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In Situ Vittrification Melt and Confinement Hood
Performance Review

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HOOD PERFORMANCE REVIEW
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Abstract

This document consolidates and organizes information available concerning in situ vitrification (ISV) melt behavior and confinement hood performance. This information is derived from reports of various scaled ISV tests conducted at the Pacific Northwest Laboratory (PNL), the Oak Ridge National Laboratory (ORNL), and the Idaho National Engineering Laboratory (INEL). The objective of this document is twofold: (1) to serve as a central reference of information concerning the reported melt and confinement hood performance under various operating conditions and (2) to identify ISV melt and hood characteristics that require alteration or further investigation through either additional field tests or laboratory experiments.

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1. INTRODUCTION

Tests of in situ vitrification (ISV) have been conducted at different scales using different soils, contaminants (both radioactive and nonradioactive) and burial pit configurations. This report assembles and organizes the information gained from these tests concerning the behavior of the molten soil/waste and performance of the confinement hood. It is prompted from a need to determine (1) the safety of the process by assessing the possibility of radioactive and/or chemical pollution, criticality, explosion, and worker hazards, (2) the suitability of ISV for the treatment of the Subsurface Disposal Area (SDA), and (3) process characteristics that require further investigation through either additional field tests or laboratory experiments.

The organization of this report is as follows. In section 2 the behavior of the molten pool is examined. Effects of soil properties, such as thermal and electrical conductivity, specific heat, and viscosity upon pooling and transient gas release rates are considered. Gas sources and the effects of gas migration through the melt are then addressed, followed by a discussion on contaminant retention and destruction. Next, pooling of dense materials, the possibility of criticality, and relevant experimental findings are discussed. Section 3 examines off-gas and particulate releases during ISV processing. Confinement hood integrity is also briefly addressed. Finally, section 4 summarizes the findings of this report.

2. MOLTEN POOL BEHAVIOR

In the ideal case the ISV process, when applied to contaminated soil, would completely destroy any organic compounds by pyrolysis and retain all contaminants and particulates in the glass product. All contaminants would be dispersed throughout the glass, alleviating any concerns of metal pooling or criticality. Gas release rates would involve no large transients and, as a result, hood design would be simple and based solely upon the steady-state gas release rate. The confinement hood would serve only as a chamber for complete combustion of the pyrolysis products. The off-gas processing trailer would not even be necessary.

However, tests of ISV have shown that organics and contaminants are not completely destroyed or retained by the melt. Pooling of metals and inhomogeneous distributions of compounds have been noted in the solidified product. Furthermore, notable transients of off-gas rates do occur, especially when the melt encounters a large void or a container of mixed organics. These phenomena are largely dependent upon soil characteristics such as thermal conductivity, electrical conductivity, specific heat, and viscosity. By proper addition of chemicals to the soil these properties can be altered and, hence, the phenomena mentioned above can be minimized.

2.1 Effects of Soil Properties on Melt Process Behavior

Several thermodynamic properties of waste or soil have been identified as having a major impact on the ISV process:

- thermal conductivity
- electrical conductivity
- specific heat
- viscosity

The addition of additives to the melt can drastically alter one or more of these properties, with corresponding changes in the behavior of the melt during processing.

Thermal conductivity of soil affects the maximum melt temperature that can be achieved and the maximum melt propagation rate. A low thermal conductivity requires a higher melt temperature for a given rate of melt propagation. A higher melt temperature results in more effluents due to their higher volatility. Very few thermal conductivity measurements are available for soil above 1000 C due to sample deformation (9). Thermal conductivity increases with temperature. Once the soil has become fused (at about 1000 C), thermal conductivity increases with temperature cubed.

Electrical conductivity of soil also increases with temperature. Low-conduction waste sites may require a reduction in the separation distance of the electrodes. If the required voltage for ISV startup exceeds the maximum supply voltage (PNL large-scale power supply has a voltage limitation of 4160 V) the electrode spacing must be decreased. An alternative is the addition of alkali oxides (Na_2O , K_2O , Li_2O , etc.) which increase the electrical conductivity. Soils with large amounts of refractory oxides (SiO_2 , Al_2O_3) tend to have higher viscosities, decreased conduction ion mobility and, hence, lower electrical conductivity (9).

The specific heat of contaminated soil is a measure of the energy required to heat the soil to vitrification temperatures. At low temperatures, there can be significant variations of specific heat for different soil compositions and moisture content. Although specific heat typically increases with increasing temperature the reduction of moisture content, as the process continues, will tend to reduce the specific heat. Finally, at higher temperatures (1500 to 2000 C), the specific heat for most soils will approach a constant value of approximately 0.25 to 0.28 cal/g C (9).

The effects of viscosity upon the behavior of the ISV melt are numerous. Highly viscous melts will have larger internal temperature gradients due to less convective circulation. There is probably less risk of pooling of heavy materials at the bottom of the melt. Since bubble rise rates decrease with increasing viscosity more vapors and gases will remain in the melt for a given operating temperature. However, since highly viscous melts require higher operating temperatures, volatilities are also higher.

