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**FLUIDIZED BED CALCINATION OF SIMULATED ZIRCONIUM FLUORIDE
WASTE IN EXPLORATORY PILOT PLANT TESTS**

J. C. Petrie, E. J. Bailey, D. W. Rhodes, and B. M. Legler

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A B S T R A C T

An exploratory pilot plant study of the fluidized bed calcination of zirconium fluoride waste with added calcium nitrate has shown that greater than 99 percent of the fluorides in the waste are retained in the calcined solids. Laboratory studies have indicated that mole ratios of calcium to fluoride considerably below the stoichiometric ratio were effective in suppressing fluoride volatilization. Corrosion tests conducted during the pilot plant study demonstrated that the austenitic stainless steels of which the Waste Calcining Facility is constructed will not be excessively corroded during calcination of zirconium fluoride waste in that facility.

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FLUIDIZED BED CALCINATION OF SIMULATED ZIRCONIUM FLUORIDE WASTE IN EXPLORATORY PILOT PLANT TESTS

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I. SUMMARY

Laboratory and pilot plant exploratory studies on calcination of simulated zirconium fluoride waste demonstrated the feasibility of processing such waste at the Waste Calcining Facility (WCF). Operating conditions for the pilot plant investigation were chosen to approximate those used at the WCF during a recent campaign on radioactive aluminum nitrate wastes.

Greater than 99 percent of the fluorides in the feed solution were retained in the solids product with calcium added to the feed as calcium nitrate in an amount stoichiometrically equal to the amount of fluoride in the feed. Subsequent laboratory studies indicated that as little as one-tenth of this amount will give comparable results in suppressing the volatilization of fluoride.

The yellow, granular product contained primarily zirconium oxide, aluminum oxide, and calcium fluoride; nitrates and trace components of the simulated waste were also present.

Corrosion rates were studied extensively throughout the calciner system on materials, both similar and dissimilar to those at the WCF, to determine the effect of corrosive fluorides. However, because of the low volatilization rate of the fluorides, corrosion was negligible. In general, austenitic stainless steels showed less corrosion than did martensitic stainless steels.

II. INTRODUCTION

Hydrofluoric acid is used as the principal component of the dissolvent in the reprocessing of zirconium-uranium alloy nuclear fuel elements at the Idaho Chemical Processing Plant (ICPP)⁽¹⁾. The waste resulting from this process is a radioactive zirconium fluoride solution complexed with aluminum nitrate which is stored underground in stainless steel tanks. As a continuation of the program to reduce radioactive liquid wastes to safer forms, laboratory and pilot plant studies were made to determine the feasibility of calcining this type of waste in the WCF. The feasibility study was made at operating conditions which closely approximated those now used at the WCF. The WCF was designed to handle radioactive aluminum nitrate waste generated during the reprocessing of aluminum-uranium alloy nuclear fuel elements. In that service the WCF operated 312 days with an on-stream factor greater than 99 percent. If the WCF can be used to process zirconium waste, its usefulness will be enhanced considerably.

The major requirement for satisfactory processing of the zirconium waste in the WCF is prevention of corrosion by the fluorides in the calciner feed. Equipment corrosion during the phase change from liquid to solid should be of no concern as the reaction occurs on the granular bed particles themselves. However, excessive volatilization of the fluorides from the feed solution during the calcination step could result in corrosion of the off-gas processing equipment at the WCF and could present a health hazard because of venting to the atmosphere.

The fluidized bed calciner used in the pilot plant study was 12 inches in diameter and 91.5 inches high. The basic components of the unit, fluidizing air distributor plate, venturi scrubber, etc., were patterned after a companion pilot unit, the two-foot-square calciner⁽²⁾. A detailed description of the pilot plant calcination equipment is given in Appendix A.

The composition of the zirconium fluoride waste calcined during the exploratory pilot plant study was selected to be within the range of composition of existing or expected waste at the ICPP. A comparison of waste compositions is given in Table I.

Table I

COMPOSITION OF ZrF_4 WASTES

Component, <u>M</u>	Existing <u>ZrF_4 Waste</u>	Future <u>ZrF_4 Waste</u>	<u>ZrF_4 Waste</u> Calcined in Pilot Plant
Acid	1.10	0.78	1.03
Zirconium	0.48	0.71	0.43
Fluoride	3.10	4.22	2.45
Aluminum	0.73	0.50	0.66
Nitrate	2.04	1.63	4.66 ^(a)
Boron	—	0.24	0.17
Tin	0.0045	0.0085	0.0057
Calcium	—	—	1.21

(a) Consists of 2.24 moles/l in original waste and 2.42 moles/l from $\text{Ca}(\text{NO}_3)_2$ which was added to suppress the volatility of fluorides.

