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PILOT-PLANT DEVELOPMENT OF A ROVER WASTE CALCINATION FLOWSHEET

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PILOT-PLANT DEVELOPMENT OF A ROVER WASTE CALCINATION FLOWSHEET

by

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Abstract

The results of eight runs, six using the 10-cm diameter and two using the 30-cm diameter pilot-plant calciners, in which simulated first-cycle Rover waste was calcined are described. The results of the tests showed that a feed blend consisting of one volume simulated first-cycle Rover waste and one or two volumes simulated first-cycle zirconium waste could be successfully calcined.

Summary

Eight runs have been made at the Idaho Chemical Processing Plant (ICPP) using pilot-plant calciners to calcine simulated first-cycle Rover waste. The first six runs (Runs RW-10-1 through RW-10-5R) were made using the 10-cm diameter calciner; the last two runs (Runs 59 and 62) were made using the 30-cm diameter calciner.

The first six runs were made to determine if pure Rover waste could be calcined or if not, at what blend ratio with zirconium waste it could be calcined. The results of the tests showed that pure Rover waste could not be successfully calcined, but that a blend of one volume Rover waste and one volume zirconium waste was calcinable on a small scale.

Two subsequent runs were made to determine if one:one and one:two (Rover to zirconium) waste blends could be successfully calcined on a large scale. The results of these runs showed that both blends could be calcined and that the physical properties of the calcine were very similar to those obtained when calcining pure zirconium wastes, i.e., average values for the attrition index, bulk density, and product weight-to-fines weight for the two runs were 9.5, 1.29 g/cm^3, and 3.35, respectively as compared to average values for zirconium calcine of 12, 1.24 g/cm^3, and 3.50.

Based on the experimental testing, a waste feed blend consisting of one volume of Rover waste and one volume of zirconium waste is a practical flowsheet for Rover waste calcination.

CONTENTS

FIGURES

TABLES

I. Introduction

A. Description of Rover Process

The Rover fuel elements are basically composed of a graphite matrix containing dispersed, pyrolytic carbon coated, uranium dicarbide fuel particles. A protective coating of niobium or niobium carbide is present on surfaces of most of the fuel elements.

The Rover fuel elements will be charged to an air-cooled burner containing a bed of alumina fluidized with oxygen. At the 750^{o}C to 850^{o}C bed temperature range in the burner, the graphite matrix reacts with oxygen to form gaseous combustion products, and the metallic carbides (uranium and niobium) react to form solid oxides. The metallic oxides and some unburned graphite will be elutriated from the burner and removed from the off-gas by filtration. This ash will be fed batchwise to a secondary burner containing alumina fluidized with oxygen. Auxilary heaters will be required to maintain a 750^{o}C to 850^{o}C temperature range to complete the burning of the graphite. Filters in the top of the secondary burner prevent escape of fine solids from the burner in the off-gas stream. Following complete burning of the graphite, the metal oxide fines will be elutriated from the secondary burner and fed to a dissolver. The uranium and some of the niobium will be dissolved in nitric and hydrofluoric acids. The dissolver solution will be complexed with aluminum nitrate and the insolubles separated before the solution is fed to the existing ICPP solvent extraction system for uranium purification. The first-cycle raffinate waste will then be sent to tanks WM-103, 104, 105, and 106 for temporary storage prior to fluidized-bed solidification. The expected waste composition for the Rover waste, along with that for normal zirconium waste, is shown in Table I.

B. Description of Liquid Waste -- Expected Waste Composition -- Unique Problems

The problem associated with the first-cycle Rover waste is the instability of the niobium. Niobium has a very narrow stability range and will precipitate as Nb_2O_5 if the niobium/fluoride ratio is changed by addition of complexing compounds such as aluminum, boron, and zirconium, or if there is a temperature increase of as little as 10°C.

C. Flowsheet Alternatives Considered

Four potential flowsheets for calcining the first-cycle Rover waste were investigated, i.e., pure Rover waste and one:five, one:two, and one:one volumetric blends of Rover and first-cycle zirconium wastes. The relatively small amount of Rover waste to be generated (approximately 125,000 gallons) justifies blending with existing zirconium wastes.

TABLE I

APPROXIMATE COMPOSITIONS OF ROVER AND ZIRCONIUM WASTES

Component	Rover Waste (M)	Zirconium Waste (M)
H^+	2.5	1.6
Al	0.17	0.67
Zr	-	0.45
B	0.066	0.20
Nb	0.066	-
Fe	-	0.0047
NH_4	0.062	-
NO_3^-	2.7	2.4
F^-	0.85	3.2
Activity (Ci/L)	0.005	3-7
Dissolved Metal Ion Content, g/L	12	61

II. Equipment and Procedures

A. Ten-cm and Thirty-cm Diameter Calciners

A flow diagram of the #3 10-cm diameter calciner used for pilot-plant Runs RW-10-1 to RW-10-5R is shown in Figure 1. A flow diagram of the 30-cm diameter calciner used for Runs 59 and 62 is shown in Figure 2. Both systems were essentially the same, i.e., the #3 10-cm diameter calciner is basically a scale-down version of the 30-cm diameter calciner.

Both systems consisted of a calciner vessel, primary and secondary cyclones, a fines collection pot, off-gas condensing systems, a venturi scrubber, and a scrub tank (the superheater, silica gel absorber, and filter system were not used on the 30-cm diameter calciner). In the 10-cm diameter calciner, product was taken out directly from the bed; in the 30-cm diameter calciner, a product overflow line and product pot system was used to collect the product.

B. Process Description

The feed simulated, as nearly as possible, the expected composition of the radioactive waste to be calcined. This simulated waste was fed to the calciner vessel at a controlled rate. The feed was atomized with air and injected into the bed. A mixture of kerosene and oxygen was also injected into the bed to produce the heat necessary for calcination. The various operating parameters for the eight calciner runs are shown in Table II.

C. Calcine Caking Tests

Samples of the calcine from the final beds of Runs 59 and 62 were put into open ceramic containers and heated in an oven at various temperatures (650-1000°C) over different lengths of time (1 to 30 days) to determine the temperature at which the calcine would cake and be difficult to retrieve from the storage bins.

