May 1995

**Idaho
National
Engineering
Laboratory**

RECEIVED

OCT 27 1995

OSTI

Pyrochemical Separation of Radioactive Components from Inert Materials in ICPP High-Level Calcined Waste

**J. A. Del Debbio
L. O. Nelson
T. A. Todd**

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

INEL-95/0154

Pyrochemical Separation of Radioactive Components from Inert Materials in ICPP High-Level Calcined Waste

J. A. Del Debbio

L. O. Nelson

T. A. Todd

Published May 1995

**Idaho National Engineering Laboratory
Lockheed Idaho Technologies Company
Idaho Falls, Idaho 83415**

**Prepared for the
U.S. Department of Energy
Office of Nuclear Energy
Under DOE Idaho Operations Office
Contract DE-AC07-94ID13223**

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ABSTRACT

Separation of radioactive components from inert materials in high-level calcined wastes has the potential of significantly reducing the cost of final disposal of the high-level wastes in a federal repository. Pyrochemical methods for separating actinides and fission products from nonradioactive components have been evaluated. Compared to aqueous processes, pyrochemical processes generate small volumes of aqueous wastes and do not require calcine dissolution.

Removal of $>99\%$ of the ^{137}Cs and ^{99}Tc by high temperature volatilization at $1000\text{--}1170^\circ\text{C}$ was demonstrated for all calcine types. Separation of inert metal oxides (ZrO_2 and Al_2O_3) from simulated zirconia calcine was demonstrated by molten salt extraction with CaCl_2 and by reduction to Al and Zr with Ca in molten CaCl_2 . It is expected that actinide oxides in actual calcine would also be removed. Although tests indicated that $>95\%$ of the Al and Zr was removed from the calcine, separation of the oxides and the metals from the molten salt by filtration was incomplete. Extensive process development would be required to demonstrate the feasibility of pyroprocessing zirconia calcine.

Chlorination of simulated alumina calcine with CO/Cl_2 mixtures resulted in an 86 wt% loss due to the conversion Al_2O_3 to CO_2 and AlCl_3 , which is volatile. Reaction rates were rapid, and separation of reaction products from the calcine residue was achieved. Chlorination of alumina calcine to separate actinides from inert materials may be feasible. Chlorination of zirconia calcine to remove Al and Zr as volatile chlorides resulted in a 14 wt% gain due to the conversion of CaF_2 to CaCl_2 and Al_2O_3 to AlF_3 . Thus, chlorination of zirconia calcines to remove inert materials is not feasible.

SUMMARY

Radioactive components represent less than 1 wt% of the high-level calcined wastes being stored at the Idaho Chemical Processing Plant. Thus, compared to direct immobilization, separation of the high-level waste (HLW) fraction from the nonradioactive constituents has the potential of reducing disposal costs by minimizing the volume of waste requiring final disposal. Aqueous processes for separating actinides and fission products from nonradioactive components using solvent extraction and ion exchange methods are being developed. These methods require calcine dissolution in nitric acid and generate large volumes of aqueous wastes. Pyrochemical methods, which generate small quantities of aqueous wastes and do not require calcine dissolution have been evaluated as alternatives to aqueous processes.

Greater than 90 wt% of zirconia calcine consists of CaF_2 , Al_2O_3 and ZrO_2 . Alumina calcine contains approximately 90 wt% Al_2O_3 . Two flowsheets for separating actinides and fission products from inert materials in zirconia calcine using molten salt methods have been developed by Lawrence Livermore National Laboratory (LLNL) and Lockheed Idaho Technologies Company (LITCO). A flowsheet for removing Al_2O_3 and other inerts from alumina calcine as volatile chlorides has been developed by LITCO. Removal of ^{137}Cs and ^{99}Tc by high temperature volatilization is common to all flowsheets. Tests with all calcine types, including actual calcine generated at the New Waste Calcination Facility (NWCF) indicated that >99% of the cesium and technetium was removed by heating at 1000-1170°C for 5 hours.

