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**^{137}Cs AND ^{131}I TRACER STUDIES ON Zr/Na AND Al/Na PILOT
PLANT CALCINE TO EVALUATE THERMAL PROCESSES AS
CALCINE PRETREATMENT OPTIONS**

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Summary

The reason for performing volatility studies on pilot plant calcine is to determine the cesium, and iodine decontamination factors as a function of time, temperature, and calcine type.

Separations processes are being evaluated for ICPP calcine to reduce the high-level waste volume requiring disposal in a geological repository. Reducing the high-level waste volume may reduce disposal cost and conserve repository space. Several aqueous separation processes may be applicable in partitioning the high-level constituents (actinides and fission products). These processes require calcine dissolution in acid prior to actinide and fission product separation. Cesium may be a difficult element to separate from the dissolved calcine because of the solutions: 1) acidity, and 2) complicated chemical matrix. Sodium, calcium, aluminum, and zirconium may interfere with cesium removal from the acidic or neutralized solution. Because of this, a thermal pretreatment option was evaluated in hopes of selectively removing cesium prior to calcine dissolution.

Results from the calcine thermal pretreatment show that 50% of the cesium from Zr/Na calcine was volatilized after 3 hours at 900°C. The percent cesium volatilization did not increase after 8 hours at this temperature. Using Al/Na calcine, 90% of the

cesium volatilized after 3 hours at 900°C. The percent cesium volatilization did not increase after 5 hours. These results indicate the presence of a non-volatile cesium compound in the calcine.

Iodine from both calcine types was volatilized to below gamma spectroscopy detection limits after 2 hours at 700°C. Increasing the mass of cesium and iodine in the calcine had little effect on the amount volatilized.

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Introduction

Recent emphasis has been placed on separating the actinides and fission products from ICPP calcine in order to reduce the high-level waste disposal volume. Reducing this high-level waste volume may not only conserve space in a high-level waste repository, but may also reduce disposal cost. Approximately 1 wt% (Ref. 1) of the ICPP calcine contributes to its radioactivity. The remaining 99 wt% is inert material resulting from fuel dissolution, solvent extraction, and calcination processes. Various aqueous separation processes have been suggested as applicable technologies to partition the bulk of the calcine's radioactivity into a fraction of its original volume.

Schulz and Bray (Ref. 2) have summarized several precipitation, ion exchange, and solvent extraction methods for the removal of cesium from alkaline and acidic waste streams. Some of these methods may be applicable for removing cesium from dissolved calcine. A recent and promising method for cesium removal uses cobalt dicarbollide in a nitrobenzene diluent (Ref. 3).

Unfortunately, nitrobenzene is an unsuitable diluent because of its toxicity.

Cesium, primarily ^{137}Cs , may be a troublesome isotope to remove from dissolved calcine by the methods discussed by Schulz and Bray because its chemistry closely resembles that of sodium and

calcium in this acidic nitrate system (nitric acid is assumed to be the most suitable solvent for calcine dissolution). Calcium is added in the calcination process to prevent fluoride volatilization (Ref. 4). Aluminum and zirconium may also interfere with cesium removal from an acidic system and from a basic system if the solution is neutralized. Cesium removal from acidic waste streams, such as those resulting from calcine dissolution, has not been thoroughly investigated. In addition, the decontamination factor (DF) for cesium removal from calcine to achieve a Class A low-level waste stream (as defined in 10 CFR 61.55) is 4200; i.e. 99.99 % of the cesium must be separated from the calcine. For these reasons, cesium separation from the calcine is receiving a great amount of attention.

Iodine may or may not require partitioning from the calcine. Concentrations of iodine in the calcine are not well known. It was included in this study in hopes of determining its chemistry during volatilizing actual ICPP calcine.

Since the calcine is generated in a fluidized bed operated at 500°C, large amounts of iodine, if any, would not be expected to be present in the calcine. However, Mincher (Ref. 5) reported 46 ug Tc/gram in zirconia calcine. Because of the presence of technetium in the calcine, iodine should not be excluded from being present until proven otherwise.

Technetium is reported (Ref. 6) to extract into CMPO based TRUEX solvent as the protonated pertechnetate (HTcO_4). Solvent extraction is a feasible process for removing technetium (and most likely iodine) from dissolved calcine. If the calcine is thermally pretreated prior to dissolution to volatilize cesium, iodine (and most likely technetium) could also be volatilized. Thermal pretreatment is appealing because it may selectively remove cesium. Removing the cesium prior to dissolution may also reduce radioactivity shielding requirements (costs) in a separations facility.

