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CALCINING SODIUM-BEARING WASTE BY BLENDING WITH ZIRCONIUM FLUORIDE WASTE

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ABSTRACT

A flowsheet, which is a method for converting wastes into granular, free flowing solids, was developed for calcining sodium-bearing waste stored at the Idaho Chemical Processing Plant (ICPP). The flowsheet consists of blending sodium-bearing waste with zirconium-fluoride waste so that the calcine product contains as much as 5% sodium; calcium nitrate is added to the blend to give a calcium-to-fluoride mole ratio of 0.7.

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SUMMARY

One of the major wastes stored at the ICPP is sodium-bearing waste. This type of waste is difficult to calcine because the sodium nitrate present causes fluidized-bed agglomeration during calcination, and chloride present can cause excessive corrosion of off-gas scrubbing equipment when volatilized from the calciner vessel and collected by the off-gas scrubbing equipment. Blending Sodium (Na) waste with zirconium fluoride waste in a ratio such that the calcine product contains 5.25 or less mole percent sodium, and adding calcium nitrate to the blend to give a calcium-to-fluoride mole ratio of 0.7, prevents fluidized-bed particle agglomeration or excessive corrosion of the off-gas system during calcination of the blend.

The calcined blend produces particles that are very hard (attrition index of 60 to 80%) and that have a high bulk density (1.7 g/cm^3). The hard calcine particles make size control during calcination a problem, and the combination of large particles (due to their hardness) and high bulk density results in difficulty in removing the particles from the calciner vessel of the WCF. This problem was circumvented by alternately calcining the blend until the mass mean particle diameter (MMPD) was greater than 0.6 mm followed by calcining the unblended zirconium (Zr) waste until the particle MMPD was less than 0.6 mm.

The blend containing calcium nitrate contains much less solids than the unblended Zr waste containing calcium nitrate. Thus, plugging in the calciner feed system should be less of a problem when using blended rather than unblended Zr waste. The caking temperature of calcine from the blend containing 5.25 mole percent sodium is 550°C; the caking temperature decreases as the sodium content of the calcine increases.

Solids precipitate from blends of Zr and Na liquid wastes within a short time after the wastes are combined. Most of these blends precipitate solid granules or flakes. Such solids would be difficult to slurry from a waste storage tank. These solids in blends containing calcium nitrate stored for a short time prior to feeding to a calciner present no problem because they are occluded in the calcium fluozirconate and are readily slurried into and through the calciner feed system. It is recommended that blends of Zr and Na wastes not be stored together in waste storage tanks, only in feed makeup tanks if possible.

I. INTRODUCTION

Aqueous radioactive waste at the ICPP is calcined in the WCF. The WCF and the New Waste Calcining Facility (NWCF) under construction are fluidized-bed calciners heated by in-bed combustion, operating at a calcination temperature of 500°C. The resulting calcine is suitable for storage as granular solids.

These facilities will be used to calcine sodium-bearing wastes. Three, 1135 m^3 (300 000 gal), storage tanks at the ICPP are currently filled with intermediate-level radioactive, sodium-bearing wastes, and a fourth tank is being filled. Na wastes include aqueous radioactive wastes from the second- and third-cycle extraction processes, several chemical laboratories, the hot pilot-plant, the multicurie cell, the remote analytical facility, the decontamination facility, the fuel storage basin, waste cell floor drains, and process equipment waste. In addition, Na wastes include aqueous radioactive wastes received from other facilities at the Idaho National Engineering Laboratory (INEL). Table 1 shows the composition of the contents in the 3 full tanks.

Na wastes contain 2 constituents, sodium nitrate and chloride, in sufficient concentrations to make calcination of these wastes in a fluidized-bed difficult. Sodium nitrate exists in the molten-undecomposed state over a large temperature range (300 to 850°C); thus, during calcination of wastes containing sodium nitrate, fluidized-bed particles tend to agglomerate over this temperature range. To overcome this problem, substances may be added to wastes to (a) lower the decomposition temperature of sodium nitrate or (b) to combine with the nitrate at a low temperature to form a compound that is stable at, and has a melting point above, the calcination temperature. Similarly, the presence of the Na wastes second principal constituent, chloride, presents certain problems. The presence of 700 to 1600 ppm chloride in a waste may cause excessive corrosion of off-gas equipment during calcination

TABLE 1. COMPOSITION OF SODIUM-BEARING WASTE STORED AT THE ICPP

	Molar Concentration in Tank Number		
Component	WM-180	WM-184	WM-186
H+	1.40	0.14	1.63
Al	0.56	0.59	0.37
Fe	0.011	0.018	0.022
Na	1.59	2.44	1.59
F	0.00065	0.0048	0.0065
NO_3	4.38	4.64	5.02
B	0.0057	0.0046	0.015
Cl	0.032	0.045	0.020 - 0.031
PO_4	0.020	0.028	0.0099
SO_4	0.035	0.00066	0.00061
Hg	0.0050	0.00073	0.0028
K	0.24	0.13	0.23
Mn	0.023	0.0045	0.023

of the waste. The waste must be treated to remove chloride prior to calcination or to retain chloride in the bed during calcination.

When developing a flowsheet for calcination of a waste, a method is usually scoped first by using a differential thermal analyzer (DTA), and then, if the DTA shows the method to be promising, more detailed testing is performed in pilot-plant calciners. However, when developing the flowsheet for blending Na wastes with first-cycle zirconium fluoride wastes, the method was first developed in pilot-plant calciners, and then the DTA was used to determine what reactions were taking place during calcination of the blends. The reason for this reversal in procedure was that blending Na and Zr wastes would be such a convenient method of adding complexing reagents to Na waste to inhibit chloride volatility and decompose or complex sodium nitrate ($NaNO_3$) to prevent bed agglomeration that this blending had been recommended as a method for calcining Na waste prior to intensive flowsheet development work.[1] While addition of nonradioactive reagents to Na wastes would probably achieve this objective, blending the Na waste with Zr waste would save chemical costs, result in a higher calciner processing rate, and result in a greater volume reduction when the liquid is converted to a solid.

Bed particle agglomeration did not occur when appropriate blends of Zr and Na wastes were calcined in pilot-plants at 400 to 500°C because sodium was complexed as Na_3AlF_6 (the cryolite flowsheet); however, excessive fluoride and chloride volatility from the bed caused excessive corrosion in the off-gas acid scrubber system. Adding calcium nitrate ($Ca(NO_3)_2$) to the blends prior to calcination sufficiently suppressed fluoride and chloride volatility from the bed during calcination to prevent excessive corrosion to acid scrubbing equipment. Flowsheets tried in the WCF during its seventh processing campaign, using 3-1/2 or greater volumes of Zr waste blended with 1 vol Na waste containing $Ca(NO_3)_2$ resulted in calcine solids that were difficult to remove from the calciner vessel and in possible buildup of excessive chloride in the off-gas scrubbing system. During its eighth processing campaign, the WCF calcined 122 m^3 (32 200 gal) of Na waste using a blend of 3-1/2 vol Zr waste and 1 vol Na waste containing $Ca(NO_3)_2$. Between the unsuccessful and successful calcinations of Na waste in the WCF (a) WCF operating techniques were modified to allow for successful removal of Na containing calcined solids from the calciner vessel (b) the maximum chloride concentration allowed in the solution of the off-gas acid scrubber was increased from 500 to 2600 ppm because an investigation showed that this solution must contain greater than 2600 ppm chloride before the scrubber would become excessively corroded,[2] and (c) more pilot-plant work was conducted to develop a calcination flowsheet for Na waste based on blending the waste with Zr waste and using $Ca(NO_3)_2$ to suppress fluoride and chloride volatility.

This report covers in detail the pilot-plant work performed to develop a flowsheet for calcining Na waste based on blends of Zr and Na wastes carried out during the period between the unsuccessful and successful calcinations of the blends in the WCF. Work carried out prior to that time in developing a calcination flowsheet for studying blends of Zr and Na wastes as a method for calcining Na wastes is summarized in this report.

II. EXPERIMENTAL EQUIPMENT AND PROCEDURES

Schematic diagrams and brief descriptions of the 10- and 30-cm-diameter calciners used to develop a calcination flowsheet for Na wastes based on blending the wastes with Zr wastes are presented in the appendix of ICP-1163, *Calcination Flowsheet Development*.[3] During the early work on the cryolite flowsheet, electric heaters were used to heat the 10- and 30-cm calciners rather than in-bed combustion.

Ten-Centimeter-Diameter Calciner Studies

Runs SBW4-8, -9, -10, -11, -12, and -13

These runs were made to study what effect varying the proportion of Na waste in the blend (using sufficient $Ca(NO_3)_2$ to give a Ca/F mole ratio of 0.7) has on calciner operability, calcine properties, fluoride volatility, and chloride volatility. The calciner's fluidized-bed was heated, with kerosene as the fuel, by in-bed combustion; a propane torch was used to raise the temperature inside the calciner above the autoignition temperature of a kerosene-oxygen mixture. The calcination temperature was 500°C.

Off-gas leaving the 10-cm-diameter calciner passed through in the following order: a primary cyclone to remove fines, a venturi scrubber (using 1-4M nitric acid) for further fines removal, a secondary cyclone, and finally a water-cooled condenser. About 3% of the total off gas was pulled through a caustic scrubber at a point between the secondary cyclone and condenser. Acid scrub was recycled to calciner feed at 15% of the gross feed rate. Samples of calcine product, calcine fines, caustic scrub, and acid scrub were taken every 8 hours. Some samples of each type were analyzed for some of their constituents. Calcine generated from Zr-Na wastes blends calcined at 500°C were combined from several different 10-cm-diameter calciner runs for use as starting beds; the starting beds used in all runs were not produced from the same calciner runs. The mass mean particle diameter (MMPD), and bulk density were determined for the calcine product every 8 hours. MMPD, bulk density, and attrition index (a measurement of particle hardness) were determined for the initial and final beds. Photographs were taken of magnified particles of the final bed produced during calcination of the blend. Bulk densities were determined for the fines every 8 hours, and weights of product and fines were noted at various times during each run.

Six 40 hour runs were made to test calcination of feed having Zr to Na wastes blend ratios of 2, 3, 4, 4-1/2, 6, and 8. Solid $Ca(NO_3)_2$ was added to all blends prior to calcination to give a Ca/F mole ratio of 0.7. Typical compositions of the Zr and Na wastes used are shown in Table 2. This Na waste is also typical of that used in 30-cm-diameter calciner Run 67 (described subsequently) and in much of the Zr-Na wastes blends work done prior to the seventh processing campaign of the WCF. The Zr waste used is typical of that stored in tank WM-185 calcined in the WCF during its eighth campaign.

TABLE 2. COMPOSITION OF SIMULATED FIRST-CYCLE ZIRCONIUM WASTE AND SODIUM-BEARING WASTE USED IN 10- AND 30-CM CALCINER RUNS (MOLARITY)

Constituent	First-Cycle Zirconium Fluoride Waste		Sodium-Bearing Waste
	WM-182 Waste	WM-185 Waste	
Zr	0.38	0.44	--
Al	0.64	0.68	0.51
H^+	1.4	1.5	1.2
B	0.16	0.20	0.008
Na	--	--	1.8
K	--	--	0.20
Mn	--	--	0.017
Hg	--	--	0.003
Fe	0.007	0.005	0.017
NO_3	2.3	2.4	4.9
F	2.5	3.2	--
Cl	--	--	0.036
PO_4	--	--	0.019
SO_4	--	--	0.06

Calcine particle size was controlled by varying the feed nozzle air ratio (NAR). Runs were started with a high NAR (1000) and the NAR was adjusted downward if the MMPD decreased below 0.45 mm. All runs were terminated voluntarily after 40 hours; excessive fluidized-bed particle agglomeration did not take place during any of the runs. Appendix A summarizes operating conditions, fluidized-bed characteristics, properties of calcined solids, and the fluoride and chloride volatility behavior of these runs.

Runs SBW4-1 and -2

These 14-hour long runs were made to test if blends having a low blend ratio of Zr to Na wastes (1 to 1 and 2 to 1) could be successfully calcined at 500°C if they contained an abnormally high Ca/F mole ratio of 1.0. Except for sampling techniques and the short duration of the runs, calciner operation was similar to that described in the previous section. Properties of the fluidized-bed and solids generated were observed at the beginning and end of the runs. Off-gas, feed, calcine, or fines were not sampled for chemical content. Calcination of the 1 to 1 blend produced dry fines; calcination of the 2 to 1 blend produced wet fines.

Thirty-Centimeter-Diameter Calciner Study (Run 67)

A 30-cm-diameter, fluidized-bed, in-bed combustion calciner was used to calcine 2 blends (a 3 vol Zr-1 vol Na wastes blend for 40 hours, then a 5 vol Zr-1 vol Na wastes blend for 72 hours) to show the desireability of a flowsheet consisting of Zr to Na wastes blend ratios ranging between 3 and 5 for testing in the WCF. The calcination temperature was 500°C; kerosene was the fuel; and a propane torch was used to raise the temperature inside the calciner above the autoignition temperature of the kerosene-oxygen mixture.

Off gas leaving the 30-cm diameter calciner passed through: a primary cyclone, a quench tower, a venturi scrubber (using 1-4M nitric acid), a knock-out pot, and a condenser, in that order. About 0.2% of the total off gas was pulled through a caustic scrubber at a point between the knock-out pot and the condenser. Scrubbing solution was recycled to calciner feed at a rate of approximately 15% of the gross feed rate. The product, fines, and acid scrub were sampled at 8-hour intervals; each batch of feed was sampled after calcium nitrate addition; the caustic scrub was sampled at cumulative operating time (COT) of 36, 52, 68, and 100 hours after passing off-gas through it for 8 hours. Some samples of each type were analyzed for some of their constituents. Calcine generated from the calcination of Zr waste at 500°C was used for a starting bed. The MMPD and bulk density were measured every 8 hours and the attrition index was measured every 16 hours on calcine product; fines bulk density was measured every 8 hours. Photographs were taken of magnified particles of product at COT 32, 50, 60, and 88 hours; and weights of product and fines were determined at various times.

The run was voluntarily terminated after 112 hours. Very little bed agglomeration had occurred during the run; the final bed weighed 74.2 kg and contained 0.59 kg of material greater than 14 mesh in size and 0.301 kg of material greater than 1/2 in. in size. Na waste composition typical of that used in Run 67 to make blends is shown in Table 2; the Zr waste of the blends is typical of that stored in WM-182 calcined during the eighth processing campaign of the WCF (see Table 2). Operating conditions, fluidized-bed characteristics, and properties of solids generated, analyses of samples taken, and temperature and pressure data for Run 67 are given in Appendices B, C, D, and E.

During the run, corrosion coupons of type 304L stainless steel were present in the off-gas line in the following positions: the inlet and outlet of the condenser, the quench tower, and the bottom and top of the knock-out pot. A coupon was also located in the acid scrub tank exit. Corrosion rates on all coupons were less than or 1 micrometer/month (0.04 mils/month). The coupon located in the top of the knock-out pot exhibited general weld decay; other coupons exhibited light general attack.

DTA and X-Ray Evaluations

Differential thermal analysis (DTA) combined with X-ray diffraction results were used to study the calcination chemistry of Zr-Na wastes blends. The equipment and techniques used in such a study are described in ICP-1084.[4] Simulated wastes were evaporated to dryness at 80°C before examination by DTA. DTA examination of the dried wastes gave temperature ranges over which different reactions occur. Separate dried samples were heated below and above the temperatures at which a given reaction occurred and were then analyzed by X-ray diffraction to determine the specific change(s) that took place. The results of these studies are given in calcination chemistry in the section on calcination of blends of zirconium and sodium wastes with calcium nitrate.

III. CALCINATION OF BLENDS OF ZIRCONIUM AND SODIUM WASTES WITHOUT CALCIUM NITRATE (CRYOLITE FLOWSHEET)

Calcination Chemistry

When the appropriate blends of Zr and Na wastes are calcined at 500°C, the sodium nitrate in the blend is converted to cryolite according to the equation:

$$6\,NaNO_3 + 2\,AlF_3 + 6\,HF \rightarrow 2\,Na_3AlF_6(\text{cryolite}) + 6\,NO + 3\,H_2O + 9/2\,O_2.$$

The cryolite is thermally stable to temperatures above 965°C. At a calcination temperature of 500°C in these blends, enough of the sodium nitrate has been decomposed to form cryolite so that the molten, undecomposed sodium nitrate is not present in concentrations sufficient to agglomerate enough particles to prevent successful fluidized-bed operations.

Pilot-Plant Flowsheet Development

Early runs[5] using pilot-plant, fluidized-bed calciners heated by bayonet type electric heaters inserted in the bed showed that blends of Zr and Na wastes containing a fluoride-to-sodium (F/Na) mole ratio greater than 1 could be calcined at 500°C without agglomeration if, prior to calcination, the blends contained 4.3 g of sugar (sucrose) per g of sodium present. Sodium nitrate is decomposed by reducing reagents, which, with the exception of weak reducing reagents such as sugar, would not remain in the oxidizing atmosphere of a calciner long enough to be effective. The same blends could not be calcined at 400°C without sugar present because caking of the calcined waste on the heaters caused the heaters to burn out. Calcining these blends caused a high generation of fines. Later runs[6], in fluidized-bed, pilot-plant calciners using in-bed combustion to heat the bed showed that blends of Na and Zr wastes could be successfully calcined at 500°C without sugar. Aluminum and fluoride were present in the blends in about 10% excess over that required for Na_3AlF_6 formation.