The processing characteristics of soils can be modified by additions of Na_2O , NaNO_3 , and CaO . Observations reported in (9) of the effects of Na_2O and CaO on soil viscosity and electrical conductivity are listed below:

- Molten soil viscosity is primarily dependent upon the composition of the base soil. Addition of Na_2O or CaO cause the viscosity to decrease for a given temperature.
- Molten PNL soil viscosity at 1325 C can be decreased from 2000 poise for base soil to almost 10 poise by increasing Na_2O concentration from 3% to 35%.
- Electrical conductivity is primarily dependent upon Na_2O concentration since both CaO and the base soil attempt to dilute the Na_2O and lower conductivity.
- Electrical conductivity of PNL soil at 1325 C can be increased from $0.01 \text{ (ohm cm)}^{-1}$ to $1.4 \text{ (ohm cm)}^{-1}$ by increasing the concentration of Na_2O from 3% to 35%.

Na_2O serves to decrease viscosity and increase electrical conductivity. CaO also decreases viscosity but tends to also decrease electrical conductivity. Hence, addition of Na_2O to a waste site will permit ISV processing at lower temperatures and may prove effective in minimizing volatilization of hazardous compounds.

Reference (15) discusses the addition of NaNO_3 , $\text{Na}_2\text{B}_4\text{O}_7$, and other compounds to INEL soil to alter the viscosity and metal integration in the melt. Results indicate that sodium nitrate selectively oxidizes graphite instead of metal and should not be used for ISV processing with graphite electrodes. Sodium tetraborate addition was not recommended since it did not eliminate voids in the vitrified block.

2.2 Gas Release

Gases other than the vapors from volatile elements can originate from the combustibles, large voids, or containers that burst. These gases are important for the following reasons:

- they provide a pathway upwards through the melt for the additional release of volatiles.
- they increase the load on the off-gas processing system.
- particulates can be entrained by the gases and carried into the off-gas processing system.
- when gases originate or travel up near the electrodes they can increase the effective electrical resistivity of the melt.
- accumulation of gases under the protective cold cap can rupture the cap, thereby increasing particulate, volatile, and heat losses.

The off-gas processing system must be capable of handling transient pulses of gas release and still maintain a slight vacuum in the confinement hood. Estimates of the combustibility limitations of the large-scale off-gas processing system have been made (4):

Combustible Liquids:	9600 lb/yd of depth, or 7 wt%
Void Volumes:	5.6 yd ³ or 152 ft ³
Combustible Packages:	1.2 yd ³ or 32 ft ³
Combustible Solids w/ 30% soil	6400 lb/yd of depth, or 4.7 wt%

These values assume transients of no more than 1 minute. The off-gas capacity of the system is limited by the magnitude and duration of the transient. However, once the transient is over, the system is fully capable of handling another transient of the same magnitude. Although, in general, transient gas generation periods account for little of the processing time the confinement

hood and off-gas processing trailer must be capable of handling any magnitude of transient.

Studies have been done to determine the duration and behavior of various transients. Experiments to determine the pressure rise and release rate of organics in sealed containers have shown maximum pressures in lecture bottles to reach 32 psig and release durations of 1.5 minutes (13). These data indicate that the containers softened, minimizing the pressure rise. Theoretical calculations had predicted pressures of several hundred psi and transient pressure waves of a few seconds (13).

Reference (16) reports results on an engineering scale test conducted by PNL on INEL soil with containers of organics. A sludge/grease mixture containing carbon tetrachloride, trichloroethylene, tetrachloroethylene, trichloroethane, and ethyl ether was placed in a half-gallon glass bottle in the center of a metal/soil mixture. A pressure transducer was plumbed into the lid of the container. The glass bottle reached a maximum internal pressure of 8.6 psig before it breached. The temperature of the soil directly adjacent to the bottle was 200 C.

Intrusion into 55 gallon drums is expected to be very fast, with very rapid release rates. A pilot-scale test was conducted by PNL where a 55 gallon drum, containing combustible waste and soil, was buried 0.3 m beneath the surface and vitrified (9). When the melt first contacted the drum rapid venting of pyrolysis gases occurred with increased particulate loading in the off-gas. This increased rate of release lasted 30 minutes.

In spite of the obvious importance of transient pressure rises due to bursting containers and sudden pyrolysis, little information to characterize these phenomena is available. Research needs to be done to determine the rate with which gases are released from various containers and how large a transient the off-gas processing system can handle without permitting a positive pressure buildup in the hood.

2.3 Retention/Destruction of Contaminants

In the course of ISV processing of hazardous waste gaseous and particulate effluents are discharged. Safety and applicability analysis of the ISV process necessitates characterization of the composition as well as the steady state and transient release rates of these effluents. Ideally, all components of the buried wastes and soil are to be retained and encapsulated by the melt. A measure of performance of the ISV process is the decontamination factor (DF), which is the ratio of the mass of an element or species entering a process to the mass exiting that process. The higher the measured DF for a particular element the better the process performance in retaining or destroying that element in the melt. It is difficult to identify a minimum DF for a process since very toxic compounds demand higher DF's than less toxic compounds. Additionally, if there is a significant amount of an element in the waste, a high DF may still result in a substantial release of that element into the off-gas processing system. However, DF's of 1000 or higher are considered good and correspond to retaining more than 99.9% of that element in the melt.

Many tests have been conducted to assess the DFs for ISV processing of various applicable waste species. These tests may be subdivided by the scale or size of the test (see Table 1) and further subdivided by whether the test was "cold" (no radioactive species present) or "hot" (radioactive species present). A summary of most soil-to-off-gas DFs measured to date is presented in Appendix A. These DFs were determined by analysis of hood and ducting smears, scrub solutions, HEPA filters from the process trailer, and samples obtained from the ISV product.