D. Undissolved Solids Tests

Samples of zirconium, Rover, 1 volume Rover:1 volume zirconium, and 1 volume Rover:2 volumes zirconium waste feeds were tested for undissolved solids present (after calcium nitrate addition). Solid calcium nitrate

SCHEMATIC DIAGRAM OF 4-INCH DIAMETER CALCINER

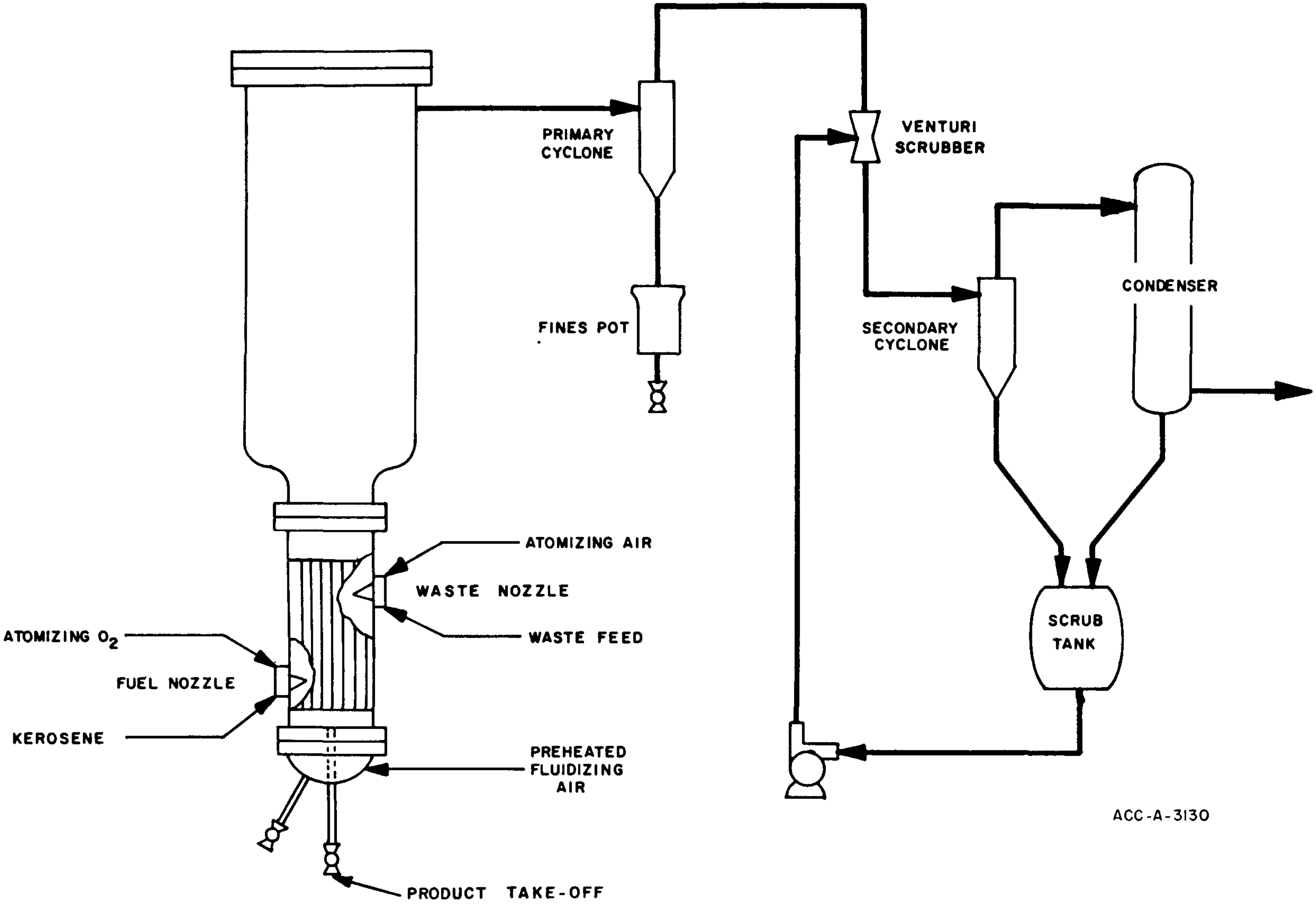
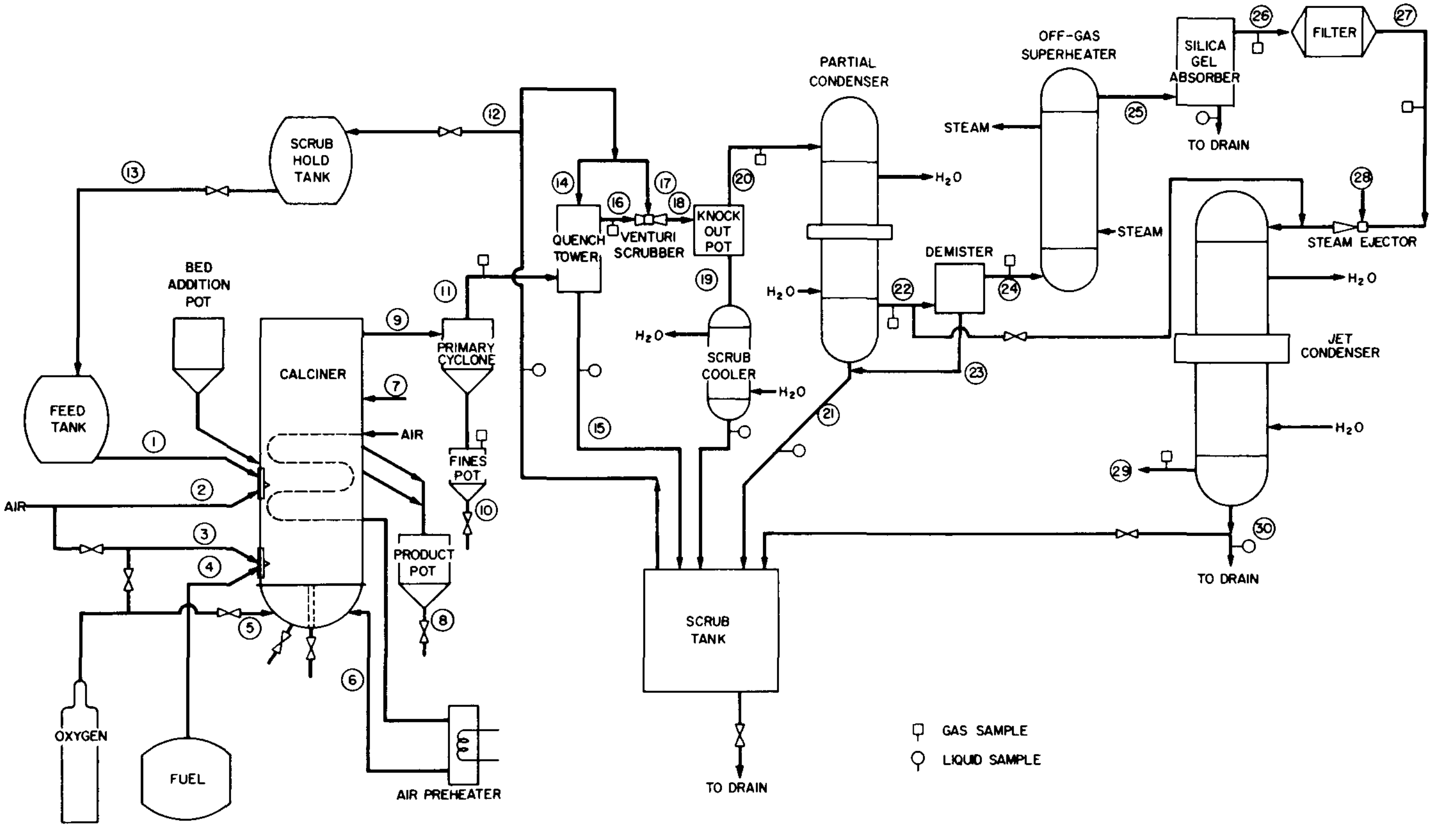