Average wt% ^{137}Cs in the calcine is 0.0035 (Ref. 1). Even though the wt% iodine in the calcine is not known, it was estimated by taking the concentration of ^{129}I in the feed prior to calcination and assuming that no iodine was volatilized during the calcination process; i.e all the iodine in the feed was calcined.

Volatilization processes were evaluated on two predominate ICPP calcine types: 1) zirconium-sodium based calcine and 2) aluminum based calcine. Run 17 calcine, generated from the 30 centimeter Pilot-Plant Calciner in March 1987, was used in these tests to simulate the zirconium-sodium based calcine, while Run 20 calcine, also generated from the 30 centimeter Pilot-Plant Calciner in May 1988, was used to simulate the aluminum based calcine. Run 20 calcine is a three-way blend calcine consisting of 7:3:1.25 volume blend of simulated WM-182 (aluminum) waste,

WM-187 (fluorinel) waste, and WM-186 (sodium) waste. Run 17 and 20 calcines were also chosen because of the complexity of their calcine matrix. Concentrations of the major elements in these calcines are shown in Table I.

Table I
Elemental Compositions Of Run 17 and 20
Pilot Plant Calcines

Element	Run 17 (wt%)	Run 20 (wt%)
Aluminum	5.61	20.0
Boron	0.962	1.22
Calcium	24.9	17.1
Zirconium	13.1	9.00
Sodium	3.5	3.4
Potassium	0.80	0.66
Cadmium	4.63	1.59
Cerium	<0.007	<0.007
Chromium	0.990	0.596
Iron	0.331	0.479
Manganese	0.088	0.047
Nickel	0.109	0.106
Selenium	<0.236	<0.236
Strontium	0.064	0.069
Cesium	<0.010	<0.010
Mercury	<0.0005	<0.0005
Chloride	2.45 mg/g	3.14 mg/g
Fluoride	17.3	12.0
Sulfur	1.07	0.54
Nitrate	5.87	3.80

note: Remainder of mass balance is oxygen

Experimental Methodology

For these tests, 10 grams of each calcine type (Run 17 and Run 20) was spiked with 10 mls of solution containing ^{137}Cs and ^{131}I . These isotopes have gamma energies detectible at 661 Kev and 364 Kev, respectively. A mixture of fines and product at a ratio of 3 to 1 comprised the 10 grams of each calcine type spiked. The porous physical nature of the calcine causes the calcine to act similar to a sponge. This allows the cesium and iodine to penetrate the inner calcine matrix and become "evenly" distributed throughout the calcine particles. One gram of calcine will absorb approximately one ml of solution.

Spiking Methodology

Ten mls of the spike solution was prepared from standard solutions of ^{137}Cs (as the nitrate salt) and ^{131}I (as iodate). The activity of the cesium standard solution was 1.41×10^{-1} uCi/ml, while the activity of the iodine standard was 5.34×10^{-2} uCi/ml.

The spike solution for the first experiment was prepared by taking three mls of the cesium standard and five mls of iodine standard and diluting the solution to a total volume of 10 mls with DI water. Two spike solutions were prepared; one for each calcine type. This spike solution provided a

total activity of 1,768 D/s ^{137}Cs and 988 D/s ^{131}I per gram of calcine, respectively.

A second spiking experiment was performed to determine the effects of cesium and iodine mass in the calcine on the volatilization decontamination factors. Non-radioactive standard solutions of cesium and iodine, prepared by the Quality Control Laboratory, were used to increase the masses of cesium and iodine in the calcine. The concentration of cesium and iodine in these solutions was 15.8 mg/ml and 0.02 mg/ml, respectively. 0.068 mls of the cesium standard and 2.10 mls of the iodine standard was added to a spike mixture containing 3 mls of the ^{137}Cs standard and 3 mls of the ^{131}I standard. This solution was allowed to equilibrate over a 24 hour period while evaporating in the calcine.

Volatilization Methodology

The spike solution was allowed to dry on the calcine for a period between 3 and 8 days at room temperature. Approximately one gram of each calcine type was placed in a quartz boat 1.61 cm (I.D.) in diameter and 2.42 cm in height. A tare weight was obtained on each quartz boat prior to the addition of calcine. A gross weight of each quartz boat was obtained after the calcine was added. This provided a net weight of calcine in each boat.

Prior to heating the calcine in the quartz boat, the activity of cesium and iodine in each sample was obtained by gamma spectroscopy using a High Purity Germanium detector on a Data General S-140 computer system. Gamma system calibration, efficiency, and counting geometry are discussed later.