At first, corrosion in the off-gas acid scrubber system was unacceptably high during calcination of Na-Zr wastes blends. This was thought to be caused by the preferential dissolution of Na_3AlF_6 rather than Al_2O_3 and ZrO_2 in the nitric acid scrub solution, thereby creating a large excess of fluoride. This corrosion was controlled by adding aluminum nitrate to the scrub solution to provide enough Al^{+3} ions in solution to adequately complex the fluoride released from the Na_3AlF_6 dissolution. However, high aluminum concentrations in the acid scrub (0.3 to 0.9<u>M</u>) caused off-gas system plugging due to $AlF_3 \cdot XH_2O$ formation.

Calcine product produced during the calcination of blends of Na and Zr waste at 500°C was very soft, having an attrition index of about 3%. The product attrition index was increased to 58% by the presence of about 0.12<u>M</u> boron in the blends.

Compatibility studies between various startup beds and blends of Na and Zr wastes indicated that severe agglomeration of bed particles occurred when a ZrO_2-CaF_2 startup bed was used. This problem was caused by high sulfate concentrations in the blend (0.11 to 0.14<u>M</u>). An analyses of Na wastes stored at ICPP indicated that some of these wastes could be as high as 0.2<u>M</u> in sulfate ion. The agglomeration problem did not occur when an Al_2O_3 startup bed was used during calcination of a Zr-Na wastes blend with high sulfate concentration at 500°C.

Blends of Zr and Na wastes contain 500 to 800 ppm chloride ions. The chloride concentration in the off-gas acid scrubber solution quickly exceeded the 500 ppm maximum chloride limit placed on the solution, to prevent excessive corrosion, when blends of Zr and Na wastes were calcined at 500°C. There appeared to be no effective method to eliminate the chloride volatility problem other than to remove chloride from the waste prior to calcination. No more work was done on the cryolite flowsheet after it was learned that chloride volatility from a fluidized-bed during calcination of blends of Zr and Na wastes at 500°C could be suppressed by adding calcium nitrate to the blends prior to calcination.

IV. CALCINATION OF BLENDS OF ZIRCONIUM AND SODIUM WASTES WITH CALCIUM NITRATE

A new process was developed which allowed the chloride and fluoride in a blend of Zr and Na wastes to be retained in solid calcine as a non-volatile species. The process involved blending 1 vol of Na waste (composition shown in Table 2) with 3 vol of Zr waste (same composition as WM-185 waste in Table 2), and adding 1/2 mole of $Ca(NO_3)_2$ per mole of fluoride in the waste blend prior to calcination at 500°C. Fluidized-bed particle agglomeration was still a problem with this process.

The calcine particles contained nodules which prevented quality fluidization. The nodules were almost eliminated by adding 0.7 moles of $Ca(NO_3)_2$ per mole of fluoride in the blend. This improved process was used at the WCF during the seventh processing campaign to calcine 8.6 m^3 (2275 gal) of Na waste. Use of this process in the WCF resulted in difficulty in removing calcine solids from the calciner vessel due to higher particle density and in possible release of excessive chloride to the off-gas scrubbing system.

Additional pilot-plant calciner studies determined how the blend ratio affected calciner operability, properties of calcined solids, and fluoride and chloride volatility. Corrosion studies showed that 2600 ppm chloride could be present in the off-gas scrubber solution before excessive corrosion begins.[2] Early in the eighth processing campaign of the WCF, it was realized that increasing the degree of fluidization by increasing the fluidizing velocity made it possible to remove solids from the calciner vessel. The WCF calcined 122 m^3 (32 200 gal) of Na waste during its eighth processing campaign as a blend of 3-1/2 vol Zr waste with 1 vol Na waste.

Calcination Chemistry

X-ray diffraction examinations of solids produced from the calcination of blends of Zr and Na wastes containing $Ca(NO_3)_2$ in pilot-plant calciner and DTA studies show the presence of CaF_2 and ZrO_2 but not the presence of cryolite. Calcium fluozirconate ($CaZrF_6 \cdot 2H_2O$) is formed when $Ca(NO_3)_2$ is added to blends of Zr and Na wastes. At least some of the CaF_2 and ZrO_2 found in solids from the calcination of Zr-Na wastes blends containing $Ca(NO_3)_2$ are present because of the decomposition of calcium fluozirconate at 500°C. Although no sodium compound(s) (other than a small amount of sodium nitrate) has been found during the examination of calcined solids by X-ray methods, it is assumed that the sodium is complexed as cryolite. Fluoride is probably retained in calcined solids as CaF_2.

It is not known why chloride is retained in calcined solids. There is evidence that chloride retention in calcine solids during calcination of blends, of Zr and Na wastes containing $Ca(NO_3)_2$ at 500°C is increased by one or more of the following (a) increase of the calcium concentration of the blends (b) increase of the aluminum-to-fluoride mole ratio of the blend, and (c) increase of the sodium concentration of the blend.[7] Essentially all the mercury present in a blend containing $Ca(NO_3)_2$ is volatilized from the bed during calcination at 500°C. The volatile mercury species has not been identified.

Pilot-Plant Flowsheet Development Prior to WCF Seventh Processing Campaign

The 10- and 30-cm, pilot-plant calciner runs used to develop a flowsheet for calcining a blend of Zr and Na wastes containing $Ca(NO_3)_2$ for the WCF during the seventh processing campaign are summarized in Table 3.[8] The Na waste used in these runs was similar in composition to that shown in Table 2; the Zr waste was similar to the WM-185 waste shown in Table 2. The Zr waste to Na waste blend ratio that would result in a maximum Na waste calcination rate in the WCF while retaining acceptable calciner operability and properties of calciner solids seemed to be 3 vol Zr waste to 1 vol Na waste.

TABLE 3. PILOT-PLANT RUNS USING BLENDS OF Zr AND Na WASTES AS FEED, 1972 to 1975

Run Number	Duration (Hours)	Objective 10-cm Calciner Runs	Comments
SC4-1a 1b 1c 1d	7 20 20 40	Scoping runs using blends of 3 and 5 vol Zr - 1 vol Na wastes, Ca/F mole ratio of 0.5, with and without $AgNO_3$	$AgNO_3$ not effective in suppressing Cl volatility
SC4-2	2	Blend of 1 vol Zr - 1 vol Na wastes with Ca/F mole ratio of 0.5 and $AgNO_3$	Clinker formation
SC4-3a 3b	19 19	Blend of 2 vol Zr - 1 vol Na wastes with Ca/F moles ratios of 0.5 and 0.25 using $AgNO_3$	Agglomerates Agglomerates
SC4-4 SC4-5	7 19	Blend of 3 vol Zr - 1 vol Na wastes, Ca/F mole ratio of 0.5 at 400°C	No notes Chloride volatilization
SC4-6 SC4-9	20 72	Blend of 3 vol Zr - 1 vol Na wastes, Ca/F mole ratio of 0.5 at 500°C	No notes Large noduled particles
SC4-7	10	Blend of 3 vol Zr - 1 vol Na wastes, Ca/F mole ratio of 0.5 at 450°C	Chloride volatilization
SC4-8	10	Blend of 3 vol Zr - 1 vol Na wastes, Ca/F mole ratio of 0.5 at 550°C	Chloride volatilization
SC4-10	20	Blend of 2.5 vol Zr - 1 vol Na wastes, Ca/F mole ratio of 0.5	Clinker formation
SC4-11	39	Blend of 3.5 vol Zr - 1 vol Na wastes, Ca/F mole ratio of 0.5	Agglomerates
SC4-12	80	Blend of 5 vol Zr - 1 vol Na wastes, Ca/F mole ratio of 0.7	No nodules on particles
SC4-13	8	Removing nodules from calcined blended waste particles by using unblended waste as feed	Successful
SC4-15	44	Blend of 3 vol Zr - 1 vol Na wastes, Ca/F mole ratio of 0.7	No nodules on particles
SC4-16	52	Blend of 3 vol Zr - 1 vol Na wastes, Ca/F mole ratio of 0.6	No nodules on particles

TABLE 3. (continued)

Run Number	Duration (Hours)	Objective	Comments
		10-cm Calciner Runs	
SC4-17	40	Blend of 3 vol Zr - 1 vol Na wastes, Ca/F mole ratio of 0.5	No nodules on particles
SC4-18	34		Nodules on particles
		30-cm Calciner Runs	
Run 49	90	Blend of 3 vol Zr - 1 vol Na wastes, Ca/F mole ratio of 0.5	Large noduled particles, clinker
Run 50	70	Blend of 4 vol Zr - 1 vol Na wastes, Ca/F mole ratio of 0.5	Large noduled particles, clinker
Run 52	140	Blend of 3 vol Zr - 1 vol Na wastes alternated with unblended Zr waste	Low Na waste depletion
Run 53	130	Blend of 3 vol Zr - 1 vol Na wastes, Ca/F mole ratio of 0.7	Particle size control problems

A Ca/F mole ratio in the blend of between 0.5 and 0.7 seemed to suppress chloride and fluoride volatility from the bed to an acceptable degree. Type 304L stainless steel coupons in off-gas lines and equipment during 30-cm calciner runs showed corrosion rates no greater than 25 micrometers/month (1 mil/month). There were no off-gas lines or equipment failures due to excessive corrosion. Nitric acid (1-4$\underline{M}$) was acceptable for use in the off-gas scrubber (no complexing agent had to be added to prevent excessive fluoride corrosion). Chloride retention in calcined solids (bed plus product plus fines) varied between 50 and 70% of that fed to the calciner. With these retentions, the chloride concentration in the acid scrub solution remained below 500 ppm and was not predicted to accumulate above that value during long-term operation, provided the acid scrub solution was recycled to the calciner feed at a rate equal to 15% of the gross calciner feed rate. Chloride retention in calcined solids was independent of calciner temperature between 400 and 550°C. Chloride retention in calcined solids was not increased by adding silver nitrate to the blend containing $Ca(NO_3)_2$.

Calcination of blends containing a Ca/F mole ratio of 0.5 at 500°C produced noduled calcine particles. Prolonged fluidization with noduled particles produces clinkers and agglomerates in the calciner vessel because these particles are not well fluidized. Calcination of blends of 3 vol or greater Zr waste and 1 vol Na waste containing a Ca/F mole ratio of 0.6 or 0.7 at 500°C does not produce noduled particles. It was difficult to control the size of particles produced by the calcination of a blend of 3 to 5 vol Zr waste and 1 vol Na waste containing Ca/F mole ratios 0.5 to 0.7 because product particles produced were so hard (attrition index of 60 to 90%).

During prolonged calcination of a blend of 3 vol Zr waste and 1 vol Na waste with a Ca/F mole ratio of 0.7 at 500°C in a 30-cm calciner, particle size had to be reduced by jet grinding. Calcine product produced by the above process had a high bulk density (1.8 g/cm^3). Fines produced from the process were soluble in nitric acid. The product bed material was so resistant to attrition that relatively few fines were produced (product-to-fines weight ratios of 2.4 or greater were obtained with this process in the 30-cm calciner). An alternate method for reducing nodules on a particle's surface to an acceptable level was to calcine a blend of 3 vol Zr waste and 1 vol Na waste having a Ca/F mole ratio of 0.5 for 30 to 40 hours and then calcine unblended Zr waste (for 8 to 12 hours) to smooth the surface of noduled calcine formed by calcining blended feed; the blended and unblended calciner feed would be alternated indefinitely. This latter method was not actively pursued because its use would result in a low, WCF, Na waste throughput.

The blend flowsheet using $Ca(NO_3)_2$ was tested in the WCF during its seventh processing campaign. The Na waste used was from tank WM-180 (Table 1); the Zr waste used was from tank WM-185 (Table 2). The test was to begin by calcining a blend of 4 vol Zr waste and 1 vol Na waste using a Ca/F mole ratio of 0.7; as the test progressed satisfactorily, the blend ratio would be lowered to 3. Actually the test in the WCF began with a blend ratio higher than 4 and was terminated before the blend ratio was reduced to 3-1/2. The test was terminated when the chloride concentration in the off-gas acid scrub solution became greater than 500 ppm. During the test there was difficulty in removing calcine product from the calciner vessel. Chloride values for the off-gas acid scrub solution during the seventh processing campaign of the WCF and for prior campaigns are suspect. Analyzing acid scrub solution requires that chloride first be volatilized from the solution. It was not realized that the presence of mercury in acid scrub solution (usually present during calcination of Zr waste and blends of Zr and Na wastes) inhibited the volatilization of chloride from the solution until mercury began to be added to calciner feed during the pilot-plant studies to be described subsequently. Mercury had not been added to calcium feed in the pilot-plant studies previously described. In the procedure currently used for determining chloride in various solutions, mercury is complexed so that it will not inhibit chloride volatility.

Flowsheet Development After the WCF Seventh Processing Campaign

Further pilot-plant calciner testing was required to better define operating parameters related to particle size control and chloride volatility. Two 14-hour, 10-cm calciner runs, six 40-hour, 10-cm calciner runs, and one 112-hour, 30-cm calciner run were made to study what effect varying the Zr to Na wastes blend ratio (using sufficient $Ca(NO_3)_2$ to give a Ca/F mole ratio of 1.0 in the 14-hour runs, and 0.7 in the other runs) has on calciner operability, calcine properties, fluoride volatility, and chloride volatility. Zirconium-to-sodium waste blend ratios of from 1 to 8 were studied. Sodium waste with a composition typical of that shown in Table 2 was used; the 10-cm calciner studies used Zr waste similar to WM-185 waste of Table 2, and the 30-cm calciner study used Zr waste similar to WM-182 waste of Table 2.

Fluidized-Bed Operation and Properties of Solids Generated

Agglomeration did not occur in any of the 10- and 30-cm calciner runs to an extent that forced the calciner shutdown prior to the scheduled shutdown time. There were the normal amounts of agglomerates at the end of each run inside the calciner and adhered to calciner surfaces, nozzles, the propane torch, and thermocouple sheaths. During the 40- hour runs in the 10-cm calciner studying Zr to Na wastes blend ratios of 2 to 1, 6 to 1, and 8 to 1, the fines produced were damp; during 40-hour runs in the 10-cm calciner for studying blend ratios of 3 to 1, 4 to 1, and 4-1/2 to 1, fines produced were dry.

In the former runs, off-gas lines and equipment plugging problems were greater than normal for operation in the 10-cm calciner; in the latter runs and in the 30-cm calciner run these plugging problems were less than normal for the calciners involved. Producing damp fines was considered an equipment problem, not a flowsheet problem. The quantity of particles larger than 14 mesh in the final beds of calciner runs was used to indicate the tendency of a given feed to agglomerate during calcination. There seemed to be no trend between the amount of larger than 14 mesh agglomerated particles formed in the final bed and the Zr to Na wastes blend ratio; also agglomerate formation seemed to be unrelated to whether unblended Zr waste or a blend of Zr and Na wastes were calcined (Figure 1).

An advantage in calcining a blend over calcining unblended Zr waste is that the amount of undissolved solids in a blend is much less than in

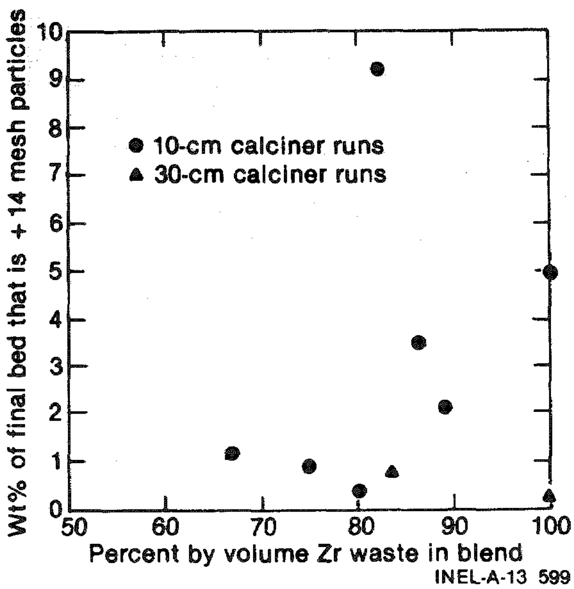

Figure 1. Tendency to form agglomerates during calcination of Zr and Na waste blends using $Ca(NO_3)_2$.

