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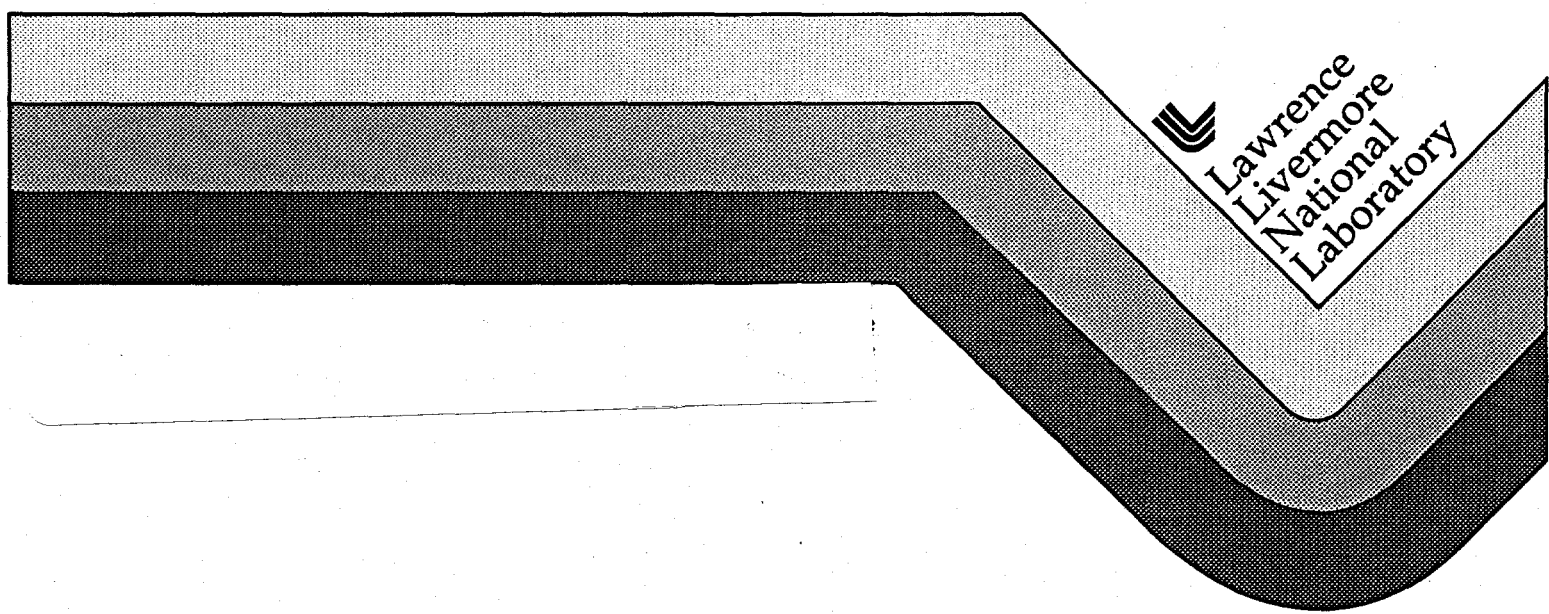
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PYROCHEMICAL PROCESSING OF IDAHO CHEMICAL PROCESSING PLANT (ICPP)

HIGH LEVEL WASTE (HLW) CALCINE

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Abstract

The feasibility of several pyrochemical approaches for separating non-radioactive constituents from ICPP HLW calcine were examined. The removal of aluminum as $AlCl_3$ from alumina calcine was successfully demonstrated. The examination of pyrochemical processes to remove non-radioactive constituents, primarily aluminium, zirconium, calcium and fluorine, from zirconia calcine showed that fluorine removal was required in order to chlorinate the calcine. A molten calcium chloride wash, a calcium reduction, and a sulfuric acid treatment were examined as possible zirconia calcine pretreatment options for fluorine removal.

Fluorine removal from simulated ICPP zirconia calcine was demonstrated by both a $CaCl_2$ wash method and a sulfuric acid treatment method. X-ray fluorescence analysis indicated that greater than 97% of the fluorine can be removed by either method. Fluorine removal by a calcium reduction using an alloying agent, zinc, or a calcium reduction using a filtration separation were also demonstrated, but the efficiencies of fluorine removal were considerably less ranging from 50 to 90%.

Regeneration of $CaCl_2$ from the salt and oxide residues of the $CaCl_2$ wash experiments was also demonstrated by an aqueous dissolution method. From the salt residue, 85% or more of the $CaCl_2$ was recovered and contained little if any CaF_2 or CaO . From the oxide residue close to 100% of the $CaCl_2$ was recovered. Because of the overall success of the $CaCl_2$ wash, it was determined to be the preferred fluorine removal process. The sulfuric acid treatment to remove fluorine is effective, but the proposed overall flowsheet has not been adequately demonstrated.

