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**DEVELOPMENT OF IN-BED COMBUSTION HEATING
FOR CALCINATION OF RADIOACTIVE WASTES**

T. K. Thompson

IDAHO NUCLEAR CORPORATION
NATIONAL REACTOR TESTING STATION
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WASTE DISPOSAL AND PROCESSING
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By

T. K. Thompson

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ABSTRACT

In-bed combustion, the burning of a hydrocarbon fuel directly in a fluidized bed, is being investigated as a method of supplying heat for fluidized-bed calcination of radioactive liquid wastes in the Waste Calcining Facility at the Idaho Chemical Processing Plant. Direct combustion of a fuel within the fluidized bed has the inherent advantage of eliminating the high metal temperatures experienced in the present circulating NaK system; the majority of the unscheduled shutdowns have resulted from metallurgical failures of the liquid metal heat transfer system. Pilot-plant studies on the calcination of synthetic aluminum and zirconium wastes by in-bed combustion in a twelve-inch calciner have demonstrated: (1) that calcined solids formed during in-bed combustion and by indirect heating have similar properties, (2) the potential for decreased air pollution as a result of the formation of small quantities of nitrogen oxides, (3) the potential for increased capacity for an existing calciner, and (4) that operation of a calciner using in-bed combustion is safe. Results from development studies indicate that in-bed combustion can be employed advantageously in the existing Waste Calcining Facility.

SUMMARY

A fluidized-bed calcination process is employed in the Waste Calcining Facility (WCF) at the Idaho Chemical Processing Plant to convert high-level radioactive liquid wastes to a free-flowing granular solid. Heat for the calcination process is currently supplied from liquid sodium-potassium eutectic (NaK) flowing through an in-bed heat exchanger bundle. Calcining capacity is limited presently by the rate of heat transfer from the exchanger bundle to the fluidized bed.

The in-bed combustion method of supplying heat for the endothermic calcination process has several inherent advantages over the liquid metal heat transfer system. A major feature of in-bed combustion is the elimination of the intermediate metallic heat transfer surfaces; thus, the calcining capacity is not limited by heat transfer resistances at the in-bed exchanger surfaces.

Pilot-plant tests using in-bed combustion were conducted in a twelve-inch diameter calciner. Objectives of the pilot-plant program on in-bed combustion were to determine: (1) the minimum stable combustion temperatures, (2) properties of the calcined solids, (3) safety implications of in-bed combustion, and (4) the general operability of the calcination process using in-bed combustion.

The minimum stable combustion temperature was found to be a strong function of nitrate concentration; the minimum operating temperature was $\sim 380^{\circ}\text{C}$ for 13 M nitric acid and $\sim 475^{\circ}\text{C}$ for 2 M nitric acid. Tests indicate that the minimum temperature is independent of bed material (alumina or zirconia).

Calcined solids produced during in-bed combustion were found to have similar properties to those produced by indirect heating. Generally, however, the solids formed during in-bed combustion contained a small amount of elemental carbon and had a lower content of total volatiles and residual nitrates.

The chemistry of the calcination reactions was altered by the use of in-bed combustion. Nitrates were converted mainly to elemental nitrogen and oxygen instead of to nitrogen oxides.

Operability of the twelve-inch pilot-plant calciner using in-bed combustion presented no major difficulty. Lower waste nozzle air ratios were used during in-bed combustion because of the additional particle break-up action resulting from the presence of the fuel nozzle. Major operational changes required for calcination using in-bed combustion are the necessity of adding oxygen to the fluidizing air and nitric acid to the scrubbing solution.

The highest rate for the waste feed rate using in-bed heaters was approximately 7 gal/hr-ft²; a feed rate of 11 gal/hr-ft² was realized during in-bed combustion calcination. Waste feed rates can probably be increased further by optimizing the operating variables involved. Since the existing WCF operates at a waste feed rate of 7.5 gal/hr-ft², a significant increase in calcining capacity is anticipated as a result of using in-bed combustion.