Table 2.1. Scale sizes of ISV tests

<u>Equipment Size</u>	<u>Electrode Separation</u>	<u>Block Size</u>
Bench Scale	10 cm	1 to 10 kg
Engineering Scale	0.23 to 0.36 m	0.05 to 1.0 t
Intermediate Scale	1.2 m	10 to 50 t
Large Scale	3.5 to 5.5 m	400 to 800 t

Careful comparison of DF values and test conditions show that there are many factors that affect the off-gas rate of a particular species. The effect of burial depth on element retention within the molten soil is very important and is illustrated in Figure 1. The closer the material is to the surface, the less likely the material will be captured by the molten glass. Results from large-scale testing show that retention continues to increase with increasing depths below 1 m. When the burial depths of some metals were increased from 1 m to 5 m an order of magnitude increase in retention was observed (5). From these results it can be inferred that retention rates for bench-, engineering-, and intermediate-scale tests are probably lower than those for large scale tests. This conclusion has implications on the ability to do scaled tests of ISV. Also, the retention of volatile materials can be significantly increased by the addition of extra soil or overburden on top of the waste.

When considering the retention of metals, especially volatile metals, the solubility of the metal and its oxidation state in the melt are also important. The most likely oxidation states for a metal in the melt are either the pure state or the lowest oxidation state that will accommodate a stable oxide (5). This is because the melt is reducing in nature.

Although the ISV process was developed primarily to treat buried inorganic, low-level radioactive wastes it has also been applied to some extent to the destruction of organic materials. Initial tests have shown that most organics are pyrolyzed at the high temperatures of the molten soil but that particulate effluents adsorb some of the organics. In tests conducted by Battelle on soil containing small amounts of PCBs, furans, and dioxins, off-gas analysis revealed concentrations of PCBs in the untreated off-gas in excess of EPA regulations, as well as much smaller concentrations of furans and dioxins (6). No PCBs were detected in the vitrified mass or in the adjacent soil other than directly adjacent to the block, where measurable concentrations of 0.7 ppm PCBs were measured (6). This concentration is below the typical lower limit imposed by EPA for a cleanup action (6).

Figure 2.1 Effect of burial depth upon retention of selected species (9).

PNL conducted an engineering-scale test on December 19, 1989 using INEL soil with an inverted, sealed, half-gallon glass container of mixed sludge and grease. Following rupture of the glass container, persistent flares appeared at the melt surface due to the combustion of the vented pressurized gases (16). This burning of organic vapors above the melt surface indicates incomplete pyrolysis within the melt. The top and bottom of the container were 27 cm and 51 cm below the surface, respectively.

Hazardous inorganic compounds can also be treated by ISV. Nitrates are destroyed by reduction to diatomic gases by the temperature and reducing conditions in the melt. Sulfates are only partially decomposed, the rest must be handled by off-gas processing. Fluorides are almost entirely dissolved into the melt; chlorides are likewise dissolved, but only up to 1 wt% of the melt. Use of a caustic scrub solution in off-gas processing will effectively treat any fluoride or chloride effluents (4).

Gas generation from combustible wastes and the formation and subsidence of a cold cap on top of the melt greatly affect the transient amount of element and particulate loss. The upward movement of gases through the melt increases the entrainment of particles and offers pathways for the increased release of volatile elements. The cold cap operates as a semi-impermeable barrier to the release of vapors and particulates. Convective and radiative cooling of the upper layer of the melt forms the cold cap. Several mechanisms can rupture the cap. Subsidence of the melt beneath the cap, accumulation of gases, or an increase in the power consumption or temperature of the melt may remove the cap.

The rate of element and particulate effluents is lowest during normal operation (1). The affect of the loss of a cold cap is dependent to some extent upon the particular element. For fission products, the loss of a cold cap can increase element release by up to an order of magnitude. For transuranics the affect is much more severe, increasing emissions by up to 4.5 orders of magnitude. Heavy metals are less affected. Increases are less than an order of magnitude. In general, the less volatile an element is, the more its emissions are increased by the loss of a cold cap.

Combustion gas releases affect fission product, transuranic, and heavy metal releases in a similar way. During gas releases, emissions of other elements can increase by up to two orders of magnitude. However, gas generation periods account for <3% of the total run times for these tests (1).

Melt composition, viscosity, and temperature interact and affect the retention factors of various elements in the melt. This is due to the dependence of off-gas rate upon volatility and mobility, which in turn is dependent upon the viscosity of the melt. A comparison study was conducted between the retention of Cs and Sr in vitrified ORNL and Hanford soils (7). Soil samples from each site were contaminated with nonradioactive Cs and Sr. The 100 poise temperatures of the ORNL and Hanford ISV glasses were 1324 and 1665 C, respectively. Table 3, taken from reference (7), summarizes their findings.

