Separation of Non-Hazardous, Non-Radioactive Components from ICPP Calcine via Chlorination

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ABSTRACT

A pyrochemical treatment method for separating non-radioactive from radioactive components in solid granular waste accumulated at the Idaho Chemical Processing Plant was investigated. The goal of this study was to obtain kinetic and chemical separation data on the reaction products of the chlorination of the solid waste, known as calcine. Thermodynamic equilibrium calculations were completed to verify that a separation of radioactive and non-radioactive calcine components was possible. Bench-scale chlorination experiments were completed subsequently in a variety of reactor configurations including: a fixed-bed reactor (reactive gases flowed around and not through the particle bed), a packed/fluidized-bed reactor, and a packed-bed reactor (reactive gases flowed through the particle bed). Chemical analysis of the reaction products generated during the chlorination experiments verified the predictions made by the equilibrium calculations. An empirical first-order kinetic rate expression was developed for each of the reactor configurations.

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1. INTRODUCTION

A significant effort is currently being expended within the Department of Energy (DOE) to develop methods to treat and dispose of Idaho Chemical Processing Plant (ICPP) high-level waste (HLW) accumulated from spent nuclear fuel reprocessing and plant decontamination activities. Since 1963, the liquid HLW accumulated at the ICPP has been solidified to a granular material (calcine) in a fluidized-bed calciner. Currently, about 3,900 m³ of calcine are stored at the ICPP in underground, concrete-encased, stainless-steel bins.

The chemical composition of the calcine varies within each bin, but may be categorized into four general types: 1) alumina, 2) zirconia, 3) zirconia-sodium, and 4) fluorinel-sodium.¹ The chemical composition of these four major calcine types is shown in Table 1. The compositions shown in Table 1 are based on the assumption that all fluoride is tied up with calcium, and all other metals (Al, Zr, Na, etc.) are oxides. In reality, the composition of calcine is more complex. The principal calcine components are aluminum oxide, calcium fluoride, calcium oxide, and zirconium dioxide. The radioactive calcine components represent less than 1.0 wt% of the calcine mass.

Calcine was originally intended to be a long-term intermediate waste form. However, radioactive components of calcine are leachable in water and therefore, calcine is not a suitable form for final disposal. As a result, a research and development program is currently underway to develop feasible and cost-effective processing and immobilization schemes to treat and dispose of calcine. The immobilization alternatives currently under consideration for the calcine include formation of glass or glass-ceramic waste form. Both alternatives involve heating a calcine/additive mixture to 1050 to 1200°C (and simultaneously applying 10 to 20 ksi for the glass-ceramic process) to form a leach-resistant monolith which would be disposed of in a repository.

Table 1
Representative Chemical Composition and
Relative Volumes of ICPP Calcined Wastes

Component	Alumina	Zirconia	Fluorinel-Na Blend 4.2:1	Zirconia-Na Blend
Al ₂ O ₃	90.6	14.4	9.6	14.1
ZrO ₂	---	23.4	17.5	19.0
CaF ₂	---	54.3	42.4	44.4
B ₂ O ₃	0.6	3.0	2.9	2.5
CdO	---	---	5.7	---
Na ₂ O	3.1	---	5.1	4.5
K ₂ O	---	---	1.1	0.9
CaO	---	3.9	12.2	12.8
Fe ₂ O ₃	0.6	0.1	0.2	0.3
Hg	2.9	---	---	---
SO ₄	1.2	---	2.6	0.3
PO ₄	---	---	0.2	0.2
Other	---	1.0	1.0	1.0
Volatiles	1	1.0	5-10	3-8
Radionuclides	<1.0	<1.0	<1.0	<1.0
Volume in Bin Sets (m ³)*	765	1244	150	1400

* An additional 300 m³ of 3-way blend calcine (a blend of aluminum, sodium, and fluorinel liquid waste) were generated in campaign H3

It has been postulated that a reduction in disposal costs would be realized if the hazardous and radioactive calcine components could be separated from the remaining calcine components prior to immobilization and disposal. Two separation schemes are currently being studied as part of the ICPP research and development program: 1) a series of

pyrochemical (high-temperature, non-aqueous) separations followed by vitrification of the radioactive waste streams and 2) a series of aqueous separations followed by vitrification of the radioactive waste streams. Each separation process has the potential to save 90 to 95% of the expected HLW immobilization and disposal costs. Therefore, development and implementation of an aqueous or pyrochemical separations process is economically attractive.

The purpose of this work was to investigate the feasibility of separating non-radioactive from radioactive calcine components via chlorination as part of the pyrochemical process development program. A schematic diagram of the proposed pyrochemical process flow sheet is shown in Figure 1. The main processing steps are: 1) calcine stabilization at 600°C to decompose nitrate salts, volatilize adsorbed CO_x, and flash residual H₂O, 2) heat treatment of the calcine at ~1000°C to volatilize Cs and possibly Cd, 3) chlorination of the calcine followed by separation of volatile chlorides (mainly non-radioactive) from the solid non-volatile oxide and chloride residue, 4) direct reduction of the solid residue to a metallic phase, 5) metal/salt separation, and 6) HLW immobilization and disposal. This work relates to Step Number 3, calcine chlorination.

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Figure 1. Schematic diagram of the proposed pyrochemical process for treating accumulated ICPP calcine.

2. LITERATURE SEARCH

Calcine consists of a mixture of metal oxides and, except for alumina calcine, fluoride salts. Several high-temperature unit operations have been identified to segregate the non-hazardous, hazardous, and radioactive calcine components. For example, a simple operation is to heat calcine to 600°C in air to decompose nitrate salts and remove 90% of the nitrogen as NO_x. Over 99% of the ¹³⁷Cs and 70% of the Cd are removed as calcine is heated to over 1000°C. Trace quantities of Cs and Cd volatilize from the calcine at temperatures as low as 600°C. However, efficient removal of Cs and Cd is not realized below temperatures of 1000°C. Other calcine components such as Tc (50wt% volatilizes in 30 minutes at 600°C), Na, and Ru may volatilize at temperatures greater than 1000°C, but no data specific to calcine are available. Actinide elements are not expected to volatilize during calcine heat treatment at 1000°C.²

A more complicated high-temperature separations process identified involves reacting calcine with chlorine and a reducing agent such as CO-Cl₂ or CCl₄. A separation would be observed as non-volatile oxides such as Al₂O₃, B₂O₃, and ZrO₂ are converted to volatile chlorides. This separations process is called chloride volatility. Chloride volatility has been used or studied for use in several separation schemes such as purification and separation of Ti, Al, Zr, Mo, Fe, U, and Pu metals from impurities. Those of particular interest to this study are investigations involving Al, Zr, U, and Pu as these elements are found in ICPP calcine. Chlorination of other metals found in ICPP calcine were not identified in the literature.

2.1 Chlorination of Aluminum Oxide

The current industrial application of alumina chlorination is in the preparation of reagent-grade AlCl₃.³⁻⁶ Chlorination of bauxite ores (see Reference 3) was investigated as a method to separate aluminum from impurities such as iron oxide (6-8wt%) and lesser quantities of

titanium and silicon. Bauxite ore samples were heat treated at 1050°C in air to remove water and to ensure formation of low density γ -alumina. Heat treatment of the ore at temperatures in excess of 1050°C produced high density (non-reactive) α -alumina. Heat-treated samples were pressed to 90% of theoretical density to prepare sample pellets for this study. Both CO-Cl₂ and CCl₄, diluted in argon were used as chlorinating reagents.

The reaction rate observed during chlorination of pure alumina samples at temperatures between 300 and 600°C showed a clear Arrhenius-type dependence (see Reference 4). The fastest chlorination rates were observed at temperatures between 600 and 700°C. No increase in reaction rate was observed at temperatures between 700 and 1050°C. The lack of reaction rate temperature dependence was attributed to: 1) reduction in specific surface area with increasing temperature (γ -alumina was converted to α -alumina), 2) decreasing reaction rate due to gas diffusion control, and 3) reaction of CO with Cl₂ (or other chlorinating reagents) prior to the desired heterogeneous chlorination reaction. The chlorination rate of α -alumina was 50 to 300 times slower than the chlorination rate of γ -alumina. The activation energy for four alumina-chlorine reactions is shown in Table 2. Additional investigation of bauxite and γ -Al₂O₃ chlorination as a means of removing aluminum from parent materials was recommended.

Table 2
Activation Energy for Four Aluminum Oxide-Chlorine Reactions

Reaction	E _{act}
$\gamma\text{-Al}_2\text{O}_3 + 1.5 \text{ C} + 3 \text{ Cl}_2 \rightarrow 2 \text{ AlCl}_3 + 1.5 \text{ CO}_2$	39
$\gamma\text{-Al}_2\text{O}_3 + 1.5 \text{ C} + 3 \text{ Cl}_2 + \text{O}_2 \rightarrow 2 \text{ AlCl}_3 + 1.5 \text{ CO}_2 + \text{O}_2$	58
$\alpha\text{-Al}_2\text{O}_3 + 3 \text{ CO} + 3 \text{ Cl}_2 \rightarrow 2 \text{ AlCl}_3 + 3 \text{ CO}_2$	37
$\gamma\text{-Al}_2\text{O}_3 + 3 \text{ CO} + 3 \text{ Cl}_2 \rightarrow 2 \text{ AlCl}_3 + 3 \text{ CO}_2$	38

2.2 Chlorination of Zirconia

The commercial production of Zr metal involves chlorination of purified ZrO_2 via the Kroll process.⁷ The chlorinator is operated at 1000°C with chlorine, but the chlorination rate can be increased dramatically with the addition of a reducing agent such as C or CO .⁸ The reactions and activation energies for two zirconia-chlorine reactions are shown in Table 3.

