecular or microparticle carry-off by escaping gas bubbles then occurs, similar to adsorptive bubble separation and ion flotation processes employed in the chemical industry to separate dilute heavy species from liquids under gas sparging conditions. Tracer absorption onto bubbles rising through the ISV melt is believed to have carried tracer material to the melt surface. Aerosolization of the surface melt (due to bubble escape) containing dilute quantities of tracer material is believed to be responsible for tracer release to the cover hood and off-gas collection system.

Although questions remain about the modeling assumptions and approximations used to estimate governing parameters, it is encouraging to note that estimates of tracer release were directly tied to testing conditions. The fractional concentration of tracer species in the melt was obtained from knowledge of tracer inventory conditions, while the rates of gas generation were estimated from the quantity and location of gas producing waste in the test pit. Because adsorptive bubble separation and ion flotation methods are well-established processes used to separate dilute heavy species from liquids under gas sparging conditions, it is reasonable to deduce that tracer release by such mechanisms may also be operable under ISV melt conditions. Specific testing for assessment of ISV off-gas induced release of heavy metal and oxide contaminants, therefore, is recommended. Methods of controlling off-gassing and adsorptive/flotation properties of contaminants during ISV melting would be expected to improve the overall retention of contaminant species within the vitrified waste.

CONTENTS

ABSTRACT	iii
SUMMARY	v
1. INTRODUCTION	1
2. REVIEW OF ISV TRACER RELEASE AND PREVIOUS ANALYSIS	3
2.1 Summary of Previous Analysis	3
2.2 Summary of Release Predictions for IFT-1 Conditions	8
3. MODEL DEVELOPMENT	11
3.1 Requirements for Adsorptive Bubble Separation	11
3.2 Aerosol Generation from Bubble Escape	12
3.2.1 Aerosol Volume per Bubble Burst (V_{aero})	13
3.2.2 Rate of Bubble Escape	15
3.2.3 Species Surface Concentration (C_{trac})	15
4. ESTIMATE OF TRACER RELEASE FOR IFT CONDITIONS	16
4.1 IFT-1 Tracer Release Estimates	16
4.2 IFT-2 Tracer Release Estimates	18
4.3 ORNL Tracer Findings	22
5. CONCLUSIONS AND RECOMMENDATIONS	25
5.1 Recommendations	25
6. REFERENCES	29
Appendix A—Description of IFT Conditions	A-1
Appendix B—Adsorptive Bubble Separation Methods	B-1
Appendix C—Aerosol Production by Bubble Bursting	C-1

FIGURES

1. Off-gassing during waste vitrification and attendant tracer release due to bubble escape and aerosolization at the melt surface	2
2. Waste configuration and tracer placement location in IFT-1 and 2	4
3. Potential mass transport modes for quiescent, dynamic, and gaseous melts	6
4. Evidence of bubble bursting at ISV melt surface	8
5. Tracer transport caused by adsorption onto rising bubbles	11
6. Gas bubble sparging through a liquid with aerosolization from bubble bursting at the liquid surface	13
7. Comparison of measured hood pressure and temperatures noted in IFT-1 and 2	20
8. Comparison of depth of soil melting, deduced from measurements of average electrode depth	21
9. Comparison of ORNL measure off-gassing flow rates and timing of ¹³⁷ Cs release (in counts per cubic foot, based on measured activity in off-gas collection hood) ..	24
10. Schematic of ISV-drum laboratory test configuration for characterization of off-gassing and tracer release	26
11. Schematic of ISV-drum laboratory test configuration for characterization of off-gassing and tracer release	28

TABLES

1. Waste inventory in the IFT-1 and 2 experiments	5
2. IFT-1 tracer release data	5
3. Mass transport predictions for IFT-1 conditions	10
4. Summary of IFT-1 conditions used to estimate tracer release	16
5. IFT-1 tracer release data	16
6. IFT-2 dysprosium release data	18
7. Comparison of ISV melting rates during melt exposure of tracer materials	22

Off-Gassing Induced Tracer Release from Molten Basalt Pools

1. INTRODUCTION

As part of U.S. Department of Energy (DOE) mandated efforts at remediation of buried radioactive waste at DOE operated sites, the Idaho National Engineering Laboratory (INEL) is conducting a testing and feasibility program to assess the suitability of *in situ* and *ex situ* thermal treatment technologies for stabilization of transuranic (TRU) waste and contaminated soils.^{1,2} The process involves heating and melting waste and soils that upon resolidification fixes waste contaminants into a stable vitrified (glass-like) form. *In situ* vitrification (ISV) uses electrical resistance heating to melt contaminated soil or buried waste in place, while *ex situ* processing requires retrieval of waste with subsequent thermal processing within a dedicated melter facility. In both cases, the desirable behavior for TRU and other contaminants is immobility during melting, so that complete contaminant retention occurs within the recrystallized glass-like product. However, organic waste components (e.g., paper, cloth, wood, and cutting oils) are generally present that are pyrolyzed at soil/waste melt temperatures ($>1,400^{\circ}\text{C}$), resulting in formation of gaseous byproducts (CO and steam) that migrate through and are released from the melt. Such off-gassing and bubble rise through the melt can enhance the migration of TRU and other heavy-metals in the melt, with the potential for their partial release from the melt surface.

Evidence for partial contaminant escape has been noted in several INEL-ISV intermediate field tests (IFT),³ where small quantities of rare-earth oxides (tracers Dy_2O_3 , Yb_2O_3 , and Tb_4O_7) were placed in the test pits to simulate the presence of PuO_2 . In IFT-1, nearly 4% tracer release occurred during soil melting and associated off-gassing, while little release was noted in IFT-2 for which off-gassing was greatly reduced. In a previous report,⁴ qualitative assessment of the test data indicated tracer release tied to off-gassing and bubble rise through the melt,^{4,5} so that further investigation of off-gas induced contaminant transport and release was initiated.

A review of the INEL-IFT data on tracer release and previous analysis indicating release tied to off-gassing is summarized in Section 2. Section 3 presents a descriptive model of tracer (and TRU) release due to bubbly flow through basaltic melts. The model assumes dissolution of heavy metal oxides (e.g., plutonium and rare-earths) into basaltic melts on a molecular and/or microparticle scale, with subsequent release of heavy metal contaminants from the melt surface due to aerosolization effects caused by the bursting and escape of gas bubbles,^{6,7} as illustrated in Figure 1. Such a process is similar to adsorptive bubble separation and ion flotation processes^{8,9} employed in the chemical industry to separate dilute heavy species from liquids under gas sparging conditions. The models are exercised in Section 4, where predictions are made of gas and tracer release for the IFT-1 and 2 conditions. Conclusions and suggestions for further research are summarized in Section 5.

Figure 1. Off-gassing during waste vitrification and attendant tracer release due to bubble escape and aerosolization at the melt surface.

2. REVIEW OF ISV TRACER RELEASE AND PREVIOUS ANALYSIS

During the summer of 1990, two IFTs were conducted^{3,10} using rare-earth oxides (Dy_2O_3 , Yb_2O_3 , and Tb_4O_7) to simulate TRU (PuO_2) behavior during soil melting. In IFT-1, all three rare-earth tracers were added to the test pit, while in IFT-2, only Dy_2O_3 was used to simulate PuO_2 behavior. In IFT-1, release of tracer material (ranging from about 1.2 wt% for Dy_2O_3 to ≈ 3.9 wt% for Tb_4O_7) occurred during soil melting and associated off-gassing, while essentially no release was observed for IFT-2 where off-gassing was greatly reduced.

Figure 2 illustrates the relative positioning of waste and tracers used in the IFT-1 and 2 experiments. Pertinent inventory information is provided in Table 1 (see also Appendix A), where it is noted that IFT-2 contained about twice the inventory of Dy_2O_3 (but no Tb_4O_7 or Yb_2O_3) than in IFT-1. After testing, the amounts of tracers were measured in retrieved samples of vitrified soil and at various locations within the collection hood, off-gas piping surfaces, scrub solution, and high efficiency particulate air (HEPA) filters (collectively referred to as the off-gas collection system). Although quantitative determination of tracer amounts was hampered by sampling uncertainties, results indicated that the majority of the tracers were retained in vitrified product. Nevertheless, as indicated in Table 2, release of tracer material was found within the off-gas collection system for IFT-1.

Although the IFT-2 contained about twice the inventory of Dy_2O_3 compared to IFT-1 (the total tracer inventory in IFT-1 was 4,004 g versus 2,282 g for IFT-2), essentially no dysprosium was found in the IFT-2 off-gas collection system. Also, although IFT-2 contained potentially more volatile waste than IFT-1, hood temperature and vacuum pressure measurements indicated a greatly reduced gas release process in IFT-2 than for IFT-1, which suggests that the more dynamic off-gassing process for IFT-1 may have been responsible for enhanced tracer release noted in that experiment. Scoping analysis of the off-gassing effects on tracer transport was initiated^{4,5} and the results are summarized in the following section.

2.1 Summary of Previous Analysis

In References 4 and 5, an order-of-magnitude assessment of the IFT-1 tracer release data was approached from consideration of the fundamental equation for mass transport from a liquid pool, which can be expressed by the equation:

$$m_{rel} = k_m A (C_{bulk} - C_{surface}) \quad (1)$$

where

A = surface area for release (cm^2)

C_{bulk} = bulk concentration of species in the melt (g/cm^3)

$C_{surface}$ = concentration at the melt surface (g/cm^3)

Figure 2. Waste configuration and tracer placement location in IFT-1 and 2.

Table 1. Waste inventory in the IFT-1 and 2 experiments.

Material	Inventories	
	IFT-1	IFT-2
Waste materials		
Combustible	666 lb	1,514 lb
Water	478 lb	1,035 lb
FLOOR-DRI	43 lb	94 lb
MICRO-CELL	143 lb	308 lb
Metal	2,473 lb	6,758 lb
Glass	485 lb	237 lb
Concrete	867 lb	600 lb
Tracers		
Dy ₂ O ₃	1.336 kg	2.282 kg
Tb ₄ O ₇	1.337 kg	—
Yb ₂ O ₃	1.331 kg	—
Tracers (total)	4.004 kg	2.282 kg
Soil		
Soil fill	54,630 lb	49,963 lb
Soil overburden	2 ft	4 ft

Table 2. IFT-1 tracer release data.

Oxide inventory	Rare earth	Hood/duct deposits	HEPA deposits	Maximum release fraction
Dy ₂ O ₃ = 1,336 g	Dy = 1,164 g	4.7–6.2 g	7.5 g	0.012
Tb ₄ O ₇ = 1,337 g	Tb = 1,137 g	28–29.9 g	14.0 g	0.039
Yb ₂ O ₃ = <u>1,331 g</u>	Yb = <u>1,169 g</u>	11–12.3 g	17.5 g	<u>0.025</u>
Total = 4,004	= 3,473 g			Average = 0.025

m_{rel} = rate of mass released from free surface (g/s).

In the above expression, k_m is the generalized mass transport coefficient (cm/s), estimated for the three mechanisms illustrated in Figure 3 (i.e., diffusion from a stagnant pool, mass transfer due to thermally induced convective currents, and mass transport due to bubble escape). Scoping calculations were presented^{4,5} to identify which mechanism would be predominant for ISV melt environments and the results are summarized below.

For quiescent liquids, molecular diffusion occurs because of concentration gradients, where the mass transport coefficient for diffusion ($k_{m,diff}$) and the associated release time constant (t_{diff}) can be approximated as

$$k_{m,diff} = \pi D/R_p \quad t_{diff} = R_p/k_{m,diff} \quad (2)$$

where

D = molecular diffusivity of tracer (cm^2/s)

R_p = pool depth (cm).

Free convection was assessed assuming that thermal gradients exist in the ISV melt, where the following convection mass transfer coefficient ($k_{m,conv}$) and associated time constant (t_{conv}) were employed:

$$k_{m,conv} = 0.36(D/R_p)Ra^{0.23}(Sc/Pr)^{0.23} \quad t_{conv} = R_p/k_{m,conv} \quad (3)$$

Figure 3. Potential mass transport modes for quiescent, dynamic, and gaseous melts.

where

- Ra = Rayleigh number ($g\beta Q\lambda R_p^5/\alpha\lambda\mu_k$)
- Sc = Schmidt number (μ_k/D)
- Pr = Prandtl number (μ_k/α)
- R_p = pool depth (cm)
- g = gravity constant (cm/s^2)
- β = thermal expansion coefficient (K^{-1})
- Q = volumetric heat source (W/cm^3)
- α = thermal diffusivity (cm^2/s)
- μ_k = kinematic viscosity (cm^2/s)
- λ = thermal conductivity (W/cm-K).

