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J. A. Del Debbio

Removal of Cesium From a High-Level Calcined Waste by High Temperature Volatilization

Lockheed
Idaho Technologies Company

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ABSTRACT

Pyrochemical methods are being evaluated for the separation of actinides and fission products from inert material in high-level waste calcine. Separation processes have the potential of reducing waste disposal costs by reducing the volume of high-level waste requiring final disposal in a repository. Tests were conducted to evaluate high temperature volatilization for removing ^{137}Cs from four types of calcines. The results for pilot plant calcines indicate greater than 99% cesium removal for alumina and fluorinel/sodium calcines heated at 1000°C and 99% removal for zirconia calcine heated at 1100°C. Tests with actual calcine generated at the New Waste Calcining Facility (NWCF) from a blend of aluminum, sodium and zirconium/fluorinel wastes resulted in 96% cesium removal at 1000°C and greater than 99% removal at 1170°C.

SUMMARY

Separation of actinides and fission products from inert materials in high-level waste (HLW) calcine has the potential of reducing HLW disposal costs by minimizing the volume of waste requiring final disposal in a repository. A pyrochemical process has been proposed in which calcine is heated at 1000°C to remove ^{137}Cs by volatilization. The calcine is then mixed with molten calcium chloride where actinide and inert metal oxides are reduced to metals with calcium. After separation of the metal component from the salt, inert metals (principally zirconium and aluminum) are separated as volatile chlorides in a chlorination step leaving actinide metals which are then incorporated into a final waste form. Tests were conducted to determine the feasibility of removing ^{137}Cs from calcine by heat treatment. The pilot plant calcines tested included Fluorinel/sodium (run LTWM-1-88), alumina (run 77) and zirconia (run 74). Experiments were also conducted at the Remote Analytical Laboratory (RAL) with actual calcine generated at the New Waste Calcination Facility (NWCF) from a blend of aluminum, zirconium/Fluorinel and sodium wastes. Volatilization of cadmium from the calcines was also determined. Other components of NWCF calcine whose volatilities were determined included Hg, ^{90}Sr , ^{99}Tc , Pu, and ^{241}Am .

Fluorinel/sodium pilot plant calcine was heated for 5 hours at 600, 700, 900, and 1000°C in separate experiments. Cesium volatilization at 900, and 1000°C was 30%, and 98% respectively. No measurable cesium volatilization occurred at 600 and 700°C. All subsequent tests were conducted at 900 and 1000°C with 5 and 10 hour run times.

Cesium volatilization in 5 hours at 1000°C for alumina and Fluorinel/sodium calcine was 99% and 99.7% respectively. Cesium removal from zirconia calcine was 90% at 1000°C and 99% at 1100°C. Cesium removal from NWCF calcine was 96% at 1000°C and 99.8% at 1170°C. A 10 hour run at 1000°C resulted in 99% cesium volatilization from NWCF calcine. Lowering the temperature to 900°C and increasing run times to 10 hours resulted in large decreases in cesium removal except for Fluorinel/sodium calcine. The results for NWCF, Fluorinel/sodium, zirconia and alumina calcines were 59%, 94%, 41% and 11% respectively. Technetium-99 removal from NWCF calcine was greater than 99% when heated at 1000°C for 5 hours. No ^{99}Tc was detected in the calcine after heating compared with 25 $\mu\text{g/g}$ before heating. No volatilization of ^{90}Sr , Pu, or ^{241}Am was detected.

Mercury was removed from NWCF calcine to below detectable limits (>94% removal) after heating at both 900 and 1000°C for 5 hours. Mercury levels in the unheated calcine were 26 $\mu\text{g/g}$. Cadmium volatilization at 1000°C and 5 hours for NWCF, Fluorinel/sodium and zirconia calcines were 65%, 69% and 54% respectively. Alumina calcine has only trace levels of cadmium.

Greater than 96% of the volatilized Cs, Cd and ^{99}Tc condensed within 20-cm of the heated zone indicating the absence of highly volatile species. Condensed volatiles dissolved readily in 3 N HNO_3 allowing the recovery of a large percentage of volatilized components.

Recovery of volatilized Cs averaged 92% for all calcines tested. Recovery of ^{99}Tc from NWCF calcine was 83%. Cadmium recovery was 89% for pilot plant calcines and 58% for NWCF calcine.