The volume of the existing zirconium waste at ICPP is only 43,500 gallons, but future wastes are expected to be accumulated at a rate on the order of 100,000 gallons per year. The existing waste was accumulated from a batch process while the future waste will accumulate from a recently installed semi-continuous process⁽¹⁾.

The feed solution for the pilot plant test was accumulated during several small-scale pilot plant studies of the zirconium fuel reprocessing scheme. Additional testing is planned after feed solutions are prepared from dissolution of scrap zirconium.

III. LABORATORY STUDIES

Laboratory studies of the calcination of zirconium fluoride waste under static conditions demonstrated that complexing the zirconium fluoride waste with calcium oxide reduced the fluoride volatilization to less than one percent⁽³⁾. Parameters affecting the volatility of fluoride which were studied in the laboratory were: (1) the Ca/F mole ratio, which was varied from 0.37 to 0.75; (2) calcining temperature, which was varied from 300°C to 600°C; and (3) nitrate concentration, which was varied from 0.9M to 3.6M.

The laboratory tests were conducted by placing a small volume of simulated feed solution in a platinum crucible which was then placed in an electrically heated stainless steel enclosure. The off-gas from the enclosure, containing decomposition products and a small amount of CO₂-free air used to purge the vessel, was passed through a caustic scrubbing solution to collect the volatilized fluorides.

Only 0.9 percent of the fluoride was volatilized at a Ca/F mole ratio of 0.5 at a calcining temperature of 400°C. Increasing the Ca/F mole ratio to 0.75 at the same calcining condition reduced the volatilization to 0.5 percent.

The nitrate content of the slurry affected the fluoride volatilization as shown in Figure 1. It should be noted that the results shown in this figure were obtained at a calcining temperature of 500°C; in contrast, the calcining temperature of the pilot plant study was 400°C which should reduce the volatilization.

Fig. 1 Percent of fluoride volatilized as affected by nitrates in the feed

Because of the promising results from the pilot plant calcination study, described in the next section of this report, additional laboratory studies were undertaken. The purpose of these additional studies was to determine if a lower Ca/F mole ratio could be used. Results of this study are given in Table II and show that a much lower Ca/F mole ratio in the simulated feed resulted in fluoride evolution comparable to that observed during the fluidized bed calcination study. The adequacy of these lower ratios remains to be demonstrated in pilot plant scale tests, which are being planned.

Table II
ZIRCONIUM FLUORIDE WASTE CALCINATION STUDIES
AT REDUCED Ca/F MOLE RATIOS

<u>Ca/F Mole Ratio</u>	<u>Weight Percent of Fluoride in Solids</u>	<u>Weight Percent of^(a) Fluoride in Scrub</u>
0	87.3	7.1
0.05	90.4	1.7
0.20	89.9	1.9

(a) More confidence should be placed on the analysis for fluoride in the scrub solution than for the fluoride analysis of the calcined solids because of the inherent difficulty in obtaining uniform samples of heterogeneous solids.

Limited pilot plant tests on the fluidized bed calcination of high sodium content, second-cycle solvent extraction waste have indicated the sodium in the second-cycle waste could serve the same purpose as calcium for suppression of fluoride volatility. The blending of these dissimilar wastes to prepare calciner feed will be the subject of future tests.

IV. CALCINER OPERATING CONDITIONS AND RUN HISTORY

Calciner operating conditions for the pilot plant study of zirconium waste calcination were chosen to simulate as closely as possible the operating conditions which are employed at the WCF to calcine aluminum nitrate wastes⁽⁴⁾. Table III compares the operating conditions used in the pilot plant tests with those used at the WCF.

Table III

CALCINER OPERATING CONDITIONS

<u>Parameter</u>	<u>Twelve-Inch-Diameter Pilot Plant Calciner</u>	<u>WCF Calciner</u>
Starting Bed	Amorphous Alumina produced at 400°C	Same
Bed Temperature	400°C	400°C
Bed Weight	180 lbs	4000 lbs
Superficial Fluidizing Velocity	1.0 ft/sec	1.0 ft/sec
Feed Rate	10 l/hr	300 l/hr ^(a)
Nozzle Air-to-Liquid Volume Ratio (NAR)	250, 500, 625, 700	500-600
Calciner Vapor Space Pressure	Below Atmospheric	Below Atmospheric

(a) Includes recycled scrubbing solution.