TABLE OF CONTENTS

	Page
ABSTRACT	i
SUMMARY.	ii
I. INTRODUCTION	1
II. THE IN-BED COMBUSTION HEATING METHOD	4
III. PILOT PLANT PROGRAM.	5
1. Apparatus.	5
2. Procedure.	7
2.1 Startup Operating Procedures.	7
2.2 Determination of Minimum Operating Temperature.	8
2.3 Steady-State Operation.	9
3. Results and Discussion	13
3.1 Minimum Operating Temperatures.	14
3.2 Oxygen Consumption.	15
3.3 Comparison of Calcined Solids Using In-Bed Combustion and Indirect Heating	16
3.4 Process Chemistry Changes Associated with In-Bed Combustion	16
3.5 Comparison of Kerosene and #2 Fuel Oil.	19
3.6 Comparison of Operating Parameters; In-Bed Combustion Versus Indirect Heating.	20
3.7 Effect of In-Bed Combustion on Calcination Capacity.	21
IV. CONCLUSIONS.	22
V. FUTURE PROGRAM	23
VI. REFERENCES	25

TABLES

<u>Table</u>	<u>Title</u>	<u>Page</u>
I.	Composition of Simulated Wastes	14
II.	Oxygen Sources with In-Bed Combustion	16
III.	Typical Properties of Calcined Product	17
IV.	Typical Properties of Calcined Fines	18
V.	Typical Calciner Off-Gas Compositions	19
VI.	Comparison of Typical Operating Parameters	21

FIGURES

<u>Figure</u>	<u>Title</u>	<u>Page</u>
1	The Waste Calcining Facility	2
2	NaK System Flow Diagram	2
3	Comparison of Heat Flow Paths	4
4	Diagram of Twelve-Inch Diameter Calciner	6
5	Nozzle Locations for Twelve-Inch Diameter Calciner	7
6	Bed Temperature During Startup Operation	8
7	Bed and Vapor Space Temperatures During Minimum Stable Combustion Temperature Determination	9
8	Interrelationships Between Process Variables for Indirect Heating	10
9	Interrelationships Between Process Variables for In-Bed Combustion	11
10	Dependence of Oxygen Utilization on Use of Air or Oxygen as Fuel Atomizing Gas	12
11	Effect of Nitric Acid Concentration on Minimum Operating Temperature	15

I. INTRODUCTION

The Waste Calcining Facility (WCF) at the Idaho Chemical Processing Plant converts high-level radioactive liquid wastes to granular solids using a fluidized-bed calcination process. Waste solutions are converted to granular, free-flowing solids which occupy about ten percent of the original solution volume. The solids provide a safer form for long-term storage of radioactive wastes⁽¹⁾. Waste solutions are sprayed⁽²⁾ into a fluidized bed, maintained at 400-500°C by means of a liquid metal heat transfer system⁽³⁾, using external atomizing nozzles. Solid wastes deposited in layers on the bed particles decompose to oxides; the off-gas (volatile decomposition products, fluidizing and atomizing gases) is decontaminated in a wet off-gas scrubbing system, silica gel adsorbers, and a filter system located downstream from the calciner vessel. The calcined solids are continuously removed and transported pneumatically to storage bins as shown schematically in Figure 1⁽⁴⁾.

Heat for the endothermic calcination reactions is currently provided by an in-bed, bayonet-tube heat exchanger through which sodium-potassium (NaK) eutectic is circulated. The liquid metal is heated in an oil-fired furnace and is circulated by an electromagnetic pump^(3,4). Liquid metal temperatures vary from about 740°C in the furnace tubes to about 650°C on the exit side of the in-bed heat exchanger. A flow diagram of the NaK system is shown in Figure 2.

Though the liquid metal heat transfer system has satisfied all design requirements, it has been responsible for several unscheduled shutdowns resulting from localized metallurgical failures caused by aging and stress at the high metal temperatures⁽⁵⁾. Eventually, part or all of the system must be replaced, preferably with components permitting a greater calcining capacity. Furthermore, future throughput requirements in the WCF dictate that either an in-bed heat exchanger of increased heat transfer capacity be installed, or that a more efficient method of heating be employed.