Note that increasing the ORNL ISV test temperature from 1325 C to 1650 C decreased the viscosity from 100 to 3 poise and increased the off-gassing concentration of Cs from 5.3 to 220 micro g/ml. However, Hanford's ISV melt off-gas concentration of Cs at 1650 C was only 17.8 micro g/ml. This discrepancy can be explained in part by the much higher viscosity of the Hanford ISV melt. However, when the T100P of the Hanford ISV products was lowered to that of the ORNL ISV product, either by addition of CaO or Na₂O, off-gas concentrations of Cs were still higher than those for the ORNL product. These observations indicate a complicated inter-relationship between composition, temperature, melt viscosity, effluent volatility (a direct function of temperature) and off-gassing rate. The effect of soil composition is small, however, in comparison to temperature and viscosity. Since viscosity decreases with temperature and volatility increases with temperature, effluents are minimized when the ISV process is operated at the lowest feasible temperature. The melt viscosity for INEL soil ranges from 4000 to 5000 poise at 1600 C (8). The significantly higher viscosity of molten INEL soil implies good retention of vapors and particulates in the melt at typical melt temperatures. However, the higher viscosity also suggests longer melt times, higher melt temperatures, and larger temperature gradients (9). Soil additions are a possible consideration to lower the melt temperature and processing time.

Table 2.2. Summary of cesium off-gas and retention results (7)

<u>Glass Product</u>	<u>Test Temperature</u>	<u>Viscosity Poise</u>	<u>Off-Gas Conc. Cs(,micro g/ml)</u>	<u>Retention (wt%)</u>
ORNL ISV	1325	100	5.3	99.865
ORNL ISV	1650	3	220	94.388
Hanford ISV	1650	100	17.8	99.592
Hanford ISV (CaO Adjusted)	1325	100	5.9	99.849
Hanford ISV (Na ₂ O Adjusted)	1325	100	12.8	99.702

2.4 Pooling, Dispersion, and Criticality

The ISV process was originally developed by PNL for immobilization and destruction of inorganic, low-level, radioactive, homogeneous wastes. The technology is now in the process of being extended to include high-level and/or inhomogeneous wastes, such as that at the INEL. This has necessitated the consideration of several new phenomena that can occur in the melt.

When processing a site with dense objects such as I-beams, nuts and bolts, etc., there may be pooling of dense molten material at the bottom of the melt. This concentration of material raises several concerns. First, the accumulated material could conceivably diffuse downward or laterally into the soil at a rate faster than the melt progression with the result that the contaminated waste would not be encompassed by the ISV melt. Experience with PCBs mixed with soil has shown that the vitrification rate is greater than the PCB diffusion rate and that any migration into the soil is unlikely (5). The very bottom of the intermediate scale ORNL solidified test melt was analyzed for composition. The unreacted soil revealed no detectable levels of Cs or Sr (7), indicating that the Cs and Sr were contained within the vitrified mass and did not migrate into the nearby soil. The effect of pooling of a material would be to increase the concentration gradient of material and thus increase the diffusion rate into the surrounding soil.

Pooling of fissionable materials is of great concern since the criticality limit of the material could be reached. This concern will be addressed later. Another concern is that a pool of liquid metal would short the electrodes causing equipment failure and unnecessary restarts. Two engineering-scale tests were conducted during FY88 to study the feasibility of ISV of INEL soils containing a high metals loading. The soil samples had a progressively increasing metallic content with depth. Results of these tests are reported in (8). The process successfully vitrified the soils with localized metal concentrations as high as 42 wt% (total metal concentrations of 16 wt%) without shorting. Examination of the solidified melts revealed large voids in the upper portion of the blocks and large pools of metal at or near the bottom of the blocks. These pools formed in spite of the very high viscosity of the melt (5000 - 6000 poise). It also was noted that the formation of a metal pool at the bottom of the melt promotes downward growth by skewing the power distribution to the bottom portion of the melt. An observation made during test 1 indicated that the metals can cause a loss of conduction between phases rather than a short, although it was also hypothesized that the loss of conduction could have been caused by formation of large voids in the melt. No conclusions were reached other than the inclusion of high concentrations of metals changes the typical resistance curve of the ISV process due to pooling and contact with electrodes.

Materials in the waste that have roughly the same specific gravity as the ISV glass are usually dispersed throughout the melt. The dispersion results in a final product that is homogeneous in terms of concentration. In 1983 vitrified blocks produced by engineering-scale and pilot-scale tests at PNL were analyzed to determine the migration and final distribution of contaminants in the melt (10). No migration of the contaminants was detected beyond the melt zone. It was concluded that the high viscosity at the melt edge prevented any migration. Contaminants were found to be uniformly distributed throughout the block in all tests. This was attributed to good convective mixing in the melt.

Other tests reported similar results. In 1982, engineering-scale tests were conducted on the performance of ISV on mixed hazardous waste including steels, ceramic and glass materials, etc. (11). Nonradioactive cesium,

strontium, and ruthenium were mixed in the soils. No contaminants were detected in the surrounding soil after the test. Ruthenium showed little dispersion. Migration of cesium and strontium in the melt was significant and occurred in all directions, decreasing near the edges of the melt. Cesium showed a somewhat preferential migration in the vertical direction, possibly due to its high volatility. Final concentrations of cesium and strontium were homogeneous throughout the melt.

An intermediate-scale test containing actual radioactive transuranic and mixed fusion elements was conducted at PNL in June, 1983. One of the objectives of this test was to characterize the behavior of the hazardous elements in the melt. Four core segments were removed and analyzed for composition. The distribution of radioactive elements within the samples and throughout the melt was found to be homogeneous with some exceptions (12). Ruthenium tended to concentrate near the top and bottom of the melt. The explanation offered was that ruthenium tends to move towards these cooler regions of the melt due to its volatility. Other radionuclides in the melt (Am, Pu, Cs, Sr, and Co) were uniformly distributed in the melt. Furthermore, the degree of uniformity increased with increasing mass of material in the melt.

