Offgas Emissions from the Vitrification of Hanford Envelope C Low Activity Waste

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OFFGAS EMISSIONS FROM THE VITRIFICATION OF HANFORD ENVELOPE C LOW ACTIVITY WASTE

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ABSTRACT

A sample of radioactive waste from Hanford tank 241-AN-102, pretreated to remove undissolved solids, ^{137}Cs, ^{90}Sr, ^{99}Tc, and transuranic elements, was melted in a bench-scale melter to produce a vitrified waste form. The pretreated waste was mixed with glass forming chemicals to give a slurry feed for the melter. Measurements of fixed gas, volatile metal, and particulate offgas emissions were performed. Only small amounts of flammable gases H_2 and CO were formed. The metals and radionuclides with the highest emissions were the more volatile metals, as expected. The more volatile species were B, Na, K, ^{99}Tc, and ^{137}Cs. Boron, ^{99}Tc, and ^{137}Cs evolved at higher rates during idling of the melter that during feeding the slurry. The composition of the particulate emissions approximated the composition of the feed.

INTRODUCTION

A small continuously fed melter was used to vitrify seven liters of pretreated Hanford Envelope C low activity radioactive waste (LAW) from tank 241-AN-102 in support of the Hanford River Protection Project- Waste Treatment Plant (RPP-WTP, or WTP). Hanford Envelope C waste contains large quantities of chelating agents and their breakdown products, such as EDTA, HEDTA, nitrilotriacetic acid, gluconic acid, and iminodiacetic acid; it is also high in sulfate. The waste is EPA listed for numerous RCRA metals and organic species. Pretreatment of the waste prior to vitrification included precipitation of ^{90}Sr by isotopic dilution and transuranic species by addition of $NaMnO_4$, cross-flow filtration to remove entrained and precipitated solids, ^{137}Cs and ^{99}Tc removal by ion exchange, and concentration by evaporation. Glass forming chemicals and minerals were then added to make up the melter feed.

Melter System Design

The design for the melter system was based on scaling the design of the WTP LAW melter. Vitrification of the radioactive pretreated waste required containment in a radiohood, as shown in Figure 1. The melter feed system, melter, and offgas treatment systems were required to function so that no listed RCRA hazardous material was emitted into the laboratory ventilation or drain systems. A major concern, due to the presence of the organic species, was the potential for producing a flammable mixture of CO and H_2 in the offgas. Control of offgas flammability was implemented by continuous monitoring for CO and H_2, with an automatic feed interlock if the percent Lower Flammable Limit (%LFL) exceeded 60%.(1)

A simplified diagram of the melter system is shown in Figure 2. The melter design is shown in Figure 3. The melter is heated with three zones of external resistance heating. Glass temperature is measured using a thermocouple installed in an Inconel™ 690 thermowell and the plenum temperature is measured by two thermocouples. Glass pouring is via an underflow weir into an overflow pipe and is accomplished by building up sufficient feed and glass in the melter such that the hydrostatic head forces the glass to be poured. A vent to atmosphere at the top of the drain tube prevents siphoning of glass.