Induction heating of the fluidized bed was considered but was rejected because more heat would be generated in the walls of the calciner vessel than in the bed. Use of external combustion chambers supplying

Figure 1
The Waste Calcining Facility

Figure 2
NaK System Flow Diagram

hot combustion gases to a heat exchanger in the bed was rejected because of the need to use firebrick to withstand the high temperatures; firebrick is not desirable in radioactive service because of the difficulty in decontaminating a ceramic material.

The combustion of a fuel within the fluidized bed was selected as an attractive alternate to the NaK heat transfer system. Several advantages of in-bed combustion are: (1) greater reliability due to the increased simplicity and elimination of the liquid metal heat transfer system, (2) heat transfer is not dependent on heat transfer surfaces within the fluidized bed, and (3) a capacity increase of approximately 50 percent in the existing WCF can be realized with in-bed combustion.

II. THE IN-BED COMBUSTION HEATING METHOD

The use of in-bed combustion to heat a fluidized bed is not new; processes involving waste disposal^(6,7) and lime manufacture⁽⁸⁾ have been reported. Air is used as both the fluidizing gas and oxygen source for combustion in these processes, resulting in fluidizing velocities of several feet per second in order to supply the necessary quantities of oxygen for combustion.

The calcination of radioactive wastes requires fluidizing velocities of about one foot per second in order to minimize elutriation of the friable product. To accomplish this, while at the same time supplying enough oxygen for combustion, pure oxygen must be added to the fluidizing gas.

In-bed combustion has inherent advantages over the liquid metal system currently in use at the WCF. In comparing the heat flow paths for these two heat transfer methods, shown in Figure 3, it is significant that the in-bed combustion process eliminates the intermediate metallic heat transfer surfaces. Metal wall temperatures are minimized with the in-bed combustion process because the hottest part of the process occurs within the fluidized bed, i.e., a large ΔT driving force between the liquid metal and the fluidized bed is not necessary for efficient heat transfer. Secondly, the capacity of the process is not limited by the heat transfer resistances of an in-bed heat exchanger⁽⁹⁾.

Figure 3
Comparison of Heat Flow Paths

III. PILOT-PLANT PROGRAM

Scoping studies to determine the operating temperature necessary for stable in-bed burning (no vapor space burning) have been reported⁽¹⁰⁾. The results of these tests indicated that temperatures greater than 650°C were required for stable burning. Since one of the main criteria for any new heat transfer system was the elimination of high metal wall temperatures, a pilot-plant program was initiated to find a method of reducing the bed temperature necessary for stable combustion. The temperature of the fluidized bed would be limited to a maximum of 500°C when calcining zirconium fluoride wastes⁽¹¹⁾ because of excessive fluoride volatility at higher temperatures.

The majority of work was conducted in a twelve-inch diameter pilot-plant calciner equipped with a wet off-gas scrubbing system. A total of 617.5 operating hours has been accumulated with the in-bed combustion system. Zirconium wastes have been calcined a total of 465.0 hours, of which the longest continuous operating period was 239.0 hours. Aluminum wastes have been calcined a total of 152.5 hours with the longest operating period being 100 hours.

1. APPARATUS

A simplified flowsheet of the pilot-plant twelve-inch diameter calciner and the fuel and waste nozzles are shown in Figures 4 and 5, respectively. The feed and fuel nozzles can be positioned one over the other as in Figure 4 or opposed as shown in Figure 5. The heart of the process is the calciner vessel with its fluidizing gas distributor plate, fuel and feed nozzles, product overflow standpipes, fluidizing air pre-heat coil, and rupture disc with a bursting pressure of 28 psia at 500°C. Off-gas leaving the top of the calciner vessel first passes through a primary cyclone separator where a large part of the elutriated solids are removed and collected in the fines pot. The off-gas is then scrubbed with ~1 M HNO_3 in the venturi scrubber, after which the gas and liquid are separated in the secondary cyclone. The off-gas then passes through a condenser and steam jet before being vented from the building.

Figure 4
Diagram of Twelve-Inch Diameter Calciner

Figure 5
Nozzle Locations for Twelve-Inch Diameter Calciner

Process control instrumentation consists of closed loop automatic control on fluidizing air, fluidizing oxygen, scrub solution, fuel, waste feed, and atomizing gases. The pressure in the calciner vessel is controlled by bleeding air to the suction side of the steam jet exhauster.

