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Summary Of Waste Calcination At The Idaho Nuclear Technology And Engineering Center

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ABSTRACT

Fluidized-bed calcination at the Idaho Nuclear Technologies and Engineering Center (INTEC, formally called the Idaho Chemical Processing Plant) has been used to solidify acidic metal nitrate fuel reprocessing and incidental wastes wastes since 1961. A summary of waste calcination in full-scale and pilot plant calciners has been compiled for future reference. It contains feed compositions and operating conditions for all the processing campaigns for the original Waste Calcining Facility (WCF), the New Waste Calcining Facility (NWCF) started up in 1982, and numerous small scale pilot plant tests for various feed types. This summary provides a historical record of calcination at INTEC, and will be useful for evaluating calcinability of future wastes.

SUMMARY

Fluidized-bed calcination has been used at the Idaho Nuclear Technology and Engineering Center (INTEC), (formerly called the Idaho Chemical Processing Plant (ICPP) since the early 1960's to solidify acidic metal nitrate wastes from fuel processing. A summary of waste calcination in full-scale and pilot plant calciners has been compiled for future reference. The summary includes feed chemical composition and process operating parameters for: 1) Waste Calcining Facility (WCF) cold operation and hot campaign H-1 through H-9 from 1961 to 1981; 2) New Waste Calcining Facility (NWCF) cold operation and hot campaigns H-1 through H-4 from 1981 to 2000; and 3) small-scale feed blend tests conducted using non-radioactive simulants in various sizes of pilot plant calciners with fluidized-beds from 4 in. diameter up to 2 foot square. These summaries provide a historical record of calcination development at INTEC, give the range of feed compositions and feed additives that have been tested, and will be useful for evaluating calcinability of future wastes.

In the calcination process, the liquid wastes are sprayed using air-atomizing nozzles into a fluidized bed of heated spherical calcine particles, evaporating water and nitric acid in the wastes and leaving behind solid-phase metal oxides. Heat was originally provided by re-circulating liquid eutectic sodium/potassium alloy through heat exchange tubes located in the bed. In 1970 the heat input was changed to in-bed combustion (IBC) of kerosene fuel, sprayed directly into the bed through oxygen atomized fuel nozzles, and the calcination temperature was increased to 500°C. NWCF testing at 600°C with IBC was performed during April-June 1999 and April-May 2000.

The successful calcination of a given waste is dependent primarily on the major chemical constituents (greater than about 0.05 molar) and the concentration (or diluteness) of dissolved solids in the waste feed. Chemical additives used for calcination have been calcium nitrate to control halide volatility, boric acid to promote amorphous alumina formation, and aluminum nitrate to dilute the sodium content in the calcine. Wastes which were difficult to calcine alone due to diluteness, inability to control particle size, or formation of agglomerates could often be calcined as blends with more amenable wastes.

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I would like to acknowledge Billie J. Newby for his years of hard work and dedication, over his 30+ years at the Idaho Chemical Processing Plant. His meticulous notes on calcination have been extremely helpful over the years. A great many others, too numerous to mention, worked on calcination development and operation over the years; and they should all be proud to have pioneered the most successful high-level radioactive waste solidification process in the Department of Energy (DOE) complex. I would also like to acknowledge R. M. Gifford for typing and preparing this report for publication.

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ACRONYMS

AI	Attrition Index
Al	Aluminum
ALD	Analytical Laboratories Department
AMSCO	A paraffin hydrocarbon solvent used in the solvent extraction processes
ANN	Aluminum Nitrate
APS	Atmospheric Protection System
BBWI	Bechtel BWXT Idaho, LLC
COT	Cumulative Operating Time
CSSFs	Calcined Solids Storage Facilities
DOE	U. S. Department of Energy
DOE-ID	U. S. Department of Energy-Idaho operations office
ENICO	Exxon Nuclear Idaho Company
F	Flouride (F^-)
H^+	Acidity
HEPA	High-efficiency Particulate Air (filter)
HLLWE	High Level Liquid Waste Evaporator
HLW	High Level Waste
IBC	In-bed Combustion
ICPP	Idaho Chemical Processing Plant
INEEL	Idaho National Engineering and Environmental Laboratory
INTEC	Idaho Nuclear Technology and Engineering Center (formerly ICPP)
LET&D	Liquid Effluent Treatment & Disposal system
LMITCO	Lockheed Martin Idaho Technologies Company
$\underline{M}$	Molarity
MMPD	Mass Mean Particle Diameter
$N^{\underline{a}}$	Acid Normality
$N^{\underline{b}}$	Base Normality
NAR	Nozzle Atomizing-air to feed Ratio
NO_3	Nitrate (NO_3^-)
NO_x	Nitrogen Oxides
NRC	Nuclear Regulatory Commission
NWCF	New Waste Calcining Facility
PEW	Process Equipment Waste
PEWE	Process Equipment Waste Evaporator
PO_4	Phosphate (PO_4^{-3})
PWL	Process Waste Lines
RAL	Remote Analytical Laboratory
RCRA	Resource Conservation and Recovery Act
SBW	Sodium-bearing Waste
SO_4	Sulphate (SO_4^{-2})
SRI	Stanford Research Institute
TBP	Tributyl Phospate
Total Solids	Total of undissolved solids and dissolved solids
TFF	Tank Farm Facility
TFT	Tank Farm Tanks
UDS	Undissolved Solids
VRF	Volume Reduction Factor (Ratio of Liquid Waste Volume to Calcine Volume)
vol	volume or volumes

WCF	Waste Calcining Facility
WINCO	Westinghouse Idaho Nuclear Company
Zr	Zirconium

Summary of Waste Calcination At the Idaho Nuclear Technology and Engineering Center

INTRODUCTION

Fluidized-bed calcination has been used at the Idaho Nuclear Technology and Engineering Center (INTEC, formerly called the Idaho Chemical Processing Plant or ICPP) since the early 1960s to convert the liquid high-level radioactive wastes from the reprocessing of spent nuclear fuel into a dry granular calcine for volume reduction and safer temporary storage. The Waste Calcining Facility (WCF), with a 2-foot square fluidizing section, began hot operation in 1963. The New Waste Calcining Facility (NWCF), with a 5-foot diameter fluidizing section, began hot operation in 1983. The following is a report summarizing the operation of the calciners on various feed compositions from 1962 through 2000, and a summary of simulated (non-radioactive) feed blends tested in the pilot plant calciners during that time to support operation of the production facilities. The portions up through NWCF campaign H1 and initial pilot plant studies of calcination of Sodium waste with aluminum nitrate were compiled by B. J. Newby prior to his retirement, with the intent that it be used for evaluation of future waste compositions for calcination. More recent plant and pilot plant data has since been added to provide a complete listing of calciner operation and testing through shutdown of the NWCF in June, 2000.

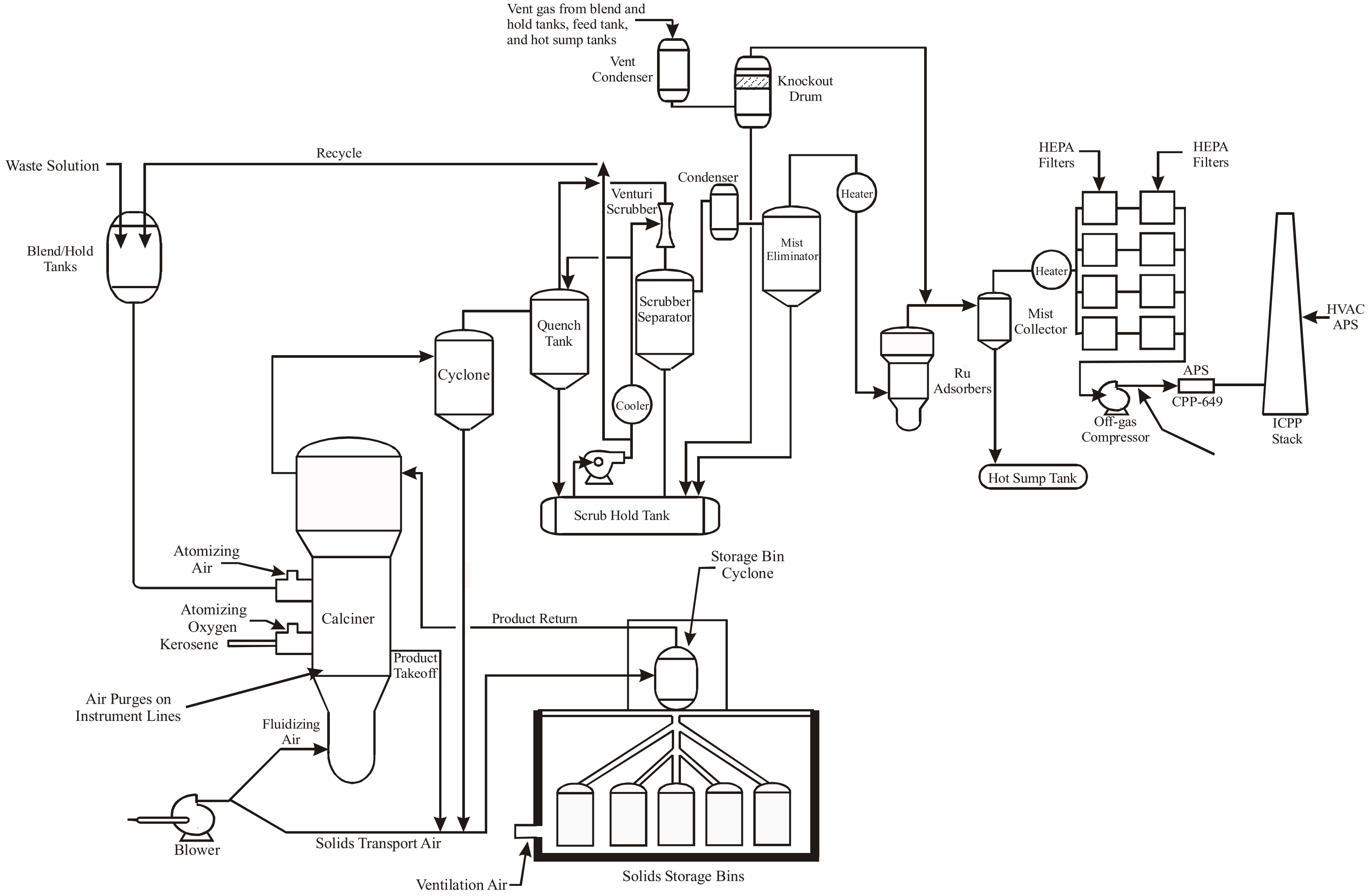
Trace elements in the wastes, including radionuclides, do not have a significant effect on the calcinability of wastes and are not included in this report. A detailed inventory of waste calcine produced by the WCF and NWCF has been prepared separately by M. D. Staiger (1999). Mr. Staiger also maintains a comprehensive file of data sources, such ICPP Production Monthly Reports.

In the calcination process, the liquid wastes are sprayed using pneumatic atomizing nozzles into a fluidized bed of heated spherical calcine particles. Until 1967, the fluidized-bed was heated to a calcination temperature of 400°C by re-circulating liquid eutectic sodium/potassium alloy through heat exchange tubes located in the bed. After 1970, heat input was changed to in-bed combustion (IBC) of kerosene fuel, sprayed directly into the bed through oxygen atomized fuel nozzles, and the calcination temperature was increased to 500°C. NWCF testing at 600°C with IBC was performed during April-June 1999 (Nenni et al. 2000 and Wood 1999) and during April-May 2000 (Swenson 2000).

At calcination temperatures, the water and nitric acid in the wastes are evaporated, leaving behind solid-phase metal compounds, mostly oxides, that form additional bed material. As the amount of solid bed material increases, the solids are drained batchwise from the calciner vessel (calcine product) and continuously from the off-gas primary cyclone (calcine fines). Both the product and fines are pneumatically transported to the Calcined Solids Storage Facilities (CSSFs), commonly known as the bin sets. The CSSFs provide interim storage of the calcine until final waste treatment for disposal in an approved high-level radioactive waste (HLW) repository.

The successful calcination of a given waste is dependent primarily on the major chemical constituents (greater than about 0.05 molar) and the concentration (or diluteness) of dissolved solids in the waste feed. It is also sometimes difficult to distinguish whether a feed failed due to chemistry or equipment problems. Dissolved solids concentration is the weight of calcine produced per volume of feed during calcination, and can be estimated from the feed composition by making assumptions about the compounds produced during calcination such as in Appendix G of Childs, Donovan, and Swenson (1982) and in O'Brien (1995). Waste which is difficult to calcine alone due to diluteness, inability to control particle size, or formation of agglomerates (e.g. sodium and potassium nitrate) could often be calcined as blends with more amenable wastes. The primary chemical additives used for calcination have been calcium nitrate to control halide volatility, and boric acid to promote amorphous alumina formation. Cold, non-radioactive aluminum nitrate has also been used as startup feed, as a diluent for sodium waste, and as an additive for dilute aluminum wastes. The calciner operating parameters are controlled to maintain an average particle size large enough to prevent excessive carry-over of particles and yet small enough to maintain adequate fluidization, and to maintain adequate level in the bed above the feed nozzles. Particle size is primarily controlled by adjusting the feed nozzle atomizing-air flow rate, but can also be affected by the fluidizing air rate and O2/Fuel ratio.

The calciners were equipped with similar offgas treatment systems to remove calcine fines and radioactive species from the calciner vessel offgas. Figure 1 shows a schematic of the NWCF calcination process, which is also representative of WCF. A hot cyclone separator removes much of the calcine fines from the offgas. The offgas is then rapidly cooled in a quench tower, and a venturi scrubber removes the majority of the remaining entrained fines. The scrub solution used in the quench tower and the scrubber contains 3-4 M nitric acid so fines are dissolved into solution. Aerosols from the venturi scrubber are removed in the scrubber separator and mist eliminator. Silica-gel bed adsorbers, designed to capture ruthenium, also serve as a prefilter for high efficiency particulate air (HEPA) filters. The offgas is reheated upstream of the HEPA filters. The calciner vessel and offgas system is maintained under a negative pressure using compressors to contain the radioactive material in the system.



NWCF Process wo.cdr

Figure 1. Schematic of the NWCF Calcination process.

COLD STARTUP OF THE WASTE CALCINING FACILITY

Information for the cold startup of the Waste Calcining Facility (WCF) from February 5, 1961 to November 21, 1962 is found in Lakey, Lohse, and Palica (1965). The startup consisted of 10 runs: the first run used water as feed to check out equipment and operational problems; the other runs used simulated $Al(NO_3)_3$-nitric acid waste to check out equipment, operational, and calcination flowsheet problems. In the various runs the feed composition for $Al(NO_3)_3$ was varied between 1.26 and 1.72 *M*, nitric acid composition between 0.44 and 2.49 *M* and sodium nitrate concentration between 0.036 and 0.172 *M*. Successful calcination flowsheets (as shown below) were employed in Runs 8 and 10.

Table 1. Successful flowsheets during cold WCF startup.

	Run #8 5/25-6/10/1962	Run #10 10/11-10/13/1962, 10/22-11/21/11962
$Al(NO_3)_3$ (*M*)	1.74	1.52
HNO_3 (*M*)	0.59	1.71
$NaNO_3$ (*M*)	0.038	0.036
Boric Acid (*M*)	0.01	0.0089
MMPD (mm)[a]	0.50 +0.20 –0.25	0.50±0.20
Bulk Density (g/cc)[a]	1.0 +0.48 –0.10	1.0 + 0.48 –0.09
NAR	300 between 5/25 and 6/24; 580 between 6/4 and 6/10	450 between 10/11, 10/13 and 10/29; 580 between 10/9 and 11/6; 650 between 11/6 and 11/21
Mole% Na	0.86	0.93
Solid Content (g/L)	92	81

a. Values are given as average and range.