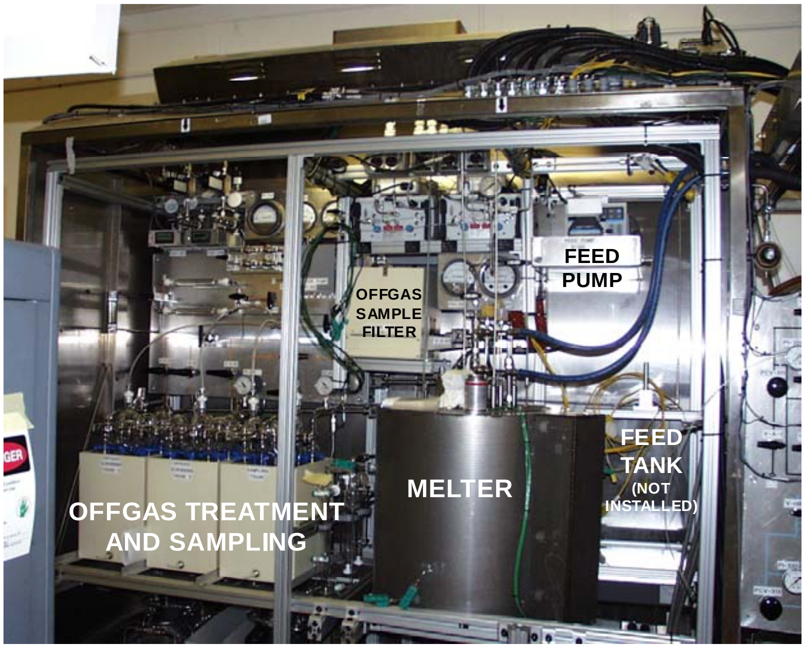

Figure 1. Melter System Photo

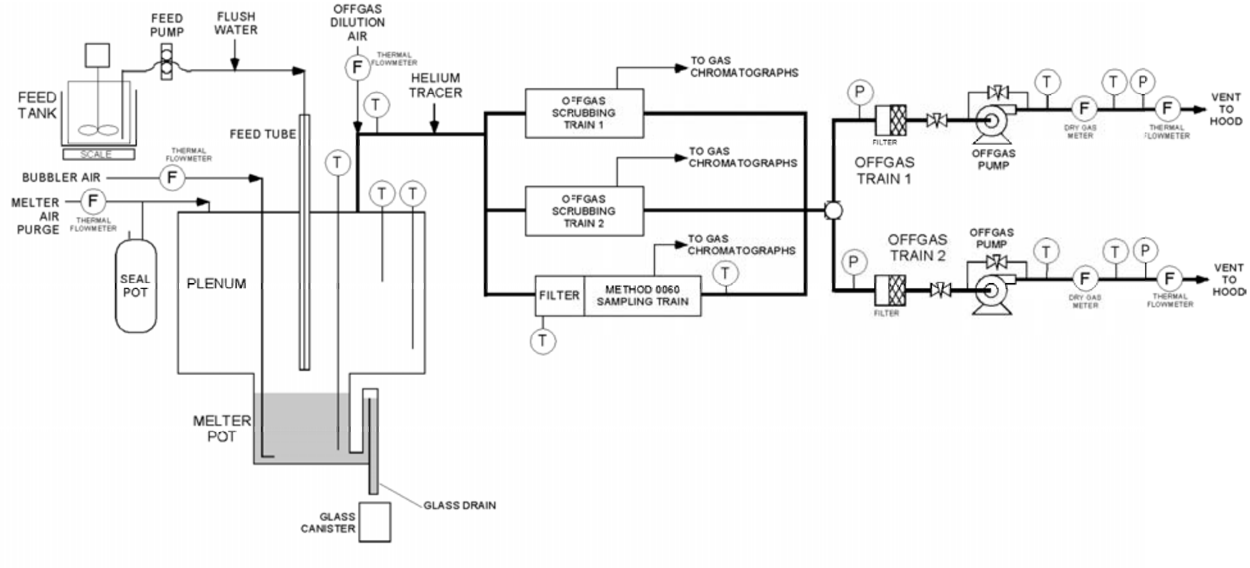

Figure 2. Simplified Schematic of Melter System

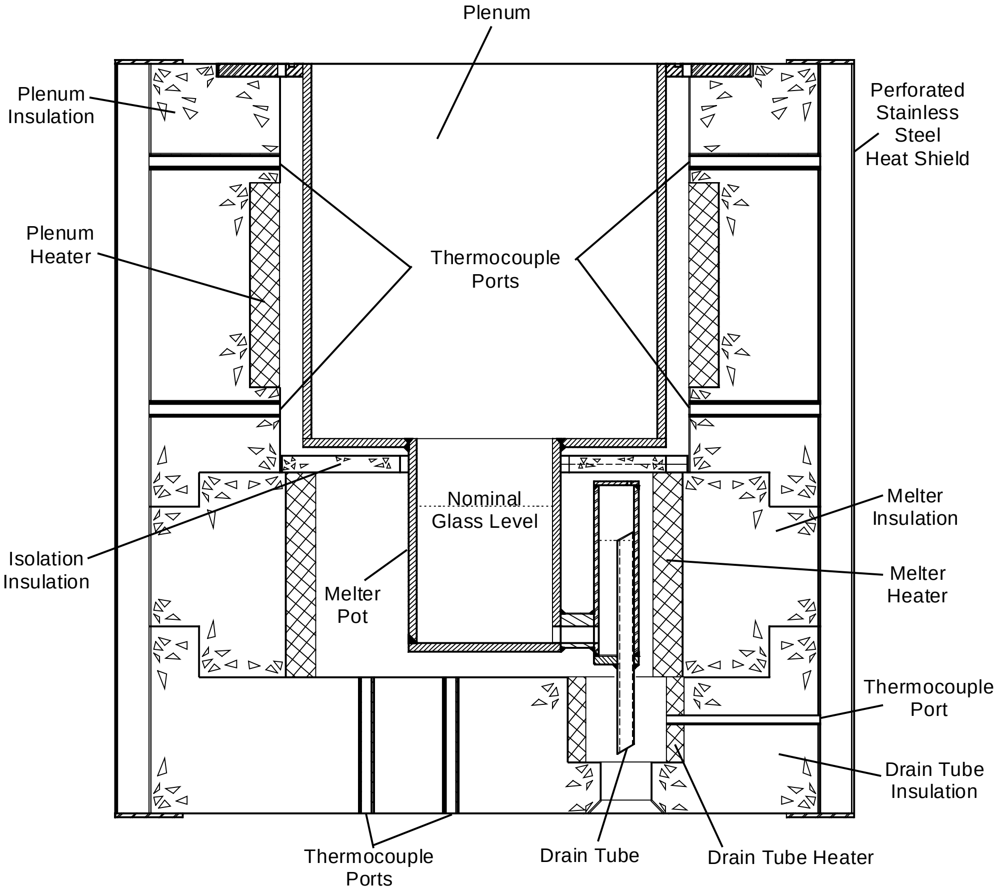

Figure 3. Melter Pot and Heater Design

Table 1 shows comparisons of the full-scale LAW melter and the small scale melter. The surface area of the melt pools was used as the scaling factor for sizing the small scale melter. Therefore, the feedrate, offgas flux, and glass production rates were scaled. The height of the melt pool could not be scaled, so the glass residence time is much less in the small scale melter; the normal glass level was 4-4.5 inches, depending on vacuum. The plenum was scaled to achieve the same residence time as in the LAW melter. The bubbler air flowrate could not be scaled since the volumetrically scaled flowrate (1.6 slpm) through a single tube in the small melter caused violent surging of the glass and cooled the melter too much.

The glass pool dynamics are much different between a melter with a 10 m^2 surface area and a 0.76 m glass depth and one with a 0.00771 m^2 surface area and 0.1 m glass depth. Therefore, the behavior of the cold cap, where the oxidation-reduction (redox) reactions occur, may be different. The evolution of metals and radionuclides from a melter is generally a combination of entrainment and volatilization. A small scale melter should be adequate to quantify volatilized metals and radionuclides since the physical process of volatilization is essentially the same regardless of melter size. However, the process of entrainment is extremely dependent on the melter plenum configuration, including its dimensions, airflow patterns, locations of heaters, etc. Short plenums tend to result in more entrainment than taller ones. The LAW melter plenum is approximately 1.4 m tall, which was impossible to implement in a small melter.