Table 3
Activation Energies for Two Zirconia-Chlorine Reactions

Reactions	E_{act}
$\text{ZrO}_2 + \text{Cl}_2 \rightarrow \text{ZrCl}_4 + \text{O}_2$	39.7 kcal/mol
$\text{ZrO}_2 + \text{C} + \text{Cl}_2 \rightarrow \text{ZrCl}_4 + \text{CO}_2$	30.5 kcal/mol

The activation energy reported for the reaction

ranged from 22.3 to 29.1 kcal over the temperature range studied. The variation in activation energy was attributed to the equilibrium reaction

2.3 Chlorination of Uranium

Chlorination of nuclear fuel was studied in an effort to recover uranium from spent nuclear fuel. The first processing step envisioned for the chlorination scheme was chlorination of the metal material surrounding the fuel (cladding) with gaseous HCl at 520 to 670 K.⁹ This chlorination step was used to convert zircaloy cladding to volatile chlorides. A more rigorous secondary chlorination was completed at 970 to 1120 K with a C-CCl_4 gaseous mixture once the cladding was removed in the initial chlorination step, . The major

components of the fuel material, U and Th, were chlorinated and volatilized as UCl_3 and ThCl_4 . Chlorination of spent fuel was successful in removing 90% of the uranium.

2.4 Chlorination of Plutonium

Chlorination of PuO_2 is used to produce Pu metal.¹⁰ Chlorination studies have been performed with several chlorinating reagents including, Cl_2 , HCl , CCl_4 , $\text{Cl}_2 - \text{CCl}_4$, and $\text{HCl} - \text{CCl}_4$. Both Cl_2 and HCl proved to be inadequate reagents as no chlorination was observed using either gas at temperatures ranging from 545 to 790°C. Pure CCl_4 and mixtures of CCl_4 with Cl_2 and Ar proved to be adequate chlorinating reagents at temperatures greater than 500°C. A $\text{CCl}_4 - \text{Cl}_2$ mixture was preferred as other CCl_4 mixtures produced a carbon deposit on the PuCl_3 product. Conversion of PuO_2 to PuCl_3 ranged from 94.2 to 95.4% using the $\text{CCl}_4 - \text{Cl}_2$ mixture. Chlorinated Pu was nonvolatile and remained in the solid phase.

2.5 CCl_4 Decomposition

Several CCl_4 decomposition studies were identified in the literature.¹¹⁻¹³ Decomposition was observed at all temperatures greater than 300°C and increased dramatically in the presence of a metal oxide catalyst such as Al_2O_3 . The CCl_4 decomposition products included C_2Cl_4 , C_2Cl_6 , C_6Cl_6 , C, and Cl_2 . Each of the pyrolysis reaction products identified in the literature could participate in chlorination reactions.

3. THEORY

Two theoretical considerations are important in the development of a chloride volatility process: 1) are the desired chlorination reactions and separations thermodynamically favorable at feasible temperatures, and 2) do the chemical and volatilization reactions occur

rapidly enough at feasible temperatures. Both of these theoretical considerations are discussed below.

3.1 Thermodynamic Equilibrium

The volatilization temperature of selected chlorinated calcine components are shown in Table 4 to illustrate the potential for separating the radioactive and non-radioactive chlorinated calcine components. AlCl_3 , BCl_3 , and ZrCl_4 have low volatilization temperatures as compared to other chlorinated calcine components. Ideally, volatile chlorinated calcine components would volatilize at temperatures above 350°C and provide a gross separation between non-radioactive and radioactive calcine components.

Rigorous thermodynamic equilibrium calculations were completed to obtain a more accurate estimate of the separation possible via calcine chlorination. The computer code selected to make equilibrium calculations was the Facility for the Analysis of Chemical Thermodynamics (F*A*C*T*). F*A*C*T* consists of an extensive database and a library of algorithms designed to complete a variety of thermodynamic computations. The database consists of the thermodynamic properties of over 3800 compounds and a number of binary solutions.¹⁴ The specific code utilized for this work was EQUILIB. The user specifies the set of reactants and state variables (T and P) and the products are calculated by EQUILIB. The equilibrium composition is the one with the lowest Gibbs energy at a specified temperature.

Table 4
Boiling Points of Chlorinated Calcine Components

Component	Pure Component Boiling (B) or Sublimation (S) Point, °C
AlCl ₃	180.85 - S
NaCl	1413 - B
BCl ₃	12.5 - S
Nitrate Salts	600 - decompose as NO _x
CaCl ₂	>1600 - B
HgCl	400 - B
KCl	1500 - B
MnCl ₂	1190 - B
ZrCl ₄	330 - S
CsCl	1303 - B
SrCl ₂	2000 - B
UCl ₃	1727 - B
PuCl ₃	787 - B
NpCl ₃	1527 - B
AmCl ₃	1750 - B

3.2 Chemical Kinetics

There are two ideal models used to describe the chemical reaction between a solid particle and a gas: a constant particle volume model and a shrinking core model as shown in Figure 2.¹⁵ Two general assumptions are made for the constant particle volume model: 1) reactant gas concentration is constant throughout the particle, and 2) reaction occurs throughout the entire particle at varying rates. Hence, the solid particle reacts continuously and progressively until chemical reaction is complete. The shrinking core model is described as follows. Reaction occurs at the particle surface where an ash layer forms as the reaction

progresses. Reactant gases and reaction products must diffuse through the ash layer for the reaction to occur at the unreacted core surface. The particle diameter remains constant throughout the entire reaction. Reaction is complete when the solid particle has been converted to ash.

Figure 2. Schematic diagram of the (a) constant particle volume and the (b) shrinking core heterogeneous chemical kinetic models.

The actual reaction mechanism is somewhere in between the two ideal cases in most real systems; as reaction occurs at the surface beneath the ash layer, and reactant gases penetrate the particle pores and react in the particle interior. However, the chemical kinetics may be adequately described by one of the ideal models in many cases.

A summary of the possible mechanistic steps which influence calcine chlorination is shown in Figure 3. Formulation of a global kinetic rate expression is practical when simplifying assumptions can be made to reduce the number of mechanistic steps (see Figure 3) to between one and three. Formulation of an overall kinetic rate expression is not practical where more than three mechanistic steps influence the overall kinetic rate. Instead, a simple first- or second-order rate expression is used to model reaction kinetics where more than three mechanistic steps influence the chemical reaction rate.

Figure 3. Schematic diagram of a solid particle undergoing chemical reaction with a gas.

The proposed calcine chlorination mechanistic steps are: 1) diffusion of reactant gas through the stagnant gaseous boundary layer surrounding the particle, 2) pore diffusion, 3) reactant gas diffusion through the ash layer, 4) adsorption of reactant gas at the particle surface, 5)

global reaction rate expression is impractical. Simplifying assumptions can be made to reduce the ten possible mechanistic steps to one to three, and formulation of a global kinetic expression is practical in many heterogeneous systems. Where more than three mechanistic steps influence the overall kinetic rate, the global kinetic rate expression may be approximated by an empirical first- or second-order rate expression (see Reference 15).

The overall rate expression developed for calcine chlorination was first-order. A dimensionless form of the first-order reaction expression developed is:

$$\frac{dX_{Ca}}{dt} = k x_A \quad (1)$$

where X_{Ca} is defined as

$$X_{Ca} = \frac{M_{Ca}^o - M_{Ca}}{M_{Ca}^o - M_{Ca,min}^f}, \quad (2)$$

and C_A is defined as the total concentration, C_{tot} times the reactant gas mole fraction, x_A . The quantity $M_{Ca,min}^f$ refers to the mass of calcine remaining at maximum conversion. The concentration of the reactant gas and the volatile reaction products was calculated from the ideal gas law.

4. EXPERIMENTAL

The purpose of calcine chlorination experiments was to gather chlorination rate data and to determine the chemical composition of the chlorination reaction products. The calcine mass remaining in the reactor after each chlorination experiment was assumed to correlate to the conversion of calcine. Chemical analyses completed on the reaction products provided chemical composition data.

4. EXPERIMENTAL

The purpose of calcine chlorination experiments was to gather chlorination rate data and to determine the chemical composition of the chlorination reaction products. The calcine mass remaining in the reactor after each chlorination experiment was assumed to correlate to the conversion of calcine. Chemical analyses completed on the reaction products provided chemical composition data.