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1. INTRODUCTION

A pyrochemical process is being considered for separating actinides and fission products from inert in high-level waste calcine. The proposed process could minimize future disposal costs by reducing the volume of waste requiring final disposal in a repository. The first step in the process involves degassing the calcine by heating to 600°C followed by heat treatment at 1000°C or higher to volatilize ^{137}Cs . The calcine is then treated with calcium in a molten salt to reduce actinide and inert metal oxides to metals. The resultant metal component is separated from the salt and chlorinated at 600°C to separate inert metals as volatile chlorides. Actinide chlorides are then reduced to metals with calcium and the metals incorporated into a final waste form. The volatilized ^{137}Cs may be condensed onto a matrix such as fiberglass, which is suitable for incorporation into a glass waste form. The condensed cesium may also be dissolved in water and the ^{137}Cs separated from condensed inert using ion exchange methods.

Removal efficiencies of fission products (principally ^{137}Cs and ^{90}Sr) and actinides must be maximized to allow disposal of the salt waste generated by the calcium reduction process as a low-level waste.

The volatility of cesium from glass, ceramics, and synthetic calcines has been described in the literature^{1,2,3} although volatilization mechanisms have not been identified. Sill⁴ has reported a cesium volatilization rate of $22.67 \pm 6.09\%/hr$ at 900°C when added as a tracer solution to a simulated granular basalt waste form. Extrapolation of this data to 1000°C indicates that 100% would volatilize in 1 hour. However, due to differences in waste form chemistry, cesium distribution and diffusion effects, cesium volatilization rates may be much lower for calcine.

This report describes experiments conducted to determine the effect of time and temperature on cesium volatilization from three pilot plant calcines and actual calcine generated at the NWCF. The pilot plant calcine types tested included zirconia (run 74), alumina (run 77), and Fluorinel/sodium (run LTWM-1-88). Zirconia and alumina calcine represent greater than 90% of the high-level waste calcine inventory. The NWCF calcine tested was generated from a blend of aluminum, zirconium/Fluorinel and sodium waste during campaign H3, phase 2 which ran from 3/93 to 10/93. Processing time of the three-way blend was approximately 40% of the total duration of the campaign. The type of waste processed, blend ratios, and feed rates change frequently during a campaign. The effects of these variables on cesium volatility is not known and was not an objective of this study. Other calcine components which may volatilize at high temperatures (>900°C) and for which data is presented include cadmium, mercury, and ^{99}Tc .

2. CALCINE CHARACTERIZATION

The elemental composition of the calcines tested is listed in Table I. The values for NWCF calcine are estimates calculated from feed compositions and blend ratios. The zirconia (run 74) and alumina (run 77) pilot plant calcines were generated in the 30-cm calciner. The Fluorinel/sodium calcine (LTWM-1-88) was produced in the 10-cm calciner. The pilot plant calcine samples tested were taken from final bed material and were not stabilized (degassed). The NWCF calcine sample was taken during calciner operation after bed turnover had occurred. Table II lists the major chemical components as determined by X-ray diffraction analysis. With

the exception of alumina calcine, the calcines tested are similar in chemical structure. The large amount of aluminum present in NWCF calcine may be present as amorphous Al_2O_3 .

Table I
Elemental Analysis (Wt.%) of Calcines Tested

	Zirconia <u>run 74</u>	Alumina <u>run 77</u>	Fluorinel/Sodium <u>LWTM-1-88</u>	<u>NWCF^a</u>
Al	11.2	46.5	6.60	20.9
B	1.10	0.20	1.10	0.96
Ca	25.0	1.20	22.3	16.8
Cd	0.09	0.01	4.90	1.28
Cl	<0.20	<0.20	0.10	0.13
Cs	0.38	0.47	0.36	b
Hg	0.10	<0.10	<0.10	26.0 ^c
F	17.4	0.80	13.0	11.4
Fe	0.10	0.40	0.35	0.76
K	<0.10	0.40	0.35	0.76
Na	0.40	1.80	3.41	2.96
NO_3^-	<1.0	1.60	11.3	6.02
$\text{SO}_4^{=}$	1.80	0.20	1.60	2.50
Sr	0.78	0.50	0.59	0.13
Zr	16.6	0.60	11.6	7.63

^a Estimates calculated from feed analyses, blend ratios, and other parameters. Cadmium, mercury and strontium values based on chemical analysis.