The intermediate-scale test melt at ORNL was analyzed for composition. Seven cores were removed from the solidified melt and four samples representative of the melt were submitted for detailed analysis. The composition of all four samples was essentially the same, both in the crystalline and in the glass phase (7). This result indicates that at some point the melt was homogeneous in terms of concentration of species. Homogeneity could have resulted from a combination of molecular diffusion and convective mixing.

Whenever a contaminated site contains fissionable materials it is necessary to evaluate if ISV processing will concentrate the materials or change the moderation properties of the site and increase the potential for criticality. Transuranic elements common to waste sites that may sustain a

nuclear reaction are listed in Table 4 (9). Included in this table are the subcritical mass limits and the estimated radionuclide content of INEL transuranic waste.

PNL (9) identified four changes which occur during the ISV process that affect the amount and degree of neutron-absorbing/reflecting material near the radionuclides:

- soil densifies and becomes glasslike.
- organics and combustibles pyrolyze and are released from the melt.
- water evaporates out of the melt area.
- metals melt and settle to the bottom of the melt zone, leaving most of the vitrified area free of metal.

The removal of moisture from the melt during ISV processing decreases the possibility of criticality and increases the minimum critical mass of plutonium. However, the existence of large quantities of organic materials in the melt increases the potential of criticality. In particular, polyethylene was identified as an organic having very good moderation characteristics. Calculations have shown that the minimum critical mass of plutonium moderated by polyethylene is 0.36 kg (9). During heating, bags, gloves, bottles, and other forms of polyethylene may melt and collect with plutonium in a more dense form at the bottom of a waste container, thus increasing the moderation of plutonium. Although considered unlikely, this phenomenon decreases the estimated critical areal concentration for plutonium to 2.4 kg/m² for a polyethylene reflected system. A conservative value of one third results in an estimated safe ISV operating limit of 0.8 kg/m² when large quantities of hydrogenated organics are present in containers (9). This same reference (9) estimates that in other cases vitrification of a waste site is possible if it has an areal plutonium concentration of < 1.0 kg/m² or if it contains a total plutonium mass of less than 0.6 kg as long as no mechanisms of concentration exist.

Table 2.3. Estimated subcritical mass limits and concentrations of radionuclides in INEL waste (9).

<u>Radionuclides</u>	<u>Subcritical Mass Limit,</u> <u>kg (as metal)</u>		<u>INEL %</u>
	<u>Water</u> <u>Reflector</u>	<u>Steel</u> <u>Reflector</u>	
²³³ U	7	--	--
²³⁷ Np	30	20	--
²³⁸ Pu	4	3	0.008
²³⁹ Pu	5	--	90.420
²⁴⁰ Pu	20	15	5.650
²⁴¹ Pu	6	--	0.000
²⁴² Pu	60	40	0.002
²⁴¹ Am	24	16	3.900

Mechanisms for plutonium concentration were also addressed in (9). These methods were identified as:

- some radionuclides may become insoluble in the ISV glass permitting some fissionable material to settle out.
- dense oxide particles may settle or pool on melt the bottom.
- possibility of reducing conditions to reduce compounds to their metallic state, allowing them to settle and form a more concentrated pool.

Vaporization and resulting condensation may also be a mechanism for concentration of plutonium.

Since the major constituents of both INEL and Hanford transuranic wastes are ²³⁹Pu and ²⁴⁰Pu, PNL performed a criticality analysis for these isotopes. Contaminated waste forms of Pu include sulfates, nitrates, hydroxides, halides, carbonates, and oxides. Of these, the oxide form is most stable. Pu

may also be incorporated into a silicate matrix during ISV. Although the ISV melt is a reducing environment, reduction of Pu from the oxide to the metallic form is not thermodynamically favorable (9).

Determination of the possibility of Pu exceeding the solubility limits of the ISV glass is dependent upon the composition of the glass and the concentration of Pu in the melt. High-level waste glasses, which are similar to ISV glass, have measured PuO_2 solubilities higher than 2% (9).

Concentration of Pu metal or oxide by settlement or pooling are generally felt to be unlikely for two reasons: "1) the ISV melt advances at a very slow rate, $< 10\text{cm/h}$, so that any PuO_2 in the upper part of the melt will have a long time to dissolve before it can concentrate in significant amounts with PuO_2 deeper in the waste site; and 2) PuO_2 is typically a fine powder that, even if it remained undissolved, will become thoroughly mixed within the glass by the characteristically strong convective currents" (9, p. 150). Support for this statement exists in some analysis done in 1983 by PNL (10). Engineering- and intermediate-scale blocks contaminated with cerium as a simulant for plutonium were analyzed for pooling and selective migration. The final concentration of cerium was found to be 14 times less than its original concentration.

On the other hand, observations of metal pooling during INEL tests raise concerns. The specific gravity of INEL melts is 2.38, while that for steel and PuO_2 is approximately 7.8 and 11.46, respectively (8). As discussed in (8), pooling of iron and stainless steel was observed during an engineering scale test with INEL soil. These pools of metal were observed near the bottom of the melt, while small spheres of metal ranging in sizes up to 1mm were dispersed throughout the melt. Since PuO_2 has a specific gravity 1.5 times that of steel, the concern of plutonium pooling on the bottom of the melt is still valid. The viscosity of the INEL melt is 40 to 50 times that of Hanford. For the same operating conditions, the increased viscosity of the INEL melt reduces the rate of pooling (terminal velocity of droplets is reduced) but also reduces any convective currents to disperse the plutonium. Note that INEL melts may be so viscous that the terminal velocity for even large plutonium droplets would be negligible.