The generation of pyrolysis gases causes bubble rise through the melt that can capture and transport tracer species in the process. The limiting or maximum mass transport coefficient for bubble rise ($k_{m,bubb}$) was estimated from the terminal bubble velocity ($V_{t,bubb}$):

$$k_{m,bubb} \approx V_{t,bubb} = 2(R_b^2)\rho_L g/9\mu \quad t_{br} = R_p/k_{m,bubb} \quad (4)$$

where

- R_b = bubble radius (cm)
- ρ_L = melt density (g/cm^3)
- t_{br} = characteristic bubble rise time (s)
- μ = melt viscosity (g/s-cm).

The other parameters are as previously defined.

Characteristic release times (t_{diff} , t_{conv} , t_{br}) were estimated in Reference 5, indicating diffusion and convection times that are much slower than transport times associated with gas bubble rise through the melt. Thus, it was concluded that tracer release by carry-off with escaping pyrolysis gas bubbles shown in Figure 4 would be the dominant release mechanism for ISV melt conditions. Therefore, a more detailed investigation of this process was performed^{4,5} for the IFT-1 conditions.

Figure 4. Evidence of bubble bursting at ISV melt surface.

2.2 Summary of Release Predictions for IFT-1 Conditions

An order-of-magnitude estimate of the IFT-1 tracer release data was approached by making use of empirically based mass transport correlations from bubble rise. The overall mass transport coefficient (k_m) was obtained from the following expression for the Sherwood number (Sh) associated with spherical bubble rise through liquids:

$$k_m = Sh(D)/d_b \quad (5)$$

where d_b is the characteristic bubble diameter, and Sh is found from the following correlation suggested in the literature:¹¹

$$Sh = 0.65 Pe^{1/2} \quad \text{for } Re < 10 \quad (6)$$

where

Re = bubble Reynolds number ($V_b \rho_L d_b / \mu$)

Pe = bubble Peclet number ($V_b d_b / D$)

$Sh =$ Sherwood number ($k_m d_b / D$)

$V_b =$ terminal bubble velocity ($V_{t,bubb}$) as given above.

Calculational results are summarized in Table 3 for the IFT-1 conditions. Using bubble diameter of $d_b = 1$ to $4 \text{ cm}^{4,5}$ and tracer diffusivities of $D = 0.1$ to $0.5 \times 10^{-6} \text{ cm}^2/\text{s}$, release fractions of 4.5 to 20% are indicated, where the lowest value (4.5%) compares favorably with the IFT-1 tracer release data of 3.9%. The 4.5% prediction is associated with the lower limit of bubble size ($d_b = 1 \text{ cm}$) and diffusivities of $0.10 \times 10^{-6} \text{ cm}^2/\text{s}$. Because these values appear physically realistic, favorable comparison between theory and the IFT-1 data is apparent from an order-of-magnitude perspective. Because the thermochemical and transport properties of PuO_2 would be similar to that of the rare-earth oxides⁵ used in the IFT, similar release of PuO_2 is indicated for dynamic off-gassing conditions as occurred for the tracers. It was also noted in References 4 and 5 that although IFT-2 contained potentially more volatile waste than IFT-1, the actual extent of gas release in IFT-2 was less than in IFT-1. Thus, the tracer release data and supporting scoping analysis indicate that tracer release is tied to off-gassing phenomena.

Although the analysis described above yields order-of-magnitude estimates of tracer for the IFT-1 conditions, the analysis is deficient in that release of entrained species depend on adequate modeling of the following effects:

- Actual off-gas mass flow rates associated with bubbly flow through the melt
- Nature of bubble escape from the melt and associated aerosolization characteristics of the ejected melt due to bubble escape
- Concentration of dissolved tracer species in the ejected aerosolized melt
- Fraction of aerosolized melt that remains entrained within the hood space above the melt.

These phenomena are examined in the remainder of this report and models are developed for quantification of such effects.

Table 3. Mass transport predictions for IFT-1 conditions.

IFT-1 conditions		Value	
Melt surface area (A)		$\approx (10 \times 10\text{-ft}) = 9.29\text{E}+4 \text{ cm}^2$	
Bulk concentration (C_{bulk})		$= (3,473 \text{ g})/(1.67\text{E}+7 \text{ cm}^3) = 2.08 \text{ E-4 g/cm}^3$	
Melt time (t_{melt})		$= 17.5 \text{ h} = 6.300 \text{ E}+4 \text{ s}$	
Melt density (ρ_L)		$= 2.2 \text{ g/cm}^3$	
Melt viscosity (μ)		$= 300 \text{ g/s-cm}$	
Gravitation constant (g)		$= 980 \text{ cm/s}^2$	

Bubble velocity and Reynolds and Peclet numbers				
$V_b = 2\rho_L g/9\mu$		$Re = V_b \rho_L d_b/\mu$		$Pe = V_b d_b/D$
$d_b, \text{ cm}$	$V_b, \text{ cm/s}$	Re	$Pe(D=0.5\text{E-6 cm}^2/\text{s})$	$Pe(D=0.1\text{E-6 cm}^2/\text{s})$
1.0	0.40	0.003	8.0 E+5	4.0 E+6
4.0	6.39	0.187	5.1 E+7	2.6 E+8

Sherwood number, mass transfer coefficient, and release rate						
$Sh = 0.65Pe^{1/2}$		$k_m (\text{cm/s}) = Sh(D)/d_b$		$m_{\text{rel}}(\text{g/s}) = k_m A(C_{\text{bulk}})$		
$d_b, \text{ cm}$	$D = 0.5 \text{ E-6 cm}^2/\text{s}$			$D = 0.1 \text{ E-6 cm}^2/\text{s}$		
	Sh	k_m	m_{rel}	Sh	$k_m, \text{ cm/s}$	m_{rel}
1.0	581	2.90 E-4	0.0056	1,300	1.30 E-4	0.0025
4.0	4647	5.81 E-4	0.0112	10,400	2.60 E-4	0.0050

Total mass and fractional release estimates				
$M_{\text{rel}}(\text{g}) = m_{\text{rel}}(t_{\text{melt}})$		$RF = M_{\text{rel}}/(3473 \text{ g})$		
$d_b, \text{ cm}$	$D = 0.5 \text{ E-6 cm}^2/\text{s}$		$D = 0.1 \text{ E-6 cm}^2/\text{s}$	
	$M_{\text{rel}}, \text{ g}$	RF	$M_{\text{rel}}, \text{ g}$	RF
1.0	353	0.10	158	0.045
4.0	707	0.20	315	0.091

3. MODEL DEVELOPMENT

Although order-of-magnitude analysis indicates tracer release tied to off-gassing, detailed assessment of the IFT-1 conditions and tracer deposits found in the off-gas collection system (hood, pipe surfaces, and scrub solution) requires adequate modeling of governing processes and consideration of actual test conditions. For example, knowledge is required concerning the adsorptive nature of the bubble surface and its ability to transport molecules or microparticles of tracer material through the melt. In addition, the amount of tracer deposited on the collection hood and associated piping will depend on the nature of bubble escape from the melt surface and the aerosolization characteristics of the ejected melt associated with such bubble escape, for which models must be developed if tracer deposition data are to be more accurately predicted. Likewise, estimation or measurement of test off-gas flow rates is required for benchmarking model predictions of tracer release with actual test data. Consideration of these factors and development of quantitative models for their prediction are presented in this section.

3.1 Requirements for Adsorptive Bubble Separation

During the vitrification and melting of buried wastes organic, components are pyrolyzed, resulting in formation of gaseous byproducts (primarily CO and steam) that migrate as bubbles (see Figure 4) or vapor streams through the melt and are released at the melt surface. Such off-gassing and bubble rise through the melt is considered the primary cause for tracer migration to the melt surface, whereby it is believed that small quantities of tracer material or TRU attach themselves to the bubble surface and rise with it, as illustrated in Figure 5. A parallel process in the chemical industry is adsorptive bubble separation,^{8,9} where dilute species separation from liquids occurs as a consequence of adsorption of such species onto the surface of bubbles rising through a liquid. Such separation can involve either charged ions, neutral molecules, or microparticles.

The primary condition required for adsorptive bubble separation⁸ to be operative is the breakdown or dissolution of dilute heavy species into individual molecules or microparticles, so that

Figure 5. Tracer transport due to adsorption onto rising bubbles.

carry-off by the less dense gas bubble is possible. As discussed in Reference 12, solubility data indicate that the rare-earth oxides (Dy_2O_3 , Tb_4O_7 , and Yb_2O_3) and PuO_2 would dissolve to at least 1.0 wt% in SiO_2 -based basalt melts. In general, TRU contamination in buried waste is much less than 1 wt%. Likewise, because the tracer composition within the IFT-1 and 2 test pits was much less than the 1 wt% solubility limit, and because these tracers (Dy_2O_3 , Tb_4O_7 , and Yb_2O_3) were added to the test pit in powder form, it is reasonable to assume that they dissolved in the ISV melt on a molecular or microparticle scale. Thus, the primary requirement for tracer molecular dissolution (or breakdown into microparticles) is satisfied for rare-earth oxides in basaltic melt. Although other factors impact the overall efficiency of the adsorptive bubble separation process (see Appendix B) (e.g., gas sparging rates, species concentration levels and ionic strength and bubble surface area), such factors are of secondary importance compared to the necessary requirement that breakdown of a dilute heavy species into microparticles or dissolution occurs.

3.2 Aerosol Generation from Bubble Escape

In addition to satisfying necessary criteria for tracer (or TRU) adsorption onto the bubble surface, the amount of tracer released from the melt will depend on the vigor of bubble escape and the aerosolization characteristics of the ejected melt. Appendix C and References 6, 7, 13, and 14 present a review of aerosol generation by the bursting bubbles, indicating that the amount of aerosol produced is related to accelerations experienced by the liquid film defining the bubble cap, as depicted in Figure 6.

Based on the assumption that the amount of aerosol produced is proportional to the liquid film cap of the bubble that protrudes above the ISV melt surface, an estimate of the contaminant or tracer release rate (m'_{trac}) from the melt surface can be expressed by the generalized equation:

$$m'_{\text{trac}} = m'_{\text{aero}} C_{\text{trac}} \quad (7)$$

where C_{trac} is the concentration mass fraction of contaminant or tracer near the liquid surface (g-contaminant/g-melt), and m'_{aero} is the mass rate of aerosol generation caused by bubble bursting at the melt surface. The mass rate of aerosol generation (m'_{aero}) can be expected to be related by some proportionality to the rate of bubble release from the melt, which can be expressed as

$$m'_{\text{aero}}(\text{g/s}) = V_{\text{aero}} \rho_L n'_b \quad (8)$$

where

V_{aero} = volume of aerosol droplet per bubble burst ($\text{cm}^3/\text{bubble}$)

ρ_L = density of the melt that is aerosolized (g/cm^3)

Figure 6. Gas bubble sparging through a liquid with aerosolization from bubble bursting at the liquid surface.

$$N'_b = \text{number of bubbles released per second from melt surface (bubbles/s).}$$

To estimate the aerosol generation rate (m'_{aero}) and the attendant mass rate of contaminant release (m'_{trac}) from the melt using the above expressions, methods must be developed to estimate the volume of aerosol droplet produced per bubble burst (V_{aero}), concentration of the contaminant (C_{trac}) in the melt film cap that is aerosolized, and rate of bubble escape from the melt surface (N'_b) caused by release of the pyrolysis gases (CO and steam). Models for estimation of these terms are developed in the following sections.

3.2.1 Aerosol Volume per Bubble Burst (V_{aero})

As discussed in Appendix C, an upper limit on the volume of aerosol droplet produced per bubble burst (V_{aero}) can be estimated by assuming that the entire volume enclosed within the liquid

film cap, just before bubble bursting, is converted into aerosolized droplets. For this assumption, the ratio of the aerosolized droplet to bubble volume (V_{aero}/V_b) can be approximated as

$$\frac{V_{aero}}{V_b} = \frac{6A_f\delta}{\pi D_b^3} \quad (9)$$

where

V_b = bubble volume

δ = thickness of the film cap

D_b = bubble diameter

and A_f is the effective surface area of the film cap at bursting, which can be approximated as:^{15,16}

$$A_f = (\pi/6) [D_b - 0.08a]^3 \quad (10)$$

where

$$a = \left[\frac{2\sigma}{(\rho_L - \rho_g)g} \right]^{1/2} \quad (11)$$

where

ρ_L = melt density (g/cm^3)

ρ_g = density of gas (g/cm^3)

g = gravitation constant (980 cm/s^2)

σ (dy/cm) = melt surface tension.

For small values of a , the ratio V_{aero}/V_b is of the same order of magnitude as the film cap thickness at rupture (δ , where δ has the units of centimeters). As indicated in Appendix C, for the bubbly flow regime, observations of the film cap thickness (δ) at rupture range from 10^{-5} to 10^{-3} cm,^{16,17} where the majority of empirical evidence^{7,17,18} indicates a film rupture thickness on the order of $\approx 10^{-4}$ cm. Thus, an average value of V_{aero} is estimated as

$$V_{aero,ave} = (10^{-4}) \left[V_b = \frac{\pi D_b^3}{6} \right] \quad (12)$$

3.2.2 Rate of Bubble Escape (N'_b)

The rate of gas bubble sparging can be estimated from test conditions, assuming all combustible gases and water vapor escape in the form of bubbles sparged through the ISV melt. Under this assumption, the rate of bubble escape can be estimated as

$$N'_b \text{ (bubbles/s)} = \frac{R_{gas} \text{ (cm}^3\text{/s)}}{V_b \text{ (cm}^3\text{/bubble)}} \quad (13)$$

where R_{gas} is the rate of gas generation (CO and steam) during ISV pyrolysis and V_b is the average bubble volume.