Three reactor configurations were utilized in an effort to elucidate the reaction kinetics and mechanisms. The reactor configurations tested were a fixed-bed (reactive gases did not directly pass through the bed), a packed/fluidized bed, and a packed-bed reactor (reactive gases passed directly through the bed). The fixed-bed reactor was used to continuously measure calcine mass during the experiment. Kinetic data collected in the fixed-bed reactor was compared to the data collected in the other two reactor configurations. The kinetic data collected in the packed/fluidized-bed and packed-bed reactors were used to determine the effect of gas velocity past the calcine particles on reaction rate. Theoretically, the reaction rate increases with increasing gas velocity as the stagnant boundary layer surrounding the particle is broken down. At sufficiently high gas velocities, the reaction rate is independent of the gas velocity and the effect of bulk gas diffusion on the overall reaction rate is eliminated.

Most experiments were completed with non-radioactive calcine due to its relative abundance, lower cost, lower hazardous and radioactive waste generation rate, and ease of handling in comparison with radioactive calcine. Non-radioactive calcine is similar to radioactive calcine stored on-site and provides a good estimation of radioactive calcine chlorination behavior. Non-radioactive calcine properties such as porosity and surface area were measured with a mercury porosimeter to enable calculation of a reaction rate per unit surface area.

4.1 Experimental Equipment

Calcine chlorination tests were conducted in a number of configurations including a fixed bed, packed/fluidized bed, and packed bed reactor. The first reactor configuration tested was a fixed-bed reactor as shown in Figure 4. Calcine was placed in a 1" OD quartz basket suspended from a balance by a thin nickel wire. Reactive gases entered the reactor beneath the basket and flowed up past the basket. Hence, the reactive gases did not flow directly through the calcine bed. The off-gas was passed through a condenser where the reaction products were collected. Residual calcine mass was recorded every 30 seconds by an IBM PC (using BalanceTalk software) connected to a Mettler PE-600 balance.

The second reactor configuration tested was a packed/fluidized-bed reactor as shown in Figure 5. Calcine was placed on quartz wool packed into the bottom of a 1"ID quartz reactor tube. Reactive gases were introduced through holes in the bottom portion of the reactor wall. This configuration was a packed bed at low gas flow rates, and a fluidized bed at high gas flow rates. Reactor off-gas was collected in the condenser. The mass of calcine was measured in the reactor before and after each experiment using a Denver Instruments 300D balance.

The third reactor configuration tested was a packed-bed reactor as shown in Figure 6. This reactor configuration was similar to the packed/fluidized-bed setup shown in Figure 5. The major difference between the two configurations is that the gas flow direction was reversed. The packed-bed reactor arrangement was used for radioactive calcine tests due to its small size compared to the other two configurations. Off-gas from the packed-bed reactor was routed through a condenser and a scrubber packed with small pieces of glass tubing and 3M NaOH. The off-gas treatment scheme facilitated the recovery of volatile radioactive species and destroyed any phosgene present.

Figure 4. Diagram of the fixed-bed reactor configuration used to study the feasibility of calcine chlorination.

Figure 5. Diagram of the packed/fluidized-bed reactor configuration used to test the feasibility of calcine chlorination.

Figure 6. Diagram of the packed-bed reactor configuration used to test the feasibility of calcine chlorination.

Both CCl_4 and CO-Cl_2 were studied as chlorinating gases. Argon was used as the carrier gas in all experiments. The CCl_4 feed rate was monitored using a Mettler PE 600 balance linked to an IBM PC in experiments conducted with CCl_4 as the chlorinating gas. A schematic of the feed system is shown in Figure 7. The CCl_4 flow rate was controlled using a gravity-fed calibrated needle valve. A bubbler did not deliver a consistent and reproducible quantity of CCl_4 to the reactor. Argon and CCl_4 were mixed in a small chamber heated to 120°C to ensure complete vaporization of the CCl_4 (boiling point of $\text{CCl}_4 = 76.8^\circ\text{C}$). A small view port was placed in the lowest area of the CCl_4 vaporization chamber to ensure that all CCl_4 fed to the reactor was volatilized. During experiments conducted with CO-Cl_2 , the reactive gas flow was metered with Johnson-Matthey flowmeters. The argon flow rate was metered with a Sierra Model 900 flow controller. The reactive gas- (CCl_4 or the CO-Cl_2 mixture) argon mixture were passed through a 3-way valve and introduced into the reactor bed.

Figure 7. Reactive gas delivery system used in calcine chlorination experiments.

4.2 Experimental Materials and Procedure

The experimental procedure utilized in the three reactor configurations was similar. Each experiment was completed with one gram of calcine, the furnace was heated to the desired temperature, and the reactive gases were introduced to the reactor. Argon was used as the carrier gas in all experiments. The calcine used in all non-radioactive experiments was produced in either Run 77 (alumina) or Run 80 (zirconia) of the 30-cm calciner pilot-plant. The composition of Run 77 and Run 80 calcine is shown in Table 5. As-formed calcine product (mean diameter of 300 μm) was used in all experiments.

Table 5
Chemical Composition of
Run 77 and Run 80 Pilot-Plant Calcine (wt%)

Component	Run 77 Calcine	Run 80 Calcine
Al_2O_3	91.4	14.4
B_2O_3	0.6	0.3
CaO	0.6	25.9
Ce_2O_3	0.1	0.1
Cr_2O_3	0.2	0.7
Cs_2O	0.5	0.3
CaF_2	1.7	34.1
Fe_2O_3	0.6	0.2
K_2O	0.2	<0.1
Na_2O	2.5	0.3
NiO	0.1	0.1
SrO	0.7	0.8
ZrO_2	0.8	22.8

4.2.1 Experimental Procedure

The experimental procedure for chlorination tests was as follows:

- 1- Heat calcine to 600°C and hold for 30 hours to decompose nitrate salts, flash residual moisture, and to volatilize incomplete combustion products such as CO_x. Heat treatment of the calcine at 600°C prior to the experiment is necessary to ensure that the mass loss measured during the experiment is due to chlorination and to volatilization of calcine components.
- 2- Place 1.0 gram of heat-treated alumina or zirconia calcine in the reactor.
- 3- Set the furnace to the test temperature.
- 4- Initiate flow of argon to the chlorination setup using the argon bypass.
- 5- Initiate chlorinating gas flow (CCl₄ or the CO/Cl₂ mixture) and start the run timer, once the temperature of the furnace and the reactor vessel have reached the desired set points. (The mass of residual calcine was monitored every two minutes in experiments completed with the thermobalance.)
- 6- Turn off the reactive gas flow, remove the reactor, and weigh the mass of alumina or zirconia calcine remaining once the desired run time is reached. Record time of reaction, mass of alumina calcine remaining, and reactive gas flows on the run data sheet.
- 7- Collect samples for chemical analysis as desired. Solid samples were scraped from the condenser and submitted with residual calcine samples for SEM, EDS, x-ray fluorescence, and mercury porosimetry analysis. Liquid

samples intended for ICP-MS analysis were prepared by dissolving the condensate in 5 M HNO_3 and then diluted to 250 ml. Residual alumina calcine samples were dissolved in phosphoric acid at 150°C to allow complete dissolution of the calcine.

4.2.2 Chlorination of CaCl_2 -Washed Zirconia Calcine

Two chlorination experiments were completed with samples of CaCl_2 -washed zirconia calcine to verify an alternative pyrochemical treatment flowsheet in conjunction with Lawrence Livermore National Laboratory (LLNL). CaCl_2 -washed samples were prepared at LLNL. The purpose for these experiments was to remove fluoride from the calcine prior to chlorination. Theoretically, if the fluoride is removed from zirconia calcine, a separation of radioactive and non-radioactive calcine components could be achieved via chlorination. CaCl_2 -washed samples were prepared by heating a 50/50 mixture of CaCl_2 -zirconia calcine to 1000°C for several hours. The molten CaCl_2 -zirconia solution was poured through a silica filter to remove the solids (mainly ZrO_2 , actinide oxides, and other metal oxides) from the molten salt (mainly CaF_2 , and CaCl_2). The solids were sent to the ICPP for chlorination experiments. An approximate chemical composition (determined by x-ray diffraction) of the CaCl_2 -washed samples is shown in Table 6.

Chlorination was completed at the ICPP with 3.0 g samples using CCl_4 and a temperature of 900°C for 30 minutes. The remainder of the experimental procedure utilized for sample chlorination was as described in Section 4.2.1.

Table 6
X-Ray Diffraction Analysis of CaCl₂-Washed
Zirconia Calcine

Element	wt%
F	<0.4
Cl	39.54
Mg	0.57
Al	4.23
Ca	35.94
Zr	18.88
Hf	.16
Ta	.23

4.2.3 Analytical Equipment

The equipment used to analyze as-formed calcine, chlorinated calcine reaction products, and residual chlorination solids was available at various locations at the Idaho National Engineering Laboratory. SEM and EDS analyses were completed at the Idaho Research Center (IRC) on an integrated Amray Model 1830 and a Kevex model Delta 5 instrument respectively. The combination of the SEM and EDS instruments provided the elemental composition of the solid phase for all elements with an atomic weight greater than 11 (boron). The mercury porosymmeter, model number Poresizer 9320 located at the IRC, was used to measure the calcine porosity and pore diameter and to estimate the calcine surface area. X-ray diffraction analyses were completed at the ICPP on a Kevex Model D5000. ICP-MS analysis was completed at the ICPP also.