^b Not determined.

^c Units are $\mu\text{g/g}$.

Table II
X-Ray Diffraction Analysis of Calcines Used in the Calcine Volatiles Tests

<u>Zirconia</u> <u>run 74</u>	<u>Alumina</u> <u>run 77</u>	<u>Fluorinel/Sodium</u> <u>LWTM-1-88</u>	<u>NWCF</u>
CaF ₂	α -Al ₂ O ₃	CaF ₂	CaF ₂
NaNO ₃	δ -Al ₂ O ₃	NaNO ₃	NaNO ₃
ZrO ₂	NaNO ₃	ZrO ₂	Ca _{0.15} Zr _{0.85} O _{1.85}
Ca _{0.15} Zr _{0.85} O _{1.85}		Ca _{0.15} Zr _{0.85} O _{1.85}	Amorphous Al ₂ O ₃
		CdO	
		CdS	

Analysis of the NWCF calcine for major radionuclides and hazardous components is listed in Table III. The analyses were performed by dissolving the calcine in concentrated HNO₃/HCl mixtures and analyzing the resultant solutions.

Table III
Analysis of NWCF Calcine Sample Used in the Calcine Volatiles Tests^a

<u>Component</u>	<u>Half-Life</u> <u>y</u>	<u>μCi/g</u>	<u>Concentration</u> <u>μg/g</u>	<u>wt. %</u>
¹³⁷ Cs	3.0 E1	2.4 E3	2.8 E1	2.8 E-3
¹³⁴ Cs	2.1 E0	3.6 E1	2.8 E-2	2.8 E-6
¹⁵⁴ Eu	8.6 E0	4.0 E1	1.5 E-2	2.8 E-6
⁹⁹ Tc	2.1 E5	4.3 E-1	2.5 E1	2.5 E-3
⁹⁰ Sr	2.9 E1	3.7 E3	2.7 E1	2.7 E-3
²⁴¹ Am	4.3 E2	1.3 E0	3.9 E-1	3.9 E-5
Total U	NA	b	<2.3E2	<2.3E-2
Total Pu	NA	1.7 E1	b	b
Cd	NA	NA	1.3 E4	1.3 E0
Sr	NA	NA	1.3 E3	1.3 E-1

^a Calcine sample taken on 6/10/93 (campaign H3) during processing of three-way blend of Aluminum (WM-182), Zirconium/Fluorinel (WM-187) and Sodium (WM-185) wastes. Blend ratio = 7Al:4.2 Zr/FI:1.3 Na.

^b Isotopic percentages needed to calculate these values were not determined.

NA = Not applicable

3. EXPERIMENTAL METHODS

3.1 Cold Tests with Pilot Plant Calcines

The test apparatus for the cold tests conducted with pilot plant calcines is illustrated in Figure 1. A weighed amount of calcine was added to a nickel weighing boat and placed inside the alumina tube. Sample weights were 21.2000 to 21.2800 grams. After purging the apparatus with argon for 15 minutes at ambient temperatures the calcine was heated at 300°C for approximately 1 hour to remove water. When condensed water vapor was no longer visible in the quartz tube outside the heated zone, the adapter and condenser were attached and the calcine was degassed at 600 - 700°C until no NO_x vapors were visible (about 1/2 hour). The calcine was then heated at the test temperature for either 5 or 10 hours. After cooling the apparatus under argon, the calcine was removed from the weighing boat and weighed. The heated calcine was sampled in a glove bag filled with argon to prevent sorption of water. Three samples of the calcine before and after heating were analyzed for cesium and cadmium to determine percent volatilization. Fluorinel/sodium calcine samples were dissolved by heating in concentrated HNO₃/HCl. Zirconia calcine before heat treatment dissolved in hot HNO₃/HCl, while samples heated to 900 and 1000°C required fusion with lithium tetraborate prior to dissolution in HNO₃. Alumina calcine before and after heating also required lithium tetraborate fusion for dissolution. Cesium was analyzed by flame emission spectroscopy and cadmium by inductively coupled plasma (ICP) techniques. Volatiles which condensed downstream of the heated zone were dissolved in 3N HNO₃ and the solutions analyzed for cesium and cadmium.