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Introduction

The Idaho Chemical Processing Plant (ICPP) at the Idaho National Engineering Laboratory (INEL) has, since 1953, reprocessed irradiated nuclear fuel to recovery uranium-235 and krypton-85. The resulting high-level waste (HLW) solutions have been calcined, since 1963, in a fluidized bed calciner. The resultant HLW calcine has been stored in underground stainless steel bins. There is currently an excess of 3700 m³ of calcined HLW. Because of federal land disposal restrictions for HLW, ICPP calcine is an unsuitable waste form for long term geologic disposal. As a result, the calcine will have to be immobilized before long term geologic disposal can be achieved. The two options being considered for immobilizing ICPP HLW calcine are a calcine/glass waste form and a glass-ceramic waste form (1,2). However both of these options will be very expensive due to the high cost of HLW disposal.

There are various compositions or types of HLW calcine in storage at INEL due to the compositional variations in irradiated nuclear fuel elements processed over the years. However, all of the HLW calcine types contain less than one percent fission products and actinides (elements that make the calcine HLW). Separation of the fission products and actinides into a HLW and the inert materials into a low-level waste (LLW) may significantly decrease disposal costs(3). Currently LLW disposal costs are orders of magnitude less than estimated HLW disposal costs. Both aqueous and pyrochemical processing methods have been proposed to remove the HLW components from the calcine. In proposed aqueous processes, actinides and fission products are separated from the non-radioactive constituents by dissolution followed by hydroxide precipitation, by ion exchange, or solvent extraction. In the proposed pyrochemical processes, the actinides and fission products are separated from the non-radioactive constituents by chloride volatilization and molten salt reduction. If processing materials can be recycled in a cost-effective manner, either approach has the potential to dramatically reduce the ICPP HLW volume while maintaining reasonable levels of LLW. This article presents pyrochemical systems that could be used to separate the HLW components from the non-radioactive components in the ICPP HLW calcine. Feasibility studies on selected operations will be presented and discussed.

Calcine Compositions

The bulk of calcines formed from INEL HLW solutions are designated as either alumina or zirconia calcine and in 1986 comprised about 20% and 75%, respectively, of the stored calcine material. The zirconia calcine is present in two main variations, plain and fluorinel - sodium blend (1). A third type of calcine stored at INEL which is very similar in composition to zirconia calcine is stainless steel calcine, and as of 1986 it comprised less than 0.1% of the stored calcine material(1). The balance of the stored calcine material is alumina and dolomite start-up material for the fluidized bed calciner. Typical compositions for alumina and zirconia calcines are given in Table I (4,5,6). Alumina calcine is composed primarily of Al₂O₃ whereas zirconia calcine contains large fractions of ZrO₂ and Al₂O₃ as well as CaF₂.

Pyrochemical Processes

The major non-radioactive constituents in the ICPP HLW calcines are Al₂O₃, ZrO₂, and CaF₂. The chlorides of both aluminum and zirconium are very volatile, sublimation points for AlCl₃ and ZrCl₄ are 178 and 331°C, respectively, whereas chlorides of actinides and fission products are relatively non-volatile. The most volatile of these are UCl₄, NpCl₄, and CsCl which have boiling points of 792, 1020, and 1290°C, respectively. The large separation in volatility between aluminum and zirconium chlorides and the actinide and fission product chlorides suggests that chlorination is a good potential means for removing aluminum and zirconium from the calcine material. This assumes, however, that the formation of mixed chloride species such as CsAlCl₄(g) are insignificant. In order to convert Al₂O₃ to AlCl₃ and ZrO₂ to ZrCl₄, carbon must be present in the chlorination process, i.e. carbochlorination. Upon chlorination the aluminum, zirconium, and boron chlorides vaporize out of the system. These chlorides can be separated from the CO and CO₂ product gas and converted to metals by a calcium or magnesium reduction. In the case of alumina calcine the remaining material consists of actinide and fission product chlorides, NaCl, and trace amounts of miscellaneous metal chlorides. In the case of zirconia

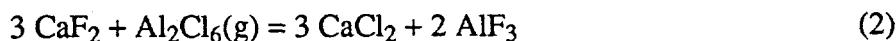
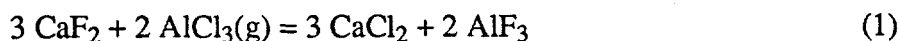
calcine the remaining material consists of CaF₂, CaCl₂, the actinide and fission product chlorides, and trace amounts of miscellaneous metal chlorides. Separation of the CaF₂ and CaCl₂ from the actinides and fission products can be accomplished by a calcium or magnesium reduction operation. To minimize waste the CaF₂ and CaCl₂ salts can be electrowon to provide the required chlorine and calcium reagents. A pyrochemical processing flowsheet for processing zirconia calcine is depicted schematically in Figure 1. Depending upon the temperature of the carbochlorination process, uranium, neptunium, and cesium may be volatilized as chlorides. If needed, these products can be returned to the chlorination vessel by means of a reflux condenser held at about 600°C. Cesium can also be removed by an initial heat treatment of the calcine. INEL has shown that greater than 99% of the cesium can be removed from alumina and zirconia calcines by heat treatment in vacuum at 1000 and 1100°C, respectively.