4.3 Experimental Methodology

Chlorination experiments were completed in the fixed-bed reactor first to allow continuous measurement of the calcine mass in the reactor and to get a feel for the behavior of calcine during chlorination. The kinetic data collected during the experiments were compared to the data found in the literature. Calcine chlorination products were submitted for chemical analyses to obtain separation data. The main drawback of the fixed-bed reactor configuration was poor gas/solid contact.

The packed/fluidized-bed reactor and the packed-bed reactor were used to determine the calcine chlorination rate with improved gas/solid contact. Calcine was removed from the reactor and weighed manually after each experiment to compile kinetic data. Thus, a new sample was required for each experiment. Initially, a series of 20 statistically designed experiments were completed in the packed/fluidized-bed reactor with an equimolar mixture of CO-Cl_2 diluted in 85 mol% argon. The purpose of the statistically-designed experiments was to determine which experimental parameter(s) (i.e., time, temperature, and gas flow rate) affected the reaction kinetics the most. The experimental design and results analyses were completed using XSTAT software. Based on the results of the statistically-designed experiments, chlorination experiments were completed with CCl_4 in place of CO-Cl_2 to determine the effect of reactive gas on the reaction rate. The use of CCl_4 allowed completion of many experiments as the reaction time was decreased substantially.

Based on the results obtained in the statistically-designed experiments, an extensive parametric study was completed in the packed/fluidized-bed and packed bed reactor with CCl_4 to determine the effect of reactive gas concentration (or mole fraction), gas flow rate, and temperature on the chlorination rate. The mole fraction of CCl_4 was varied from 0.08 to 0.46, the total gas flow rate was varied from 100 to 1404 ml/min (25°C, 1 atm), and the temperature was varied from 500 to 800°C, to complete the parametric study. The

parametric study data was analyzed to elucidate the reaction kinetics and to compare the performance of the two reactor configurations.

The drawback of the packed/fluidized-bed reactor was poor filtration of the reactor off-gas. Hence, separation data was not collected in the packed/fluidized-bed reactor. The packed-bed reactor was used to determine the separation achieved via chlorination. Non-radioactive samples tested in the packed-bed reactor were submitted for ICP-MS analysis. Radioactive samples tested in the packed-bed reactor were submitted to analytical chemistry for radioanalysis.

5. RESULTS

The results obtained from the calcine chlorination study are presented below. Results include thermodynamic equilibrium calculations, elemental analysis of reaction products, SEM photographs, EDS elemental phase composition, phases determined by x-ray diffraction, calcine pore size and surface area measured with a mercury porosymmeter, and residual calcine mass and/or calcine conversion.

5.1 F*A*C*T* Thermodynamic Equilibrium Calculations

The basic assumptions used to complete equilibrium calculations were: 1) ideal gas behavior; 2) ideal pure solids for condensed phases; and 3) a basis of 100 grams of calcine, 250 grams of CCl_4 , and 1000 grams of argon. Calculations were completed using the calcine compositions for Run 77 (alumina) and Run 80 (zirconia) pilot plant calcine with 0.002 g of U_2O_3 added to estimate the behavior of actinide elements. Also, excess chlorinating reagent and argon were added to in the calculations to simulate long chlorination times. The results of the equilibrium calculations are summarized in Table 7.

Table 7
Calculated Chemical Composition of Alumina and Zirconia Calcine
Chlorinated at 600°C

Component	Solids (g)	
	Run 77 (Alumina) Calcine	Run 80 (Zirconia) Calcine
Al ₂ O ₃	4.40	0.00
AlF ₃	0.00	23.7
B ₂ O ₃	0.12	0.00
CaO	0.22	0.00
CaCl ₂	1.75	98.32
CaF ₂	0.41	1.00
Fe ₂ O ₃	0.18	0.00
K ₂ O	0.02	0.00
Mn	0.50	0.00
Na ₂ O	0.62	0.00
SO ₄	1.20	0.00
ZrO ₂	0.34	0.00
NaCl	4.68	0.00
KCl	0.11	0.00
Gases (g)		
AlCl ₃	218.23	0.02
BCl ₃	1.61	0.00
FeCl ₃	0.85	0.00
ZrCl ₄	0.64	43.12
CsCl	0.002	0.002
UCl ₃	0.0025	0.0025
Total Gas	221.33	43.14
Initial Weight	100.00	100.00
Final Weight (solids)	14.5	123.02
% Mass Change	-85.5	23.02

5.2 Analytical Results

Analytical results include SEM photographs, EDS elemental analysis, x-ray diffraction analysis, mercury porosimetry measurements, ICP-MS analysis of calcine chlorination products, and radioanalysis of radioactive calcine chlorination products.

5.2.1 Analytical Results for Zirconia Calcine

Analyses completed on chlorinated zirconia calcine included SEM, EDS, mercury porosimetry, and x-ray diffraction of residual solid material. No measurable quantities of volatile reaction products were collected. The SEM micrographs of unreacted zirconia calcine and chlorinated zirconia calcine (see Figure 8) revealed that little visible change had taken place during calcine chlorination.

An elemental map of chlorinated zirconia calcine (chlorinated at 600°C in the fixed-bed reactor) generated with EDS is shown in Figure 9. This map is a composite image revealing the relative abundance of the elements chlorine, zirconium, calcium, oxygen, aluminum, fluorine, and sulphur. Isocolorometric areas are indicative of a particular element. It appears that high concentrations of chlorine are located near high concentrations of calcium. High concentrations of fluorine appear to be near high concentrations of aluminum and calcium. The elemental analysis completed with EDS is shown in Table 8.

Figure 9. SEM elemental map of chlorinated zirconia pilot-plant calcine.

Table 8
EDS Analysis of Residual Solids from Chlorinated Zirconia Calcine

Element	Composition (Mol %)
O	39.6
F	12.16
Na	0.55
Al	3.73
Cl	25.68
K	0.4
Ca	13.48
Sr	0.46
Zr	3.93

Results obtained from x-ray diffraction of zirconia calcine and chlorinated zirconia calcine (chlorinated at 600°C in the fixed-bed reactor with CO-Cl₂) are shown in Table 9. The compounds identified in the chlorinated zirconia calcine verify the observations of the elemental map. The major components of chlorinated zirconia calcine were CaClF, ZrO₂, and CaF₂. Other components identified included Ca_{0.15}Zr_{0.85}O_{1.85}, CaO, CaCl₂, and AlF₃.

Table 9
X-Ray Diffraction Analysis Results of Zirconia Calcine

Sample	Principal Constituents	Minor Constituents
Before Chlorination	CaF ₂	AlF ₃ , CaSO ₄ , and ZrO ₂
After Chlorination	CaClF, ZrO ₂ , and CaF ₂	Ca _{0.15} Zr _{0.85} O _{1.85} , CaO, CaCl ₂ , AlF ₃ , and CaCl ₂ ·6H ₂ O

Mercury porosymmetry results of zirconia and chlorinated zirconia calcine (chlorinated at 600°C with CO-Cl₂) are shown in Table 10. The total pore area, total intrusion volume, the pore diameter, and the porosity of zirconia calcine appear to decrease during chlorination.

Table 10
Mercury Porosymmetry Results of Zirconia Calcine
Before and After Chlorination

Sample	Total Intrusion Volume (ml/g)	Total Pore Area (m ² /g)	Average Pore Diameter (μm)	Bulk Density (g/ml)	Porosity (%)
Before Chlorination	0.1471	7.092	0.0829	2.2035	32.40
After Chlorination	0.0649	3.42	0.0759	2.6926	17.47

5.2.2 Analytical Results for Zirconia Calcine Washed with CaCl₂

Zirconia calcine was blended with an equal weight of CaCl₂, heat treated at 1000°C, and filtered to remove residual oxides in an effort to remove fluoride from the calcine prior to treatment via chlorination (see Section 4.2.2). The residual oxide material collected during the CaCl₂ wash was subjected to chlorination with CCl₄ at 900°C. The solid sample weight decreased from 3.0 g to 2.3 g (23 wt%) during chlorination which indicated volatilization of some sample components. The off-gas condensate was subjected to x-ray diffraction analysis. The components identified in the off-gas were mainly C₆Cl₆, a degradation product of CCl₄ and a trace of Zr. The volatile components which caused the weight loss observed in the experiment were not identified.

5.2.3 Analytical Results for Alumina Calcine

Analyses of chlorinated alumina calcine included SEM, EDS, x-ray diffraction, mercury porosymmetry, and ICP-MS. SEM micrographs of unreacted alumina calcine, alumina calcine chlorinated at 600°C in the fixed-bed reactor with CO-Cl_2 , and condensed reaction product are shown in Figure 10. The average particle size appears to decrease during reaction. This decreasing particle size is verified by visual inspection of chlorinated alumina calcine as compared to as-formed calcine in all chlorination experiments. This decreasing particle size can be attributed to attrition rather than a shrinking core reaction mechanism as full-size, low density, calcine particles are visible in the SEM photographs. Visual inspection of chlorinated calcine product also corroborates this result as full-size low-density calcine particles are observed to cling to the sample bottle wall after all chlorination experiments.

(a)

(b)

(c)

Figure 10. SEM photographs of chlorinated alumina pilot-plant calcine and condensed volatile species; a) Photograph before chlorination (20x), b) Photograph after chlorination (15x), and c) Photograph after chlorination (100x).