Figure 1. Cold Calcine Volatiles Test Apparatus for Pilot Plant Calcines

Fluorinel/sodium (run LTWM-1-88) calcine was tested at 600 - 1000°C with purge rates in the range of 0.3-4 slpm to determine optimum conditions for cesium volatilization. Run times for these tests were 5 hours. Based on the results of these tests, zirconia (run 74) and alumina (run 77) calcines were tested at 900 and 1000°C with a purge rate of 2 slpm. For tests conducted at 2 slpm, a quartz wool plug was substituted for the glass frit in the adapter to reduce pressure drops.

3.2 Hot Tests with NWCF Calcine

The apparatus used for the hot tests with NWCF calcine is illustrated in Figure 2. A calcine sample was weighed in the platinum crucible, lowered into the alumina tube, and suspended just above the alumina support rod by means of the platinum wire. Sample weights ranged from 1.9500 - 2.1300 grams. Purging, drying and degassing operations were similar to those described for the cold tests. The calcine was heated to the test temperature for either 5 or 10 hours. After the alumina tube cooled to near ambient temperatures, and while the system was being purged, the deionized water was drained from the bubbler vessel and collected for analysis. Draining the bubbler vessel while under the argon purge prevented water from entering the bubbler tube, thus enabling determination of the extent of volatiles deposition in the bubbler and bubbler tube separately. The bubbler vessel was then rinsed with 3N HNO_3 and the rinse collected for analysis. The bubbler tube was disconnected from the adapter and rinsed twice with 3N HNO_3 .

Figure 2. Remote Hot Calcine Volatiles Test Apparatus for NWCF Calcine

The adapter was then removed and rinsed twice with 3N HNO₃. The platinum crucible containing the calcine was removed and weighed. The calcine was then removed and the platinum crucible weighed to determine the weight of the calcine after heating. Variations in the weight of the crucible were insignificant.

The alumina tube was removed and the section outside the heated zone was soaked twice in 3N HNO₃. The solutions were collected for analysis. The platinum wire and crucible were also rinsed and the solutions analyzed. The two rinses of each part of the apparatus were analyzed separately for the first two runs to determine efficiency of deposit removal. However, for the majority of the tests, the two rinses were combined when analyses indicated relatively small amounts in the second rinses.

The heated calcine was analyzed for the components in Table III to determine their volatilities. Calcine samples before and after heating were dissolved by heating in concentrated HNO₃/HCl mixtures. Based on determination of undissolved solids, calcine dissolution was 96% and 99% for two samples heated at 900°C and 99% for two samples heated at 1000°C. Runs were conducted at 900°C for 5 and 10 hours, and at 1000°C for 5 and 10 hours. The purge rate was 0.6 slpm. Two 5 hour runs at 900 and 1000°C with a purge rate of 2 slpm were also conducted. As in the cold tests, the glass frit in the adapter was replaced with quartz wool for tests with the higher purge rate.

4. DATA ANALYSIS

Percent volatilization of cesium and cadmium from pilot plant calcines was calculated with equation 1.

$$\%V = \frac{(F_1 w_1 - F_2 w_2)}{F_1 w_1} \times 100 \quad (1)$$

where,

- %V = percent volatilization
- F₁ = weight fraction in calcine before heating
- F₂ = weight fraction in calcine after heating
- w₁ = calcine weight before heating, g
- w₂ = calcine weight after heating, g

When only one run was conducted, the error was estimated by propagating the error (2σ) associated with measurements of F₁ and F₂ through equation 1. The propagation of error formula used is equation 2^{5,6}.

$$SV = \frac{100w_2 \sqrt{F_2^2 (S_{F_1})^2 + F_1^2 (S_{F_2})^2}}{w_1 F_1^2} \quad (2)$$

where,

SV = standard deviation for % volatilization

S_{F_1} = standard deviation (2σ) for weight fraction of component before heating.

S_{F_2} = standard deviation (2σ) for weight fraction of component after heating.