Once the initial cesium and iodine activities for each sample had been obtained, the calcine was placed in an oven at 700, 800, or 900°C for 1, 2, or 3 hours. This allowed decontamination factors to be determined as a function of time and temperature. Cesium and iodine in the gas phase should never come to equilibrium with that in the solid phase because of: 1) the large oven volume, 2) the movement of air through the oven by convection, and 3) the movement of air through the oven when the oven door was opened. This test configuration simulated an open system with infinite air flow. After heating, the samples were allowed to air cool, then were reweighed and recounted.

Decontamination factors were obtained by taking the ratio of the initial activity over the final activity. Percent cesium and iodine volatilized was determined by taking the difference between the initial and final activities and dividing this difference by the initial activity.

$$DF = \frac{\text{Activity Before Heating}}{\text{Activity After Heating}} \quad (1)$$

$$\% \text{ Cs, I Volatized } = \frac{\text{Initial Activity} - \text{Final Activity}}{\text{Initial Activity}} \times 100 \quad (2)$$

After the final activity was measured, some of the samples were randomly chosen and recounted again in an unused quartz boat. An accurate weight of the calcine in the boat was obtained. Recounting was done to ensure cesium and iodine were not absorbing on the quartz boat and providing erroneous decontamination factor calculations. No significant difference in activity was seen when the calcine was recounted in the unused boat, indicating that cesium and iodine were not absorbing onto the quartz boat.

Volatilization tests using pilot plant calcine containing non-radioactive cesium were also performed so that cesium volatility comparisons could be made between spiked calcine and calcine containing cesium from the calcination process. This comparison verified the method of spiking the calcine with ^{137}Cs to determine its DF. Run 74 (Zr/Na) and Run 77 (Alumina) 30-cm pilot-plant calcines were used for these tests because of their high non-radioactive cesium concentrations. One gram of each calcine type was placed in

an alumina crucible. The crucibles containing the calcine were then placed in an oven at 900°C for 1, 2, or 3 hours. After heating, the calcine was dissolved in 10 mls of 8 M HNO_3 . The dissolved calcine samples were analyzed for cesium by Atomic Absorption Spectroscopy.

Gamma Counting

Counting geometry was maintained by placing the quartz boat in a 13 dram vial. This also prevented contamination of the counting equipment. Since the diameter of the 13 dram vial was larger than the diameter of the quartz boat, a styrofoam sleeve was fabricated for each sample that immobilized the boat at the bottom of the vial. In the second set of experiments, the quartz boats were slightly smaller in diameter than a 5 dram counting vial. This eliminated the need for the styrofoam sleeve. This counting system ensured a reproducible geometry for the samples.

Gamma Efficiency Calibration

Two gamma efficiency calibrations were performed using standards prepared from the ^{131}I stock solution of 5.34×10^{-2} uCi/mL and ^{137}Cs stock solution of 1.41×10^{-2} uCi/mL. A standard for the 13 dram vial geometry was prepared by adding 0.50 mL of ^{131}I solution, 0.25 mL of ^{137}Cs solution,

and 0.25 mL of deionized H₂O to a quartz boat. The boat was then sealed to prevent evaporation and placed in a 13 dram counting vial using the styrofoam sleeve mentioned earlier. A standard for the 5 dram vial geometry was prepared by adding 0.80 mL of ¹³¹I solution and 0.20 mL of ¹³⁷Cs solution to a quartz boat. This boat was also sealed to prevent evaporation and placed in a 5 dram counting vial.

Both standards were centered against a High Purity Germanium detector of 73% relative efficiency and counted until > 20,000 counts were obtained in the ¹³¹I and ¹³⁷Cs primary photopeaks, 364 Kev and 661 Kev respectively. This ensured a random counting error of less than 1%. The absolute efficiency factor was calculated for each photopeak by dividing the net count rate observed by the decay corrected disintegration rate of the isotope.

$$EFF \text{ Factor} = \frac{[Total \text{ Peak Integral/Count Time (sec)}]_{std}}{[Decay \text{ Corrected Activity (Dis/Sec)}]_{std}} \quad (3)$$

Efficiency factors for cesium and iodine counted in the 13 dram vials were determined to be 0.048 and 0.056, respectively. Efficiency factors in the 5 dram vials were 0.049 for cesium and 0.069 for iodine.