Table I Composition of ICPP Calcines

Component	Type of Calcine and Composition, wt%		
	Alumina	Zirconia	Fluorinel - Na Blend
Al ₂ O ₃	82-95	13-17	9
Na ₂ O	1-3		4.8
K ₂ O			1.2
ZrO ₂		21-27	17-18
CaF ₂		50-56	41-42
CaO		2-4	12
SO ₃			3
B ₂ O ₃	0.5-2	3-4	3.0-3.4
CdO			6.7-7.0
Misc.	0.5-1.5	0.5-1.5	0.5-1.5
Fission Products and Actinides	<1	<1	<1

Thermochemical Analysis

The flowsheet depicted in Figure 1 was analyzed using chemical reaction and thermochemical equilibria calculations. These calculations validated most operations in the flowsheet except for the removal of alumina from the zirconia calcine. Zirconia calcine contains a significant fraction of fluorine, in the form of CaF₂, which reacts with the aluminum chloride product to form AlF₃ which is non-volatile. AlF₃ is formed by the following reactions.



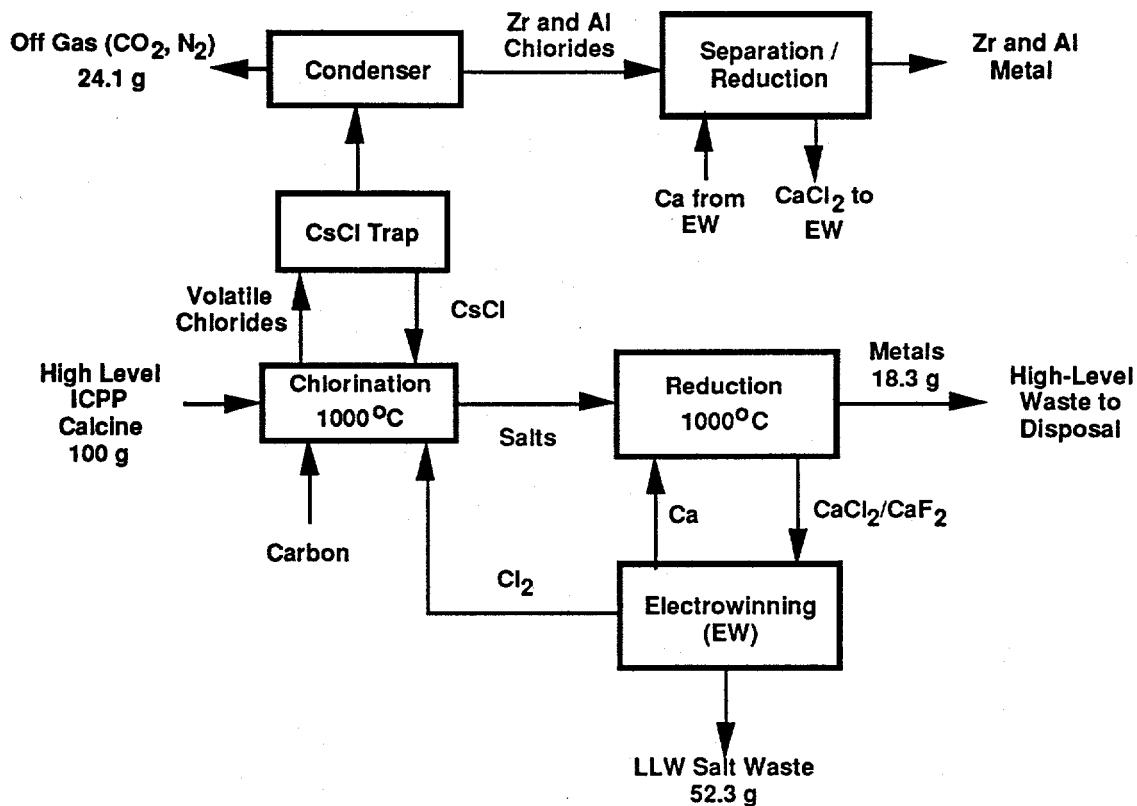


Figure 1: Baseline pyrochemical flowsheet for treating zirconia ICPP HLW calcine

These reactions have a free energy changes of -233 kJ and -235 kJ at 600°C, respectively.

Chlorination experiments at INEL verified that aluminum would be removed from alumina calcine but would not be removed from the zirconia calcine. Chlorination of radioactive and simulated non-radioactive alumina calcine using equimolar CO-Cl₂ gas in argon at 600°C resulted in a 85-86 percent weight loss. Experiments with simulated non-radioactive zirconia calcine under the same conditions resulted in a 14 percent weight gain. To remove aluminum from the zirconia calcine by vaporization of aluminum chloride, a pretreatment process is required to remove fluorine before a chlorination operation. The following three pretreatment options were examined at Lawrence Livermore National Laboratory (LLNL): a molten calcium chloride wash, a calcium reduction, and a sulfuric acid treatment.