Cold studies in the WCF confirmed Idaho Chemical Processing Plant (ICPP) laboratory and pilot plant studies and Stanford Research Institute theoretical considerations that the presence of $NaNO_3$ aids alpha alumina formation in the calcination of ICPP $Al(NO_3)_3$-HNO_3 waste, and the presence of the 0.01 to 0.06 *M* boric acid aids amorphous alumina formation and suppresses α-Al_2O_3 formation during the calcination of ICPP $Al(NO_3)_3$-HNO_3 waste (Newby et al. 1978b). The cold WCF studies showed that formation of amorphous Al_2O_3 is preferred over α-Al_2O_3 because: a) amorphous Al_2O_3 is less erosive to equipment than α-Al_2O_3 and produces less fines; b) fines from amorphous Al_2O_3 will dissolve in nitric acid, while α-Al_2O_3 fines did not; and c) an amorphous, Al_2O_3 product has a higher attrition resistance. WCF cold studies showed that the presence of 0.01 *M* H_3BO_3 in $Al(NO_3)_3$-HNO_3 waste feed would keep α-Al_2O_3 in calcined solids produced below 0.5% and undissolved solids (UDS) in acid scrub below 0.2wt%. It was thought that increasing the boric acid concentration in $Al(NO_3)_3$-HNO_3 feed to 0.05 *M* caused caking of aluminum around feed nozzle. Feed $NaNO_3$ concentration was not increased above 0.038 *M* when 0.01 *M* boric acid was present so it was not known at what $NaNO_3$ feed concentration that 0.01 *M* boric acid would cease effectively suppressing α-Al_2O_3 formation. At given operating conditions particle size decreased as bed α-Al_2O_3 content increased (decrease of particle size caused bed temperature to decrease with the NaK heating system due to reduced heat transfer). Bed α-Al_2O_3 concentration could be kept at 10-15% when the feed had a $NaNO_3$ concentration of 0.038 *M* (no boron present); increasing the feed $NaNO_3$ concentration to 0.060 *M* (no boron present) increased the α-Al_2O_3 content of the bed to 75%. In general when boric acid was present in $Al(NO_3)_3$-HNO_3 feed containing $NaNO_3$ being calcined as compared to the same feed without boron being calcined: dissolved aluminum concentration in acid scrub was higher, undissolved solids in scrub was less, and the acid in the scrub was used up more quickly. Bed properties for α-Al_2O_3 were: high bulk density, small particle size, low intra-particle porosity, and low nitrate content. The cold run in the WCF showed that nozzle atomizing-air to feed ratio

(NAR) could effectively control product size; size control became easier when the bed contained little or no α-Al_2O_3 (was essentially amorphous Al_2O_3). It was found that extremely fine solids (<200 microns) do not act as nuclei for particle growth.

WCF CAMPAIGN H-1

During this campaign (December 8, 1963 – October 15, 1964), the WCF calcined $Al(NO_3)_3$ wastes from WM-185, -187, and –183 without difficulty except for failure of bellows on 2 valves on acid scrub recycle to feed line. Composition of the principal feeds calcined from these wastes are shown in Table 2 through Table 4. About 5 ½ batches of feed from WM-180 (calcined in H-2 campaign where compositions are given) were calcined (waste with high ammonium concentration). Decided to calcine WM-180 waste in future campaign because scrub solution samples appeared milky and percent of undissolved solids began to increase; also, a potentially explosive compound, Mellons base, was possibly found in undissolved solids of the scrubbing system. It was later found that a synthetic Mellons base was stable at calcination and calcine storage temperatures (Rhodes 1973). Waste from WM-188 could not be calcined because the aluminum concentration was too low and bed height could not be maintained. Composition of WM-188 waste was: 1.08 $\underline{M}$ Al and 0.53 $\underline{M}$ H^+ (Commander et al. 1966).

Principal feeds calcined: WM-185 waste, WM-185 waste and acid scrub recycle, WM-187 waste plus concentrate from waste evaporator and first cycle raffinate from the BNL fuel processing run, WM-187 waste, WM-183 waste, WM-183 waste and acid scrub solution and hot sump tank solution, WM-183 waste and acid scrub solution and evaporated hot sump tank solution and non-evaporated hot sump tank solution. Solution from the waste evaporator and hot sump tank solution recycled to feed was made necessary by failure of bellows on 2 valves on the acid scrub recycle line. The first leak was from a valve in the off-gas cell. From February through most of August leaking solution was allowed to go through the cell floor drain to the hot sump tank, from which it was transferred to an evaporator to be evaporated down along with dilute waste from normal sources, and was finally transferred to WM-187. In late August leakage from valve in off-gas cell stopped and a second valve in the calciner cell leaked, the leak went down the cell drain to the hot sump tank. During part of the remaining campaign acid scrub solution and solution from the hot sump tank (unevaporated) was recycled to feed. During the rest of the campaign, acid scrubbing solution plus hot sump tank solution that had been evaporated plus hot sump tank solution that had not be evaporated was recycled to feed. Boric acid was present in all feed (0.01 $\underline{M}$ B) to prevent formation of α-Al_2O_3. Bed mass mean particle diameter (MMPD) ranged between 0.45 and 0.65 min. during the campaign; bulk density of bed between 0.94 and 1.21 g/cm^3. The calciner vessel was heated with coils of hot NaK inside the bed.

Table 2. Feed compositions with WM-185 H-1.

	WM-185	12/27/1963 to 1/26/1964	1/27/1964 to 2/26/1964	1/27/1964 to 2/26/1964	2/27/1964 to 3/26/1964		3/27/1964 to 4/26/1964	
H^+	0.59	1.58	1.86	0.56	0.94	0.56	0.56	0.93
Al	1.74	1.47	1.46	1.64	1.54	1.67	1.65	1.53
Hg	0.011	0.008	0.008	0.010	0.011	0.011	0.010	0.011
NH_4	0.059	0.042	0.041	0.056	<0.25	0.057	0.056	<0.25
B	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.008
Na	0.039	0.027	0.027	0.037	0.005	0.037	0.037	0.005
Si								
PO_4			Days filters lasted: 95, 100, 98, 93, 30					
SO_4								
NO_3	5.40	5.72	5.95	5.09	5.36	5.17	5.13	5.32

Table 3. Feed compositions with WM-187 during H-1.

	WM-187	Added 11,000 gal Conc. Scrub to WM-187	4/27/1964 to 5/26/1964	5/27/1964 to 6/26/1964	6/27/1964 to 7/26/1964	
H^+	0.98	1.04	0.90	0.94	0.98	0.77
Al	1.61	1.60	1.39	1.45	1.51	1.42
Hg	0.012	-	0.010	0.011	0.011	0.019
NH_4	<0.25	-	<0.25	<0.25	<0.25	<0.05
B	0.008	-	0.008	0.008	0.008	0.008
Na	0.005	-	0.004	0.005	0.005	0.047
NO_3	5.60	5.64	4.90	5.11	5.32	5.1`9
Si						0.002
PO_4						0.009
SO_4						0.012

Table 4. Feed compositions with WM-183 during H-1.

	WM-183	7/27/1964 to 8/26/1964	8/27/1964 to 9/26/1964	9/27/1964 to 10/26/1964
H^+	0.82	1.20	1.59	2.06
Al	1.5	1.39	1.33	1.26
Hg	0.020	0.017	0.015	0.013
NH_4	<0.05	<0.05	<0.05	<0.05
Na	0.05	0.04	0.04	0.03
B	-	0.008	0.008	0.008
Si	0.002	0.002	0.001	0.001
PO_4	0.010	0.008	0.007	0.007
SO_4	0.013	0.011	0.010	0.009
NO_3	5.50	5.51	5.72	5.98

Production monthly reports that cover the first campaign are No. 45 (Ayers 1964a) to No. 55 (Ayers 1964b). Original waste compositions were obtained from Lakey (1962).

WCF CAMPAIGN H-2

During Campaign H-2 it was difficult to calcine aluminum nitrate waste containing 0.76 to 1.05 M NH_4NO_3:

A) Bed-level dropped to 3 to 4" above the feed nozzles (usually ~6 to 8" above nozzles) and remained there despite all efforts to raise the level. Had to operate with product take-off closed. All product (as fines) was elutriated to off-gas and separated by the primary cyclones (Ayers 1966b).

B) Off-gas filters would become plugged and have to be changed in less than 30 days (Ayers 1966d. Filters usually last 90 to 100 days. Alternating a feed high in ammonium ion with one having no or a small amount of ammonium (a waste containing no ammonium ion to which off-gas acid and scrub had been recycled) reduced product elutriation to an acceptable level, allowed control of bed height, and increased filter life from 48 to 100 days (Ayers 1966d; Lakey 1962). The number of feed batches of waste high in ammonium alternated with a given number of feed batches low in ammonium varied. This probably meant that feed batches high in ammonium nitrate would be changed to feed batches low in ammonium nitrate whenever maintaining bed height became a problem. Size of bed particles varied between 0.47 and 0.75 mm; bulk density of bed particles varied between 0.71 and 1.30 g/cm^3.

Blending feeds so that the feed was low in ammonium nitrate seemed to keep off-gas filter plugging down but did not seem to be as effective in reducing fines carryover as alternating feeds high in ammonium nitrate concentration with those low ammonium nitrate concentration. Bed level was easier to maintain and fines carryover less noticeable when feed was blended resulting in reducing the feed ammonium concentration from 0.42 to 0.22 M; the same blending increased feed sodium concentration from 0.074 to 0.16 M which may also have caused the desired effect (Amberson 1967a). Boric acid was present in all feed to promote formation of amorphous alumina. Aluminum feed compositions are shown in Table 5.

Feeds calcined included: a) WM-183 with and without acid scrub recycle; b) WM-183 concentrated with acid scrub recycle; c) WM-182 with and without acid scrub recycle; d) WM-180 (contains ammonium nitrate) with and without acid scrub recycle, e) WM-180 concentrated plus acid scrub recycle; f) blends of WM-186, WL-101, WM-185, and WM-182 unconcentrated or concentrated plus acid scrub recycle; g) blends in f) plus waste materials from WM-100, WM-101, and WL-101; and h) blends of WM-180 and WM-182 concentrated and unconcentrated plus acid scrub recycle. The acid scrub recycle rate averaged ~25% of the calciner feed rate when calcining diluted feed. When calcining concentrated feed, the recyle rate was reduced to ~15%. Ammonium concentration in acid scrub varied between 0.11 and 0.6 M. WCF second processing campaign lasted between April 1, 1966 and March 24, 1968. The WCF used the direct heating NaK system during this campaign.

Hot Zr waste tank WM-188 was also calcined during the second WCF campaign between November 13, 1967 and February 26, 1968. In general the operation was smooth, but much time was expended in determining operating parameters for controlling product size. MMPD varied between 0.39 and 1.02 mm with the typical size being between 0.60 and 0.80 mm, bulk density varied between 1.29 and 1.88 g/cm^3. High efficiency particulate air (HEPA) filters on off-gas line lasted a satisfactory period of time (~100 days). For a while the product take-off line did not operate properly and product was removed through a valve in the calciner vessel but began working because of no apparent reason (the reason the drain line did not work was not apparent either). There was plugging in the inlet of the venture scrubber which could temporarily be removed by treatment with 13 M HNO_3. Solids carry over to acid scrub system was higher than expected.

The only composition of the Zr waste from Tank WM-188 calcined during the second WCF campaign that could be found was in Lohse and Hales (1970). This composition is in Table 6. The composition is described as a typical composition; the waste must have already been diluted by $Ca(NO_3)_2$ solution because a calcium concentration was given in Lohse and Hales (1970); the aluminum concentration seems to be unreasonably high based on compositions given for the waste in Tank WM-188 calcined during Campaign H-3.

Table 5. Aluminum feed compositions calcined during WCF H-2.

Constituents (*M*)	WM-183	WM-182	WM-180	Blend	Blend	Blend	Blend	Blend	Blend	Blend
Al	1.5	1.62-1.68	1.59-1.63	1.44-1.48	1.53	1.70	1.80	1.65	1.70	1.52
H^+	0.82	1.16-1.18	0.07-0.16	1.09-1.26	1.91	1.34	1.32	1.31	1.17	1.30
NH_4^+	Not present	Not present	1.05	0.76-0.82	0.08	0.51	0.24	0.42	0.22	0.39
Na	0.05	0.096-0.11	0.018	0.026-0.03	0.10	0.07	0.10	0.074	0.16	0.11
Hg	0.02	0.018-0.019	0.012-0.014	0.014-0.015	0.019	0018	0.020	0.017	0.015	0.008
B	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.008
Si	0.002									
NO_3	5.5	6.2	6.0	6.4	6.7	7.0	7.1	6.8	6.6	6.4
PO_4	0.01									
$SO_4^=$	0.01									

References: Lakey 1962; Ayers 1966a; Ayers 1966b; Ayers 1966c; Ayers 1967a; Ayers 1967b; Amberson 1967a and Amberson 1967b

Table 6. Typical composition of Zr waste calcined during Campaign H-2.

Component	Concentration
Zr, *M*	0.3
F, *M*	2.3
Al, *M*	0.7
$NaNO_3$, *M*	0.05
Boric Acid, *M*	0.02
$Ca(NO_3)_2$, *M*	1.2
Acid, *M*	1.5

WCF CAMPAIGN H-3

During this campaign (August 14, 1968 through June 3, 1969) Zr wastes from WM-188 and 189 plus acid scrub plus $Ca(NO_3)_2$ solution were calcined for most of the time, and Al waste from WM-185 plus acid scrub and boric acid solution was calcined for one week. This campaign is covered in CPP Production Monthly Report No. 101 (Amberson 1968) through No. 111 (Amberson 1969) and a report on the Third Processing Campaign of WCF (Bendixsen, Lohse, and Hales 1971). Compositions of wastes calcined were calculated from WM tank waste compositions found in CPP production monthly reports and/or the campaign report, (Bendixsen, Lohse, and Hales 1971) volumes of various solutions put in a feed make-up tanks found in the Monthly Production Reports, and recycle acid scrub solution compositions from WCF Run H-3 daily reports. The blended feed compositions are shown in Table 7 and 8. In making these calculations it was assumed that carry-over and dissolution of all fines compounds in acid scrub solutions were the same as for the Al_2O_3 in the product.

Control of particle size was done mostly by using the waste NAR, but when MMPD approached 1.0 mm water was inserted into bed through 1 of 3 nozzles or feed was diluted with water in the feed makeup or WM tank. During Campaign H-3 MMPD varied between 0.54 and 0.93 mm and the bulk density between 1.19 and 1.80 g/cm^3 for Zr waste calcine. In both the second and third campaigns a NAR of 750 to 800 was required to maintain a stable particle size (0.6 to 0.8 mm) when calcining Zr-type waste as compared to a NAR of 400 to 550 required for Al-type waste (stable size of 0.56-0.70 mm). Dilution of the salt concentration in WM-188 by decontamination solutions and surface water collected from the sump in the permanent storage tank vault enclosure lowered the fluoride concentration in WM-188 from its original value. This dilution resulted in an excess of $Ca(NO_3)_2$ (Ca/F mole ratio of 0.75) added to the feed during 6 weeks of operation. This excess caused the changes noted in the footnote of Table 7 plus an abnormally high carryover of solids to the quench tower from the cyclone. The problem was corrected by correcting the fluoride concentration of WM-188 and adding a Ca/F mole ratio of 0.55 to calciner feed. Calcine product having NO_3^- concentration of 15% required a NAR of 620 while solids having a nitrate composition of 1% required a NAR of 770.

Size of particles could not be controlled from calcining WM-189 waste by using only NAR (if a decent feed rate was maintained). Size was controlled by adding water to the bed through 1 of 3 nozzles (reduced feed rate to an unacceptable level) or adding water to a feed makeup tank or WM tank.

During calcination of WM-189 waste the solids transport system and calciner cyclone progressively showed a poorer performance. These problems were attributed to high nitrate content of calcine solids (21 wt%). High nitrate content of calcine indicated excess calcium in calciner feed stream which originated from the dolomite initial start-up bed used (contained $CaCO_3$). The fines carried to the quench system being largely dolomite in composition resulted in a recycle rich in calcium. When this stream was blended with calciner feed already containing a Ca/F mole of 0.55 resulting in calciner feed enriched with Ca. The excess calcium remained in the calciner bed in the nitrate form. This was solved by calcining $Al(NO_3)_3$ waste for about one week.

The WCF used NaK circulated through coils in the bed to heat the bed during H-3.

Table 7. Waste blends calcined during WCF Campaign H-3.

	Zr Waste WM-188				Zr Waste WM-189	Zr Waste WM-189
Constituents ($\underline{M}$)	1/16 – 1/26/1969, 8/14 – 11/12/1968	12/13 – 12/26/1968	12/27 – 1/15/1969[a]	1/16 – 1/27/1969	1/27 – 2/5/1969[b]	2/6 – 2/19/1969[c]
H^+	1.04-1.96	1.24	1.45	1.04	1.61	1.29
Al	0.36-0.44	0.31	0.33	0.35	0.37	0.30
B	0.077-0.093	0.078	0.082	0.089	0.10	0.080
Ca	0.76-0.92	0.89	0.94	0.74	1.03	0.82
Zr	0.18-0.22	0.16	0.16	0.18	0.22	0.18
Fe	0.003-0.004	0.004	0.004	0.005	0.003	0.002
K	0.002	0.002	0.002	0.002	0.001	0.001
F	1.39-1.67	1.19	1.25	1.35	1.87	1.50
NO_3	2.81-3.96	3.31	3.50	2.80	3.83	3.06

	Zr Waste WM-189	Zr Waste WM-189	WM-189 Zr Waste	WM-185 Al Waste[f]
Constituents ($\underline{M}$)	2/20 – 2/26/1969[d]	2/27 – 3/6/1969[e]	3/7 – 3/19, 3/27-4/3, 4/27 – 6/4/1969	4/13 – 4/10/1969
H^+	1.45	1.49	1.72-1.85	0.74
Al	0.33	0.34	0.36-0.41	0.96
B	0.090	0.092	0.081-0.93	
Ca	0.93	0.95	0.65-0.74	
Zr	0.20	0.20	0.17-0.20	
Fe	0.003	0.003	0.003	
K	0.001	0.001	0.001	0.019
F	1.68	1.73	1.18-1.35	
NO_3	3.45	3.54	3.38-3.75	3.62

a. Ca/F mole ratio too high (~.75): problems in keeping MMPD from getting too small; NO_3 content in product increased from ~2 to 17 wt%; probable agglomeration in bed (difficulty in removing bed from calciner vessel), plugging of cyclone display jet followed by an increase in fines carry-over to the scrub system, MMPD at a given NAR and feed rate becomes smaller.

b. When calcining this feed MMPD could not be controlled with a NAR of 920 using a feed rate of 95 gph (maximum NAR possible at that feed rate). Particle size controlled at NAR of 920 by diluting feed with 20 vol% waste (over kill). Later used ~ 7 ½ vol% dilution factor.

c. Using 20 vol% dilution factor.

d. Using 10 vol% dilution factor.

e. Using 7 ½ vol% dilution factor.

f. The composition of this waste comes from Bendixsen, Lohse, and Hales (1971). In Campaign H-1 (WCF) an Al waste containing 1.08 $\underline{M}$ Al was too low in Al concentration to maintain bed height. The WM-185 waste must not have been calcined for a long enough period for failure to maintain bed height to matter.