The activities (dis/sec) for ¹³¹I and ¹³⁷Cs in the spiked calcine samples were calculated by dividing the net count

rate in the photopeaks (counts/sec) by the absolute efficiency factors for the given isotope.

$$\text{Activity (Dis/Sec)} = \frac{\text{Total Peak Integral/Count Time (sec)}}{[\text{Absolute Efficiency Factor}]} \quad (4)$$

Another efficiency calibration at a geometry 10 cm from the detector was also performed. The absolute efficiency at 10 cm was less than that against the detector since the efficiency decreases proportionally to $1/(\text{distance})^2$. However, the sample volume and specifically the sample depth normal to the detector become less critical at increased distances. Counts were performed at the 10 cm geometry and compared to those done against the detector face to determine if minute differences in calcine depth, i.e. sample weight, caused any significant bias at the near detector geometry. Samples counted in the near and far configuration showed good agreement, therefore the samples were counted against the detector to allow for higher efficiency and shorter analysis times.

Results/Discussion

Spiked Calcine

Tables II and III show the activities of cesium and iodine before and after heating for Run 17 calcine samples. Good agreement in the initial activities of both these isotopes between samples shows that a homogeneous mixture of calcine was taken from the spiked calcine. Weights of these samples before and after heating are shown in Appendix A.

Table II

Cesium Activities in Run 17 Calcine Before and After Heating

Sample	¹³⁷ Cs Activity Before Heating (D/S/G)	¹³⁷ Cs Activity After Heating (D/S/G)	% Change
700°C for 1 hr	1390	1376	-1%
700°C for 2 hr	1494	1434	-4%
700°C for 3 hr	1490	1474	-1%
800°C for 1 hr	1337	1352	1%
800°C for 2 hr	1525	1408	-8%
800°C for 3 hr	1350	1150	-15%
900°C for 1 hr	1415	1108	-22%
900°C for 2 hr	1344	945	-30%
900°C for 3 hr	1388	750	-46%
900°C for 8 hr	1192	624	-48%

Table III

Iodine Activities in Run 17 Calcine Before and After Heating

Sample	¹³¹ I Activity Before Heating (D/S/G)	¹³¹ I Activity After Heating (D/S/G)	% Change
700°C for 1 hr	894	39	-96%
700°C for 2 hr	947	4	-100%
700°C for 3 hr	941	3	-100%
800°C for 1 hr	846	ND	100%
800°C for 2 hr	960	ND	-100%
800°C for 3 hr	859	ND	-100%
900°C for 1 hr	904	ND	-100%
900°C for 2 hr	874	ND	-100%
900°C for 3 hr	893	ND	-100%

ND = None Detected

To ensure the percent cesium volatilized calculations were accurate and not artificially low due to cesium absorbing onto the quartz boats, samples heated at, 700°C for 3 hours, 800°C for 3 hours, and 900°C for 2 hours, were transferred to unused and preweighed quartz boats. Prior to recounting, a gross weight of each boat and calcine was obtained. No difference was seen in the activities of the recounted samples and the first activities measured after heating. This signifies that no cesium was absorbed onto the quartz boat and the determination of the percent cesium volatilized is accurate. Weights and activities of the recounted samples are shown in Appendix A.

Run 17 data is graphically shown in Figure 1. From this figure, maximum decontamination factors can be extrapolated for the open volatilization system. At 900°C, the maximum DF is 2, a maximum DF of 1.5 is estimated at 800°C, and at 700°C the maximum DF is estimated to be 1.04 (essentially no DF).

Figure 1

Zr/Na Calcine Cesium Volatility

Cesium and iodine results from tests conducted using Run 20 calcine are shown in Tables IV and V. As in the initial activities of Run 17 calcine, there is good agreement in the initial activities between samples of Run 20 calcine. Weights of each sample before and after heating are shown in Appendix B.

Table IV

Cesium Activities in Run 20 Calcine Before and After Heating

Sample	¹³⁷ Cs Activity Before Heating (D/S/G)	¹³⁷ Cs Activity After Heating (D/S/G)	% Change
700°C for 1 hr	1608	1580	-2%
700°C for 2 hr	1755	1684	-4%
700°C for 3 hr	1467	1416	-3%
800°C for 1 hr	1565	1267	-19%
800°C for 2 hr	1442	1006	-30%
800°C for 3 hr	1415	928	-34%
900°C for 1 hr	1194	429	-64%
900°C for 2 hr	1204	258	-80%
900°C for 3 hr	1388	140	-88%
900°C for 5 hr	980	205	-79%