EDS elemental analysis of alumina calcine chlorinated at 600°C in the fixed-bed reactor with CO-Cl₂ and condensed reaction product is shown in Table 11. Many of the elements identified in the unreacted calcine are not identified in the condensed reaction product.

Table 11
SEM and EDS Analysis of Residual Calcine from Alumina
Calcine Chlorination Experiments

Element	Residual Solids Average Composition (mol%)	Condensed Volatile Reaction Product Composition (mol%)
O	55.54	60.83
Mg	1.3875	0.00
Al	36.0975	11.87
P	1.61	0.00
S	1.5525	0.00
Cl	2.465	27.29
Ca	1.3	0.00
Mn	0.005	0.00
Fe	0.02	0.00
Cu	0.035	0.00

X-ray diffraction results for alumina calcine chlorinated at 600°C in the fixed-bed reactor with CO-Cl₂ and condensed reaction product are shown in Table 12. Compounds of aluminum are the principal components of each sample. Major components are present in the sample in concentrations greater than 15 wt%. Minor components can be present in concentrations less than 15 wt%.

Table 12
X-Ray Diffraction Analysis of
Unreacted and Chlorinated Alumina Calcine

Sample	Major Constituents	Minor Constituents
Before Chlorination	$\gamma\text{-Al}_2\text{O}_3$	$\alpha\text{-Al}_2\text{O}_3 \approx 2\%$, $\delta\text{-Al}_2\text{O}_3$ and amorphous Al_2O_3
After Chlorination	None Identified	$\alpha\text{-Al}_2\text{O}_3 \approx 6\%$, $\gamma\text{-Al}_2\text{O}_3$, $\beta\text{-Al}_2\text{O}_3$, CaSO_4 , and CaCl_2
Condensed Off-gas from Chlorination	$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$	CaSO_4 , CaF_2 , $\text{Ca}(\text{ClO})_2 \cdot 3\text{H}_2\text{O}$, and $\text{Ca}(\text{PO}_3)_2$

The results of mercury porosimetry measurements on unreacted and reacted alumina calcine (chlorinated at 600°C with CO-Cl_2 in the fixed-bed reactor) are shown in Table 13. The total pore diameter, total intrusion volume, and porosity increased, whereas the total pore area decreased during chlorination.

Table 13
Mercury Porosymmetry Results of Alumina Pilot-Plant Calcine
Before and After Chlorination

Sample	Total Intrusion Volume (ml/g)	Total Pore Area (m^2/g)	Average Pore Diameter (μm)	Bulk Density (g/ml)	Porosity (%)
Before Chlorination	0.3972	63.872	0.0249	1.1878	47.18
After Chlorination	0.5275	46.383	0.0455	1.0957	57.79

ICP-MS analysis of alumina calcine chlorinated in the packed-bed reactor at 600°C with an equimolar CO-Cl_2 mixture for two hours and condensed reaction product is shown in Table

14. Nearly all calcine components are associated with the volatilized reaction products, and a clean separation between components was not achieved.

Table 14
Elemental Analysis of Off-Gas and Residual Solid Samples Taken
During Chlorination of Non-Radioactive Alumina Calcine

Element	Run #				
	Before	1		2	
		Solids (g)	Condensate (g)	Solids (g)	Condensate (g)
Al	0.465	0.0902	0.380	0.147	0.325
B	0.002	0.000154	7.8×10^{-4}	4.76×10^{-4}	4.38×10^{-4}
Cs	0.004	$<8 \times 10^{-5}$	3.25×10^{-5}	$<8 \times 10^{-6}$	2.3×10^{-5}
Na	0.002	7.68×10^{-4}	2.1×10^{-3}	8.16×10^{-4}	2.0×10^{-3}
Sr	0.005	5.76×10^{-6}	$<2.5 \times 10^{-6}$	5.1×10^{-6}	3.25×10^{-6}
Total	0.478	0.091	0.382	0.148	0.327

5.2.4 Analytical Results for Radioactive Calcine

The calcine used for radioactive calcine chlorination tests was retrieved from a sample storage rack at the Remote Analytical Laboratory (RAL). The sample was labelled as 3-way blend calcine (a blend of liquid sodium waste, aluminum waste, and non-radioactive aluminum nitrate calcined in the New Waste Calcliner Facility). The composition of this material was thought to closely correspond to the alumina calcine currently stored in the on-site bin storage area. However, as the test progressed, it was obvious that the material retrieved for this test was not alumina calcine as little off-gas condensate was collected during the chlorination experiment. Chemical analysis of the calcine (available after the tests were completed) revealed that CaF_2 was present in the calcine. Hence, separation of radioactive and non-radioactive components was not achieved as limited amounts of chlorine

reacted with the calcine to produce non-volatile chlorides such as CaCl_2 and AlF_3 as demonstrated with non-radioactive zirconia calcine chlorination tests. All glassware was rinsed and the rinsate was sent to a counting room to determine the presence of certain radionuclides. Three experiments were completed at 600°C with the radioactive calcine: two with CO-Cl_2 diluted in argon and one (a blank) with argon only. Radioanalysis of unreacted calcine and condensed reaction product are shown in Table 15 for Cs.

Table 15
Analytical Results from Radioactive Calcine Chlorination Tests

Sample	1	2	Blank
Unreacted Calcine Analytical Results			
^{134}Cs (g)	2.89×10^{-12}	2.89×10^{-12}	2.89×10^{-12}
^{137}Cs (g)	6.97×10^{-6}	6.97×10^{-6}	6.97×10^{-6}
Analytical Results from Chlorination Experiments			
^{134}Cs in Condenser (g)	1.08×10^{-12}	7.82×10^{-13}	6.47×10^{-15}
^{137}Cs in Condenser (g)	3.09×10^{-6}	2.25×10^{-6}	2.38×10^{-8}
^{134}Cs in Bubbler (g)	0	1.92×10^{-15}	0
^{137}Cs in Bubbler (g)	0	6.73×10^{-9}	9.02×10^{-10}
^{134}Cs Collected in off-gas (Mass Fraction)	0.374	0.271	0.002
^{137}Cs Collected in off-gas (Mass Fraction)	0.443	0.322	0.003

Radioactive Cs was chlorinated and volatilized from the residual calcine solids. Run numbers 1 and 2 were completed under identical conditions for nearly two hours; however the carbon monoxide flow rate for Run 2 dropped 90% after 100 minutes. The blank run was

completed under the same conditions as Run 1 and 2 except Cl_2 and CO were not introduced to the reactor.

5.3 Chemical Kinetics

Experiments were completed in all reactor configurations (see Figure 4, 5, and 6) to determine the rate of calcine mass change due to pilot-plant calcine chlorination. The majority of the mass loss experiments were completed with simulated alumina calcine since the results of thermodynamic calculations showed that a gross separation of zirconia calcine components via chlorination was not feasible. A few zirconia calcine chlorination experiments were completed to verify the results of the equilibrium calculations.

5.3.1 Fixed-Bed Mass Change Results for Alumina and Zirconia Calcine

The results from experiments completed in the fixed-bed reactor were plotted as calcine mass remaining in the reactor as a function of reaction time. The results for an alumina calcine chlorination experiment completed at 600°C with equimolar CO-Cl_2 are shown in Figure 11. The mass loss rate increased from 0 to 175 minutes as the reactive gases penetrated the calcine bed. A constant mass loss rate was observed from 175 to 275 minutes as the calcine mass remaining in the reactor dropped from 0.80 to 0.30 grams. The reaction was complete (0.15 g calcine remaining in the reactor or 85% mass loss) after approximately seven hours.

The mass of calcine increased during the first 15 minutes of the experiment in experiments completed with zirconia calcine. No mass change occurred after 15 minutes. The overall mass loss results observed during each of the experiments completed in the fixed bed apparatus are shown in Table 16. The calcine mass decreased a maximum of 86% during chlorination of simulated alumina calcine and increased a maximum of 14% during chlorination of simulated zirconia calcine. The initial reaction rate observed for alumina calcine was $0.07 \text{ (g-calcine volatilized) / (g-calcine hour)}$.

Table 16
Observed Mass Loss of Chlorinated Alumina and Zirconia Calcine

Run #	Calcine Type	Run Duration	% Mass Change
1	Alumina	8 hours	-85
2	Alumina	8 hours	-86
3	Zirconia	4 hours	+14
4	Zirconia	4 hours	+14

Figure 11. Measured residual mass of Run 77 (alumina) calcine during chlorination with a CO-Cl₂ mixture at 600°C.

5.3.2 Packed-Fluidized Bed Mass Change Results for Alumina Calcine

The results from the statistically-designed chlorination experiments completed with equimolar CO-Cl_2 diluted in 85% Ar are shown in Table 17. The temperature was varied from 600 to 800°C, the total gas flow rate was varied from 250 to 500 ml/min, and the time was varied from 1 to 3 hours. Statistical analysis of the mass remaining at the end of the experiment revealed that time was the variable that affected the mass loss observed during the experimental runs, whereas the gas flow rate and temperature did not appreciably affect the calcine mass loss rate. The statistical model generated from the experimental results indicated that the maximum mass loss rate would be obtained at a temperature of 800°C and a total gas flow rate of 375 ml/min. The reaction rate observed during the statistically designed experiments varied from 0.10 to 0.17 (g-calcine volatilized) / (g-calcine · hour).