An additional concern is, even if there is not enough plutonium in the melt for criticality, that any amount of pooling would create a hot spot in the melt. This hot spot would remain after the melt cooled. The existence of hot spots in the solidified mass could change the leaching characteristics of the glass.

Very limited research has been done to date on the dependence of leaching upon temperature and this research was only for the leaching of sodium at temperatures below 90 C (5). Results of this research show that leaching rates follow an Arrhenius relation with an activation energy of 20 kcal/mole and increase with temperature. At 90 C the measured hydration rate was about 2mm²/yr. No mention was made over thermal degradation of the vitrified glass material due to long term high temperature exposure.

3. OFF-GAS BEHAVIOR AND HOOD PERFORMANCE

Although most gases and particulates are retained in the melt some do escape by various mechanisms. These effluents must be processed to prevent the release of potentially dangerous substances into the atmosphere. A confinement hood is typically placed above the melt to capture and direct the releases to a treatment system. A slight negative pressure is maintained in the hood to ensure all effluents are caught. The discussion in this section will center on the ISV process releases and the structural integrity of the confinement hood.

3.1 Temporal and Spatial Distribution of Effluents and Particulates

Incorporated in the ISV processing system is a metal hood located above the melt. The purpose of this hood is two-fold. It provides support for the four electrodes and serves to confine and direct any particles, volatilized hazardous materials, and acid gases released by the melt to the off-gas processing trailer. The capture of melt releases is ensured by maintaining a slight vacuum in the hood. Although several different hood designs have been used throughout the development of ISV technology some general observations can be made of off-gassing and particulate loading.

In the course of the July 1987 pilot-scale test at ORNL, detailed off-gas analysis was performed. Scrub solution samples were taken at 2 hour intervals during the run (3). The confinement hood was smear sampled at five 10 by 10 cm areas. Four of the five sections of off-gas ducting was also smear sampled.

The pH of the scrub solutions rose from neutral to above 10 within a few hours of the start of the test. Five hours into the test the starter path of Na_2CO_3 had to be reinitiated. The resulting heating and decomposition led to a pulse of Na and dissolved solids in the scrub solutions. Thus, for the first 18 hours of operation, the total solids content of the scrub solution rose rapidly, due to the entrainment of Na_2CO_3 and loose soil under the hood. Most of these solids were suspended rather than dissolved. After 24 hours, the pH of the scrub solution began to drop, to below 4. At first, this

behavior was attributed to the melt front hitting the limestone rocks directly above the waste and producing carbonic acid. The rate of accumulation of particulates in the scrub solution also dropped. Solids were equally dissolved and suspended in the scrub. Formation of a cold cap on the melt was probably the cause of this reduced solids accumulation. The pH continued to fall, even below the limit of carbonic acid. Eventually, alkaline wash solution was added to the scrub tanks to protect them from corrosion. This raised the pH at the end of the test. Samples from the barrels of scrub solution showed that sulfate was the predominant anion present, indicating that SO_2 was the principal contributor to the low pH.

Analysis of the spatial distribution of cesium, lithium, sodium, calcium, magnesium, and strontium demonstrated that over 90% of these materials that were entrained in the off-gas was captured by the scrub solution (96% of the cesium and 92% of the Sr, (14)). Solids and elements such as aluminum, iron, and silicon were more distributed between the hood, ducting, and scrub solution. The primary HEPA filter collected 3.5% of the released Cs and 1.7% of the Sr (14). The final HEPA filter did register amounts of Cs and Sr, but the quantities could not be measured. A suggested improvement was the incorporation of a HEPA filter at the exit of the confinement hood (before the processing trailer) after the initial time period of significant particulates. This HEPA filter would capture the much lower levels of particulates later in the process and could be simply dropped into the melt at the end of use.

Reference (1) describes the particulate mass loading as a function of time for four intermediate-scale tests involving radionuclides and organics. Initial peak mass loadings of 900 to 1400 mg/m^3 occurred within 2 hours of the initiation of the tests. This was attributed to the entrainment of graphite and glass frit startup material. Mass loadings then sharply decreased to 50 mg/m^3 during normal operation. During times of cold cap subsidence the particulate loadings slightly increased due to the loss of the filtering effect of the cold cap. Combustion gas releases also increased the mass loadings. Average particle sizes ranged from 1.4 mm during combustion gas release periods to 0.1 mm during cold cap subsidence with a mean of 0.7 to 0.8 mm during startup and normal operation.

Reference (2) discusses the spatial distribution of contaminants in the off-gas system during PNL's first large scale radioactive test. In general, less than 10% of the total mass released to the off-gas system collected on the hood (2.3% of the silicon and <1% of F⁻, Cl⁻, and SO₄). Exceptions noted were alkali earths (Mg 9.3%, Ca 12%, Sr 17%) and phosphates (26%). Reference (4) noted that during a pilot scale radioactive test cobalt (20%) also tended to accumulate on the hood surface. Reference (12) stated that only a small percentage of elements remained on the soil and glass surface inside the hood. From 65 to 92% of radionuclides released were removed by the scrub solution. More than 97% of the radionuclides were removed from the off-gas system before the first HEPA stage. No gamma emitting radionuclides were detected on the second stage HEPA filter. Also, more volatile elements such as Cs and Ru are released as smaller particles. Thus, these are the most likely materials to reach the HEPA stage. Reference (2), however, noted that a significant amount of aluminum was not retained by the scrub system and was carried to the HEPA filters.