Table 1. Comparison of Small Scale Melter and LAW Melter Designs

MELTER		LAW Melter	Small Scale Melter
Diameter	cm	357 *	10.2
* (if LAW melter were cylindrical rather than rectangular)			
Glass Depth	m	0.76	0.10-0.11
Surface Area	m^2	10.0	0.00771
Surface Area Scale Factor to Full-Scale Melter			1296.6
Glass Volume	liter	7620	0.840
Mass of Glass in Melter	kg	20955	2.31
Glass Production Flux (glass/hr/melt surface area)	kg/hr/m^2	41.67	
Glass Production Rate	Mt/d	10	-
	kg/hr	416.7	0.321
OFFGAS			
Glass Surface Area / Vapor Space Volume	m^{-1}	0.538	
Melter Vapor Space Volume	liter	18580	14.33
Feedrate / Surface Area	liter/hr/m^2	51.00	
Offgas Flux from Feed	kg/hr/m^2	45.8	
Offgas Residence Time in Plenum	sec	27.7	

At the melter exit, a measured quantity of air was immediately introduced to cool the offgas from the melter exit temperature to about 200-350°C. This air addition is similar to the film cooler air that would be introduced in the WTP melter, but no film cooler was actually used in the small melter. The offgas from the melter was directed to any of three offgas scrubbing trains. Two of these were specifically only for scrubbing the offgas, while the third was for sampling via modified EPA SW-846 Method 0060.(2) The Method 60 equipment and methods used followed the method as closely as possible, given the constraints of working in the radiohood. Note that the offgas sampling train served as the actual offgas treatment system during sampling. Impingers containing sodium hydroxide were added before the silica gel to remove acid gases and activated carbon traps were added after the silica gel to remove organics. By extension of Method 60, sampling for additional metals beyond those described by the method and sampling for radionuclides was also performed.

Measurements

The Method 60 sampling train is specified for 17 hazardous air pollutant metals, as given in Table 2. The additional metals and radionuclides of interest to the WTP are also listed. The offgas sampling train was simplified by not measuring mercury; due to its volatility, all mercury fed is evolved to the offgas, so no measurement was needed.

Table 2. EPA Method 60 Metals, Additional Metals and Radionuclides Measured

Method 60	Sb	As	Ba	Be	Cd	Cr	Co	Cu	Pb	Mn	Hg	Ni	P	Se	Ag	Tl	Zn
Added Metals	Al	B	Ca	Fe	K	Li	Mg	Mo	Na	P	Si	Sn	V	Zr			
Radionuclides	Total Alpha	Total Beta	^{60}Co	^{65}Zn	^{79}Se	^{90}Sr (^{90}Y)	^{94}Nb	^{99}Tc	^{103}Ru	^{106}Ru/ ^{106}Rh	^{113}Sn	^{125}Sb	^{134}Cs	^{137}Cs	^{144}Ce	^{152}Eu	
	^{154}Eu	^{155}Eu	^{224}Ra	^{233}U	^{234}U	^{235}U	^{236}U	^{237}Np	^{238}U	^{238}Pu	^{239}Pu ^{240}Pu	^{241}Am	^{241}Pu	^{242}Cm	^{244}Cm		

The application of Method 60 for the added metals and radionuclides has not been qualified by the EPA. However, in lieu of appropriate methods, both SRTC and BWXT Y-12 at Oak Ridge have shown that this method can be used for many metals.(3,4) Metals of interest that have proven to be difficult to quantify are B, Ca, Si, Na, K, Fe, Cr, and Al due to their abundance throughout the environment, in the glassware used in the method, and in the materials of construction of the melter system (Inconel™ 690, stainless steel). The radionuclides ^{14}C, ^{129}I, and tritium were not measured due to the difficulty in quantifying these and also due to limitations on space for installation of additional sampling equipment.

Measurement of the offgas flowrate was done by both a tracer gas method (5) and a calibrated dry gas meter (DGM).(6) The tracer gas was He; it and N_2, O_2, CO, CO_2, H_2, and CH_4 were measured by gas chromatography (GC). The composition of the offgas was used to determine the molecular weight to correct the dry gas meter readings. The He tracer and DGM flow measurements tracked each other reasonably well, with an average difference of less than 1 slpm. The air inleakage into the melter typically ranged from 1-3 slpm.

The melter feed system consisted of an approximately 19-liter, agitated, cylindrical feed tank that was placed on a calibrated scale for feedrate determination. A peristaltic pump was used to deliver the melter feed to the melter via a water-cooled feed tube. The design melter feedrate of about 6-7 ml/min could not be achieved due to feed tube plugging; the actual feedrate was typically 15-20 ml/min.

Results

Two melter campaigns were performed with non-radioactive simulants to test the system. Fixed gas and particulate emissions were measured during the second of these runs. A comparison of the simulant and radioactive waste composition is shown in Table 3. All simulant concentrations have been adjusted to the same Na^+ basis of 7.63M. The simulant was made to be similar to the feed to the Sr/TRU precipitation process, (7) and was then subjected to the precipitation process so that a more realistic simulant would result. The concentrations of most of the major components in the surrogate were very similar to the actual waste, with the exception of TIC. Several of the trace components were significantly different from the actual waste.