Combining Equations 8, 12, and 13, the mass rate of aerosol generation (m'_{aero}) can be expressed as

$$m'_{aero,ave} \text{ (g/s)} = V_{aero,ave} \rho_L N'_b = (10^{-4}) \rho_L R_{gas} \quad (14)$$

3.2.3 Species Surface Concentration (C_{trac})

For present purposes, the tracer concentration (C_{trac}) at the bubble surface can be assumed to be similar to the average tracer concentration in the melt (C_{bulk}), which can be estimated from the tracer inventory and the average melt depth during exposure of the tracer material to melting conditions. Making use of the above expressions, an estimate of the rate and total mass release of tracer material is presented in the following section for the IFT conditions.

4. ESTIMATE OF TRACER RELEASE FOR IFT CONDITIONS

An estimate of tracer release from the melt surface can be obtained by multiplying Equation 14 by the tracer concentrations in the melt (C_{trac}) and the average melt time (t_{melt}) over which gas sparging would have induced such a release; thus the total release (M_{trac}) can be determined from the following expression:

$$M_{\text{trac}} (\text{g}) = V_{\text{aero,ave}} \rho_L N'_b \cdot C_{\text{trac}} t_{\text{melt}} = (10^{-4}) \rho_L R_{\text{gas}} C_{\text{trac}} t_{\text{melt}} \quad (15)$$

where the parameters are as previously defined. Estimates for the IFT-1 and 2 conditions are presented below.

4.1 IFT-1 Tracer Release Estimates

Values for R_{gas} , C_{trac} , and t_{melt} are estimated in Appendix A and summarized in Table 4 for the IFT-1 conditions, based on the assumption that individual tracer release occurs during the time period when ISV melting reached the respective waste layers in which each tracer was placed. Using these values and $\rho_L \approx 2.2 \text{ g/cm}^3$, calculational results for tracer release fractions are presented in Table 5 and compared with the IFT-1 release data.

Table 5 compares actual and predicted release fractions for the three tracers. As indicated, the predictions compare favorably with the IFT-1 rare-earth release data, indicating that off-gassing and bubble fractation could well have been responsible for the release of small quantities (1 to 4%) of plutonium oxide simulants (Dy_2O_3 , Tb_4O_7 , and Yb_2O_3) during ISV melting. It is particularly encouraging that such calculational success is tied to estimates of pyrolysis gas and steam release from the melt, based on known combustible and water inventories within the IFT-1 test pit.

Table 4. Summary of IFT-1 conditions used to estimate tracer release.

Layer	Tracer	t_{melt}	C_{trac}	R_{gas}
1	Dy	18,000 s	1.32 E-4	4.65 E+4 cm ³ /s
2	Tb, Yb	9,000 s	1.74 E-4	12.17 E+4 cm ³ /s

Table 5. IFT-1 tracer release data.

Layer	IFT-1 release data		Model predictions	
	Tracer inventory	Release fraction	Amount	Release fraction
1	Dy=1,164 g	0.010–0.012	24.3 g	0.021
2	Tb=1,137 g	0.037–0.039	41.9 g	0.037
2	Yb=1,169 g	0.024–0.025	41.9 g	0.036

Although release predictions compare favorably with the test data, some of the nuances concerning modeling assumptions should be recognized. The underlying hypothesis for tracer release is that it occurs as a consequence of molecular or microparticle carry-off by escaping gas bubbles. Clear evidence for bubble escape from the ISV melt is illustrated in Figure 4, which is from a video taken at the ISV melt surface, indicating continuous gas release in the form of bubbles bursting at the melt surface. Thus, the assumption of tracer release due to carry-off by escaping gas bubbles is reasonable.

With respect to the assumption that flotation of tracer material to the melt surface occurs as molecules or microparticles attached to such bubbles, similar to the bubble fractionation (also called adsorptive bubble separation) process described in References 8 and 9, it would be necessary that the tracer material be dissolved in the melt on either a molecular scale or as microparticles. Estimates (see Appendix A) indicate bulk tracer concentrations on the order of ≈ 0.01 to 0.02 wt% for IFT-1 conditions, while solubility data indicate that the rare-earth oxides (Dy_2O_3 , Tb_4O_7 , and Yb_2O_3) and PuO_2 would dissolve to at least 1.0 wt% in basaltic melts.¹² Because IFT-1 tracer concentrations are well below solubility limits and the tracers were added to the test pit in powder form, molecular solution or microparticle suspension for rare-earth oxides (and PuO_2) appears justified. Thus, the assumption of tracer carry-off by absorption onto escaping gas bubbles, analogous to bubble fractionation or adsorptive bubble separation methods in the chemical industry,^{8,9} is reasonable.

Important parameters impacting calculational results are the fractional concentration of tracer species in the melt (C_{trac}), assumptions regarding the rates of gas release during melting/tracer release (R_{gas}), and the melt time over which tracer release occurs (t_{melt}).

Estimates of C_{trac} were based on known tracer inventory conditions and the assumption that the tracer is distributed evenly within a rectangular melt pool (i.e., from the melt surface to original tracer burial location). Somewhat different geometric conditions impacting C_{trac} might equally apply, where the assumption of pool consolidation of ≈ 50 vol% on melting and subsidence is considered approximate, as is the assumption of rectangular geometry. A smaller pool size and hemispherical geometry would increase estimates of C_{trac} at the same tracer inventory conditions. However, tracer diffusional and convective migration would likewise impact the manner in which tracer material is distributed within the melt, where partial migration to outside the melt boundary would be expected and thus reduce somewhat tracer concentration estimates. Migration effects thus tend to counter geometric simplifications. Uncertainties regarding tracer concentration (C_{trac}) estimates can only be resolved through deliberate efforts at controlling tracer dispersion within the melt. For order-of-magnitude assessment of tracer release, the simplifying assumption used here regarding C_{trac} appears reasonable.

The volumetric gas release rate (R_{gas}) was estimated from known inventories of organic (e.g., paper, wood, and cloth) and aqueous-based (e.g., sludge and concrete) materials contained within each layer of the test pit. The melt time (t_{melt}) for each layer was based on the time period over which gases were released from the pyrolysis of organics and sludge dryout for that particular layer. It is also assumed that tracer release occurs during the time it takes the ISV melt front to pass through the particular waste layer in which a specific tracer was located. Steam generation associated with soil moisture was ignored, because it is believed that such moisture was released early in the ISV melting transient, before the tracer material (contained within the waste drums) was subjected to ISV melting.

Gas sparging through the melt occurs during ISV processing of wastes located at deeper burial positions, so that gas bubbles rising from lower depths can also carry tracer material to the melt surface. However, this effect is counteracted by the visual observation of vapor and gas migration to the peripheral sides of the melt pool,³ where such gases would not be available for sweeping of tracer material through the melt pool. The assumption that all gaseous material (associated with the waste layer in which tracer material was buried) is released through the ISV melt pool and available for tracer carry-off, tends to offset the potential contribution of gas generation from lower layers. For these reasons, the simplifying assumption is made that only the gaseous waste within the same layer that tracer materials exist, contributes to tracer transport. Accurate estimates of the volumetric gas sparging rates through the ISV melt require dedicated off-gassing measurements, which are not within the charter of the IFT experiments.

4.2 IFT-2 Tracer Release Estimates

Based on a similar assumption used in estimating R_{gas} , C_{trac} , and t_{melt} for IFT-1; calculational results for dysprosium release are presented in Table 6 for IFT-2. Model predictions indicate an IFT-2 dysprosium release fraction of 0.027. Post-test hood/piping smear analysis and off-gas HEPA filter and scrub tank data indicate no significant differences between pretest and post-test dysprosium concentrations. Thus, test findings indicate no dysprosium release for the IFT-2,⁶ while model predictions indicate 2.7% release. The salient question is why dysprosium release was not measured for the IFT-2 experiment, while model predictions clearly indicate flotation of dysprosium due to bubble rise through the melt.

One noteworthy factor is that although IFT-2 contained potentially more volatile waste than IFT-1, the actual amount of released gas during the conduct of IFT-2 was less than in IFT-1.

Table 6. IFT-2 dysprosium release data.

Governing equation			
$M_{\text{trac}} (\text{g}) = (10^{-4}) \rho_L R_{\text{gas}} C_{\text{trac}} t_{\text{melt}}$			
Parameter values			
$t_{\text{melt}} =$	50,400 s	$R_{\text{gas}} =$	3.73 E+4 cm ³ /s
$C_{\text{trac}} =$	1.28 E-4	$\rho_L =$	2.2 g/cm ³
Calculation			
<u>IFT-2 release data</u>		<u>Model predictions</u>	
<u>Dysprosium Inventory</u>	<u>Release fraction</u>	<u>Amount released</u>	<u>Release fraction</u>
1,988 g	0.00	52.9 g	0.027

Although direct measurements of off-gassing are not available, qualitative estimates of gas release can be deduced from Figure 7, where a comparison of hood temperature and vacuum pressure measurements are presented for the two experiments. The data for IFT-2 show three negative spikes in hood vacuum pressure and a corresponding temperature increase, indicative of three significant gas release events. By comparison, 14 spiking events are noted for IFT-1, suggesting a more frequent and dynamic off-gassing process in IFT-1. The greater amount of off-gassing noted for IFT-1 is consistent with the experimental observation of greater tracer carry-off by escaping gas bubbles.

As shown in Figure 8, a faster melting rate in IFT-1 compared to IFT-2 may have also contributed to more dynamic off-gassing and thus tracer carry-off in IFT-1 than in IFT-2. Likewise, evidence exists³ for a greater amount of gas escape at ISV pool periphery (i.e., at the melt-solid soil boundary) associated with the slower melting rates for the IFT-2. Gas escape at the sides of the ISV melt pool would reduce the tracer flotation potential. It is also interesting to note that the IFT-2 incorporated the use of graphite electrodes, where partial gas venting along the electrode surface was noted, which would tend to reduce the potential for tracer and heavy metal flotation associated with bubble rise through the melt pool. On the other hand, silica (SiO_2)-coated electrodes were used (to limit oxidation of the graphite rods) in the IFT-1, where wetting between the SiO_2 coating and SiO_2 -based melt would be expected (and occurred as evidenced by rod adhesion to solidified/vitrified melt). ISV melt/electrode wetting would tend to limit the potential for gas venting at the electrode surface, so that greater gas release through the IFT-1 melt pool proper would be expected, and result in greater tracer carry-off by bubble flotation.

Data from other ISV tests¹⁹ suggest that heavy-metal elements buried at greater depths are preferentially retained in the vitrified melt. This empirical observation is consistent with the apparent reduced amount of tracer release for the IFT-2 (dysprosium buried at ≈ 5 ft) as compared to the IFT-1 (dysprosium buried at ≈ 2 ft; terbium and ytterbium buried at ≈ 3.5 ft). However, a counteracting observation from the IFT-1 is the larger fractional release of terbium and ytterbium tracers (buried at ≈ 3.5 ft) than dysprosium (buried at ≈ 2 ft).

Such differences in test pit configuration and operations could well have influenced the amounts of tracer release. Additionally, several aspects of the tracer sampling for the IFT-2 experiment confound its interpretation. The use of the post-test smear data from IFT-1 as pretest smear data for IFT-2 is suspect, where the IFT-1 tracer hood deposits (post-test smear samples) may have been lost during hood relocation to the IFT-2 test pit. As discussed in Reference 3, smear data suggest this possibility and reduce the confidence in use of the post-test smear data from IFT-1 as pretest smear data for IFT-2. Despite these sampling concerns, the data nevertheless suggest less tracer release for IFT-2 than for IFT-1.

Clearly, the numerous differences between the two tests and experimental uncertainties do not allow for definitive quantitative predictions of tracer release from off-gassing. Nevertheless, the fact remains that the more active gas release process noted for IFT-1 would have enhanced tracer flotation and release to the off-gas collection system, as modeling predictions indicate.

In addition to the INEL test observations on rare-earth oxide behavior, Oak Ridge National Laboratory (ORNL) performed vitrification studies of simulated contaminated soil seepage pits,²⁰ in which rare-earth oxides were added as tracer materials. The ORNL test findings are summarized in the following section.

R93 1491

Figure 7. Comparison of measured hood pressure and temperatures noted in IFT-1 and 2.

T83 1422

Figure 8. Comparison of depth of soil melting, deduced from measurements of average electrode depth.