The first zirconia flowsheet tested involves contacting the calcine with molten CaCl_2 at 800-900°C to dissolve the CaF_2 and to separate the actinide and inert metal oxides by filtration. The combined oxides are then chlorinated with CCl_4 and the inert metal chlorides are separated from the actinide chlorides by volatilization. The actinide chlorides are reduced with Ca and converted to a metallic waste form or converted to oxides for immobilization in glass. The fission products (principally ^{90}Sr) remain in the salt which is disposed of as low-level waste (LLW). The results of CaCl_2 wash tests conducted by LLNL with simulated zirconia calcine indicated that >99% of the ZrO_2 and Al_2O_3 was separated by filtration and that 75-90% of the F dissolved in the CaCl_2 . However, 60% of the molten CaCl_2 did not pass through the filter and filtration rates were too slow to be practical.

The second zirconia flowsheet tested is the calcium reduction flowsheet in which the calcine is reacted with Ca in molten CaCl_2 to reduce the actinide and inert metal oxides to metals. The metals are separated from the molten salt by filtration, and chlorinated with Cl_2 at 600°C to separate volatile inert metal chlorides from actinide chlorides. The other process steps are similar to the calcium chloride wash flowsheet. Calcine reduction tests conducted with simulated zirconia calcine at 800-1000°C resulted in 100% reduction of Al_2O_3 and 95% reduction of ZrO_2 . Filtration of the molten salt to remove the Al and Zr metal particulates was very slow and resulted in only partial separation. The addition of Zn (m.p. 400°C) to coalesce the metals into a metallic button was unsuccessful. At least 78% of the Sr was not reduced and remained in the filtered salt. In an actual process, the salt would be disposed of as a LLW.

The process for treating alumina calcine consists of chlorination of inert oxides with CCl_4 or CO/Cl_2 at 600°C to separate them from radioactive components as volatile chlorides. The principal products would be AlCl_3 and BCl_3 with traces of FeCl_3 and ZrCl_4 . The inert chlorides are then oxidized and converted into a LLW waste glass. The nonvolatile actinide chlorides and fission products are reduced with Ca and oxidized for conversion into a HLW glass. Experiments in which simulated alumina calcine was chlorinated with CO/Cl_2 in Ar at 600°C resulted in 100% conversion of Al_2O_3 to AlCl_3 and CO_2 . Analysis of the residual calcine indicated that 100% of the cesium volatilized under these test conditions,

probably as CsCl_2 . This indicates the importance of removing cesium upstream of the chlorination process in order to separate radioactive components from inert materials.

Although a chlorination process for treating alumina calcine may be feasible, application of pyrochemical methods for separating radioactive components from inert materials for all calcine types would be difficult. Many of the process steps in the proposed flowsheets have not been demonstrated, and, compared to aqueous processes, a much longer development time would be required to determine feasibility. Therefore, it is recommended that further development of pyrochemical methods should not be considered.

CONTENTS

ABSTRACT	iii
SUMMARY	v
1. INTRODUCTION	1
2. CALCINE CHARACTERIZATION	1
3. PROCESS FLOWSHEET DEVELOPMENT	1
3.1 Volatilization of ^{137}Cs and ^{99}Tc	2
3.2 Calcium Chloride Wash Process for Treating Zirconia Calcines	4
3.3 Calcium Reduction Process for Treating Zirconia Calcines	6
3.4 Zirconia Calcine Chlorination	8
3.5 Chlorination of Alumina Calcine	9
4. CONCLUSIONS	10
5. REFERENCES	11

FIGURES

1. Calcium Chloride Wash Flowsheet for Treating Zirconia Calcines	5
2. Calcium Reduction Flowsheet for Treating Zirconia Calcines	7
3. Process Flowsheet for Pyrochemical Treatment of Alumina Calcine	10

TABLES

1. Calculated Normalized Composition (wt%) and Volume of ICPP Calcined Wastes	2
2. Radiochemical Analysis of Calcine	2
3. Percent Volatilization of Semivolatile Components in Four Calcine Types	3
4. Percent Distribution of Major Elements in Calcium Chloride Wash Tests	6
5. Percent Distribution of Major Elements in Calcium Reduction Tests	8
6. Mass Change Data for Zirconia Calcine Chlorination Experiments	8
7. Mass Change Observed During Calcine Chlorination Experiments	9

Pyrochemical Separation of Radioactive Components from Inert Materials in ICPP High-Level Calcined Waste