Table 3. Pretreated AN-102 Simulant and Rad Waste Compositions

By ICP-ES:	Simulant mg/L	Rad Waste mg/L
Al	8047	8388
B	32	22
Ca	122	176
Cd	<0.05	32.9
Cr	109	117
Cu	13	5.6
Fe	2	4
K	1597	1235
Li	6	<0.2
Mg	0.2	0.1
Mn	45	1.3
Mo	31	35
Ni	180	200
Pb	66	80
Si	24	71
Ti	<0.01	<0.2
Zn	1	2
Zr	0.3	1
Na	175541	175400
Na (M)	7.63	7.63
Carbon		
TOC	11004	10970
TIC	10169	21500
Anions by IC:		
Fluoride	1278	1060
Formate	6901	6450
Chloride	4202	1860
Nitrite	46325	46600
Nitrate	112802	119700
Sulfate	7009	7570
Phosphate	1920	2170
Oxalate	1483	1010
Hydroxide	NA	24800
Carbonate	NA	58400

Radionuclides by ICP-Mass Spectroscopy:	Rad Waste mg/L
mass 99	3.2
mass 230	<0.006
mass 231	<0.006
mass 232 (Th)	1.71
mass 233	<0.006
mass 234 (U)	<0.006
mass 235 (U)	0.0113
mass 236 (U)	<0.006
mass 237 (Np)	0.0853
mass 238 (Pu & U)	1.07
mass 239 (Pu)	0.0169
mass 240 (Pu)	<0.006
mass 241 (Am & Pu)	0.00879
mass 242 (Pu)	<0.006
mass 243 (Am)	<0.006
mass 244 (Cm)	<0.006
mass 245 (Cm)	<0.006
mass 246	<0.006
From ICP-MS:	**µCi/mL**
^{99}Tc	0.0543
By Radiochemistry:	**µCi/mL**
^{60}Co	0.05
^{134}Cs	ND
^{137}Cs	0.07
^{154}Eu	0.04
^{155}Eu	0.03
^{241}Am	0.03
^{90}Sr	1.79
^{99}Tc	0.06
Total Alpha	0.1
Total Beta	6.85

The additives used for glass formation are shown in Table 4. Each of the glass formers contained various impurities. Most of the impurities were major components of other glass formers, except for Mn, K, Ni, Cr, carbonate, ^{238}U and ^{232}Th (from zircon); these were present at up to 0.4 wt%. The targeted waste sodium loading in the glass was 11.8 wt% as Na_2O. Sucrose was also added for redox control.

Table 4. Glass Formers

Kyanite Raw (Al_2SiO_5)	Olivine (Mg_2SiO_4)
Boric Acid (H_3BO_3)	SiO_2
Wollastonite ($CaSiO_3$)	TiO_2
Fe_2O_3	ZnO
Li_2CO_3	Zircon $ZrSiO_4$

The concentrations of offgases measured by the gas chromatographs are shown for a typical feeding period during the radioactive run in Figure 4. Evolution of NO_x was seen by the presence of the yellow-brown color of NO_2 in some of the glassware. No NO above the detection limit of about 2% was seen. At several times, trace amounts of methane, ethane, propane, and isobutane and about 0.1% N_2O were found.

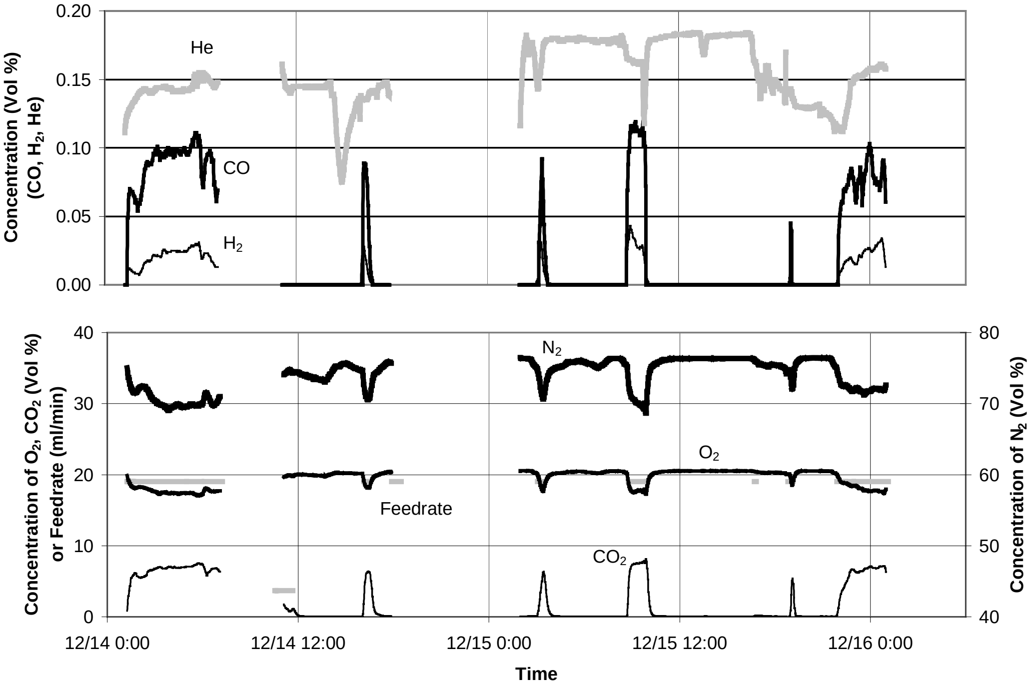

Figure 4. Radioactive Run Offgas Compositions

During feeding, the glass temperature typically ranged from 1080-1130°C. The plenum temperature, offgas flowrate, and offgas temperature are shown for the radioactive run in Figure 5. The plenum temperature dropped to about 550°C, within the 400-600°C WTP range for the two longest feeding periods. On 12/14, the plenum temperature appears to have reached a steady state temperature for several hours. The time from the start of feeding to reaching steady state was about 4-5 hours. During the feeding periods, the cold cap coverage was typically 80-90% of the surface area of the melter. (The cold cap is the unreacted and partially reacted feed material that floats on top of the molten glass.)