Table 8. First cycle Zr waste calciner feeds successfully calcined during WCF Campaign H-3 (August 14, 1968 – June 3, 1969).

Constituents (*M*)	WM-188 8/14 – 8/ 26/1968	WM-188 8/27 – 9/26/1968	WM-188 9/27 – 10/26/68	WM-188 10/27 – 11/12/1968	WM-188 1/16 – 1/26/1969	WM-189 3/7 – 3/19/1969	WM-189 3/27 – 4/23/1969 and 4/11/ - 4/26/1969	WM-189 4/27 – 5/26/1969	WM-189 5/27 – 6/4/1969
H^+	1.86	1.56	1.78	1.96	1.24	1.77	1.91	1.88	1.82
Al	0.41	0.44	0.37	0.36	0.35	0.37	0.41	0.40	0.36
B	0.086	0.093	0.079	0.077	0.089	0.084	0.093	0.091	0.082
Ca	0.86	0.92	0.79	0.076	0.089	0.084	0.75	0.73	0.66
Zr	0.20	0.19	0.18	0.18	0.18	0.18	0.20	0.20	0.18
Fe	0.0034	0.0028	0.0031	0.0030	0.0046	0.0031	0.0035	0.0034	0.0031
K	0.002	0.002	0.002	0.002	0.002	0.0013	0.0014	0.0014	0.0012
F	1.56	1.67	1.43	1.39	1.35	1.22	1.36	1.32	1.19
NO_3	3.97	3.74	3.75	3.27	2.79	3.46	3.81	3.72	3.46

WCF CAMPAIGN H-4

During Campaign H-4 (August 3, 1970 through January 5, 1971), the WCF calcined first cycle Zr waste from WM-187 and WM-189 (plus acid scrub recycle). $Al(NO_3)_3$ waste from WM-183 was also calcined for a short period of time. This was the first campaign using in-bed combustion.

The Zr waste was calcined successfully using in-bed combustion to heat the bed. The greatest problem was to keep bed height and particle size from decreasing. The campaign was begun using Zr waste from WM-189 (plus recycled acid scrub) but bed level decreased continually, so after 1 day of operation, WCF calcined waste from WM-187 (plus recycled scrub) which was a more concentrated waste then WM-189 in hopes of improving solid production. Finally one fuel and one feed nozzle (upper ones) was removed (taken off-line) and bed level increased. Efforts to increase MMPD also failed; MMPD stabilized at a value of 0.40 to 0.44 mm. Increasing MMPD was tried using waste from WM-187 by: a) reducing feed nozzle atomizing air to 700 scfh; b) lowering bed temperature from 500 to 475^oC; c) decreasing air fluidizing air flow to 155 scfh (0.65 ft/sec superficial velocity); d) minimizing oxygen flow to fuel nozzles; and e) operating 92 h on hot Al waste from WM-183. During this period MMPD of bed material ranged between 0.33 and 0.45 mm.

In prior runs, the normal NAR operating value of Al waste to control MMPD at 0.6 mm was 600; this value for Zr waste was ~750. In the 4th campaign, the NAR was reduced to ~180 to stabilize the size near 0.4 mm. The reason for such a low NAR is believed to be bed particle attrition caused by the fuel nozzle. Run H-4 is described in ICPP Monthly Production Report No. 125 (Amberson 1970) through No. 130 (Amberson 1971a)**,** and Wielang, Lohse, and Hales (1972).

Calciner feed compositions calcined during 4th campaign were calculated using following assumptions and/or information: a) volumes of various solutions put in feed make-up tanks were found in ICPP Monthly Production Reports No. 125 through No. 130 (Amberson 1970 through Amberson 1971a)**;** b) WM-187 waste composition used was found in Rhodes (1972); c) the latest composition for WM-189 waste that could be found was a March 1969 analyses found in Bendixsen, Lohse, and Hales (1971) (waste had been added to WM-189 between March 1969 and August 1970), d) the only analyses for WM-183 waste found was in Lakey (1962) and waste had been both removed from and added to WM-183 between December 1962 and August 1970; and e) no daily reports could be found for WCF Run H-4; the H^+ and Al concentrations of acid scrub recycle used in calculating Run H-4 calciner feeds was the average H^+ and Al concentrations of scrub recycle solutions from WCF Run H-5 daily reports over periods in Run H-5 where $Ca(NO_3)_2$ was added to Zr feed (diluted with acid scrub recycle) as a concentrated solution (appropriate daily reports over period September 1971 through January 1972); it was assumed that the carry-over of and dissolution of all fines' constituents in acid scrub solutions were the same as for Al_2O_3.

The latest composition that could be found for the $Al(NO_3)_3$ waste in WM-183 is in Table 9. This waste was calcined for 92 h in the period August 27 through September 26, 1970.

The composition of Zr calciner feeds calcined during WCF Run H-4 are given in Table 10.

Table 9. Composition of $Al(NO_3)_3$ waste in WM-183 as of 1960.

H^+ (N) Acid	0.82
Al (*M*)	1.5
Hg (g/L)	4.11
NH_4 (*M*)	<0.05
Ru (g/L)	0.034
NO_3 (*M*)	5.5
Fe (g/L)	0.29
Cl (g/L)	<0.005
Te (g/L)	0.008
Mo (g/L)	0.079
Na (g/L)	1.15
Si (g/L)	1.15
PO_4 (g/L)	0.97
SO_4 (g/L)	1.24

Table 10. WCF Campaign H-4 August 3, 1970 through January 5, 1971 in-bed combustion.

	First Cycle Zr Waste Calciner Feeds Successfully[a] Calcined (Waste from WM-187; Concentrations in Molar)			
	8/8 – 8/26/1970	8/27 – 9/26/1970	9/27 – 10/26/1970	11/27 – 12/26/1970
H^+	1.46	1.20-1.46	1.25	1.26
Al	0.52	0.42	0.44	0.45
B	0.15	0.12	0.13	0.13
Ca	1.33	1.08	1.51	1.15
Zr	0.36	0.29	0.30	0.31
Fe	0.003	0.0026	0.0028	0.0028
Na	0.0021	0.0017	0.0018	0.0018
F	2.43	1.97	2.75	2.09
NO_3	4.44	3.59	5.37	3.83
Cl	0.00027	0.00022	0.00023	0.00024

a. Had to remove “A” fuel and feed nozzle before bed level increased even when using WM-187 waste. Eventually put “A” nozzles back in service again using WM-187 waste and bed level was okay; perhaps hadn’t adjusted other operating parameters to suitable values during first part of run.

Table 11. WCF Campaign H-4 August 3, 1970 through January 5, 1971 in-bed combustion.

First Cycle Zr Waste Calciner Feed Which Didn't Contain Enough Dissolved Solids to Build Bed[a] (Waste from WM-189) August 3 – August 7, 1970	
H^+	1.35
Al	0.44
B	0.10
Ca	0.80
Zr	0.22
Fe	0.0038
K	0.0015
F	1.46
NO_3	3.42

a. Had to remove "A" fuel and feed nozzle before bed level increased even when using WM-187 waste. Eventually put "A" nozzles back in service again using WM-187 waste and bed level was okay; perhaps hadn't adjusted other operating parameters to suitable values during first part of run.

WCF CAMPAIGN H-5

During Campaign H-5, the WCF calcined first cycle Zr waste from WM-189 (plus acid scrub recycle), first cycle $Al(NO_3)_3$ waste from WM-183 (plus acid scrub recycle), and stainless steel sulfate waste (plus acid scrub recycle).

The concentrations of WM-183 and WM-189 wastes used in feed calcinations were those given from WCF Campaign H-6, thus, feeds calculated would be only approximate because wastes were added to tanks WM-183 and –189 during WCF Campaign H-5 and between Campaigns H-5 and H-6. Also in making these calculations: a) volumes of various solutions put in feed make-up tanks were found in monthly production reports No.138 (Amberson 1971b) through No. 186 (Amberson 1972b); b) the H^+ and Al concentrations of acid scrub recycle solutions were found in WCF Run H-5 daily reports; and c) it was assumed that the carry-over of and dissolution of all fines constituents in acid scrub solutions were the same as for Al_2O_3 (roughly true based on 12" calciner pilot plant runs).

Stainless steel sulfate waste was tested twice unsuccessfully during the last part of the H-5 Campaign as a blend with $Al(NO_3)_3$ using an Al/SO_4 mole ratios of 0.73 and 1.2 during the first attempt (increased the Al^+ concentration to stabilize bed) and an Al/SO_4 mole ratio of 1.2 during the second attempt (the sulfate waste was added to an Al_2O_3 bed). During both attempts the WCF had to be shut down within a few days due to high pressure drops across the final HEPA filters. The blend compositions are given in Table 12 and the MMPD varied from 0.50 – 0.65 mm, NAR from 170 – 482, and bulk density from 1.34 – 1.49 g/cc. $Al(NO_3)_3$ was added to the stainless-steel sulfate waste to inhibit sulfate volality.

During Run H-5, adding $Ca(NO_3)_2$ to Zr waste as a solid rather than as a saturated aqueous solution was successfully calcined. Zr feed calcined successfully in Campaign H-5 is shown in Table 12 and was only slightly more concentrated in dissolved solids than the zirconium feed calcined unsuccessfully in first part of Campaign H-4 (wouldn't build bed). Perhaps proper operating parameters hadn't been determined yet for the in-bed, fluidized-bed calcination of Zr feed when calcining the earlier Zr feed. During zirconium feed calcination, the MMPD was 0.22 – 0.50 mm, NAR was 168 – 293, and bulk density was 1.42 – 1.66 g/cm^3.

$Al(NO_3)_3$ waste calcined on January 28 through January 29, 1972 contained such a small amount of dissolved solids that the bed was elutriated at a higher rate than it could be formed even when adding ~0.7 mm Dolomite bed material to calciner vessel. Bed was not made until the $Al(NO_3)_3$ waste was switched to Zr feed, yet during the last part of Campaign H-5, an $Al(NO_3)_3$ waste having only slightly more solids than the previously calcined $Al(NO_3)_3$ waste was calcined 31 days and built bed during that time. When bed couldn't be built in Campaign H-5: MMPD = ~0.36 mm, bulk density = ~1.49 g/cc, and NAR = ~345. When bed could be built: MMPD = 0.56 – 0.77 mm; bulk density. = 1.14 – 1.37 g/cc and NAR = 359 – 545. This successful calcined $Al(NO_3)_3$ feed appeared to have created excessive fines because the pressure across the WC-912 solids storage cyclone increased after the cyclone was unplugged and after an electric heater was installed in the cyclone vault to prevent moisture in the transport air stream from condensing and caking solids inside WC-912 cyclone.

Average final HEPA filter on-stream time for each filter was 9 days in the five campaign and 69 days for the fourth campaign which may have been due to the dilute feeds processed in the fifth campaign which produced more fines.

Between WCF Campaigns H-5 and H-6, to 106,600 gallons of WM-183 aluminum waste was added: 6,900 gallons of possibly decon solution, 2,900 of possibly first cycle Al waste, and 41,000 gallons of first cycle stainless steel nitrate waste. During WCF Campaign H-5 there were only 2 WM tanks containing High Level $Al(NO_3)_3$ wastes (WM-180 and –183). Letters dated shortly after Campaign H-5 (Wielang 1972; Newby 1972a; Newby 1972b) give the approximate compositions of Al raffinates as 1.16 $\underline{M}$ Al, 0.99 $\underline{M}$ H^+, and 4.6 $\underline{M}$ NO_3. These results agree more with Campaign H-1 results than results previously given for Campaign H-5 $Al(NO_3)_3$ feeds. The feed used on January 28 through January 29, 1972 could not be calcined and was more dilute in Al concentration than $Al(NO_3)_3$ feed that could not be calcined during Campaign H-1. The other two campaign H-5 $Al(NO_3)_3$ feeds that could be calcined were more concentrated in Al concentration than Campaign H-1 feed that couldn't be calcined.

Table 12. WCF Campaign H-5 September 23, 1971 to May 11, 1972 in-bed combustion.

	1st Cycle Zr Waste Calciner Feeds Successfully Calcined[a] (Waste from WM-189, Concentrations in Molar except where otherwise noted)					
	9/23 – 9/26/1971	9/27 - 10/26/1971	10/27 - 11/26/1971	11/27 - 12/26/1971	12/27/1971-1/3/1972 1/23-2/23/1972	1/29 – 2/23/1972
H^+	1.33	1.13	1.16	1.16	1.28	1.38
Al	0.47	0.34	0.34	0.34	0.36	0.40
B	0.11	0.10	0.10	0.10	0.11	0.12
Ca	0.93	0.84	0.85	0.84	0.90	0.97
Zr	0.23	0.20	0.21	0.20	0.22	0.23
Fe (g/L)	0.23	0.20	0.21	0.20	0.22	0.23
F	1.69	1.53	1.54	1.53	1.64	1.75
NO_3	3.78	3.06	3.14	3.12	3.36	3.33

a. Compositions are based on WCF Campaign H-6 values for WM-189 from G. W. Pelletier that have not previously been published.

Table 13. Stainless steel sulfate wastes (not successfully calcined).

	5/3 – 5/5/1972	5/10 – 5/11/1972
H^+ *M*	2.49	2.30
Al *M*	0.47	0.60
B *M*	0.03	0.03
Cr *M*	0.014	0.013
Ni *M*	0.007	0.006
Fe *M*	0.05	0.04
NO_3 *M*	3.44	3.68
SO_4 *M*	0.38	0.35

Table 14. Aluminum Nitrate wasted calcined (waste from WM-183).

	Not Successfully Calcined[a]	Successfully Calcined[b]	
	1/28 – 29/1972	3/28 – 4/15/1972 4/10 – 4/26/1972	4/26 – 5/3/72
H^+ *M*	1.41	1.08	0.95
Al *M*	0.97	1.22	1.09
NO_3 *M*	4.43	4.86	4.31
B *M*	0.008	0.008	0.008

a. Because of dilute nature of this waste, when calcined, fluidized bed in the calciner was elutriated at a higher rate than it could be formed. Dolomite startup bed material was added to the calciner vessel in an effort to stabilize the bed level but it wasn't stabilized until the calciner switch to first cycle Zr waste.

b. Successfully calcined feed may have created excessive fines because the pressure across the WC-912 solids storage cyclone increased even after the cyclone was unplugged and an electric heater was installed in the cyclone vault to prevent moisture in the transport air stream from condensing and caking solids inside the WC-912 cyclone.

WCF CAMPAIGN H-6

During Campaign H-6 (May 25, 1973 to May 8, 1974), the WCF calcined: first cycle Zr waste from tanks WM-188 and –189 (plus acid scrub recycle); first cycle $Al(NO_3)_3$ waste from WM-183 (plus acid scrub recycle); and blends of first cycle Zr waste and stainless steel sulfate waste (plus acid scrub recycle). The assumption made to calculate feed compositions calcined during Campaign H-6 are explained in the following 3 sections describing calcination of each of the 3 different types of wastes calcined during Campaign H-6.

The trouble encountered in calcining Zr waste from tank WM-189 was that it was too dilute and there was trouble maintaining bed level. Eventually a more concentrated waste (WM-188 waste) was added to the waste in tank WM-189 and the blend was calcinable.

The $Al(NO_3)_3$ waste in WM-183 was quite dilute and had to be concentrated before it could be calcined over long periods of time. The $Al(NO_3)_3$ waste in tank WM-183 was a blend with stainless steel nitrate waste, and the presence of constituents from the latter waste was blamed for more fines being produced than usual.

Blends of Zr stainless steel sulfate waste were successfully calcined ranging from 6.4 to 5 volumes Zr waste per 1 volume steel waste. After successfully calcining stainless steel sulfate waste as a blend with Zr waste, all the stainless steel sulfate waste was transferred to two 300,000 gallon tanks containing first cycle Zr waste (18,800 gallon to tank WM-188 and 18,000 gallons to tank WM-189) (Amberson 1974d).