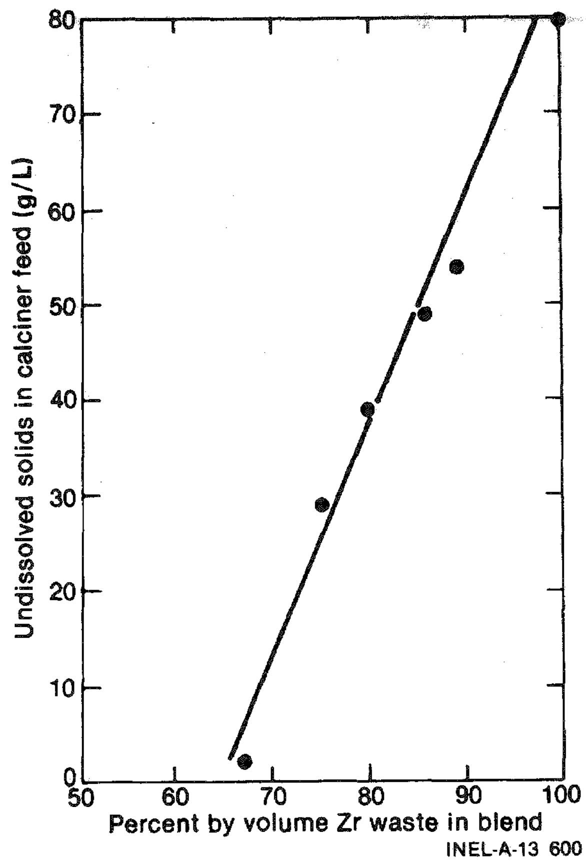

Figure 2. Relationship of undissolved solids in feed to the Zr to Na waste blend ratio.

the unblended Zr waste when $Ca(NO_3)_2$ is added (Figure 2). Also the amount of undissolved solids in calciner feed decreases as the proportion of Na waste in the blend increases (Figure 2). Since the plugging problems in the feed system of a calciner are related to quantity of undissolved solids in the feed, plugging problems in the feed system of a calciner are common when calcining Zr waste but limited when calcining a blend of Zr and Na waste.

Fluidized-bed operation and properties of solids generated for the 10-cm calciner runs are tabulated in Appendix A. Operation conditions for the 30-cm calciner run are tabulated in Appendix B and E, and properties of the fluidized-bed and solids generated are tabulated in Appendix C. Surfaces of calcine particles produced from the calcination at 500°C of a blend of 1 vol Zr waste and 1 vol Na waste containing a Ca/F mole ratio of 1.0 contained numerous nodules. Surfaces of calcine particles produced from the calcination at 500°C of a blend of 2 vol Zr waste and 1 vol Na waste containing a Ca/F mole ratio of 1.0 and blends of 2 to 8 vol Zr waste and 1 vol Na waste containing a Ca/F mole ratio of 0.7 contained only few nodules and were only slightly rougher than surfaces of calcine produced from unblended Zr waste. Figure 3 illustrates (a) calcine containing highly noduled surfaces produced by calcining a blend containing insufficient $Ca(NO_3)_2$ to inhibit nodule formation (b) calcine containing a few nodules (typical of calcine from blends of 2 to 8 vol Zr-1 vol Na waste with a Ca/F mole ratio of 0.7) produced by calcining the same blend with enough $Ca(NO_3)_2$ to inhibit nodule formation, and (c) a type of calcine never experiencing agglomeration due to surface nodules produced by calcining Zr waste.

MMPD was controlled by the waste NAR in 10-cm calciner runs. A high waste NAR (1200) is obtainable in the 10-cm calciner. In each 10-cm calciner run an initial NAR of about 1000 was used; the NAR was decreased if the product MMPD decreased below 0.45 mm, while the NAR was increased if the product MMPD increased above 0.60 mm. In the 30-cm calciner, product MMPD was effectively controlled by a combination of waste NAR and the oxygen-to-fuel ratio (Figure 4). Product MMPD increased from 0.44 to 0.61 mm between COT 36 and 56 hours, waste NAR was increased to greater than 300 and the oxygen-to-fuel ratio to greater than 2000 at COT 52 hours, and the MMPD began to decrease after a 4 hour time lag. At a COT of 100 hours, the oxygen-to-fuel ratio was purposely decreased from about 2300 to less than 1950 while attempting to keep the waste NAR constant; the product MMPD increased after an 8 hour time lag.

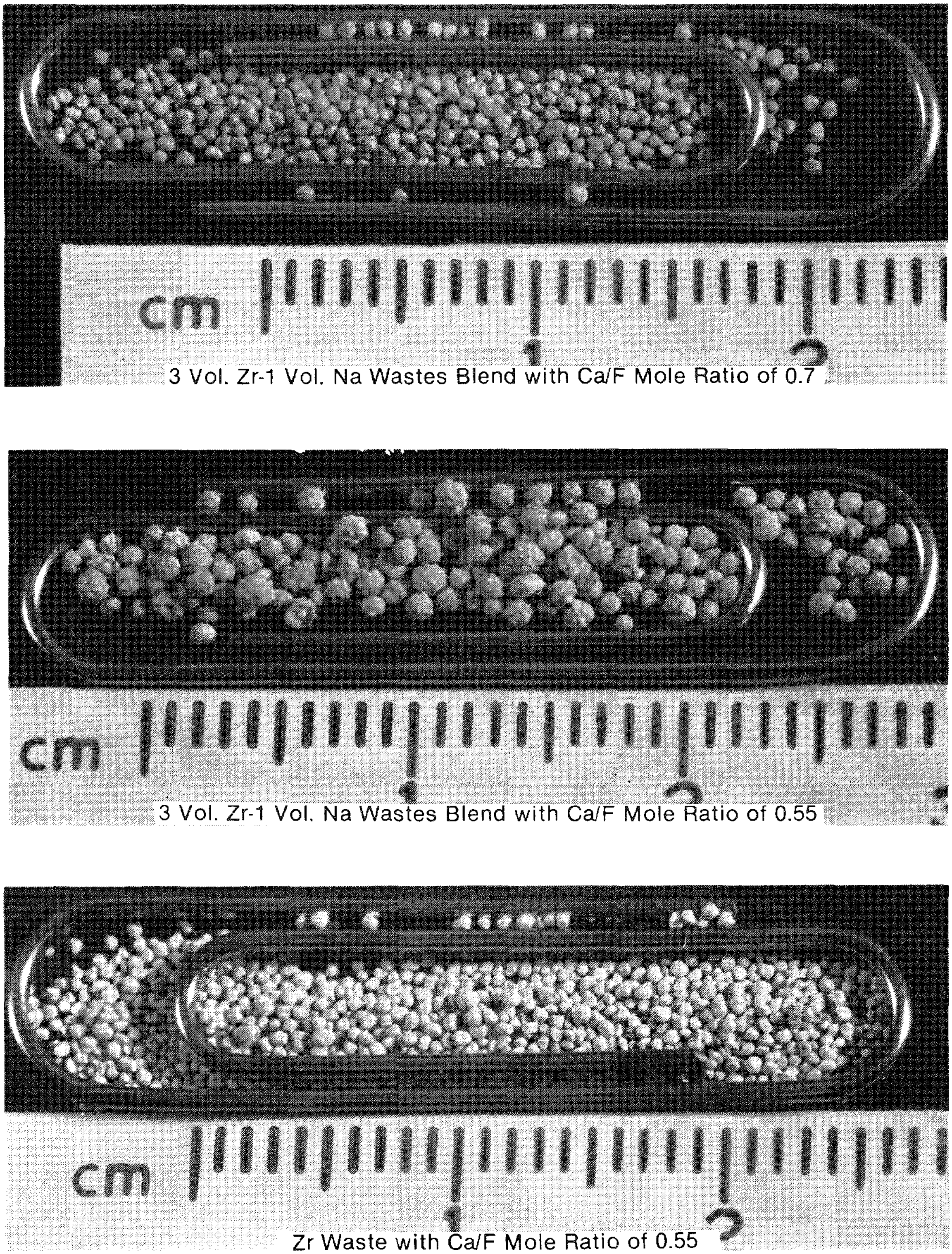

Figure 3. Magnified calcine particles with and without nodules.

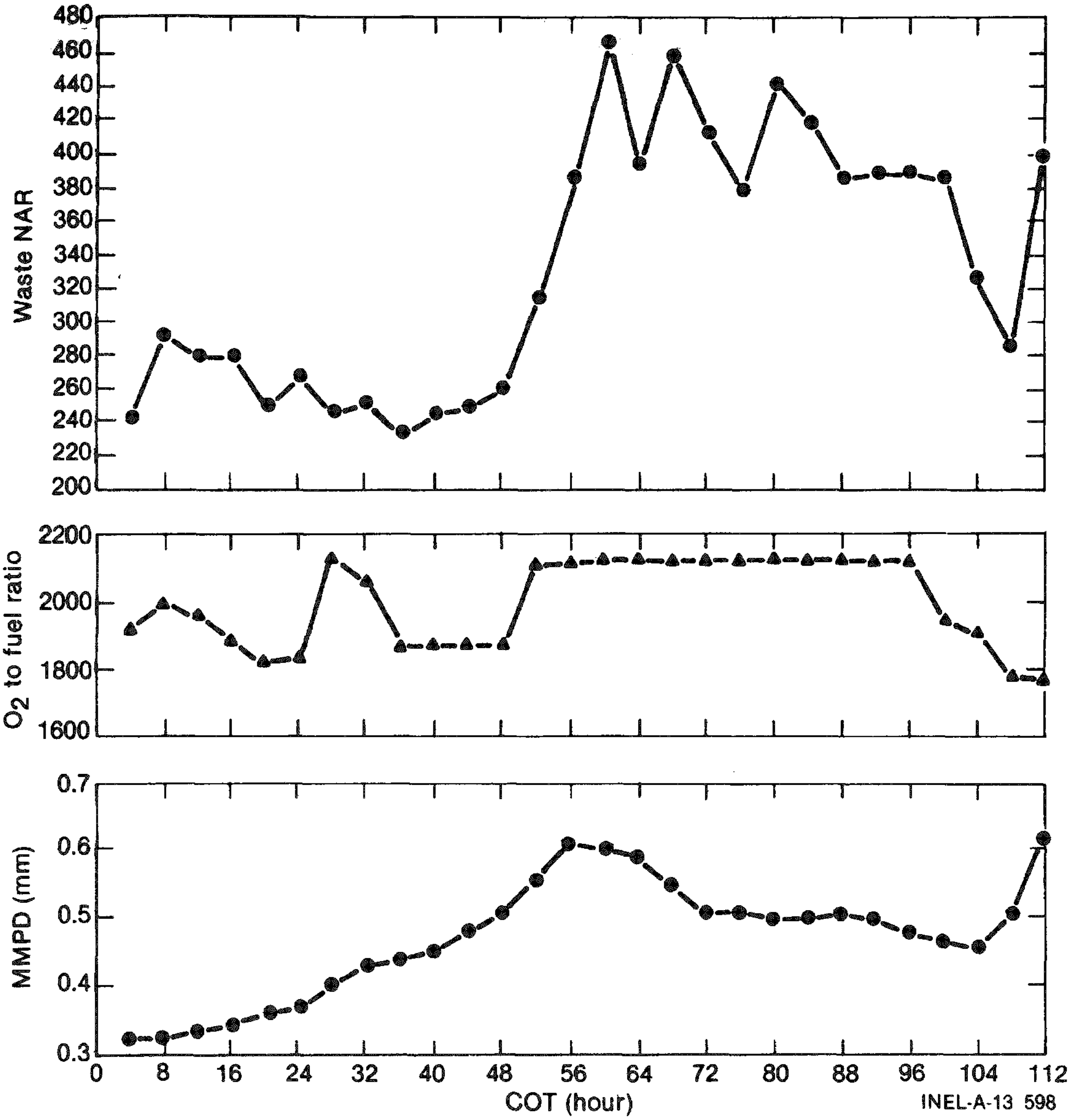

Figure 4. Control of MMPD using waste NAR and O_2 to fuel ratio in the 30-cm calciner.

Roughly, attrition index of calcine produced increased as the proportion of Na waste in the blend increased (Figure 5). As one might expect from such a relationship, fines production rate roughly decreased and the product-to-fines ratio roughly increased as the proportion of Na waste in the blend increased. The information from operating the 30-cm calciner 40 hours using a blend of 3 vol Zr waste and 1 vol Na waste is not included in Figure 5 because the calciner was not close enough to equilibrium conditions to give values that would always be truly representative of the 3 to 1 blend. The calcine production rate, calcine bulk density, and possibly the fines bulk density are independent of the proportion of Na waste in the blend (Figure 6).

When calcining the same waste in a 10- and 30-cm calciner, the product produced in the 30-cm calciner has a lower bulk density than does the product produced in the 10-cm calciner. The product bulk densities obtained from the 10-cm calciner compare more closely to the ones obtained in the WCF than do bulk densities obtained from the 30-cm calciner. Calcination of blends of simulated 2 to 8 vol WM-185 (Zr) waste

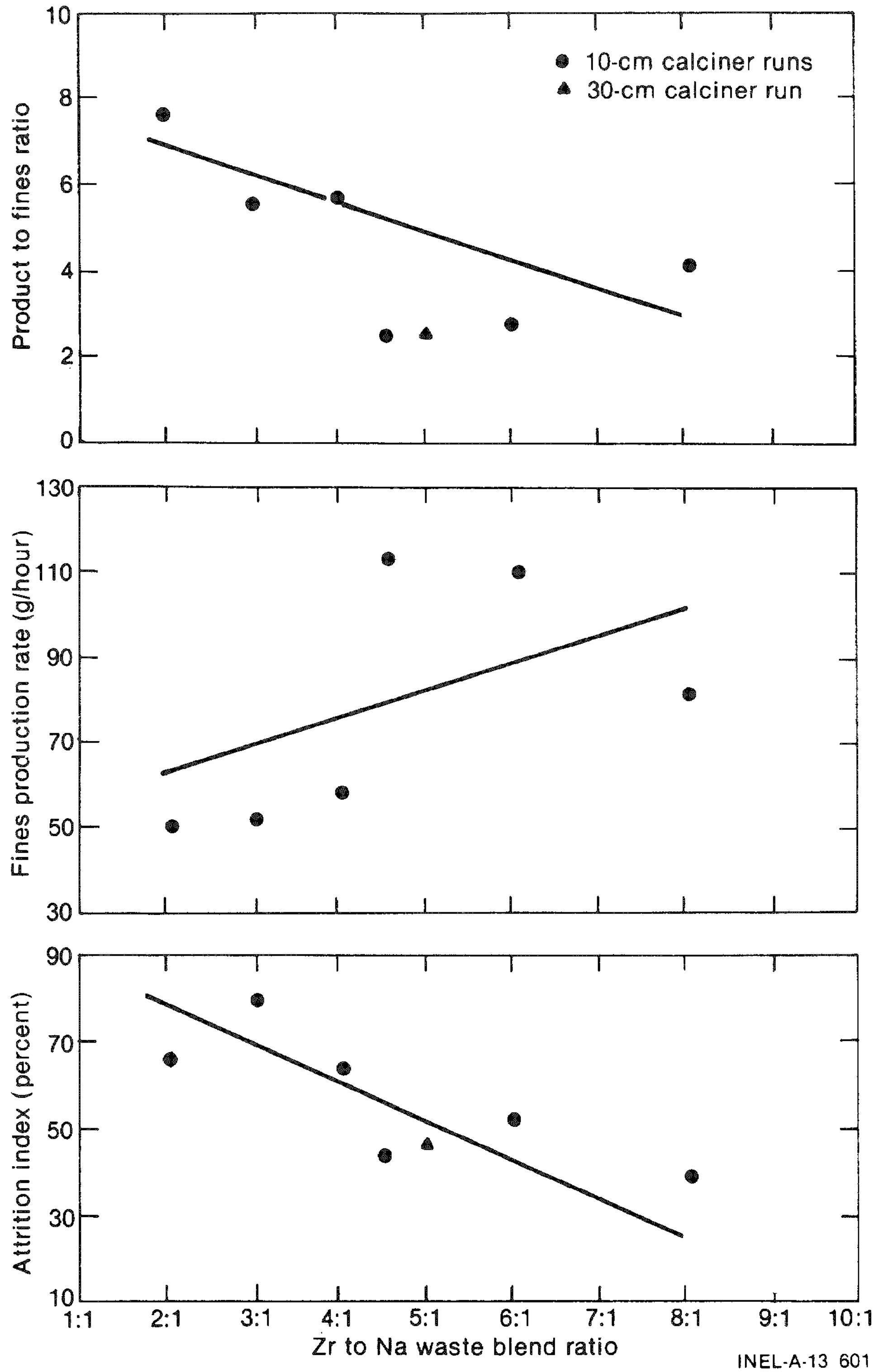

Figure 5. Relationship of particle hardness and fines production to Zr to Na waste blend ratio.

