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VOLATILIZATION OF HEAVY METALS AND RADIONUCLIDES FROM SOIL HEATED IN AN INDUCTION "COLD" CRUCIBLE MELTER

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ABSTRACT
The behavior of heavy metals and radionuclides during high-temperature treatment is very important for the design and operational capabilities of the off-gas treatment system, as well as for a better understanding of the nature and forms of the secondary waste. In Russia, a process for high-temperature melting in an induction heated "cold" crucible system is being studied for vitrification of Low Level Waste (LLW) flyash and SYNROC production with simulated high level waste (HLW).

This work was done as part of a Department of Energy (DOE) funded research project for thermal treatment of mixed low level waste (LLW). Soil spiked with heavy metals (Cd, Pb) and radionuclides (Cs-137, U-239, Pu-239) was used as a waste surrogate. The soil was melted in an experimental lab-scale system that consisted of a high-frequency generator (1.76 MHz, 60 kW), a "cold" crucible melter (300 mm high and 90 mm in diameter), a shield box, and an off-gas system. The process temperature was 1350-1400°C. Graphite and silicon carbide were used as "sacrificial" conductive materials to start heating and initial melting of the soil batch. The off-gas system was designed in such a manner that after each experiment, it can be disconnected to collect and analyze all deposits to determine the mass balance. The off-gases were also sampled during an experiment to analyze for hydrogen, NO_x, carbon dioxide, carbon monoxide and chlorine formation.

This paper describes distribution and mass balance of metals and radionuclides in various parts of the off-gas system. The leach rate of the solidified blocks identified by the PCT method is also reported.

INTRODUCTION
In selecting a thermal treatment for mixed wastes, distribution of radionuclides and toxic metals produced by different melter designs has to be evaluated to evaluate the capabilities of the technology. One of the alternative melter designs is a high-frequency induction cold

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crucible.[1,2] The main advantages of the cold crucible over other designs are as follows: higher temperature capability, small dimensions yielding a small working inventory, high productivity, and low corrosion due to generation of the protective lining slag "cold skull" on the water-cooled metal tubes. Also, the melts have very active hydrodynamic regimes which produces good mixing. This is very important to obtain the mass balance and partitioning data for the selected elements, as well as to quantify the gaseous products.

Soils from the Idaho National Engineering and Environmental Laboratory (INEEL), contaminated with radioactive and hazardous components were used as a waste stream for lab-scale cold crucible tests at Khlopin Radium Institute (KRI), St. Petersburg, Russia, in collaboration with the SIA RADON, Moscow, Russia, and the INEEL, Idaho Falls, ID, USA. The work was funded by the U.S. DOE through the Mixed Waste Focus Area (MWFA).

EXPERIMENTAL PROGRAM

Description of Lab-Scale Cold Crucible System

The lab-scale cold crucible system shown in Figure 1 consists of the cold crucible, installed in a protective metal box equipped with an off-gas system where gases can be periodically sampled.