First Cycle Zirconium Waste Calcined During WCF Run H-6 (WM-188 and WM-189 Wastes)

The compositions used for WM-188 and –189 feeds calcined in the WCF prior to adding waste in WM-188 to wastes in WM-189 are based on WCF H-6 values from G. W. Pelletier that have not previously been published. The approximate composition of the first cycle Zr waste calcined from tank WM-189 after WM-188 waste had been added to the waste in tank WM-189 was calculated using the compositions for each waste, the volume of WM-188 waste added, the volume of WM-189 waste, plus the jet dilution experienced during the operation found in Amberson (1973f). The composition of the combined wastes in WM-189 is given in Table 16.

WM-189 waste apparently was too dilute (didn't contain enough dissolved and undissolved solids) to build bed and maintain bed height and was calcined for short periods of time before switching to WM-188 waste which was sufficiently concentrated in dissolved and undissolved solids to build bed and maintain bed height. Finally, when WM-188 waste was combined with WM-189 waste, the combined wastes were sufficiently concentrated in dissolved and undissolved solids to build bed and maintain bed height. During calcination of Zr feed:

MMPD = $0.46^{+0.50}_{-0.15}\,mm$ (average and range of 60 samples)

Bed bulk density = $1.49^{+0.14}_{-0.30}$ g/cc (average and range of 60 samples)

NAR = 1.54^{+200}_{-57} (average and range of 97 determinations)

Table 15. First cycle zirconium waste calcined during WCF Run H-6 (WM-188 and WM-189 wastes).[a]

Constituents	WM-188 and –189 Wastes Combined in Tank WM-189	WM-189 Feed Calcined Unsuccessfully during 5/25-5/31/1973	WM-188 Feed Calcined Successfully 6/5-25/1973	WM-188 Calcined Successfully 7/25-8/11/1973	WM-188 Feed Calcined Successfully 8/2-26/1973
H^+ (*M*)	1.65	1.11	1.20	1.20	1.15
Al (*M*)	0.52	0.39	0.42	0.42	0.42
B (*M*)	0.17	0.11	0.14	0.14	0.14
Ca (*M*)		0.83	1.14	1.16	1.15
Zr (*M*)	0.36	0.22	0.28	0.28	0.28
Fe (g/L)	0.36	0.22	0.28	0.28	0.28
F (*M*)	2.84	1.52	2.07	2.10	2.09
NO_3 (*M*)	2.21	3.54	4.18	4.18	4.20

a. Volumes of various process streams used to calculate feed compositions are those found in ICPP Monthly No. 159 (Amberson 1973e) to No. 166 (Amberson 1974a). Compositions of recycle streams were from the WCF Run H-6 "Daily Reports."

Table 16. First cycle zirconium waste calcined during WCF Run H-6 (WM-188 and WM-189 wastes).*

Constituents	WM-188 Feed Calcined Successfully 8/27-9/16/1973	Combined WM-188 and -189 Feeds Calcined Successfully 10/25-11/26/1973	Combined WM-188 and –189 Feeds Calcined Successfully 11/27-12/3/1973 12/11-12/26/1973	Combined WM-188 and –189 Feed Calcined Successfully 12/27/1973-1/16/1974
H^+ (*M*)	1.18	1.08	1.15	1.22
Al (*M*)	0.40	0.37	0.40	0.40
B (*M*)	0.14	0.12	0.12	0.13
Ca (*M*)	1.14	0.98	0.99	1.10
Zr (*M*)	0.27	0.23	0.24	0.26
Fe (g/L)	0.27	0.23	0.24	0.26
F (*M*)	2.08	1.78	1.80	1.99
NO_3 (*M*)	4.10	2.91	3.73	3.98

Aluminum Nitrate Waste Calcined During WCF Run H-6 (WM-183 Waste)

To 106,600 gallons of WM-183 first cycle aluminum raffinate waste, between Campaign H-5 and H-6, was added: 6,900 gallons of possible decon solution; 2,900 gallons of possible first cycle Al waste; and 41,000 gallons of first cycle stainless steel nitrate waste (Amberson 1972c; Amberson 1972d; Amberson 1972e; Amberson 1973a; Amberson 1973b; Amberson 1973c; Amberson 1973d). Assuming that the composition of WM-183 waste and stainless-steel nitrate waste prior to the above additions to WM-183 was that given in Bower (1974) Table XI and assuming that assuming that the $Al(NO_3)_3$, and H^+ composition for WM-183 waste provided by G. W. Pelletier for WCF H-6 was after the above additions, then the composition of WM-183 waste and blended feeds would be roughly as shown in Table 17.

Table 17. Aluminum nitrate waste calcined during WCF Run H-6 (WM-183 waste).

Constituents (*M*)	WM-183 Waste	WM-183 Feed Calcined during 5/27-6/26/1973, 6/20-26/1973, 7/20-8/1/1973	WM-183 Feed Calcined during 4/10-26/1974	WM-183 Feed Calcined during 4/27-5/8/1974
Al	0.80	1.28	1.24	0.98
Cr	0.011	0.016	0.015	0.010
Ni	0.0045	0.0064	0.0060	0.0041
Fe	0.041	0.058	0.055	0.038
Na	0.004	0.0056	0.0054	0.0037
Gd	0.0029	0.0041	0.0039	0.0027
NH_4	0.018	0.025	0.024	0.017
Mo	0.0014	0.0019	0.0019	0.0013
Ru	0.00025	0.00036	0.00034	0.00023
H^+	1.0	1.40	1.34	0.90
NO_3	1.7	3.16	3.23	2.78
B	-	0.008	0.008	0.008

Most of the time WM-183 waste was concentrated prior to transferring it to the feed blend tank. Between March 28 and April 19, 1974, when calcining concentrated WM-183 waste, the off-gas final filters had to be changed out frequently, and material removal from the filters turned out to be ammonium magnesium aluminum fluoride hydrate. WM-183 waste was never analyzed for magnesium, but small amounts of ammonium and fluoride were present. The calciner gross feed rate was reduced from ~125 to 75 gph, and this stopped the need for frequent filter changeouts. During the period between April 26 and May 8, there was high solids carryover to the scrubbing system and plugging of the transport air return line and the solids storage cyclone. An X-ray diffraction analysis of the bed material showed a substantial amount of alpha and gamma alumina present. It was suggested that the greater than normal fines generation was caused by the presence of alpha and gamma alumina and that components present in the electrolytic waste (which had been added to WM-183 waste) probably caused the shift from amorphous to the crystalline alumina species (Amberson 1974c). It is more likely that the greater than normal fines generation rate was caused by the insufficient dissolved solids content of the WM-183 waste (<1.0 *M* Al). During calcination of Al feed

MMPD = $0.66^{+0.19}_{-0.12}\,mm$ (average and range of 11 samples)

Bed bulk density = $1.24^{+0.05}_{-0.05}$ g/cm^3 (average and range of 11 samples)

NAR = 154^{+212}_{-75} (average and range of 27 determinations)

Blends of First Cycle Zirconium Waste and Stainless Steel Sulfate Waste Calcined During WCF Run H-6

Between January 16-30, 1974 a blend of ~6.4 vol. Zr from WM-189 (actually a blend of WM-188 and WM-189 wastes) and 1 vol. stainless steel sulfate waste was successfully calcined; between January 31, 1974 and February 6, 1974 a blend of ~5 vol. Zr waste from WM-189 (actually a blend of WM-188 and WM-189 wastes) and 1 vol. stainless steel sulfate waste was successfully calcined. The approximate concentrations of feeds calcined are in Table 18. In making these calculations: a) the approximate composition of first cycle Zr waste calcined from WM-189 after WM-188 waste had been added to the waste in tank WM-189 was calculated using the composition of each waste from WCF H-6 data from G. W. Pelletier and using the volume of WM-188 waste added to the volume of WM-189 waste plus the jet dilution experienced during this operation found in Amberson (1973f); b) the composition of stainless steel sulfate waste is the that found in Newby et al. (1978b); c) volumes of various process streams used to calculate feed compositions are those found in Amberson (1974a) and Amberson (1974b); and d) compositions of recycle streams were from the WCF H-6 “Daily Reports”. During calcination of blends of first cycle zirconium feed and stainless steel sulfate feed

MMPD = $0.43^{+0.13}_{-0.06}\,mm$ (average and range of 7 samples)

Bed bulk density = $1.57^{+0.06}_{-0.05}$ g/cm^3 (average and range of 7 samples)

NAR = 126^{+44}_{-100} (average and range of 16 determinations)

Table 18. Blends of first cycle zirconium waste and stainless steel sulfate waste calcined during WCF Run H-6.

Constituents	~6.4 Vol. Zr Waste – 1 Vol. S.S. SO_4 Waste Successfully Calcined 1/16-26/1974	~6.4 Vol. Zr Waste – 1 Vol. S.S. SO_4 Waste Successfully Calcined 1/27-30/1974	~5 Vol. Zr Waste – 1 Vol. SS. SO_4 Waste Successfully Calcined 1/31-2/6/1974
H^+ (<u>*M*</u>)	1.35	1.41	1.40
Al (<u>*M*</u>)	0.36	0.39	0.43
B (<u>*M*</u>)	0.11	0.12	0.12
Zr (<u>*M*</u>)	0.23	0.24	0.24
Ca (<u>*M*</u>)	0.96	0.99	0.95
Fe (ppm)	0.24	0.26	0.25
Cr (<u>*M*</u>)	0.002	0.002	0.002
Ni (<u>*M*</u>)	0.0008	0.0008	0.002
F (<u>*M*</u>)	1.75	1.79	1.73
NO_3 (<u>*M*</u>)	3.74	3.94	3.89
SO_4 (<u>*M*</u>)	0.058	0.062	0.075

WCF CAMPAIGN H-7

During Campaign H-7 (June 8, 1975 to January 24, 1977) the WCF calcined (when calcining, all wastes were combined with acid scrub recycle): first cycle Zr waste from tank WM-189, -187, and –185; 1 vol. Na waste from tank WM-180 concentrated to a sp. gr. of 1.27 blended with 4 vol. of WM-187 waste; 1 vol. unconcentrated Na waste from tank WM-180 blended with 4 vol. of WM-187 waste; and 1 vol. unconcentrated Na waste from tank WM-180 blended with 10 vol. of WM-185 waste. The assumptions made to calculate feed compositions calcined during Campaign H-7 are explained in the 2 sections following describing calcination of each of the 2 different types of wastes calcined during Campaign H-7.

There were problems with restrictions in the transport air line every time the first cycle Zr waste in tank WM-189 was calcined (Amberson 1975a; Amberson 1975b); there were also problems with the plugging of silica gel absorbers and off-gas filters (Amberson 1975a; Amberson 1975b). The latter problem was solved when steam was turned off to the WC-305 heater and turned onto the adsorber coils (Amberson 1975a; Amberson 1975b). Transport air line plugging was eliminated by calcining 4 batches of WM-187 waste and then 2 batches of WM-189 waste (Amberson 1974d). If the sulfate in WM-189 waste caused the problems, and assuming the concentration of SO_4 in stainless steel sulfate waste given in Newby et al. (1978b) is correct and 18,000 gallons of stainless steel sulfate waste (plus jet dilution) were added to 146,300 gal of WM-189 waste (Amberson 1974d), the sulfate concentration in the WM-189 waste being calcined in Run H-7 would have been 0.61 $\underline{M}$. Calcination of blends of Zr waste and stainless steel sulfate waste in WCF Run H-6 for 20 successive days indicated presence of 0.061 $\underline{M}$ sulfate should be no problem. WM-189 waste was probably so hard to calcine because it had become too dilute due to addition of acid scrub recycle solution, solutions found in the tank sump, and decontamination solutions to the waste tank WM-189 while calcining it.

Calcium nitrate ($Ca(NO_3)_2$) was added as a solid to the calciner feed some of the time during Campaign H-7, and no adverse effect was noted.

Blends of Zr and Na wastes were calcined during Campaign H-7. One batch of 200 gallons of WM-180 sodium waste concentrated to a sp. gr. of 1.27 blended with 800 gal. of WM-187 waste and 3 different batches of 1 vol. unconcentrated WM-180 waste blended with 4 vol. of WM-187 waste were calcined between June 14 and June 25, 1976 with a cumulative operating time (COT) of ~6 days; a total of 600 gal. of Na waste was calcined. Very little nozzle plugging was experienced. However, chloride concentration of the acid scrub increased markedly (from 273 ppm on June 22 to 909 ppm on June 23), and the blend seemed to generate more fines when calcined than did the straight waste as evidenced by frequent plugging of the calciner cyclone and WC-148 and an increase in the ΔP across the solids storage cyclone. Difficulty was experienced in transfer of bed material to solid storage and particle size increased. Examination of calcine under a scanning electron microscope showed some evidence of nodule formation. A feed preparation error on the second batch calcined resulted in a Ca/F mole ratio of 0.85. This could have led to bed clinker formation if such feed had been calcined for very long. Between January 5 and 11, 1977, 1075 gal. of Na waste from WM-180 was calcined as a blend of 1 vol. unconcentrated WM-180 waste and 10 vol. WM-185 waste. Chloride buildup in acid scrub solution was twice the normal rate, and calcine examined under an electron microscope indicated a bonding scale building up on particles.

First Cycle Zirconium Wastes Calcined During WCF Run H-7 (WM-185, -187, and –189 Wastes)

During Campaign H-7: 43,950 gal. of first cycle Zr waste from tank WM-189, 266,150 gal. of Zr waste from WM-187, and 63,500 gal. of Zr waste from WM-185 were calcined. The feed blends for WM-187 and WM-185 are shown in Table 19 and 20. No attempt was made to calculate the actual composition of feeds from WM-189 because of the addition of stainless steel sulfate waste, decontamination solutions, scrub recycle solutions, tank sump solutions, and others to the waste in tank WM-189 since its last reported composition during H-6 and before it was calcined during H-7. In calculating feeds from WM-185 and –187, Rhodes (1972) analyses were used for the wastes because when Rhodes analyzed these waste the tanks were essentially full and very little solution had been added to or removed from tanks WM-187 and –185 between September 1971 and Campaign H-7. As Campaign H-7 progressed the composition used to calculate feeds from the waste in WM-187 would become more and more diluted than it originally was because acid scrub recycle solutions, tank sump solutions, and decontamination solutions were added back to tank WM-187 as WM-187 waste was being calcined. The composition of WM-187 feed being fed to the WCF was found in the WCF Run "H-7" Daily Report from May 3, 1976. The composition of this feed was very close to the calculated composition of the feed for that time except for Zr, Fe, and F. If the calcium concentration for the feed on the daily report was correct and a Ca/F mole ratio of 0.55 had been used, the fluoride concentration on the daily report must be incorrect. During calcination of Zr feed:

MMPD = $0.44^{+0.33}_{-0.27}$ *mm* (average and range of 110 samples)

Bed bulk density = $1.56^{+0.28}_{-0.38}$ g/cc (average and range of 110 samples)

NAR = 145^{+164}_{-53} (average and range of 154 determinations)

Table 19. WM-187 first cycle Zr waste calciner feeds successfully calcined during WCF H-7.

Species[a]	6/8-6/26/1975	6/27-7/26/1975[b]	9/26-10/18, 10-23-10/26/1975	10/27-11/17/1975	4/21-4/26/1976[c]	4/27-5/26/1976	5/27-6/26/1976	6/27-7/18/1976
H^+	1.25	1.22	1.33	1.43	0.97	1.30	1.51	1.31
Al	0.48	0.44	0.54	0.54	0.42	0.47	0.54	0.47
Zr	0.32	0.29	0.36	0.35	0.24	0.31	0.36	0.32
B	0.15	0.13	0.16	0.15	0.10	0.14	0.16	0.14
Fe (g/L)	0.18	0.15	0.18	0.18	0.12	0.16	0.19	0.16
Na (mg/L)	47	41	49	47	33	43	50	43
Ca	1.17	1.11	1.31	1.26	0.90	1.18	1.33	1.17
F	2.12	2.01	2.39	2.29	1.63	2.14	2.42	2.12
NO_3	3.99	4.15	4.58	4.38	3.30	4.06	4.58	4.01

a. Concentrations in Molar except where otherwise noted.
b. Batching sequence was 4 batches WM-187 waste and 2 batches WM-189 waste.
c. This was too short a time (4 days) to really test the calcinability of this flowsheet.

Table 20. WM-185 first cycle Zr waste calciner feeds successfully calcined.[a]

Species[a]	12/4 – 12/26/1976	12/27/1976 – 1/24/1977
H^+	1.30	1.12
Al	0.57	0.46
Zr	0.35	0.29
B	0.16	0.13
Fe (g/L)	0.20	0.17
Na (mg/L)	23	19
Ca	1.34	1.07
F	2.44	1.94
NO_3	4.59	3.78

a. Concentrations in Molar except where otherwise noted.