Molten Calcium Chloride Wash

In this approach, fluorine in the form of CaF₂ is removed from the calcine by washing it out with molten CaCl₂. Pure CaF₂ has a melting point of 1423°C whereas a mixture of 50 mol% CaF₂ and 50 mol% CaCl₂ has a melting point of about 800°C (7). Therefore, CaF₂ in the calcine could be removed by adding sufficient amounts of CaCl₂ at temperatures greater than the salt phase melting point and filtering out the non-soluble oxide residue. In addition, some of the CaO present in the calcine will be dissolved by the CaCl₂ and washed out with the CaF₂. A potential weakness with this approach is the possibility that actinides and fission products may dissolve in the salt and be washed out with CaF₂.

Calcium Reduction

In this approach, the calcine oxides are reduced by calcium metal in the presence of molten CaCl₂. Calcium oxide is one of the most stable oxides and therefore all of the other oxides in the calcine material will be reduced to metal in the presence of calcium. However, cesium and strontium can form stable chlorides in the presence of CaCl₂. The product CaO is soluble in CaCl₂ and CaF₂. Calcium reduction is a standard pyrochemical process by which several

actinide oxides, fluorides, and chlorides are reduced to metal. A potential weakness with this approach is that the metal and salt phases must be easily separable. Calcium reductions of actinide compounds result in a metal phase that is much denser (18 g/cc) than the salt (2 g/cc) and usually has a low melting point such that a well formed metal button is produced in the bottom of the vessel. The metals reduced from the zirconia calcine material will be primarily aluminum and zirconium which form high melting phases and are considerably less dense than the actinides. Thus, the metal may not be easily separated from the salt.

Sulfuric Acid Pretreatment

In this approach, fluorine in the form of HF(g) is removed by reacting the zirconia calcine material with concentrated sulfuric acid. Industrial processes (8) use this approach to make HF(g) from CaF₂ generating CaSO₄ in the process. A potential weakness with this process is that the HF(g) generated, the concentrated sulfuric acid, and the heat required for the reaction form a very reactive environment which suggests that special container materials might be required to avoid corrosion. However, industrial process to generate HF(g) from CaF₂ and H₂SO₄ are carried out in vessels of low silicon steel. The temperature in the reaction zone for this process is held between 150 and 300°C (8). Thus, low silicon steel would be expected to be an adequate container for a sulfuric acid treatment of ICPP HLW calcine. The sulfuric acid treatment process also complicates the process flowsheet because sulfates are formed. In the carbochlorination step, gaseous sulfur containing materials will be formed which would need to be converted back to sulfuric acid and recycled in order to minimize waste.

Process Feasibility Studies

Process feasibility studies were performed at LLNL using zirconia calcine for each of the three pretreatment options. Since the preliminary chlorination tests showed that the alumina calcine could be readily chlorinated only the zirconia calcine was examined for pretreatment.

Reagents

Simulated zirconia calcine, obtained from INEL, was used for all experiments. Both the CaCl₂ wash experiments and the calcium reduction experiments were conducted in vertically-mounted tube furnaces under argon atmosphere. Samples were placed in round bottom MgO crucibles which were contained by a stainless steel vessel which sits down in the furnace.

Anhydrous CaCl₂ was used for both the CaCl₂ wash experiments and the calcium reduction experiments. Since CaCl₂ is extremely hygroscopic and not readily available in anhydrous form, anhydrous fused CaCl₂ salt cakes were produced by the Lawrence Livermore National Laboratory - Salt Preparation Facility. The salt cakes were stored under inert atmosphere until needed.

The simulated zirconia calcine used in the calcium chloride wash and the calcium reduction experiments was heat treated to remove residual moisture and nitrates that may have been present. The calcine, normally about 500g, was heated at around 600°C for about 4 hours in a MgO crucible which was open to the glove box atmosphere such that the moisture could vent to the box. Weight losses due to moisture, nitrates, and other volatiles in the simulated calcine varied from 0.5 to 1.6 wt%. The simulated calcine material used in the sulfuric acid treatments was not heat treated before use. The presence of any moisture will not effect this treatment.

Chemical Analysis

Product materials and the calcine starting material were analyzed by X-ray fluorescence. Fused solids were submitted directly for analysis. Granular and powdery materials were pelletized by cold pressing before being analyzed. As a pellet or fused solid, detectability of the fluorine is greatly increased and is estimated to be ± 0.3 - 0.4 wt%. Fluorine is not detectable in loose powder samples. Detectability for elements heavier than fluorine was estimated to be ± 0.1 wt%. The concentrations of elements lighter than fluorine could not be accurately determined with X-ray fluorescence. Therefore, oxygen compositions were estimated by mass balance using the reagent compositions and the weights of the reagent and product materials. Some of the starting

calcine material as a pressed pellet was also submitted for analysis. The composition of the simulated calcine was in good agreement with compositions reported by INEL.