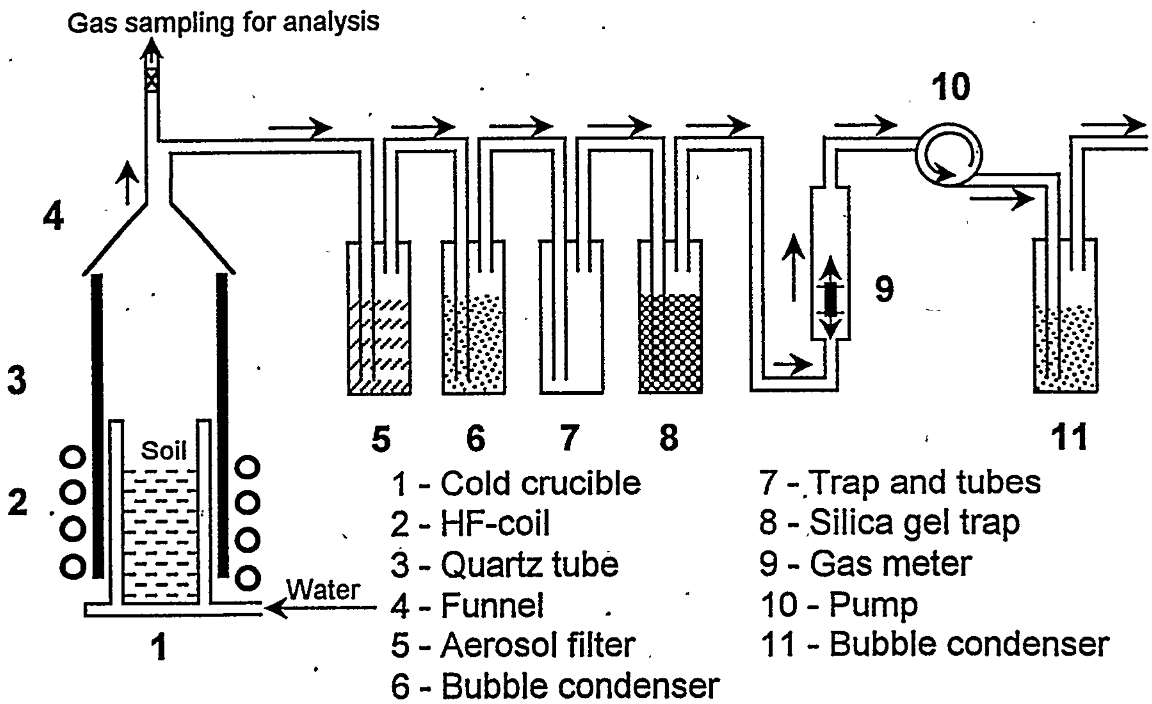

Figure 1. Schematic of Off-Gas System Design

The cold crucible itself is a vessel formed by copper tubes placed within a copper induction coil. The tubes are internally water-cooled, so even when the feed is melting at

1350-1400°C the tubes remain cool producing a protective "cold skull" slag layer between the melt and the tubes. The cold crucible is 300 mm high and 90 mm in diameter, with a processing volume of 800 cm^3. The crucible is surrounded by a four-turn inductor energized by a high frequency (1.76 MHz) 60 kW generator.

To collect all products generated during various stages of thermal treatment, a quartz tube was installed between the outer walls of the crucible and the inductor. Off-gases flowed upward through the tube and gathered under a quartz funnel, then passed through an aerosol filter packed with fine fiber glass wool (5), a bubble condenser (6), reservoir (7), silica gel trap (8) and a final bubble condenser (11). The pump (10) provided the vacuum, and flow was measured by a rotameter (9).

After each experiment, the off-gas system was dismantled to analyze samples taken from its various parts. The off-gases were first sampled in vacuum gas pipettes (500 cm^3) and in the liquid absorbent. Such gas components as carbon dioxide, carbon monoxide and hydrogen were analyzed by chromatography with an error of ± 10%, but NO_x and chlorine were analyzed by an iodine metric method with an accuracy of ± 15%. In some experiments, prior to washing the quartz tube, samples of the deposits on the tube's internal surfaces were collected for X-ray analysis.

Soil Characterization and Batch Preparation

All experiments were performed with the soil received from INEEL. The soil had the following chemical composition (wt. %): Al_2O_3 - 13.0; SiO_2 - 73.0; Fe_2O_3 - 4.5; MgO - 5.0.; CaO - 4.0; Na_2O - 0.5, with the density of 1.08 g/cm^3. Tables I and II show the differential thermal analysis DTA and X-ray analysis data for the soil.

TABLE I

Differential Thermal Analysis (DTA) Results for INEEL Actual Soil

t°C	Transformation
120 (-)	Free water loss
400 (-)	Crystalline water loss, recrystalization of illite
660 (-)	Crystalline water loss for chlorite
840 (-)	Decomposition $CaCO_3$; $MgCa(CO_3)_2$
	Total mass loss ~ 13 %wt

Sample batches for the experiments were prepared by mixing the high silica soil with sodium carbonate (Na_2CO_3) to reduce the electric resistivity, as well as nitrates of the heavy and toxic metals U, Ce, Cd, and Pb to provide the required contaminant concentrations. Two experiments were also made with soil spiked with Cs–137 and Pu–239 added in the form of nitric acid solutions. A well-mixed batch was charged into the cold crucible that, together with the inductor, was placed into the shielded process box. Finally, the off–gas system was connected by the quartz tube.