FIGURE 1. SCHEMATIC DIAGRAM OF #3 10-cm DIAMETER CALCINER



1	FEED	11	CYCLONE OFF-GAS	21	PARTIAL CONDENSER CONDENSATE
2	FEED ATOMIZING AIR	12	SCRUB TO HOLD TANK	22	PARTIAL CONDENSER OFF-GAS
3	FUEL ATOMIZING GAS	13	SCRUB RECYCLE TO FEED	23	DEMISTER DRAIN
4	FUEL	14	SCRUB TO QUENCH	24	DEMISTER OFF-GAS
5	FLUIDIZING OXYGEN	15	QUENCH RECYCLE	25	SUPERHEATER OFF-GAS
6	HEATED FLUIDIZING AIR	16	QUENCH OFF-GAS	26	ABSORBER OFF-GAS
7	MISCELLANEOUS PURGES	17	SCRUB TO VENTURI	27	FILTER OFF-GAS
8	CALCINE PRODUCT	18	VENTURI OFF-GAS	28	STEAM
9	CALCINER OFF-GAS	19	SCRUB RECYCLE	29	OFF-GAS TO STACK
10	CALCINE FINES	20	KNOCKOUT POT OFF-GAS	30	JET CONDENSATE

FIGURE 2. SCHEMATIC DIAGRAM OF 30-cm DIAMETER CALCINER

TABLE II

OPERATING PARAMETERS FOR EIGHT ROVER WASTE FLOWSHEET RUNS

Run #	Feed	Gross Feed Rate (L/h)	Fuel	Fuel Rate (L/h)	Waste NAR[a]	O_2/Fuel Ratio	Fluidizing Velocity (m/s)	Recycle Rate (L/h)	Bed Temp (°C)	Starting Bed	Run Time (h)
RW-10-1	2 Zr: 1 Rover	2.08	Kerosene	0.57	680	1690	0.27	0.00	500	ZrO_2-CaF_2	11.0
RW-10-2	5 Zr: 1 Rover	2.20	Kerosene	0.60	612	1720	0.27	0.00	507	Final Bed from RW-10-1	11.0
RW-10-3	Pure Rover	2.73	Kerosene	0.75	460	1557	0.26	0.00	500	Final Bed from RW-10-2	9.5
RW-10-4	1 Zr: 1 Rover	2.08	Kerosene	0.57	607	2035	0.26	0.00	500	ZrO_2-CaF_2	12.0
RW-10-5	1,2 Zr: 1 Rover	1.98-2.04	Kerosene	0.54-0.56	508-748	1698-2327	0.26	0.00	500	Final Bed from RW-10-4	62.0 (1:1) 66.0 (2:1)
RW-10-5R	1 Zr: 1 Rover	1.98-2.04	Kerosene	0.54-0.56	508-748	1698-2327	0.26	0.00	500	Final Bed from RW-10-5	112.0
R 59	1 Zr: 1 Rover	35.35	Kerosene	4.73-6.81	119-200	1900-2450	0.25-0.26	5.30	500	ZrO_2-CaF_2	100.0
R 62	2 Zr: 1 Rover	35.23	Kerosene	5.15-7.38	122-200	1800-2420	0.26-0.27	5.28	500	Final Bed from Run 59	108.0

[a]Ratio of liquid feed rate to atomizing air rate at feed nozzle pressure and 21°C.

($Ca(NO_3)_2$) was added to each sample to give a Ca^{+2}/F^- mole ratio of 0.55. The samples were heated at 55°C for 24 hours and then dried in a vacuum drier after which the undissolved solids were weighed.

III. Experimental Testing and Results

A. Ten-cm Diameter Calciner Runs RW-10-1 through RW-10-5R

The primary objective of these runs was to determine the maximum first-cycle Rover waste and first-cycle zirconium waste blend that could be successfully calcined with solid calcium nitrate ($Ca(NO_3)_2$) added for fluoride complexing (0.55 Ca/F mole ratio).