4.3 ORNL Tracer Findings

Past waste disposal operations at ORNL involved the placement of over a million curies of radioactive liquid waste in seepage trenches between 1951 and 1966. In planning for remediation of such sites, ISV technology has been identified as a leading candidate because of the high risks associated with various retrieval options. To this end, an ISV demonstration test was conducted in the spring of 1991,²⁰ in which the retention/release characteristics of various volatile and nonvolatile tracer materials were incorporated into a simulated soil seepage test pit, composed of crushed dolomitic limestone (17 wt% MgO, 29 wt% CaO) and backfill soil with a moisture content of 18 vol% water ($\approx 2,500$ L). Contaminant simulants added to the test pit included radioactive isotopes of volatile cesium (^{137}Cs) and nonvolatile strontium (^{90}Sr), as well as lesser amounts of ^{60}Co , ^{241}Am , and $^{239}\text{Pu}/^{240}\text{Pu}$. Rare-earth oxide tracers (CeO_2 , La_2O_3 , and Nd_2O_3) were also added as surrogates for TRU. On-line gas monitoring and aerosol sampling allowed for qualification of release of volatile and nonvolatile species from the melt.

In the ORNL test, soil melting occurred over a 5-day period, during which time 2.4 wt% of volatile ^{137}Cs was released from the melt and captured as particulates in filters located in the off-gas containment hood. However, greater than 99.993 wt% retention of ^{90}Sr , ^{241}Am , and $^{239}\text{Pu}/^{240}\text{Pu}$ was estimated from post-test analysis of the recrystallized product, where core sampling revealed large-scale crystal formation on melt cooldown rather than a vitrified product. The greater amount of crystallization in the ORNL test (versus primarily vitrification in the INEL-IFT) is considered²⁰ due to the low sodium and high calcium/magnesium content of the ORNL soil/limestone mixture. In addition, post-test sample analysis indicated greater than 99.9995 wt% retention of the rare-earth oxides (CeO_2 , La_2O_3 , and Nd_2O_3). This nearly complete retention occurred despite significant off-gassing as the soil dried out (water release during soil melting was estimated to be 1,700 L, compared to an initial water content of 2,500 L).

Although differences in testing conditions for the ORNL and INEL-IFT experiments make it difficult to draw definitive conclusions concerning tracer release behavior, it is interesting to note the differences in melting rates and gas release behavior for these experiments. As indicated in Table 7, slow melting rates are evident for the ORNL and IFT-2 experiments with nil rare-earth tracer release, compared to the faster melting rate for IFT-1 in which tracer release was observed. Observations³ for the IFT-2 also indicate gas escape at the peripheral melt-solid boundary during slow melting, while in IFT-1 off-gassing occurred at the interior of the melt pool.

Table 7. Comparison of ISV melting rates during melt exposure of tracer materials.

Test	Melting rate ^a	Tracer release
INEL IFT-1	≈ 17 cm/h	1.2 to 3.9%
INEL IFT-2	≈ 4.4 cm/h	none
ORNL	≈ 2.3 cm/h	none

a. ISV melting rate during period of melt exposure at tracer placement depth.

Observations from recent small-scale ISV tests,^a which incorporated the use of graphite vent rods, indicate significant gas venting along the surface of graphite rods. The IFT-2 and ORNL tests incorporated graphite electrodes, where similar venting along the electrode surface would be expected. Such venting at the IFT-2 and ORNL electrodes would tend to reduce the potential for tracer and heavy metal flotation associated with bubble rise through the melt pool. On the other hand, SiO₂-coated electrodes were used (to limit oxidation of the graphite rods) in the IFT-1, where wetting between the SiO₂ coating and SiO₂-based melt would be expected (and occurred as evidenced by rod adhesion to solidified/vitrified melt). ISV melt/electrode wetting would limit the potential for gas venting at the electrode surface, so that greater gas release by bubble rise through the IFT-1 melt pool proper would be expected, resulting in greater tracer carry-off by bubble flotation.

A second factor relates to differences in gas composition and the timing of its release. In the IFT-2 and ORNL tests, the vast majority of gas release is associated with steam generation (i.e., dryout of soil moisture in the ORNL experiment; a steam generation from aqueous based sludge in the IFT-2). Steam release from moisture dryout largely precedes local soil melting and is released early in the ISV melting transient. This effect is shown in Figure 9, where the high initial ORNL off-gas flow rates are considered to be associated with early steam release due to soil dryout, which precedes the time at which cesium and other tracer materials were exposed to melting.

For the IFT-1, similar quantities of both CO gas and H₂O vapor are estimated from pit inventory conditions (see Appendix A). The CO gas would be released only on melt front penetration to the depth at which organic materials were pyrolyzed and thus available for tracer flotation.

Because information on gas release effects impacting tracer release is primarily qualitative in nature, specific testing is recommended to investigate overall off-gassing effects that influence heavy-metal and rare-earth oxide release under ISV conditions. Recommendations for such testing are suggested in the following section.

a. R. K. Farnsworth and B. M. Gardner, *Quick-Look Report on ISV Lab Test Series-1*, EG&G Idaho, Inc., WTD-93-052, January 1993.

R93 1359

Figure 9. Comparison of ORNL measure off-gassing flow rates and timing of ^{137}Cs release (in counts per cubic foot, based on measured activity in off-gas collection hood).²⁰

5. CONCLUSIONS AND RECOMMENDATIONS

Test data from recent INEL ISV field tests were assessed relative to rare-earth tracer release during ISV and melting of simulated buried waste. In these tests, small quantities of rare-earth oxides (tracers Dy_2O_3 , Yb_2O_3 , and Tb_4O_7) were mixed with waste material to simulate the presence PuO_2 . In the first test, IFT-1, 1 to 4 wt% tracer release was noted,³ which is believed to have been associated with the release of pyrolysis gases (i.e., CO and steam) from vitrification of buried organic waste and steam generated from dryout of aqueous-based sludge. Little tracer release, however, was noted in the second test, IFT-2, for which off-gassing was greatly reduced.^{4,5}

Analysis is presented indicating that dissolution of tracer oxides into basaltic melts can be expected, with subsequent tracer molecular or microparticle absorption onto gas bubbles rising through the melt. Analogous processes for tracer flotation by escaping gas bubbles is adsorptive bubble separation and ion flotation, which are employed in the chemical industry to separate dilute species from liquids under gas sparging conditions. Subsequent aerosolization of the surface melt by bursting/escaping gas bubbles is believed to be responsible for release of tracer species to the off-gas collection system. Improved methods of controlling off-gassing during ISV would be expected to improve the overall retention of heavy-metal contaminants.

Although questions remain about overall modeling assumptions and approximations used to estimate governing parameters, it is encouraging to note that estimates of tracer release were directly tied to testing conditions. For example, tracer concentrations were estimated from inventory conditions, while rates of gas generation were estimated from measured melting rates and the quantities of combustible and sludge waste contained within the test pits. Likewise, adsorptive bubble separation methods and aerosolization caused by bubble escape at the surface melt are known processes used to separate dilute heavy species from liquids under gas sparging conditions. Thus, it is reasonable to deduce that tracer release by such mechanisms may be operable under ISV conditions. Specific testing conditions are discussed below for more in-depth evaluation of such off-gas/tracer-release phenomena.

5.1 Recommendations

During 1992, three small-scale laboratory vitrification tests were conducted at INEL^b to provide data on soil permeability effects on vapor transport and the influence of graphite vent rods on gas pressure relief and particulate generation. These tests were conducted in 110-gal steel drums containing well-characterized INEL soil (i.e., composition, moisture content, oxide content, and permeability). The test drums were instrumented with thermocouples and pressure transducers strategically placed to provide on-line pressure and temperature data. Particulate sampling data were also obtained using an isokinetic particle sampling system and smear sampling for particle deposition onto the surface of the off-gas collection hood.

An assessment of the test data^b indicates melt pressure relief and gas venting for the test, which incorporated the use of graphite vent rods. Figure 10 illustrates the manner in which ISV gases are

b. R. K. Farnsworth and B. M. Gardner, *Quick-Look Report on ISV Lab Test Series-1*, EG&G Idaho, Inc., WTD-93-052, January 1993.

Figure 10. Schematic of ISV-drum laboratory test configuration for characterization of off-gassing and tracer release.

vented from the melt at the graphite rod surface. Isokinetic stack sample and smear data offer evidence that the amount of entrained particles released to the off-gas system was substantially less for the test using the graphite vent rod compared to a similar test, which however did not incorporate the use of a graphite vent rod. Such test results offer indirect support for the hypothesis that reduced gas percolation through the interior of the melt pool would lead to reduced tracer release. It is interesting to note that the IFT-2 and ORNL tests also incorporated graphite electrodes, where similar venting along the electrode surface would be expected, thus reducing the potential for tracer flotation associated with bubble rise through the melt pool. On the other hand SiO_2 -coated electrodes were used in the IFT-1, where wetting between the SiO_2 coating and the SiO_2 -based melt would be expected. Wetting contact at the ISV-melt/electrode interface would limit the potential for gas venting at the surface of the coated electrode, so that greater gas release through the IFT-1 melt pool proper would be expected and greater tracer carry-off by bubble flotation. It is suggested that the ISV-drum tests³ be adapted for a more in-depth investigation of gas sparging and adsorptive bubble separation effects on heavy metal release.

The proposed testing configuration, similar to previous ISV-drum tests, is illustrated in Figure 11. The test drums should contain relatively moisture-free/well-characterized soil, laced with known inventories of the rare-earth oxides (Dy_2O_3 , Yb_2O_3 , and Tb_4O_7). The rare-earth tracers should be tagged by previous neutron activation so that their respective release rates can be measured using an on-line radioisotopic monitor. The ISV drum apparatus could be modified to include the capability for controlled CO (or CO_2) gas injection through the melt, with no additional combustible materials (e.g., paper, wood, and cloth) or aqueous-based sludge added to the soil. Controlled well-characterized gas injection should coincide with the time at which the ISV melt front encompasses the location of the tagged tracer material. The ISV melting rate should be relatively slow to facilitate estimation of tracer concentration levels within the ISV melt. Measurements of gas inflow and off-gassing collection rates would be desirable. On-line capability for video recording of bubble gas escape from the ISV melt surface would be beneficial to assay for both bubble size and bursting characteristics, as well as quantification of the rate of bubble escape. An aerosol monitoring system (e.g., cascade impactor, multistage cyclone, and isokinetic particle sampler) should be incorporated into off-gas collection hood for assay of melt and tracer aerosol generation characteristics. Testing under similar conditions, with and without graphite vent rods, would yield valuable information concerning the possible use of vent rods as a remediation technique for reduction of off-gas induced heavy metal transport and release. Under well-controlled and well-instrumented conditions, one should be able to benchmark test results against modeling predictions, so that definitive conclusions regarding bubble flotation of heavy-metals can be made.

Figure 11. Schematic of ISV-drum laboratory test configuration for characterization of off-gassing and tracer release.

6. REFERENCES

1. T. L. Eddy et al., *Thermal Processing System Concepts and Considerations for RWMC Buried Waste*, EGG-WTD-10058, February 1992.
2. A. D. Donaldson, R. J. Carpenedo, and G. L. Anderson, *Melter Needs Development Assessment for RWMC Buried Waste*, EGG-WTD-9911, February 1992.
3. R. A. Callow, L. E. Thompson, and J. R. Weidner, *In Situ Vitrification Application to Buried Waste: Final Report of Intermediate Field Tests at Idaho National Laboratory*, EGG-WTD-9807, August 1991.
4. A. W. Cronenberg and R. A. Callow, *Predictions of PuO_2 and Tracer Compound Release from ISV Melts*, EGG-WTD-10172, April 1992.
5. A. W. Cronenberg, R. A. Callow, and R. E. McAtee, "Use of Rare Earth Tracers as Pu Simulates in ISV Studies," *Proc. 8th Annual Waste Management Symposium, Tucson, Arizona, March 1-5, 1992*.
6. T. Ginsberg, "Aerosol Generation by Liquid Breakup Resulting from Sparging of Molten Pools of Corium by Gases Released During Core/Concrete Interactions," *Nuclear Science and Engineering* (89), 1985, pp. 36-48.
7. M. Tomaides and K. T. Whitby, "Generation of Aerosols by Bursting of Single Bubbles," *Fine Particles*, B. Y. H. Liu (Ed.), Academic Press, New York, 1976.
8. R. Lemlich, *Adsorptive Bubble Separation Techniques*, Academic Press, New York, 1972.
9. R. H. Perry et al., "Novel Separation Processes," *Perry's Chemical Engineers' Handbook*, Section 17, McGraw-Hill Book Co, New York, 1984.
10. R. A. Callow and L. E. Thompson, "In Situ Vitrification: Application to Buried Waste," *Proc. Waste Management Symposium, Tucson, Arizona, 1991*.
11. G. H. Geiger and D. R. Poirier, *Transport Phenomena in Metallurgy*, Addison-Wesley Pub. Co., Reading, Massachusetts, 1973.
12. R. E. McAtee and M. Beal, *Comparison of the High Temperature Chemistry of Plutonium and Rare Earths: A Review Study*, EGG-WTD-9801, September 1991.
13. T. Ginsberg, "Aerosol Generation From Sparging of Molten Pools of Corium by Gases Released During Core-Concrete Interactions," *Proceedings of the International Meeting on LWR Severe Accident Evaluation, Cambridge, Massachusetts, August 28 to September 1, 1983*, paper TS11.4.