2. PROCEDURE

2.1 Startup Operating Procedures

During startup the fluidized bed is heated to the desired temperature by use of heated fluidizing air in accordance with WCF operation. Once the desired bed temperature is reached, 13 M HNO_3 is fed to the waste feed nozzle and atomized with air. Immediately after the flow of nitric acid begins, the fuel flow is started to the fuel atomizing nozzle and atomized with air. Within seconds, spontaneous ignition of the fuel takes place. Once ignition occurs, oxygen should be added to

the fluidizing gas to control above-bed burning. Temperatures during a typical startup are shown in Figure 6; startup has been achieved at temperatures as low as 335°C.

Figure 6
Bed Temperature During Startup Operation

2.2 Determination of Minimum Operating Temperature

Tests were conducted to determine the minimum operating temperature that could be maintained using various concentrations of nitric acid as the thermal load on the process. The procedure used for this series of tests was to preheat the fluidized bed with internal electrical resistance heaters to a temperature greater than the expected ignition temperature using air as both the fluidizing and atomizing gas. When the desired temperature was reached, the heaters were shut off and nitric acid solution and fuel flows were then initiated in that order. After ignition, the fuel rate and the oxygen/air ratio in the fluidizing and atomizing gases were set at specified values throughout the test. The acid feed rate was then slowly increased, thereby increasing the thermal load and decreasing the bed temperature. Eventually a condition was

reached where the bed and vapor space temperatures were equal; this point was defined as the minimum stable combustion temperature. At this point, any increase in acid feed rate causes above-bed burning which is undesirable because of the associated decrease in combustion efficiency. A typical plot of bed temperature during a run to determine the minimum stable combustion temperature is shown in Figure 7.

Figure 7
Bed and Vapor Space Temperatures During Minimum Stable
Combustion Temperature Determination

2.3 Steady-State Operation

The steady-state operation of the calcination process using in-bed combustion is more complicated than operation using an indirect heat transfer method of heating the fluidized bed (in-bed electrical resistance heaters). A comparison of the relationships between the process variables for indirect heating and in-bed combustion can be made by referring to Figures 8 and 9, respectively; the independent variables are shown as six-sided polygons and the first-order dependent variables are defined as dependent variables having both inputs and outputs and are shown as rectangles. The second-order dependent variables are defined as dependent variables having inputs only and are shown as ovals. Feedback to the independent variables is shown by dashed lines. Waste nozzle air/feed ratio, fluidizing velocity, bed temperature, and waste feed rate are independent variables in both processes; however, the

Figure 8
Interrelationships Between Process Variables for Indirect Heating

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Figure 9
Interrelationships Between Process Variables for In-Bed Combustion

fuel nozzle air/fuel ratio is an additional independent variable with in-bed combustion. The greater complexity of in-bed combustion is indicated by the number of first-order dependent variables; in-bed combustion has eight first-order dependent variables whereas indirect heating has only three.

The current process control instrumentation consists of automatic controllers to control flow of fuel, feed, scrubbing solution, fluidizing and atomizing gases, and the calciner pressure. No attempts have been made to link the independent and dependent variables by automatic control in these exploratory studies.

After the startup period, pure oxygen is added to the fluidizing gas to maintain the fluidizing velocity at ~ 1 ft/sec while supplying sufficient oxygen to insure complete combustion of the fuel. The fuel atomizing gas is also switched from air, used in startup, to pure oxygen for steady-state operation. Using pure oxygen to atomize the fuel results in a more intimate mixture of fuel droplets and oxygen--and consequently reduces the fluidizing and atomizing oxygen required for in-bed burning--as illustrated in Figure 10.

Figure 10
Dependence of Oxygen Utilization on Use of Air or Oxygen
as Fuel Atomizing Gas

Studies to date have indicated that about three days of operation are required to minimize the oxygen consumption rate for both zirconium and aluminum nitrate simulated wastes. During this "conditioning" period the oxygen rate can slowly be reduced using the operational guideline of allowing only in-bed burning; an explanation for this phenomenon is not yet available.