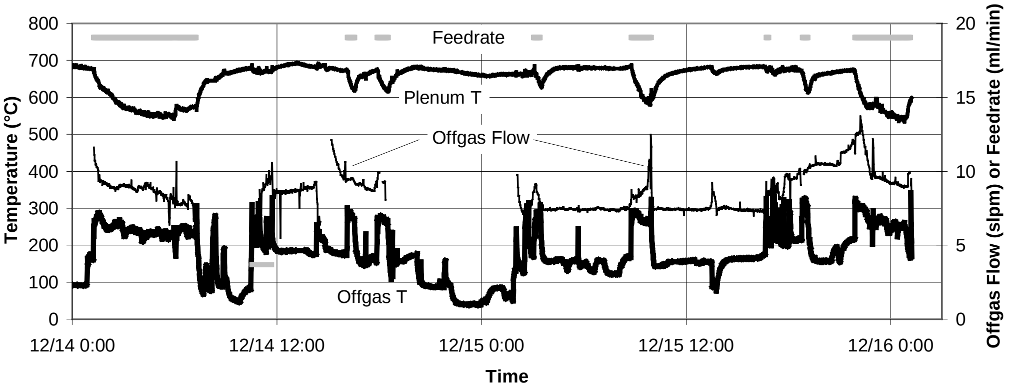

Figure 5. Radioactive Run Offgas & Plenum Temperature and Offgas Flow Data

Material balances on carbon fed versus detected as CO and CO_2 closed to within 3.1% and 5.3%, respectively, for the simulant and radioactive runs, which confirms that the CO and CO_2 measurements were good. Redundant CO_2 measurements gave differences less than 7%.

The rate of generation of offgases from the feed is controlled by the temperature and redox chemistry in the cold cap. These offgases generated then react in the plenum via the water-gas shift, oxidation, and other gas phase reactions. A model for the evolution of H_2 and CO from glass melters has been developed by SRTC.(8,9) This model predicts the concentrations of H_2 and CO as a function of the true plenum gas temperature and the concentrations of oxidizing and reducing species in the feed. The true plenum gas temperature must be determined by an energy balance because the plenum thermocouple readings are affected by the radiant shine from the hot glass and melter walls.

The %LFL for a mixture of CO and H_2 is:

$$\%\mathrm{LFL} = 100\left(\frac{C_{CO}}{12.5} + \frac{C_{H_2}}{4.0}\right)$$

where C_i = concentration in volume %.

The %LFL is dependent on offgas flowrate (dilution by air), the feedrate, and the concentration of the organic species (TOC) in the feed. To compare data on different bases, the %LFL equation can be rewritten to compare quantities that are only dependent on the molar ratios of CO and H_2 evolved to the TOC feedrate (e.g., mol CO / mol TOC fed $\equiv R_{CO/TOC}$). From this analysis, the equation is then:

$$\mathrm{Constant} \times \%\mathrm{LFL} = \frac{R_{CO/TOC}}{12.5} + \frac{R_{H_2/TOC}}{4.0}$$

where the right hand side is independent of flows and concentrations. Therefore, plotting “Constant x %LFL” can be used to compare data from different systems. Figure 6 shows the data for this work along with data from a SRTC Defense Waste Processing Facility (DWPF) pilot melter.(10) The model line fits the data well; all of the data from this work shows much lower flammability than the DWPF pilot work.

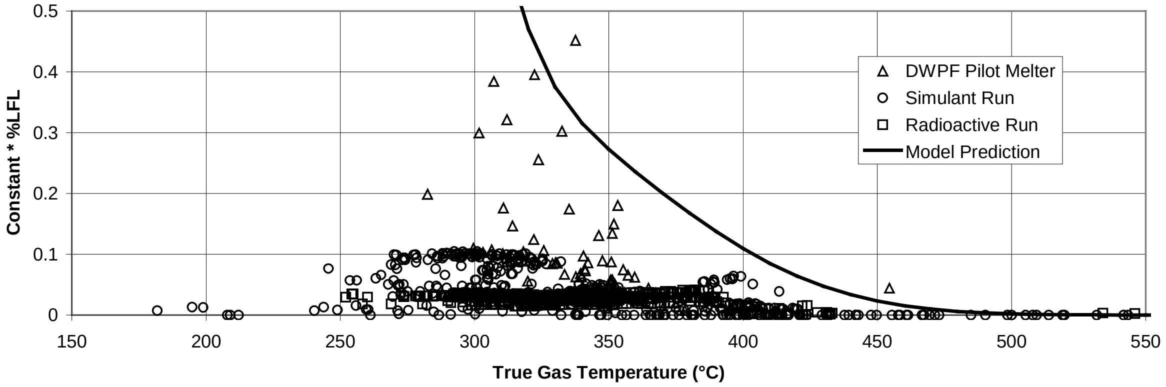

Figure 6. Scaled %LFL versus True Gas Temperature

Some of the melter offgas condensates and carbon traps were analyzed for volatile and semivolatile organics by GC-MS using techniques similar to EPA methods. Organics found in the greatest quantities are shown in Table 5. The diethyl phthalate is probably from the plastic sample bottles used. The prevalence of nitriles may be a result of the organics being scrubbed in the Method 60HNO_3/H_2O_2 impingers. No nitriles were detected on the carbon beds.