Some product materials and the calcine starting material were also analyzed by X-ray powder diffraction. Samples which were known to contain a large fraction of CaCl_2 were loaded onto a diffraction slide and protected on both sides with cellophane tape before submitting for analysis. Even with these precautions, the samples containing CaCl_2 were still found to absorb significant amounts of moisture during the analysis. The calcine starting material was found to contain CaF_2 and tetragonal ZrO_2 . Presumably CaO is dissolved in ZrO_2 thus stabilizing the tetragonal phase. No alumina or calcia (CaO) phases were detected. Possibly they are present as a glassy phase and were therefore not detected.

Molten Calcium Chloride Wash Experiments and Results

A series of five molten calcium chloride wash experiments were performed on the simulated zirconia calcine. In general the experiments consisted of placing the zirconia calcine and CaCl_2 into a porous crucible, placing the porous crucible into a high density MgO crucible, heating the mixture until molten, stirring, and raising the porous crucible in order to allow the salt to drain away from the undissolved calcine. Three types of porous crucibles were used, low density MgO , a fused silica reactor containing a coarse frit (90 to 150 μm pore size), and carbon felt. Reagent weights, product weights, and run parameters for all of the calcium chloride wash experiments are given in Table II.

Table II Experimental parameters and results from molten calcium chloride wash experiments.

Experiment	CW01	CW02	CW03		CW04	CW05	
			wash 1	wash 2		wash 1	wash 2
Feed Calcine (g)	500.0	499.9	494.9	868.4 ¹	497.2	199.6	432.4 ¹
Feed CaCl_2 (g)	1358.1	1363.9	1448.9	1400.0	1449.9	500.5	500.2
Product Oxide Residue (g)	857.8	679.3	868.4	775.0	1035.4	437.4	482.5
Product Salt Residue (g)	1000.3	1000.4	818.2	1314.8	853.7	290.9	463.8
Salt Hold Up (g)		178.4	253.9	154.2	46.5	14.9	5.8
Run Temperature ($^{\circ}\text{C}$)	1000	900	850	850	850	1000	1000
Stir Rate (rpm)	200	220	200	200	0	0	0
Homogenization Time (hr)	4	6.2	4	6	15	0	0
Filtration Time (hr)	16	20.2	10	26	24	72	72
Fluorine Removal by Mass Balance ² (%)	60.3	71.0	61.6	71.8	52.2	46.1	53.8
			89.2 combined			75.1 combined	
Fluorine Removal by X-Ray Fluorescence (%)	64.3	80.0	>97 combined		76.9	50.0 combined	

¹product salt residue from first wash

²assumes CaO dissolves in the salt

In experiments CW01, CW02, and CW03, low density MgO crucibles were used as the filtration device. These seemed to work well but the rate at which the molten CaCl_2 drained was rather slow, approximately 60 grams per hour. Fluorine removal for a single wash was as high as 80% and fluorine removal for a double wash, CW03, was at least 97% by X-ray fluorescence analysis. Assuming that CaO dissolved completely in the salt phase, the fluorine removal was

calculated by mass balance to be 60.3, 71.0 and 89.2% for experiments CW01, CW02, and CW03 where experiment CW03 was a double wash experiment. If CaO did not dissolve at all in the salt, the calculated fluorine removal is slightly higher and the elemental compositions are only affected a few percent.

Using the X-ray fluorescence data, fluorine removal from the calcine is calculated from the fluorine compositions in the salt and oxide residues and the total mass of the salt and oxide residues by the equation below.

$$\%R = 100 W_F(S)M(S)/[W_F(O)M(O) + W_F(S)M(S)] \quad (3)$$

Where %R is the percent fluorine removal, $W_F(S)$ and $W_F(O)$ are the weight percent compositions of fluorine in the salt and oxide residues, and $M(S)$ and $M(O)$ are the total masses of salt and oxide residue. The salt hold up in the filtration device is assumed to be the same in composition as the salt residue and is included in the total mass of the salt residue for the calculation. In this manner, the fluorine removal for experiments CW01, CW02, and CW03 was calculated to be 64.3%, 80.0 %, and greater than 97%. In experiment CW03, the double wash experiment, the fluorine was below detectable and the percent fluorine removal was calculated assuming 0.3 wt% as the detectability limit for fluorine.

The salt and oxide residues from calcium chloride wash experiments CW02 and CW03 were submitted for X-ray analysis. The salt residues were found to be CaCl_2 with some CaClF . The oxide residues were found to contain CaCl_2 , CaClF , and ZrO_2 or CaZrO_3 .