14. D. A. Powers, J. E. Brockmann, and A. W. Shiver, "VANESA: A Mechanistic Model for Radionuclide Release and Aerosol Generation During Core Debris Interactions with Concrete," NUREG/CR-4308, SAND85-1370, July 1986.
15. Y. Toba, "Drop Production by Bursting of Air Bubbles on the Sea Surface: Theoretical Study of the Shape of Floating Bubbles," *Journal of the Oceanographic Society of Japan* (15), October 1959.
16. F. MacIntyre, "Flow Patterns in Bursting Bubbles," *Journal of Geophysical Research* (77), September 1972.
17. J. A. Quinn, "Breaking Bubbles and the Water-to-Air Transport of Particulate Matter," *Chemical Engineering Science* (30), 1975, p. 1177.
18. D. S. Azbel et al., "Acoustic Resonance Theory for the Rupture of Film Cap of a Gas Bubble at a Horizontal Gas-Liquid Interface," *Two Phase Momentum, Heat and Mass Transfer in Chemical Process and Energy Engineering Systems*, Vol. 1, Hemisphere Publ. Co., 1978, pp. 159-170.
19. J. L. Buelt et al., *In Situ Vitrification of Transuranic Wastes: Systems Evaluation and Applications Assessment*, Battelle Pacific Northwest Laboratory, PNL-4800, Supplement 1, 1987.
20. B. P. Spalding et al., *Tracer-Level Radioactive Pilot-Scale Test of In Situ Vitrification for Stabilization of Contaminated Soil Sites at ORNL*, ORNL/TM-12201, November 1992.

Appendix A

Description of IFT Conditions

Appendix A

Description of IFT Conditions

A-1. IFT-1 DESCRIPTION

This appendix describes testing conditions for intermediate field tests (IFT)-1 and IFT-2 experiments that are pertinent to an assessment of off-gassing and tracer release noted in these tests.^{1,2}

The IFT-1 test pit consisted of several distinct waste layer into which rare-earth oxide (Dy_2O_3 , Tb_4O_7 , and Yb_2O_3) tracers were placed for simulation of PuO_2 behavior. The top layer consisted of 0.6 m (2 ft) of soil overburden without any waste or tracer materials. The next four layer were approximately 1.5-ft deep, with various amounts of combustible materials, aqueous-based sludge, metals, glass, and concrete (≈ 33 wt% water), which were contained within cardboard and wooden boxes and steel cans. As illustrated in Figures A-1 and A-2, the waste containing cans and boxes were randomly dispersed within each distinct waste layer. The first two layers below the soil overburden also contained small quantities of the rare-earth oxide powders, which were also placed in cans containing simulated waste material. The waste pit inventory conditions are summarized in Tables A-1 and A-2, and the geometric conditions are illustrated in Figure A-3.

Below the overburden layer was waste layer-1 (also called the top layer), which consisted of randomly-dispersed waste boxes and cans mixed with fill dirt. The dysprosium oxide (Dy_2O_3) tracer material was dispersed in several of the waste cans comprising layer-1. The next layer (layer-2) consisted of randomly-dispersed waste boxes and cans mixed with fill dirt. Ytterbium oxide (Yb_2O_3) was placed in cans at the bottom tier of layer-2, while in the top tier of layer-2 were cans containing terbium oxide (Tb_4O_7). Layers-3 and 4 contained different mixtures of boxes and cans with different amounts of sludge, metal, and combustible materials that were free of any tracer material. The inventories of tracer, combustibles (cloth, paper, wood), and water (from sludge and concrete) for each layer are as summarized in Table A-3.^{1,2}

In situ melting (ISV) for the IFT-1 was initiated on June 12, 1990, and proceeded for approximately 5 hours when an electrode power cable failed at a melt depth of 46 to 51 cm (18 to 20 in.). After cable replacement, the test was restarted (on June 14) at the constant power of 300 kW for an additional 18 hours. The electrode depth history is illustrated in Figure A-4.

Pyrolysis gases (primarily CO) and steam were continuously released during ISV melting in the form of bubbles observed at the melt surface.² In addition, rapid gas surging was also noted and occurred in 14 separate events, characterized by measured sharp temperature increases and pressure spikes in the off-gas collection hood. Concentrations of O_2 and CO were monitored at the off-gas stack throughout the test and are shown in Figure A-5. The O_2 concentration generally averaged between 20 and 21% during the test; however, short periods of reduced oxygen were measured at times associated with gas surging from the melt and increased CO release (both from gas combustion in the hood and increased CO release from the melt). Unfortunately, quantitative information on gas

Figure A-1. Waste cans and boxes in top waste layer of the IFT-1 test pit.

Figure A-2. Backfilling of waste cans containing Tb_4O_7 and boxes for waste layer 2 of the IFT-1 test pit.

Table A-1. Indication of IFT-1 test pit composition and placement.^a

Layers	Depth	Contents
Overburden	0–2.0 ft	2-in. starter path SDA lakebed soil
Waste layer 1	2.0–3.5 ft	Cans: 15 s, ^b 29 c, 5 c-g, 1 m, 1 w Boxes: 5 metal
Waste layer 2	3.5–5.0 ft	Cans: 17 s, 24 c, 7 c-g, 2 m, 1 w Boxes: 4 metal, 1 cement/glass
Waste layer 3	5.0–6.5 ft	Cans: 10 s, 30 c, 7 c-g, 8 m, 1 w Boxes: 4 metal, 1 cement/glass
Waste layer 4	6.5–8.0 ft	Cans: 20 s, 21 c, 2 c-g, 6 m, 1 w Boxes: 3 metal, 2 cement/glass
Underburden	8.0–10.0 ft	SDA lakebed soil

a. Engineering Design File, EDF-ISV-034.

b. These designations indicate the contents of the cans: s = sludge cans; c = combustible cans; c-g = concrete/glass cans; m = metal cans; w = wood cans. These cans contained the following approximate amounts of material: sludge can (s) - 10.716 lb (7.71 - H₂O, 0.70 - FLOOR DRI, 2.307 - MICRO-CEL E); combustible can (c) - 4.154 lb (1.637 - cloth, 2.517 - paper); concrete/glass can (c-g) - 17.440 lb (11.035 - concrete, 6.405 - glass); metal can (m) - 8.235 lb (4.118 - carbon steel, 4.118 stainless steel); wood can (w) - 4.875 lb; pallet - 13.5 lb of wood. Boxes contained the following, approximate amounts of material: metal - 123.0625 lb (50% carbon steel); concrete/glass - 246.375 lb (158.75 - concrete, 87.625 - glass).

Table A-2. Waste material composition for IFT-1 test pit (in pounds).

Materials	Total	Item weight	Waste deposit layers			
			Top	2nd	3rd	Bottom
Combustibles	665.5					
Cans		451.5				
Paper		261.75	72.99	60.40	75.51	52.85
Cloth		170.25	47.47	39.29	49.11	34.38
Wood		19.50	4.88	4.87	4.88	4.87
Boxes		214.0				
Cardboard		160.00	40.00	40.00	40.00	40.00
Pallet (wood)		54.00	0.00	13.50	13.50	27.00
Sludge (cans only)	664.4					
Water		478.0	478.00	115.65	131.06	77.10
Floor Dri		43.4	43.40	10.50	11.90	7.00
Micro-Cel		143.0	143.00	34.50	39.20	23.10
Metals	2,473.0					
Cans		504.0				
Stainless		70.00	4.12	8.24	32.94	24.70
Carbon steel		434.00	93.37	97.49	130.94	112.20
Boxes		1,969.0				
Stainless		984.50	307.65	246.13	246.13	184.59
Carbon steel		984.50	307.65	246.13	246.13	184.59
Concrete/glass	1,351.75					
Cans		366.25				
Concrete		231.75	55.18	77.25	77.25	22.07
Glass		134.50	32.03	44.83	44.83	12.81
Boxes		985.5				
Concrete		635.00	0.00	158.75	158.75	317.50
Glass		350.50	0.00	87.62	87.63	175.25
Totals of columns	5,154.65	5,154.65	1,125.99	1,306.66	1,314.80	1,407.20

Figure A-3. Illustration of tracer placement of IFT-1 test pit.

Table A-3. Summary of inventories for layers containing tracer material.

Layer	Tracer oxide (tracer)	Combustibles	Sludge water	Concrete
Overlayer	—	—	—	—
1	$Dy_2O_3=1,336$ g ($Dy=1,164$ g)	≈ 165 lb (74.84 kg)	≈ 116 lb (52.62 kg)	≈ 55.2 lb (25 kg)
2	$Tb_4O_7=1,337$ g ($Tb=1,137$ g) $Yb_2O_3=1,331$ g ($Yb=1,169$ g)	≈ 158 lb (71.67 kg)	≈ 131 lb (59.42 kg)	236 lb (107 kg)
3	—	≈ 183 lb (83.00 kg)	≈ 77 lb (34.93 kg)	236 lb (107 kg)
4	—	≈ 159 lb (72.12 kg)	≈ 154 lb (69.85 kg)	≈ 340 lb (154.2 kg)

Figure A-4. History of electrode and melt depth for the IFT-1.

R93 1390

Figure A-5. Qualitative data on gas release during IFT-1.

release rates are unavailable, so that IFT-1 gas release estimates must be assessed from the inventories of water and combustible materials present in the IFT-1 test pit.

After testing, the amounts of tracers were measured in retrieved samples of vitrified soil and at various locations within the collection hood, off-gas piping surfaces, scrub solution, and HEPA filters (collectively referred to as the off-gas collection system). Although quantitative determination of tracer amounts was hampered by sampling uncertainties, results indicate that the majority of the tracers were retained in the vitrified product. Nevertheless, several percent of the tracer material was found within the off-gas collection system for IFT-1, as indicated in Table A-4. The tracer release results presented in Table A-4 form the basis for comparisons used in this report.

A-2. ESTIMATE OF IFT-1 CONDITIONS FOR ASSESSMENT OF TRACER RELEASE

As discussed in Section 4, an estimate of the amount of rare-earth release from off-gassing and aerosolization of droplets at the melt surface (containing trace quantities of such rare earth material) can be obtained from the following expression:

$$M_{trac} (g) = (10^{-4}) \rho_L R_{gas} C_{trac} t_{melt}$$

where $\rho_L = 2.2 \text{ g/cm}^3$, and the following parameters must be estimated from knowledge of the IFT-1 conditions:

C_{trac} = fractional concentration of tracer species in the melt

R_{gas} = rate of gas release during melting/tracer release (g/s)

t_{melt} = melt time over which tracer release occurs (s).

Estimates for each are presented in the following sections.

Table A-4. IFT tracer release data.

Oxide Inventory	Rare Earth	Hood/Duct Deposits	Scrub Solution	Release Fraction
Dy ₂ O ₃ = 1,336 g	Dy = 1,164 g	4.7-6.2 g	7.5 g	0.010-0.012
Tb ₄ O ₇ = 1,337 g	Tb = 1,137 g	28-29.9 g	14.0 g	0.037-0.039
Yb ₂ O ₃ = 1,331 g	Yb = 1,169 g	11-12.3 g	17.5 g	0.024-0.025
Total = 4,004 g	Total = 3,473 g			Average ≈ 0.025

A-2.1 Fractional Concentration (C_{trac}) and Release Time (t_{melt})

As noted in Figure A-1 and Table A-1, dysprosium (Dy_2O_3) was placed in the first layer containing waste, at a depth of between 2.0 to 3.5 ft below the soil surface. For present purposes, C_{trac} and t_{melt} can be estimated assuming that the majority of dysprosium release occurs during melting of the waste layer in which it was originally placed (layer-1). The fractional concentration of dysprosium can be estimated using layer-1 thickness ($\Delta = 1.5$ ft soil), modified by a factor of two ($\Delta_{\text{melt}} = 0.5\Delta_{\text{soil}}$) to account for density differences between the original soil and its molten state¹ (subsidence of waste pit from 40 to 70 vol%). The melt time (t_{melt}) is based on the electrode position information shown in Figure A-4, from which the time associated with melting of the layer-1 thickness can be deduced. Based on these assumptions, C_{trac} and t_{melt} are estimated in Table A-5 to be

$$C_{\text{trac}} (\text{Dy}) = 1.32 \text{ E-4} \quad t_{\text{melt}} (\text{Dy}) = 18,000 \text{ s}$$

The concentration can be compared with solubility data, indicating that the rare-earth oxides (Dy_2O_3 , Tb_4O_7 , and Yb_2O_3) and PuO_2 would dissolve to at least 1.0 wt% in SiO_2 -based basalt melts.³ Noting that the density of basaltic melts is on the order of 2.2 g/cm³, a mass fraction of ≈ 0.0132 wt% is estimated for dysprosium. Because this weight fraction is well below the solubility limit (1 wt%) and because dysprosium was added to the test pit in powder form, it is reasonable to assume that dysprosium (as well as the other tracers) is dissolved in the melt on a molecular scale.