J. A. Del Debbio
L. O. Nelson
T. A. Todd

1. INTRODUCTION

Since 1963, calcination of aqueous wastes from reprocessing of DOE-owned spent nuclear fuels has resulted in the accumulation of approximately 3800 m³ of high-level waste (HLW) at the Idaho Chemical Processing Plant (ICPP). The waste is in the form of a granular solid called calcine and is stored on site in stainless steel bins which are encased in concrete. Due to the leachability of ¹³⁷Cs and ⁹⁰Sr and possibly other radioactive components, the calcine is not suitable for final disposal. Hence, a process to immobilize calcine in glass is being developed. Since radioactive components represent less than 1 wt% of the calcine, separation of actinides and fission products from inert components is being considered to reduce the volume of HLW requiring final disposal. Current estimates indicate that compared to direct vitrification, a volume reduction factor of 10 could result in significant cost savings.

Aqueous processes, which involve calcine dissolution in nitric acid followed by separation of actinide and fission products by solvent extraction and ion exchange methods, are being developed. Pyrochemical separation methods, which generate small volumes of aqueous wastes and do not require calcine dissolution, have been evaluated as alternatives to aqueous processes. This report describes three proposed pyrochemical flowsheets and presents the results of experimental studies conducted to evaluate their feasibility. The information presented is a consolidation of three reports^{1,2,3}, which should be consulted for experimental details.

2. CALCINE CHARACTERIZATION

Calculated compositions and volumes of ICPP calcined wastes are listed in Table 1³. As indicated, calcine consists primarily of Al₂O₃, ZrO₂ and CaF₂. This was confirmed by x-ray analysis of alumina and zirconia calcine retrieved from bin set 2 in 1978⁴. Radiochemical analyses of the retrieved calcine and calcine generated from a blend of aluminum, zirconium/Fluorinel and sodium wastes during the last (6/93) calcination campaign are listed in Table 2. Due to the oxygen rich atmosphere during calcination, it is assumed that the actinides are present as oxides. Strontium-90 and ¹³⁷Cs may be present as fluorides and/or oxides depending on how much fluoride is present during calcination.

3. PROCESS FLOWSHEET DEVELOPMENT

Lockheed Idaho Technologies Company (LITCO) and Lawrence Livermore National Laboratory (LLNL) have developed several flowsheets for the separation of actinides and fission products (¹³⁷Cs and ⁹⁰Sr) from inerts in zirconia calcines^{2,3}. These calcines include zirconia, Fluorinel/Na and zirconia/Na. Lockheed Idaho has developed a flowsheet for the pyroprocessing of alumina calcine in order to separate the inert Al₂O₃ from radioactive components. In this section, two selected zirconia flowsheets and the alumina calcine flowsheet will be described as well as the results of laboratory tests conducted to support the flowsheets. Also, test results for the direct chlorination of zirconia calcine to remove inerts from radioactive components are presented.

Table 1. Calculated Normalized Composition (wt%) and Volume of ICPP Calcined Wastes

Component	Alumina	Zirconia	Fluorinel-Na Blend	Zirconia-Na Blend
Al ₂ O ₃	89.5	14.2	8.9	13.3
ZrO ₂	trace	23.2	16.1	17.9
CaF ₂	trace	53.7	39.1	41.9
B ₂ O ₃	0.6	3.0	2.7	2.4
CdO	trace	trace	5.3	4.3
Na ₂ O	3.1	trace	4.7	0.9
K ₂ O	trace	trace	1.0	12.1
CaO	trace	3.9	11.2	0.3
Fe ₂ O ₃	0.6	0.1	0.2	trace
HgO	3.1	trace	trace	0.3
SO ₄ ⁼	1.2	trace	2.4	0.2
PO ₄ ⁼	trace	trace	0.2	trace
Other	1.0	1.0	0.92	1.0
Volatiles	1.0	1.0	8.0	5.7
Radionuclides	<1.0	<1.0	<1.0	<1.0
Volume ^a , m ³	765	1244	150	1400

a. An additional 300 m³ was generated from various blends of aluminum, zirconium/Fluorinel and sodium wastes during campaign H3 (6/93).