TABLE II

X-ray Data for INEEL Actual Soil

Mineral composition	Chemical composition	Concentration, wt%
α–quartz	SiO_2	43
oligoclase	$(Ca_xNa_{1-x})Al_{2-x}Si_{2+x}O_8$	14
calcite	$CaCO_3$	10
dolomite	$CaMg(CO_3)_2$	7
chlorite	$(Mg,Fe)_{6-2x}(Al,Fe)_{2x}[OH]_8\{Si_{4-2x}Al_{2x}O_{10}\}$	9
illite	$K_{<1}(Al,Fe)_2[OH]_2\{AlSi_3O_{10}\}nH_2O$	17

RESULTS

The initial melt in the crucible is formed by inductive heating of small pieces of graphite or silicon carbide placed on the batch surface in the crucible. Once the melt starts forming, heating of the whole bulk continues until all the material is melted. The process has three different stages of melting as shown in Figure 2, and depends on the power consumption. A steady state melt temperature was maintained at 1350-1400°C.

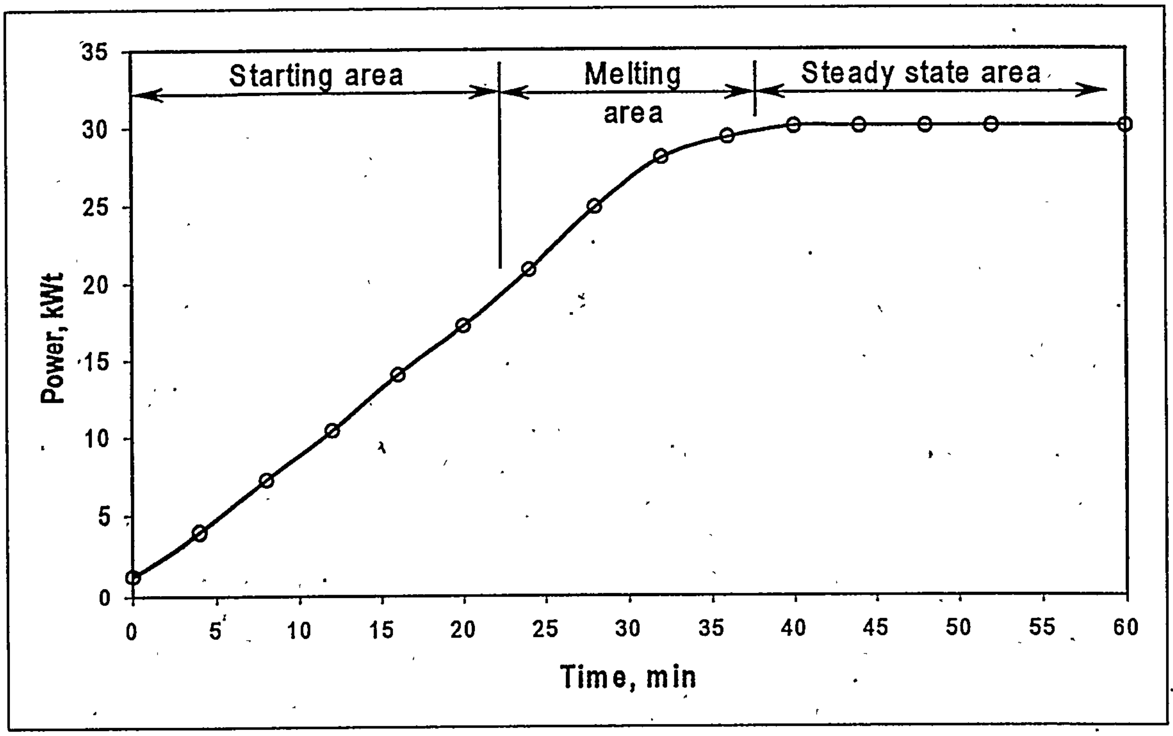

Figure 2. Power Consumption of the Cold Crucible at Various Stages of the Melting Process

Generation of Off-Gases

Generation of off-gases during high-temperature melting in the cold crucible can be caused by the following processes:

- decomposition of carbonates and nitrates in the batch;
- interaction of graphite or silicon carbide with oxygen and/or soil moisture;
- NO_x generation from air components in the high-frequency inductive field at high temperatures.