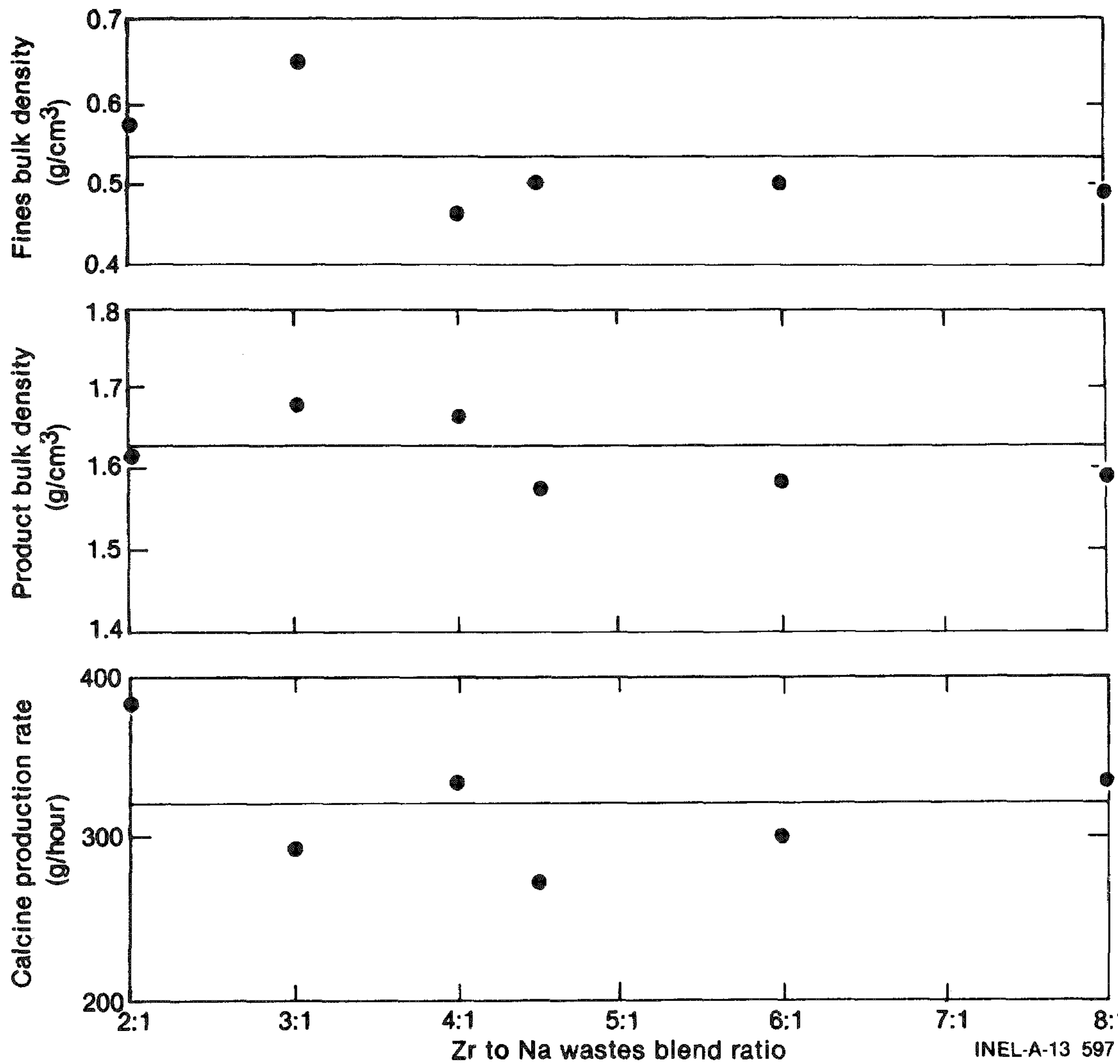

Figure 6. Calcine production and bulk densities as a function of the Zr to Na waste blend ratio using a 10-cm calciner.

and 1 vol WM-180 (Na) waste in the 10-cm calciner at 500°C gave products with bulk densities averaging 1.6 g/cm^3. In the eighth campaign, calcination of a blend of 3-1/2 vol WM-182 (Zr) waste and 1 vol Na waste at 500°C in the WCF gave product with a bulk density of 1.7 g/cm^3. Calcination of a blend of simulated 5 vol WM-182 waste and 1 vol WM-180 waste at 500°C in the 30-cm calciner gave product with a bulk density of 1.3 g/cm^3.

Calcine from the 30-cm (but not from the 10-cm) calciner had a tendency to set up into very fragile agglomerates when allowed to cool without agitation. When these agglomerates were allowed to cool without agitation to 150, 70, or 24°C, they readily broke up when poured once from one bucket to another; once broken up, the calcine did not agglomerate again even when heated for 2-1/2 days at 500°C and allowed to cool to 24°C without agitation.

Behavior of Volatiles

The composition of product, fines, off-gas acid scrub solution, off-gas caustic scrub solution, and feed are summarized in Appendix D for the 30-cm calciner run.

Fluoride Volatility. Fluoride volatility information is summarized in Table 4. In all runs the amount of calcium in all off-gas, acid scrubbing solution samples taken was enough to combine with all the fluoride present in the same samples as CaF_2. Thus, all the fluoride present in the acid

TABLE 4. FLUORIDE BEHAVIOR IN OFF-GAS

Run Number	SBW4-8	SBW4-9	SBW4-10	SBW4-11	SBW4-12	SBW4-13	Run 67	
Zr to Na Wastes blend ratio	4-1/2	3	8	6	2	4	3	5
Ca ($\underline{M}$) in acid scrub[a]	$0.3^{+0.3}_{-0.2}$	0.07 ± 0.04	0.29 ± 0.02	$0.6^{+0.2}_{-0.1}$	$0.39^{+0.15}_{-0.13}$	$0.42^{+0.03}_{-0.02}$	0.12[b]	0.08 ± 0.01
F($\underline{M}$) in acid scrub[a]	$0.5^{+0.3}_{-0.4}$	$0.13^{+0.08}_{-0.06}$	$0.40^{+0.06}_{-0.04}$	$0.8^{+0.2}_{-0.1}$	$0.47^{+0.06}_{-0.10}$	$0.45^{+0.02}_{-0.01}$	0.18[b]	0.11 ± 0.01
Zr($\underline{M}$) in acid scrub[b]	0.13	0.012	0.062	0.19	0.10	0.092	0.019	0.010 ± 0.002[a]
Al($\underline{M}$) in acid scrub[b]	0.34	0.032	0.11	0.28	0.15	0.16	0.050	$0.037^{+0.003}_{-0.007}$[a]
B($\underline{M}$) in acid scrub[b]	0.075	0.072	0.10	0.13	0.034	0.033	0.012	$0.007^{+0.000}_{-0.001}$[a]
percent of F fed to calciner escaping acid scrubber as gaseous fluoride[a]	$0.5^{+0.3}_{-0.2}$	$0.67^{+0.09}_{-0.13}$	$0.20^{+0.06}_{-0.05}$	$0.25^{+0.05}_{-0.04}$	$0.26^{+0.04}_{-0.05}$	$0.25^{+0.03}_{-0.04}$	0.26[b]	$0.41^{+0.09}_{-0.06}$

a. The numbers given represent the average, maximum, and minimum values obtained during a given run.
b. The acid scrub was analyzed only once for these values during a run.

scrub solution had probably been entrained as CaF_2 in fines contained in the off-gas. Also in all runs there was always enough zirconium, aluminum, and boron present in the acid scrubbing solution samples to complex the fluoride present and thus prevent excessive fluoride corrosion to the acid scrubber equipment.

The amount of volatile fluoride escaping the acid scrubber seemed to be independent of the proportion of Na waste in the blend. The amount of volatile fluoride escaping the acid scrubber in the various 10- and 30-cm calciner runs varied between 0.15 and 0.81% of the fluoride fed to the calciner. In general, there was no increase in fluoride concentration in the acid scrubbing solution as a run progressed.

Chloride Volatility. Chloride retention in calcine solids (product plus bed plus fines) was excellent (90%) in all 10-cm calciner runs and was slightly less (68%) in the 30-cm calciner run (see Table 5). Although solids chloride retention of the 30-cm calciner run was less than in the 10-cm calciner runs, it was almost identical to the solids chloride retention observed in the 30-cm calciner Run 53 (70%) during which a blend of 3 vol Zr and 1 vol Na wastes having a Ca/F mole ratio of 0.7 was calcined at 500°C.[9] Chloride retention in calcine solids seemed to be independent of the proportion of Na waste in the blend (Table 5), and more chloride was retained in the product than in the fines. In general, chloride concentration in the off-gas acid scrub solution did not buildup as the run progressed and remained below 500 ppm. Studies using calcium or magnesium nitrate to suppress chloride and fluoride volatility during calcination of Zr-Na wastes blends in a 10-cm diameter calciner indicated chloride retention in calcine solids increases as the aluminum to fluoride mole ratio of the feed increases.[10] This did not seem to be the case in the runs described in this report. Perhaps some other calciner feed characteristic is contributing to the excellent retention of chloride in calcine solids, such as the high Ca/F mole ratio (0.7) in blends having low Na concentration or the presence of sodium itself.

Mercury Volatility. Mercury behavior during calcination of Zr-Na wastes blends containing $Ca(NO_3)_2$ at 500°C was observed for the 30-cm calciner run, but not for the 10-cm calciner runs. Less than 0.1% of the mercury fed to the calciner was found in calcine solids (bed plus product plus fines). The mercury material balance was poor, varying between 26 and 55% (averaging 40%). It was thought that the poor mercury material balance was caused by basing the amount of mercury escaping the off-gas acid scrubber on the amount of mercury found in the 6M sodium hydroxide, a poor absorber of mercury, contained in the caustic scrubber. However, the mercury found in a 12M hydrochloric acid scrubber (which should be a good mercury absorber) placed in series with the caustic scrubber during an 8 hour operating period would have improved the average mercury material balance from a value of 40% of the mercury accounted for to a value of 60% based on information obtained during a 30-cm calciner run completed several months later.

Caking Temperatures

Calcine stored in storage bins heated by fission-product decay becomes difficult to remove from the bins when the temperature of the calcine rises above a given value (caking temperature) dependent upon the waste used to make calcine. It is imperative that the temperature of calcine stored in a bin not rise above the caking temperature if the calcine is to be retrieved.

The calcine from zirconium fluoride waste that will be stored in bins in the future may be heated as high as 400 to 500°C by fission product decay. Blending this waste with Na waste (an intermediate level radioactive waste) should produce calcine that will not be heated to as high of a temperature as the unblended waste. Figure 7 shows the caking temperatures of calcine produced by calcining different blends of Zr and Na wastes containing $Ca(NO_3)_2$. Caking temperatures of calcine were determined by heating the simulated calcine (bed granules without fines) in open crucibles and observing temperatures (to the nearest 50°C) at which the calcine begins to cake and stick to crucible surfaces. According to Figure 7, calcine produced from the blend of Zr and Na wastes calcined in the eighth processing campaign of the WCF (blend of 3-1/2 vol WM-182 waste and 1 vol WM-180 waste having a Ca/F mole ratio of 0.7) would have a caking temperature of 550°C.

Stability of Blends of Zirconium and Sodium Wastes

The two major wastes produced and stored at the ICPP are Zr and Na wastes. Because waste storage tank space is limited, it may be desirable at

TABLE 5. CHLORIDE BEHAVIOR DURING CALCINATION OF Zr-Na WASTES BLENDS CONTAINING A Ca/F MOLE RATIO OF 0.7

Run Number	SBW4-8	SBW4-9	SBW4-10	SBW4-11	SBW4-12	SBW4-13	67	
Zr to Na wastes blend ratio	4-1/2	3	8	6	2	4	3	5
Al/F mole ratio in feed[a]	$0.27^{+0.04}_{-0.02}$	0.49 ± 0.03	$0.26^{+0.03}_{-0.02}$	$0.25^{+0.00}_{-0.01}$	$0.31^{+0.01}_{-0.02}$	$0.27^{+0.04}_{-0.03}$	0.27	0.32 ± 0.03
Percent of total chloride in: calcine solids[a,b]	92^{+6}_{-3}	92^{+5}_{-7}	88^{+3}_{-2}	86 ± 1	92^{+3}_{-2}	88^{+2}_{-4}	75 ± 4	64^{+10}_{-7}
Fines	36^{+18}_{-15}	16^{+7}_{-6}	22^{+16}_{-13}	28^{+14}_{-18}	9^{+3}_{-4}	11 ± 7	27 ± 10	22^{+3}_{-4}
Product plus bed	56^{+21}_{-20}	76^{+11}_{-5}	66^{+14}_{-18}	58^{+19}_{-15}	83 ± 7	76^{+14}_{-16}	48 ± 6	41^{+7}_{-4}
Acid scrub	6^{+2}_{-4}	6^{+5}_{-4}	12^{+2}_{-3}	14 ± 1	6^{+2}_{-1}	4^{+3}_{-2}	10 ± 2	7^{+4}_{-3}
Off-gas leaving acid scrub	2 ± 1	<1.4	<1.0	<1.0	$1^{+0.7}_{-0.3}$	8^{+7}_{-4}	3	$2^{+0.4}_{-0.1}$
Percent of total chloride accounted for[a]	113^{+57}_{-29}	81^{+46}_{-37}	77^{+19}_{-26}	85^{+32}_{-33}	99^{+32}_{-17}	122^{+39}_{-47}	87 ± 4	73^{+14}_{-9}

a. The numbers given represent the average, maximum, and minimum values obtained during a given run.
b. Fines plus product plus bed.

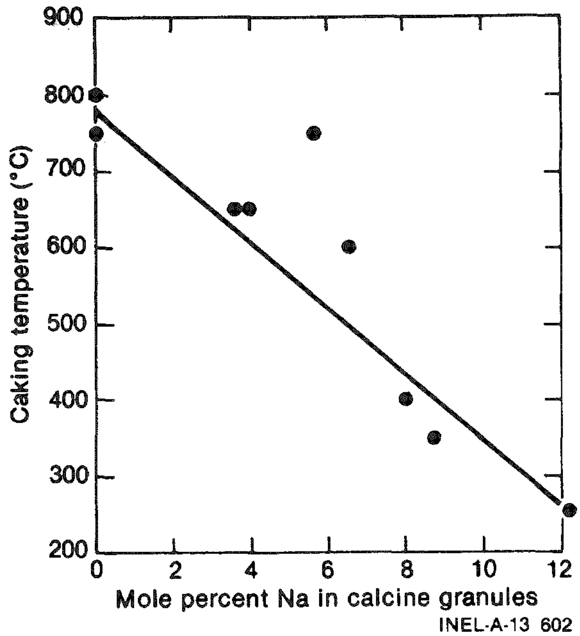

Figure 7. Variation of caking temperature with sodium content of calcine.

some time to store blends of Zr and Na wastes in storage tanks. Table 6, using Na waste similar to that indicated in Table 2 and Zr waste similar to that of the WM-185 waste in Table 2, summarizes information that should be considered when storing such blends. The upper temperature limit recommended for the storage of blends of Zr and aluminum wastes is 35°C, this should apply to blends of Zr and Na wastes also.[11] Blends of 1 to 100 vol Zr and 1 vol Na wastes are unstable within 1 day; solid content of these blends do not increase after being stored for a given time — this given time interval depends on the blend. Solids formed in blends of 2 to 10 vol Zr waste and 1 vol Na waste could not be removed from storage tanks because they are present as flakes or granules. The amount of solids present increase as the storage temperature increases and generally decreases as the proportion of Na waste in the blend decreases. The solids formed when $Ca(NO_3)_2$ is added to any blend, including the solids present after a blend has been mixed for a short time, are easily dispersed into solution. This would be the situation where blends are stored in feed makeup tanks just prior to being fed to the WCF.

Experience in the WCF during the Eighth Processing Campaign

During the eighth processing campaign, 576 m^3 (152 200 gal) of WM-182 (Zr) waste and 122 m^3 (32 200 gal) of WM-180 (Na) waste were simultaneously calcined. The Na waste was calcined at 500°C as a blend of 3-1/2 vol WM-182 waste and 1 vol WM-180 waste containing a Ca/F mole ratio of 0.7. The calcine produced from the blend was so hard that calcined particles reached an MMPD of 0.7 mm. The large particles also had a high bulk density (1.7 g/cm^3). The large, hard, heavy particles required a fluidizing air rate greater than that used for calcine from unblended Zr waste to satisfactorily remove bed from the calciner vessel.

Since only a limited volume of off-gas can be handled by the WCF off-gas cleanup system, increasing the fluidizing air rate decreases the WCF waste throughput. The problem was solved by alternately calcining the blend until product MMPD became greater than 0.6 mm, and then calcining unblended Zr waste until the product MMPD was less than 0.6 mm (this also decreased the bulk density). The length of time that the blended wastes could be calcined before it became necessary to calcine unblended waste varied, but a good average would be for every 8 days that the blended wastes were calcined it was necessary to calcine the unblended waste for a day.

Prior to operating the WCF by alternately calcining unblended WM-182 waste and a blend of WM-182 and WM-180 wastes, unblended WM-182 was calcined for about 2 months. During these 2 months, typically (a) the fluidizing air rate was 4.8 to 5.4 m^3/min, 170 to 190 scfm, (b) the gross feed rate was 0.23 to 0.49 m^3/hour (60 to 130 gph), and (c) the recycle rate of acid scrub to feed was 20% of the gross feed rate. During the next 4-1/2 months, the WCF alternately calcined WM-182 waste and a blend of WM-182 waste and WM-180 waste. During this 4-1/2 month period typically (a) the fluidizing air rate was 5.9 to 8.2 m^3/min (210 to 290 scfm) (b) the gross feed rate was 0.23 to 0.38 m^3/hour (60 to 100 gph), and (c) the recycle rate of acid scrub to feed was 12% of the gross feed rate. During the 4-1/2 months that Na waste was calcined in the WCF, the chloride concentration in the off-gas acid scrubber solution increased from 650 to roughly 2600 ppm.