Hood reuse considerations required the identification of a hood interior coating that would immobilize any particulates attached to the inner hood surface (9). This coating would be sprayed onto the inner surface at the conclusion of a run, prevent the loss of any particulates during movement of the hood, and combust due to high interior temperatures during the next run. Desirable properties were identified as (9):

- adherence to vertical surfaces coated with moisture and particles,
- spray application capability,
- easily removed,
- economical, nonflammable, and nontoxic

Seven fixatives were tested by PNL. The fixative selected by PNL for use was polyvinyl alcohol.

3.2 Confinement Hood Integrity

Surges of off-gas due to the bursting of containers and rapid pyrolysis result in pressure and temperature transients. These transients prompt questions concerning the structural integrity of the confinement hood. The large-scale hood designed by PNL incorporates a temperature design limit of 550 C and a pressure limitation of 6 inches of water. To eliminate the possibility of small cracks forming in the hood due to thermal stresses the hood is fabricated from individual stainless steel panels which are bolted together. This construction allows the hood panels to expand and contract independently. A radiative heat shield is installed under the central region of the molten zone to reduce the skin temperature of the hood panels. Currently, the pilot-scale hood at the INEL is constructed of stainless steel panels bolted and spot welded together. No heat shield is incorporated in the design. As a result, substantial warpage, buckling, and popping sounds have been noted during tests.

4. SUMMARY

A technical summary of published ISV test results and observations concerning melt and confinement hood performance has been presented. Although tests were of many different scales and involved different soil constituents, several general observations may be made.

1. Although significant amounts of contaminants are released from the melt during normal ISV processing, the off-gas processing system is effective in removing the contaminants. One reference, however, mentions problems the process system may have with aluminum.
2. Particulate release rates are greatest during the early part of processing and during pyrolysis gas releases.
3. The significantly higher viscosity of molten INEL soil implies good retention of vapors and particulates in the melt. However, the higher viscosity also suggests longer melt times and higher melt temperatures and temperature gradients.
4. Since viscosity decreases with temperature and volatility increases with temperature, effluents are minimized when the ISV process is operated at the lowest feasible temperature. Soil additions are a possible consideration to lower the melt temperature and processing time.
5. Additional overburden and cold-cap retention are other possible techniques for minimizing the quantity of material processed by the off-gas system.
6. More information is needed to assess the hood and off-gas processing system performance during transient releases. Research needs to be done on the rate with which gases are released from various containers and the maximum transients the off-gas processing system and confinement hood can handle without permitting a positive pressure buildup in the hood.

7. Significant migration of contaminants from the melt into the surrounding soil was never noted. The possibility of gas migration into the surrounding soil during processing and subsequent escape into the environment has not been adequately resolved.
8. Pooling of dense materials in the melt was noted in some tests. Pooling tended to increase the melt propagation rate by skewing the power dissipation region to the lower part of the melt.
9. Criticality concerns arising from the possible pooling of radioactive constituents have not been sufficiently resolved although it is questionable if there will ever be enough radioactive material in a melt for criticality. However, any pooling of radioactive material may result in a local "hot spot" or region that will remain at an elevated temperature for a long period of time.
10. Tests are needed to resolve the long term stability and leaching characteristics of the ISV glass at elevated temperatures.

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APPENDIX A
DECONTAMINATION FACTORS FOR VARIOUS ELEMENTS AND TESTS

Trace Element	Ref.	DF	Test Scale	Burial Depth	Notes
Nonvolatile	Simulated	Fission/Fission	Products		
Co	1	8×10^1	Intermediate	0.8 m	Test 4A. Mixed w/PNL soil and tributyl phosphate (TBP) in 55 gal drum.
	3	6.7×10^2	Intermediate	0-2 m	ORNL seepage trench
^{60}Co	4	1.8×10^3	Intermediate		PNL crib waste
Mo	1	$> 1 \times 10^5$	Intermediate	0.8 m	Test 4A. Mixed w/PNL soil in 55 gal. drum.
	1	2×10^2	Intermediate	0.4 m	Test 4B. Mixed w/PNL soil in one of four 5 gal metal canisters.
Sr	1	5×10^4	Intermediate	0.5 m	Test 2. PNL soil mixed w/Cs, Sr, and lanthanides in a 5 gal metal canister.
	1	2×10^3	Intermediate	0.8 m	Test 3. PNL soil, combustibles, and trace elements in 55 gal drum.
	1	8×10^2	Intermediate	0.8 m	Test 4A. Mixed w/PNL soil and TBP in 55 gal drum.
	1	1×10^3	Intermediate	0.4 m	Test 4B. Mixed w/PNL soil in one of four 5 gal metal canisters.
	3	5.0×10^5	Intermediate	1.5 m	ORNL seepage trench
^{90}Sr	4	3.2×10^3	Intermediate		PNL crib waste