Blends of First Cycle Zirconium Waste and Sodium Waste Calcined During WCF Run H-7

During Campaign H-7, 1675 gallons of Na waste (tank WM-180) was calcined as a blend with WM-187 and –185 wastes. In calculating feeds from WM-180 waste, Rhodes (1972) analyses were used for unconcentrated waste because when Rhodes analyzed this waste the tank was essentially full, and solutions added to the tank between September 1971 and the start of Campaign H-7 changed the volume of the tank less than 10%. During Campaign H-7, the only solution put into tank WM-180 was solution that had been removed from the tank. The composition of WM-180 waste concentrated to a sp.gr. of 1.27 is given in the WCF Run "H-7" Daily Report for June 10, 1976, and this composition was used in the calculations use for calculating the compositions of the blends using this Na waste. The Zr-Na waste blends were not calcined long enough to see if the blends could be calcined successfully. The Cl concentration in offgas acid scrub would have leveled off at a concentration below that excessively corrosive to materials of construction in the acid scrubber (maximum chloride concentration allowed in the WCF, offgas, and acid scrub solution to prevent excessive corrosion was 2600 ppm) (Newby 1980a). Based on pilot plant work and later calcination of these blends in plant calciners, these blends should not have been plugging transport lines, absorbers, and offgas filters when calcined. During calcination of blends of first cycle Zr and Na waste:

MMPD = $0.43^{+0.08}_{-0.05}$ *mm* (average and range of 7 samples)

Bed bulk density = $1.63^{+0.23}_{-0.08}$ g/cc (average and range of 7 samples)

NAR = 214^{+133}_{-72} (average and range of 11 determinations)

Table 21. Blends of first cycle Zirconium waste and sodium waste calcined during WCF Run H-7.

Constituents	1 Vol. WM-180 Waste Concentrated to a sp.g. of 1.27 – 4 vol. WM-187 Waste 6/14/1976	1 Vol. Unconcentrated WM-180 Waste – 4 Vol. WM-187 Waste 6/15/1976[a] and 6/22-6/25/1976
H^+ (*M*)	1.49	1.48
Al (*M*)	0.55	0.52
Zr (*M*)	0.30	0.30
B (*M*)	0.13	0.13
Fe (g/L)	0.26	0.24
Na (*M*)	0.24	0.22
K (*M*)	0.039	0.034
Ca (*M*)	1.41	1.69 *M* on 6/15/1976[a]; 1.39 *M* on 6/22-6/25/1976
F (*M*)	2.01	1.99
NO_3 (*M*)	5.58	5.94[a], 5.34 *M*

a. Batch on June 15, 1976 had a Ca/F mole ratio of 0.85 rather than 0.70. This might have clinkered the bed if such a feed had been calcined very long.

Table 22. Blends of first cycle Zirconium waste and sodium waste calcined during WCF Run H-7.

Constituents	1 Vol. Unconcentrated WM-180 Waste – 10 Vol. WM-185 Waste 1/5 – 1/11/1977
H^+ (*M*)	1.12
Al (*M*)	0.46
Zr (*M*)	0.27
B (*M*)	0.12
Fe (g/L)	0.18
Na (*M*)	0.079
K (*M*)	0.012
Ca (*M*)	1.25
F (*M*)	1.79
NO_3 (*M*)	4.43

WCF CAMPAIGN H-8

During Campaign H-8 (September 13, 1977 through September 29, 1978), the WCF calcined (when calcining, all wastes were combined with acid scrub recycle): first cycle Zr waste from tanks WM-185 and –182; 1 vol. Na waste from tank WM-180 blended with 3 ½ vol. WM-182 waste, 1 vol. Na waste from tank WM-180 blended with 3 ½ vol. WM-188 waste, and 1 vol. Na waste from tank WM-180 blended with 3 ½ vol. WM-189 waste (WM-189 and WM-188 wastes were first cycle Zr wastes). Pelletier (1979) said that Zr-Na waste blends were calcined varying between 3.5 vol. Zr waste – 1 vol. Na waste and 8 vol. Zr waste – 1 vol. Na waste. Only two production monthly reports covering the time period that Zr-Na wastes were being calcined told what blend ratios were being calcined (McMillian 1978a; McMillian 1978b); in both reports a blend of 3 ½ vol. Zr waste – 1 vol. Na waste was being calcined. The assumptions made to calculate feed compositions calcined during Campaign H-8 are explained in the two sections following describing calcination of each of the two different types of wastes calcined during Campaign H-8.

During the campaign, the $Ca(NO_3)_2$ used as feed additive was found to contain more phosphate than the $Ca(NO_3)_2$ used in the past, and this increased nozzle plugging. Phosphate combines with the feed to give a crystalline Ca-Zr phosphate. The plant producing the $Ca(NO_3)_2$ had changed their process for making $Ca(NO_3)_2$ which had resulted in more phosphate present. At first the problem was solved by adding $Ca(NO_3)_2$ as a liquid rather than as a solid. It was found that a polymer, Betz 1100, would flocculate Ca-Zr phosphate which precipitated from the lower grade $Ca(NO_3)_2$; however, based on pilot plant experience, it was decided to add the high phosphate containing $Ca(NO_3)_2$ as a solid which increased nozzle plugging but was not severe enough to require switching to liquid $Ca(NO_3)_2$. Higher quality $Ca(NO_3)_2$ was received later.

Fluorapatite [$Ca_5(PO_4)_3F$] was tested as a start up bed. Excessive bed material was last during heatup and the initial feed phases of startup, and dolomite addition was required to maintain an adequate bed level because there was not sufficient fluorapatite on hand.

The biggest problem when calcining Zr-Na waste blends was keeping particle size from becoming too large. Methods used to control particle size are discussed in the section on calcination of Zr-Na waste blends for H-8.

First Cycle Zirconium Waste Calcined During WCF Run H-8 (WM-185 and –182 Wastes)

During Campaign H-8, 208,900 gallons of first cycle waste from tank WM-185, 212,500 gallon of Zr waste from WM-182, 1,600 gallons of Zr waste from WM-188, and 1,700 gallons of Zr waste from WM-189 were calcined; at least 112,700 gallons of this waste was calcined as blend with Na waste (WM-180 waste). Blends of Zr and Na waste are discussed in a later section. Calcination of Zr waste using $Ca(NO_3)_2$ as the only additive will be discussed in this section. The small amounts of WM-188 and WM-189 wastes transferred to WCF) to obtain samples of the wastes in tanks, and were subsequently calcined as blends with Na waste. There are no samplers on the tank farm tanks WM-180 through WM-190, so the tank farm wastes were normally transferred to the WCF feed tanks for sampling. After sampling, the solution was usually returned back to the tank farm.

In calculating feeds from WM-185 waste, Rhodes (1972) analyses were used for these feeds because when Rhodes analyzed these wastes the tanks were essentially full and very little solution had been added to tank WM-185 between September 1971 and Campaign H-8. Also, very little solution, if any, was added to tank WM-185 during Campaign H-8 while WM-185 waste was being calcined. The composition of WM-182 waste found in ACI-357 (1978) was taken, but since this document was dated September 1978 (date when Campaign H-8 ended), the analyses must represent the waste before or during Campaign H-8. This analyses for WM-182 was the only one that could be found. Tank WM-182 was essentially full before Campaign H-8 and had become that way in May 1974 (Amberson 1974c) and nothing was returned to tank WM-182 between May 1974 and the time when solution from the tank was being calcined. While the solution was being calcined in Campaign H-8 some decontamination solution was returned to tank WM-182 but the dilution would have been less than 10 vol%. During calcination of Zr feed:

MMPD = $0.46^{+0.22}_{-0.08}$ (average and range of 37 samples)

Bed bulk density = $1.46^{+0.23}_{-0.14}$ g/cc (average and range of 37 samples)

NAR = 122^{+253}_{-63} (average and range of 113 determinations)

Table 23. WM-185 first cycle zirconium feeds successfully calcined during WCF H-8.

	9/13-9/26/1977	9/27-10/18/1977 10/19-10/26/1977	10/27-11/26/1977	11/27-12/14/1977 12/21-12/31/1977	1/1-1/9/1978 1/13-1/31/1978
H^+	1.36	1.25	1.21	1.21	1.18
Al	0.55	0.54	0.51	0.45	0.45
Zr	0.31	0.31	0.29	0.26	0.27
B	0.15	0.15	0.14	0.13	0.13
Na (g/L)	0.023	0.022	0.021	0.019	0.019
Ca	1.23	1.23	1.16	1.04	1.06
F	2.24	2.23	2.10	1.89	1.92
NO_3	4.80	4.65	4.36	3.99	4.03

Note: Concentrations in molar except when otherwise noted.

Table 24. WM-182 first cycle zirconium feeds successfully calcined during WCF H-8.

	2/1-2/3/1978 2/7-2/28/1978	3/1-3/3/1978	4/3-4/16/1978
H^+	1.35	1.28	1.16
Al	0.53	0.51	0.55
Zr	0.27	0.23	0.26
B	0.12	0.11	0.12
Na (g/L)	1.38	1.21	1.34
Ca	0.99	0.85	0.95
F	1.80	1.55	1.74
NO_3	4.32	3.76	4.10

Note: Concentrations in molar except when otherwise noted.

Blends of First Cycle Zirconium Waste and Sodium Waste Calcined During WCF Run H-8

During Campaign H-8, 32,200 gallons of Na waste (tank WM-180) was calcined - mostly as blends with WM-182 waste, but also as one batch of a blend of WM-180 and –189 and one batch of WM-180 and –188. Those two batches were calcined to obtain samples of WM-188 and –189 tank farm wastes for analysis. The analyses that were run on each batch of Na-Zr waste feed fed to the WCF Run H-8 were found and that is what is reported below. Nitrate analyses were not requested so were calculated by: using monthly production reports for volumes of the components making-up calciner feed;

assuming the blend used in all feed was 3.5 vol. WM-182 waste – 1 vol. WM-180 waste; and assuming the composition of WM-182 and WM-180 waste was that reported in ACI-357 (1978). The biggest problem with calcining Zr-Na waste blends was keeping bed particle size from getting too large. To control particle size: the feed atomizing air rate had to be increased by a factor of 3-4 over that used in calcining Zr waste; at the higher particle size fluidized air flow had to be increased (the higher fluidizing air flow and feed atomizing air rate placed a heavier load on the off-gas system and limited gross feed rate to ~100 gal/hr); from the Daily Reports it appeared that when MMPD reached 0.7 to 0.8 mm using the Na-Zr blend the feed would be switched to Zr waste until the MMPD came down to ~0.5 mm. The chloride concentration of acid scrub solution ranged between ~1000 and 2700 ppm. During calcination of Zr-Na waste blends:

MMPD = $0.60^{+0.28}_{-17}\ mm$ (average and range of 63 samples)

Bed bulk density = $1.67^{+0.11}_{-0.22}$ g/cc (average and range of 62 samples)

NAR = 450^{+301}_{-324} (average and range of 74 determinations)

There were 16 feed batches for which sufficient constituents were analyzed to determine mole % Na+K in solids that would be produced from the feed (if the batches where Na was calculated on batches of feed were subtracted, we would have a total of 10 batches rather than 16 batches having sufficient analyses). Only 3 of the 16 batches contained 5.3 mole% Na+K or less, while 9 of the 16 batches would produce solids having greater than 10 mole% Na+K. A Na+K content greater than 10 mole% should have caused agglomeration for Na-Zr blends; however, none of the batches clinkered the calciner bed. If the analyses truly represents the concentration of constituents in the feed batches calcined, these solids produced may cake in the storage bins; however, the presence of other types of calcine around may prevent the caking or make the caking of solids less hard.

Table 25. Zr-Na waste blend feeds calcined during WCF Run H-8.

Species	4/10-4/19/1978[a]	4/20-5/30/1978[a]	5/31-6/6/1978[a]	6/7-6/12/1978[a]	6/13-6/19/1978[a]	6/20-6/24/1978[a]	6/25-7/3/1978[a]
H^+ (*M*)	2.03	2.25	2.94	2.78	2.72	2.25	2.42
Al (*M*)	0.58	0.35	0.20	0.25	0.26	0.26	0.28
Zr (*M*)	0.17	0.09	0.09	0.13	0.14	0.08	0.18
B (*M*)	0.15	0.056	0.058	0.09	0.09	0.053	0.12
Na (*M*)	0.27	0.31	0.24	0.37	0.47	0.23	0.28
K (*M*)	0.040	0.047	0.036	0.055	0.070	0.034	0.042
Ca (*M*)	0.8	0.4	0.37	0.71	0.73	0.39	0.74
F (*M*)	1.27	0.51	0.50	0.99	1.03	0.52	0.98
NO_3 (*M*)	4.29	3.44	3.31	3.99	4.03	3.35	4.19
	Solids contain 6.2 mole% Na+K	Solids contain 13.4 mole% Na+K	Solids contain 12.2 mole% Na+K	Solids contain 11.2 mole% Na+K	Solids contain 12.5 mole% Na+K	Solids contain 10.9 mole% Na+K	Solids contain 8.0 mole% Na+K
Solid content (g/L)	156.5	103.8	86.1	137.2	150.5	88.55	140.5

a. Blends should not have been calcined because resulting solids would contain more than 5.3 mole% Na+K.

Table 26. Zr-Na waste feed blends calcined during WCF Run H-8.

Species	7/14-7/15/1978	7/16-7/28/1978	7/29-8/4/1978	8/15-8/17/1978[c]	8/18-8/26/1978[c]	8/27-9/2/1978[c]	9/3-9/10/1978[c]	9/11-9/18/1978[c]	9/19-10/1/1978[c]
H^+ (<u>*M*</u>)	2.82	2.46	2.42	2.89	4.63	3.18	2.84	3.40	2.92
Al (<u>*M*</u>)	0.33	0.38	0.31	0.34	0.24	0.42	0.35	0.33	0.24
Zr (<u>*M*</u>)	0.32	0.14	0.13	0.10	0.12	0.09	0.20	0.12	0.069
B (<u>*M*</u>)	0.19	0.083	0.088	0.063	0.077	0.06	0.088	0.073	0.039
Na (<u>*M*</u>)	0.29	0.12	0.14	No Anal.[a]	No Anal.[a]	No Anal.[b]	No Anal.[b]	No Anal.[b]	No Anal.[b]
K (<u>*M*</u>)	0.043	0.018	0.021	No Anal.[a]	No Anal.[a]	No Anal.[b]	No Anal.[b]	No Anal.[b]	No Anal.[b]
Ca (<u>*M*</u>)	1.36	0.58	0.50	0.47	0.45	0.43	0.82	0.61	0.46
F (<u>*M*</u>)	1.62	0.83	0.68	0.65	0.67	0.61	1.22	0.73	0.66
NO_3 (<u>*M*</u>)	5.43	3.87	3.72	3.67	3.63	3.53	4.31	3.89	3.51
	Solids contain 5.3 mole% Na+K	Solids contain 4.1 mole% Na+K	Solids contain 5.4 mole% Na+K	Solids contain 10.2 mole% Na+K	Solids contain 11.1 mole% Na+K	Solids contain 11.0 mole% Na+K	Solids contain 7.6 mole% Na+K	Solids contain 9.8 mole% Na+K	Solids contain 12.8 mole% Na+K
Solid content (g/L)	221.6	108.1	99.0	107.1	102.5	108.1	152.2	125.6	98.1

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a. Calculated values = 0.28 <u>M</u> Na, 0.041 <u>M</u> K.

b. Calculated values = 0.30 <u>M</u> Na, 0.044 <u>M</u> K.

c. Blends should not have been calcined because resulting solids would contain more than 5.3 mole% Na+K.

WCF CAMPAIGN H-9

During Campaign H-9, June 16, 1979 through March 16, 1981, the WCF calcined (when calcining, all wastes were combined with acid scrub recycle): first cycle Zr waste from tanks WM-182, 1-85, -188, and –189; 5, 7, 8, and 10 vol. WM-182 (Zr waste) waste with 1 vol. Na waste from WM-180; 4 ½ and 6 vol. WM-188 (Zr waste) waste with 1 vol. Na waste from WM-180; and 7 and 9 vol. WM-189 (Zr waste) waste with 1 vol. Na waste from WM-180. WM-185 waste already contained a significant sodium concentration (0.20 M). The chemical concentrations of all wastes used in Campaign H-9 and the concentrations of these wastes at various times over the period that they were calcined are found in Childs, Donovan, and Swenson (1982). In calculating feed blends for the WCF, information from the following sources were used: a) the waste chemical compositions found in Childs, Donovan, and Swenson (1982); b) flow rates of process streams found in appropriate monthly production reports during the campaign; and c) the chemical concentrations of acid scrub recycle solutions found in appropriate WCF daily reports during the campaign.

There were many forced shutdowns during Campaign H-9 due primarily to equipment deterioration. The primary factor contributing to shutdowns was a defective distributor plate (grid) which could not provide adequate fluidization. Agglomerates were largely initiated by poor fuel atomization due to eroded fuel nozzle caps. Under poorly fluidized conditions, high feed rates and excessive water flushing also contributed to agglomeration. Poor fluidization allowed bed condition to deteriorate making bed removal difficult, causing high temperature spreads in the bed, and resulting in high fines carryover (contributing to cyclone/fines jet plugging). Experience in Campaign H-9 showed that the WCF ran best at near 100 gph in terms of offgas system capacity, IBC control, product take-off capacity, and feed makeup time for calcium nitrate dissolution.

Based on laboratory and pilot plant results, the water flush (of feed nozzles) system was converted to 150 psi air. Air flushing was extremely successful for clearing restrictions and reduced agglomeration potential compared to water flushing.