CCl_4 was used as the chlorinating reagent in place of CO-Cl_2 to chlorinate alumina calcine in the packed/fluidized bed reactor after the statistically-designed experiments were completed. A complete listing of residual mass data collected in the packed/fluidized-bed reactor with CCl_4 is shown in Appendix A. The results from chlorination experiments completed with various CCl_4 mole fractions at 600°C are shown in Figure 12 to illustrate the effect of CCl_4 mole fraction on the reaction rate. The calcine conversion appears to be linear until the conversion reaches approximately 0.50, and then begins to decrease. Hence, the conversion rate is equal to the initial rate until the conversion is 0.50

The results from chlorination experiments completed at 500, 600, 700, and 800°C are shown in Figure 13 to illustrate the effect of temperature on reaction rate. The initial kinetic chlorination rate constant (assuming linear chlorination rate) is plotted as a function of temperature. The rate constant increased significantly between 500 and 600°C, and then decreased between 700 and 800°C. The calcine chlorination rate observed with CCl_4 in the temperature range studied varied between 1.44 and 11.6 (g-calcine volatilized) / (g-calcine · hour).

The results from chlorination experiments completed at various gas flow rates are shown in Figure 14 to illustrate the effect of gas flow rate on reaction rate. The calcine conversion appears to be independent of CCl_4 mole fraction above 0.08.

Table 17
Experimental Conditions Used in Statistically-Designed
Calcine Chlorination Experiments with CO-Cl_2

Run #	Temperature of Reactor ($^{\circ}\text{C}$)	Total Gas Flow rate* (ml/min)	Reaction Time (hours)	Mass Remaining (grams)
1	600	250	1	0.84
2	800	250	1	0.83
3	600	500	1	0.90
4	800	500	1	0.83
5	600	250	3	0.74
6	800	250	3	0.58
7	600	500	3	0.71
8	800	500	3	0.70
9	600	375	2	0.76
10	800	375	2	0.68
11	700	250	2	0.70
12	700	500	2	0.72
13	700	375	1	0.89
14	700	375	3	0.66
15	700	375	2	0.79
16	700	375	2	0.78
17	700	375	2	0.73
18	700	375	2	0.74
19	700	375	2	0.75
20	700	375	2	0.73

* 20°C , 1 atm, 85 mol% Ar - balance equimolar CO-Cl_2 mixture

Figure 12. Conversion of calcine by chlorination with CCl_4 at 500°C in a packed/fluidized-bed reactor setup.

Figure 13. Reaction rate constant for the reaction of alumina calcine with CCl_4 at various temperatures.

Figure 14. Conversion of calcine by chlorination with CCl₄ at 600°C in a packed/fluidized-bed reactor.

5.3.3 Packed-Bed Mass Change Results for Alumina Calcine

Initially, CCl_4 was used as the chlorination reagent in the packed-bed reactor. A complete list of the experimental calcine mass loss results for the packed-bed reactor configuration is presented in Appendix B. The results from a series of chlorination experiments are shown in Figure 15 for a reactor temperature of 600°C , a time of three minutes, and various CCl_4 mole fractions as noted. Variation of the data points shown in Figure 17 was due partially to the inability to accurately meter CCl_4 at the Ar flow rates tested. The reaction rate varied between 1.8 and 8.4 (g-calcine volatilized)/(g-calcine · hour).

Figure 15. Conversion of calcine by chlorination with CCl_4 at 600°C in a packed-bed reactor at various superficial reactive gas velocities.

Calcine chlorination experiments were completed in the packed-bed reactor using both a CO-Cl_2 mixture and CCl_4 as the chlorinating reagent to determine the time required to completely chlorinate calcine and to determine experimental parameters for radioactive calcine tests. The residual calcine mass observed during these experiments is shown in Table 18. The reaction is

complete after approximately two hours using CO-Cl₂ while it is nearly complete after 15 minutes using CCl₄ as the chlorinating reagent.

Table 18
Mass Change of Alumina Calcine during Chlorination
in a Packed Bed Reactor

Run #	Initial Mass (g)	Final Mass	Time
1*	1.00	0.24	15 Minutes
2**	1.00	0.24	2 Hours
3**	1.00	0.34	2 Hours***

* Experiment completed with CCl₄ as the chlorinating reagent

** Experiment completed with CO-Cl₂ as the chlorinating reagent

*** Carbon monoxide flow rate decreased during final 15 minutes of experiment.

The chlorination experiments with actual radioactive calcine were completed with CO-Cl₂ diluted in argon using the packed bed configuration due to environmental concerns with CCl₄. The radioactive calcine used in the tests was made from a blend of sodium waste (liquid HLW high in sodium resulting from decontamination operations), aluminum waste (liquid HLW resulting from reprocessing aluminum-clad fuel) and non-radioactive aluminum nitrate (added to ensure efficient calcination). No analytical results for calcium or fluoride were available prior to the experiment. The mass loss observed during the chlorination experiments is shown in Table 19. The mass of calcine increased during the chlorination experiments.

Table 19
Mass Change Results Observed During Calcine Chlorination
Experiments Completed with Actual Radioactive Calcine

Run #	Ar Flow Rate (ml/min)	CO Flow Rate (ml/min)	Cl ₂ Flow Rate (ml/min)	Calcine Mass Before (grams)	Calcine Mass After (grams)
1	200	20	20	1.00	1.12
2	200	20	20	1.00	1.09
Blank	200	0	0	1.00	1.04

6. DISCUSSION

Two considerations were considered in the investigation of calcine chlorination: 1) does a separation between radioactive and non-radioactive calcine components occur and 2) does the separation occur rapidly enough at suitable temperatures to design a process. The experimental results will be discussed to evaluate calcine chlorination on the basis of the two considerations. First, the equilibrium calculations are compared to the experimental results. Second, the chlorination kinetics are discussed and an empirical first-order rate expression is presented for the packed-bed reactor. Third, kinetic mechanistic steps are discussed and possible simplifying assumptions are presented

6.1 Thermodynamic Equilibrium Calculations and Observed Separation Results

Preliminary thermodynamic equilibrium calculations completed to ascertain the feasibility of calcine chlorination as a method to separate radioactive and non-radioactive alumina calcine components were not promising for zirconia calcine as no significant volatile species were predicted and the mass of calcine was predicted to increase. However, for alumina calcine, the calculation results were favorable.

6.1.1 Zirconia Calcine Equilibrium Calculations and Experimental Results

Separation of radioactive and non-radioactive zirconia calcine components via chlorination was not favorable according to thermodynamic equilibrium calculations (see Table 7). The major calcine components predicted were CaCl_2 , AlF_3 , and ZrCl_4 . Other volatile species predicted during the calculations were CsCl and UCl_3 . The only major volatile species was ZrCl_4 . The major reaction predicted during chlorination was

with a heat of reaction of -45.5 kcal / mole at 600°C.

Analytical results of unreacted and reacted zirconia calcine samples showed good agreement with the equilibrium calculations except for Zr as no volatile reaction products were collected during chlorination experiments. X-ray diffraction completed on chlorinated zirconia calcine showed the presence of AlF_3 and CaClF (see Table 9). No Al_2O_3 was identified in either unreacted or reacted zirconia calcine samples. The EDS elemental map (see Figure 9) showed the Cl in close proximity with calcium indicating chlorination of CaF_2 (see Equation 3).

Areas of Cl-free zones are visible in the elemental map also. This is attributed to reaction between calcine and chlorine at the particle surface only. Reaction did not penetrate into the calcine particle further due to sintered CaClF at the particle surface. The melting temperature of pure CaClF was estimated to be 735°C from an equilibrium phase diagram of CaF_2 and CaCl_2 .²⁰ The CaClF melting point may be even lower in the presence of impurities. Hence, sintering of the chlorinated zirconia calcine surface may account for the incomplete reaction observed during chlorination experiments.

The thermodynamic calculations were inaccurate for zirconia calcine in that no $ZrCl_4$ was identified as a reaction product in any of the experiments. This is due to both the extremely low chlorination kinetic rate of ZrO_2 at $600^\circ C$ and the sintering action of the chlorinated calcium compounds.

Mass loss was observed in chlorination experiments completed with zirconia calcine treated with $CaCl_2$. However, $ZrCl_4$ was not identified as a reaction product. Instead, the only major compound identified in the condensed off-gas was a degradation product of CCl_4 , C_6Cl_6 . Zr was detected in minor quantities with x-ray fluorescence. Hence, chlorination does not appear to be an effective method for separating radioactive and non-radioactive zirconia calcine components.

6.1.2 Alumina Calcine Equilibrium Calculations and Observed Separations

Equilibrium calculations indicated that a separation between radioactive and non-radioactive alumina calcine components was feasible. The major volatile species predicted were $AlCl_3$, BCl_3 , $FeCl_3$, $ZrCl_4$, UCl_3 , and $CsCl$ (see Table 7). Hence, two radioactive species were predicted to volatilize. The calculated components of the residual solid was unreacted Al_2O_3 , $NaCl$, and other unreacted oxides and non-volatile chlorides. A mass reduction of 85.5 wt% was predicted by the equilibrium calculations. The major chemical reaction predicted was

with a ΔH_{rxn} of -21.9 kcal/mole at $600^\circ C$.