The variation of bed temperature serves as a useful indication of fluidization quality. The temperature spread within the fluidized bed is less than 15°C during normal operation. These temperature ranges occur at fluidizing velocities 2 to 2.5 times the calculated incipient fluidizing velocity^(11,12); the fluidizing velocity is based on the superficial cross-sectional area of the calciner. At fluidizing velocity/incipient fluidizing velocity ratios of less than 2, poor fluidization leading to the formation of agglomerates in the fluidized bed can occur. This condition is indicated by a bed temperature spread greater than 15°C.

3. RESULTS AND DISCUSSION

Several operating characteristics were observed during the scoping studies and pilot-plant tests. Above-bed burning was defined as the condition where the vapor-space temperature was greater than the fluidized-bed temperature. The use of pure oxygen in the fluidizing and atomizing gases during startup is undersirable because of the possibility of forming an explosive fuel-oxygen mixture in the vapor space.

Stable burning at a given temperature was defined as the condition of self-sustained combustion entirely within the fluidized bed while using no external ignition sources. It is postulated that the following criteria must be satisfied for stable combustion to occur in fluidized beds:

1. The bed temperature must be greater than or equal to the autoignition temperature of the fuel-oxygen mixture.
2. The flame velocity must be equal to or greater than the actual interstitial velocities in the fluidized bed.

3. The ignition lag time (time delay between introduction of an ignition source and combustion) must be less than the residence time of the combustible mixture in the fluidized bed.

A theoretical analysis of the in-bed combustion process was not attempted due to a lack of information regarding the functional dependence of flame velocity, ignition lag, and autoignition temperature upon temperature, pressure, and oxygen concentration in fluidized systems.

3.1 Minimum Operating Temperatures

Preliminary tests made with both simulated aluminum and zirconium wastes showed that the aluminum wastes had a lower minimum operating temperature than the zirconium wastes at identical conditions of excess fluidizing oxygen using air to atomize the fuel. The results of these studies indicated that the minimum operating temperature for stable in-bed burning was 392°C for aluminum waste and 460°C for zirconium waste. Later tests have shown that operation is possible at temperatures considerably lower than these mentioned above by using pure oxygen to atomize the fuel. Zirconium wastes, for example, have been calcined in pilot-plant tests at 420°C with no above-bed burning by atomizing the fuel with oxygen instead of air. Typical compositions of simulated aluminum and zirconium wastes are shown in Table I.

TABLE I
COMPOSITION OF SIMULATED WASTES

Component	Waste Type	
	Aluminum	Zirconium
Al ⁺³ (g/l)	38.6	9.0
NO ₃ ⁻ (M)	5.2	3.8
H ⁺ (M)	1.2	1.4
H ₂ ⁺ (g/l)	0.6	---
B ₂ ⁺ (g/l)	0.5	1.0
Cr ⁺³ (g/l)	0.4	0.4
Zr ⁺⁴ (g/l)	---	23.0
Ca ⁺² (g/l)	---	37.3
F ⁻ (M)	---	1.6
Total Solids (g/l)	82	127
Undissolved Solids (g/l)	0.2	54
Density (g/l)	1.256	1.200

Other tests using various concentrations of nitric acid showed a strong dependence of minimum operating temperature upon acid (ie, nitrate) concentration. The lowest operating temperature was achieved with the most concentrated feedstock (13 M nitrate). Results of these tests indicate the minimum combustion temperature is independent of bed material. A plot of minimum operating temperature versus acid concentration for both sand and alumina beds is shown in Figure 11.

Figure 11
Effect of Nitric Acid Concentration on Minimum Operating Temperature

3.2 Oxygen Consumption

Oxygen is supplied to the process in the fluidizing and atomizing gas streams and also in the nitrates present in the waste feed. A typical material balance on the oxygen sources is shown in Table II. The smallest amount of fluidizing and atomizing oxygen used to date was 97 percent* of the theoretical amount required for complete combustion and occurred during a steady-state operating period of 33 hours.

*The oxygen utilization is defined as 100 times the amount of oxygen in the fluidizing and atomizing gas streams divided by the stoichiometric amount of oxygen required for complete combustion of the fuel. This does not include the oxygen present as nitrates in the waste feedstock.