Percent volatilization of radionuclides from NWCF calcine was calculated with equation 3.

$$\%V = \frac{(D_1 w_1 - D_2 w_2)}{D_1 w_1} \times 100 \quad (3)$$

where,

D_1 = disintegrations/second (d/s) per gram of calcine before heating

D_2 = disintegrations/second (d/s) per gram of calcine after heating

Standard deviations for % volatilization were calculated with equation 2 substituting D_1 and D_2 for F_1 and F_2 .

Radionuclide decontamination factors (DF) and standard deviations were calculated with equations 4 and 5 respectively.

$$DF = \frac{D_1}{D_2} \quad (4)$$

$$S_{DF} = DF \sqrt{\left(\frac{S_{D_1}}{D_1}\right)^2 + \left(\frac{S_{D_2}}{D_2}\right)^2} \quad (5)$$

where S_D is the standard deviation (2σ).

The percent of the amount volatilized which was recovered was determined by equation 6.

$$\%R = \frac{T_r}{T_v} \times 100 \quad (6)$$

where,

%R = percent recovered
 Tr = total mass or d/s in rinse solutions
 Tv = total mass or d/s volatilized

5. RESULTS AND DISCUSSION

5.1 Volatilization of Semivolatile Components

Table IV lists the results of initial scoping tests to determine the effect of temperature on the volatilization of cesium and cadmium from pilot plant calcine. The data indicate that temperatures in excess of 900°C are required to remove appreciable amounts of these components. The effect of argon purge rate on cesium and cadmium volatilization from Fluorinel/sodium pilot plant calcine is indicated in Figure 3. A large effect on the diffusion rate of vapor phase species occurred between 0.3 and 2 slpm. The results shown in Table IV and Figure 3 established 1000°C and 2 slpm as the conditions resulting in the maximum volatilization rate.

Volatilization data for semivolatile components of four calcine types is summarized in Table V. The data indicate that >99% of the cesium can be removed in 5 hours from all the calcines tested by heating to 1000°C (for Fluorinel/sodium and alumina calcine) and 1100°C (for zirconia and NWCF calcine). Increasing the heating time to 10 hours at 1000°C for NWCF calcine resulted in 99% cesium removal with a purge rate of 0.6 slpm.

Table IV
 Effect of Temperature on Volatilization of Cesium and Cadmium from Fluorinel/Sodium
 Pilot Plant Calcine (Run LTWM-1-88)

<u>Temperature, °C</u>	<u>% Volatilized</u>	
	<u>Cs</u>	<u>Cd</u>
600	ND	ND
700	ND	ND
900	30	5.6
1000	98	73

Argon purge rate = 0.3 slpm
 Run time = 5 hours
 ND = None detected

Figure 3. Percent Volatilization vs. Argon Purge Rate

Table V
Percent Volatilization of Semivolatile Components in Four Calcine Types

Temp, °C	NWCF 3-way blend ^a					Fluorine/Sodium run LTWM-1-88				Zirconia run 74			Alumina run 77			
	900		1000		1170	900	1000	1100	900	1000	1100	900	1000	1100		
Time, h	5	10 ^b	5	10 ^b		5	10	5		5	10	5		5	10	5
Cs	47±5.6	59±5.4	96 (27±3.5) ^c	99 (94±10) ^c	99.8 (380) ^c 99.8 (537) ^c	84 ^d ±4.2	94±1.0	99.7 >99 >99	>99 >99	22±5.5	41±4.3	93 ^d ±5.8	>99 >99	2.5±7.0	11±6.4	99 >99 89
Cd	33±8.3	39±7.9	ND	65±4.3	81,86	23 ^d ±6.3	27±7.0	69 ^d ±3.0	82,83	11±6.2	16±6.1	69 ^d ±3.2	82,83	c	c	c
Hg	>94	>94	>94	>94												
¹³⁴ Cs	57±7.2	69±6.0	>99	99 (102±29) ^c												
⁹⁹ Tc	94±1.5	ND	94±1.2	>99 (>528) ^c												

^a Blend of Al, Zr/Na and Na wastes processed during campaign H3, 3/93-10/93.

^b Purge rate = 0.6 slpm.

^c Decontamination Factor.

^d Average of 3 runs. Standard deviation is = 2σ.

^e No Cd data due to very small amounts (0.01 wt%) present.