The results from SEM,EDS, and x-ray diffraction analysis verified Equation (4) as $AlCl_3$ was found in the off-gas samples. However, these analyses failed to indicate the presence of Cs. ICP-MS analysis of reacted calcine and condensed off-gas were necessary to detect Cs. Other volatile species detected in trace quantities with ICP-MS included Cs, Na, and Sr. However,

only a fraction of the original mass of these trace elements was recovered in the residual solids and the condensed off-gas samples. It is possible that variations in the calcine composition or analytical error could account for the missing trace elements. Additional unit operations would be required to separate trace radioactive species (such as CsCl and UCl_3) from other volatile non-radioactive components such as AlCl_3 to utilize chlorination as a treatment method for alumina calcine.

6.2 Alumina Calcine Chlorination Kinetics

The reaction rate observed during alumina calcine chlorination experiments was dependent on chlorinating reagent, reactant gas flow, reactant gas concentration, reactor configuration, and temperature. A parametric study was completed in an effort to develop an overall kinetic rate expression. General correlations between some experimental parameters and the reaction rate were found. However, the effect of some experimental parameters on the reaction rate defied simple explanation. The effect of each experimental parameter on reaction rate and formulation of a kinetic model are discussed below.

6.2.1 Temperature Effects and Activation Energy

The effect of temperature on the reaction rate constant typically follows the Arrhenius Law. The activation energy calculated with the Arrhenius law between 500 and 600°C for alumina calcine chlorination was 6.7 kcal/mole. This is much lower than the literature-reported values for reaction of Al_2O_3 and bauxite ore with various mixtures of C-Cl_2 and CO-Cl_2 diluted in Ar (see Section 2.1). The rate constant observed during chlorination experiments did not follow the Arrhenius Law over the entire temperature range studied (see Figure 13). The failure of the Arrhenius Law to describe the effect of temperature on the reaction rate constant was due to four major causes: 1) a shifting reaction mechanism over the wide temperature range studied, 2) the $\alpha\text{-Al}_2\text{O}_3$ phase transition, 3) CCl_4 decomposition, and 4) increasing effect of

mass-transfer resistance with increasing temperature. The shifting reaction mechanism is consistent with results reported in the literature for Al_2O_3 chlorination.

Alumina calcine consists of several Al_2O_3 phases including relatively chlorination-resistant α - Al_2O_3 . The fraction of α - Al_2O_3 in the calcine increases during chlorination due to three main causes. First, reactive Al_2O_3 phases are chlorinated and volatilized. Second, the phase transformation of subphases of Al_2O_3 to α - Al_2O_3 at temperatures much lower than the typical phase transformation temperature (1050°C) in the presence of impurities (see Reference 3). Third, the heat of reaction (see Equation 4) increases the calcine surface temperature enough to allow the α - Al_2O_3 phase transition to occur (see Reference 3). Detailed calcine surface temperature measurements and phase transformation temperature studies would be required to verify this theory.

As the temperature of the bulk gas increases, the amount of CCl_4 decomposing prior to calcine chlorination increases. Hence, as the temperature is increased, the concentration of CCl_4 reaching the calcine particle decreases.

6.2.2 Reactor Configuration Effects

The alumina calcine chlorination rate was different in each of the experimental reactor configurations tested. The fastest chlorination rates were observed in the packed/fluidized-bed configuration and the slowest rates were observed in the fixed-bed configuration. The difference in rates observed in the different reactors is due to the transport of reactant gas to the stagnant gas boundary layer surrounding the particle. Several models were evaluated in an effort to develop a theoretical kinetic model.

6.3 Alumina Calcine Chlorination Reaction Mechanisms and Kinetic Model.

There are 10 mechanistic steps (see Section 3.2) which could affect calcine chlorination kinetics. These mechanistic steps (resistances to reaction) and an empirical kinetic model for the observed data in the packed/fluidized-bed and packed-bed reactor are discussed below.

6.3.1 Packed/Fluidized-Bed Reaction Kinetics

The development of an overall theoretical rate expression for alumina calcine is not practical at this stage of investigation. Of the 10 possible reaction mechanisms identified, five to six could be included in formulating the overall rate expression. To include these five mechanisms in the overall rate expression the following parameters must be measured experimentally: Thiele modulus, D_e , k_{ads} , k_{rxn} , CCl_4 decomposition, and the physical and transport properties for the CCl_4 -Ar system.

The resistance of bulk gas diffusion on the reaction rate was demonstrated in experiments completed in the packed/fluidized bed. The effect of bulk gas diffusion on reaction rate was diminished as the flow rate of reactive gas was increased (see Figure 16) above 3500 ml/min. Flow rates higher than 3500 ml/min did not change the chlorination rate.

The reaction rate was not a function of reactant gas mole fraction at higher gas flow rates and CCl_4 mole fractions above 0.16 (see Figure 14) in the packed/fluidized bed. Further increases in reaction rate were not observed at CCl_4 mole fractions as high as 0.44. This may be due to control of the reaction rate by a Langmuir-Hinshelwood mechanism. Once all available adsorption sites are occupied, higher concentrations of reactant gases (such as CCl_4) will not increase the reaction rate. An alternative cause for the constant reaction rate at high CCl_4 mole fractions could be carry-over of small particulates in the off-gas. Larger-scale reactors would need to be tested to verify the reaction kinetics observed in the packed-fluidized bed reactor to complete scale-up of this process.

6.3.2 Packed-Bed Reactor Kinetics

The discussion presented for kinetic effects in the packed/fluidized bed reactor is applicable to the kinetic effects observed in the packed-bed reactor with the exception of the bulk gas diffusion resistance. The reaction rate was not influenced by the bulk gas flow rate. Hence, this effect would not be included in a theoretical reaction expression for the packed-bed reactor.

The kinetic results from experiments completed in a packed-bed reactor setup showed a dependence on the reactant concentration (or reactant gas mole fraction), and a first-order rate expression was applied to the results. A plot of the kinetic results from packed-bed reactor experiments is shown in Figure 16. The first-order rate fit (see Equation 2) gives a correlation coefficient of 0.98. The first-order rate fit appears to provide an adequate model for the chlorination kinetics observed in a packed-bed reactor.

Figure 16. Alumina calcine conversion observed during experiments completed in a packed-bed reactor with carbon tetrachloride at 600°C.

7. CONCLUSIONS AND RECOMMENDATIONS

Based on the calcine chlorination experimental work conclusions and recommendations are made. The conclusions are:

- 1- The thermodynamic equilibrium calculations completed on F*A*C*T* showed good agreement with experimental results.
- 2- An empirical first-order reaction expression provided a good model of calcine chlorination kinetics in a packed-bed reactor
- 3- The calcine chlorination rate was approximately eight times faster with CCl_4 as compared to CO/Cl_2 .
- 4- Several kinetic mechanisms influence the rate of alumina calcine chlorination: bulk gas diffusion, pore diffusion, adsorption of reactant gas at the solid surface, decomposition or reaction of reactant gas, and chemical reaction at the surface. Diffusion through the ash layer did not affect the kinetic rate.
- 5- Chlorination of alumina calcine yields a separation of some calcine components. However, chlorination does not result in a clean separation of radioactive and non-radioactive calcine components at temperatures above 600°C .
- 6- Chlorination of zirconia calcine results in a mass increase and no separation between calcine components occurs.

The following recommendations are made for future calcine chlorination investigations:

- 1- Measure the following calcine properties: Thiele modulus, D_e , k_{ads} , k_{rxn} , k_{des} , and CCl_4 decomposition and/or CO/Cl_2 gas phase reaction.
- 2- Measure the following physical and transport reactive gas ($\text{CCl}_4\text{-Ar}$ and $\text{CO/Cl}_2\text{-Ar}$) properties: viscosity, binary diffusion coefficient, density.
- 3- Complete additional chlorination experiments to optimize the chlorination temperature with respect to kinetics and radioactive/non-radioactive component separation.
- 4- Investigate methods to remove trace radioactive chlorides from non-radioactive chlorides.

- 5- Complete surface temperature measurements to ensure that the bulk temperature measured in the reactor accurately represents the actual surface temperature of the calcine particle.
- 6- Complete Al_2O_3 phase transition studies at the surface temperature measured during chlorination experiments.
- 7- Recommended alumina calcine chlorination reactor configuration and parameters are: fluidized-bed reactor configuration (maximum rate), reactor temperature of 600°C (maximum rate), and CCl_4 as the reactant gas. If necessary, a packed bed of calcine could be used to deplete the residual CCl_4 in the fluidized reactor. The calcine in the packed bed could be batch-fed to the fluidized bed counter-current to the effluent gas flow.