Table 2. Radiochemical Analysis of Calcine

Calcine	Concentration, µg/g						
	¹³⁷ Cs	⁹⁰ Sr	⁹⁹ Tc	Total U	Total Pu	²³⁷ Np	²⁴¹ Am
Alumina ^a	6.9E1	3.7E1	ND	5.0E1	3.2	5.0	9.7E-2
Zirconia ^a	2.2E1	1.7E1	ND	3.1E1	5.9	1.1	2.5E-2
3-way blend ^b	2.8E1	2.7E1	2.5E1	<2.3E2	3.9E-1	ND	3.9E-1

a. Retrieved calcine. Values are from ICP-1189 (reference 4).

b. Calcine generated during campaign H3 (6/93) from a blend of aluminum, zirconium/Fluorinel and sodium wastes. Values are from INEL-94/0028 (reference 1).

ND - Not Determined.

3.1 Volatilization of ¹³⁷Cs and ⁹⁹Tc

Removal of ¹³⁷Cs and ⁹⁹Tc from calcine prior to pyroprocessing is common to all flowsheets. Studies were conducted to evaluate removal of ¹³⁷Cs from calcine by high temperature volatilization. The calcines tested included simulated zirconia, alumina and Fluorinel/Na types and actual calcine generated at the New Waste Calcination Facility (NWCF). Experimental details and test results have been reported by Del Debbio¹. In addition to cesium, volatilization of ⁹⁹Tc, Cd and Hg was also studied. A summation of the test results is listed in Table 3. The data indicate that greater than 99% (DF > 100) of the ¹³⁷Cs

Table 3. Percent Volatilization of Semivolatile Components in Four Calcine Types

Temp, °C	Actual Calcine ^a					Fluorinel/Sodium				Zirconia			Alumina			
	900		1000		1170	900		1000	1100	900		1000	1100	900		1000
Time, h	5	10 ^b	5	10 ^b	5	5	10	5	5	5	10	5	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	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	76, 76	86	e	e	e
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 actual calcine based on ¹³⁷Cs analysis.
 4. ND = No data.

and ^{99}Tc can be removed from calcine by heat treatment at 1000-1170°C. A decontamination factor of 100 is sufficient to allow the calcine to be designated a Nuclear Regulatory Commission (NRC) Class B low-level waste (LLW) with respect to ^{137}Cs . Condensed cesium compounds were soluble in water, which suggests that collection of cesium by aqueous dissolution of the condensate followed by sorption on zeolite is feasible. Technetium condensates are expected to be soluble in water and can be treated in the same manner^{1, 5}. Condensed cadmium compounds (principally CdO) were not soluble in water but dissolved readily in 3N HNO_3 . As is indicated in Table 3, 65-86% cadmium volatilization can be expected during heat treatment of cadmium-containing calcines. Methods would have to be developed for collection and disposal of the cadmium.

X-ray diffraction studies of heat treated calcines indicated that no significant structural changes which would affect downstream processes had occurred.

3.2 Calcium Chloride Wash Process for Treating Zirconia Calcines

A process for removing actinides and fission products from zirconia calcines is schematically illustrated in Figure 1. The calcine is heat treated at 600°C to remove H_2O and CO_2 and to decompose nitrates, releasing NO_x . This step is sometimes referred to as calcine stabilization. Cesium-137 and ^{99}Tc are removed by volatilization at 1000-1100°C, condensed, dissolved in water and sorbed on zeolite for incorporation into a high-level waste form. The calcine then undergoes a two-step wash cycle in which it is contacted with molten CaCl_2 to dissolve the CaF_2 . The molten salt/calcine mixture is then filtered to separate the undissolved actinide and inert metal oxides from the molten salt. The actinide and inert metal oxides are chlorinated with CCl_4 to separate the inert metals as volatile chlorides. The actinide chlorides are then reduced to metals with calcium in molten CaCl_2 and separated for incorporation into a metallic wasteform or converted to oxides for producing a glass waste form.

Volatile inert metal chlorides from the chloride volatility step are thermally oxidized and disposed of as LLW. Excess CCl_4 can be condensed and recycled to the chlorinator.

The CaCl_2 from the wash step is separated from the CaF_2 and CaO by aqueous dissolution. The undissolved CaF and CaO is disposed of as LLW. The CaCl_2 solution is evaporated. The condensate is recycled to the aqueous dissolution step and the CaCl_2 is recycled to the wash step. Fission products are disposed of as a LLW salt.