TABLE 6. STABILITY PROPERTIES OF BLENDS OF ZIRCONIUM AND SODIUM WASTES STORED FOR SIX MONTHS

Blend	Storage Temperature °C	Time Blend Became Unstable	Time Solid Content of Blend Ceased Increasing	Nature of Solids in Blends	Quantity of Solids After 6 Months Storage	
					Packed Volume of Solids (cm^3/L)	Weight of Solids (g/L)
1 vol Zr-1 vol Na	35	Immediately	After 19 hours	Fine, colloidal, gelatinous	51	37
2 vol Zr-1 vol Na	35	After 1-1/2 hours	After 19 hours	Colloidal, fine, and gelatinous; after 98 days changed into granules that could be dispersed only with difficuly	17	156
3 vol Zr-1 vol Na	35	After 3 hours	After 19 hours	Same as above but changed into granules after 17 days of storage	26	254
4 vol Zr-1 vol Na	35	After 3 to 19 hours	After 19 hours	Same as above but changed into granules after 10 days of storage, granules larger than above	30	264
5 vol Zr-1 vol Na	35	After 3 to 19 hours	After 6 days	Colloidal, fine, and gelatinous; after 10 days changed into flakes that could be dispersed only with difficulty	23	197
10 vol Zr-1 vol Na	24	Within 5 hours	After 85 days	Granular, difficult to disperse	3.3	1.8
	35	Within 5 hours	After 21 days	Granular, difficult to disperse	6.7	2.6
25 vol Zr-1 vol Na	24	After 1 day	After 85 days	Fine, easily dispersed	3.3	1.0
	35	After 1 day	After 78 days	Fine, easily dispersed	5.8	1.1
50 vol Zr-1 vol Na	24	After 1 day	After 177 days	Fine, easily dispersed	1.7	0.4
	35	After 1 day	After 105 days	Fine, easily dispersed	5.0	0.6
75 vol Zr-1 vol Na	24	After 1 day	After 177 days	Fine, easily dispersed	2.5	0.3
	35	After 1 day	After 105 days	Fine, easily dispersed	5.0	0.4
100 vol Zr-1 vol Na	24	After 1 day	After 177 days	Fine, easily dispersed	1.7	0.2
	35	After 1 day	After 112 days	Fine, easily dispersed	5.0	0.3

V. CONCLUSIONS AND RECOMMENDATIONS

Conclusions

1. ICPP sodium-bearing waste can be calcined in a fluidized-bed at 500°C as a blend with Zr waste if $Ca(NO_3)_2$ is added. This method was proven in the WCF during the eighth processing campaign when 122 m^3 (32 200 gal) of Na waste was calcined.

2. Calcine from blends of Zr and Na wastes containing 5.3 mole percent sodium is relatively free from fluidized-bed agglomeration and has a caking temperature of 550°C.

3. The presence of $Ca(NO_3)_2$ in Zr-Na wastes blends to give a Ca/F mole ratio of 0.7 effectively suppresses fluoride and chloride volatility when the blends are calcined and produces calcine product that is relatively smooth and contains few nodules.

4. The undissolved solids content of feed from blends of Zr-Na wastes (having a Ca/F mole ratio of 0.7) increased, the attrition index of product decreased, and the product to fines ratio decreased as the proportion of Na waste in the blend decreased.

5. Fluidized-bed agglomeration, smoothness and nodule content of product, product density, chloride retention in calcine solids, and fluoride volatility seem to be independent of the proportion of Na waste in the blend over the range 2 to 8 vol WM-185 waste and 1 vol Na waste (Table 2 gives waste compositions). Calcination at 500°C of a 1 to 1 blend of the same wastes produces calcine product containing many nodules.

6. Calcination of the blend containing 5.3 mole percent sodium having a Ca/F mole ratio of 0.7 produces hard calcine (attrition index 60 to 80%) with a high bulk density (1.7 g/cm^3).

7. The undissolved solids content of Zr-Na waste blends containing a Ca/F mole ratio of 0.7 is sufficiently low so that plugging of calciner feed equipment should be a less frequent problem.

8. Size of calcine product can be controlled by variation of waste NAR in the 10-cm calciner, variation of the waste NAR and oxygen-to-fuel ratio in the 30-cm calciner, and alternately calcining a blend of Zr-Na wastes blend with unblended Zr waste in the WCF.

9. Blends of Zr and Na liquid wastes are unstable over a wide blend ratio within a day. Over a large range of blend ratios solids are produced as granules or flakes which are difficult to disperse into a solution; these solids probably could not be removed from a storage tank. Solid content varies from 5 to 50 cm^3/L depending on the blend ratio.

Recommendations

1. A Zr to Na waste blend ratio producing calcine having a sodium mole percent of 5.25 should be used to calcine Na waste. This blend ratio will provide a maximum Na waste throughput rate in the WCF while maintaining suitable calciner operations. The calcine has a reasonably high caking temperature (550°C). This blend ratio provides a safety factor from blend ratios that might produce bed agglomeration or caking in the storage bins. (The method used to calculate sodium mole percent in calcine is described in Appendix F.)

2. Control particle size and agglomeration by using the appropriate waste NAR, oxygen-to-fuel ratio, and fluidizing air rate. Using waste NAR and the oxygen-to-fuel ratio to control particle size is preferable over alternately calcining the blended Zr-Na wastes with unblended Zr waste.

3. Use a Ca/F mole ratio of 0.7 in the Zr-Na wastes blend.

4. The relationship between particle size and density and the fluidizing air rate using Leva's equation[12] should be used to prevent particle agglomeration. Leva's equation is:

$$G_{mf} = \frac{688\,(Dp)^{1.82}\,(\rho g\,(\rho p\text{-}\rho g))^{\,0.941}}{\mu^{0.882}}$$

where

G_{mf} = mass flux of gas at minimum fluidization (lb/hour·ft^2)

D_p = mean particle diameter (in.) =

$$\frac{1}{\sum_{i=1}^{N} X_i/S_i}$$

(X_i being the fraction retained on screen and S_i being the geometric mean of screen sizes)

ρ_g = density of gas (lb/ft^3)

ρ_p = density of particles (lb/ft^3)

μ = viscosity (centipoise).

Since the minimum superficial fluidizing velocity (U_{mf}) is $G_{mf}/3600\rho_g$, then

$$U_{mf} = \frac{\frac{688}{3600}\,(D_p)^{1.82}\,(\rho_p\text{-}\rho_g)^{\,0.941}}{\mu^{0.882}\,(\rho_g)^{\,0.0592}}$$

where

U_{mf} = minimum superficial fluidizing velocity (ft/s).

5. It may be desirable to test Ca/F mole ratios less than 0.7 in the WCF, and if no problems are encountered, this lower Ca/F mole ratio should be used.

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APPENDIX A

TEN-cm CALCINER RUNS USING BLENDS OF ZR-NA WASTES WITH $Ca(NO_3)_2$

APPENDIX A

TEN-cm CALCINER RUNS USING BLENDS OF ZR-NA WASTES WITH $Ca(NO_3)_2$

The following appendix presents 2 tables showing 10-cm calciner runs.

TABLE A-1. OPERATING CONDITIONS

Calcination Temperature = 500°C, Acid Scrub Recycle Rate = 15% of Feed Rate, $Ca(NO_3)_2$ Added As Solid, Waste Feed Rate = 2L/hour, Feed Nozzle = 40 100 Liquid, 120 Air, Fuel (Kerosene) Nozzle = 2050 Liquid, 67-6-20-70° Air; Nozzles Are Spraying System Co. Nozzles

Run Number	SBW4-1	SBW4-2	SBW4-8	SBW4-9	SBW4-10	SBW4-11	SBW4-12	SBW4-13
Zr/Na wastes blend ratio	1	2	4-1/2	3	8	6	2	4
Ca/F mole ratio	1.0	1.0	0.7	0.7	0.7	0.7	0.7	0.7
Al/F mole ratio	0.38	0.32	0.30	0.32	0.23	0.23	0.29	0.26
Run duration (hours)	14	14	40	40	40	40	40	40
Fluidizing air rate L/s (scfm)[a]	$0.76 \pm 0 (1.60 \pm 0)$	$0.86 \pm 0 (1.83 \pm 0)$	$0.88^{+0.05}_{-0.10}$ $(1.86^{+0.10}_{-0.22})$	$0.78 \pm 0 (1.66 \pm 0)$	$0.76^{+0}_{-0.02}$ $(1.60^{+0}_{-0.04})$	$0.76^{+0.02}_{-0.009}$ $(1.61^{+0.04}_{-0.02})$	$0.75 \pm 0 (1.59 \pm 0)$	$0.75 \pm 0 (1.59 \pm 0)$
Feed atomizing air pressure kPa (psig)[a]	$150^{+12}_{-37} (21.3^{+1.7}_{-5.3})$	$87^{+2.8}_{-4.2} (12.6^{+0.4}_{-0.6})$	$92^{+4}_{-3} (13.4^{+0.6}_{-0.4})$	$92^{+18}_{-10} (13.4^{+2.6}_{-1.4})$	$85^{+15}_{-2} (12.3^{+2.2}_{-0.2})$	$132^{+33}_{-15} (19.2^{+4.8}_{-2.2})$	$149^{+3}_{-4} (21.6^{+0.4}_{-0.6})$	$137^{+1}_{-6} (19.8^{+0.2}_{-0.8})$
Feed atomizing air rate L/S (scfm)[a]	$0.46 \pm 0 (0.98 \pm 0)$	$0.52 \pm 0 (1.10 \pm 0)$	$0.57 \pm 0 (1.20 \pm 0)$	$0.57 \pm 0 (1.20 \pm 0)$	$0.53^{+0.02}_{-0.009}$ $(1.13^{+0.04}_{-0.02})$	$0.52 \pm 0 (1.10 \pm 0)$	$0.58^{+0.00}_{-0.01}$ $(1.23^{+0.00}_{-0.03})$	$0.58 \pm 0 (1.23 \pm 0)$
Kerosene feed rate L/hour[a]	0.71 ± 0.07	$0.78^{+0.05}_{-0.04}$	$0.60^{+0.09}_{-0.05}$	$0.56^{+0.09}_{-0.07}$	$0.62^{+0.08}_{-0.10}$	$0.65^{+0.06}_{-0.09}$	$0.73^{+0.05}_{-0.06}$	$0.75^{+0.07}_{-0.06}$
Fuel Nozzle O_2 rate L/s (scfm)[a]	$0.38 \pm 0 (0.81 \pm 0)$	$0.28^{+0.05}_{-0.09}$ $(0.59^{+0.11}_{-0.19})$	$0.35 \pm 0 (0.75 \pm 0)$	$0.35 \pm 0 (0.75 \pm 0)$	$0.33 \pm 0 (0.70 \pm 0)$	$0.34 \pm 0 (0.73 \pm 0)$	0.33 ± 0.005 (0.69 ± 0.01)	$0.36 \pm 0 (0.76 \pm 0)$
NAR	833 ± 0	935 ± 0	1020 ± 0	1020 ± 0	962^{+32}_{-27}	935 ± 0	1034^{+11}_{-63}	1038^{+7}_{-42}
Startup bed	Calcine from 3 vol Zr-1 vol Na wastes blend with Al/F mole ratio = 0.33 and Ca/F mole ratio = 0.7	Same as for run SBW4-1	Combined calcine from runs SBW4-1 and 2	Same as for run SBW4-8	Combined calcine from runs SBW4-8 and 9	Same as for run SBW4-10	Same as for run SBW4-10	Same as for run SBW4-10
Bed turn-over percent	52.7	71.8	83.8	87.9	89.8	88.8	88.0	90.5

a. The numbers represent the average, maximum, and minimum values obtained during a given run.

TABLE A-2. FLUIDIZED-BED CHARACTERISTICS

Run Number	SBW4-1	SBW4-2	SBW4-12	SBW4-9	SBW4-13	SBW4-8	SBW4-11	SBW4-10
Zr to Na wastes blend ratio	1	2	2	3	4	4-1/2	6	8
Ca/F mole ratio	1.0	1.0	0.7	0.7	0.7	0.7	0.7	0.7
Product								
Production rate (g/hour)	440	674	381	292	331	274	299	331
Density (g/cm^3)[a]	1.63	1.58	$1.61^{+0.02}_{-0.03}$	$1.68^{+0.06}_{-0.08}$	$1.66^{+0.06}_{-0.05}$	$1.57^{+0.02}_{-0.03}$	1.58 ± 0.05	1.59 ± 0.04
MMPD (mm)[a]	0.6625	0.6146	$0.6080^{+0.0644}_{-0.0538}$	$0.5913^{+0.1161}_{-0.047}$	$0.5748^{+0.0470}_{-0.0441}$	$0.5966^{+0.0098}_{-0.0201}$	$0.5875^{+0.1392}_{-0.0647}$	$0.6151^{+0.1063}_{-0.1128}$
Fines								
Production rate (g/hour)	33	44	50	52	58	113	110	81
Density (g/cm^3)[a]	0.895 ± 0.025	0.525 ± 0.035	$0.57^{+0.06}_{-0.05}$	$0.65^{+0.17}_{-0.23}$	$0.46^{+0.03}_{-0.09}$	$0.50^{+0.11}_{-0.06}$	$0.50^{+0.04}_{-0.07}$	$0.49^{+0.03}_{-0.08}$
Product to fines ratio	13.3	10.6	7.7	5.6	5.7	2.4	2.7	4.1
Starting bed								
MMPD (mm)	0.5625	0.5625	0.5758	0.6376	0.5758	0.6376	0.5758	0.5758
Density (g/cm^3)	1.71	1.71	1.65	1.58	1.65	1.58	1.65	1.65
Attrition index of -32 +35 Mesh fraction (percent)	69.6	69.6	68	56	68	56	68	68
Final bed								
MMPD (mm)	0.6625	0.6146	0.5182	0.5713	0.5307	0.5964	0.5468	0.5023
Density (g/cm^3)	1.63	1.58	1.58	1.68	1.61	1.56	1.53	1.55
Attrition index of -32 +35 Mesh fraction (percent)	68	85.2	66	80	64	43	52	39
wt% of bed that is +14 Mesh Particles	--	--	1.1	1.0	0.41	9.2	3.5	2.1
wt% of bed that is +1/2-in Agglomerates	--	--	0.083	0.88	insignificant	2.1	1.6	1.0

a. The numbers given represent the average, maximum, and minimum values obtained during a given run.

APPENDIX B

OPERATING CONDITIONS DURING CALCINATION OF BLENDS OF 3 AND 5 VOL Zr WASTE AND 1 VOL Na WASTE HAVING A Ca/F MOLE RATIO OF 0.7 FOR THIRTY-cm CALCINER RUN 67

APPENDIX B

OPERATING CONDITIONS DURING CALCINATION OF BLENDS 3 AND 5 VOL Zr WASTE AND 1 VOL Na WASTE HAVING A Ca/F MOLE RATIO OF 0.7 FOR THIRTY-cm CALCINER RUN 67

The following tables present operating conditions.