Table V

Iodine Activities in Run 20 Calcine Before and After Heating

Sample	¹³¹ I Activity Before Heating (D/S/G)	¹³¹ I Activity After Heating (D/S/G)	% Change
700°C for 1 hr	1025	ND	-100%
700°C for 2 hr	1000	ND	-100%
700°C for 3 hr	916	ND	-100%
800°C for 1 hr	971	ND	100%
800°C for 2 hr	917	ND	-100%
800°C for 3 hr	937	ND	-100%
900°C for 1 hr	835	ND	-100%
900°C for 2 hr	864	ND	-100%
900°C for 3 hr	839	ND	-100%

ND = None Detected

To ensure no cesium absorbed onto the quartz, thus causing erroneously low cesium volatility activities, samples ran at 700°C for 3 hours, 800°C for 3 hours, and 900°C for 3 hours were transferred to unused quartz boats and recounted. No difference in activities was seen showing an insignificant amount of cesium on the glass. Weights and activities of these recounted samples are shown in Appendix B.

Figure 2 shows the percent cesium volatilized as function of time and temperature in Run 20 calcine. As seen in this figure, up to 90% of the cesium was volatilized after 5 hours and 900°C. At these conditions a cesium DF of 10 was achieved. A cesium DF of 2 is achieved at 800°C, and 1.04 at 700°C.

Figure 2

Al/Na Calcine Cesium Volatility

Spiked Calcine With Increased Cs and I Mass

The effects of cesium and iodine mass on volatilization decontamination factors was also evaluated. Non-radioactive cesium, as cesium chloride, and iodine, as potassium iodide, was mixed with solution of ^{137}Cs and ^{131}I . Enough cesium and iodine was added to the calcine to result in 0.0107 wt% and 0.00042 wt%, respectively. Aliquots of Run 17 and 20 calcine were then weighed, counted, heated at 800 and 900°C for 1, 2, and 3 hours, and recounted.

Tables VI and VII show the activities of cesium and iodine for Run 17 calcine before and after heating. As in previous tests, all the iodine was volatilized from the calcine.

Table VI

Cesium Data From Run 17 Calcine With Increased Cesium Mass

Sample	^{137}Cs Activity Before Heating (D/S/G)	^{137}Cs Activity After Heating (D/S/G)	% Change
800°C for 1 hr	1427	1560	9%
800°C for 2 hr	1424	1520	7%
800°C for 3 hr	1465	1497	2%
900°C for 1 hr	1425	1307	-8%
900°C for 2 hr	1475	1154	-22%
900°C for 3 hr	1389	923	-34%

Table VII

Iodine Data From Run 17 Calcine With Increased Iodine Mass

Sample	¹³¹ I Activity Before Heating (D/S/G)	¹³¹ I Activity After Heating (D/S/G)	% Change
800°C for 1 hr	160	ND	-100%
800°C for 2 hr	160	ND	-100%
800°C for 3 hr	164	ND	-100%
900°C for 1 hr	163	ND	-100%
900°C for 2 hr	168	ND	-100%
900°C for 3 hr	161	ND	-100%

ND = None Detected

Cesium volatilized at 800°C in this test does not correlate with the initial results shown in Table II. Results at 900°C show that 34% of the cesium volatilized after 3 hours with a maximum of 60% after 10 hours (Figure 3). Cesium volatility is lower at both 800 and 900°C compared to the test where CsCl was not added. This may be attributed to the formation of ¹³⁷CsCl which is less volatile at these temperatures or is less mobile in the gas phase through the calcine.

Figure 3

Tables VIII and IX show the results of cesium and iodine volatility with increased mass using Al/Na calcine. All of the iodine was again volatilized, indicating iodine mass has little effect on its volatility. Results show that 28% of the cesium volatilized after 3 hours at 800°C and 84% after 3 hours at 900°C. These results do agree with those where CsCl was not added. This may indicate that the low results found in the Zr/Na calcine are attributed to a slower migration of CsCl through that calcine matrix rather than CsCl being less volatile than Cs₂O.