Run RW-10-1 utilized a waste feed blend of one volume simulated first-cycle waste and two volumes simulated first-cycle zirconium waste. There were no equipment failures during the run. The run was highly successful in that the objective was met and no serious problems were encountered in calcining the blended wastes. The only problem in the run was a plugged feed nozzle. After this was corrected, the atomizing air rate to the feed nozzle was increased and no further plugging occurred. No nozzle caking or bed agglomeration was observed. The bulk densities of the product and fines were 1.25 g/cm^3 and 0.60 g/cm^3, respectively. The attrition resistance index of the final bed was 18.4 and the mass-mean particle diameter (MMPD) was 0.38 mm.

Run RW-10-2 used a waste feed blend of one volume simulated first-cycle Rover waste and five volumes simulated first-cycle zirconium waste to determine the effect on calcination when a diluted feed was used. The run was successfully completed and no serious problems were encountered in calcining the blended wastes. Several small problems were encountered such as a plugged feed nozzle, a stuck float on the feed rotameter, and difficulty in removing the bed. No nozzle caking occurred, but several agglomerates approximately one-quarter inch in diameter, were observed in the final bed. These small agglomerates probably caused the difficulty in removing the bed; they may have formed during one period when a plugged feed nozzle caused a high bed temperature before the situation was corrected. The bulk densities of the product and fines were 1.12 g/cm^3 and 0.60 g/cm^3, respectively. The attrition resistance index and MMPD of the final bed were 12.4 and 0.47 mm, respectively.

Run RW-10-3 attempted to calcine pure, simulated, first-cycle Rover waste. The scheduled run was completed, although serious problems were encountered, as expected,due to the dilute nature of the feed, with feed nozzle plugging, high bed attrition, and agglomerates in the bed. The feed nozzle plugging was caused by a cake (approximately 3.8 cm high) of unsintered calcine that formed around the nozzle. The probable cause of the nozzle cake and agglomerates (broken off nozzle cake) in the bed was poor feed atomization resulting from the decreased rate of feed atomizing air and fluidizing air. These air streams were decreased below their normal ranges in an attempt to build bed by decreasing the attrition of the soft calcine (3.8 attrition index). If the air streams had been left at their normal levels, probably no nozzle caking or agglomerates would have formed, but excessive fines would have been generated and little product produced resulting in a decreasing bed level. The bulk density, attrition resistance index, and MMPD of the final bed were 1.13 g/cm^3, 3.8, and 0.47 mm, respectively.

Run RW-10-4 used a waste blend of one volume simulated first-cycle Rover waste and one volume simulated first-cycle zirconium waste. The run was highly successful. The waste blend calcined readily without any nozzle caking or bed agglomeration. The bulk densities of the product and fines were 1.31 g/cm^3 and 0.48 g/cm^3, respectively. The MMPD of the final bed was 0.39 mm.

Since Run RW-10-4 was successful, a long-term run was scheduled for the 10-cm diameter calciner.

Run RW-10-5 started up and operated normally with a one volume Rover and one volume zirconium waste blend until 61.5-hours cumulative operating time (COT) when the bed temperatures started to split leading to a shutdown at 62.0-hours COT. Investigation showed that the bed contained many agglomerates and a large clinker had formed around the fuel nozzle. The run was restarted using a feed blend of one volume Rover and two volumes zirconium waste. A shutdown occurred at 95-hours COT when the feed supply was depleted. Upon finishing feed make-up, the run was restarted with the one-to-two blend and allowed to run until 128-hours COT when planned shutdown occurred.

Since Run RW-10-5 appeared to be a borderline case (operated almost successfully) for the one-to-one ratio, Run RW-10-5R was started using the one-to-one blend. Only one unscheduled shutdown occurred during this run and that was due to water in the kerosene line at 47.9-hours COT. The run was then continued until scheduled shutdown at 112-hours COT. A large agglomerate was found around the feed nozzle and three-quarters of the way around the vessel wall. Since this is a problem inherent with the 10-cm calciner and not necessarily due to the feed blend, this flowsheet was determined to be satisfactory for testing in the larger pilot-plant calciner.

The product MMPD is shown as a function of run time in Figure 3; it is seen that all MMPDs are within practical operating limits. The product weight to fines weight ratios (P/F) averaged 1.63 for the run.

B. Thirty-cm Diameter Calciner Run 59

Since RW-10-5R was successful, a long-term run (Run 59) was scheduled in the 30-cm diameter calciner. The objective of this run, to evaluate the operability of calcining a feed blend consisting of one volume simulated Rover first-cycle waste and one volume simulated zirconium first-cycle waste, with solid calcium nitrate ($Ca(NO_3)_2$) added for fluoride volatility control, was successfully demonstrated.

There were two equipment failures during the run. At 1-hour COT the kerosene pump failed and caused a 6-hour shutdown. At 71-hours COT the main masterflex feed pump failed, but caused no downtime. The feed was switched to the auxiliary pump and the run continued until scheduled shutdown at 100-hours COT. The only flowsheet problem encountered in the run was minor bed agglomeration. At 8-hours COT it was seen that the product contained many small, fragile agglomerates; however, they did not increase in size or quantity throughout the rest of the run.