Particle size control was a problem when calcining Zr-Na waste blends. Experience in Campaign H-9 suggested that particle size control was only feasible with dilute blends and then only if high NAR's (500-600) were used before the particle size grew beyond about 0.45 mm. Lower feed rates (80-100 vs >100 gph) also appeared to help. The effect of the O_2/fuel ratio was indeterminate when varied between 1800 and 2400. The highest mole% Na+K found in any calculated blend composition was 5.8%; almost always the mole% was below 5.3%. The solids content of calculated blended feeds was 123 g/L or greater; no mention was made of problems with building bed and maintaining bed height when calcining these feeds. The solids content of Na blended WM-185, -188, and –187 feeds varied between 116 and 208 g/L; no mention was made of problems with building bed or maintaining bed height when calcining these feeds. Most of the unblended WM-182 feeds had a solids content of ~100 g/L and bed could not be built using such a dilute feed after spraying cold $Al(NO_3)_2$ solution on starting bed. Usually, WM-182 feed was calcined after a Zr-Na waste blends to decrease particle size. An attempt was made to use fluorapatite as a starting bed from June 1979 to March 1980. Due to high bed elutriation rates during calciner startups which required frequent supplemental bed additions, the use of fluorapatite was abandoned and dolomite was used (dolomite was more readily available in small quantities than fluorapatite). Compared to dolomite, fluorapatite was less erosive to piping; had a higher attrition index and thus would not produce as many fines; had more dense and spherical particles giving lower elutriation rates. During calcination of Zr feed:

MMPD = $0.36^{+0.28}_{-10}$ *mm* (average and range of 173 samples)
Bed bulk density = $1.52^{+0.27}_{-0.45}$ g/cm^3 (average and range of 178 samples)
NAR = 184^{+415}_{-111} (average and range of 381 determinations)

During calcination of Zr-Na blends:

MMPD = $0.43^{+0.30}_{-0.12}$ *mm* (average and range of 80 samples)
Bed bulk density = $1.45^{+0.19}_{-0.34}$ g/cm^3 (average and range of 83 samples)
NAR = 363^{+396}_{-263} (average and range of 176 determinations)

WM-182 Zr Waste Feeds

Most WM-182 Zr waste feeds did not contain enough dissolved and undissolved solids to build bed and/or maintain bed height; this happened while calcining these feeds during June 16, 1979 and June 21-26, 1979. The WM-182 waste feeds calcined from August 17 to September 2, 1979 were used to reduce bed particle size after having calcined Zr-Na wastes blends; feeds calcined between August 17 and August 31, 1979 may have contained enough solids to build bed and/or maintain bed height (their solids content was marginal to do so) if calcined for a longer period of time, but the feeds calcined on September 1 through September 2, 1979 should not have had enough solids to build bed and/or maintain bed height if calcined for longer periods of time. Feeds calcined between September 25 and September 30, 1979 were calcined after calcination of WM-189 waste feeds; Smolen (1979) says that during this period when WM-189 and –182 feeds were calcined, the size of bed particles was stabilized at 0.35-0.40 mm and bed level control was excellent. If WM-182 waste feeds had been calcined much longer, bed particle size should have begun decreasing.

Table 27. WM-182 Zr waste feeds calcined during WCF H-9.

Species	6/16/1979 and 6/21-6/26/1979	8/17-31/1979	9/1-2/1979 and 9/25-30/1979
H^+ (*M*)	0.94	1.08	1.10
Al (*M*)	0.42	0.32	0.34
Zr (*M*)	0.14	0.16	0.15
B (*M*)	0.073	0.077	0.078
Fe (*M*)	0.006	0.0074	0.0064
Na (*M*)	0.038	---	0.041
Ca (*M*)	0.54	0.71	0.58
F (*M*)	0.99	1.09	1.06
NO_3 (*M*)	3.45	3.59	3.55
UDS (g/L)	14.1	14.4	13.9
Solid Content (g/L)	103	119	101

WM-189 Waste Feeds

Processing of first-cycle Zr waste from Tank WM-189 was accompanied by feed nozzle plugging (especially from the bottom transfer line which draws waste only 2” from the bottom of WM-189) and particle agglomeration. Feed nozzle plugging was caused by solids on the bottom of the tank drawn into the nozzles; extra solids on the tank’s bottom might have been caused by fact that WM-189 waste was actually a dilute Na-Zr wastes blend and such a blend is unstable, and by the fact that solids will precipitate from Zr wastes when their acidity exceeds 1.5 N, which WM-189 did exceed. WM-189 waste’s tendency to agglomerate was probably also caused by the fact that it was a dilute blend, and these blends are more susceptible to agglomeration due to higher concentrations of low melting constituents when process upsets or equipment failures do occur. During the period January 16 through 24, 1981, one batch of WM-185 waste was alternated with 1 batch of WM-185 waste to reduce WM-189 waste particle agglomeration. WM-182 waste was as concentrated in Na as was WM-189 waste but didn’t have agglomeration problems. WM-182 waste also had feed nozzle plugging problems when the volume of waste in WM-182 became quite low. WM-185 waste was much more concentrated in Na than either WM-182 and WM-189 wastes and didn’t have agglomeration problems.

Table 28. WM-182 Zr waste feeds calcined during WCF H-9.

Dates	9/21-25/1979	1/16-24/1981 (1 batch WM-185 Feed Alternated with 1 Batch WM-189 Feed)	2/11-28/1981	3/1-16/1981
H^+ (*M*)	1.38	1.64	1.58	1.45
Al (*M*)	0.42	0.43	0.41	0.37
Zr (*M*)	0.19	0.24	0.23	0.21
B (*M*)	0.098	0.11	0.10	0.10
Fe (*M*)	0.0071	0.0056	0.0057	0.0055
Na (*M*)	0.041	0.040	0.012	0.012
Ca (*M*)	0.70	0.86	0.78	0.76
F (*M*)	1.27	1.56	1.42	1.38
NO_3 (*M*)	3.83	4.12	4.00	3.82
UDS (g/L)	15.4	5.6	1.0	6.2
Solid Content (g/L)	125	131	120	116

WM-188 Waste Feed

A WM-188 waste feed was calcined during the period March 4 and March 9, 1979 in order to reduce particle size which had built-up during calcination of a Zr-Na waste blend (Smolen 1980). The WM-188 blended feed compositions are provided in Table 29.

WM-185 Waste Feed

When calcining WM-185 waste feed: the calciner was shut down 5 different times; there were plugging problems with the primary cyclone discharge, product take-off and product drain lines; and agglomerates were found in bed samples taken. These problems were blamed on equipment failures rather than on failure of the chemical flowsheet used. Concentration of WM-185 waste feeds calcined are shown in Table 29. Note the relatively high concentration of Na in WM-185 waste feeds. Potassium concentrations were not known and are not reported because either the feeds weren’t analyzed for K or the analyses gave inconsistent results. The highest mole% Na in solids produced by calcining WM-185 waste feeds was 3.8%. Apparently, samples of calcine from WM-185 waste feeds showed less agglomerates present than samples from WM-189 waste feeds (which contained much less Na than WM-185 waste).

Table 29. WM-188 and WM-185 waste feeds calcined during WCF H-9.

	WM-188 Feed	WM-185 Feed								
	8/4-9/1979	3/19-31/1980	4/13-23/1980 and 4/25-30/1980	5/17-31/1980	6/1-3/1980	10/13-31/1980	11/1-12/1980	12/9-31/1980	1/1-16/1981 and (1/16-24/1981 – alternated with 1 batch WM-185 feed) 1/24-31/1981	2/1-10/1981
H^+ (*M*)	1.33	1.30	1.26	1.29	1.69	1.37	1.38	1.42	1.46	1.58
Al (*M*)	0.50	0.68	0.63	0.64	0.64	0.54	0.54	0.50	0.50	0.51
Zr (*M*)	0.25	0.26	0.29	0.28	0.25	0.27	0.27	0.28	0.29	0.28
B (*M*)	0.14	0.13	0.13	0.013	0.15	0.15	0.15	0.14	0.15	0.14
Fe (*M*)	0.0086	0.0039	0.0059	0.0040	0.0037	0.0081	0.0078	0.0055	0.0056	0.0057
Na (*M*)	---	0.16	0.16	0.16	0.15	0.21	0.21	0.20	0.10	0.11
Ca (*M*)	0.89	1.05	1.04	1.07	1.27	1.02	1.01	0.88	0.94	0.91
F (*M*)	1.61	1.90	1.90	1.94	2.31	1.85	1.83	1.61	1.72	1.66
NO_3 (*M*)	4.13	4.53	4.27	4.49	5.46	4.68	4.68	4.25	4.34	4.40
UDS (g/L)	16.5	7.1	6.9	8.0	24	6.7	7.5	6.4	6.3	6.1
Solid Content (g/L)	151	181	181	180	208	174	174	143	149	146

BLENDS OF ZIRCONIUM AND SODIUM WASTES

As in previous WCF campaigns, particle size control was a problem when calcining Na-Zr wastes blends. When calcining feeds from a blend of 8 vol. WM-182 waste and 1 vol. WM-180 waste (WM-182 wastes was a dilute Zr waste) operating conditions (NAR's, feed rates, fluidizing air velocities) were found that would hold particle size constant. Usually when particle size became large the feed was switched from a Zr-Na wastes blend feed to a feed of unblended Zr wastes.

Table 30. Composition of blends of Zr and Na wastes calcined during WCF H-9.

	5 vol. WM-182 – 1 vol. WM-180 6/27-30/1979	4.5 vol. WM-188 – 1 vol. WM-180 7/20-31/1979	4.5 vol. WM-188 – 1 vol. WM-180 8/1-3/1979	6 vol. WM-188 1 vol. WM-180 8/10-16/1979	8 vol. WM-182 – 1 vol. WM-180 9/3-16/1979 and 9/18-21/1979	10 vol. WM-182 – 1 vol. WM-180 12/2-5/1979	8 vol. WM-182 – 1 vol. WM-180 12/6-20/1979	7 vol. WM-182 – 1 vol. WM-180 12/21-31/1979	7 vol. WM-189 – 1 vol. WM-180 1/1-17/1980	9 vol. WM-189 – 1 vol. WM-180 2/22-29/1980
H^+ (*M*)	0.91	1.20	1.35	1.21	1.14	1.10	1.09	1.17	1.40	1.46
Al (*M*)	0.44	0.5	0.49	0.47	0.32	0.39	0.34	0.33	0.34	0.52
Zr (*M*)	0.12	0.18	0.19	0.21	0.14	0.14	0.15	0.14	0.13	0.16
B (*M*)	0.064	0.10	0.11	0.12	0.072	0.074	0.073	0.072	0.077	0.089
Fe (*M*)	0.012	0.014	0.015	0.014	0.011	0.0096	0.0097	0.0066	0.011	0.013
Na (*M*)	0.18	0.16	0.18	0.14	0.15	0.13	0.15	0.16	0.15	0.15
K (*M*)	0.028	0.030	0.032	0.025	0.020	0.013	0.019	0.022	0.025	0.024
Ca (*M*)	0.62	0.86	0.89	0.94	0.67	0.71	0.71	0.70	0.73	0.87
F (*M*)	0.89	1.23	1.27	1.34	0.95	1.01	1.02	1.00	1.04	1.25
NO_3 (*M*)	3.71	4.15	4.41	4.45	3.84	3.46	3.46	3.45	3.84	4.56
UDS (g/L)	14.1	15.9	16.5	16.5	13.9	9.3	9.3	9.3	9.4	10.6
Mole% Na+K	5.8	4.1	4.4	3.4	4.9	3.8	4.6	5.1	4.8	3.8
Solid Content (g/L)	127	160	166	168	124	124	125	123	125	152

NWCF COLD STARTUP

During cold testing of the NWCF (Phase I October 28 through November 20, 1981 and Phase II May 19 through June 17, 1982), the Calciner calcined three different types of feed. During Phase I a typical $Al(NO_3)_3$ solution used in the WCF for startup and stabilization of operation and a feed simulating a blend of 2.2 $\underline{M}$ $Al(NO_3)_3$ and Na waste was to be calcined; during Phase II a typical $Al(NO_3)_3$ solution used in the WCF for startup and stabilization of operation and a feed simulating a blend of aluminum nitrate and Na waste more concentrated in sodium than the blend calcined in Phase I were planned. The concentrations of the feed without blending them with recycled acid scrub were to be: a) $Al(NO_3)_3$ solution – 1.8 $\underline{M}$ $Al(NO_3)_3$ and 0.02 $\underline{M}$ boron; b) a simulated blend of 6 vol. 2.2 $\underline{M}$ $Al(NO_3)_3$ and 1 vol. Na waste – 1.95 $\underline{M}$ Al, 0.6 $\underline{M}$ H^+, 0.02 $\underline{M}$ B, 6.7 $\underline{M}$ NO_3, 0.29 $\underline{M}$ Na; and c) a simulated blend of 2 vol. 2.2 $\underline{M}$ $Al(NO_3)_3$ and 1 vol. Na waste – 1.68 $\underline{M}$ Al, 0.6 $\underline{M}$ H^+, 0.2 $\underline{M}$ B, 6.2 $\underline{M}$ NO_3, and 0.67 $\underline{M}$ Na. The Na waste being simulated contained 0.51 $\underline{M}$ Al, 1.80 $\underline{M}$ Na, and 0.20 $\underline{M}$ K. Sodium containing feeds used in the NWCF Cold Startup were of interest because they simulated the best alternative method tested to date in pilot-plant calciners to calcining Na waste as a blend with Zr waste. The calcination periods for calcining the 2 different blends of 2.2 $\underline{M}$ $Al(NO_3)_3$ and Na waste were too short to determine the calcination characteristics in calcining this type of blend. However, 2 major problems encountered in calcining simulated blends of 2.2 $\underline{M}$ $Al(NO_3)_3$ $Al(NO_3)_3$ and Na waste in the NWCF and in 30-cm calciners were: a) preventing calcine particles from becoming too small, and b) generation of too many fires. Two 2.2 $\underline{M}$ $Al(NO_3)_3$-Na waste blends in 30-cm calciner runs were simulated by using only $Al(NO_3)_3$, nitric acid, boric acid and sodium nitrate (Newby 1981a; Newby 1986), and two were simulated by adding all the non-radioactive constituents to the blend (Newby 1986). Even though the 2 to 1 flowsheet produced more fines than expected in the NWCF, the tall fines column (due to improper operation) seemed to be the cause of excessive fines carryover to the scrubbing systems. Calcined solids produced during the NWCF cold startup stored in a grain bin and 300 to 600 c.c. bed samples of calcined 2.2 $\underline{M}$ $Al(NO_3)_3$ – Na waste blends, unlike calcine from 30 cm calciner studies (Newby 1986), were not caked when examined about 4 years after being produced. Feed compositions, MMPD's and bulk density of bed material were obtained from computer readouts giving analyses of acid scrub, feed, and calcine samples; the feed NAR was obtained from a computer readout of "Daily Technical Reports"; and time intervals over which various feeds were calcined were obtained from feed makeup data sheets.

Table 31. Composition of $Al(NO_3)_3$ feeds calcined during NWCF cold startup.

	Composition of $Al(NO_3)_3$ Feed		
	10/28-11/2/1981	5/19-24/1982	6/3-9/1982
H^+ ($\underline{M}$)	$0.16^{+0.190}_{-0.142}$	$0.29^{+1.25}_{-0.38}$	$0.50^{+0.35}_{-0.36}$
Al ($\underline{M}$)	$1.72^{+0.47}_{-0.12}$	$1.66^{+0.38}_{-0.81}$	1.85 ± 0.12
B ($\underline{M}$)	$0.011^{+0.000}_{-0.000}$	$0.0071^{+0.0012}_{-0.0021}$	0.17 ± 0.05
NO_3 ($\underline{M}$)	Not Determined	6.39 ± 0.60	6.36 ± 1.07
UDS (g/L)	53^{+92}_{-46}	$14.2^{+32.6}_{-8.8}$	36 ± 21
MMPD (mm)	$0.402^{+0.087}_{-0.054}$ (11 determns)	$0.408^{+0.147}_{-0.077}$ (18 determns)	$0.251^{+0.180}_{-0.008}$ (19 determns)
Bulk Density (g/cc)	$1.18^{+0.11}_{-0.12}$ (11 determns)	$1.26^{+0.37}_{-0.19}$ (18 determns)	$1.02^{+0.15}_{-0.12}$ (19 determns)
NAR	265^{+141}_{-67} (5 determns)	214^{+115}_{-56} (6 determns)	180^{+71}_{-38} (7 determns)
Solid Content (g/L)	141	99	136

Note: Values given are the average and range for the data.

At the start of a typical campaign in the WCF or NWCF, an $Al(NO_3)_3$ solution containing a small amount of boron was always used as a feed for startup and stabilization of operation; the same feed was also usually used for startup and stabilization of operation during startup after shutdowns occurring within the same campaign. The composition of this feed is shown here because readily available literature doesn't contain this information. There did not seem to be any problem in being able to control the particle size of calcined solids produced from calcining this feed. The $Al(NO_3)_3$ feed calcined between May 19, 1982 and May 24, 1982 did not seem to have a high enough solid content to build bed or maintain bed height, but "Daily Technical Report" information showed this not be the case. Perhaps the period over which this information was obtained was not long enough to show trends; steady-state operation requires a minimum of ~12 days in the NWCF (Childs 1982a).