Table A-5. Estimate of dysprosium tracer concentration fraction (F_{trac}) and melt time (t_{melt}) for IFT-1.

ISV melt properties	Value
Melt density (ρ)	2.2 g/cc
Melt surface area (A)	$\approx (10 \times 10 \text{ ft}) = 9.29\text{E}+4 \text{ cm}^2$
IFT-1 dysprosium concentration	
$I_{\text{trac}} = \text{Total dysprosium tracer inventory} = 1,164 \text{ g}$	
$X = \text{Soil depth at tracer location} = 2 \text{ to } 3.5 \text{ ft} = 61 \text{ to } 107 \text{ cm}$	
$X_{\text{ave}} = \text{Average soil depth at tracer location} \approx 86 \text{ cm}$	
$X_{\text{melt}} = \text{Average depth of molten pool (1/2 soil depth)} = X_{\text{ave}}/2 = 43 \text{ cm}$	
$V_{\text{pool}} = \text{Melt volume} = X_{\text{melt}} (A) = (43 \text{ cm})(9.29\text{E}+4 \text{ cm}^2) \approx 4.0 \text{ E}+6 \text{ cm}^3$	
$C_{\text{bulk, trac}} = I_{\text{trac}}/V_{\text{pool}} = (1,164 \text{ g})/(4.0 \text{ E}+6 \text{ cm}^3) = 2.91 \text{ E-4 g/cm}^3$	
$C_{\text{trac}} = C_{\text{bulk, trac}}/\rho_L = (2.91 \text{ E-4 g-Dy/cm}^3)/(2.2 \text{ g-melt/cm}^3) = 1.32 \text{ E-4}$	
Melt time	
$t(61 \text{ cm; Figure A-4}) = 7 \text{ h}$	$t(107 \text{ cm; Figure A-4}) = 12 \text{ h}$
$t_{\text{melt}} \approx (12 \text{ h} - 7 \text{ h}) = 5 \text{ h} = 18,000 \text{ seconds}$	

In a similar manner, Tb_4O_7 and Yb_2O_3 were buried in the second waste layer at a buried depth of between 3.5 ft (≈ 107 cm) to 5.0 ft (≈ 152 cm) below the soil surface (see Figure A-3 and Table A-1). Again it is assumed that the majority of terbium and ytterbium tracer release occurs during melting of the waste layer in which they were placed (layer-2) and that volume of the melt is half that of soil. Thus, the fractional concentration of terbium and ytterbium can be estimated based on a layer depth of between 107 and 152 cm. Based on these assumptions, C_{trac} and t_{melt} are estimated in Table A-6 to be

$$C_{trac} (Tb/Yb) = 1.74 E-4$$

$$t_{melt} (Tb/Yb) = 9,000 s$$

A-2.2 Rate of Gas Release (R_{gas})

The volumetric rates of gas release (R_{gas}) from pyrolysis and sludge dryout are estimated based on the inventories of organic materials and sludge contained within each waste layer, which are given in Tables A-2 and A-3. Similar to the assumptions made for estimating tracer release behavior, it is again assumed that the pyrolysis gases (primarily CO) and steam from sludge waste (soil moisture not included) are released from the waste layers in which they are contained. Likewise, the time period

Table A-6. Estimate of terbium and ytterbium tracer concentration fraction (C_{trac}) and melt time (t_{melt}) for IFT-1.

ISV melt properties	Value
Melt density (ρ)	2.2 g/cm ³
Melt surface area (A)	$\approx (10 \times 10 \text{ ft}) = 9.29E+4 \text{ cm}^2$

IFT-1 terbium and ytterbium concentrations

$$I_{trac} = \text{Total terbium and ytterbium tracer inventory} = 1,137 + 1,169 \text{ g} = 2306 \text{ g}$$

$$X = \text{Soil depth at tracer location} = 3.5 \text{ to } 5.0 \text{ ft} = 107 \text{ to } 152 \text{ cm}$$

$$X_{ave} = \text{Average soil depth at tracer location} \approx 130 \text{ cm}$$

$$X_{melt} = \text{Average depth of molten pool (1/2 soil depth)} = X_{ave}/2 = 65 \text{ cm}$$

$$V_{pool} = \text{Melt volume} = X_{melt} (A) = (65 \text{ cm})(9.29E+4 \text{ cm}^2) \approx 6.03 E+6 \text{ cm}^3$$

$$C_{bulk,trac} = I_{trac}/V_{pool} = (2306 \text{ g})/(6.03 E+6 \text{ cm}^3) = 3.82 E-4 \text{ g/cm}^3$$

$$C_{trac} = C_{bulk,trac}/\rho_L$$

$$= (3.82 E-4 \text{ g-tracer/cm}^3)/(2.2 \text{ g-melt/cm}^3) = 1.74 E-4$$

Melt time

$$t(107 \text{ cm; Figure A-2}) = 12.0 \text{ h}$$

$$t(107 \text{ cm; Figure A-4}) = 14.5 \text{ h}$$

$$t_{melt} = (14.5 \text{ h} - 12 \text{ h}) = 2.5 \text{ h} = 9,000 \text{ seconds}$$

for such gas release is based on the time it takes the ISV melt front to penetrate that particular layer. For order-of-magnitude purposes, it can also be assumed that all paper, wood, and cloth material have a similar cellulose composition, yielding similar pyrolysis byproducts.³

Pyrolysis byproduct	Weight fraction
Carbon (retained in melt)	0.10
CO-gas (released)	0.80
H ₂ O-steam (released)	0.10

The water content (≈ 33 wt%) of the buried concrete is based on standard water of hydration values. Using the inventories given in Tables A-2 and A-3, the following gas composition are estimated:

Layer	Organic material	Water	Gas composition	t_{melt}
1	Total = 74.84 kg CO ≈ 59.9 kg H ₂ O ≈ 7.5 kg	Sludge = 52.62 kg Concrete = 8.25 kg	CO ≈ 59.9 kg H ₂ O ≈ 68.4 kg	18,000 s
2	Total = 71.67 kg CO ≈ 57.3 kg H ₂ O ≈ 7.2 kg	Sludge = 59.42 kg Concrete = 35.31 kg	CO ≈ 57.3 kg H ₂ O ≈ 102 kg	9,000 s

To obtain the volumetric rates of gas release (R_{gas} , cm³/s), the ideal gas law is employed, $PV = MRT$, where the gas volume (V) is estimated for the above gas compositions ($V = MRT/P$). Noting that IFT-1 was conducted at near atmospheric conditions (≈ 1 atm) and that the released bubbles are large enough (1 to 5 cm in diameter) to be free of surface tension effects, a pressure (P) of 1 atm can be assumed. In addition the melt temperature of basalt is assumed, i.e., $\approx 1,720$ K; while the gas constants for steam (H₂O) and CO can be estimated as

$$R_u = \text{universal gas constant} = 82 \text{ atm-cm}^3/\text{gmole-K}$$

$$M = \text{molecular weight} = 18 \text{ g/gmole-H}_2\text{O}; 28 \text{ g/gmole-CO}$$

$$R_{\text{steam}} = R_u/M = 4.55 \text{ atm-cm}^3/\text{g-K}$$

$$R_{\text{CO}} = R_u/M = 2.93 \text{ atm-cm}^3/\text{g-K}$$

Applying the ideal gas law, the following volumetric rates of gas release are estimated for each waste layer:

Layer	Gas composition, M	Volume, $V = MRT/P$	t_{melt}	$R_{\text{gas}} = V/t_{\text{melt}}$
1	CO =59.9 kg H ₂ O =68.4 kg	=3.02 E+8 cm ³ =5.35 E+8 cm ³ Total =8.37 E+8 cm ³	18,000 s	4.65 E+4 cm ³ /s
2	CO =57.3 kg H ₂ O =103.0 kg	=2.89 E+8 cm ³ =8.06 E+8 cm ³ Total =10.95 E+8 cm ³	9,000 s	12.17 E+4 cm ³ /s

Table A-7 summarizes parameter values (C_{trac} , R_{gas} , t_{melt}) necessary for estimation of the tracer releases during the IFT-1.

Table A-7. Summary of IFT-1 conditions used to estimate tracer release.

Layer	Tracer	t_{melt}	C_{trac}	R_{gas}
1	Dy	18,000 s	1.32 E-4	4.65 E+4 cm ³ /s
2	Tb, Yb	9,000 s	1.74 E-4	12.17 E+4 cm ³ /s

A-3. IFT-2 DESCRIPTION

Unlike IFT-1, only Dy₂O₃ was incorporated into the IFT-2 test pit that, as shown in Figure A-6, was buried below a 4-ft soil overburden and placed in the center of a 2-ft layer consisting of three layers of stacked cans that contained mixed waste (paper, cloth, glass, sludge, etc). Just below the waste cans was a layer of boxes that were stacked on top of wooden pallets. The waste inventory conditions for each of the three can layers are summarized in Tables A-8 and A-9. The 2.282 kg of Dy₂O₃ powder was dispersed within 10 waste cans located in the center of the stacked drum region (mid-can region), so that tracer release would have occurred concurrently with melting of the mid-can region. The inventories of tracer, combustibles (cloth, paper, wood), and water (sludge; concrete at 33 wt%) for this mid-can region are as summarized in Table A-10.

The IFT-2 was initiated on July 11, 1990. Figure A-7 presents the electrode depth history. Although observations indicate very limited gas release during the melting phase of this test, for present purposes the IFT-2 gas release rates are estimated in a similar manner to that for IFT-1, based on the inventories of water and combustible materials present in the test pit.

Post-test analysis of vitrified samples taken after the IFT-2 experiment was completed indicated test that the vast majority of the dysprosium tracer material was found to be associated with the ISV recrystallized soil. Hood/piping smear data, as well as results from high efficiency particulate air (HEPA) filter analysis and scrub tank data, indicate that there were no significant differences between tracer pretest concentrations and post-test concentrations. On this basis, no release of tracer material (Dy₂O₃) was deduced for the IFT-2 experiment.¹

Figure A-6. Illustration of tracer placement in IFT-2 test pit.

Table A-8. Indication of IFT-2 test pit composition and placement.

Layers	Depth	Contents
Overburden	4 ft	2-in. deep starter path SDA lakebed soil
Waste deposit	5 ft	Cans: 47 s, ^b 63 c, 16 c-g, 16 m, 3 w Cans: 33 s, 78 c, 21 c-g, 10 m, 2 w Cans: 54 s, 61 c, 13 c-g, 14 m, 2 w Boxes: 48 metal/soil Pallets: 4 wooden at 79 lb each
Underburden	3 ft	SDA lakebed soil

a. Engineering Design File, EDF-ISV-034.

b. These designations indicate the contents of the cans: s = sludge cans; c = combustible cans; c-g = concrete/glass cans; m = metal cans; w = wood cans. These cans contained the following, approximate amounts of material: sludge can (s) - 10.72 lb (7.72 - H₂O, 0.70 - FLOOR DRI, 2.307 - MICRO-CEL E); combustible can (c) - 3.96 lb (1.901 - cloth, 2.059 - paper); concrete/glass can (c-g) - 16.73 lb (12.0 - concrete, 4.73 - glass); metal can (m) - 6.58 lb (3.29 - carbon steel, 3.29 stainless steel); wood can (w) - 3.14 lb; pallet - 79.0 lb of wood. Boxes contained the following, approximate amounts of material: metal/soil - 119.521 lb (50% carbon steel) or 244.021 lb soil.

Table A-9. Waste material composition for IFT-2 test pit (in pounds).

Materials	Total	Item weight	Waste deposit layers				
			Top can	Mid can	Bot can	Boxes	Pallets
Combustibles	1,513.5						
Cans		813.5					
Paper		411.50	128.24	159.13	124.13		
Cloth		380.00	118.43	146.94	114.63		
Wood		22.00	9.42	6.29	6.29		
Boxes		700.0					
Cardboard		384.00				384.00	
Pallet (wood)		316.00					316.00
Sludge (cans only)	1,436.5						
Water	1,034.5	1,034.50	362.85	254.77	416.88		
Floor Dri	93.8	93.80	32.90	23.10	37.80		
Micro-Cel	308.2	308.20	108.10	75.90	124.20		
Metals	6,757.95						
Cans		1,020.95					
Stainless		131.60	52.64	32.90	46.06		
Carbon steel		889.35	306.39	284.90	298.06		
Boxes		5,737.0					
Stainless		2,868.50				2,868.50	
Carbon steel		2,868.50				2,868.50	
Concrete/glass	12,549.50						
Cans		836.50					
Concrete		600.00	192.00	252.00	156.00		
Glass		236.50	75.68	99.33	61.49		
Boxes							
Soil	11,713.00	11,713.00				11,713.00	
Totals of columns	22,257.45	22,257.45	1,386.65	1,335.26	1,385.54	17,834.00	316.00

a. Engineering Design File, EDF-ISV-034.