Semivolatile Simulated Fission/Fission Products

Cs	1	2×10^3	Intermediate	0.5 m	Test 2. PNL soil mixed w/Cs, Sr, and lanthanides in a 5 gal metal canister.
	1	3×10^1	Intermediate	0.8 m	Test 3. PNL soil, combustibles, and trace elements in 55 gal drum.
	1	6×10^1	Intermediate	0.8 m	Test 4A. Mixed w/PNL soil and TBP in 55 gal drum.
	1	2×10^2	Intermediate	0.4 m	Test 4B. Mixed w/PNL soil in one of four 5 gal metal canisters.
	2	2.3×10^2	Large	6.1 m	LSRT of PNL crib 216-Z-12
	3	8.3×10^2	Intermediate	1.5 m	ORNL seepage trench
^{137}Cs	4	1.3×10^2	Intermediate		PNL crib waste
^{106}Ru	4	5.6×10^2	Intermediate		PNL crib waste
Sb	1	8×10^2	Intermediate	0.8 m	Test 4A. Mixed w/PNL soil and TBP in 55 gal drum.
	1	3×10^1	Intermediate	0.4 m	Test 4B. Mixed w/PNL soil in one of four 5 gal metal canisters.
Te	1	1×10^2	Intermediate	0.8 m	Test 4A. Mixed w/PNL soil and TBP in 55 gal drum.
	1	2	Intermediate	0.4 m	Test 4B. Mixed w/PNL soil in one of four 5 gal metal canisters.

Simulated Transuranics

Ce	1	7×10^2	Intermediate	0.8 m	Test 3. PNL soil, combustibles, and trace elements in 55 gal drum.
	1	9×10^1	Intermediate	0.8 m	Test 4A. Mixed w/PNL soil and TBP in 55 gal drum.
La	1	2×10^2	Intermediate	0.5 m	Test 2. PNL soil mixed w/Cs, SR, and lanthanides in a 5 gal metal canister.
	1	1×10^3	Intermediate	0.8 m	Test 3. PNL soil, combustibles, and trace elements in 55 gal drum.
	1	9×10^1	Intermediate	0.8 m	Test 4A. Mixed w/PNL soil and TBP in 55 gal drum.
Nd	1	5×10^3	Intermediate	0.4 m	Test 4B. Mixed w/PNL soil in one of four 5 gal metal canisters.
	1	1×10^2	Intermediate	0.5 m	Test 2. PNL soil mixed w/Cs, Sr, and lanthanides in a 5 gal metal canister.
	1	1×10^3	Intermediate	0.8 m	Test 3. PNL soil, combustibles, and trace elements in 55 gal drum.
	1	1×10^2	Intermediate	0.8 m	Test 4A. Mixed w/PNL soil and TBP in 55 gal drum.
	1	5×10^3	Intermediate	0.4 m	Test 4B. Mixed w/PNL soil in one of four 5 gal metal canisters.
^{239}Pu	2	5.1×10^6	Large	6.1 m	LSRT of PNL crib 216-Z-12
	4	4.5×10^3	Intermediate		PNL crib waste
^{241}Am	2	2.0×10^9	Large	6.1 m	LSRT of PNL crib 216-Z-12

Heavy Metals

Cd	1	3	Intermediate	0.8 m	Test 3. PNL soil, combustibles, and trace elements in 55 gal drum.
	1	3	Intermediate	0.8 m	Test 4A. Mixed w/PNL soil and TBP in 55 gal drum.
	1	4	Intermediate	0.4 m	Test 4B. Mixed w/PNL soil in one of four 5 gal metal canisters.

Inorganics/Organics/Other

Cl ⁻	2	1.2×10^0	Large	0-7 m	LSRT of PNL crib 216-Z-12
F ⁻	2	6.8×10^2	Large	0-7 m	LSRT of PNL crib 216-Z-12
NO ₃ ⁻	2	5.3×10^1	Large	0-7 m	LSRT of PNL crib 216-Z-12
PO ₄ ⁼	2	8.6×10^1	Large	0-7 m	LSRT of PNL crib 216-Z-12
SO ₄ ⁼	2	1.5×10^0	Large	0-7 m	LSRT of PNL crib 216-Z-12
Al	2	6.6×10^4	Large	0-7 m	LSRT of PNL crib 216-Z-12
	3	9.1×10^4	Intermediate	0-2 m	ORNL seepage trench
B	3	2×10^1	Intermediate	0-2 m	ORNL seepage trench
Ba	3	1.1×10^5	Intermediate	0-2 m	ORNL seepage trench
Ca	2	1.9×10^5	Large	0-7 m	LSRT of PNL crib 216-Z-12
	3	7.1×10^4	Intermediate	0-2 m	ORNL seepage trench
Fe	2	1.1×10^5	Large	0-7 m	LSRT of PNL crib 216-Z-12
	3	1.4×10^3	Intermediate	0-2 m	ORNL seepage trench
Li	3	6.4×10^4	Intermediate	0-2 m	ORNL seepage trench
Mg	2	1.6×10^5	Large	0-7 m	LSRT of PNL crib 216-Z-12
	3	1.2×10^4	Intermediate	0-2 m	ORNL seepage trench
Mo	3	1.8×10^1	Intermediate	0-2 m	ORNL seepage trench
Na	3	1.4×10^2	Intermediate	0-2 m	ORNL seepage trench
P	3	6.5×10^2	Intermediate	0-2 m	ORNL seepage trench
Si	2	1.5×10^5	Large	0-7 m	LSRT of PNL crib 216-Z-12
	3	3.5×10^4	Intermediate	0-2 m	ORNL seepage trench
Zn	3	3.1×10^1	Intermediate	0-2 m	ORNL seepage trench
Zr	3	1.1×10^3	Intermediate	0-2 m	ORNL seepage trench

END

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