TABLE B-1. MAJOR FLOWRATES, RUN 67

COT (HOURS)	FUEL (L/HR)	WASTE (L/HR)	FLUID AIR (M3/HR)	WASTE ATOM. AIR (M3/HR)	FUEL ATOM. O2 (M3/HR)	PURGES (M3/HR)	WET OFFGAS (M3/HR)	DRY OFFGAS (M3/HR)	OFFGAS DEW POINT (C)	SCRUB TO VENT. (L/HR)	VENTURI SCRUB RETURN (L/HR)	COND. TO DRAIN (L/HR)	SCRUB TANK ACC. (L/HR)	SCRUB RECYCLE TO FEED (%)
4	5.9	42.0	34.3	10.29	11.32	0.40	111.0	53.2	81.4	43.32	180.00	25.20	24.67	13.7
8	5.7	36.5	34.5	10.67	11.32	0.40	103.1	53.8	79.2	41.74	180.00	25.20	24.67	13.7
12	5.8	36.9	35.3	10.54	11.37	0.40	104.6	54.7	79.5	42.53	138.90	25.60	2.93	13.7
16	6.1	36.9	35.5	10.59	11.55	0.40	105.0	54.8	79.5	46.45	97.80	26.00	12.59	6.3
20	6.3	41.6	35.2	10.59	11.50	0.40	110.0	54.3	80.7	47.23	100.50	25.60	5.52	6.3
24	6.2	39.0	35.1	10.60	11.48	0.40	108.9	54.2	80.3	47.23	103.20	25.20	3.79	13.2
28	5.7	41.6	35.2	10.36	12.24	0.40	111.8	54.9	80.6	47.23	110.10	25.50	7.42	13.2
32	5.7	40.7	35.1	10.55	11.82	0.40	110.6	54.6	80.7	47.23	117.00	25.80	12.08	13.2
36	5.9	43.2	35.2	10.31	11.18	0.40	113.0	53.9	81.6	42.53	108.90	25.50	4.14	14.5
40	6.0	40.7	35.3	10.21	11.24	0.40	109.9	53.8	81.1	42.53	100.80	25.20	3.79	14.5
44	6.0	41.6	35.1	10.55	11.35	0.40	110.9	53.9	80.6	45.67	150.60	25.35	5.52	13.2
48	5.9	39.0	35.2	10.36	11.11	0.40	107.5	53.6	80.2	45.67	200.40	25.50	6.04	13.2
52	5.9	47.5	35.3	15.30	11.93	0.40	123.7	59.5	81.0	42.53	169.20	24.75	5.00	14.9
56	5.7	39.0	35.0	15.29	11.44	0.40	112.7	58.9	78.9	42.53	138.00	24.00	8.97	14.9
60	5.9	36.9	38.3	17.35	13.50	0.40	117.0	66.1	76.5	42.53	113.00	25.80	8.11	14.3
64	6.1	43.7	38.3	17.31	14.13	0.40	125.6	66.4	78.5	42.53	88.00	27.60	7.07	14.3
68	6.1	37.7	31.4	17.11	13.99	0.40	112.1	59.2	78.3	42.53	92.00	27.30	3.97	13.8
72	5.9	42.0	31.3	17.02	13.66	0.40	116.4	58.8	79.2	42.53	96.00	27.00	7.94	13.8
76	6.0	40.7	34.1	15.08	14.03	0.40	115.5	60.1	78.4	42.53	102.00	29.40	3.62	14.5
80	6.1	35.2	34.2	15.44	14.13	0.40	109.9	60.7	76.9	42.53	108.00	31.80	8.97	14.5
84	5.9	36.9	34.5	15.20	13.75	0.40	112.7	60.2	77.8	42.53	124.40	26.90	0.34	14.0
88	6.0	39.9	34.6	15.32	14.00	0.40	116.7	60.6	78.8	42.53	140.80	22.00	10.18	14.0
92	6.0	38.6	34.7	15.14	14.06	0.40	115.2	60.6	78.7	42.53	119.90	25.10	0.17	14.0
96	5.9	39.0	34.7	15.26	13.73	0.40	113.7	60.5	78.3	42.53	99.00	28.20	0.86	13.6
100	6.2	39.4	34.6	15.25	12.06	0.40	112.8	58.7	78.9	42.53	103.50	30.30	5.35	13.6
104	6.2	45.8	34.3	15.11	11.87	0.40	119.4	58.1	80.8	42.53	108.00	32.40	11.04	14.2
108	6.2	47.5	31.1	14.00	10.97	0.40	116.0	52.9	82.7	42.53	104.10	29.40	5.69	14.2
112	6.0	34.8	31.6	14.36	10.66	0.40	101.8	53.5	79.4	42.53	100.20	26.40	6.21	14.2

RECYCLE RATE IS BASED ON FEED WITH CALCIUM (SCRUB/FEED WITH CA + SCRUB)

TABLE B-2. CALCINER DATA, RUN 67

COT	AVERAGE BED PRESSURE		TEMPERATURES		WASTE TO FUEL RATIO	O2 TO FUEL RATIO	O2 INPUT	CO	CO2	COMBUSTION EFFICIENCY
			AVERAGE BED	VAPOR SPACE						
(HOURS)	(KPA)	(PSI)	(C)	(C)			(% TH)	(%)	(%)	(%)
4	102.7	14.9	498.+- 3.5	476.	7.12	1921.	92.7	2.25	8.80	90.0
8	102.0	14.8	501.+- 3.1	483.	6.43	1996.	96.3	3.05	13.40	90.9
12	103.5	15.0	496.+- 2.8	477.	6.40	1972.	95.2	1.10	3.80	89.0
16	103.7	15.1	490.+- 3.4	472.	6.04	1889.	91.2	1.85	6.60	89.3
20	103.3	15.0	494.+- 3.6	478.	6.62	1832.	88.4	2.25	8.40	89.6
24	102.5	14.9	492.+- 2.8	475.	6.25	1841.	88.8	2.65	11.60	90.9
28	102.5	14.9	494.+- 2.9	475.	7.27	2142.	103.4	1.20	7.20	93.0
32	103.3	15.0	494.+- 2.6	473.	7.12	2067.	99.7	1.40	7.60	92.4
36	103.4	15.0	483.+-21.3	474.	7.28	1883.	90.9	3.80	14.60	89.9
40	103.5	15.0	494.+- 5.6	473.	6.80	1878.	90.6	2.80	14.80	92.2
44	102.1	14.8	496.+- 4.0	473.	6.89	1883.	90.9	2.75	17.20	93.2
48	103.0	14.9	494.+- 4.4	475.	6.57	1870.	90.2	2.60	15.40	92.9
52	102.9	14.9	494.+- 4.2	475.	7.99	2008.	96.9	1.95	12.80	93.5
56	102.3	14.8	494.+- 3.2	471.	6.88	2017.	97.4	1.60	10.40	93.5
60	101.6	14.7	494.+- 4.3	475.	6.30	2308.	111.4	1.70	14.00	94.7
64	101.5	14.7	494.+- 4.1	481.	7.15	2312.	111.6	1.70	14.60	94.9
68	100.0	14.5	497.+- 4.2	481.	6.17	2289.	110.5	1.70	16.40	95.4
72	99.1	14.4	495.+- 3.8	476.	7.12	2316.	111.8	1.70	14.00	94.7
76	99.1	14.4	495.+- 3.6	476.	6.80	2346.	113.2	1.00	6.80	93.7
80	100.0	14.5	496.+- 3.3	482.	5.76	2312.	111.6	0.50	2.60	92.1
84	99.7	14.5	492.+- 3.7	469.	6.21	2316.	111.8	1.70	15.00	95.0
88	100.4	14.6	494.+- 4.7	472.	6.61	2322.	112.1	1.70	16.40	95.4
92	101.0	14.7	492.+- 3.5	471.	6.40	2333.	112.6	1.50	14.60	95.4
96	100.6	14.6	493.+- 4.0	476.	6.57	2311.	111.5	1.15	10.00	94.9
100	101.1	14.7	493.+- 3.8	472.	6.36	1946.	93.9	1.85	10.40	92.6
104	101.9	14.8	495.+- 4.2	475.	7.39	1916.	92.5	1.80	10.00	92.5
108	104.0	15.1	495.+- 4.3	475.	7.72	1783.	86.0	2.90	18.80	93.5
112	104.1	15.1	492.+- 4.9	473.	5.81	1782.	86.0	2.60	15.20	92.8

TABLE B-3. RUN 67 FEED BATCH DATA (COT IN HOURS, VOL IN L)

LS	COT	FEED BATCH	FEED BATCH VOL W/O CA	FEED BATCH VOL	FEED TANK VOL	FEED TANK VOL AFTER FEED TRANSFER	SCRUB HOLD VOL	FEED TANK VOL AFTER SCRUB TRANSFER	SCRUB HOLD VOL AFTER TRANSFER
161	1	1	237.	277.	5.	307.	93.0	348.	44.7
160	7	2	237.	252.	82.	366.	44.7	366.	44.7
160	15	3	237.	275.	77.	383.	44.7	408.	24.0
160	23	4	237.	275.	103.	409.	73.0	449.	26.1
160	33	5	237.	275.	77.	375.	159.2	421.	108.2
160	41	6	237.	264.	98.	399.	139.2	434.	93.0
160	50	7	237.	270.	52.	324.	125.4	361.	77.1
160	57	8	237.	275.	58.	356.	141.3	399.	90.9
160	66	9	237.	275.	72.	393.	146.8	431.	95.1
160	74	10	237.	275.	93.	391.	157.9	436.	106.8
160	84	11	237.	275.	76.	383.	146.8	414.	96.4
160	93	12	237.	275.	88.	392.	97.8	434.	49.5
169	102	13	237.	275.	62.	363.	98.5	409.	48.1

APPENDIX C

FLUIDIZED-BED OPERATION AND PROPERTIES OF SOLIDS GENERATED DURING CALCINATION OF BLENDS OF 3 AND 5 VOL Zr WASTE AND 1 VOL Na WASTE HAVING A Ca/F MOLE RATIO OF 0.7 FOR THIRTY-cm CALCINER RUN 67

APPENDIX C

FLUIDIZED-BED OPERATION AND PROPERTIES OF SOLIDS GENERATED DURING CALCINATION OF BLENDS OF 3 AND 5 VOL Zr WASTE AND 1 VOL Na WASTE HAVING A Ca/F MOLE RATIO OF 0.7 FOR THIRTY-cm CALCINER RUN 67

The following tables show fluidized-bed operation and properties of solids generated during calcination.

TABLE C-1. PRODUCT SIZE DISTRIBUTION, RUN 67

CUMULATIVE OPERATING TIME (HOURS)	WEIGHT FRACTION RETAINED ON SCREEN													MMPD (MM)
	COMBINED SIZE RANGE (MESH)													
	14	16	20	24	28	32	35	48	65	100	150	200	-200	
0	0.0	0.0	0.0	0.0030	0.0244	0.0976	0.2530	0.4939	0.1128	0.0152	0.0	0.0	0.0	0.39
8	0.0	0.0	0.0	0.0	0.0081	0.0203	0.0650	0.4756	0.3902	0.0407	0.0	0.0	0.0	0.32
16	0.0	0.0	0.0	0.0	0.0099	0.0396	0.0990	0.5743	0.2673	0.0099	0.0	0.0	0.0	0.34
24	0.0	0.0	0.0	0.0	0.0134	0.0379	0.1648	0.7149	0.0690	0.0	0.0	0.0	0.0	0.37
32	0.0	0.0	0.0	0.0025	0.0175	0.1000	0.4850	0.3775	0.0175	0.0	0.0	0.0	0.0	0.43
40	0.0	0.0	0.0	0.0033	0.0299	0.2060	0.4983	0.2492	0.0133	0.0	0.0	0.0	0.0	0.45
48	0.0	0.0	0.0	0.0061	0.1103	0.4671	0.2894	0.1225	0.0046	0.0	0.0	0.0	0.0	0.51
56	0.0	0.0	0.0039	0.0775	0.5853	0.2481	0.0659	0.0155	0.0039	0.0	0.0	0.0	0.0	0.61
64	0.0	0.0	0.0047	0.1530	0.4743	0.1460	0.0607	0.1075	0.0502	0.0035	0.0	0.0	0.0	0.59
72	0.0	0.0	0.0081	0.1008	0.2581	0.1129	0.1855	0.2621	0.0685	0.0040	0.0	0.0	0.0	0.51
76	0.0	0.0	0.0116	0.1197	0.2587	0.1120	0.1351	0.3166	0.0463	0.0	0.0	0.0	0.0	0.51
80	0.0	0.0	0.0096	0.1093	0.2026	0.0997	0.1672	0.3859	0.0225	0.0032	0.0	0.0	0.0	0.50
88	0.0	0.0	0.0102	0.1119	0.2108	0.1323	0.2282	0.2660	0.0392	0.0015	0.0	0.0	0.0	0.51
96	0.0	0.0	0.0081	0.0647	0.1456	0.1752	0.2668	0.2857	0.0512	0.0027	0.0	0.0	0.0	0.48
104	0.0	0.0	0.0039	0.0193	0.1004	0.2124	0.2973	0.3205	0.0425	0.0039	0.0	0.0	0.0	0.46
108	0.0	0.0	0.0080	0.0578	0.1833	0.2709	0.2490	0.2112	0.0199	0.0	0.0	0.0	0.0	0.51
112	0.0	0.0075	0.0503	0.2010	0.2764	0.2513	0.1935	0.0201	0.0	0.0	0.0	0.0	0.0	0.62

TABLE C-2. FLUIDIZED BED DATA, RUN 67

COT (HOURS)	DENSITY (G/ML)	WEIGHT (KG)	HEIGHT (CM)	MMPD (MM)	FLUIDIZING VELOCITIES BELOW FUEL NOZ (M/S)	ABOVE FUEL NOZ (M/S)	TOP OF BED (M/S)	THEORETICAL INCIPIENT (M/S)	REPLACEMENT TIME - 90% (HOURS)
4	1.22	61.8	70.1	0.32	0.26	0.38	0.83	0.05	52.
8	1.22	61.8	73.8	0.32	0.26	0.38	0.78	0.05	69.
12	1.26	64.5	58.5	0.33	0.26	0.38	0.78	0.05	46.
16	1.30	68.5	75.8	0.34	0.26	0.38	0.77	0.06	51.
20	1.32	72.6	76.6	0.36	0.26	0.39	0.82	0.06	50.
24	1.35	71.2	75.1	0.37	0.26	0.39	0.81	0.07	33.
28	1.34	71.2	75.1	0.40	0.26	0.39	0.84	0.08	39.
32	1.34	72.6	74.8	0.43	0.26	0.38	0.82	0.09	42.
36	1.35	75.3	75.9	0.44	0.26	0.37	0.82	0.09	39.
40	1.37	76.6	77.2	0.45	0.26	0.38	0.81	0.10	48.
44	1.36	76.6	75.5	0.48	0.26	0.39	0.83	0.11	48.
48	1.36	80.6	79.5	0.51	0.26	0.38	0.80	0.12	38.
52	1.33	79.3	78.2	0.56	0.26	0.39	0.92	0.14	45.
56	1.30	79.3	78.2	0.61	0.26	0.38	0.84	0.17	40.
60	1.34	80.6	79.5	0.60	0.29	0.42	0.88	0.15	48.
64	1.33	78.0	76.9	0.59	0.29	0.43	0.95	0.14	45.
68	1.34	75.3	74.2	0.55	0.24	0.39	0.86	0.12	46.
72	1.35	72.6	70.0	0.51	0.24	0.38	0.90	0.10	34.
76	1.30	72.6	71.6	0.51	0.26	0.41	0.89	0.11	40.
80	1.31	76.6	75.5	0.50	0.26	0.41	0.84	0.10	68.
84	1.32	69.9	68.9	0.50	0.26	0.40	0.86	0.10	41.
88	1.34	69.9	70.4	0.51	0.26	0.41	0.89	0.11	48.
92	1.34	69.9	70.4	0.50	0.26	0.40	0.87	0.10	56.
96	1.34	73.9	74.5	0.48	0.26	0.40	0.87	0.10	71.
100	1.32	71.2	71.8	0.47	0.26	0.39	0.85	0.10	39.
104	1.30	72.6	73.2	0.46	0.26	0.38	0.90	0.09	51.
108	1.32	72.6	71.6	0.51	0.23	0.35	0.86	0.11	44.
112	1.35	75.3	72.6	0.62	0.23	0.34	0.75	0.16	45.

TABLE C-3. SOLIDS PRODUCTION DATA, RUN 67

COT (HOURS)	FUEL NAR	WASTE NAR	FLUIDIZING VELOCITY (M/S)	PRODUCT RATE (KG/HR)	FINES RATE (KG/HR)	FINES TO SCRUB (KG/HR)	TOTAL SOLIDS RATE (KG/HR)	THEORY SOLIDS RATE (KG/HR)	PROD/FINE RATIO	ATTRITION INDEX	CYC EFF (%)	VOLUME REDUCTION
4	1929.	242.	0.26	2.75	4.05	0.23	7.03	5.93	0.68	24.	95.	5.2
8	2018.	291.	0.26	2.05	1.60	0.23	3.88	5.93	1.28	24.	87.	9.9
12	1966.	280.	0.26	3.25	1.13	0.14	4.51	5.73	2.89	24.	89.	9.2
16	1882.	280.	0.26	3.10	1.25	0.04	4.39	5.54	2.48	24.	97.	10.0
20	1835.	250.	0.26	3.35	0.77	0.07	4.19	5.58	4.32	24.	92.	10.9
24	1857.	269.	0.26	4.90	1.67	0.09	6.67	5.62	2.93	24.	95.	6.9
28	2161.	246.	0.26	4.20	1.25	0.13	5.58	5.74	3.36	24.	91.	8.0
32	2070.	254.	0.26	4.02	1.13	0.16	5.31	5.87	3.58	24.	87.	8.3
36	1884.	234.	0.26	4.42	0.77	0.20	5.40	5.81	5.71	28.	79.	8.9
40	1879.	246.	0.26	3.65	0.88	0.24	4.77	5.75	4.17	31.	78.	9.8
44	1911.	252.	0.26	3.70	0.52	0.21	4.43	6.08	7.05	35.	72.	11.2
48	1882.	261.	0.26	4.90	0.92	0.18	6.00	6.41	5.30	38.	84.	7.8
52	2022.	317.	0.26	4.05	1.67	0.14	5.87	6.37	2.42	42.	92.	8.8
56	2045.	388.	0.26	4.57	1.07	0.11	5.76	6.33	4.26	45.	91.	7.3
60	2355.	469.	0.29	3.88	1.07	0.10	5.05	6.68	3.60	49.	91.	7.9
64	2361.	395.	0.29	3.95	1.75	0.10	5.80	7.04	2.26	52.	95.	7.4
68	2372.	459.	0.24	3.80	2.25	0.12	6.17	6.97	1.69	49.	95.	6.6
72	2419.	414.	0.24	4.85	1.72	0.15	6.73	6.90	2.81	45.	92.	6.9
76	2450.	379.	0.26	4.15	2.00	0.09	6.24	6.26	2.07	42.	96.	6.9
80	2395.	444.	0.26	2.60	1.92	0.02	4.55	5.63	1.35	38.	99.	8.7
84	2403.	419.	0.26	3.95	1.52	0.07	5.54	6.14	2.59	39.	96.	7.0
88	2393.	388.	0.26	3.38	1.90	0.11	5.39	6.65	1.78	40.	94.	8.0
92	2388.	393.	0.26	2.88	1.90	0.10	4.87	6.42	1.51	41.	95.	8.5
96	2379.	394.	0.26	2.40	1.80	0.09	4.29	6.20	1.33	42.	95.	9.9
100	1990.	387.	0.26	4.25	1.77	0.07	6.10	6.71	2.39	43.	96.	7.0
104	1946.	328.	0.26	3.30	1.80	0.06	5.16	7.21	1.83	44.	97.	9.0
108	1774.	287.	0.23	3.82	1.07	0.11	5.01	6.34	3.56	45.	91.	10.0
112	1771.	402.	0.23	3.82	1.17	0.15	5.15	5.47	3.26	46.	88.	8.2
TOTAL				415.8	169.6	11.2	597.	693.	2.45			

APPENDIX D

ANALYSES OF SAMPLES TAKEN DURING CALCINATION OF BLENDS OF 3 AND 5 VOL Zr WASTE AND 1 VOL Na WASTE HAVING A Ca/F MOLE RATIO OF 0.7 FOR THIRTY-cm CALCINER RUN 67

APPENDIX D

ANALYSES OF SAMPLES TAKEN DURING CALCINATION OF BLENDS OF 3 AND 5 VOL Zr WASTE AND 1 VOL Na WASTE HAVING A Ca/F MOLE RATIO OF 0.7 FOR THIRTY-cm CALCINER RUN 67

Appendix D contains tables that show an analysis of samples taken during calcination.