Table VIII

Cesium Data From Run 20 Calcine With Increased Cesium Mass

Sample	¹³⁷ Cs Activity Before Heating (D/S/G)	¹³⁷ Cs Activity After Heating (D/S/G)	% Change
800°C for 1 hr	1728	1702	-2%
800°C for 2 hr	1725	1499	-13%
800°C for 3 hr	1434	1035	-28%
900°C for 1 hr	1551	823	-47%
900°C for 2 hr	1482	338	-77%
900°C for 3 hr	1482	239	-84%

Table IX

Iodine Data From Run 20 Calcine With Increased Iodine Mass

Sample	¹³¹ I Activity Before Heating (D/S/G)	¹³¹ I Activity After Heating (D/S/G)	% Change
800°C for 1 hr	160	ND	-100%
800°C for 2 hr	154	ND	-100%
800°C for 3 hr	150	ND	-100%
900°C for 1 hr	156	ND	-100%
900°C for 2 hr	157	ND	-100%
900°C for 3 hr	164	ND	-100%

ND = None Detected

Figure 4 shows that a maximum of 50% Cs volatility occurs after 10 hours at 800°C and 100% may be volatilized after 5 hours at 900°C. It is expected that a maximum of 90% volatility is achieved rather than the 100% extrapolated from Figure 4. These results also compare to those tests where CsCl was not added (Figure 2).

Figure 4

Inert Calcine Cesium Volatility

Run 74 and 77 pilot plant calcines were tested to determine any possible differences in cesium volatility from calcine "spiked" with cesium as opposed to the more realistic pilot plant calcine generated from cesium addition to the feed prior to calcination. Run 74 and 77 pilot plant calcines were selected for this test because they are similar in chemical composition to Run 17 and 20 calcines. Chemical compositions of these calcines are shown in Table X. These two pilot plant calcines were also chosen because of their high cesium concentrations. Run 74 calcine contains 0.5 wt% cesium and Run 77 contains 0.43 wt% cesium.

A 3:1 product to fines ratio of each calcine was used for these tests. Since complete dissolution of each calcine type is unachievable (95% dissolution for Run 74 calcine and 60% dissolution for Run 77 calcine), cesium concentrations were measured in unheated calcine samples. Approximately 1 gram of unheated calcine from both runs was dissolved/leached in 10 mls of 8 M HNO_3 to determine the initial cesium concentration. The calcine samples sat in a hot water bath at 90°C for 8 hours and sat for 7 days prior to analysis to ensure all the cesium would go into solution. Cesium concentrations from the leachates were compared to the previously determined analytical results shown in Table X. Results shown in Table X were obtained by performing a lithium borate fusion on the calcine to achieve a 100% calcine

Table X
Elemental Composition Of Run 74 and 77 Pilot Plant Calcines

Element	Run 74 (wt%)	Run 77 (wt%)
Aluminum	11.2	46.5
Boron	1.1	0.19
Calcium	25.0	1.21
Zirconium	16.6	0.55
Sodium	0.4	1.80
Potassium	<0.1	0.18
Cadmium	<0.1	<0.04
Cerium	0.1	0.07
Chromium	0.4	0.13
Iron	0.1	0.40
Manganese	0.2	<0.01
Nickel	0.1	0.08
Selenium	<0.24	<0.24
Strontium	0.7	0.53
Cesium	0.5	0.43
Mercury	0.1	0.05
Chloride	<0.25 mg/g	<0.25 mg/g
Fluoride	17.4	0.77
Sulfur	1.8	0.19
Nitrate	<0.1	1.5

note: Remainder of mass balance is oxygen

dissolution and accurate cesium results. The heated calcine samples were leached concomitantly with the unheated samples. Initial cesium concentrations from the unheated calcine samples were determined to be 0.57 wt% for Run 74 calcine and 0.44 wt% for Run 77 calcine. These results agree with the values shown in Table X.

Results from this test are shown Tables XI and XII. As seen in these tables, 60% of the cesium from Run 74 Zr/Na calcine volatilized after 3 hours at 900°C while only 25% of the cesium volatilized from the Run 77 alumina calcine. Analytical results and calcine sample weights from this test are shown in Appendix D.

Table XI
Cesium Volatility Results From Run 74 Zr/Na Calcine

Sample	Cesium wt Before Heating (grams)	Cesium wt After Heating (grams)	% Cesium Volatilized
1 Hour	0.00675	0.00400	-41 %
2 Hours	0.00740	0.00410	-46 %
3 Hours	0.00653	0.00260	-60 %

Table XII

Cesium Volatility Results From Run 77 Alumina Calcine

Sample	Cesium wt Before Heating (grams)	Cesium wt After Heating (grams)	% Cesium Volatilized
1 Hour	0.00487	0.00480	-1.5 %
2 Hours	0.00552	0.00450	-19 %
3 Hours	0.00481	0.00360	-25 %

Figure 5 compares the cesium volatilization from Run 17 calcine with that from Run 74 calcine. As seen from this figure, cesium volatility from the spiked Run 17 calcine agrees with cesium volatilities from Run 74 calcine. After 3 hours at 900°C, 50% of the cesium was volatilized from the spiked Run 17 calcine, while 60% of the cesium was volatilized from the Run 74 calcine.