Several CaCl_2 wash experiments with simulated zirconia calcine were conducted at LLNL. The objective of the tests was to determine the feasibility of separating the CaF_2 from the inert metal oxides (Al_2O_3 , ZrO_2) by dissolution of the CaF_2 in molten CaCl_2 and filtering the mixture to separate the metal oxides. A porous MgO crucible, carbon felt and a coarse silica frit with a 90-150 μm pore size were tested as filtration devices. For tests with the MgO crucible and silica frit, 1400g of CaCl_2 were added to 500g calcine. Tests with carbon felt were conducted using 500g of CaCl_2 and 200g of calcine. A summation of the test results is listed in Table 4. The results indicate that 99% of the Al_2O_3 and ZrO_2 was separated from the molten salt and that 75-90% of the F (as CaF_2) dissolved in the CaCl_2 . A large amount (60 wt%) of the oxide residues consisted of CaCl_2 which did not pass through the filters. This is evidenced by the high percentage of Cl found in the oxide residues. Inert metal oxides coated with CaCl_2 may be difficult to chlorinate. The CaCl_2 may have to be remelted and chlorination conducted in the melt.

Figure 1. Calcium Chloride Wash Flowsheet for Treating Zirconia Calcines

A large percentage (69-89%) of the Sr remained in the salt residue in the double wash tests. Thus, a large percentage of the ^{90}Sr would have to be disposed of as a LLW salt. The results for double wash test CWO3 indicate that greater than 93% of the Cs remained in the salt residue. However, at least 99% of the Cs will be removed in the volatilization step upstream of the CaCl_2 wash.

Filtration rates were slow, particularly when the calcine/ CaCl_2 mixture was not stirred (run CWO5). The use of coarser filters and pressurized systems to achieve acceptable filtration rates would have to be investigated.

Table 4. Percent Distribution of Major Elements in Calcium Chloride Wash Tests

Run #	CWO3 ^a		CWO4		CWO5 ^a	
Filter	MgO crucible		silica frit		carbon felt	
Filtration Rate, g/h	60		40		10	
Temperature, °C	850		850		1000	
	Oxide Residue	Salt Residue	Oxide Residue	Salt Residue	Oxide Residue	Salt Residue
Al	> 99	< 1	> 99	< 1	> 99	< 1
Zr	> 99	< 1	> 99	< 1	> 99	< 1
Cl	25	75	43	57	ND	ND
F	< 3	> 97	24	76	ND	ND
Sr	11	89	31	69	17	83
Cs	< 7	> 93	ND	ND	ND	ND

a. Double wash tests
ND - Not Determined

No tests have been conducted in support of the remaining elements of the flowsheet. Chlorination of the washed calcine to separate volatile inert metal chlorides from actinide chlorides and oxidation of the inert metal chlorides to allow disposal as LLW would have to be demonstrated. Reduction of actinide chlorides in molten salts has been used extensively to produce actinide metals⁶. Therefore, reduction of actinide chlorides from the chloride volatility step should be feasible. However, due to the trace levels of actinides present in the calcine (see Table 2), a scavenger metal, such as cadmium, would be required to separate the reduced actinides from the molten CaCl_2 .

3.3 Calcium Reduction Process for Treating Zirconia Calcines

A flowsheet based on initial calcium reduction of the calcine to separate inert and actinide oxides from CaF_2 is illustrated in Figure 2. The calcine is heat treated to remove residual NO_x , H_2O and CO_x . Cesium-137 and ^{99}Tc are separated by high temperature volatilization. Calcium is then added to a molten CaCl_2 /calcine mixture to reduce inert metal oxides (Al_2O_3 and ZrO_2) and actinides to metals. The metals are removed from the salt by filtration and chlorinated. Volatile inert metal chlorides are then separated from nonvolatile chlorides. The actinide chlorides are reduced to metals in molten CaCl_2 with calcium, separated by filtration and incorporated into a metallic waste form. The salt residue from the first calcium reduction step is dissolved in HCl to convert the CaO generated to CaCl_2 which is recycled to the calcium reduction step after vacuum drying. Inert metal chlorides are oxidized and disposed of as LLW. Fission products remain with the salt which is disposed of as LLW.