Dynamics of off-gas generation and their compositions during melting of the same batch type with graphite and silicon carbide as starter materials are shown in Figures 3 and 4. With graphite, off-gases continue to be evolved over a longer period because the graphite burning continues well after the steady state melt is achieved. On the contrary, the silicon carbide doesn't burn out, but dissolves in the forming melt. The total amount of each gas and its ratio to the other gases in the mixture were approximately equal, thereby indicating the soil composition affects generation of off-gases more significantly than the feed material composition.

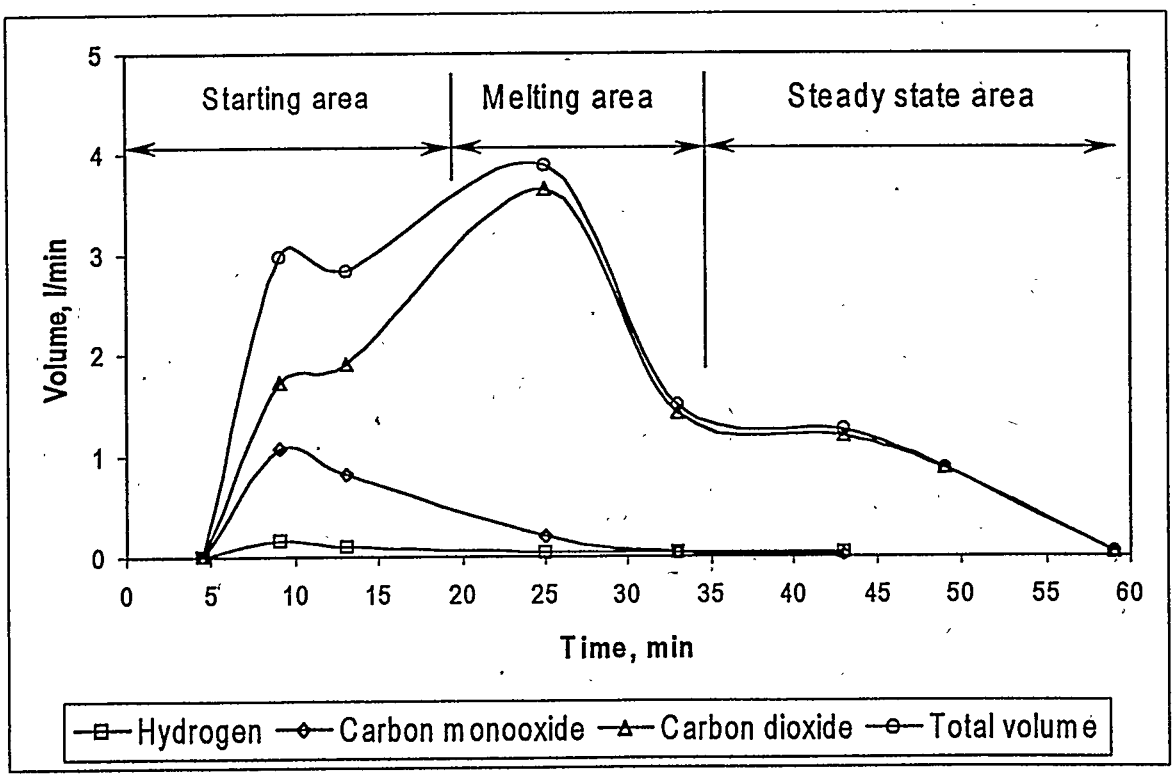

Figure 3. Release of Off-Gases during Melting with Graphite

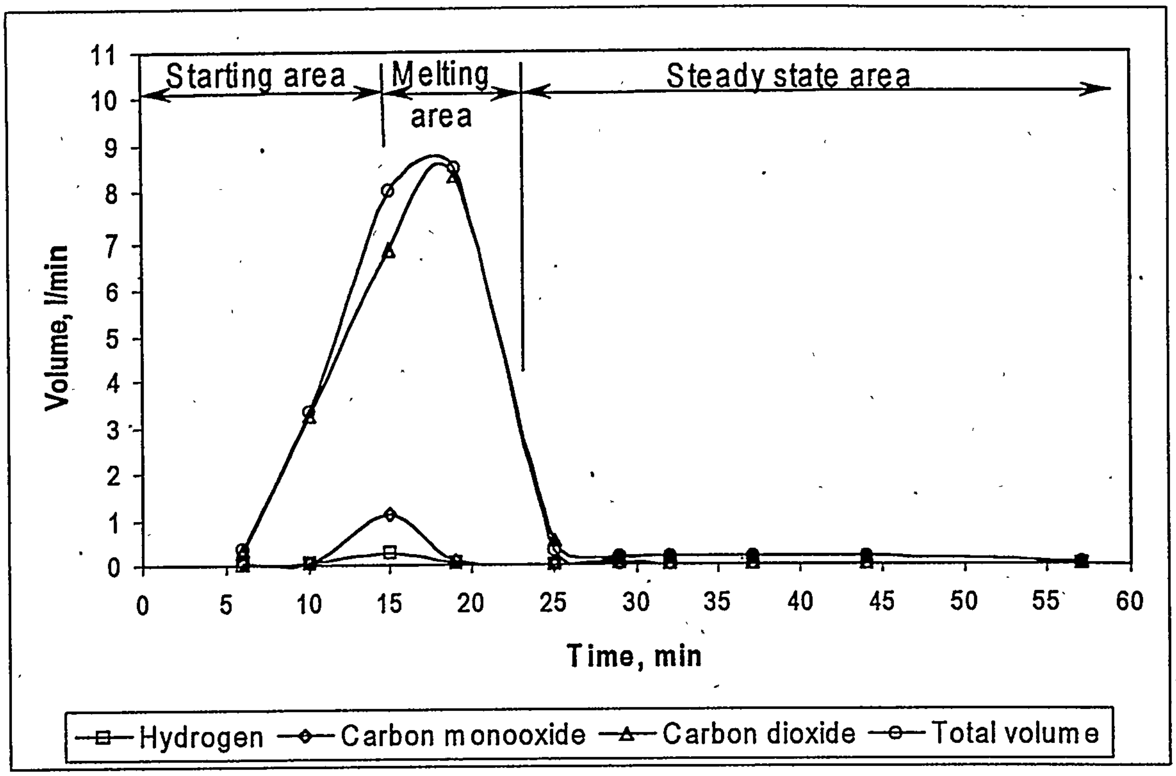

Figure 4. Release of Off-Gases during Melting with SiC

When 50g batches of additional soil were added into an established melt, some short-term intensification of off-gas generation was observed, but the relative ratios amongst off-gases remained the same as during the startup heating. In two experiments, NaCl was added into the soil batch to assess whether the chloride would somehow affect the volatility of any of the heavy metals. Analysis of the gaseous mixture indicated the presence of some free Cl_2 and HCl, 0.03 and 0.06 vol. %, respectively. Generation of white NaCl aerosol vapors that precipitated on the quartz tube, the funnel and the walls of the aerosol trap were observed.

Glass Properties

A cracked dark-green glass block surrounded by unmelted slag was left after the melt was cooled in the cold crucible. The glass density was 2.6 g/cm^3, and the glass block mass was, on average, 65% of the total feed mass. Leach test results of the glass using the Product Consistency Test (PCT) (ASTM C 1285-94) procedure are shown in Table III.