Cesium volatilization agreement between these two similar calcines validates the spiking methodology and supports the low decontamination results found in the spiking test. It is interesting to note that there is very little difference in cesium volatilities even though Run 74 calcine contains 1000 times more cesium by mass than did the Run 17 spiked calcine.

Figure 5

Figure 6 compares the cesium volatility results from Run 20 Al/Na calcine to cesium volatility results from Run 77 Alumina calcine. Run 20 and 77 calcine compositions do not compare as nicely as did Run 17 and 74, therefore, the good agreement found in the Zr/Na calcines was not expected for these aluminum type calcines. As shown in Figure 6, cesium volatilities for the spiked Run 20 Al/Na calcine are three times better than the volatility found in the Run 77 alumina calcine.

Figure 6

Cesium Volatility at 900 Celsius With Inert and Spiked Aluminum Type Calcine

The difference in volatility is attributed to the difference in calcine composition rather than cesium mass or the means cesium was introduced to the system. Results between Run 17 and Run 74 calcine support this conclusion. Regardless of the reason for the low cesium volatilities obtained for Run 77 calcine, the data shows that a lower decontamination factor was obtained in the alumina calcine containing cesium that was added to the feed prior to calcination, as apposed to cesium being spiked into the calcine.

Conclusions

Cesium decontamination factors resulting from a thermal process are dependant on time, temperature, and the calcine type. Complete cesium volatility (greater than the minimum required DF of 4200) was not achievable in either type of spiked calcine at 900°C after 6 hours. Aluminum-sodium calcine types resulted in the best cesium volatilization of 90%. This correlates to a cesium DF of 10. With zirconium type calcine, a maximum of 50% cesium volatility is achievable after 10 hours at 900°C. This correlates to a DF of 2 which is considerably lower than the required DF of 4200.

The cesium DF may be increased by increasing the temperature but temperatures above 900°C may result in an undesirable liquid calcine molt. Iodine will certainly be volatilized at 900°C, but liquid solvent extractions may be a more suitable separations process. The possible presence of a non-volatile cesium compound in both calcine types might make high DFs virtually impossible to achieve by thermal treatment.

The calcine also caked up at 900°C but the cake was easily broken up. This may indicate that a fluidized bed is required to volatilize the cesium at 900°C.

In these tests, the effects of calcine mass on cesium volatility

were not evaluated. Increasing the mass of calcine heated may reduce the cesium decontamination factor. If further tests are felt necessary, this variable should be investigated, as well as the effects of calcine particle size on cesium volatility.

Cesium volatility results between Run 17 calcine (spiked with ^{137}Cs) and Run 74 calcine (generated from pilot plant feed containing cesium) agree even though Run 74 calcine contained 1000 times more cesium. Cesium volatility results between Run 20 calcine (spiked with ^{137}Cs) and Run 77 calcine (generated from pilot plant feed containing cesium) do not agree. The disagreement is most likely due to differences in the calcine compositions rather than cesium mass or the means cesium was introduced to the system.

Appendix A

Table I

Weights of Run 17 Calcine Samples Before and After Heating

Sample	Calcine Weight Before Heating (grams)	Calcine Weight After Heating (grams)	% Change
700°C for 1 hr	1.0046	0.8552	-15%
700°C for 2 hr	0.8355	0.7436	-11%
700°C for 3 hr	0.7368	0.6520	-12%
800°C for 1 hr	0.6981	0.6195	-11%
800°C for 2 hr	1.0815	0.9481	-12%
800°C for 3 hr	1.0574	0.9399	-11%
900°C for 1 hr	1.0496	0.9404	-10%
900°C for 2 hr	1.2360	1.1052	-11%
900°C for 3 hr	1.2470	1.1163	-10%

Table II

Weights and Activities of Run 17 Calcine
Transferred To Unused Quartz Boats

Sample	Weight of Calcine Prior to Transfer	¹³⁷ Cs Activity Before Transfer (D/S/G)	Weight of Calcine After Transfer	¹³⁷ Cs Activity After Transfer (D/S/G)	% Change in ¹³⁷ Cs Activity
700°C for 3 hrs	0.6520	1474	0.6229	1616	+10%
800°C for 3 hrs	0.9399	1150	0.7891	1151	0%
900°C for 2 hrs	1.1052	750	0.9203	800	+7%