The major difference between the operating conditions of the calciner units was that the scrubbing solution was not recycled and mixed with incoming fresh feed in the pilot plant study. Recycling part of the scrubbing solution to the feed during the recent processing campaign at the WCF increased slightly the nitric acid content and reduced the metallic salt content of the incoming fresh feed.

The chronological operating history of the exploratory zirconium fluoride waste calcination study in the pilot plant is summarized in Figure 2. Operating problems, caused by feed line plugging, plagued the early portion of the run, as shown in Figure 2, but these were overcome by modifying the feed system. Other operating problems encountered during the run were minor, and after plugging in the feed transfer lines was eliminated, the run was not interrupted again.

Scrubbing solution was recycled to the venturi scrubber during the pilot plant calcination of the zirconium waste to simulate that operating condition at the WCF. The composition of the recycled stream did not reach equilibrium because the de-entrainment cyclone collected only about 60 percent of the scrubbing solution input, and a leak developed in one of the recycle pumps. Fresh water make-up was routinely added to the scrubbing solution surge tank. However, samples of the scrubbing solution recycle and product streams were routinely collected and analyzed to facilitate material balances.

V. DISCUSSION OF RESULTS

1. Fluoride Balance

Less than 1.0 percent of the fluoride in the feed calcined in the pilot plant test was volatilized, based on the analysis of samples of the off-gas and feed. Table IV gives the results of these analyses and the calculated volatilization rates. The remaining 99+ percent of the fluoride in the feed was calcined to form solid calcium fluoride.

Table IV

VOLATILIZATION RATE OF FLUORIDES

<u>Sample Number</u>	<u>Fluoride Rate to Calciner (g-moles/hr)</u>	<u>Fluoride Rate in Off-Gas (g-moles/hr)</u>	<u>Percent Volatilized</u>
1	21.09	0.126	0.60
2	23.87	0.233	0.98
3	27.87	0.117	0.43
4	21.79	0.132	0.61
5	21.14	0.102	0.48
6	24.90	0.116	0.47
7	25.60	0.121	0.47
8	29.44	0.110	0.37

Fig. 2 Chronological operating history

The off-gas sample point was located downstream from the primary cyclone and upstream from the venturi scrubber to give the most representative gas sample with a minimum amount of entrained solids. The off-gas sample did not include the fluorides associated with the entrained solids.

A steady state fluoride balance was not obtainable because the limited supply of feed was exhausted before the chemical composition of the calciner product had reached steady state. Approximately 2068 g-moles of fluoride were fed to the calciner during the run, and the calcined solids (product, fines, and the final bed) accounted for about 2058 g-moles of fluoride, or 99.5 percent of the input. By difference, the volatilization of fluorides was 0.5 percent, which compares favorably with that observed in the off-gas samples listed in Table IV.

The total fluoride content of the scrubbing solution and condensate streams was greater than that in the off-gas entering the scrubber. This result is attributed to the leaching of fluorides from the entrained solids by these aqueous streams. Figure 3 contains a plot of the amount of fluoride in the scrubbing solution and condensate streams expressed as a percentage of the fluoride in the calciner feed.

Fig. 3 Percent of fluoride collected in off-gas scrubbing solution and condensate solution

2. Properties of Calciner Product and Fines^(a)

2.1 Chemical Composition of the Calcined Solids

The product contained CaF_2 which was identified by X-ray diffraction analysis of samples of the overflow product and elutriated fines. A large amount of amorphous material was present but can not be identified absolutely. As the calcium and the fluoride content of the solids is accounted for by calcium fluoride, the other compounds are assumed to be the oxides of aluminum and zirconium.

Figure 4 presents a plot of the composition of the product as it changed throughout the run and the average chemical composition of the fines. The values shown on Figure 4 were calculated from the chemical analysis for Zr, Al, Ca, and F. The high rate of change of the product composition, particularly during the early part of the run, is due to the exponential rate of "washout" of the alumina starting bed (see Appendix B). The chemical composition of the product theoretically was within 90 percent of equilibrium at the end of the run.