TABLE III

Average PCT Leach Data for Glass Melted in Cold Crucible
(7 days, 90°C, 0.1-0.15 mm)

Elements	U	Cd	Ce	Cs-137	Pb	Pu-239
Leaching (mg/l)	0.638	0.014	0.0095	3.1 ($3.5 \cdot 10^5$ Bq/l)	0.054	0.00475 ($11.1 \cdot 10^3$ Bq/l)

For the mass balance calculation in each experiment, the glass samples were dissolved in an acid mixture of HNO_3 and HF (1:1). The solutions were analyzed by atomic absorption spectroscopy and emission spectral analysis.

Behavior of Heavy Metals and Radionuclides

After each experiment, the off-gas system was dismantled and the distribution of the feed batch components in various parts of the off-gas system was evaluated. Sample analytical results from the off-gas system components and the overall material balance in one of the experiments are shown in Table IV.

TABLE IV

Contaminants in Off-Gas System and Mass Balance (Graphite)

Off-gas System Components	Content (mg)				
	U	Cd	Pb	Ce	Na
Quartz tube (3)	0.092	7.094	4.091	0.014	112.501
Funnel (4)	0.038	0.026	0.042	0.001	60.010
Aerosol trap (5)	0.425	31.091	11.231	0.002	608.020
Bubble condenser (6)	0.018	0.024	0.044	0.006	67.920
Trap and tubes (7)	0.064	0.012	0.029	0.001	55.035
Silica gel trap (8)	0.002	0.048	0.102	0.002	320.012
Bubble condenser (11)	0.003	0.175	0.021	0.003	0.511
Total release (%)	**0.051**	**5.161**	**2.088**	**0.095**	**1.030**
Glass (anal.)	1328.80	664.80	694.46	30.20	111740.00
Initial content	1342.49	758.41	745.45	31.57	118876.00
Mass balance (%)	99.03	92.73	95.25	95.76	95.03

Table IV shows that the greatest amount of the analyzed elements, including sodium, was found in the area nearest to the cold crucible on the quartz tube (3), the funnel (4) and the aerosol trap (5). Their distribution was not equal: cadmium, lead and sodium deposited on the surface of the quartz tube and to a greater extent in the aerosol trap, while cerium precipitated in the lowest part of the quartz tube right above the cold crucible.

Experimental results obtained using silicon carbide as the "sacrificial" conductive material are shown in Table V. ^{239}Pu and ^{137}Cs behavior analyzed by the radiometric method were similar to the Ce and Na distribution respectively. X-ray analysis of the solid deposits from the quartz tube indicated the presence of all components found in the feed batch. Samples from even the area nearest to the cold crucible on the quartz tube showed the presence of Na_2PbO_3.

TABLE V
Contaminants in Off-Gas System and Mass Balance (SiC)

Off-gas System Components	Content (mg)							
	U	Cd	Pb	Ce	Na	Cs		^{239}Pu
						mg	Bk	Bk
Quartz tube (3)	0.150	9.0	7.7	0.042	213.6	17.7	$5 \cdot 10^6$ (3)–(5)	10
Funnel (4)	0.016	2.4	2.0	0.024	44.0	4.0		—
Aerosol trap (5)	0.456	0.76	2.2	—	5746.0	253.5		—
Bubble condenser (6)	0.026	0.33	0.23	0.007	95.7	7.5	$1.4 \cdot 10^5$	—
Trap and tubes (7)	—	0.010	0.1	—	1.8	0.08	$3.6 \cdot 10^3$ (7)–(8)	—
Silica gel trap (8)	—	0.104	0.09	—	328.0	0.11		—
Bubble condenser (11)	—	0.13	0.02	—	1.4	0.12	$2 \cdot 10^3$	—
Total release (%)	**0.05**	**1.7**	**1.67**	**0.003**	**5.68**	**12.85**	**12.9**	**0.001**
Glass (anal.)	1355.0	747.7	734	2568.8	113241.0	2202.8	$4 \cdot 10^7$	10^6
Initial content	1324.8	720.0	692	2534.4	106560.0	1900.8	$3.5 \cdot 10^7$	10^6
Mass balance (%)	97.8	98.0	96.0	98.7	99.8	99.1	—	—

The same detailed results are summarized for experiments in which the starting batch composition or starting heat conditions were changed as shown in Table VI.