The product MMPD is plotted versus the cumulative operating time (COT) in Figure 4. The MMPD decreased from 0.53 mm at 8-hours COT to 0.38 mm at 48-hours COT. The MMPD remained fairly constant (0.38 to 0.40 mm) from 48 to 100-hours COT. The product bulk density increased from 1.19 g/cc at 8 hours to 1.24 g/cc at 56 hours and remained fairly constant (1.23 to 1.26 g/cm^3) to 100-hours COT. The bulk density of the fines varied between 0.43 and 0.55 g/cm^3. The attrition index of

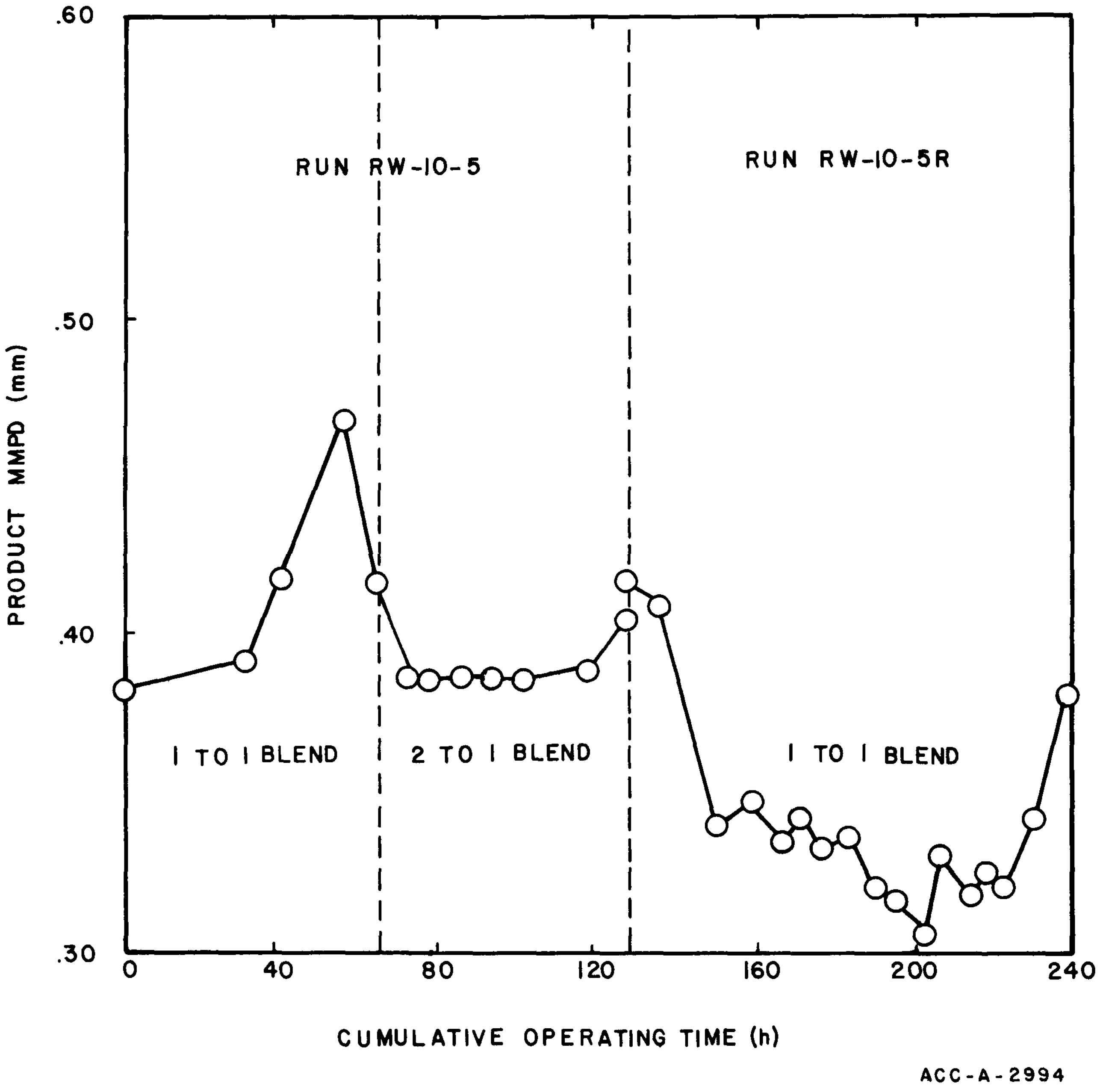


FIGURE 3. PRODUCT PARTICLE SIZE VERSUS CUMULATIVE OPERATING TIME
RUNS RW-10-5 AND RW-10-5R

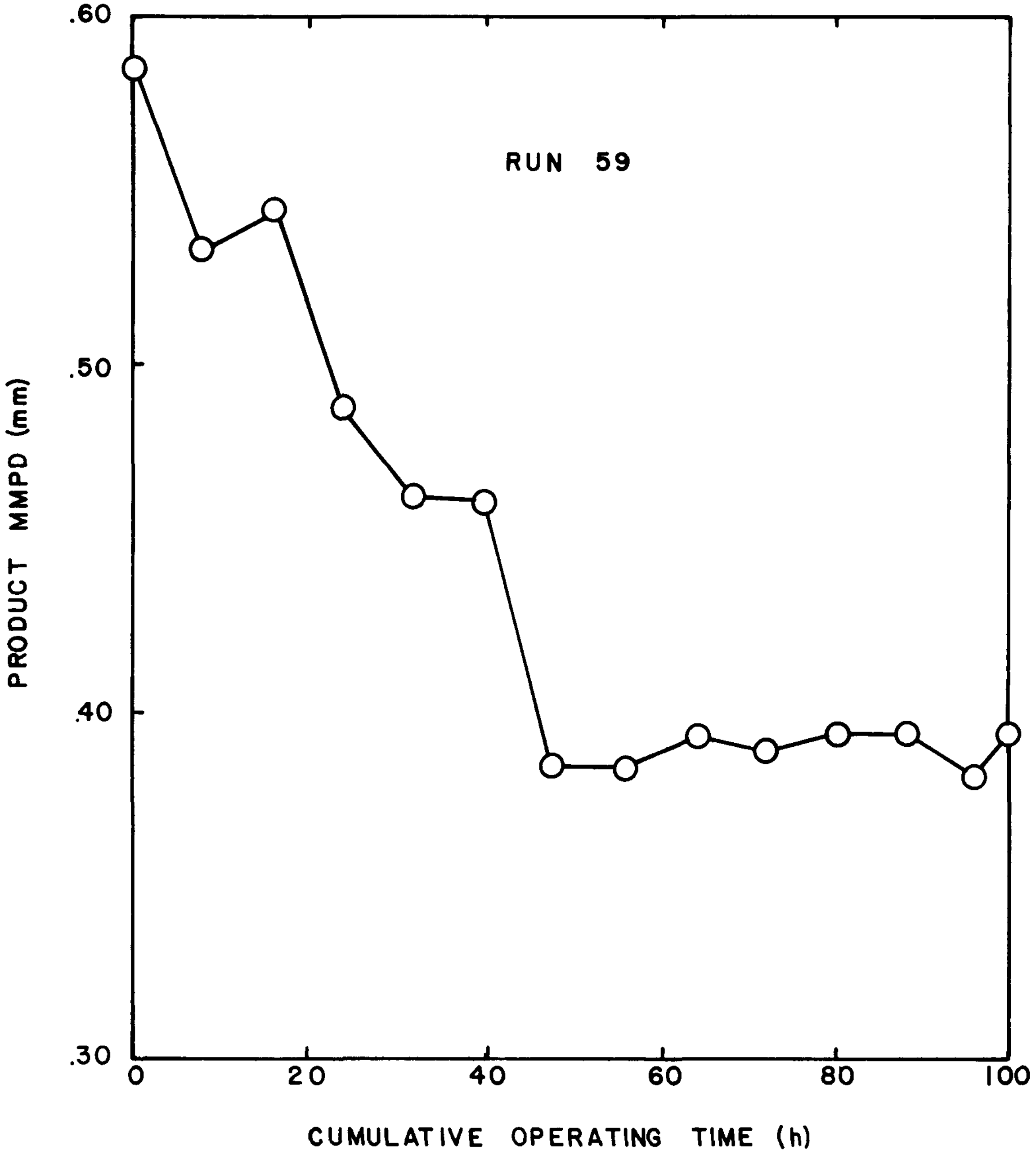


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FIGURE 4. PRODUCT PARTICLE SIZE VERSUS CUMULATIVE OPERATING TIME
RUN 59

the final bed was 8.6. The ratio of product weight to fines weight (P/F) varied between 2.32 and 7.15 with an average of 3.67.

The chemical compositions of various feed, scrub, and condensate solutions as determined by analytical chemistry are shown in Table III. The chemical compositions of the final product and fines are shown in Table IV. There was sufficient aluminum (Al^{+3}) present in the scrub and condensate to complex all fluoride (F^-) present.

Coupons composed of type 304-L stainless steel had been installed at various points in the 30-cm calciner for corrosion testing. The coupons are removed and analyzed after each run. The results for this run are shown in the next section.

C. Thirty-cm Diameter Calciner Run 62

Thirty-cm diameter calciner Run 62 was completed April 22, 1977. The objective of the run, to demonstrate calcining a feed blend consisting of one volume simulated Rover first-cycle waste and two volumes simulated zirconium first-cycle waste, with solid calcium nitrate ($Ca(NO_3)_2$) added for fluoride volatility control, was successfully completed.

There were three equipment failures during the run. At 53-hours cumulative operating time (COT), the pump for the CO/CO_2 analyzer failed and at 66-hours COT, the primary cyclone plugged. Neither of these caused a shutdown. At 76 hours the feed line to the constant-head feed tank became plugged and caused a one-half hour shutdown. After clearing out the feed line, the run was restarted and continued without further problems until normal shutdown at 108-hours COT.