Appendix B

Table I

Weights of Run 20 Calcine Samples Before and After Heating

Sample	Calcine Weight Before Heating (grams)	Calcine Weight After Heating (grams)	% Change
700°C for 1 hr	1.1400	1.0325	-9%
700°C for 2 hr	1.0774	0.9604	-5%
700°C for 3 hr	1.0102	0.9159	-9%
800°C for 1 hr	0.8333	0.7557	-9%
800°C for 2 hr	0.8429	0.7669	-9%
800°C for 3 hr	1.2508	1.1442	-9%
900°C for 1 hr	1.2358	1.1396	-8%
900°C for 2 hr	1.2346	1.1266	-9%
900°C for 3 hr	1.2227	1.1208	-8%

Table II

Weights and Activities of Run 20 Calcine
Transferred To Unused Quartz Boats

Sample	Weight of Calcine Prior to Transfer	¹³⁷ Cs Activity Before Transfer (D/S/G)	Weight of Calcine After Transfer	¹³⁷ Cs Activity After Transfer (D/S/G)	% Change in ¹³⁷ Cs Activity
700°C for 3 hrs	0.9159	1416	0.9145	1495	+6%
800°C for 3 hrs	1.1442	928	1.1446	913	-2%
900°C for 3 hrs	1.1208	140	1.0686	70	-50%

Appendix C

Table I

Weights of Run 17 Calcine Samples Before and After Heating
With Increased Cesium and Iodine Mass

Sample	Calcine Weight Before Heating (grams)	Calcine Weight After Heating (grams)	% Change
800°C for 1 hr	1.1668	1.0351	-11%
800°C for 2 hr	1.5344	1.3562	-12%
800°C for 3 hr	1.2744	1.1199	-12%
900°C for 1 hr	0.9857	0.8738	-11%
900°C for 2 hr	1.1519	1.0135	-12%
900°C for 3 hr	1.1389	1.0086	-11%

Table II

Weights of Run 20 Calcine Samples Before and After Heating
With Increased Cesium and Iodine Mass

Sample	Calcine Weight Before Heating (grams)	Calcine Weight After Heating (grams)	% Change
800°C for 1 hr	0.9971	0.9177	-8%
800°C for 2 hr	1.1748	1.0767	-8%
800°C for 3 hr	1.3569	1.2611	-7%
900°C for 1 hr	1.1672	1.0792	-8%
900°C for 2 hr	0.9877	0.9106	-8%
900°C for 3 hr	1.2878	1.1898	-8%

Appendix D

Data From Tests Using Run 74 Calcine

Sample	Sample wt Before Heating (grams)	Sample wt After Heating (grams)	Analytical Cs Results (ug/ml)
Initial	1.3592	*	770
1 Hour	1.1449	1.1074	400
2 Hours	1.2979	1.2550	410
3 Hours	1.1450	1.0933	260

* = Sample not heated

wt% Cs in Run 74 Calcine:

$$\text{Initial Sample} = \frac{(770 \text{ ug Cs/ml}) (10 \text{ ml})}{(1 \times 10^6 \text{ ug/g}) (1.3592 \text{ g sample})} \times 100 = 0.57 \text{ wt\% Cs} \quad (1)$$

grams cesium in sample before heating:

$$(\text{Sample wt}) (0.0057 \text{ grams Cs/gram sample}) = \text{grams Cs} \quad (2)$$

grams cesium in sample after heating:

$$\frac{(\text{Analytical Sample Results}) (10 \text{ ml})}{1 \times 10^6} = \text{grams Cs} \quad (3)$$

Data From Tests Using Run 77 Calcine

Sample	Sample wt Before Heating (grams)	Sample wt After Heating (grams)	Analytical Cs Results (ug/ml)
Initial	1.0232	*	450
1 Hour	1.1316	1.0728	480
2 Hours	1.1737	1.1141	450
3 Hours	1.1846	1.1310	360

* = Sample not heated

wt% Cs in Run 77 Calcine:

$$\text{Initial Sample} = \frac{(450 \text{ ug Cs/ml}) (10 \text{ ml})}{(1 \times 10^6 \text{ ug/g}) (1.0232 \text{ g sample})} \times 100 = 0.44 \text{ wt\% Cs} \quad (4)$$

grams cesium in sample before heating:

$$(\text{Sample wt}) (0.0044 \text{ grams Cs/gram sample}) = \text{grams Cs} \quad (5)$$

grams cesium in sample after heating:

$$\frac{(\text{Analytical Sample Results}) (10 \text{ ml})}{1 \times 10^6} = \text{grams Cs} \quad (6)$$

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