Fig. 4 Product and fines composition

(a) Solids produced by the calciner are separated into two types. Those solids elutriated from the bed and collected by the primary cyclone are called fines. Those solids collected by the product overflow standpipe inside of the calciner vessel are called product.

Fig. 5 Nitrate content of product and fines

Both product and fines contained nitrates complexed within the solids as shown in Figure 5. The steady decrease in the nitrate content of the product from about five weight percent to about one weight percent indicates a different complexing mechanism for containing nitrates in this product than in the alumina which constituted the starting bed. The decrease in the nitrate content of the product is probably directly associated with the decrease in its alumina content.

2.2 Physical Properties of the Calcined Solids^(b)

The physical properties of the product and fines are summarized and shown in Figure 6. Theoretically, about 90 percent of the starting bed had been replaced by freshly generated product at the end of the 95-hour operating period.

2.21 Crystalline Structures

The only crystalline structure noted in X-ray diffraction analyses of the product and fines was that of calcium fluoride. No alpha alumina was detected; however, trace amounts of crystalline silicon dioxide were found, probably from a sand starting bed somewhere

^(b) See Appendix B for definition of terms and a description of the methods used to determine the physical properties of the calcined solids.

in the history of the alumina starting bed used for this calcination study. An unidentified crystalline substance was noted on a limited number of the samples of the fines material but was never noted in samples of the product. The unidentified substance constituted only a minor part of the fines material.

2.22 Bulk Densities

The bulk density of the product increased steadily from 0.9 to 1.2 g/cc and remained constant at 1.2 g/cc during the last 24 hours of the run. The bulk density of the fines was relatively constant throughout the run, varying from 0.35 to 0.41 g/cc.

2.23 Intra-particle Porosity

The intra-particle porosity of the product did not deviate significantly from about 0.4 during the run, although both the absolute density and the particle density increased slightly as shown in Figure 6 (the absolute density and particle density are used to calculate the intra-particle porosity). The absolute density of the final product was about 3.3 g/cc; the particle density of the final product was about 1.9 g/cc.

2.24 Color and Shape

The yellow product particles had a spherical shape similar to the usual alumina product. It is expected that the product from calcination of zirconium fluoride wastes can be readily transported pneumatically in a manner similar to that used for the alumina product.

2.3 Thermal Stability of Calcined Product

A sample of the calcined product from the zirconium fluoride waste was heated for 24 hours at 800°C in a small section of stainless steel tubing to determine if the product would degrade under bin storage conditions⁽³⁾⁽⁵⁾. A small air purge was passed through the solids into two caustic scrubbers connected in series. After the test, chemical analysis of the caustic scrubbing solution showed that nearly all of the nitrate in the product volatilized, but that only a small amount of the fluoride was released. An X-ray diffraction analysis of the product which had been heated showed the presence of crystalline ZrO_2 as well as that of the crystalline CaF_2 which was found in the original product.

CPP-S-3432

Fig. 6 Physical properties of the product and fines

CPP-S-342C

Fig. 7 Solids collection rates

2.4 Solids Disposition

The theoretical product rate from the twelve-inch-diameter calciner, based on a feed rate of 10 l/hr of the composition given in Table I, was about 1.9 kg/hr. This value was calculated under the assumption that the following simplified major reactions occurred during calcination:

The assumption is not completely valid because some nitrates and water are retained in the calcined solids, and trace compounds in the feed were neglected. Based on the equilibrium bulk density of the product, 1.2 g/cc, the liquid volume was reduced by a factor of about 6.2:1. The addition of solid calcium nitrate to the liquid feed did not increase the liquid volume significantly although the calcium fluoride accounted for about 40 weight percent of the product. If a Ca/F mole ratio as low as indicated by the recent laboratory tests, can be used, the volume reduction factor should be nearly doubled.

Figure 7 is a plot of the rates at which solids were collected in the following process streams: product overflow from the bed; fines collected by the primary cyclone, the venturi scrubber, and the off-gas condenser. The collection rates for the dry solids, product, and fines, were determined by periodically weighing the material collected in the collection pots; the collection rates of the aqueous streams were determined by periodic rate checks on the respective streams and analysis of the liquid samples for total solids dried to a constant weight at the calcination temperature.