In experiment CW04, a quartz reactor with a porous frit fused into the bottom of the reactor was used as the filtration device. Although, the rate at which CaCl_2 drained was even slower than for the low density MgO crucibles, about 40 grams per hour, this reactor worked well as a filtration medium. Upon cool down, however, the porous frit cracked and broke away from the rest of the quartz reactor. Both the salt and oxide residues had solidified at the time so that the analytical results were not affected. Although the salt hold up in the frit was considerably smaller than the salt hold up in the porous MgO crucibles, a large amount of CaCl_2 was held up with the calcine material which at first appearance suggested a poor removal efficiency of fluorine. Assuming that all of the CaF_2 and CaO dissolved uniformly in the molten CaCl_2 , the fluorine removal was calculated to be only 52.2% by mass balance. The X-ray fluorescence analysis however, indicated that about 76.9% of the fluorine was removed. If the oxide residue is relatively homogenous, this suggests that it is an advantage not to stir the melt in the calcium chloride wash experiments. Since the solution was not stirred, the CaF_2 was apparently washed out preferentially toward the beginning of the experiment. The CaCl_2 above the mixture apparently stayed relatively clean of fluorine and settled down into the calcine material on the bottom of the reactor displacing the fluoride salt.

In experiment CW05, a 1/2 cm thick carbon felt was used as the filtration medium. The salt filtration rate was the slowest for this experiment, 5 grams per hour, but the filtration device still seemed to work well. The mixture was not stirred before filtration which was probably the reason for the slow rate. Assuming all of the CaF_2 and CaO dissolved uniformly, the fluorine removal was calculated to be 46.1% in wash 1 and 53.8% in wash 2. Combined removal was calculated to be 75.1%. X-ray fluorescence of the samples shows that 50.0% of the fluorine was removed after the two washes.

In each of the calcium chloride wash experiments, a large amount of CaCl_2 remains with the calcine material. This CaCl_2 can be removed by an aqueous dissolution process and reused. In a similar manner, the CaCl_2 in the salt residue can be removed by an aqueous dissolution process. This is due to the large difference in solubility of CaCl_2 versus CaF_2 and CaO . The solubility of CaCl_2 in water at 25°C is 45.3g per 100g of solution whereas the solubilities of CaF_2 and CaO in water at 25°C are 0.0017 and 0.113g per 100g of solution, respectively (9). Aqueous dissolution experiments on both the salt and oxide residues were performed. Following dissolution the undissolved solids were separated from the solution containing the CaCl_2 . The

CaCl₂ was recovered from the solution by evaporation of the water. These experiments resulted in CaCl₂ recoveries from salt and oxide residues of 84 to 100 percent. X-ray diffraction of products from salt residue dissolution, showed that the soluble phase was CaCl₂ with a trace amount of CaClOH and the insoluble phase was CaF₂ with a trace amount of CaClOH.

A 3 gram sample of the oxide residue from experiment CW03 was chlorinated by INEL at 900°C in a quartz reaction vessel in a flow of CCl₄ and argon. After chlorination the sample had lost 23 percent of its weight. The maximum it could have lost would have been 30 percent since the material contained about 70 percent CaCl₂. This is a significant improvement from the untreated zirconia concine which showed a 14 percent weight increase when chlorinated at 600°C. The condensed vapors were analysed by XRF and some zirconium was detected. However, aluminum was not detected. Chlorination of the oxide residue in a molten salt should be examined since studies have shown increased reaction rates when carbochlorinating in a molten salt (10,11,12).

Calcium Reduction Experiments and Results

A series of eight calcium reduction experiments were performed on the simulated zirconia calcine. In general the experiments consisted of placing the heat treated calcine and CaCl₂ into a MgO crucible. The mixture was heated in a pyrochemical furnace to between 800 and 1000°C then stirred at 200 to 300 rpm with a tantalum stirring rod. Calcium was added in about 10 g increments to minimize temperature spikes caused by the exothermic reactions. Between calcium additions, the system temperature was allowed to return to baseline before adding more calcium. The calcium reduction process normally took between 2 and 6 hours to complete. After all the calcium had been added, the stirring speed was reduced to between 50 and 100 rpm for at least 15 minutes to facilitate phase disengagement after which the stirrer was stopped and raised from the melt. The mixture was allowed to sit at temperature for at least a half an hour to allow further metal/salt phase disengagement. The system was then shut down and allowed to cool. Reagent weights, product weights, and run parameters for all of the calcium reduction experiments are given in Table III.

In a variation of the calcium reduction experiments, zinc was added to help the metal coalesce into a metal button. The zinc can then be removed from the metal by vacuum distillation. Zinc is very volatile relative to the major metal constituents, aluminum and zirconium. In another variation of the calcium reduction experiments, separation of the metal particulates in the black salt from the calcium reduction by means of a filtration medium was attempted. Two filter mediums were tested, Kao-wool™ blanket and carbon felt.