The 6 vol. 2.2 M $Al(NO_3)_3$ – 1 vol. Na waste flowsheet run in the NWCF cold setup was a duplicate of Run 86 made in the unenclosed 30-cm calciner pilot plant (Newby 1981a). Bed particle size was easily controlled when calcining this blend in both the NWCF and 30-cm calciner. In both calciners a large quantity of fines were produced; however, fines generation was reduced to a satisfactory level in Run 86 (increasing product-to-fines ratio from 1.5 to 2.5) by keeping fluidizing air low (fluidizing velocity below nozzle of 0.65 ft/s or 0.20 m/s), bed height sufficiently high (~6 in. or 15-cm above the feed nozzle), and using a NAR of ~200. Although the 6 to 1 flowsheet in the NWCF produced a lot of fines, improper operation of the tall fines column seemed to be the cause of excessive fines carryover to the scrubbing system. There would also probably have been less fines when calcining the 6 to 1 flowsheet in the NWCF if a lower NAR had been used (the NWCF was operated at an average NAR between 200 and 389 for 10 of the 18 days that the 6 to 1 blend was calcined and was operated for 8 days at an average NAR between 150 and 200). There was very little tendency of fluidized-bed particles to agglomerate in Run 86; there was no mention of agglomeration problems during calcination of the 6 to 1 blend in the NWCF. Neither calciner had problems building bed and maintaining bed height when calcining the 6 to 1 blend. Bulk density of bed material in the NWCF (1.17 g/cm^3) was greater than the product produced during Run 86 (0.92 g/cm^3). Analyses of pilot-plant samples indicated that the particle size distribution of fines formed calcining the 6 to 1 blend and Zr waste feeds were virtually identical; the fines from calcining the 2 to 1 Al-Na feed were distinctly smaller (Schindler 1982). The average mole% Na in calcined solids produced from the 6 to 1 blend in the NWCF was slightly higher than that desired in blends of Zr and Na wastes (5.3 mole%) and ranged between 5.5 and 6.4 mole%.

Table 32. Compositions of feeds containing blends of 6 vol. 2.2 M $Al(NO_3)_3$ – 1 vol. Na waste.

	11/3-12/1981	11/13-20/1981	6/10/1982
H^+ (*M*)	$0.41^{+0.20}_{-0.18}$	$0.65^{+0.31}_{-0.25}$	0.44±0.33
Al (*M*)	$1.93^{+0.38}_{-0.81}$	$2.00^{+0.09}_{-0.17}$	1.84±0.01
B (*M*)	$0.018^{+0.004}_{-0.008}$	$0.023^{+0.013}_{-0.006}$	0.036±0.08
Na (*M*)	$0.29^{+0.07}_{-0.12}$	$0.34^{+0.05}_{-0.03}$	0.33
NO_3 (*M*)	$6.62^{+0.88}_{-2.45}$	$6.92^{+0.30}_{-0.61}$	5.47
UDS (g/L)	130^{+143}_{-102}	77^{+63}_{-69}	15±5
MMPD (mm)	$0.354^{+0.066}_{-0.026}$ (7 determns)	$0.334^{+0.019}_{-0.043}$ (19 determns)	$0.311^{+0.040}_{-0.058}$ (4 determns)
Bulk Density (g/cc)	$1.04^{+0.12}_{-0.044}$ (7 determns)	$1.30^{+0.10}_{-0.09}$ (19 determns)	1.10±0.12 (4 determns)
NAR	277^{+112}_{-119} (10 determns)	189^{+62}_{-45} (8 determns)	158 (1 determns)
Mole% Na	5.5	6.1	6.4
Solid Content (g/L)	254	209	138

Table 33. Composition of feeds containing blends of 2 vol. 2.2 $\underline{M}$ $Al(NO_3)_3$ – 1 vol. Na waste.

	5/24/1982 – 6/2/1982	6/11/1982 – 6/15/1982
H^+ ($\underline{M}$)	$0.67^{+0.20}_{-0.26}$	$0.92^{+0.29}_{-0.49}$
Al ($\underline{M}$)	$1.78^{+0.39}_{-0.49}$	$1.66^{+0.19}_{-0.24}$
B ($\underline{M}$)	$0.11^{+0.16}_{-0.10}$	$0.18^{+0.04}_{-0.103}$
Na ($\underline{M}$)	$0.76^{+0.21}_{-0.24}$	0.68 ± 0.03
NO_3 ($\underline{M}$)	$6.59^{+0.83}_{-1.14}$	$6.24^{+0.81}_{-1.48}$
UDS (g/L)	23^{+90}_{-20}	11^{+19}_{-9}
MMPD (mm)	$0.321^{+0.078}_{-0.121}$ (26 determns)	0.346 ± 0.053 (15 determns)
Bulk Density (g/cc)	$1.09^{+0.08}_{-0.11}$ (26 determns)	$1.11^{+0.11}_{-0.07}$ (15 determns)
NAR	255^{+107}_{-54} (10 determns)	173^{+41}_{-46} (5 determns)
Mole% Na	12.9	12.1
Solid Content (g/L)	182	160

The 2 vol. 2.2 $\underline{M}$ $Al(NO_3)_3$ – 1 vol. Na waste flowsheet run in the NWCF cold startup was a duplicate of Run 87 made in the unenclosed 30-cm calciner pilot plant; the 2 to 1 blend in the NWCF was also similar to run 97 in the unenclosed 30-cm calciner pilot plant and Run 3 in the enclosed 30-cm calciner pilot plant (Newby 1981a; Newby 1986). Runs 3 and 97 used as feed a 2 to 1 blend simulated by adding all the non radioactive constituents to the blend, whereas, in Run 87 and the NWCF the Na waste was simulated using aluminum and sodium nitrates and boric acid only. Run 87, 97, and 3 produced more fines than did Run 86 (6 to 1 blend). Product-to-fines ratios were 0.84, 0.77, <1.0, and 1.2, respectively. The 2 to 1 blend in the NWCF was shown to be potentially troublesome from a fines generation standpoint (Childs 1982a), but an attempt could not be found where fines generation rates between the 2 to 1 and 6 to 1 blend calcined in the NWCF was compared. Bed agglomeration tendencies (portion of final bed particles that are >14 mesh) showed bed agglomeration tendencies were more likely in Runs 87 and 3 (agglomeration tendency of Run 97 was not measured) than in Run 86. No bed agglomeration problem was noted while calcining the 6 to 1 blend in the NWCF, but it was stated that during calcination of the 2 to 1 blend calcine particles did not grow beyond 0.425 mm without agglomerating (Childs 1982a). The mole% Na in calcined solids generated when the 2 to 1 blend was calcined in he NWCF was ~12 mole%. There may have been a problem in keeping particles from becoming too small when calcining the 2 to 1 blend in Runs 3 and 97 and in the NWCF; however during the 13 days that the 2 to 1 blend was calcined in the NWCF, the average NAR was between 200 and 362 during 9 days and between 125 and 185 for 4 days; the particle MMPD went as low as 0.20 mm when the NAR was at ~360. Average bulk density of bed material in the NWCF during calcination of the 2 to 1 blend was 1.10 g/cm^3; and bulk densities of calcine product produced during Runs 3, 87, and 97 were 1.51, 0.98, and 1.03 g/cm^3, respectively. Drums of calcined product from Runs 3 and 97 observed after being stored at <35°C for 1 year were a solid cake and caked on the surface, respectively. Samples (300 to 600cc) of bed material generated during calcination of the 2 to 1 blend in the NWCF stored at <35°C for 4 years were free flowing. The 6 to 1 blend with an Al/Na mole ratio of 6.7 appeared to have better calcination properties than did the 2 to 1 blend, i.e. a credible flowsheet for calcining Na waste as a blend with $Al(NO_3)_3$ and H_3BO_3 would use a 2.2 $\underline{M}$ $Al(NO_3)_3$ to Na waste blend ratio of greater than 2.0 and an Al/Na mole ratio of 2.5. Blends of sodium waste with 2.2 $\underline{M}$ $Al(NO_3)_3$ with an Al/Na+K mole ratio of 4 were later calcined successfully during NWCF hot Campaign H-4.

NWCF CAMPAIGN H-1

During Campaign H-1 (September 8, 1982 through June 16, 1984) the NWCF calcined (when calcining: all wastes were combined with acid scrub recycle): first cycle Zr waste from tanks WM-182, -185, -187, and –188; a waste that was already a blend of Na and Zr wastes (WM-189) and a Na waste (WM-184) that were always calcined as a blend with other Zr and/or graphite matrix nuclear rocket (Rover) wastes; Rover waste (fed to calciner from tank WM-102); aluminum nitrate waste; and blends of 1 vol. WM-189 with 1 and 2 vol. WM-182, 2 vol. WM-189 with 3 vol. WM-182, 1 vol. WM-189 with 2 and 3 vol. WM-185, 1 vol. WM-189 with 3 and 4 vol. WM-188, 2, 2.5, and 3 vol. WM-188 with 1 vol. WM-189 and 1 vol. Rover, 4 vol. WM-188 with 1 vol. WM-189, 9 vol. WM-187 with 1 vol. WM-184, 2 vol. WM-188 with 2 vol. Rover and 1 vol. WM-189, 2 and 4 vol. Rover with 1 vol. WM-189, 1.5 vol. WM-187 with 1 vol. WM-189 and 2 vol. Rover with 1 vol. WM-189 and 1 vol. WM-187. The sources of the chemical composition of wastes will be given when discussing calcination of individual wastes. The chemical compositions of acid scrub between September 8, 1982 and January 31, 1983 were the averages of scrubs produced from calcining Zr wastes and from calcining Zr-Na waste blends found in Donovan (1983b). Chemical composition of scrubs produced between March 23, 1983 and June 16, 1984 were obtained from a computer read out giving all analyses of all scrub samples taken between March 23, 1983 and June 16, 1984. Flow rates of process streams were found in 3 different types of monthly reports issued between September 1982 and June 1984: 1) Production Department Monthly Reports from B. R. Wheeler to Paul W. Smith or D. L. Condotta or from R. C. Mairson to J. F. Erben; 2) Westinghouse Idaho Nuclear Company, Inc. Monthly Progress Reports edited by H. V. Chamberlain; and 3) Monthly Reports from W. A. Mickelson to R. C. Mairson.

The NWCF was forced to shut down a number of times, but all shutdowns were due to equipment problems.

There were very few problems calcining first cycle zirconium feed during NWCF Run H-1. This zirconium waste feed always contained enough dissolved and undissolved solids to build and maintain bed height. The mole % Na+K of calcined solids was always less than 2.0%. Except at the beginning of Run H-1 and just before emptying tank WM-182, first cycle Zr waste was not calcined for long periods of time. When calcine produced from blends of Na and Zr waste and/or Rover waste became too large, calciner feed would be switched to Zr waste for a short time until particle size was reduced. With this technique for controlling particle size using appropriate NAR and fluidizing air rates particle size was kept between 0.244 and 0.543 mm when calcining blends of Na and Zr waste and/or Rover waste. The chemical compositions of WM-182, -185, -187, and –188 wastes were found in Donovan (1982a), Donovan (1983a), and Parker (1983b).

The old chloride corrosion limit for the 304L stainless steel scrub system in the WCF was 2600 ppm (Cl = Cl conc. in µg/mL ÷ scrub sp.gr.). The chloride concentration of scrub stayed below that limit between September 8, 1982 and April 14, 1983. Chloride concentration increased from 2614 ppm on April 14, 1983 to 6,400 ppm on May 8, 1983; a deep recycle was made from NCC-108 (a scrub surge vessel) to WM-189 on May 8, 1983 which reduced chloride in scrub to 2,750 ppm; by August 1, 1983 Cl in scrub had increased to 9,700 ppm and another recycle reduced Cl to ~4000 ppm. The chloride in the acid scrub remained higher than 2600 ppm for the remainder of the runs but remained less than 9,700 ppm (ranged between 2000 and 9,700 ppm during the run). The scrub was only analyzed for mercury once during Run H-1; a sample submitted for analyses on May 8, 1983 analyzed 35 g/L (0.17 *M*) in mercury which was much higher in mercury concentrations than the mercury concentration in wastes stored in ICPP waste storage tanks. Usually in calculating the mercury concentration in a calciner feed,

Table 34. First-cycle zirconium wastes calcined during NWCF H-1.

	WM-182				WM-185					WM-188		WM-187	
	9/8-9/20/1982 9/22/1982 9/28-9/30/1982	10/1-13/1982	11/23-11/29/1982	12/30-31/1982	1/1-1/23/1983	9/21/9182	1/23-25/1983	3/23-31/1983	6/11-13/1983	6/30/1983	2/10-14/1984	9/12-22/1983	6/5/1984
H^+ (*M*)	1.17	1.36	1.42	1.48	1.47	1.08	1.36	1.39	1.33	1.27	1.40	1.54	1.53
Al (*M*)	0.42	0.48	0.51	0.53	0.49	0.40	0.47	0.57	0.49	0.43	0.46	0.48	0.49
Zr (*M*)	0.27	0.32	0.33	0.35	0.33	0.22	0.27	0.26	0.26	0.17	0.17	0.32	0.31
B (*M*)	0.16	0.18	0.19	0.20	0.19	0.13	0.15	0.15	0.14	0.12	0.13	0.14	0.13
Fe (*M*)	0.0032	0.0039	0.0041	0.0042	0.0043	0.0082	0.0099	0.012	0.011	0.0087	0.0090	0.0071	0.0073
Na (*M*)	0.010	0.012	0.012	0.013	0.012	0.033	0.038	0.050	0.049	0.069	0.074	0.026	0.026
K (*M*)	0.0020	0.0023	0.0024	0.0025	0.0024	0.0049	0.0058	0.0073	0.0073	0.0089	0.0094	0.0061	0.0059
Ca (*M*	1.03	1.20	1.27	1.32	1.22	0.80	0.96	1.10	0.98	0.77	0.80	1.16	1.11
Hg (*M*)	--	--	--	--	--	0.0020	0.0025	0.0029	0.014[a]	0.014[a]	0.0026	0.025[a]	0.0026
F (*M*)	1.87	2.19	2.31	2.40	2.22	1.45	1.74	2.00	1.78	1.40	1.45	2.11	2.01
NO_3 (*M*)	3.90	4.54	5.24	4.97	4.79	3.45	4.26	4.87	4.26	3.66	3.87	4.71	4.47
Cl (µg/mL)	390	445	386	426	542	455	588	134	567	608	538	1169[a]	902
UDS (g/L)	26	29	29	31	37	20.6	31	38	19	28	28	24	18.6
Mole% Na+K	0.23	0.23	0.22	0.24	0.23	0.87	0.84	0.98	1.1	1.8	1.9	0.54	0.55
Solid Content (g/L)	171	198	207	217	209	142	176	199	166	145	150	190	180

a. Values based on scrub analyses. Others used scrub values estimated from feed.

the scrub mercury concentration was assumed to be the percent of calciner feed mercury concentration equal to what the average percent of Al, Fe, B, and Zr scrub concentrations are to the concentration of these constituents in calciner feed. The majority of mercury in calciner feed volatizes and is collected in the acid scrub, so it is possible the high mercury value was correct. If the mercury concentrations found in the scrup spl. Submitted on May 8, 1983 was used to determine mercury concentrations in calciner feed the mercury concentration in calciner feed would be greater by a factor of ~4. Cl concentrations in WM-182, -185, -187, and –188 were <50 μg/ml, 123 μg/ml, 115 μg/ml, and 170 μg/ml, respectively. During calcination of Zr feed:

MMPD = $0.312^{+0.187}_{-0.072}\,mm$ (average and range of 69 determinations)

Bed bulk density = $1.48^{+0.17}_{-0.40}$ g/cm^3 (average and range of 68 determinations)

NAR = 262^{+472}_{-161} (average and range of 90 determinations)

Blends of WM-189 Waste and Zirconium Waste and/or Rover Waste

WM-189 waste was a hybrid waste – already a blend of Na and Zr wastes being less concentrated in Na and K than a normal Na waste and less concentrated in F and Zr than a normal Zr waste. During Campaign H-1, decontamination solutions and acid scrub solutions were emptied into tank WM-189 at various times during the campaign. For this reason analyses of appropriate spls from tank WM-189 taken at 4 different times during the campaign were used to calculate composition of calciner feeds. The composition of these samples are found in Childs (1982b), Donovan (1982b), Parker (1983a), and from analytical results for a sample taken from WM-189 during May of 1984. Analyses of Zr wastes blended with WM-189 waste are given in the section on first cycle Zr wastes; analyses of Rover wastes blended with WM-189 waste are given in the following section on Rover Waste. Scrubs were not analyzed for Na or K; for calculating Na and K feed concentrations it was assumed that the percent of Na or K concentration in scrub as compared to the concentration of Na or K concentration in feed was equal to the average % of the concentrations of Al, Fe, B, and Zr in scrub compared respectively to the concentrations of Al, Fe, B, and Zr in feed.