2.5 Particle Size Control

The mass median particle diameter (MMPD) increased steadily throughout the run, probably as a result of: (1) a low initial NAR, (2) no seed addition during the early part of the run, and (3) the high viscosity of the complexed feed. The MMPD and size distribution of the product are plotted in Figure 8. In the first attempt to control the particle size of the calciner bed, the NAR was increased to 500 from the starting value of 250 after 21.5 hours of actual operation. After 20 additional hours of operation with a NAR of 500, the NAR was increased to 625. When the particle size continued to grow after operating for ten hours at a NAR of 625, the NAR was increased to 700.

Seed addition, to provide additional nuclei for particle growth, was started with the batch addition of 1170 grams alumina (104 to 417 microns in diameter), to the calciner bed about 59 hours after the start of the run. About 7.5 hours later, routine addition of 150 grams of alumina seeds (104 to 295 microns in diameter) every 30 minutes was initiated and continued to the end of the run.

Fig. 8 Product MMFD and size distribution

The MMPD was still increasing at the end of the 95-hour run although the weight percentage of the product smaller than 417 microns had increased from about five to eleven percent (see Figure 8).

To determine if the high NAR and seed addition would have controlled the MMPD of the product had calciner feed been available for an extended run, the mathematical model for particle growth determinations was applied to the conditions of this calcination study⁽⁵⁾. To test the accuracy of the mathematical model, the computer program was set up to run parallel to the actual operating conditions as well as to run beyond the end of the actual run for any desired length of time. For example, after 61 hours of actual operation, the product MMPD was 0.74 mm compared to the mathematically predicted value of 0.71 mm. Near the end of the run, 32 hours later, the product MMPD was 0.83 mm and the MMPD predicted by the mathematical model was 0.81 mm. The computer study was extended for 200 hours beyond the starting of routine seed addition. The theoretical MMPD was 0.84 mm at 100 additional hours and 0.65 at a total of 200 additional hours, thus indicating that the particle growth rate would have been controlled had additional calciner feed been available for an extended run.

2.6 Corrosion Studies

Corrosion rates during the calcination of zirconium fluoride waste were determined throughout the pilot plant calciner system by test coupons and by measurements taken on existing equipment. Particular attention was focused on testing materials in services similar to those in which they are used at the WCF. Also, other materials were tested for potential use in future fluidized bed calciners. The materials tested and their observed corrosion rates are listed in Table V⁽⁴⁾. Corrosion rates greater than 2.0 mils/month are considered unacceptable for calciner service.

In general, the chromium-nickel (austenitic) grades of steel showed more resistance than did the straight chromium (martensitic) grades of steel. Similar corrosion test results were obtained at Brookhaven National Laboratory during testing of zirconium fluoride waste calcination in a Rotary Ball Kiln⁽⁷⁾.

Corrosion rates on Groups 1, 2, and 3 may be biased upward as, inadvertently, the venturi scrubber water supply was left on at a normal flow rate of 1.5 l/min during an otherwise normal shutdown of the calciner equipment. All pertinent operating data had been collected and the final bed had been dumped and set aside for weighing by the time the scrubber water had backed through the off-gas line to the calciner vessel. The calciner vessel temperature was about 120°C when this water began flowing into the vessel. When steam was noted flowing out of the calciner vessel drain lines, the water source was traced to the venturi scrubber water supply which was then shut off. All lines were drained, and the electrical heaters and the fluidizing air were turned on to dry out the calciner vessel and off-gas lines. The temperature in the calciner vessel reached 320°C during the two-hour drying period.

Table V

CORROSION RATES DURING ZIRCONIUM FLUORIDE CALCINATION
TWELVE-INCH-DIAMETER PILOT PLANT CALCINER

<u>Type of Exposure</u>	<u>Material</u>	<u>Corrosion Rate (mils/month)</u>
1. Ambient temperature feed solution with $\text{Ca}(\text{NO}_3)_2$ added	ss Type 304L	0.01
	ss Type 304L welded to ss Type 347	0.42
	ss Type 347 welded to ss 17-4PH	0.67
	ss Type 347	0.60
2. Fluidized bed of granular product (400°C)	ss Type 304L	< 0.10
	Inconel	0.40
	ss Type 440C	42.50(a)
3. Hot calciner off-gas	Inconel - X	0.41
	K - Monel	0.11
	TimKin 16-25-6 (Cr-Ni-Mo)	0.04
	Nichrome (HR)	0.34
	Tophet "A"	0.20
	70% Copper - 30% Nickel	34.40
	Monel	0.08
	ss Type 310	0.05
	ss Type 316	0.03
	ss Type 329	0.01
	Boron Carbide	3.20
4. Hot aqueous scrubbing solution (50°C)	ss Type 304	< 0.10
5. Cooled aqueous scrubbing solution (30°C)	Silicon Carbide	2.50
	ss Type 304L welded to ss Type 347	0.04
	ss Type 347 welded to 17-4PH at 900°F	0.10
	ss Type 347 welded to 17-4PH at 1100°F	0.11
	ss Type 347 welded to 17-7PH at 900°F	0.28