TABLE II
OXYGEN SOURCES WITH IN-BED COMBUSTION
(Typical Operating Conditions-Zirconium Wastes)

	<u>Air Rate</u>	<u>Oxygen Rate</u>	<u>% Theoretical O₂*</u>
Fluidizing Air Rate	= 529 g-mole/hr	111 g-mole/hr	24%
Waste Atomizing Air Rate	= 124 g-mole/hr	26 g-mole/hr	6%
Fluidizing Oxygen Rate		282 g-mole/hr	62%
Fuel Atomizing Oxygen		<u>44 g-mole/hr</u>	<u>9%</u>
Total Oxygen in Fluidizing and Atomizing Gases	=	463 g-mole/hr	101%
Oxygen Present in Nitrates in Waste Feed		<u>171 g-mole/hr</u>	<u>37%</u>
Total Oxygen Supplied to Process		634 g-mole/hr	138%

*Needed to oxidize fuel completely to CO₂ and H₂O.

3.3 Comparison of Calcined Solids Using In-Bed Combustion and Indirect Heating

The properties of the calcined solids and overhead fines produced by the in-bed combustion process are very similar to those produced using indirect heating. The main exceptions are lower content of total volatiles and residual nitrates and the presence of elemental carbon in the solids produced using in-bed combustion. Small variations in calcium, fluoride, zirconium, and aluminum are due to slight differences in the waste feed composition used in the various runs. A comparison of the physical and chemical properties for both alumina and zirconia product and fines are shown in Tables III and IV, respectively.

3.4 Process Chemistry Changes Associated With In-Bed Combustion

The nitrates in the feed are converted primarily to nitrogen oxides during calcination using indirect heating. Part of these oxides--largely NO, NO₂ and N₂O₄--combine with the aqueous scrubbing solution in the venturi scrubber to form nitric acid in which the elutriated fines are soluble. With in-bed combustion, nitrates are converted mainly to elemental nitrogen and oxygen instead of nitrogen oxides, hence, reducing the formation of nitric acid in the aqueous scrubbing system. This necessitates the addition of nitric acid to the scrubbing system in order to dissolve the elutriated fines when using in-bed combustion

TABLE III

TYPICAL PROPERTIES OF CALCINED PRODUCT
(Twelve-inch Diameter Calciner)

Feed	Component	Conventional Indirect Heating	In-Bed Combustion
Zirconium	Al (wt%)	7.1	7.0
	NO ₃ (wt%)	3.0	0.2
	C (wt%)	---	0.07
	Ca (wt%)	30.0	30.0
	F (wt%)	17.0	16.0
	Zr (wt%)	16.5	16.5
	Total Volatiles (wt%)	3.0	0.5
	Absolute Density (g/cc)	3.2	3.3
	Particle Density (g/cc)	2.2	2.1
	Bulk Density (g/cc)	1.3	1.2
	Intra-Particle Porosity	0.4	0.4
Aluminum	Al (wt%)	46.0	46.0
	NO ₃ (wt%)	4.5	2.2
	C (wt%)	---	0.1
	Total Volatiles (wt%)	8.1	3.1
	Absolute Density (g/cc)	2.6	2.5
	Particle Density (g/cc)	1.4	1.4
	Bulk Density (g/cc)	0.9	1.0
	Intra-Particle Porosity	0.45	0.41

TABLE IV

TYPICAL PROPERTIES OF CALCINED FINES
(Twelve-inch Diameter Calciner)

Feed	Component	Conventional Indirect Heating	In-Bed Combustion
Zirconium	Al (wt%)	7.2	8.5
	NO ₃ (wt%)	7.5	1.8
	C (wt%)	---	0.20
	Ca (wt%)	30.5	28.5
	F (wt%)	23.0	26.0
	Zr (wt%)	17.2	16.8
	Total Volatiles (wt%)	9.5	4.5
	Absolute Density (g/cc)	3.3	3.2
	Bulk Density (g/cc)	0.45	0.40
Aluminum	Al (wt%)	44.0	44.8
	NO ₃ (wt%)	18.0	5.0
	C (wt%)	---	0.18
	Total Volatiles (wt%)	16.5	11.0
	Absolute Density (g/cc)	2.2	2.4
	Bulk Density (g/cc)	0.16	0.35

heating. However, the potential for nitrogen oxides polluting the air is reduced significantly due to the formation of less NO, NO₂ and N₂O₄ in the calcination process with in-bed combustion heating. A typical analysis of calciner off-gas with both types of heating is shown in Table V.