The only flowsheet problem encountered was the same type of problem that occurred in Run 59. At 8-hours COT, the product contained numerous, small, fragile agglomerates; however, they did not increase in size or quantity throughout the rest of the run and were completely absent from the final bed after the feed had been turned off. This problem has not been observed during calcination of straight zirconium waste.

TABLE III

CHEMICAL ANALYSES OF FEED, SCRUB, AND CONDENSATE SOLUTIONS

Sample	Chemical Specie, M: H^+	F^-	Al^{+3}	Zr	Ca^{+2}	Nb
R-59-RF-1 (Rover Waste	2.30	0.79	0.141	<.006	7.6 E-4	0.0511
R-59-ZF-1 (Zirconium Waste)	1.55	3.58	0.68	0.48	2.0 E-4	0.0100
R-59-Feed Batch 1	2.10	0.98	0.385	0.20[a]	1.04	0.0161
R-59-Feed Batch 2	2.10	0.97	0.381	0.20[a]	1.08	0.0152
R-59-Feed Batch 3	1.81	0.97	0.384	0.20[a]	1.02	0.0152
R-59-Scrub COT 8	3.49	0.134	0.031	0.016	6.7 E-2	0.0005
R-59-Scrub COT 48	5.23	0.40	0.112	0.050	0.239	0.0010
R-59-Scrub COT 100	2.27	0.30	0.090	0.038	0.183	0.0013
R-59-Condensate COT 100	1.31	137 μg/mL	<.020	<.006	1.9 E-3	<0.0005

[a]These figures are approximate based upon the compositions of the Rover and zirconium wastes.

TABLE IV

CHEMICAL ANALYSES OF FINAL PRODUCT AND FINES

Sample	Chemical Specie, wt%: B	F^-	Al^{+3}	Zr	Ca^{+2}	Nb
R-59-P-100 (Final Product)	1.5	1.07	10.7	14.8	33.3	1.5
R-59-JP-100 (Final Fines)	1.7	7.23	12.8	13.7	31.8	1.7

The mass mean particle diameter (MMPD) is plotted versus cumulative operating time in Figure 5. The MMPD varied throughout the run between 0.32 and 0.38 mm. The MMPD remained nearly constant (0.35 to 0.38 mm) from 64 to 108-hours COT except at 80-hours COT where it was 0.33 mm (probably due to weighing errors). The product bulk density remained nearly constant (1.29 to 1.35 g/cm^3) throughout the run. The bulk density of the fines varied between 0.64 and 1.1 g/cm^3. The attrition index of the final bed was 10.4. The ratio of the product weight to fines weight varied between 2.38 and 5.27 with an average of 3.03.

The chemical composition of various feed, scrub, and condensate solutions are shown in Table V. The chemical compositions of the final product and fines are shown in Table VI. There is sufficient aluminum (Al^{+3}) present in the scrub and condensate to complex all fluoride (F^-) present.