- NOTES: 1. Results are for one run at stated conditions except where indicated differently.
 2. Purge rates = 2 slpm except where noted.
 3. Cesium volatilization data for NWCF calcine based on ¹³⁷Cs analysis.
 4. ND = No data.

In terms of decontamination factors, the data indicate that a cesium DF of at least 100 is possible. With the exception of Fluorinel/sodium calcine, cesium volatility was greatly lower at 900°C than at 1000°C and varied considerably between the four calcine types. Factors to which the variations may be attributed include differences in the cesium chemistries, the formation of different cesium phases during heating, and porosity differences resulting in varying cesium diffusion rates.

Cadmium volatilization at 1000°C was not very large for any of the calcines tested. Heating NWCF calcine at 1000°C for 10 hours resulted in 65% of the cadmium being volatilized. Cadmium removal in the 81-86% range was obtained by heating NWCF, fluorinel/sodium and zirconia calcine at temperatures greater than 1000°C. However, significant melting of a component of Fluorinel/sodium calcine occurred causing severe agglomeration. The NWCF and zirconia calcines were slightly agglomerated. Mercury volatilization was >94% in 5 hours at 900 and 1000°C.

Volatilization of ^{134}Cs and ^{99}Tc from NWCF calcine was 99% or greater at 1000°C. No ^{99}Tc was detected in the calcine after heating as compared with 23 $\mu\text{g/g}$ in the unheated calcine. As expected, volatilization of ^{134}Cs paralleled that of ^{137}Cs . No significant volatilization of ^{90}Sr , Pu or ^{241}Am was detected.

The percent of volatilized Cs, Cd and ^{99}Tc that was recovered by dissolving the condensed deposits in 3 N HNO_3 is listed in Table VI. With the exception of cadmium recovery from NWCF calcine, percent recoveries were high. An analysis of the distribution of condensed deposits outside the heated zone indicated that greater than 96% of the volatilized components from all tests condensed within 20-cm of the heated zone. The areas of deposition were the quartz tube and adapter of the cold test apparatus (see Figure 1) and the alumina tube and adapter of the hot test apparatus (see figure 2). Temperatures in the quartz and alumina tubes were estimated to be about 200°C, hence this data suggests the absence of highly volatile vapor phase components. No Hg was detected in the dissolved condensed deposits. This may have been due to Hg levels being below detectable limits.

The heated calcines indicated no major structural changes. Fluorinel/sodium and NWCF calcine heated at 1000°C for 5 hours resulted in NaNO_3 decomposition and partial conversion of ZrO_2 to $\text{Ca}_{0.15}\text{Zr}_{0.85}\text{O}_{1.85}$. Calcium fluoride remained a major component of both calcines. Zirconia calcine heated to 1100°C for 5 hours retained CaF_2 , ZrO_2 and $\text{Ca}_{0.15}\text{Zr}_{0.85}\text{O}_{1.85}$ as the major compounds. Alumina calcine heated to 1000°C for 5 hours showed no structural changes.

Table VI
Percent Recovery of Volatilized Components

	NWCF 3-way blend ^a	Fluorinel/Sodium run LTWM-1-88	Zirconia run 74	Alumina run 77
Cs	86 ^b ±7	98 ^b ±12	89 ^c ±5.6	94 ^d
Cd	58 ^b ±6	86 ^b ±8	91 ^d	^e
⁹⁹ Tc	83 ^d			

^a Blend of Aluminum, Zirconium/Na and Sodium wastes processed during campaign H3, 3/93-10/93.

^b Average of five 5 hour runs at 900 - 1000°C. Purge rates ranged from 0.6-2 slpm

^c Average of 2 runs at 900°C (5 and 10h) and 1 run at 1000°C (5h). Purge rate = 2 slpm

^d One run

^e No data due to small amounts (0.01 wt%) of Cd present.

5.2 Characterization of Condensed Semivolatiles

Condensation of volatilized components of Fluorinel/sodium, zirconia and alumina calcines outside the heated zone was first visible at a calcine temperature of 900°C and appeared as a white deposit. As the temperature was increased to 1000°C, the white deposit became heavier, and in the case of cadmium-containing calcines (Fl/Na and zirconia), deposition of a black and brown substance identified as CdO occurred. In addition to CdO, heating Fluorinel/sodium calcine which contains a large amount of cadmium (4.9 wt%) above 900°C resulted in deposition of cadmium metal. Cadmium in the zirconia calcine tested is a contaminant and may not be present in actual zirconia calcine.