TABLE V
TYPICAL CALCINER OFF-GAS COMPOSITIONS
(Dry Basis-Mole Percent)

<u>Component</u>	<u>In-Bed Combustion (145% Theoretical O₂)</u>	<u>Indirect Heating (In-bed electrical heaters)</u>
N ₂	71.0	65.9
O ₂	16.0	15.2
N ₂ O	0.15	0.23
NO + NO ₂ , N ₂ O ₄	0.52	18.7
CO ₂	11.3	----
CO	1.0	----
CH ₄	0.02	----

3.5 Comparison of Kerosene and #2 Fuel Oil

Kerosene and No. 2 fuel oil were investigated as possible fuels for in-bed combustion. The theoretical oxygen consumption per BTU of heat generated is equal for both fuels. Thermal efficiencies of the in-bed combustion process were 61 percent for kerosene and 58 percent for No. 2 fuel oil while calcining simulated aluminum nitrate waste. The thermal efficiency for in-bed combustion is defined as:

$$100 \times \left[\frac{\Delta H_{\text{Calcination}} + \Delta H_{\text{Products}}}{\Delta H_{\text{Combustion}}} \right]$$

where:

$\Delta H_{\text{Calcination}}$ = The heat required to convert all metallic ions to oxides, decompose nitrates to N₂ and O₂, and vaporize all water at 25°C (Btu/hr).

$\Delta H_{\text{Product}}$ = The heat required to raise the temperature of the calcination and combustion products, inerts, and excess oxygen from 25°C up to the bed temperature (Btu/hr).

$\Delta H_{\text{Combustion}}$ = The theoretical heat released from the complete combustion of the fuel to gaseous H_2O and CO_2 at 25°C (Btu/hr).

The overall thermal efficiency of the WCF is about 35 percent for the complete system including the NaK furnace. This is based on the theoretical heat input in the form of burning fuel in the NaK furnace and heat outputs in the form of the endothermic calcination reactions (at 25°C) and the enthalpy required to raise the calcination reaction products and fluidizing and atomizing gases from 25°C up to bed temperature.

3.6 Comparison of Operating Parameters; In-Bed Combustion Versus Indirect Heating

A comparison of typical operating parameters for calcining aluminum and zirconium wastes in the twelve-inch diameter pilot-plant calciner using in-bed combustion and indirect heating (in-bed electrical heaters) is shown in Table VI. These data are based on over 600 hours of operation with in-bed combustion and about 3500 hours using the in-bed electrical heaters.

The nozzle air ratio is the volumetric ratio of atomizing gas to liquid at calciner conditions and affects the amount of in-bed "grinding" or attrition of bed particles⁽²⁾. A lower waste nozzle air rate is used with in-bed combustion because of the greater "grinding" action caused by the presence of an additional fuel nozzle in the calciner.

Fluidizing velocities are calculated on different bases for the two methods of heating. With indirect heating, the fluidizing velocity is based on the fluidizing air only, whereas with in-bed combustion it includes the additional gas from combustion products, excess oxygen, inerts, and atomizing gases. Atomizing gases are considered with in-bed combustion because the atomizing nozzles are located at lower bed levels and contribute significantly to fluidization throughout the remaining

TABLE VI
COMPARISON OF TYPICAL OPERATING PARAMETERS
(Twelve-Inch Diameter Calciner)