(a) The ss Type 440C test coupons fell from their mountings above the electrical heaters and worked their way down through the bed to the air distributor plate where they were found at the end of the operating period. Therefore, the tabulated corrosion rate may be biased because of possible erosion in the neighborhood of the air distributor caps.

VI. CONCLUSIONS AND RECOMMENDATIONS

The study on fluidized bed calcination of simulated zirconium fluoride wastes has demonstrated the feasibility of processing this type of radioactive waste at the WCF under conditions comparable to those employed during the recently concluded processing campaign on radioactive aluminum nitrate wastes. By addition of stoichiometric amounts of calcium nitrate to the waste, greater than 99 percent of the fluoride was retained in the solids. Adding calcium nitrate to the simulated waste produced an easy-to-handle flocculent precipitate which caused no trouble in pumping when adequate flow velocities of the solution were maintained.

Corrosion rates on materials similar to those in use at the WCF indicate that only the stainless steel Type 440C caps on the feed atomizing nozzles need to be changed. However, additional testing should be conducted because of the relatively short exposure time to the potentially corrosive environment and the possibility of biased results on some of the test coupons.

The calcined product contained by weight about 25 percent ZrO_2 , 30 percent Al_2O_3 , and 40 percent CaF_2 . The remainder consisted of nitrates and trace compounds. The presence of CaF_2 was verified by X-ray analysis of samples of the calcined solids; the presence of the oxides is assumed, and these weight percents were calculated from chemical analyses for aluminum and zirconium.

Several additional pilot plant studies are planned to determine optimum operating conditions and quantities of feed additives for fluidized bed calcination of zirconium fluoride wastes. Included in future testing will be: (1) tests to evaluate using less calcium nitrate as indicated by recent laboratory studies; (2) tests with blends of zirconium fluoride and high sodium content, second-cycle wastes in lieu of calcium nitrate, and, (3) tests to determine optimum physical and chemical properties of the calcined product as affected by varying calciner operating conditions.

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APPENDIX A. EQUIPMENT DESCRIPTION

The twelve-inch-diameter calciner was constructed in 1961 and has been operated and modified intermittently to supply support data for the WCF. About 1400 operating hours were logged during the pilot plant work on calcination of aluminum nitrate waste prior to the calcination of zirconium fluoride waste.

The process flowsheet for the twelve-inch-diameter calciner was adapted from those used in the earlier pilot plant calciners, a six-inch-diameter unit⁽⁸⁾ and a two-foot-square unit⁽²⁾. The twelve-inch-diameter calciner is more highly instrumented and is more flexible than either of its predecessors. Table VI compares the operating ranges of the three pilot plant calciner units⁽⁹⁾.

Table VI

COMPARISON OF NORMAL OPERATING RANGES OF PILOT PLANT CALCINERS

<u>Variable</u>	<u>Six-Inch Diameter</u>	<u>Two-Foot Square</u>	<u>Twelve-Inch Diameter</u>
Vapor Space Pressure	Above Atmospheric	Above Atmospheric	Above or Below Atmospheric
Fluidizing Air Velocity	0.6-4.5 ft/sec	0.5-1.5 ft/sec	0.5-2.5 ft/sec
Nozzle Air-to-Liquid Ratio	200-750	150-900	150-1100
Bed Volume	0.4 ft ³	14.5 ft ³	2.4-3.2 ft ³
Off-Gas Recycle as Fluidizing Air	None	None	Yes
Scrub Product Recycled to Venturi	None	None	Yes

Equipment details of the twelve-inch-diameter calciner are given in the following sections.

The process flow sheet used with the twelve-inch-diameter calciner is shown in Figure 9. Dotted lines represent the portions of the process not used during the calcination of zirconium fluoride.

Fig. 9 Process flowsheet for the twelve-inch-diameter calciner

1. Calciner Vessel

The calciner vessel is constructed of a 91.5-inch length of 12-inch Schedule 40 pipe. The vessel and its components are fabricated from Type 347 stainless steel. The arrangement and location of the various components attached to the calciner vessel are shown in Figure 10. Both the top plate and plenum are flanged to the vessel so that the unit can be opened for inspection or modification as required.