TABLE VI
Total Heavy Metals Release Depending on Experimental Conditions

#	**Batch composition (wt%)**	**Feed material**	**Total release, %**				**Melting time, min**	**Note**
			U	**Pb**	**Cd**	**Ce**		
1	Soil-65; Na_2CO_3-35; $Cd(NO_3)$-0.2; $Pb(NO_3)_2$-0.16; $UO_2(NO_3)_2$-0.3; $Ce(NO_3)_3$-0.03	Graphite	0.048	2.2	5.07	0.063	60	
2	Soil-65; Na_2CO_3-35; $Cd(NO_3)$-0.2; $Pb(NO_3)_2$-0.16; $UO_2(NO_3)_2$-0.3; $Ce(NO_3)_3$-0.03	Graphite	0.353	5.23	7.44	0.85	60	Batch additions during melting
3	Soil-65; Na_2CO_3-35; $Cd(NO_3)$-0.2; $Pb(NO_3)_2$-0.16; $UO_2(NO_3)_2$-0.3; $Ce(NO_3)_3$-0.03; $Cs(NO_3)$-0.3 (^{137}Cs-$4 \cdot 10^7$Bk) ^{239}Pu-10^6Bk	SiC	0.05	1.67	1.7	0.003	60	$Ce(NO_3)_3$ 10 times more
4	Soil-64; Na_2CO_3-194; $Cd(NO_3)$-0.2; $Pb(NO_3)_2$-0.16; $UO_2(NO_3)_2$-0.3; $Ce(NO_3)_3$-0.03; NaCl-16.6	Graphite	0.66	29.5	34.5	1.19	90	NaCl added

Higher volatilization of sodium, cadmium and lead was observed during the experiments with sodium chloride in the batch. Uranium and cerium behavior was also affected, but to a much lesser degree. Such differences in the behavior of the toxic metals can be explained by the greater volatilization of cadmium and lead chlorides formed under high temperatures and in the presence of chloride.

To study the mechanism of metals loss to the off-gas, i.e. mechanical carryover of the batch particles from the surface versus actual volatility during melting, the quartz tube (3) was replaced immediately after a steady state melt condition was achieved. Analytical results of the deposits formed on the internal surface of the quartz tube during the initial heating using graphite as the starter material, and those deposited after the steady state was achieved are shown in Table VII.

TABLE VII

Gaseous Phase Components Depending on Melting Stages

Melting stages	t min	Element, mg			
		U	Cd	Pb	Na
Prior to steady state	45	0.12	22.0	16.0	96.0
Steady state regime	16	0.027	0.176	0.2	48.0

The experimental data show that the bulk of the heavy and toxic metals goes into the gaseous phase during the startup heating and graphite burning. During the steady state conditions, the amounts in the gaseous phase are decreased. This is not believed to be attributable to simply a diminished amount of metal remaining in the melt after the initial heating and losses. As can be seen in Table VI (#3), offgas generation is much less when silicon carbide is used as the startup material and this is reflected by a decrease in carryover of metals. These data indicate that the major reason for loss of heavy metals is their mechanical entrainment from the batch caused by intensive startup heating and offgas evolution.

CONCLUSIONS

The cold-crucible melter is believed to be an important alternative melting method for radioactive wastes, offering many design advantages over other melter designs. These experiments demonstrate that loss of metals to the offgas system is largely controlled by mechanical entrainment rather than actual volatility. This means that extrapolation of melter performance characteristics from the bench scale will be affected by physical scale factors that control gas phase dynamics over the melt surface. This entrainment can be significantly affected by the selection of melt initiating materials, particularly materials such as graphite that burn vigorously at melt temperatures causing a rapid release of gases which readily entrains fine particles. Loss of actinides is much less than transition metals, and the small amount that is lost appears to redeposit significantly just outside the melting zone.

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Fig. 1. Schematic of Off-Gas System Design
Fig. 2. Power Consumption of the Cold Crucible at Various Stages of Melting Process
Fig. 3. Release of Off-Gases During Melting with Graphite
Fig. 4. Release of Off-Gases During Melting with SiC