Feed	Operating Parameters	Conventional Indirect Heating	In-Bed Combustion
Aluminum Waste	Fluidizing Velocity (ft/sec)	~1	~1.2
	Waste Nozzle Air Ratio	500	325
	Fuel Nozzle Air Ratio	---	700
	Mass Median Particle Diameter (mm)	0.6	0.6
	Bed Temperature (°C)	400	480
	Feed Rate (1/hr)	10	15
	Product Rate (lbs/hr)	~2	~2.5
	Fines Rate (lbs/hr)	~0.2	~.5
Zirconium Waste	Fluidizing Velocity (ft/sec)	~1	~1.7
	Waste Nozzle Air Ratio	650	500
	Fuel Nozzle Air Ratio	---	700
	Mass Median Particle Diameter (mm)	0.65	0.8
	Bed Temperature (°C)	400	480
	Feed Rate (1/hr)	16	30
	Product Rate (lbs/hr)	~3.5	~6.5
	Fines Rate (lbs/hr)	~0.3	~0.8

bed. With indirect heating, the atomizing nozzle is submerged in the bed only 5 to 8 inches and does not materially affect fluidization throughout the whole bed.

3.7 Effect of In-Bed Combustion on Calcination Capacity

The highest waste feed rate attained to date in the twelve-inch diameter pilot-plant calciner was 11.3 gal/hr-ft² using in-bed combustion. The maximum rate with the indirect electrical heaters used previously was ~7 gal/hr-ft². Since the existing WCF operates at 7.5 gal/hr-ft², a significant increase in calcining capacity is expected through the use of in-bed combustion.

IV. CONCLUSIONS

The in-bed combustion method of heating has the proven capability of increasing the capacity of the twelve-inch pilot-plant unit by about 50 percent. In-bed combustion eliminates the dependence on an internal heat exchanger operating at the high temperatures associated with a liquid metal heat transfer system. Operating procedures developed during 600 hours of operation using a twelve-inch diameter pilot-plant calciner are considered safe. Calcination of aluminum nitrate and zirconium-complexed fluoride wastes yields solids having properties essentially identical to those produced using indirect methods of supplying process heat. The major operational changes required for calcination using in-bed combustion are the need to add pure oxygen to the fluidizing air and nitric acid to the scrub solution. Air pollution by NO_2 release is reduced with in-bed combustion because of the shift in the nitrate decomposition reaction to yield N_2 and O_2 instead of NO_2 . All findings to date indicate that the in-bed combustion heating method can be successfully employed in the WCF.

V. FUTURE PROGRAM

Additional studies are planned in the areas listed below:

1. Process Upset Studies

Studies to date indicate that the in-bed combustion process is inherently stable due to the "heat sink" action of the fluidized bed over periods of 3-5 minutes from the onset of a perturbation, providing the original disturbance is corrected. It would be desirable to know the effects of process upsets over longer periods of time. Upsets to be investigated will be waste feed interruptions, oxygen interruptions--both atomizing and fluidizing--, and long-term above-bed burning. Various corrective actions for each perturbation will be determined as well as the time required for the process to return to steady-state operation.

2. Calcination of Zirconium Wastes at 450°C

It is desired to operate the WCF at 450°C while calcining zirconium wastes because of oxygen economics. All of the pilot-plant runs to date have been at higher temperatures due to the developmental nature of the experiments; however, zirconium wastes have been successfully calcined at 440°C for about 8 hours of operation while using pure oxygen to atomize the fuel. A long-term run in the twelve-inch diameter calciner is required to provide oxygen utilization and combustion efficiency data over a steady-state operating period at an operating temperature of 450°C.

3. Off-gas Filter Studies

Tests are planned to study the use of sintered metal filters for off-gas cleanup in place of the wet scrubbing system. By eliminating the scrubbing solution recycle stream to feed makeup, an increase of up to 30 percent in the capacity of the WCF could be realized. Additional benefits would be realized by eliminating the corrosion occurring in the wet scrubbing system. Areas of interest include corrosion measurements, decontamination factors, process effects, and cleanability of the filters.

4. Investigation of the Basic Mechanisms of In-Bed Combustion

Studies are planned to investigate further the basic mechanisms of in-bed combustion in order to formulate a mathematical model of the process. The mathematical model will then be used to define process control characteristics.

5. Calcination of New Types of Wastes

Development studies are required on the in-bed combustion calcination of wastes other than aluminum or zirconium that are currently stored at ICPP and new types of wastes that will be encountered in future fuel processing programs. These wastes are:

- a) stainless steel raffinate from electrolytic dissolution
- b) aluminum-zirconium co-processing wastes
- c) high sodium second-cycle wastes
- d) sulfate wastes.

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