Table A-10. Summary of IFT-2 inventories for mid-can region containing Dy₂O₃ tracer material.

Tracer oxide (tracer)	Organic materials	Water
Dy ₂ O ₃ = 2,282 g	≈312 lb (141.5 kg)	Sludge ≈254.8 lb
(Dy = 1,988 g)		<u>Concrete ≈83.2 lb</u>
		Total ≈338 lb (153.3 kg)

Table A-11. Estimate of dysprosium tracer concentration fraction (C_{trac}) and melt time (t_{melt}) for IFT-2.

ISV melt properties	Value
Melt density (ρ_L)	2.2 g/cc
Melt surface area (A)	$\approx (10 \times 10 \text{ ft}) = 9.29\text{E}+4 \text{ cm}^2$

IFT-1 dysprosium concentration

$$I_{\text{trac}} = \text{Total dysprosium tracer inventory} = 1,988 \text{ g}$$

$$X = \text{Soil depth at tracer location} = 4.5\text{--}5.5 \text{ ft} = 137.2\text{--}167.6 \text{ cm}$$

$$X_{\text{ave}} = \text{Average soil depth at tracer location} \approx 152 \text{ cm}$$

$$X_{\text{melt}} = \text{Average depth of molten pool (1/2 soil depth)} = X_{\text{ave}}/2 = 76 \text{ cm}$$

$$V_{\text{pool}} = \text{Melt volume} = X_{\text{melt}} (A) = (43 \text{ cm})(9.29\text{E}+4 \text{ cm}^2) \approx 7.06 \text{ E}+6 \text{ cm}^3$$

$$C_{\text{bulk,trac}} = I_{\text{trac}}/V_{\text{pool}} = (1,988 \text{ g})/(7.06 \text{ E}+6 \text{ cm}^3) = 2.8 \text{ E-4 g/cm}^3$$

$$C_{\text{trac}} = C_{\text{bulk,trac}}/\rho_L = (2.8 \text{ E-4 g-Dy/cm}^3)/(2.2 \text{ g-melt/cm}^3) = 1.28 \text{ E-4}$$

Melt Time

$$t(137.2 \text{ cm; Figure A-7}) = 30 \text{ h}$$

$$t(167.6 \text{ cm; Figure A-7}) = 44 \text{ h}$$

$$t_{\text{melt}} \approx 14 \text{ h} = 50,400 \text{ seconds}$$

$$C_{\text{trac}}(\text{Dy}) = 1.28 \text{ E-4}$$

$$t_{\text{melt}}(\text{Dy}) = 50,400 \text{ s.}$$

This concentration is likewise well below the solubility limit (1 wt%), and since dysprosium was added to the test pit in powder form, it is reasonable to assume that it is dissolved in the melt on a molecular scale.

A-4.2 Rate of Gas Release (R_{gas})

The volumetric rates of gas release (R_{gas}) from pyrolysis are estimated based on the inventories of combustible materials and water contained within mid-can layer (see Tables A-9 and A-10). Similar to assumptions made for the IFT-1, it is presumed that carry-off of dysprosium is associated with release of pyrolysis gases (CO and steam) contained in the mid-can layer where it was placed. Likewise, it is also assumed that such release occurs during the time period it takes the ISV melt front to penetrate the particular layer in which the tracer material was placed (i.e., mid-can layer).

Similar to assumptions regarding IFT-1, it is presumed that all paper, wood, and cloth material have a similar cellulose composition, yielding similar pyrolysis byproducts.³

T93 1410

Figure A-7. History of electrode and melt depth for the IFT-2.

A-4. ESTIMATE OF IFT-2 CONDITIONS FOR ASSESSMENT OF TRACER RELEASE

Similar to the IFT-1, estimates of tracer release from off-gassing and aerosolization of droplets at the melt surface require knowledge of the following IFT-2 conditions:

C_{trac} = fractional concentration of tracer species in the melt

R_{gas} = rate of gas release during melting/tracer release (g/s)

t_{melt} = melt time over which tracer release occurs (s).

Estimates for each are presented in the following sections.

A-4.1 Fractional Concentration (C_{trac}) and Release Time (t_{melt})

For present purposes, C_{trac} and t_{melt} can be estimated assuming that the majority of dysprosium release occurs during melting of the waste layer in which it was originally placed. Thus, the fractional concentration of dysprosium can be estimated using mid-can conditions at depth between about 4.5 ft (137.2 cm) and 5.5 ft (167.6 cm), adjusted for melt subsidence. Based on these assumptions, C_{trac} and t_{melt} are estimated in Table A-11 to be

Pyrolysis byproduct	Fraction
Carbon (retained in melt)	0.10
CO gas (released)	0.80
H ₂ O steam (released)	0.10

Using the inventories given in Tables A-9 and A-10, the following gas composition are estimated for the IFT-2 mid-can layer:

Combustibles	Sludge water	Gas composition	t_{melt}
Total = 141.5 kg CO ≈ 113.2 kg H ₂ O ≈ 14.15 kg	153.3 kg	CO ≈ 113.2 kg H ₂ O ≈ 167.5 kg	50,400 s

Similar to the estimation of the IFT-1 off-gassing conditions, the volumetric rates of gas release (R_{gas} , cm³/s) for IFT-2 was based on the ideal gas law ($PV=MRT$). Noting that IFT-2 was conducted at atmospheric conditions (≈ 1 atm) close to the melt temperature of basalt (≈ 1,720 K), the following volumetric rate of gas release is estimated:

$$R_u = \text{universal gas constant} = 82 \text{ atm-cm}^3/\text{gmole-K}$$

$$M = \text{molecular weight} = 18 \text{ g/gmole-H}_2\text{O}; 28 \text{ g/gmole-CO}$$

$$R_{\text{steam}} = R_u/M = 4.55 \text{ atm-cm}^3/\text{g-K}$$

$$R_{\text{CO}} = R_u/M = 2.93 \text{ atm-cm}^3/\text{g-K}$$

Gas composition, M	Volume, $V=MRT/P$	t_{melt}	$R_{\text{gas}}, V/t_{\text{melt}}$
CO ≈ 113.2 kg H ₂ O ≈ 167.5 kg	≈ 5.7 E+8 cm ³ ≈ 13.1 E+8 cm ³ Total ≈ 18.8 E+8 cm ³	50,400 s	3.73 E+4 cm ³ /s

Table A-12 summarizes parameter values (C_{trac} , R_{gas} , t_{melt}) necessary for estimation of the tracer releases during the IFT-2.

Table A-12. Summary of IFT-2 conditions used to estimate tracer release.

Tracer	t_{melt}	C_{trac}	R_{gas}
Dy	50,400 s	1.28 E-4	3.73 E+4 cm ³ /s

A-5. REFERENCES

1. R. A. Callow et al., *In Situ Vitrification Application to Buried Waste: Final Report of Intermediate Field Tests at Idaho National Engineering Laboratory*, EGG-WTD-9807, August 1991.
2. A. W. Cronenberg and R. A. Callow, *Predictions of PuO₂ and Tracer Compound Release from ISV Melts*, EGG-WTD-10172, April 1992.
3. R. E. McAtee and M. Beal, *Comparison of the High Temperature Chemistry of Plutonium and Rare Earths: A Review Study*, EGG-WTD-9801, September 1991.

Appendix B

Absorptive Bubble Separation Methods

Appendix B

Adsorptive Bubble Separation Methods

This appendix presents an overview of the Adsorptive Bubble Separation process and its potential impact on the transport of tracer/PuO species from basaltic melts during in situ vitrification (ISV).

During ISV, melting organic components are pyrolyzed, resulting in formation of gaseous byproducts (e.g., CO, CO₂, and H₂O) that migrate through the melt and are released at the surface. Such off-gassing and bubble rise through the melt can enhance the migration potential of transuranic (TRU) (and simulate) species. A parallel process in the chemical industry is that of Adsorptive Bubble Separation, where dilute species separation from liquids occurs as a consequence of adsorption of such species onto the surface of bubbles rising through a liquid. Such separation can involve either charged ions, neutral molecules, or microparticles. Factors known to impact the efficiency of the adsorptive bubble separation process are gas sparging rates, species concentration levels, bubble surface area, and ionic strength,¹ which are discussed here relative to their influence on TRU and simulate (Dy₂O₃, Yb₂O₃, Tb₄O₇) release under ISV melt conditions.

B-1. OVERVIEW OF ADSORPTIVE BUBBLE SEPARATION METHODS

As discussed in Reference 1, all methods of separation, whether physical or chemical, are based on differences in properties. For example, distillation is based on differences in volatility, while liquid extraction is based on differences in solubility. Adsorptive Bubble Separation techniques (sometimes referred to as the adsubble process), although less familiar, are of equal importance in the chemical processing industry. Such separation occurs as a consequence of adsorption of dissolved species (either charged ions, neutral molecules, or microparticles) at the surfaces of bubbles rising through a liquid, thereby concentrating and separating such species from the liquid.

As illustrated in Figure B-1,¹ adsorptive bubble separation techniques can be divided into two main groups. The larger group is called foam separation and requires the generation of a foam (large vapor bubbles separated by thin liquid films) to carry off the dissolved material. Examples of separation techniques involving foaming are foam fractionation, froth flotation, and ion flotation, all of which involve the carry-off of dissolved material from a solution via adsorption at the meniscus (liquid interface) between bubbles.

Nonfoaming adsorptive bubble separation processes are also common and occur under less pronounced bubbling conditions. Examples of nonfoaming separation processes are bubble fractionation and solvent sublimation. Bubble fractionation is the transfer of material from a liquid by bubble adsorption and attachment, where bubble rise results in species deposition at free surface of the liquid. Solvent sublimation is the similar transfer to an immiscible liquid above the main liquid.

Bubble fractionation is the simplest of these separation techniques and applies equally well to colloidal and microparticle suspensions, as well as the separation of charge ions and neutral molecules from solutions. As a technique of separation, it suggests itself as a method for concentration or

T93 1414

Figure B-1. Classification of adsorptive bubble separation mechanisms.¹

removing substances present at low concentration levels and without the necessity of foaming. Bubble fractionation is a prime candidate for tracer/TRU release under ISV off-gassing conditions, since in most cases off-gassing occurs as isolated bubbles or as a column of bubbles but not as a true foam.^{2,3} Aspects of bubble fractionation as applied to ISV conditions are discussed below.

B-2. FACTORS INFLUENCING BUBBLE SEPARATION EFFICIENCY

Species concentration, the rates of bubble sparging, bubble surface area, and ionic strength (for ion flotation) are some of the primary factors influencing the efficiency of the bubble separation process,^{1,2} and are assessed here in terms of their influence under ISV melt conditions. It should be noted that the lanthanum-oxide tracers (Dy_2O_3 , Yb_2O_3 , Tb_4O_7) employed in the Idaho National Engineering Laboratory (INEL)-ISV tests can be considered either dissolved as individual molecules³ within the melt and thus subject to simple "bubble fractionation," or as an equilibrium mixture of charged ions at different valance states, and therefore, subject to "ion fractionation."

B-2.1 Bubble Sparging Rate Effects

Investigations concerning ion flotation have been performed at different gas bubbling flow rates to float fine particles and ions.¹ Results are summarized in Figure B-2 for the removal of Sr^{+2} ions from an aqueous solution. As indicated 100% removal is achieved in ≈ 5 minutes at bubble flow rates of ≈ 6.5 L/h, while it takes nearly 25 minutes to achieve an equivalent removal at 1.25 L/h. Thus, the volumetric rate of bubble sparging clearly has a pronounced impact on separation efficiency.

Figure B-2. Variation in Sr^{+2} ion flotation with gas bubble flow rates (A = 1.25 L/h; B = 2.75 L/h; C = 6.5 L/h).¹

B-2.2 Concentration Effects

It has been observed¹ that ion flotation is most efficient at concentrations in the range of 10^{-5} to 10^{-3} moles/L where typical behavior is shown in Figure B-3 for the flotation of yttrium ions (Y^{+3}) in aqueous solutions. As the ion concentration is raised from the lowest values, the stability of the bubbles increases resulting in increasing efficiency for ion flotation and separation. It decreases, however, as the concentrations are raised still further, because in parts of the system localized excess ion concentrations exist that cannot be floated in an efficient manner at finite bubble concentrations. Under such conditions, flotation is impaired. Thus, there exists a maximum ion concentration at which separation is most efficient.

Differences in the concentrations of the rare-earth tracers (Dy_2O_3 , Yb_2O_3 , Tb_4O_7) used in the INEL-ISV tests could have accounted for differences in the releases of these tracers, where concentration effects would also apply to PuO removal from basaltic melts.