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Appendix A

Table A.1
Experimental Raw Data from Calcine Chlorination Experiments Completed
in a Packed/Fluidized Bed Reactor

Run #	T _{reactor}	Reaction Time (min)	Argon Gas Flow Rate (ml/min)	M ^o _{CCl₄} (g)	M ^f _{CCl₄} (g)	M ^o _{Calcine} (g)	M ^f _{Calcine} (g)
1	600	1	200	-1.93	-2.54	1	0.92
2	600	2	200	-0.59	-1.78	1	0.85
3	600	3	200	-0.57	-2.36	1	0.79
4	600	4	200	-3.14	-5.51	1	0.72
5	600	5	200	-0.59	-3.58	1	0.65
6	600	1	200	-0.61	-1.65	1	0.90
7	600	2	200	-0.68	-2.75	1	0.74
8	600	3	200	-6.41	-9.48	1	0.62
9	600	4	200	-0.80	-4.82	1	0.52
10	600	6	200	-1.46	-7.78	1	0.30
11	600	2	200	-0.21	-0.64	1	0.93
12	600	4	200	-0.16	-0.82	1	0.92
13	600	4	200	-2.75	-6.68	1	0.6
14	600	3	200	-8.23	-11.16	1	0.68
15	600	2	200	-1.93	-3.86	1	0.79
16	600	1	200	-5.3	-6.28	1	0.90
17	600	4	200	-1.82	-5.61	1	0.59
18	600	3	200	-7.09	-9.93	1	0.67
19	600	2	200	-7.48	-9.48	1	0.79
20	600	3	300	-2.97	-7.18	1	0.64
21	600	3	400	-0.46	-6.72	1	0.58
22	600	3	600	-2.39	-10.16	1	0.51
23	600	3	800	0	-12.1	1	0.42
24	600	2	275	0	-1.05	1	0.82
25	600	4	275	0	-2.33	1	0.58
26	600	6	275	0	-3.55	1	0.39
27	600	3	275	0	-1.73	1	0.69
28	600	3	550	0	-3.42	1	0.56
29	600	3	825	0	-4.98	1	0.49
30	600	3	1100	0	-6.55	1	0.47
31	600	3	1375	0	-8.88	1	0.47
32	600	2	351	0	-0.46	1	0.94
33	600	4	351	0	-0.81	1	0.84

Table A.1 (continued)

Run #	T _{reactor}	Reaction Time (min)	Argon Gas Flow Rate (ml/min)	M ^o _{CCl₄} (g)	M ^f _{CCl₄} (g)	M ^o _{Calcine} (g)	M ^f _{Calcine} (g)
34	600	6	351	0	-1.3	1	0.73
35	600	3	351	0	-0.70	1	0.89
36	600	3	351	0	-1.12	1	0.79
37	600	3	351	0	-1.67	1	0.71
38	600	3	1404	-7.9	-10.3	1	0.76
39	600	3	702	0	-1.22	1	0.84
40	600	3	1053	-3.43	-5.05	1	0.78
41	600	1	1404	0	-0.73	1	0.97
42	600	2	1404	0	-1.48	1	0.91
43	600	4	1404	0	-2.96	1	0.69
44	600	1	1404	0	-1.53	1	0.88
45	600	1	1270	0	-1.71	1	0.83
46	600	2	1270	0	NR (-3)	1	0.67
47	600	3	1270	0	-4.65	1	0.52
48	600	4	1270	0	-6.14	1	0.42
49	600	1	1135	0	-1.93	1	0.89
50	600	2	1135	0	-4.38	1	0.54
51	600	4	1135	0	-9.06	1	0.31
52	600	3	423	0	-1.47	1	0.73
53	600	3	846	0	-2.74	1	0.59
54	600	3	1387	0	-4.89	1	0.48
55	600	3	900	0	-25.74	1	0.31
56	600	3	1000	0	-14.72	1	0.38
57	600	3	300	0	-4.33	1	0.37
58	600	3	400	0	-5.85	1	0.34
59	600	3	600	0	-8.75	1	0.31
60	600	3	800	0	-11.72	1	0.38
61	600	1	1320	0	-1.52	1	0.85
62	600	2	1320	0	-3.05	1	0.66
63	600	3	1320	0	-4.80	1	0.45
64	600	4	1320	0	-6.16	1	0.34
65	600	3	330	0	-1.21	1	0.77
66	600	2	660	0	-1.62	1	0.76
67	600	3	990	0	-3.60	1	0.47
68	600	3	660	0	-2.34	1	0.57
69	600	1	1320	0	-1.59	1	0.91
70	600	2	1320	0	-2.96	1	0.78
71	600	3	1320	0	-4.23	1	0.48
72	600	4	1320	0	-6.26	1	0.42

Table A.1 (continued)

Run #	T _{reactor}	Reaction Time (min)	Argon Gas Flow Rate (ml/min)	M ^o _{CCl₄} (g)	M ^f _{CCl₄} (g)	M ^o _{Calcine} (g)	M ^f _{Calcine} (g)
73	600	3	330	0	-1.25	1	0.81
74	600	3	660	0	-2.43	1	0.67
75	600	3	990	0	-3.62	1	0.51
76	600	5	100	0	NR (-1)	1	0.78
77	600	10	100	0	NR (-2)	1	0.54
78	600	15	100	0	NR (-3)	1	0.29
79	600	20	100	0	NR (-4)	1	0.14
80	600	1	100	0	-0.57	1	0.91
81	600	2	100	0	-1.14	1	0.78
82	600	3	100	0	-1.76	1	0.65
83	600	4	100	0	-2.44	1	0.58
84	600	5	100	0	-3.17	1	0.41
85	600	6	100	0	-3.92	1	0.33
86	600	7	100	0	-4.44	1	0.27
87	600	8	100	0	-4.94	1	0.24
88	600	9	100	0	-5.16	1	0.19
89	600	10	100	0	-6.06	1	0.15
90	600	11	100	0	-6.36	1	0.12
91	600	12	100	0	-7.02	1	0.16
92	700	1	100	0	-0.60	1	0.94
93	700	2	100	0	-1.26	1	0.83
94	700	3	100	0	-1.81	1	0.78
95	700	4	100	0	-2.22	1	0.7
96	700	5	100	0	-2.92	1	0.64
97	700	6	100	0	-3.61	1	0.6
98	700	7	100	0	-4.34	1	0.5
99	700	8	100	0	-4.91	1	0.47
100	700	10	100	0	-6.06	1	0.41
101	700	2	100	0	-1.87	1	0.7
102	700	4	100	0	-3.77	1	0.44
103	700	6	100	0	-5.59	1	0.18
104	700	12	100	0	-7.38	1	0.26
105	700	14	100	0	-8.55	1	0.2
106	700	16	100	0	NR (-9.6)	1	0.13
107	700	5	100	0	-0.97	1	0.87
108	700	10	100	0	-1.91	1	0.75
109	700	15	100	0	-2.19	1	0.63
110	700	20	100	0	-3.92	1	0.51
111	800	5	100	0	-4.65	1	0.67

Table A.1 (continued)

Run #	T _{reactor}	Reaction Time (min)	Argon Gas Flow Rate (ml/min)	M ^o _{CCl₄} (g)	M ^f _{CCl₄} (g)	M ^o _{Calcine} (g)	M ^f _{Calcine} (g)
112	800	10	100	0	-9.84	1	0.34
113	800	15	100	0	-13.38	1	0.19
114	800	21	100	0	-20.49	1	0.05
115	800	2.5	100	0	-2.40	1	0.83
116	800	7.5	100	0	-7.17	1	0.49
117	800	12.5	100	0	-12.13	1	0.20
118	800	10	100	0	-1.99	1	0.87
119	800	20	100	0	-3.89	1	0.75
120	800	30	100	0	-5.53	1	0.65
121	800	1	100	0	-0.62	1	0.89
122	800	2	100	0	-1.24	1	0.93
123	800	4	100	0	-2.33	1	0.85
124	800	6	100	0	-3.42	1	0.77
125	800	10	100	0	-6.31	1	0.58
126	800	15	100	0	-9.28	1	0.4
127	800	20	100	0	-11.78	1	0.27
128	800	25	100	0	-15.28	1	0.15

Appendix B

Table B.1
Experimental Raw Data from Calcine Chlorination Experiments Completed
in a Packed Bed Reactor

Run #	T _{reactor}	Reaction Time (min)	Argon Gas Flow Rate (ml/min)	M ^o _{CCl₄} (g)	M ^f _{CCl₄} (g)	M ^o _{Calcine} (g)	M ^f _{Calcine} (g)
1	600	3	351	0	-0.69	1	0.90
2	600	3	702	0	-1.22	1	0.91
3	600	3	1053	0	-1.75	1	0.89
4	600	3	1404	0	-2.20	1	0.90
5	600	3	275	0	-2.09	1	0.79
6	600	3	550	0	-3.43	1	0.71
7	600	3	825	0	-3.87	1	0.75
8	600	3	1100	0	-5.54	1	0.81
9	600	3	1375	0	-8.61	1	0.75
10	600	3	330	0	-1.15	1	0.88
11	600	3	660	0	-2.28	1	0.85
12	600	3	990	0	-3.40	1	0.85
13	600	3	1320	0	-4.67	1	0.82
14	600	3	300	0	-4.43	1	0.64
15	600	3	400	0	-5.85	1	0.64
16	600	3	600	0	-8.94	1	0.65
17	600	3	800	0	-8.76	1	0.58