TABLE D-1. ANALYSES OF RUN 67 FEED

COT (hours)	H+ (M)	F (M)	NO_3^- (M)	Al (M)	Na (M)	Zr (M)	Ca (M)	Cl (μg/mL)	B (M)	Hg (μg/mL)	Sp.Gr. (g/mL)	Mole Ratios Ca/F	Mole Ratios Ca/Na	Mole Ratios Al/F
Calciner Feed Concentration														
1	1.07	1.69	5.32	0.46	0.38	0.26	1.30	289	0.116	354	1.302	0.769	3.42	0.272
43	1.20	1.75	5.79	0.62	0.25	0.26	1.55	305	0.106	386	1.324	0.886	6.20	0.354
93	1.11	1.71	5.53	0.49	0.26	0.25	1.65	263	0.109	354	1.309	0.965	6.35	0.287

TABLE D-2. COMPOSITION OF FINES PRODUCED DURING RUN 67

COT (hours)	wt% F	wt% Na	wt% Zr	wt% Ca	wt% Al	wt% Cl	wt% NO_3^-	Hg	Bulk Density (g/cm^3)
8	a	a	a	a	7.20	a	a	a	0.780
32	12.40	5.00	12.90	25.70	7.90	0.22	12.10	4×10^{-4}	0.670
64	12.30	3.50	12.10	31.10	7.20	0.12	11.70	4×10^{-4}	1.110
96	10.80	4.00	13.40	30.80	8.50	0.15	14.30	3×10^{-4}	0.970
112	9.14	4.90	12.80	26.00	7.80	0.22	15.60	4×10^{-4}	0.660

a. No analyses.

TABLE D-3. COMPOSITION OF PRODUCT PRODUCED DURING RUN 67

COT (hours)	wt%								Densities (g/cm^3)		
	F	Na	Zr	Ca	Al	Cl	NO_3^-	Hg	Particulate	Bulk	Bed Void
8	a	a	a	a	a	a	a	a	2.50	1.22	0.51
32	5.61	3.30	13.50	31.40	9.60	0.10	9.10	9×10^{-5}	2.45	1.34	0.45
64	5.16	3.00	12.10	33.90	8.60	0.12	9.10	6×10^{-5}	2.39	1.33	0.44
96	3.80	2.80	11.60	34.00	9.70	0.12	9.12	6×10^{-5}	2.41	1.34	0.44
112	6.68	3.00	12.20	34.10	10.20	0.12	8.20	4×10^{-5}	2.38	1.35	0.43

a. No analyses.

TABLE D-4. COMPOSITION OF ACID SCRUB DURING RUN 67

COT (hours)	F (M)	Na (M)	Zr (M)	Ca (M)	B (M)	Al (M)	Cl (μg/mL)	NO_3^- (M)	H+ (N[a])	Hg (ppm)	Density (g/mL)
32	0.18	0.075	0.019	0.115	0.012	0.050	147	1.33	0.62	390	1.050
64	0.12	0.060	0.012	0.092	0.007	0.040	114	2.11	1.14	330	1.070
96	0.10	0.047	0.009	0.068	0.006	0.030	111	1.61	0.64	297	1.050
112	0.10	0.081	0.008	0.072	0.007	0.040	141	2.30	1.10	410	1.070

TABLE D-5. COMPOSITION OF CAUSTIC SCRUB DURING RUN 67

	mg/L				
COT (hours)	F	Cl	Ca	Al	Hg
36	55.2	5.70	20.00	10.8	69
52	41.2	2.60	20.00	8.1	43
68	66.0	2.80	40.00	13.5	64
100	57.2	3.10	20.00	13.5	59

TABLE D-6. BEHAVIOR OF VOLATILES IN RUN 67

	Cl (days)					Hg (days)					Na (days)					F (days)				
	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
Percent of total volatile in:																				
Fines	36.7	17.2	18.4	23.8	25.0	0.06	0.03	0.04	0.04	0.03	27.6	15.5	27.6	33.6	27.4	18.6	9.6	16.1	18.2	11.9
Product + bed	42.2	54.2	38.2	36.7	48.6	0.03	0.02	0.02	0.01	0.007	46.2	53.0	52.3	43.1	58.6	21.4	21.8	13.9	9.8	31.4
Acid scrub	12.1	8.2	5.9	4.3	11.1	26.2	18.0	12.9	8.1	22.9	4.7	3.8	3.8	1.9	7.2	2.5	1.7	1.0	0.63	1.2
Off-gas escaping acid scrub[b]	a	3.1	2.1	2.5	2.6	a	29.7	29.7	41.3	34.6	a	a	a	a	a	a	0.28	0.38	0.54	0.42
Percent of volatile in acid scrub which came from fines	21.4	41.8	22.3	23.4	95.9	0.01	0.03	0.02	0.02	0.06	41.5	83.4	53.5	72.4	151	51.9	122	114	113	351
Percent of total volatile accounted for	90.9	82.7	64.6	67.2	87.3	26.3	47.8	42.6	49.4	57.6	78.5	72.3	83.7	78.7	93.2	42.5	33.3	31.4	29.1	44.9

a. Information not available.

b. Based on component collected in caustic scrubber containing 6 M NaOH.

APPENDIX E

TEMPERATURE AND PRESSURE DATA OBTAINED DURING CALCINATION OF BLENDS OF 3 AND 5 VOL Zr WASTE AND 1 VOL Na WASTE HAVING A Ca/F MOLE RATIO OF 0.7 FOR THIRTY-cm CALCINER RUN 67

APPENDIX E

TEMPERATURE AND PRESSURE DATA OBTAINED DURING CALCINATION OF BLENDS OF 3 AND 5 VOL Zr WASTE AND 1 VOL Na WASTE HAVING A Ca/F MOLE RATIO OF 0.7 FOR THIRTY-cm CALCINER RUN 67

The tables in Appendix E present temperature and pressure data for the 30-cm calciner run 67.

TABLE E-1. THERMOCOUPLE LOCATIONS, RUN 67

TR901 THERMOCOUPLE LOCATIONS		TR902 THERMOCOUPLE LOCATIONS	
1 -- OUTLET OF FEED COOLER	8 -- FUEL ATOMIZING O2	1 -- PRODUCT POT	13 -- VAPOR 2.1 METER E WALL
2 -- OUTLET OF SCRUB EM FLOWMETER	9 -- OUTLET OF PARTIAL COND.	2 -- AMBIENT E OF FINES POT	14 -- VAPOR 1.79 METERS E WALL
3 -- FEED ATOMIZING AIR	10 -- FUEL	3 -- PRIMARY CYCLONE OUTLET	15 -- FLUID AIR PREHEATER OUTLET
4 -- OUTLET OF VENTURI SCRUBBER	11 -- AMBIENT AIR	4 -- VESSEL 2.2 METERS E WALL	16 -- FINES POT INLET
5 -- OUTLET OF QUENCH TOWER	12 -- OUTLET OF DEMISTER	5 -- VESSEL 1.87 METER E WALL	17 -- VAPOR 1.49 METERS E WALL
6 -- INLET OF AIR PREHEATER	13 -- OUTLET OF HEAT EXCHANGER	6 -- VESSEL 1.56 METERS E WALL	18 -- BED 58.4 CM N WALL
7 -- WATER OUTLET OF JET COND.	14 -- SILICA GEL ADSORBER	7 -- VESSEL 1.25 METERS E WALL	19 -- VAPOR 1.26 METER W WALL
	15 -- INLET TO FINAL FILTER	8 -- BED 78.7 CM W WALL	20 -- BED 11.4 CM S WALL
		9 -- BED 78.7 CM S WALL	21 -- VESSEL 11.4 W WALL
		10 -- VESSEL 78.7 CM N WALL	22 -- BED 11.4 CM E WALL
		11 -- BED 11.4 CM N WALL	23 -- BED 58.4 CM S WALL
		12 -- VAPOR 97 CM E WALL	

TABLE E-2A. THERMOCOUPLE READINGS, RUN 67

INPUT DATA - TR901(1-15) ALL UNITS ARE DEGREES C

LS	COT	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	TIC 903	TIC 904
31	4	18.	31.	21.	76.	177.	174.	7.	21.	31.	26.	23.	20.	21.	21.	21.	316.	521.
30	8	17.	38.	0.	66.	141.	170.	8.	19.	26.	24.	20.	21.	21.	21.	19.	316.	521.
30	12	19.	37.	0.	76.	143.	174.	8.	19.	29.	26.	18.	18.	18.	18.	18.	315.	527.
30	16	33.	40.	0.	72.	79.	175.	8.	19.	29.	25.	16.	19.	19.	23.	18.	316.	521.
30	20	26.	41.	0.	73.	81.	178.	8.	21.	29.	26.	21.	20.	19.	23.	17.	316.	521.
30	24	20.	32.	0.	72.	105.	168.	8.	21.	30.	26.	21.	20.	19.	23.	17.	316.	527.
30	28	21.	32.	0.	72.	94.	171.	8.	21.	29.	26.	21.	21.	19.	23.	17.	316.	527.
30	32	19.	31.	0.	71.	88.	169.	8.	22.	29.	27.	23.	21.	20.	20.	18.	316.	529.
30	36	19.	23.	0.	80.	151.	170.	8.	22.	30.	27.	22.	20.	19.	19.	19.	314.	529.
30	40	19.	27.	0.	85.	162.	167.	8.	21.	31.	25.	19.	18.	23.	22.	19.	314.	527.
30	44	19.	27.	0.	75.	165.	168.	8.	21.	30.	24.	20.	20.	21.	20.	19.	314.	528.
30	48	20.	26.	0.	72.	161.	166.	8.	21.	29.	24.	19.	20.	21.	20.	20.	314.	526.
30	52	23.	27.	0.	78.	162.	163.	8.	20.	30.	23.	19.	19.	21.	20.	19.	316.	527.
30	56	18.	27.	0.	76.	135.	158.	8.	21.	29.	24.	23.	22.	21.	20.	19.	316.	527.
30	60	19.	25.	0.	65.	171.	160.	8.	21.	29.	24.	20.	21.	21.	20.	19.	314.	527.
30	64	18.	28.	0.	72.	141.	171.	8.	21.	30.	24.	20.	20.	21.	20.	20.	314.	526.
30	68	20.	28.	0.	73.	133.	176.	8.	21.	30.	25.	20.	20.	20.	20.	19.	316.	532.
30	72	19.	27.	0.	73.	120.	175.	8.	21.	30.	26.	21.	20.	19.	19.	19.	316.	521.
30	76	17.	29.	0.	72.	157.	172.	8.	21.	29.	26.	22.	19.	19.	19.	19.	316.	527.
30	80	18.	29.	0.	72.	142.	177.	8.	21.	30.	27.	23.	20.	20.	19.	19.	316.	527.
30	84	17.	30.	0.	72.	102.	168.	8.	19.	30.	25.	21.	18.	18.	18.	18.	316.	527.
30	88	20.	31.	0.	70.	78.	168.	8.	20.	28.	24.	19.	20.	20.	19.	18.	316.	526.
30	92	19.	30.	0.	69.	76.	165.	8.	18.	28.	22.	17.	19.	19.	19.	17.	316.	527.
30	96	20.	28.	0.	74.	166.	178.	8.	18.	31.	24.	17.	18.	18.	18.	16.	316.	527.
30	100	18.	30.	0.	76.	91.	168.	8.	18.	31.	23.	19.	18.	18.	18.	16.	316.	527.
30	104	22.	25.	0.	75.	96.	171.	8.	23.	31.	27.	23.	21.	20.	20.	19.	316.	529.
30	108	18.	25.	0.	77.	173.	170.	8.	22.	31.	27.	18.	16.	16.	16.	21.	316.	527.
39	112	15.	24.	0.	75.	156.	166.	8.	18.	30.	23.	23.	23.	23.	22.	17.	316.	527.

TABLE E-2B. THERMOCOUPLE READINGS, RUN 67

INPUT DATA - TR902(1-23) ALL UNITS ARE DEGREES C

LS	COT	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	DORIC	TRC905
41	4	300.	23.	385.	329.	375.	323.	417.	500.	500.	402.	498.	433.	0.	431.	198.	140.	450.	500.	476.	497.	454.	492.	500.	501.	521.
40	8	253.	19.	384.	326.	373.	319.	418.	503.	503.	400.	500.	427.	0.	432.	194.	127.	453.	503.	483.	501.	450.	496.	504.	504.	524.
40	12	270.	19.	378.	325.	372.	319.	416.	497.	497.	400.	497.	431.	0.	427.	193.	199.	450.	497.	477.	493.	452.	491.	497.	500.	527.
40	16	301.	15.	375.	325.	371.	318.	412.	493.	493.	396.	491.	426.	0.	426.	186.	70.	444.	490.	472.	487.	445.	484.	491.	495.	516.
40	20	311.	20.	381.	327.	375.	323.	421.	497.	496.	399.	494.	430.	0.	432.	196.	80.	453.	495.	478.	491.	450.	487.	495.	496.	521.
40	24	280.	20.	381.	324.	374.	318.	412.	493.	493.	400.	491.	425.	0.	427.	197.	96.	445.	493.	475.	491.	445.	486.	494.	495.	516.
40	28	274.	22.	375.	323.	372.	319.	414.	495.	497.	400.	495.	431.	0.	427.	196.	90.	447.	496.	475.	493.	448.	490.	495.	498.	521.
40	32	275.	23.	374.	318.	370.	318.	412.	495.	496.	400.	493.	428.	0.	424.	197.	73.	443.	496.	473.	493.	446.	489.	496.	497.	524.
40	36	297.	17.	376.	317.	372.	318.	413.	496.	497.	401.	492.	431.	0.	429.	197.	190.	448.	451.	474.	494.	448.	452.	496.	500.	526.
40	40	285.	18.	375.	314.	367.	314.	410.	498.	499.	397.	495.	429.	0.	425.	187.	123.	443.	496.	473.	490.	437.	483.	495.	500.	527.
40	44	325.	17.	383.	319.	371.	317.	415.	499.	499.	411.	496.	431.	0.	427.	189.	57.	445.	498.	473.	496.	438.	488.	497.	499.	527.
40	48	286.	19.	376.	375.	368.	316.	415.	495.	496.	413.	494.	431.	0.	430.	187.	50.	444.	497.	475.	492.	427.	485.	497.	498.	526.
40	52	300.	22.	378.	315.	367.	312.	412.	496.	498.	418.	494.	432.	0.	426.	187.	81.	444.	497.	475.	492.	418.	486.	493.	499.	524.
40	56	285.	21.	371.	315.	365.	312.	409.	495.	497.	418.	494.	430.	0.	422.	188.	77.	438.	496.	471.	492.	412.	488.	497.	498.	524.
40	60	260.	22.	371.	319.	366.	312.	414.	495.	497.	420.	493.	431.	0.	425.	188.	62.	443.	497.	475.	491.	425.	486.	498.	498.	524.
40	64	236.	18.	377.	324.	371.	319.	423.	496.	497.	418.	494.	431.	0.	429.	191.	121.	450.	497.	481.	491.	438.	488.	498.	498.	529.
40	68	330.	22.	379.	325.	373.	319.	423.	499.	500.	419.	496.	432.	0.	431.	189.	115.	451.	500.	481.	494.	435.	489.	500.	501.	527.
40	72	313.	22.	377.	324.	372.	320.	417.	497.	498.	418.	494.	431.	0.	429.	196.	105.	447.	495.	476.	493.	440.	488.	498.	498.	527.
40	76	277.	22.	375.	325.	372.	320.	415.	497.	498.	418.	495.	430.	0.	429.	199.	117.	447.	497.	476.	494.	441.	489.	497.	498.	527.
40	80	285.	22.	373.	326.	372.	322.	424.	497.	499.	419.	496.	433.	0.	429.	200.	121.	453.	497.	482.	495.	443.	490.	500.	500.	527.
40	84	310.	23.	375.	319.	365.	315.	410.	494.	494.	415.	491.	425.	0.	423.	193.	131.	441.	494.	469.	490.	438.	485.	495.	498.	524.
40	88	310.	21.	373.	321.	367.	315.	411.	496.	496.	416.	492.	427.	0.	426.	193.	135.	440.	497.	472.	491.	435.	485.	498.	496.	524.
40	92	290.	19.	369.	320.	366.	312.	410.	495.	494.	415.	492.	426.	0.	425.	188.	122.	441.	494.	471.	490.	433.	486.	495.	495.	521.
40	96	266.	18.	370.	323.	371.	321.	421.	495.	494.	416.	493.	429.	0.	431.	198.	130.	450.	497.	476.	490.	440.	486.	495.	495.	524.
40	100	272.	21.	372.	320.	371.	317.	413.	495.	494.	417.	492.	426.	0.	423.	198.	128.	443.	495.	472.	490.	440.	486.	496.	496.	524.
40	104	266.	22.	370.	323.	367.	318.	416.	497.	497.	417.	495.	431.	0.	428.	198.	117.	447.	497.	475.	492.	442.	487.	498.	499.	524.
40	108	324.	18.	363.	318.	365.	318.	415.	495.	497.	416.	495.	430.	0.	425.	193.	99.	445.	497.	475.	492.	433.	487.	499.	501.	527.
49	112	325.	17.	558.	315.	363.	313.	412.	495.	495.	417.	494.	429.	0.	425.	190.	82.	442.	495.	473.	485.	436.	485.	495.	500.	527.