In the calcium reduction tests, about 500g of heat treated (at 1000°C) calcine were added to 3500g of CaCl_2 in a MgO crucible. The mixture was heated at $800\text{--}1000^\circ\text{C}$ and stirred at 200–300 rpm. After calcium was then added in 10g increments over a 30-minute period. After calcium addition, the stirring rate was reduced to 50–100 rpm for 15 minutes to allow metal/salt phase disengagement. The stirrer was then removed and the mixture remained at temperature for 1/2 hour, after which the system was allowed to cool to room temperature. The reduced metal appeared as dark particulates embedded in the salt. An attempt to separate the metal particulates by heating the metal/salt mixture to 900°C and filtering it through a carbon felt for 20 hours resulted in only partial separation. About 205g of the salt remained

Table 5. Percent Distribution of Major Elements in Calcium Reduction Tests

	<u>Black Salt^a</u>	<u>White Salt</u>
Al	100	0
Zr	95	4.6
Ca	27	73
Cl	27	73
F	50	50
Sr	22	78
Cs	ND	ND

a. Portion of salt containing metal particulates

Reactants: Zirconia Calcine, 500.5g, CaCl₂, 3184.1 g,

Calcium, 185.1 g

ND - Not Determined

3.4 Zirconia Calcine Chlorination

Direct chlorination of zirconia calcine to remove Zr and Al as volatile chlorides (ZrCl₄ and AlCl₃) was evaluated. Two chlorination experiments were completed with zirconia calcine using a CO/Cl₂ gas mixture as the chlorinating gas. The mass change observed during these experiments is shown in Table 6. As can be seen, the calcine mass increased during chlorination. The mass increase was due to the displacement of oxygen from Al₂O₃ and a gain of chlorine according to the following reaction:

The occurrence of this reaction is supported by elemental and x-ray analysis of the products, and by thermodynamic calculations.

Table 6. Mass Change Data for Zirconia Calcine Chlorination Experiments

<u>Run No.</u>	<u>Run Duration (hours)</u>	<u>% Mass Change</u>
1	4	+14
2	4	+14

The reaction does not progress to completion because the outside layer of the calcine reacts and fuses, forming a barrier which inhibits chlorination throughout the entire particle. No further zirconia calcine chlorination experiments were conducted. However, if other pyrochemical process unit operations (e.g., direct reduction or CaCl₂ wash) could be used in conjunction with chlorination of zirconia calcine, additional experiments could be conducted to determine the feasibility of zirconia calcine chlorination followed by direct reduction.

3.5 Chlorination of Alumina Calcine

A schematic diagram of the pyrochemical process for treating alumina calcine is shown in Figure 3. The calcine is heat treated at 600°C to remove residual NO_x, H₂O, and CO_x. The calcine is heated at 1000°C to remove volatile radioactive components such as ¹³⁷Cs and ⁹⁹Tc. The calcine is then chlorinated with CCl₄ or CO/Cl₂ at 600°C to volatilize nonhazardous, nonradioactive compounds such as AlCl₃, BCl₃, and ZrCl₄. The volatilized nonradioactive components are oxidized to allow chlorine recycle and to provide a more stable LLW. The nonvolatile radioactive components are reduced, oxidized and immobilized for disposal as HLW.

Prior to chlorination experiments, a series of thermodynamic equilibrium calculations were completed. Based on equilibrium calculations for alumina calcine, the maximum separation possible was 86 wt% mass loss. The following reactions were predicted by the calculations:

Hence, some chlorination reactions produce volatile species such as AlCl₃ and BCl₃, and other reactions produce nonvolatile species such as NaCl. A separation is achieved due to the difference in vaporization temperatures for the radioactive and nonradioactive chlorinated calcine components.

Several experiments were completed using nonradioactive alumina calcine to verify the separation by chlorination. The experimental results obtained during calcine chlorination experiments agreed well with the predictions obtained from the thermodynamic equilibrium calculations. The mass change observed during chlorination of simulated alumina calcine at 600°C with equimolar CO-Cl₂ diluted in Ar is shown in Table 7. As seen in Table 7, chlorination of alumina calcine resulted in a mass reduction of up to 86% due to volatilization of AlCl₃ and other volatile chlorinated species.

Table 7. Mass Change Observed During Calcine Chlorination Experiments^a

<u>Run #</u>	<u>Calcine Type</u>	<u>Mass Change Observed</u>
1	Alumina	86 wt% loss
2	Alumina	86 wt% loss

a. Experiments were completed at 600°C with equimolar CO-Cl₂ diluted in Ar.