Coupons of type 304-L stainless steel had been installed at various points in the 30-cm calciner for corrosion testing. These coupons were removed after the run and submitted for analysis. The results for this run and Run 59 are as follows (data for Run 57 which used straight zirconium waste are included for comparison):

	Corrosion Rates (μm/month)		
Coupon Location	Run 59	Run 62	Run 57
Top of Condensor	10.41 (0.41 mil/mo)	7.0 (0.28 mil/mo)	21.08 (0.85 mil/mo)
Scrub Tank-Pump Exit	1.78 (0.07 mil/mo)	0.4 (0.2 mil/mo)	10.92 (0.43 mil/mo)
Quench Tower	Not Tested	11.0 (0.43 mil/mo)	34.8 (1.37 mil/mo)
Condensor Bottom-Gas Outlet	2.29 (0.09 mil/mo)	0.2 (0.01 mil/mo)	1.02 (0.04 mil/mo)
Bottom of Knock-out Pot	18.80 (0.74 mil/mo)	15.0 (0.59 mil/mo)	62.48 (2.46 mil/mo)
Impingement Plate-Top of Knockout Pot	21.59 (0.85 mil/mo)	10.0 (0.39 mil/mo)	149.0 (5.87 mil/mo)

D. Calcine Caking Tests

The caking temperature was found for calcine produced by calcining one and two volumes of simulated first-cycle zirconium (ZF) waste blended with one volume of simulated Rover waste. The calcine from the one volume Rover: one volume ZF wastes blend was from the final bed of 30-cm

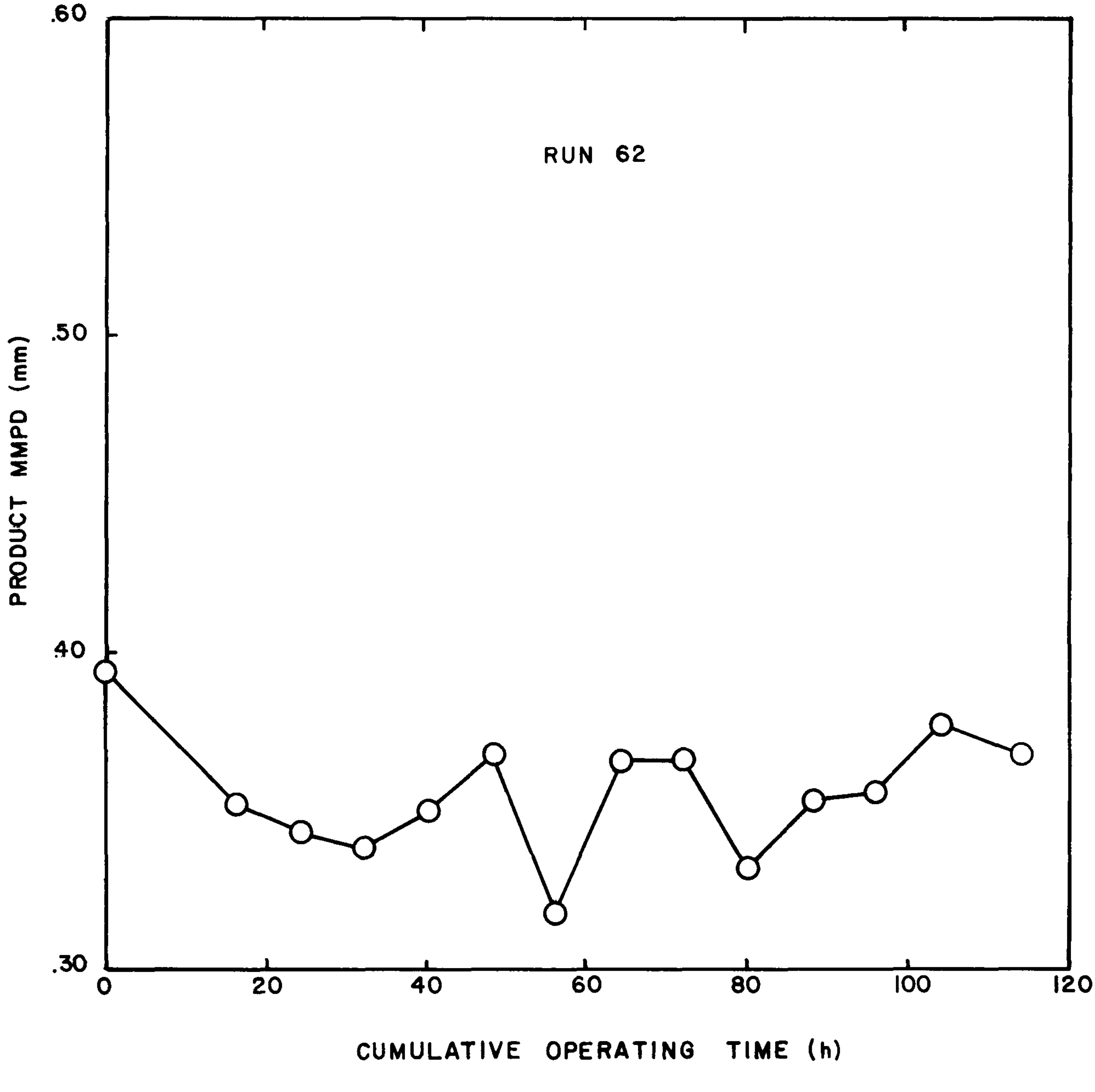

FIGURE 5. PRODUCT PARTICLE SIZE VERSUS CUMULATIVE OPERATING TIME RUN 62

TABLE V

CHEMICAL ANALYSES OF FEED, SCRUB, AND CONDENSATE SOLUTIONS (M)