Experiments CR01, CR02, and CR03, were standard calcium reduction experiments, however, no consolidated buttons were formed. The product consisted of salt that was separated into a white salt upper layer and a black salt lower layer. The black salt which was about 50% denser than the white salt ranged from about 1/4 to 1/2 of the salt cake product by volume. Only in experiment CR01 were the white and black salts separated and weighed. In this experiment, the calculated yield of metal was 149.5g and the black salt weighed 1138.3g. Assuming that the fluorine is distributed evenly throughout the salt, fluorine removal by mass balance was calculated to be 72.2%. The percent fluorine removal was also calculated from the fluorine compositions and the masses of white and black salt by the following equation.

$$\%R = 100 W_F(W)M(W)/[W_F(B)M(B) + W_F(W)M(W)] \quad (4)$$

Where %R is the percent fluorine removal, W_F(W) and W_F(B) are the weight percent compositions of fluorine in the white and black salt, and M(W) and M(B) are the masses of white and black salt. In this manner, the percent fluorine removal for experiment CW01 was calculated to be 50.5%. Assuming the amounts of black and white salt in experiment CW02 were the same as in experiment CW01, the percent fluorine removal was calculated to be about 73.0%. Samples from experiment CW03 were not submitted for analysis.

In experiments CR04, CR05, and CR06, zinc was added during and after the reduction in order to help the product metal coalesce and produce a well formed metal button. These reduction experiments were generally conducted at lower temperatures in order to decrease the volatilization of zinc, which has a boiling point of 907°C. Experiments CR04 and CR06 resulted in white and black salt phases, and similar to the first three experiments there were no metal buttons formed. In experiment CR05, the product mixture after the reduction was treated by vacuum distillation at 850°C for 16 hours. Unlike the other experiments, no separation in white and black salt layer was observed.

Table III Experimental parameters and results from calcium reduction experiments.

Experiment				With Zinc			With Filtration	
	CR01	CR02	CR03	CR04	CR05	CR06	CR07	CR08
Feed Calcine (g)	500.5	500.0	480.9	500.0	497.8	499.4	498.8	498.7
Feed CaCl ₂ (g)	3184.1	3184.8	3182.9	1350.0	2700.2	4926.0	4277.9	4097.2
Feed Calcium (g)	185.1	216.2	184.7	159.1	293.0	300.0	185.0	185.0
Feed Zinc (g)	0.0	0.0	0.0	35.3	55.8	100.0	0.0	0.0
Total Product Salt (g)		3634.5	3560.3	1981.7	3464.2 ¹	5746.5		
Product White Salt (g)	2568.5						3220.9	2601.7
Product Black Salt (g)	1138.3						1695.9	2142.2
Sweeps (g)	---	---	---	---	82.1	82.5	---	---
Run Temperature (°C)	960	963	974	983	753	833	899	900
Stir Rate (rpm)	425	275	300	200	235	300	300	300
Stir Time (hr)	1.2	1.4	1.4	4.5	2.3	5.8	3.0	2.0
Soak Time (min)	0	0	0	25	20	70	120	120
Fluorine Removal by Mass Balance (%)	72.2	---	---	---	---	---	67.5	55.9
Fluorine Removal by X-Ray Fluorescence (%)	50.5	73.0	---	---	---	---	78.1	(80.5 ²) 67.5
								(90.2 ²)

¹Salt weight after attempted vacuum distillation, at 850°C for 16 hours

²fluorine removal after filtration

Experiments CR07 and CR08 were standard calcium reductions similar to experiments CR01-CR03 except that filtration of the metal flakes in the black salt was attempted by means of a filtration device. After both experiments CR07 and CR08, the salt separated, as expected, into an upper white salt layer and a lower black salt layer. The black salt was about 1/4 by volume in experiment CR07 and about 1/2 by volume in experiment CR08 of the total salt cake. By mass balance, the fluorine removal before filtration was calculated to be 67.5% and 55.9% for experiment CR07 and CR08, respectively. The X-ray fluorescence data showed that 78.1% and 67.5% of the fluorine was removed from calcium reduction experiments CR07 and CR08. After filtration in experiment CR08, the X-ray fluorescence data showed that about 90% of the fluorine was removed.

In the calcium reduction experiments, the sum of the product weights were generally less than the sum of the reagent weights. In experiments CR05 and CR06, the sweeps were weighed and the discrepancy between reagent and product weights was negligible. The sweeps are small fragments of salt obtained during break-out from the MgO crucibles and from the tantalum stirrer. They are not easily assigned to either the white or black salt phases. The larger discrepancy between reagent and product weight totals in experiments CR01, CR02, and CR03 was due to not accounting for the salt stuck to the MgO pieces during break-out.