The only visible deposit due to heating NWCF calcine at 1000°C was a black powder. Analysis by emission spectrometry determined that the only metal present was cadmium. X-ray diffraction analysis indicated that the compound was amorphous. This compound was presumed to be amorphous CdO.

Figures 4 and 5 are photographs of condensed semivolatiles from heating alumina and zirconia calcine at 1000°C for 20 hours. Elemental and X-ray diffraction analyses of the deposits are listed in tables VII and VIII respectively. The elemental analysis indicated that on a mole % basis, fluoride and sulfur (as SO₄²⁻) were the major nonmetals present. Thus, in addition to Cs₂SO₄, cesium condensed in combination with fluoride as an amorphous compound or compounds. This material is shown as the white deposit in Figures 4 and 5. Sodium was a major component of the condensed deposits that resulted from heating alumina calcine, and may have condensed as an amorphous fluoride.

Figure 4. Condensed Semivolatiles from Heating Alumina Calcine at 1000°C for 20 Hours.

Figure 5. Condensed Semivolatiles from Heating Zirconia Calcine at 1000°C for 20 Hours.

The cesium component of the condensed volatiles was completely soluble in deionized water. Thus, in a full scale process, separation of cesium for further processing may be feasible by ion exchange methods. Condensed S and CdO was not soluble in deionized water but completely dissolved in 3N HNO₃. The treatment of a cadmium waste stream will have to be considered especially when processing Fluorinel/Na calcine.

Table VII
Elemental Analysis of Condensed Semivolatiles

	<u>Alumina Calcine</u>		<u>Zirconia Calcine^a</u>	
	<u>Wt%</u>	<u>Mole %</u>	<u>Wt%</u>	<u>Mole %</u>
Cs	50	15	50	25
Na	12	19	0.72	2.0
B	1.8	6.4	1.1	6.5
Al	1.1	1.5	0.57	1.3
Cd	0.82	0.30	17	9.7
F	26	54	12	42
SO ₄ ⁻	7.9	3.1	17	11
Cl	0.74	0.80	1.7	3.1
NO ₃ ⁻	0.2	0.14	0.29	0.30
Totals	100.6	100.2	100.4	100.9

^a White deposit shown in Figure 5.

Table VIII
X-ray Diffraction Analysis of Condensed Semivolatiles

<u>Alumina Calcine</u>	<u>Zirconia Calcine</u>
Cs ₂ SO ₄	Yellow Deposit - Sulfur
Amorphous	White Deposit - Cs ₂ SO ₄
Material	- Amorphous
	- Material
	Brown Deposit - CdO

6. CONCLUSIONS

1. Removal efficiencies for ^{137}Cs and ^{99}Tc of 99% (DF=100) should be possible by heating Fluorinel/sodium, alumina and NWCF calcine to 1000°C for 5-10 hours. Removal of 99% of the cesium from zirconia calcine requires heating to 1100°C. A decontamination factor of 100 for ^{137}Cs is sufficient to allow designation of high-level waste calcine as a Class B waste with respect to ^{137}Cs . A Class A designation requires a DF of 4200 which tests indicate is not possible by heating calcine at 1000°C.
2. High cadmium removal efficiencies (>90%) are not possible by heating calcine at 1100°C. Heating Fluorinel/Na calcine at this temperature results in melting, which causes severe agglomeration.
3. Removal of condensed ^{137}Cs , ^{99}Tc and Cd compounds for further processing can be accomplished by dissolution in 3N HNO_3 . Condensed cesium compounds can be removed by dissolution in deionized water. This should facilitate separation by ion exchange methods such as using zeolites which can be incorporated into a high-level waste glass.
4. Heat treatment of Fluorinel/sodium calcine at 1000°C should not result in significant agglomeration particularly if a fluidized bed or rotary kiln is used. These methods should result in increased diffusion rates for semivolatiles and therefore maximize removal efficiencies. Zirconia and alumina calcines can be heated to 1100°C without significant agglomeration or major structural changes.

7. REFERENCES

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