B-2.3 Ionic Strength Effects

It has been observed that the presence of salts decreases the efficiency of ion flotation process. Figure B-4 illustrates the effect of the presence of phosphate anions, PO_4^{-3} , sulfate anions, SO_4^{-2} , and chloride anions, Cl^{-1} , on the separation of dichromate ($\text{H}_2\text{Cr}_2\text{O}_7$) ions from aqueous solutions. As indicated, the presence of the weaker Cl^{-1} anions results in a small reduction in the separation of the dichromate ions from solutions; however, if the stronger PO_4^{-3} anions are present a large reduction in the flotation of the dichromate ions occurs. Such results illustrate the impact of ionic charge on overall separation efficiency.

Figure B-3. Dependence of flotation efficiency on Y^{3+} ion concentration levels.¹

Figure B-4. Effect of the addition of anions of different charge on the separation of dichromate ions from aqueous solutions.¹

B-3. REFERENCES

1. R. Lemlich, *Adsorptive Bubble Separation Techniques*, Academic Press, New York, 1972.
2. R. H. Perry et al., "Novel Separation Processes," *Perry's Chemical Engineers' Handbook*, Section 17, McGraw-Hill Book Co, New York, 1984.
3. A. W. Cronenberg, R. A. Callow, and R. E. McAtee, "Use of Rare Earth Tracers as Pu Simulates in ISV Studies," *Proc. 8th Annual Waste Management Symposium, Tucson, Arizona, March 1-5, 1992*.
4. A. W. Cronenberg and R. A. Callow, *Predictions of PuO₂ and Tracer Compound Release from ISV Melts*, EGG-WTD-10172, April 1992.

Appendix C

Aerosol Production by Bubble Bursting

Appendix C

Aerosol Production by Bubble Bursting

Aerosol generation from bubble sparging through liquids occurs as a consequence of bubble bursting at the pool surface, where accelerations experienced by liquid film defining the bubble cap govern the overall amount of liquid aerosol dispersed into the atmosphere. As illustrated in Figure C-1, two types of behavior have been observed in studies of aqueous systems.^{1,2,3} At low gas flow rates, the bursting of single bubbles produce individual fine aerosol droplets, while for high gas flow rates, jetting of liquid occurs, which disintegrates into droplets that are fairly large (on the order of 100 μ). The gas mass flow rate not only influences the aerosolization process but also bubble size. It has been observed that for bubble diameters larger than about 2 mm, the aerosol is largely dictated by the accelerations experienced by liquid films during the bursting process. There is evidence that when large bubbles burst, they also inject small (<1 mm) bubbles into the liquid. It is the bursting of these larger bubbles that is of primary interest here.

Ginsberg^{1,2} and Powers³ have reviewed the literature on the amount of aerosol created by the bursting of relatively large bubbles, where several models have been proposed, which are summarized here.

Figure C-1. Predictions of mechanical aerosolization using the Azbel model where $E = V_{\text{aero}}\rho_1/V_{\text{bubb}}\rho_g$ (calculations assuming $\rho_1 = 1.0 \text{ g/cm}^3$, $\sigma = 400 \text{ dyne/cm}$, $M = 15$, $T = 2,200 \text{ K}$, and $P = 1 \text{ atm}$) (from Reference 3).

C-1. FILM CAP MODEL

An upper limit on the volume of aerosol droplet produce per bubble burst (V_{aero}) can be estimated by assuming that all the volume enclosed within the liquid film cap,^{4,5} just before bubble bursting, is converted into aerosolized droplets. Under this assumption, the ratio of the droplet to bubble volume (V_{aero}/V_b) can be approximated as

$$\frac{V_{aero}}{V_b} = \frac{6A_f\delta}{\pi D_b^3}$$

where

V_b = bubble volume

δ = thickness of the film cap

D_b = bubble diameter

A_f = effective surface area of the film cap at bursting,

which can be approximated as^{1,2}

$$A_f = (\pi/6) [D_b - 0.08a]^3$$

where

$$a = \left[\frac{2\sigma}{(\rho_L - \rho_g)g} \right]^{1/2}$$

and

ρ_L = density of melt (g/cm³)

ρ_g = density of gas (g/cm³)

g = gravitation constant, 980 cm/s²

σ = melt surface tension (dy/cm).

Since in general $\rho_L \gg \rho_g$, so that "a" is small and $V_{aero}/V_b \approx 1$. For the "bubbly flow" regime, the film cap thickness (δ) at rupture has been observed to be in the range 10^{-5} to 10^{-3} cm⁴ with an average value of 10^{-4} ,⁶ thus the volume of the aerosolized melt can be approximated as

$$V_{aero} = (10^{-4}) (V_{bubb}) = (10^{-4}) [\pi D_b^3 / 6].$$

C-2. ENTRAINMENT MODEL

Azbel et al.⁷ assumed that the entire mass of liquid in the film cap is ejected as droplets. The model considers that film-cap rupture occurs from the growth of oscillation disturbances driven by acoustic vibrations in the liquid. Azbel's result for the volume of the film cap can be written as

$$V_{aero} = V_{bubb} \left[\frac{3K_1}{2\pi\rho_g D_b} \right] \left[\frac{\left(1 - \frac{D_b^2}{2k_2} + \frac{9D_b^4}{16k_2^2} \right)^{1/2} + \left(\frac{D_b^2}{4k_2} - 1 \right)}{\left(1 + \frac{3D_b^2}{4k_2} \right) - \left(1 - \frac{D_b^2}{2k_2} + \frac{9D_b^4}{16k_2^2} \right)^{1/2}} \right]$$

where

D_b = bubble diameter

ρ_g = gas density

ρ_L = liquid density

K_1 = $1.15(\pi\sigma/c^2)$

σ = liquid surface tension

c = speed of sound in gas ($\approx 1.08E+4(T/M)^{1/2}$)

T = temperature (K)

M = molecular weight of gas

k_2 = $6\sigma/g(\rho_L - \rho_g)$

g = acceleration due to gravity

E = $V_{aero}\rho_L/V_{bubb}\rho_g$

Predictions obtained from the Azbel model are shown as a function of bubble diameter (D_b) in Figure C-1. The ratio of aerosolized mass to that of the gas bubble ($E = V_{aero}\rho_L/V_{bubb}\rho_g$) is indicated to rise to a maximum for bubble sizes of slightly less than 1 cm. The ratio then varies slowly, about 10^{-4} for larger bubbles. For aerosolized water droplets and steam gas bubbles, a value

of $E = 10^{-4}$ corresponds to $V(\text{aerosol})/V(\text{bubble}) \approx 10^{-8}$. Comparison of this value to that predicted using the film cap model by Toba⁴ indicates that not all the film is aerosolized as assumed in the Azbel model.

C-3. TOMAIDES-WHITBY EMPIRICAL DATA

Tomaides and Whitby⁸ measured the size distribution of water droplets resulting from the surface rupture of 5.5-mm diameter air bubbles in a 0.1% NaCl solution of water. The number of aerosol droplets observed per bubble rupture was ≈ 200 at a droplet diameter of $\approx 10 \mu\text{m}$, so that the volume of liquid ejected per bubble burst is

$$V_{\text{aero}} = 1.2 E^{-6} (V_{\text{bubb}}) .$$

C-4. GARNER, ET AL. EMPIRICAL DATA

Garner, et al.⁹ measured the rate of entrainment of liquid aerosol droplets in air bubble experiments using water, ethyl alcohol, and benzene systems. For bubble diameters in the range of 6 to 12 mm, they measured aerosol droplets in the 8 to 52 μm diameter range, with a peak in the distribution at $\approx 12 \mu\text{m}$. The measured entrainment rate (E) was in the range of about 0.02 to 0.05 for single bubbles. Assuming a density ratio $\rho_L/\rho_g \approx 1,000$, the volume of entrained droplets is thus estimated to be

$$V_{\text{aero}} = 3.5 E^{-5} (V_{\text{bubb}}) .$$

In the same series of single-bubble experiments, the effect of "impure" liquids was studied. The measured effect of the impurities was to increase the delay time for bubble rupture while the bubble is at the liquid surface. The measured entrainment rate for bubbles bursting from a pool of water containing a suspension of calcium carbonate was in the range of $E = 1.3 E^{-4}$ to $2.3 E^{-4}$ for bubbles in the same diameter range as in the pure liquid experiments. This leads to an entrained liquid volume of about

$$V_{\text{aero}} = 2.0 E^{-7} (V_{\text{bubb}})$$

for the water/ CaCO_3 -air system studied. Note that the entrainment rates for the "pure" and "impure" liquids are divergent by two orders of magnitude.

C-5. CIPRIANO-BLANCHARD EMPIRICAL DATA

Cipriano and Blanchard¹⁰ also measured bubble and aerosol spectra in a laboratory simulation of breakup of ocean waves. Their data, obtained in a "multibubble" experiment, suggest that most aerosolized droplets have a diameter of about 10 μm for bubbles $> 1 \text{ mm}$ in diameter. Their results indicate that the rate of droplet production per bubble increases with bubble diameter, while the volume of liquid aerosol per bubble decreases. For 10-mm bubbles, the results of Cipriano and Blanchard¹⁰ suggest the following correlation:

$$V_{aero} = 4.0E-6 (V_{bubb}) .$$

C-6. SUMMARY

Figure C-2 summarizes various estimates for the volume of aerosolized liquid droplets generated per bubble burst at the surface of a liquid pool. As indicated, the data are scattered over nearly three orders of magnitude, suggesting a strong dependence on liquid impurities as noted by Garner.⁹

a. F. H. Garner, et al., "The Size Distribution and Entrainment of Droplets," *Transaction of the Institution of Chemical Engineers* (32), 1954, pp. 222-234.

b. R. J. Cipriano and D. C. Blanchard, "Bubble and Aerosol Spectra Produced by a Laboratory Breathing Wave," *Journal of Geophysical Research* (86), September 1981, pp. 8085-8092.

c. M. Tomaides and K. T. Whitby, "Generation of Aerosols by Bursting of Single Bubbles," *Fine Particles*, B. Y. H. Liu (Ed.), Academic Press, New York, 1976.

d. D. S. Azbel et al., "Acoustic Resonance Theory for the Rupture of Film Cap of a Gas Bubble at a Horizon Gas-Liquid Interface," *Two Phase Momentum, Heat and Mass Transfer in Chemical Process and Energy Engineering Systems*, Vol. 1, Hemisphere Publishing Co., 1978, pp. 159-170.

Figure C-2. Estimates of the aerosol droplet volume produced per bubble (V_{aero}/V_{bubb}) at various bubble diameters (D_b).

C-7 REFERENCES

1. T. Ginsberg, "Aerosol Generation From Sparging of Molten Pools of Corium by Gases Released During Core-Concrete Interactions," *Proceedings of the International Meeting on LWR Severe Accident Evaluation, Cambridge, Massachusetts, August 28 to September 1, 1983*, paper TS11.4.
2. T. Ginsberg, "Aerosol Generation by Liquid Breakup Resulting from Sparging of Molten Pools of Corium by Gases Released During Core/Concrete Interactions," *Nuclear Science and Engineering* (89), 1985, pp. 36-48.
3. D. A. Powers, J. E. Brockmann, and A. W. Shiver, "VANESA: A Mechanistic Model for Radionuclide Release and Aerosol Generation During Core Debris Interactions with Concrete," NUREG/CR-4308, SAND85-1370, July 1986.
4. Y. Toba, "Drop Production by Bursting of Air Bubbles on the Sea Surface: Theoretical Study of the Shape of Floating Bubbles," *Journal of the Oceanographic Society of Japan* (15), October 1959.
5. F. MacIntyre, "Flow Patterns in Bursting Bubbles," *Journal of Geophysical Research* (77), September 1972.
6. J. A. Quinn, "Breaking Bubbles and the Water-to-Air Transport of Particulate Matter," *Chemical Engineering Science* (30), 1975, p. 1177.
7. D. S. Azbel et al., "Acoustic Resonance Theory for the Rupture of Film Cap of a Gas Bubble at a Horizontal Gas-Liquid Interface," *Two Phase Momentum, Heat and Mass Transfer in Chemical Process and Energy Engineering Systems, Vol. 1*, Hemisphere Publishing Co., 1978, pp. 159-170.
8. M. Tomaiides and K. T. Whitby, "Generation of Aerosols by Bursting of Single Bubbles," *Fine Particles*, B. Y. H. Liu (Ed.), Academic Press, New York, 1976.
9. F. H. Garner et al., "The Size Distribution and Entrainment of Droplets," *Transactions of the Institution of Chemical Engineers* (32), 1954, pp. 222-234.
10. R. J. Cipriano and D. C. Blanchard, "Bubble and Aerosol Spectra Produced by a Laboratory Breaking Wave," *Journal of Geophysical Research* (86), September 1981, pp. 8085-8092.11

**DATE
FILMED**

9/12/94

END