Two additional experiments were completed with simulated alumina calcine to determine if a separation between fission products and nonradioactive calcine components is feasible. The analytical results from these two experiments indicated that all calcine components, including Cs, volatilized from the calcine during chlorination. Hence, a clean separation between radioactive and nonradioactive components was not achieved. These results emphasize the importance of removing Cs upstream of the calcine chlorination step.

Figure 3. Process Flowsheet for Pyrochemical Treatment of Alumina Calcine

4. CONCLUSIONS

Tests with zirconia calcine have indicated that separation of actinides and fission products from inerts by a pyrochemical process can best be accomplished with a process based on the separation of CaF_2 from ZrO_2 and Al_2O_3 using a CaCl_2 wash (Figure 1). The CaCl_2 wash is preferable to calcium reduction because of the inability to separate the Al, Zr and Cr metal reduction products from the molten salt and the generation of additional LLW in the form of NaCl from the HCl scrubber (Figure 2). Although the CaCl_2 wash was successful in separating the ZrO_2 and Al_2O_3 from the molten salt, filtration rates were slow and would have to be improved significantly to make the process feasible. Separation efficiencies for ^{90}Sr are such that 70-90% would remain in the LLW salt. This condition would have to be acceptable for the process to be feasible. Chlorination of the separated inert metal oxides in residual salt and thermal oxidation of the inert metal chlorides would have to be demonstrated.

Chlorination of alumina calcine at 600°C to remove 90 wt% of the calcine as AlCl_3 may be feasible. However, formation of volatile UCl_6 with subsequent decomposition to UCl_5 and UCl_4 may occur⁷. These compounds would have to be recycled to the residual calcine. Other actinide chlorides such as UCl_3 , PuCl_3 , NpCl_3 and AmCl_3 are expected to be stable^{8,9,10}. Chlorination of zirconia calcine to remove ZrO_2 and Al_2O_3 as volatile chlorides is not feasible. The desired reaction products, ZrCl_4 and AlCl_3 are not produced.

Pyrochemical processes of the type being considered for the treatment of calcine have not achieved the advanced stage of development reached by aqueous phase processes. The pyrochemical treatment of calcine to separate actinides and fission products from inerts involves many process steps most of which have not been demonstrated. Extensive experimental studies over a number of years will be required to obtain the necessary data and acquire expertise in high temperature systems and molten salt processes. For these reasons, it is recommended that pyrochemical processes should not be given further consideration as a calcine treatment option.

5. REFERENCES

1. J. A. Del Debbio, Removal of Cesium from a High-Level Calcined Waste by High Temperature Volatilization, INEL - 94/0028 (November 1994)
2. M. C. Bronson, B. B. Ebbinghaus, D. C. Riley, L. O. Nelson and J. A. Del Debbio, Pyrochemical Processing of Idaho Chemical Processing Plant (ICPP) High-Level Waste (HLW) Calcine, Lawrence Livermore National Laboratory Report, UCRL-JC-119349 (November 1994)
3. L. O. Nelson, Separation of Hazardous and Radioactive Calcine Components via Chlorination, INEL-95/0146 (April 1995)
4. B. A. Staples, G. S. Pomiak and E. L. Wade, Properties of Radioactive Calcine Retrieved from the Second Calcined Solids Storage Facility at ICPP, ICP-1189 (March 1979)
5. J. A. Rard, Critical Review of the Chemistry and Thermodynamics of Technetium and Some of its Inorganic Compounds and Aqueous Species, UCRL-53440 (September 1983)
6. J. G. Reavis: in Molten Salt Techniques (D. G. Lovering and R. S. Gale, eds.), pp 38-47, Plenum Press, New York (1987)
7. J. E. Bullard and J. J. Betchul, Journal of the American Ceramic Society, Vol. 63, No. 7-8 (July-August 1980)
8. D. Brown, Halides of the Lanthanides and Actinides, pp 154-155, John Wiley and Sons (1986)
9. S. Fried, "The Preparation of Anhydrous Americium Compounds," Journal of the American Chemical Society, 73:416 (1951)
10. Plutonium Handbook: A Guide to the Technology, Volume 1, O. J. Wick, ed., p 363, American Nuclear Society (1980)