Table 5. Organics in Offgas Condensate and Carbon Trap Samples

Condensate	(µg/L)	**Condensate**	(µg/L)	**Carbon Beds**	(µg/g)
Pyridinecarbonitriles	390-520	1-Propene, 1-chloro-, (E)-	49	Methyl formate	25-27
But-2-enedinitrile	200-490	Quinoline	42	Acetic acid, methyl ester	9-55
Diethyl Phthalate	280-300	Isoquinoline	15	Formic acid	20
1,3-Benzenedicarbonitrile	240	Propanedinitrile, methylene-	34		
1,2-Benzenedicarbonitrile	94	Tributyl phosphate	30		
Benzonitrile, 4-hydroxy	60-140	Quinazoline	21		

One particulate sample taken by modified EPA Method 60 during the simulant run was taken while the melter was idled for about 35 minutes, so the particulate collected was only due to volatilization of the glass. As expected, the major component found was boron, which was the most volatile species present in significant amounts. Two offgas particulate samples were taken during the radioactive run. From the concentrations measured in the offgas, the decontamination factor for each species was determined (decontamination factor [DF] is defined as the mass flow in ÷ mass flow out). These DF data are summarized in Table 6 along with the same data expressed as percent retained (in the glass). The elements in this table highlighted in boldface are the ones that are most abundant in the feed. The highest DFs (~4,700-40,000) were found for Zr, Mg, Ca, Mn, Fe, Ti, Li, Zn, and Al. The DF for total particulate was 26720. Previous work (11) with a DWPF pilot melter gave a total particulate DF of about 2600, so the small scale melter had an overall DF that was about 10 times the DWPF pilot value. High DFs would also be expected for the other transition metals, and these ranged from ~250-2000. The DFs of these elements may be lower because they are present in smaller quantities, which result in larger percentage analytical errors.

Table 6. Decontamination Factors and Percents Retained for Elements & Radionuclides

Elements	Mean DF	Percent Retained	Percent as Particulate	Duratek Data Percent Retained	Elements	Mean DF	Percent Retained	Percent as Particulate	Duratek Data Percent Retained
Total Particulate	26720	-	-	-	K	227	99.56	95.6	98.97
Zr	34416	>99.99	95.4	>99.99	Be	NA	NA	50	
Mg	20939	>99.99	33.5	>99.99	Sb	NA	NA	88.9	
Ca	15354	>99.99	57.6	99.98	Tl	NA	NA	61.1	
Mn	9001	99.99	85.9	99.95	As	NA	NA	50	
Fe	7290	99.99	90.5	99.99	Se	NA	NA	94.4	
La	<6459	<99.98	50.0						
Ti	6166	99.98	98.3	99.97					
Li	5474	99.98	98.6	99.94	**Radiochemical**				
Zn	4928	99.98	87.6	99.96	^{60}Co	<2750	<99.96	74.2	
Al	4495	99.98	88.7	99.99	^{137}Cs	82	98.79	99.8	96.96 *
Sn	3666	99.97	62.6		^{154}Eu	<2953	<99.97	92.4	
Sr	3452	99.97	90.2		^{155}Eu	<1316	<99.92	90	
P	2442	99.96	75.9		^{241}Am	<724	<99.86	92.5	
V	<2349	<99.96	53.2		Alpha Count	9770	99.99	92.3	
Ni	1980	99.95	63.1		Beta Count	806	99.88	99.9	
Ba	1723	99.94	72.5		^{90}Sr	2622	99.96	98.3	
Pb	1506	99.93	83.6		^{99}Tc	7.44	86.55	99.9	
Co	1213	99.92	84.2		ND: Pu^{238}, Pu^{239}/Pu^{240}, Pu^{241}, Ra^{226}, Cs^{134}, Eu^{152},Ru^{103}, Ru^{106}/Rh^{106}, Sb^{125}, Am^{241}, Ce^{144}, Sn^{113},Cm^{244}, Zn^{65}, Nb^{94}				
Ag	<688	<99.85	50.0						
Cd	675	99.85	90.1						
Na	646	99.84	94.6	99.77	**ICP-MS**				
Si	351	99.71	96.2	99.99	^{99}Tc	6.73	85.13	99.7	
Mo	302	99.67	91.2		mass 232 (Th)	9562	99.99	82.5	
Cr	235	99.57	97.0	99.23	mass 238 (Pu & U)	10126	99.99	70	
B	230	99.56	42.2	99.81	All other masses between 230 & 246	~<430	~<99.8		
Cu	229	99.56	90.3					* non-radioactive Cs	

NA: not available, not measured in feed
"<": at least on measurement less than a blank
ND: not detected in feed or offgas

The DF for silicon is lower than expected due to the difficulty in performing the blank correction for the quartz filter paper; Mg and Ca also had high blank concentrations. Most of the metals found in the offgas are probably due to entrainment of feed or glass particles, as evidenced by the prevalence of the glass formers and sodium. The particulate percentage of the offgas emissions of most of the transition metals are greater than 90%, with the exception of metals present near their blank values (Cd, Co, Cu, Ni). A comparison of the percents retained between this work and from a Duratek (12) RPP-WTP pilot-scale melter shows similar trends, with K, B, Cr and Na having the lower values.