Sulfuric Acid Treatment Experiments and Results

The sulfuric acid treatment of the simulated zirconia calcine was accomplished in two steps. In the first step about 25g of calcine, not previously heat treated, was placed in a Teflon reactor vessel. Concentrated H₂SO₄ was introduced into the reactor vessel. The entire vessel was heated to between 160 and 270°C to convert the CaF₂ to CaSO₄ and drive off HF(g) in the process. In the second step of the treatment process, the calcine residue was placed into a graphite or porcelain crucible and heated to between 380 and 430°C. In this step, any unreacted H₂SO₄ was volatilized from the material and any Zr(SO₄)₂ which may have formed was decomposed to ZrO₂. Decomposition of Zr(SO₄)₂ occurs at about 407°C.

The four sulfuric acid treatment experiments were very similar. Reagent weights and volumes, product weights, run parameters, and fluorine removal for the four experiments are summarized in Table IV.

Table IV Experimental parameters and results from sulfuric acid treatment experiments.

Experiment	SA01	SA02	SA03	SA04
Feed Calcine (g)	25.00	25.00	25.00	25.00
Feed H ₂ SO ₄ (ml)	15	35	35	45
H ₂ SO ₄ conc. (M)	10.2	18.1	18.1	18.1
Reaction Product (g)	34.95	49.13 ¹ (50.07)	51.21	51.71
Max. 1 st Temp. (°C)	160	173	256	268
1 st Heating Time (min)	60	120	95	75
Max. 2 nd Temp. (°C)	400	380	407	430
2 nd Heating Time (min)	45	45	30	20
Fluorine Removal by Mass Balance (%)	----	100	100	100
Fluorine Removal by X-Ray Fluorescence (%)	38.0	>97	>97	>97

¹Value is low because some material was lost when transferring from the Teflon reactor to the graphite crucible. The number in parenthesis is probably more accurate and includes an estimated amount of the material that was lost.

The percent fluorine removal can be calculated from the fluorine compositions and the masses of the starting and product residues by the following equation.

$$\%R = 100 W_F(C)M(C)/[W_F(S)M(S) + W_F(C)M(C)] \quad (4)$$

where %R is the percent fluorine removal, $W_F(C)$ and $W_F(S)$ are the weight percent compositions of fluorine in the starting calcine material and the product sulfate residue, and $M(C)$ and $M(S)$ are the masses of starting calcine material and the product sulfate residue. X-ray fluorescence data of the reacted materials shows that the fluorine removal in experiments SA01, SA02, SA03, and SA04 are 38.0%, >97%, >97%, and >97%, respectively. For experiments SA02, SA03, and SA04, fluorine in the product residues was undetectable by X-ray fluorescence. Thus, the fluorine was taken to be less than 0.3 wt%. The oxygen concentrations in the product residues were calculated by assuming that the boron and zirconium constituents are present as oxides and the remaining constituents are present as sulfates. Cesium and strontium are not expected to be lost in the sulfuric acid treatment and are expected to remain with the sulfated calcine material.

After the sulfuric acid treatment, the product calcine contains a large portion of sulfate material. The sulfate material should be just as suitable for carbochlorination as the oxide residue from the calcium chloride wash experiments. In order for this approach to be attractive, the sulfates will need to be converted back to sulfuric acid for reuse. Thus, waste generation would be minimized. No experiments were conducted to demonstrate further processing or regeneration of sulfuric acid from the sulfated material.

Conclusions

Feasibility studies have shown that pyrochemical processes can be used to separate non-radioactive constituents from ICPP HLW calcine. The removal of aluminum as $AlCl_3$ from alumina calcine was successfully demonstrated. The examination of pyrochemical processes to remove non-radioactive constituents, primarily aluminium, zirconium, calcium and fluorine, from zirconia calcine showed that fluorine removal was required in order to volatilize the aluminum from calcine. A molten calcium chloride wash, a calcium reduction, and a sulfuric acid treatment were examined as possible zirconia calcine pretreatment options for fluorine removal.

Of the three methods of fluorine removal, the sulfuric acid treatment was the most successful overall. Complete removal was demonstrated in three different experiments. However, the product material is composed of sulfates. This complicates further processing since the sulfates will ultimately need to be converted back to H_2SO_4 and recycled in order for this pretreatment method to be attractive. The calcium reduction pretreatment method was the least successful. The highest fluorine removal was about 90% when filtration was employed.

The calcium chloride wash experiments showed that complete fluoride removal can be achieved although two or more washes and significant quantities of $CaCl_2$ may be required. However, the $CaCl_2$ in both the salt and oxide residues is easily removed by aqueous dissolution and can be recovered for reuse. In addition, the oxide residue can be chlorinated with the $CaCl_2$ present. The $CaCl_2$ would then be separated from the radioactive components in a subsequent reduction operation. Preliminary studies on the chlorination of the oxide residue resulting from the calcium chloride wash experiments indicated a high efficiency due to weight loss.

Follow on studies should be performed on large scale samples to demonstrate the chlorination and subsequent aluminum and zirconium removal from calcium chloride washed calcine. In addition a detailed cost analysis should be performed between the various separation options.

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