The necessary heat to effect the calcination reaction is supplied by 39 electrical heaters. The 1/2-inch-diameter inconel-sheathed electrical heaters are arranged in a bundle as shown in Figure 11. The amount of electrical power delivered to the heaters, which in turn controls the operating bed temperature, can be controlled automatically or manually through pneumatic positioners on a bank of six powerstats. The maximum heat which can be delivered to the twelve-inch-diameter calciner is 160,500 Btu/hr.

Calcined particles within the size range of the desired product are occasionally thrown from the surface of the bed by bursting air bubbles. To prevent these particles from being carried into the off-gas stream, a baffle (see Figure 12) is located 72 inches above the fluidizing air distributor plate. Because of the slanted arrangement of the louvers in the baffle, the particles are deflected back to the fluidized bed or against the walls of the calciner vessel. Virtually no product-sized particles were found in the fines collected in the primary cyclone.

The calcined product is continuously removed from the calciner vessel through either of two 1-1/2 inch diameter overflow lines located at 37.5 and 48.5 inches above the air distributor plate (see Figure 10). The upper product take-off line is a vertical standpipe while the lower take-off line terminates at the wall of the calciner vessel. The product is collected in a small vessel for periodic sampling and weighing of the calciner product. The choice of product take-off lines depends upon the desired bed height. The equilibrium bed height normally resulting from using the upper product take-off is about 36 inches; for the lower product take-off the equilibrium bed height is about 25 inches. During the zirconium fluoride waste calcination study, the upper product take-off was used.

Three possible nozzle locations are provided in the twelve-inch-diameter calciner. These locations are at 4 inches, 25.5 inches, and 31.5 inches above the air distributor plate. Only the nozzle port at the 25.5-inch level has been used to date.

Feed is introduced into the fluidized bed for calcination by a pneumatic atomizing nozzle using air to atomize the liquid stream at the calciner wall. The normal operating range for the NAR (nozzle air to liquid volume flow ratio) is from 250 to 700 at a liquid flow rate of 10 l/hr, although the flow ratio can be varied between 150 and 1100 at the 10 l/hr liquid rate. No operating difficulty was experienced in atomizing the simulated zirconium fluoride waste which contained the flocculent precipitate.

TYPICAL PRESSURE PROBE DETAIL

CPP - S - 3431

Fig. 10 Calciner vessel details

Fig. 11 Electrical heater bundle

Fig. 12 Baffle in vapor space of calciner vessel

A bed addition pot, connected to the calciner vessel at 56 inches above the distributor plate, is designed to allow bed addition at any time during the startup procedure or during actual operation. The "seeds" added to the bed during the zirconium calcination test to control the particle size were added through the bed addition pot.

Off-gas from the calciner vessel is routed to the primary cyclone through a 1-1/2 inch-diameter outlet at the center of the top flange.

2. Plenum and Fluidizing Air Distributor Plate

The plenum and the fluidizing air distributor plate were made separable as shown in Figure 13. The units are gasketed by metal at the flange of the plenum and secured together by a packed nut located at the bottom outlet of the plenum.

Twenty air distributor caps are arranged on the distributor plate with each 1-inch-diameter cap surmounting a 7/32-inch-diameter orifice in the plate. This arrangement has provided adequate fluidization for the twelve-inch-diameter calciner.

3. Primary Cyclone and Fines Collection Pot

The first unit in the solids de-entrainment apparatus is a simple cyclone. Figure 14 shows details of the primary cyclone and fines collection pot. The primary cyclone normally collects about 90 percent of the fines elutriated from the calciner vessel.

Fines continuously removed from the off-gas by the primary cyclone are collected in a pot for periodic sampling and weighing. A 3/4-inch-diameter line connects the primary

Fig. 13 Plenum and the fluidizing air distributor plate

cyclone to the collection pot. An electrical heating tape is wound around the inter-connecting line to prevent off-gas condensation in the line. A small gas flow down the inter-connecting line is maintained by a water jet pulling the gases from the collection pot through a porous metal filter located within the fines collection pot.