The DFs reported for ^{60}Co, ^{154}Eu, ^{155}Eu, and ^{241}Am are all based on values that were below the detection limits, and so are based on the detection limits. The DF for ^{90}Sr (~2675) is close to that found for total Sr (~3450). The Cs DF was approximately 82, which is very close to the DF of 130 found for measurements of non-radioactive Cs in the DWPF pilot melter.(13) The percent retained measured in this work for ^{137}Cs (99.79%) is much larger than that found for non-radioactive Cs by Duratek (96.96%).(12) The ^{99}Tc percent retained was low at 85.2-86.6, which is expected due to the volatility of both $NaTc_2O_4$ and Tc_2O_7. The DFs for masses 232 and 238 and alpha counts were very high, as to be expected with the nonvolatile actinides. Most of the radionuclides were found predominately on the filter, except for masses 232 and 238. It seems unusual that these actinide metals (82.5 and 70.0 %, respectively) would have a smaller particulate fraction than more volatile elements such as Cs or Tc. These low measurements for masses 232 and 238 (alpha emitters) are supported by the low particulate percentage for alpha count (92.3). Masses 232 and 238 (Th & U) were present in the zircon flour glass former, so masses 232, 238 and Zr would be expected to have similar DFs. The DF for Zr (34400 – 40200) is of similar magnitude to those of mass 232 Th (9562 – 18950) and mass 238 U (10130 – 16010). The major beta emitter, ^{90}Sr, had a DF of 2622 which is of similar magnitude to the beta count (806).

The percents retained for ^{137}Cs and ^{99}Tc were 99.79% and 85.2-86.6, respectively. However, these same values, when calculated from the feed concentrations and the glass analyses, were found to be much lower. Table 7 compares the percents retained in the glass calculated by these two methods along with values determined elsewhere from other melter studies.

Table 7. Radionuclide Percents Retained in Glass

This Work				**Referenced Work**	
Radionuclide	**Method***	**Percent Retained (Glass / Feed)**	**Percent Retained Calculated from Offgas Measurements**	**Percent Retained**	**Source**
^{60}Co	Rad. Chem.	95.5 ± 9.9	<99.96		
^{137}Cs	Rad. Chem.	73.1 ± 11.0	99.79	96.96 102.1 ± 5.1 95.65	Duratek (12) DWPF Melter (14) DWPF Pilot Melter (14)
^{154}Eu	Rad. Chem.	98.3 ± 15.7	<99.97		
^{155}Eu	Rad. Chem.	109. ± 57.	<99.92		
^{241}Am	Rad. Chem.	37.0 ± 5.9	<99.86		
^{90}Sr	Rad. Chem.	93.1 ± 19.5	99.98		
^{99}Tc	Rad. Chem.	28.0 ± 0.6	86.6	99.13 69.09	DWPF Melter (14) DWPF Pilot Melter (14)
^{99}Tc	ICP-MS	30.8 ± 4.1	85.2		
Total Alpha	Rad. Chem.	37.6 ± 1.7	99.99		
Total Beta	Rad. Chem.	67.0 ± 20.4	99.88		
mass 232 (Th)	ICP-MS	80.4 ± 68.6	>99.99		
mass 235 (U)	ICP-MS	73.0 ± 11.5	<99.93		
mass 237 (Np)	ICP-MS	48.8 ± 3.2	<99.91		
mass 238 (Pu & U)	ICP-MS	88.9 ± 56.2	>99.99		

Note: ± uncertainties shown are one standard deviation.
* Rad. Chem.: Radiochemical analysis; ICP-MS: Inductively Coupled Plasma- Mass Spectrometry

The high percent retained values for ^{60}Co, ^{154}Eu, ^{155}Eu, and ^{90}Sr agree very well. However, note that the uncertainties for the glass/feed calculated values for ^{154}Eu and ^{155}Eu are very high. The amounts retained for masses 232 and 238 calculated from glass/feed are also low, but again the uncertainties are high. The glass/feed values for total alpha, total beta, ^{241}Am, and masses 235 and 237 are also much lower than the offgas values. These low values were not expected and we can offer no explanation for them.

The percents retained for ^{137}Cs and ^{99}Tc from the two methods are consistent in that by either calculation they are lower than the other values, i.e., the major metals and nonvolatile radionuclide ^{90}Sr, but the absolute values are much different. As shown by the data in Table 7 (from previous melter studies at SRTC), the volatility of ^{99}Tc was much higher in the SRTC research melter which had a small cold cap versus the larger DWPF melter, which was operated with a significant (>90%) cold cap. About 31% of the ^{99}Tc was lost in the research melter, while virtually no loss was found for the DWPF melter. For these same conditions, 4% or less ^{137}Cs was lost from these and the Duratek melter.

A hypothesis that could account for the actual losses of ^{99}Tc and ^{137}Cs is as follows. Feeding of the LC melter comprised only a relatively small portion of the total time the system was operated; there was significant idling time with no cold cap. We can assume that both of these radionuclides were evolved during feeding at the DF values calculated from the offgas data during feeding, but at some unknown higher rates during idling. To estimate these unknown rates of volatilization, the addition of feed and volatilization were modeled for the entire run. The rate of volatilization was then determined to make the final concentrations in the glass equal to those measured.

Figure 7 shows: the amount of glass produced throughout the run ; an indicator of can number; and the hypothetical concentration of ^{99}Tc in the glass. The final concentration was set to be 0.0065 μCi/g glass. The maximum possible Tc^{99} in the glass was 0.0216 μCi/g glass; this calculated amount accounts for the loss of Tc^{99} measured during feeding (from the measured DF). A similar graph can be drawn for ^{137}Cs , but is not shown here. The final concentration of ^{137}Cs was 0.0255 μCi/g glass and the maximum possible was 0.0346 μCi/g glass.

This analysis was complicated by the way the glass sample was taken. Approximately 500 g of glass was taken from both can 5 and can 6. Each can's glass was crushed and mixed to get a somewhat representative sample of all the glass in the can. Each 500 g sample was then put through a reheat and cool-down cycle, wherein the glass was maintained at 1150°C for four hours. We assumed that Tc^{99} and Cs^{137} both volatilized during these reheats. After the reheats, the two 500 g samples were again crushed and mixed together. The final glass sample was from this mixture.