TABLE E-3. PRESSURE GAUGE LOCATIONS, RUN 67

PRESSURE GUAGE LOCATIONS

PI901 -- STEAM TO JET	PI902 -- FEED SUPPLY	PI903 -- SCRUB SUPPLY	PI904 -- SCRUB TANK GUAGE PRES.
PI905 -- FUEL SUPPLY	PI906 -- FUEL NOZZLE LIQUID	PI907 -- OXYGEN SUPPLY	PI908 -- FEED NOZZLE LIQUID
PI909 -- FEED NOZZLE GAS	PI910 -- FLUIDIZING AIR PREHTR INLT	PI911 -- FLUIDIZING AIR SUPPLY	PI912 -- QUENCH TWR INLET (ABS)
PI913 -- VENT SCRB EXIT (ABS)	PI914 -- KNOCKOUT POT EXIT (ABS)	PI915 -- FEED ATOM AIR SUPPLY	PI916 -- AIR BLEED TO JET
PI917 -- PARTIAL COND EXIT (ABS	PI918 -- STEAM JET INLET (ABS)	PI919 -- FUEL NOZZLE GAS	PI920 -- ATMOSPHERIC PRESSURE
PI922 -- INSTRUMENT AIR	PI923 -- 50 PSI AIR		

TABLE E-4A. PRESSURE GAUGE READINGS, RUN 67

INPUT DATA - PI(1-11), PSI AND KPA

LS	COT	901		902		903		904		905		906		907		908		909		910		911	
51	4	5.0	34.	7.0	48.	0.0	0.	1.6	11.	72.5	500.	0.0	0.	48.0	331.	3.7	25.	29.0	200.	4.0	28.	51.5	355.
50	8	5.0	34.	6.0	41.	0.0	0.	1.7	12.	72.5	500.	0.0	0.	48.5	334.	3.7	25.	30.0	207.	3.7	25.	51.5	355.
50	12	3.0	21.	5.6	39.	0.0	0.	1.6	11.	72.0	496.	0.0	0.	49.0	338.	3.7	25.	31.0	214.	4.0	28.	51.3	354.
50	16	3.0	21.	5.3	37.	0.0	0.	1.5	10.	72.0	496.	0.0	0.	49.0	338.	3.8	26.	34.0	234.	4.1	28.	51.3	354.
50	20	5.0	34.	5.1	35.	0.0	0.	1.4	10.	72.0	496.	0.0	0.	48.0	331.	3.9	27.	34.0	234.	4.0	28.	51.3	354.
50	24	3.0	21.	8.5	59.	0.0	0.	1.4	10.	72.0	496.	0.0	0.	47.8	329.	3.8	26.	33.0	227.	4.0	28.	51.2	353.
50	28	5.0	34.	7.0	48.	0.0	0.	1.3	9.	72.5	500.	0.0	0.	67.0	462.	3.8	26.	35.0	241.	3.9	27.	51.3	354.
50	32	5.0	34.	6.0	41.	0.0	0.	1.3	9.	72.5	500.	0.0	0.	67.5	465.	3.9	27.	33.0	227.	3.8	26.	51.5	355.
50	36	5.0	34.	6.0	41.	0.0	0.	1.4	10.	72.3	498.	0.0	0.	68.5	472.	4.0	28.	34.0	234.	3.9	27.	51.5	355.
50	40	5.0	34.	6.0	41.	0.0	0.	1.6	11.	72.0	496.	0.0	0.	69.0	475.	4.3	30.	36.0	248.	4.0	28.	51.5	355.
50	44	4.0	28.	7.0	48.	0.0	0.	1.4	10.	71.8	495.	0.0	0.	68.9	475.	4.5	31.	27.0	186.	4.0	28.	51.0	351.
50	48	4.0	28.	6.0	41.	0.0	0.	1.5	10.	72.0	496.	0.0	0.	68.9	475.	4.6	32.	36.0	248.	4.0	28.	51.0	351.
50	52	4.5	31.	5.5	38.	0.0	0.	1.4	10.	72.0	496.	0.0	0.	68.5	472.	4.0	28.	53.5	369.	4.0	28.	51.5	355.
50	56	4.5	31.	5.1	35.	0.0	0.	1.3	9.	72.3	498.	0.0	0.	68.5	472.	3.8	26.	52.0	358.	4.0	28.	51.3	354.
50	60	4.5	31.	5.5	38.	0.0	0.	1.3	9.	71.5	493.	0.0	0.	66.0	455.	3.8	26.	62.5	431.	4.0	28.	51.5	355.
50	64	4.5	31.	5.3	37.	0.0	0.	1.2	8.	72.0	496.	0.0	0.	64.5	444.	4.1	28.	63.0	434.	4.0	28.	51.3	354.
50	68	4.0	28.	5.9	41.	0.0	0.	1.0	7.	71.8	495.	0.0	0.	64.0	441.	3.8	26.	68.7	473.	3.5	24.	51.5	355.
50	72	4.0	28.	5.5	38.	0.0	0.	1.0	7.	71.5	493.	0.0	0.	65.5	451.	3.8	26.	68.8	474.	3.4	23.	51.0	351.
50	76	5.0	34.	5.5	38.	0.0	0.	1.0	7.	72.0	496.	0.0	0.	65.5	451.	3.6	25.	53.0	365.	3.5	24.	50.5	348.
50	80	5.0	34.	5.3	37.	0.0	0.	1.0	7.	72.0	496.	0.0	0.	64.5	444.	3.7	25.	56.0	386.	3.7	25.	51.0	351.
50	84	7.0	48.	5.0	34.	0.0	0.	1.0	7.	72.5	500.	0.0	0.	65.0	448.	3.8	26.	54.0	372.	3.6	25.	51.6	356.
50	88	6.0	41.	5.0	34.	0.0	0.	1.3	9.	72.5	500.	0.0	0.	64.8	447.	3.8	26.	54.0	372.	3.6	25.	51.5	355.
50	92	3.0	21.	4.9	34.	0.0	0.	1.1	8.	72.0	496.	0.0	0.	65.0	448.	4.0	28.	53.0	365.	3.7	25.	51.5	355.
50	96	3.5	24.	4.9	34.	0.0	0.	1.2	8.	71.5	493.	0.0	0.	65.5	451.	4.0	28.	53.5	369.	3.7	25.	51.5	355.
50	100	4.0	28.	5.0	34.	0.0	0.	1.3	9.	71.5	493.	0.0	0.	68.1	469.	3.7	25.	54.0	372.	3.7	25.	51.5	355.
50	104	5.0	34.	5.0	34.	0.0	0.	1.5	10.	71.0	489.	0.0	0.	67.0	462.	3.7	25.	53.8	371.	3.8	26.	51.3	354.
50	108	5.0	34.	5.0	34.	0.0	0.	1.5	10.	71.0	489.	0.0	0.	67.5	465.	4.0	28.	58.0	400.	4.0	28.	51.5	355.
59	112	5.0	34.	5.0	34.	0.0	0.	1.5	10.	71.8	495.	0.0	0.	68.0	469.	4.0	28.	58.0	400.	4.0	28.	51.6	356.

TABLE E-4B. PRESSURE GAUGE READINGS, RUN 67

INPUT DATA - PI(12-23) PSI AND KPA

LS	COT	912		913		914		915		916		917		918		919		920		922		923	
59	4	14.0	96.	13.5	93.	13.4	92.	94.0	648.	0.0	0.	12.6	87.	13.1	90.	39.0	269.	12.3	85.	20.5	141.	50.0	345.
59	8	14.0	96.	13.4	92.	13.3	92.	96.5	665.	0.0	0.	12.5	86.	13.0	90.	39.0	269.	12.3	85.	20.5	141.	50.0	345.
59	12	14.1	97.	13.4	92.	13.3	92.	94.0	648.	0.0	0.	12.5	86.	12.9	89.	39.0	269.	12.3	85.	20.5	141.	50.0	345.
59	16	14.0	96.	13.3	92.	13.3	92.	95.0	655.	0.0	0.	12.4	85.	12.9	89.	39.0	269.	12.3	85.	20.5	141.	50.0	345.
59	20	14.0	96.	13.3	92.	13.2	91.	95.0	655.	0.0	0.	12.5	86.	12.9	89.	39.0	269.	12.3	85.	20.5	141.	50.0	345.
59	24	13.8	95.	13.2	91.	13.2	91.	98.0	675.	0.0	0.	12.5	86.	12.8	88.	39.0	269.	12.3	85.	20.5	141.	50.0	345.
59	28	13.8	95.	13.2	91.	13.1	90.	93.0	641.	0.0	0.	12.5	86.	12.9	89.	42.0	289.	12.3	85.	20.5	141.	50.0	345.
59	32	13.9	96.	13.3	92.	13.2	91.	97.0	668.	0.0	0.	12.6	87.	13.0	90.	42.0	289.	12.3	85.	20.4	141.	50.0	345.
59	36	14.0	96.	13.3	92.	13.3	92.	95.0	655.	0.0	0.	12.6	87.	13.0	90.	40.0	276.	12.3	85.	20.4	141.	50.0	345.
59	40	14.0	96.	13.4	92.	13.3	92.	93.0	641.	0.0	0.	12.6	87.	13.0	90.	39.0	269.	12.3	85.	20.4	141.	50.0	345.
59	44	13.8	95.	13.2	91.	13.2	91.	97.0	668.	0.0	0.	12.5	86.	12.8	88.	39.0	269.	12.3	85.	20.5	141.	50.0	345.
59	48	13.9	96.	13.3	92.	13.3	92.	93.0	641.	0.0	0.	12.5	86.	12.8	88.	39.0	269.	12.3	85.	20.5	141.	50.0	345.
59	52	13.8	95.	13.2	91.	13.1	90.	94.0	648.	0.0	0.	12.6	87.	12.8	88.	41.0	283.	12.3	85.	20.5	141.	50.0	345.
59	56	13.8	95.	13.2	91.	13.1	90.	98.0	675.	0.0	0.	12.5	86.	12.8	88.	41.0	283.	12.3	85.	20.5	141.	50.0	345.
59	60	13.7	94.	13.1	90.	13.0	90.	97.0	668.	0.0	0.	12.6	87.	12.7	88.	48.0	331.	12.3	85.	20.5	141.	50.0	345.
59	64	13.8	95.	13.1	90.	13.0	90.	96.5	665.	0.0	0.	12.6	87.	12.7	88.	48.0	331.	12.3	85.	20.5	141.	50.0	345.
59	68	13.6	94.	12.8	88.	12.8	88.	94.0	648.	0.0	0.	12.6	87.	12.7	88.	50.0	345.	12.3	85.	20.5	141.	50.0	345.
59	72	13.6	94.	12.8	88.	12.7	88.	93.0	641.	0.0	0.	12.7	88.	12.7	88.	49.0	338.	12.3	85.	20.5	141.	50.0	345.
59	76	13.6	94.	12.8	88.	12.7	88.	91.0	627.	0.0	0.	12.7	88.	12.7	88.	49.0	338.	12.3	85.	20.4	141.	49.5	341.
59	80	13.5	93.	12.9	89.	12.8	88.	96.0	662.	0.0	0.	12.7	88.	12.8	88.	51.0	351.	12.3	85.	20.4	141.	49.8	343.
59	84	13.5	93.	12.9	89.	12.8	88.	94.0	648.	0.0	0.	12.6	87.	12.6	87.	49.0	338.	12.3	85.	20.4	141.	50.0	345.
59	88	13.8	95.	13.1	90.	13.0	90.	97.0	668.	0.0	0.	12.5	86.	12.6	87.	49.0	338.	12.3	85.	20.6	142.	50.0	345.
59	92	13.7	94.	12.9	89.	12.9	89.	94.5	651.	0.0	0.	12.5	86.	12.5	86.	49.0	338.	12.3	85.	20.5	141.	50.0	345.
59	96	13.6	94.	13.0	90.	13.0	90.	96.1	662.	0.0	0.	12.4	85.	12.5	86.	48.0	331.	12.3	85.	21.0	145.	50.0	345.
59	100	13.7	94.	13.0	90.	13.0	90.	96.0	662.	0.0	0.	12.4	85.	12.6	87.	41.0	283.	12.3	85.	20.5	141.	50.0	345.
59	104	13.9	96.	13.1	90.	13.1	90.	94.0	648.	0.0	0.	12.6	87.	12.9	89.	41.0	283.	12.3	85.	20.5	141.	50.0	345.
59	108	14.1	97.	13.5	93.	13.4	92.	92.5	637.	0.0	0.	12.6	87.	12.8	88.	42.0	289.	0.0	0.	20.2	139.	50.0	345.
59	112	14.1	97.	13.4	92.	13.4	92.	96.0	662.	0.0	0.	12.5	86.	12.8	88.	42.0	289.	0.0	0.	20.5	141.	50.0	345.

APPENDIX F

CALCULATION OF SODIUM MOLE PERCENT IN CALCINE

APPENDIX F

CALCULATION OF SODIUM MOLE PERCENT IN CALCINE

In calculating the sodium mole percent of calcine produced from a Zr-Na wastes blend, we only considered the major constituents: aluminum, zirconium, fluoride, calcium, and oxide. During calcination of the blend, all the sodium (Na) is assumed to form Na_3AlF_6; the remaining fluoride (not used in Na_3AlF_6) is assumed to form CaF_2; the remaining aluminum (not used in Na_3AlF_6) is assumed to form Al_20_3; the remaining calcium (not used in CaF_2) is assumed to form Ca0; and the zirconium (Zr) is assumed to form $Zr0_2$.

As an example of this calculation, calculate the mole percent of Na in a blend of 3 vol WM-182 waste (Table 2) with 1 vol of the Na waste of Table 2. Concentration of major constituents in the blend are:

1. Sodium (Na) $= \frac{1.8\underline{M} \times 1}{4} = 0.45\underline{M}$

2. Aluminum (A1) $= \frac{(0.51\underline{M} \times 1) + (0.64\underline{M} \times 3)}{4} = 0.61\underline{M}$

3. Fluoride (F) $= \frac{2.5\underline{M} \times 3}{4} = 1.88\underline{M}$

4. Calcium (Ca) = Ca/F mole ratio is 0.7 or $\frac{Ca}{1.88\underline{M}} = 0.7$ or $Ca = 0.7 \times 1.88\underline{M} = 1.32\underline{M}$

5. $Zr = \frac{0.38\underline{M} \times 3}{4} = 0.28\underline{M}$.

Thus, calcine from 1 L of blend contains: 0.45 moles of Na, 0.61 moles of Al, 1.88 moles of F, 1.32 moles of Ca, and 0.28 moles of Zr; but the moles of oxide (O) are unknown.

To calculate moles of 0:

1. 0.45 moles of Na, 0.15 moles of Al (1 mole of Al/every 3 moles of Na used), and 0.9 moles of F (2 moles of F/mole of Na used) are used to form Na_3AlF_6.

2. (1.88 — 0.9) moles of F and 0.49 moles of Ca (1 mole of Ca/every 2 moles of F used) are used to form CaF_2.

3. There are (0.61 — 0.15) moles of Al, (1.32 — 0.49) moles of Ca, and 0.28 moles of Zr to form oxides.

4. moles of oxide = 0.69 moles as Al_20_3 + 0.83 moles as Ca0 + 0.56 moles as $Zr0_2$ = 2.08 moles.

Thus mole percent of Na in calcine =

$$\frac{0.45\,(Na)}{0.45(Na) + 0.61(A1) + 1.88(F) + 1.32(Ca) + 0.28(Zr) + 2.08(0)}\,(100)$$

$$= 6.8\%$$

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