PRIMARY CYCLONE DETAIL TWELVE-INCH-DIAMETER CALCINER

Fig. 14 Primary cyclone and fines collection pot

Fig. 15 Venturi scrubber

6. Condenser

A shell-and-tube heat exchanger is used to remove condensable acids from the off-gas before it enters the off-gas compressor. Details of this condenser are given on Figure 17. The condensate stream is collected from the condenser at a normal rate of 10 liters/hr.

7. Vacuum System

The off-gas was vented from the condenser to the suction side of an off-gas compressor which is used to supply a vacuum for the calciner unit. The vacuum system for the twelve-inch-diameter calciner is shown schematically in Figure 18. The solids in the off-gas dictated that a water sealed compressor, such as the Nash Hytor, be used to supply the vacuum for the calciner system.

4. Venturi Scrubber

A venturi scrubber is located downstream of the primary cyclone. Details of the venturi scrubber are given in Figure 15. Although four liquid ports are provided at the throat of the venturi, only two are normally used. Liquid to the venturi scrubber is normally supplied at a rate of 90 liters/hr.

5. Scrub De-entrainment Cyclone

The atomized scrubbing solution is "air-lifted" vertically by the off-gas about 12 feet to a scrub de-entrainment cyclone (see Figure 16 for details of the cyclone). The scrubbing solution separated from the off-gas is cooled and then collected in a surge tank for eventual recycle to the venturi scrubber. Fresh water can also be used in the venturi scrubber.

Fig. 16 Liquid de-entrainment cyclone

When the calciner system is operated with the vapor space in the calciner vessel above atmospheric pressure, the vacuum system is by-passed and the off-gas is vented to the atmosphere.

Summary

The twelve-inch-diameter calciner is highly versatile in that operating parameters can be varied over a wide range. The twelve-inch-diameter pilot plant calciner is much more automated than its predecessors--the six-inch-diameter calciner and the two-foot-square calciner⁽⁹⁾. It is expected that the twelve-inch-diameter calciner will be the main "workhorse" during future pilot plant calcination studies conducted at ICPP.

APPENDIX B. GLOSSARY OF TERMS

1. The percent of original bed remaining at any time can be calculated from the following formula:

$$x = 1 - e^{\left(\frac{Pt}{W}\right)}$$

where: x = weight fraction of original bed at time, t

W = weight of original bed

P = product rate per hour

t = time in hours

The validity of the equation depends on perfect mixing in the bed and on steady state conditions regarding the product rate and bed weight. The product rate, P , includes only the solids collected as overflow material and not that part of the product elutriated from the calciner vessel.

2. The crystalline structure of the calcined solids was determined by X-ray diffractational analysis. Materials not showing a crystal structure are defined as amorphous.

3. The bulk density of the calcined solids, both product and fines, was determined by pouring the material through a funnel into a graduated cylinder for measuring the untapped volume. The known volume of the material was then weighed and the mass per unit volume of the substance was calculated. The volume determined in this manner includes the material volume, inter-particle void volume, and the intra-particle pore volumes.

4. The absolute density of the solids, both product and fines, is the density of the material excluding all intra-and inter-particle voids. Carbon tetrachloride was used in a displacement method as it is assumed that the carbon tetrachloride penetrates all voids in the solids.

5. The particle density of the product was determined by mercury displacement. Mercury fills the inter-particle voids but, because of the high surface tension of mercury at normal pressures, does not fill the intra-particle voids. This method is not used on the fines as they are too small for this method to work satisfactorily.

6. Intra-particle porosity of the product was calculated from the following formula:

$$\text{Intra-particle porosity} = \frac{\rho_a - \rho_p}{\rho_a}$$

where: ρ_a = absolute density

ρ_p = particle density

The term intra-particle porosity refers to the void fraction within each particle.

7. The superficial fluidizing velocity is defined as the linear velocity which would be attained by the fluidizing air in the empty calciner vessel at the operating temperature and pressure.

8. The feed nozzle air-to-liquid ratio (NAR) refers to the volumetric flow ratio of the atomizing air stream to the liquid feed stream. The air volume was determined at the metering temperature (ambient) and the pressure in the vapor space of the calciner vessel above the fluidized bed (vapor space).

9. The mass median particle diameter (MMPD) and the size distribution of the product particles were determined by screening samples of the product through successively smaller Tyler mesh screens. The results of the particle size distribution determinations shown in Figure 8 of this report are given as cumulative percent finer than the screen size given. The MMPD of the product was calculated from the size distribution analysis by accumulatively multiplying the weight percent of product on each screen by an appropriate factor..

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