The addition to the melter was modeled as a simple stirred tank, while the volatilization was modeled as an exponential decay.

Addition:

$$C_o = \frac{C_i\left(e^{k_A t} - e^{k_A t_o}\right) + C_{oi} e^{k_A t_o}}{e^{k_A t}}$$

where C_i = concentration of species in melter feed on an oxide basis (μCi/g glass)
C_o = concentration of species in the glass in the melter (μCi/g glass)
t = time (min)
t_o = initial time (min)
m = melter feedrate on oxide basis (g feed as oxide / min)
M = mass of glass in melter (g)
C_{oi} = initial concentration of species in the melter at $t = t_o$ (μCi/g glass)
k_A = m/M

Note: C_i is adjusted for loss of species to offgas during feeding (DF).

Volatilization:

$$\frac{C_o}{C_{oi}} = e^{-k_V(t-t_o)}$$

where C_o, C_{oi}, t are as defined above; t_o = time at start of the loss by volatilization (min), and k_V is a constant.

The hypothesized volatility shown in Figure 7 does not seem unreasonable. This analysis is based on limited data with significant uncertainty, but the basic conclusion is still reasonable. It appears that the volatilities of both ^{137}Cs and ^{99}Tc, when compared on a rate basis, are much more of a concern during idling of the melter than during feeding. Therefore, quantification of volatility during idling may be an important measurement that should be made.

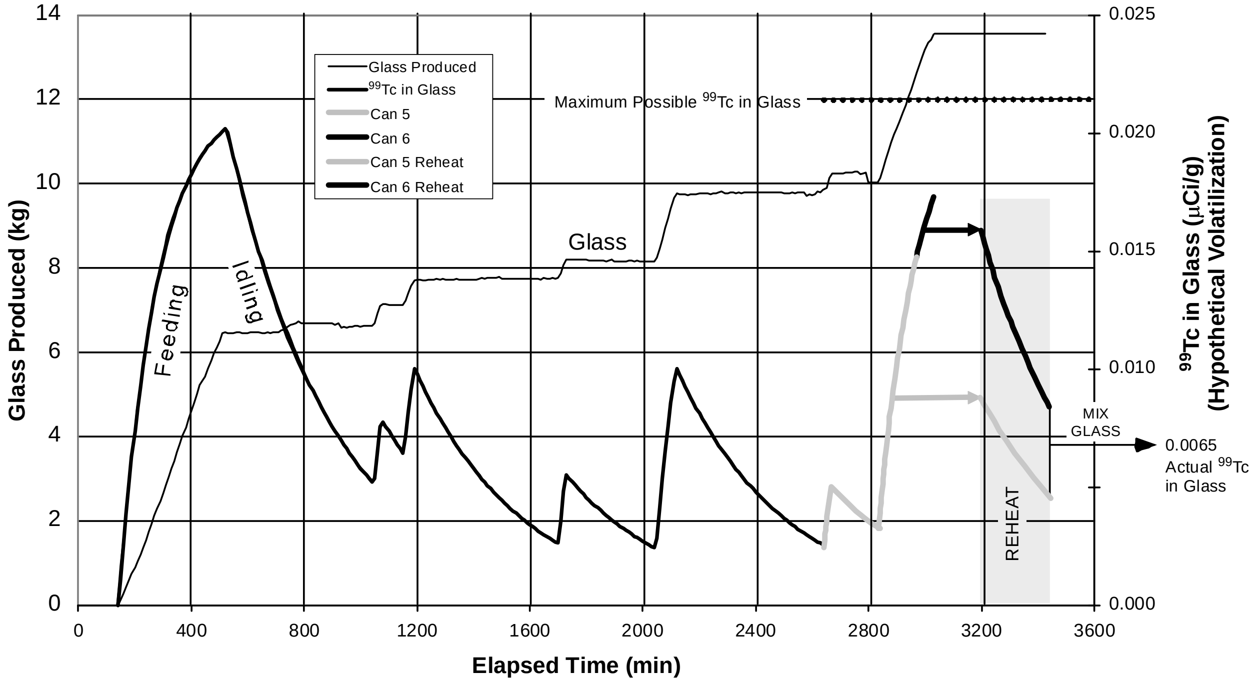

Figure 7. Hypothetical Volatilization of ^{99}Tc.

Conclusions

The relative emission rates for most of the non-radioactive elements were in the ranges expected. The particulate collected tended to mimic the composition of the feed, indicating the expected entrainment as the primary mechanism of emission. The volatile sampling showed that the most volatile element was boron, as expected. Mg, Tl, Ca, Sn, and P also showed more volatility than the other metals. The least volatile were Li, Zr, Ti, Fe, Ca, Al, and Zn. The overall particulate DF was found to be about 27,000 and the more abundant metals ranged from 4700 to 40,000. The DFs for ^{137}Cs and ^{99}Tc were about 82 and 7, respectively. The ^{137}Cs DF is in good agreement with previous studies. The DFs for alpha count, ^{90}Sr, mass 238, and mass 232 were over 10^3, which indicates these components were retained in the glass at >99.9%. Beta count (mostly ^{90}Sr) was retained at 99.8%.

Comparison of DFs measured during feeding for ^{137}Cs and ^{99}Tc suggests that much more of these volatile radionuclides were retained in the glass versus measured dissolved glass/feed ratios. These data have been explained by consideration of the overall idle times vs. feed times of the melter and by the additional 4-hr melt and cooling that was performed on the analyzed melter glass.

Offgas composition measurements by gas chromatography showed the main offgas component from the feed was CO_2. NO_x was also present, as seen visually in the offgas glassware. Insignificant quantities of H_2 and CO were found during feeding.

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