Sample	H^+	F^-	Al^{+3}	Zr	Ca^{+2}	Nb
R-62-Z (Zirconium Waste)	1.38	3.52	0.67	0.47	.00019	0.004
R-62-RA (Rover Waste)	2.48	0.86	0.087	<0.006	.00007	0.065
R-62-RB (Rover Waste)	2.54	0.86	0.201	<0.006	.00662	0.045
R-62-Feed Batch 2	1.77	2.34	0.438	0.114	1.13	0.009
R-62-Feed Batch 10	1.88	2.32	0.461	0.187	0.967	0.016
R-62-Feed Batch 22	2.01	2.07	0.455	0.076	0.922	0.014
R-62-Scrub COT 8	2.76	0.18	<0.039	0.019	0.057	0.0004
R-62-Scrub COT 48	1.77	0.48	0.075	0.043	0.116	0.0009
R-62-Scrub COT 108	2.70	0.51	0.087	0.056	0.146	0.002
R-62-Condensate COT 108	1.65	0.017	<0.039	<0.011	0.00422	<0.0001

TABLE VI

CHEMICAL ANALYSES OF PRODUCT AND FINES

		Chemical Specie, wt%				
Sample	B	F^-	Al^{+3}	Zr	Ca^{+2}	Nb
R-62-Product COT 16	1.4	18.5	7.8	15.4	30.9	1.29
R-62-Fines COT 16	1.5	16.8	7.8	16.2	29.6	1.04
R-62-Product COT 108	2.4	17.9	7.7	16.5	29.8	0.92
R-62 Fines COT 108	1.4	18.5	7.5	16.2	28.4	0.78

diameter calciner Run 59; the calcine from the one volume Rover: 2 volumes ZF wastes blend was from the final bed of 30-cm calciner Run 62. Neither calcine caked when heated in an open ceramic container for one month at 650°C. Both calcines formed very soft cakes within 2 weeks when heated at 700°C.

E. Undissolved Solids Present in Various Feed Blends

The amount of undissolved solids present in four feed blends is shown in Table VII. The amount of undissolved solids present is dependent upon the fluoride (F^-) molarity (which determines the amount of calcium nitrate added); no unique problems occur with Rover waste.

TABLE VII

UNDISSOLVED SOLIDS PRESENT IN THE VARIOUS FEED BLENDS[a]

Feed Sample	Undissolved Solids (g/L)	Fluoride (F^-) $\underline{M}$
Zirconium Waste	84.15	3.59
Rover Waste	12.65	0.83
1 volume Rover:1 volume Zirconium	52.65	2.21
1 volume Rover:2 volumes Zirconium	64.90	2.67

[a]With calcium nitrate added to provide a Ca/F mole ratio of 0.55.

IV. Discussion of Results

Ten-centimeter diameter pilot-plant calciner scoping studies, using the expected Rover waste composition, showed that calcination of pure Rover waste is impractical due to high bed attrition and agglomeration. Further testing using various feed blends, ranging from one volume Rover: five volumes zirconium to one volume Rover: one volume zirconium, showed that feed blends as concentrated as one volume Rover waste mixed with one volume zirconium waste can be successfully calcined.

Since it is desirable to process the Rover waste as rapidly as possible (the waste will be stored in singly contained tanks), further testing was done using the 30-cm pilot-plant calciner to demonstrate the most concentrated Rover waste blending ratio on a larger scale. Thirty-cm diameter calciner Run 59 using a one volume Rover first-cycle waste:one volume zirconium first cycle waste feed blend and Run 62 using a one volume Rover first-cycle waste:two volumes zirconium first-cycle waste feed blend were successfully completed. Both Run 59, a 100-hour run, and Run 62, a 108-hour run, were smooth throughout their duration with the only downtime occurring due to minor equipment problems.

In both cases, several small, fragile agglomerates were found in the product samples taken after eight hours of operation. The agglomerates consisted of from two to ten particles weakly bonded together which probably made up less than 1% of the product weight. The exact amount of agglomerates in the product could not be determined since none of the agglomerates survived the screening operation. The agglomerates did not increase in size or quantity during the remainder of either run and they disappeared from the final bed during fluidization after the feed had been shut off. These agglomerates should not adversely affect plant-scale fluidized-bed calcination.

The Rover blend products are very similar to zirconium product as shown in Table VIII. In both runs, the calcine product was slightly softer than that produced when calcining straight zirconium waste.

TABLE VIII

COMPARISON OF PRODUCT PROPERTIES FOR ROVER AND ZIRCONIUM WASTE CALCINE

Feed Blend	Product weight/ Fines weight	Bulk Density (g/cc)	Attrition Resistance
1 volume Rover first-cycle waste:1 volume Zirconium first-cycle waste	3.67	1.26	8.6
1 volume Rover first-cycle waste:2 volumes Zirconium first-cycle waste	3.03	1.32	10.4
Zirconium first-cycle waste	3.50	1.24	12.0

No more plugging of the feed system should be encountered than experienced when operating on straight zirconium waste. Erosion and corrosion rates for either blend are expected to be similar to that experienced with zirconium waste.

For storage considerations, the calcine resulting from the Rover blends is slightly different from zirconium calcine. The Rover calcine begins sticking together slightly at $\sim$700^{o}C while straight zirconium calcine does not exhibit this stickiness until approximately 800^{o}C. Based upon the projected bin temperatures for Bin Sets #3 and #4, no problems should occur from storing the Rover calcine in these bins.

V. Conclusions

1. Pure first-cycle Rover waste can not be successfully calcined due to high bed attrition and agglomeration.
2. A one volume first-cycle Rover waste and one volume first-cycle zirconium waste blend successfully calcines to a product with an attrition resistance index of 8.6, a bulk density of 1.26 g/cm^3, and an average product weight/fines weight of 3.67.
3. A one volume first-cycle Rover waste and two volumes first-cycle zirconium waste blend successfully calcines to a product with an attrition resistance index of 10.4, a bulk density of 1.32 g/cm^3, and an average product weight/fines weight of 3.03.
4. The small fragile agglomerates found in the product during 30-cm diameter calciner Runs 59 and 62 should not adversely affect fluidized-bed calcination.
5. The corrosion that occurs during calcination of a one:one or one:two blend of first-cycle Rover and first-cycle zirconium wastes is comparable to that which occurs when calcining first cycle zirconium waste.

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