The greatest problem encountered in calcining blends of WM-189 and Zr wastes was keeping the size of calcine product particles from becoming too large even though while calcining these blends in Campaign H-1 the mole% Na+K in the calcined solids was 4.6 mole% or less. When calcine particles from blends of WM-189 and Zr waste became too large calciner feed was switched to Zr waste until particle size became suitably small again; changing the blend ratio, the NAR, and the fluidizing air rate was also used to control particle size. The time periods that a blend of WM-189 and Zr waste could be calcined before having to switch to Zr waste feed was quite long: 40 days between October 14 and November 23, 1982, 30 days between November 30 and December 30, 1982, 41 days between April 1 and June 11, 1983, 17 days between June 13 and June 30, 1983, and 19 days between June 1 and June 30, 1983. On April 13, 1983 the Ca/F mole ratio was reduced from 0.70 to 0.65 and on April 28, 1983 further reduced from 0.65 to 0.60. No adverse effect was noticed by decreasing the Ca/F mole ratio except an increase in Cl concentration in the acid scrub increasing from 2,600 ppm on April 14, 1983 to 6,400 ppm on May 8, 1983; a deep recycle was made from NCC-108 (a scrub surge vessel) to WM-189 on May 8, 1983 and the Ca/F mole ratio was increased from 0.60 to 0.70 which reduced the scrub Cl content to 2,750 ppm. Although increasing the Ca/F mole ratio from 0.60 to 0.70 decreased the rate that Cl concentration increased in acid scrub solution, the increase of the Ca/F mole ratio did not stop the increase of Cl concentration in acid scrub; another deep recycle from NCC-108 to WM-189 was needed

Table 35. Blends of WM-189 and zirconium waste calcined during NWCF H-1.

	1 Vol. WM-182 – 1 Vol. WM-189 10/14-10/21/1982	2 Vol. WM-182 – 1 Vol. WM-189 10/21-10/31/1982	2 Vol. WM-182 – 1 Vol. WM-189 11/1-11/9/1982	3 Vol. WM-182 – 2 Vol. WM-189 11/9-11/22/1982 and 11/30/1982	3 Vol. WM-182 – 2 Vol. WM-189 12/1-12/29/1982	2 Vol. WM-185 – 1 Vol. WM-189 1/25-1/31/1983
H^+ (<u>M</u>)	1.55	1.55	1.58	1.58	1.66	1.70
Al (<u>M</u>)	0.51	0.49	0.52	0.53	0.55	0.48
Zr (<u>M)</u>	0.20	0.23	0.25	0.23	0.24	0.20
B (<u>M</u>)	0.12	0.14	0.14	0.13	0.13	0.11
Fe (<u>M)</u>	0.017	0.013	0.013	0.015	0.016	0.016
Na (<u>M</u>)	0.21	0.15	0.15	0.18	0.19	0.19
K (<u>M)</u>	0.031	0.023	0.024	0.027	0.028	0.027
Ca (<u>M</u>	0.99	1.14	1.22	1.15	1.19	0.91
Hg (<u>M)</u>	0.0019	0.0020	0.0021	0.0023	0.0024	0.0020
F (<u>M)</u>	1.41	1.63	1.74	1.64	1.70	1.31
NO_3 (<u>M</u>)	5.68	5.62	5.85	5.89	6.14	5.29
Cl (µg/mL)	495	431	395	416	450	541
UDS (g/L)	18	20	21	20	21	19
Mole% Na+K	4.6	3.1	2.9	3.6	3.7	4.4
Solid Content (g/L)	182	194	206	199	207	171

to reduce the acid scrub Cl concentration when the concentration became too high (9,700 ppm) after which the acid scrub Cl concentration reduced to ~4000 ppm. During the rest of the campaign, except for short periods of time, calciner feeds other than blends of WM-189 and Zr feeds were being calcined. The chloride concentration of WM-189 waste was ~550 µg/mL (450 ppm). During the calcination of WM-189-Zr waste blends:

MMPD = $0.362^{+0.092}_{-0.118}\ mm$ (average and range of 204 determinations)

Bed bulk density = $1.52^{+0.38}_{-0.18}$ g/cm^3 (average and range of 203 determinations)

NAR = 504^{+413}_{-356} (average and range of 216 determinations)

Table 36. Blends of WM-189 sodium waste and zirconium waste calcined during NWCF H-1.

	3 Vol. WM-185 – 1 Vol. WM-189 1/31/1983	3 Vol. WM-185 – 1 Vol. WM-189 4/1-4/30/1983	3 Vol. WM-185 – 1 Vol. WM-189 5/1-5/31/1983	3 Vol. WM-185 – 1 Vol. WM-189 6/1-6/11/1983 and 6/13-6/25/1983	3 Vol. WM-188 – 1 Vol. WM-189 6/25-6/30/1983	4 Vol. WM-188 – 1 Vol. WM-189 7/1-7/20/1983	4 Vol. WM-188 – 1 Vol. WM-189 9/1-9/3/1983	1.5 Vol. WM-187 – 1 Vol. WM-189 5/14-5/17/1984, 5/18/1984, 5/20-5/24/194, 5/26-5/29/1984	1.5 Vol. WM-187 – 1 Vol. WM-189 6/1-6/4/1984 and 6/6-6/8/1984
H^+ (*M*)	1.70	1.48	1.47	1.39	1.30	1.42	1.44	1.68	1.65
Al (*M*)	0.46	0.51	0.52	0.52	0.46	0.47	0.47	0.46	0.44
Zr (*M*)	0.20	0.23	0.23	0.23	0.15	0.15	0.16	0.21	0.21
B (*M*)	0.12	0.15	0.15	0.15	0.13	0.13	0.14	0.12	0.11
Fe (*M*)	0.014	0.016	0.016	0.016	0.015	0.014	0.014	0.015	0.015
Na (*M*)	0.16	0.14	0.14	0.14	0.16	0.15	0.147	0.15	0.14
K (*M*)	0.023	0.021	0.022	0.021	0.023	0.019	0.021	0.041	0.037
Ca (*M*	0.96	1.02	1.04	1.09	0.84	0.88	0.91	1.04	0.99
Hg (*M*)	0.0021	0.0029	0.0019	0.014	0.014	0.022	0.026	0.0047	0.0043
F (*M*)	1.37	1.54	1.54	1.55	1.20	1.26	1.30	1.48	1.41
NO_3 (*M*)	5.29	4.91	4.91	4.89	4.18	4.37	4.51	4.75	4.59
Cl (µg/mL)	519	454	620	655	683	1,091	1274	633	1030
UDS (g/L)	19.5	22.6	21	20	27	30	34	15.3	16.5
Mole% Na+K	3.7	3.0	2.9	2.9	4.1	3.7	3.6	3.7	3.5
Solid Content (g/L)	173	185	186	190	164	169	177	178	172

Table 37. Blends of WM-189 Na waste, zirconium waste, and Rover waste calcined during NWCF H-1.

	3 Vol. WM-188 – 1 Vol. WM-189 – 1 Vol. Rover 7/20-7/30/1983	2.5 Vol. WM-188 – 1 Vol. WM-189 – 1 Vol. Rover 7/30-7/31/1983	2.5 Vol. WM-188 – 1 Vol. WM-189 – 1 Vol. Rover 8/1-8/13/1983	2 Vol. WM-188 – 1 Vol. WM-189 – 1 Vol Rover 8/13-8/31/1983	2 Vol. WM-188 – 1 Vol. WM-189 – 1 Vol. Rover 1/16-1/27/1984	2 Vol. WM-188 – 1 Vol. WM-189 – 2 Vol Rover 1/27-1/31/1984	2 Vol. WM-188 – 1 Vol. WM-189 – 2 Vol. Rover 2/1-2/10/1984, 2/14-2/29/1984	2 Vol. WM-188 – 1 Vol. WM-189 – 2 Vol. Rover 3/1-3/6/1984, 3/11-3/17/1984	2 Vol. WM-188 – 1 Vol. WM-189 – 2 Vol. Rover 4/19-4/20/1984	2 Vol. Rover - 1 Vol. WM-189 – 1 Vol. WM-187 6/8-6/14/1984
H$^+$ (*M*)	1.40	1.40	1.41	1.41	1.36	1.30	1.30	1.27	1.46	1.55
Al (*M*)	0.47	0.47	0.49	0.50	0.51	0.52	0.51	0.56	0.49	0.44
Zr (*M*)	0.13	0.19	0.20	0.13	0.11	0.096	0.10	0.099	0.096	0.11
B (*M*)	0.13	0.13	0.13	0.13	0.12	0.11	0.12	0.12	0.10	0.11
Fe (*M*)	0.016	0.017	0.018	0.019	0.014	0.011	0.011	0.013	0.097	0.0096
Na (*M*)	0.13-0.17[a]	0.14-0.19[a]	0.14-0.20[a]	0.15-0.20[a]	0.15-0.20[a]	0.12-0.20[a]	0.12-0.20[a]	0.13-0.21[a]	0.10-0.18[a]	0.087-0.19[a]
K (*M*)	0.017-0.026[a]	0.020-0.027[a]	0.021-0.028[a]	0.022-0.031[a]	0.022-0.030[a]	0.017-0.030[a]	0.018-0.031[a]	0.019-0.031[a]	0.022-0.036[a]	0.023-0.041[a]
Ca (*M*	0.77	0.74	0.77	0.74	0.75	0.71	0.72	0.74	0.62	0.64
Hg (*M*)	0.022	0.022	0.014	0.014	0.0022	0.0018	0.0018	0.0019	0.0027	0.0026
Nb (*M*)	0.0017	0.0019	0.0019	0.0022	0.0033	0.0052	0.0054	0.0054	0.0035	0.0044
F (*M*)	1.10	1.06	1.10	1.05	1.07	1.02	1.03	1.06	0.89	0.92
NO$_3$ (*M*)	4.01	3.98	4.08	4.03	4.29	4.12	4.01	4.21	3.72	3.57
Cl (µg/mL)	1120	1130	802	816	374	337	545	822	359	947
UDS (g/L)	25	24	24.5	23.6	20.9	17.5	17.4	19.5	16.4	11.5
Mole% Na+K	3.5-4.6[a]	3.7-4.9[a]	3.6-5.0[a]	4.0-5.3[a]	4.0-5.3[a]	3.5-5.5[a]	3.4-5.5[a]	3.5-5.5[a]	3.3-5.7[a]	3.0-6.0[a]
Solid Content (g/L)	151-155[a]	156-161[a]	161-167[a]	151-156[a]	146-151[a]	134-142[a]	136-144[a]	143-151[a]	122-131[a]	118-128[a]

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a. Of analyses found for Rover samples taken, only one sample was analyzed for Na and K (submitted 7/19/1983); the lower volume assumes Rover waste in the blend had some Na concentration as samples submitted 7/19/1983.

Blends of WM-189, Zirconium Waste, and Rover Waste

As with blends of WM-189 and Zr wastes, the greatest problem encountered in calcining blends of WM-189, Rover, and zirconium wastes (Table 37) was keeping the size of calcine product particles from being too large. The size of particles produced from blends of WM-189, Zr wastes, and Rover waste was controlled by switching to zirconium waste feed or diluted aluminum nitrate for a short period of time, varying of the NAR, changing the blend ratio, and/or changing the fluidizing air rate. The time period that a blend of WM-189, Zr, and Rover wastes could be calcined before having to switch to Zr waste or aluminum nitrate feed was quite long: 45 days between July 20 and September 3, 1983; 25 days between January 16 and February 10, 1984; and 25 days between February 10 and March 6, 1984. Only one analysis of samples of Rover waste was found where Rover waste was analyzed for Na and K content; this sample, submitted for analysis on July 19, 1983, showed Rover waste having a relatively high Na and K concentration (0.25 $\underline{M}$ and 0.041 $\underline{M}$ respectively). NCC-101 (a blend tank) from which this Rover sample was taken is also used to hold Na waste, and these high Na and K values could have been from the heel. If it was assumed that all Rover waste calcined contained 0.25 $\underline{M}$ Na and 0.041 $\underline{M}$ K, the Na+K mole% of calcine produced from calcining blends of WM-189, Zr, and Rover wastes varied between 4.6 and 6.0 mole%. If it was assumed that all Rover waste samples not analyzed for Na and K concentration contained no Na or K, the Na+K mole% of calcine produced from calcining blends of WM-189-Rover-Zr waste varied between 3.0 and 4.0 mole%. During the calcination of WM-189-Zr waste-Rover blends:

MMPD = $0.375^{+0.168}_{-0.086}$ *mm* (average and range of 97 determinations)

Bed bulk density = $1.53^{+0.23}_{-0.22}$ g/cm^3 (average and range of 96 determinations)

NAR = 540^{+788}_{-366} (average and range of 108 determinations)

Blends of WM-189 and Rover Waste

In calcining blends of WM-189 and Rover wastes, there was a problem keeping particle size from getting too large even though adjustments were made to the feed NAR and fluidizing air to control size and the blend ratio was changed from 2 Vol. Rover – 1 Vol WM-189 waste to 4 Vol. Rover – 1 Vol. WM-189 waste. In order to control MMPD, the calcination of the Rover waste – WM-189 waste blends was alternated with calcination of straight Rover waste or a blend of WM-189 and Zr waste. The Rover waste – WM-189 waste blends were run 1 to 8 days before alternating with straight Rover waste or a blend of Rover waste and WM-189 waste for 15 hours (one batch) to 7 days. The probable reason for difficulty in controlling bed particle size for these blends of Rover and WM1-189 wastes was that there was probably too much Na+K in the particles being produced. Of analyses found for Rover waste samples submitted to the Analytical Section, only one (submitted to the Analytical Section on July 19, 1983), had Na and K concentrations; this spl of Rover waste contained 0.25 $\underline{M}$ Na and 0.041 $\underline{M}$ K, solids produced from calcining blends of Rover and WM-189 wastes would contain from 9.4 to 9.8 mole% Na+K as compared to the 5.3 mole% Na+K recommended for such solids. If it was assumed that all Rover wastes not analyzed for Na or K contained no Na or K, the solids produced from calcining blends of Rover and WM-189 wastes contained from 3.0 to 5.0 mol% Na+K. Scrubs were not analyzed for Na or K; for calculating Na or K feed concentration it was assumed that the percent of Na and K concentration in scrub as compared to the concentration in feed was equal to the average percent of concentrations of Al, Fe, B, and Zr in scrub compared respectively to the concentrations of Al, Fe, B, and Zr in feed. Blends of Rover and WM-189 waste were not calcined for a sufficient length of time to note any trends.

During the calcination of blends of Rover and WM-189 wastes:

MMPD = $0.345^{+0.115}_{-0.091}$ *mm* (average and range of 29 determinations)

Bed bulk density = $1.37^{+0.24}_{-0.15}$ g/cm^3 (average and range of 28 determinations)

NAR = 420^{+226}_{-248} (average and range of 30 determinations)

Table 38. Blends of WM-189 and Rover waste calcined during NWCF H-1.

	2 Vol. Rover – 1 Vol. WM-189 4/20/1984 and 4/24-4/26/1984	4 Vol. Rover – 1 Vol. WM-189 5/2/1984, 5/3-5/11/1984, 5/17/1984, 5/18-5/20/1984, and 5/29-5/31/1984	4 Vol. Rover – 1 Vol. WM-189 4/26-4/30/1984
H$^+$ (*M*)	1.53	1.52	1.47
Al (*M*)	0.48	0.46	0.49
Zr (*M*)	0.046	0.045	0.042
B (*M*)	0.091	0.11	0.96
Fe (*M*)	0.0105	0.0073	0.0072
Na (*M*)	0.11-0.24[a]	0.068-0.26[a]	0.064-0.24[a]
K (*M*)	0.029-0.051[a]	0.018-0.049[a]	0.017-0.046[a]
Ca (*M*	0.366	0.41	0.37
Hg (*M*)	0.0027	0.0028	0.0027
Nb (*M*)	0.0057	0.0079	0.0069
F (*M*)	0.52	0.59	0.53
NO$_3$ (*M*)	3.24	2.98	3.06
Cl (µg/mL)	367	513	318
UDS (g/L)	7.9	6.6	6.9
Mole% Na+K	5.0-9.7[a]	3.0-9.8[a]	3.0-9.4[a]
Solid Content (g/L)	86-103[a]	84-104[a]	80-98[a]

a. Analyses found for Rover samples taken only one sample was analyzed for Na+K (submitted June 19, 1983); the lower volume assumes no Na or K in Rover waste; the upper volume assumes Rover waste in blend had the same Na concentration as sample submitted July 19, 1983.

Blends of Na Waste (WM-184) and Zirconium Waste (WM-187)

A blend of 9 Vol. Zr waste (from WM-187) and 1 Vol. Na waste (from WM-184) was calcined between September 3 and September 12, 1983. On September 11 agglomerates appeared in the fluidized bed (Wheeler 1983). To reduce the agglomerates, the feed was changed to straight Zr waste on September 12, 1983. The composition of the calciner feed from the blend of WM-187 waste and WM-184 waste is shown in Table 39. The composition of WM-184 waste used to calculate the feed is that given in Caldwell (1983). The WM-184-WM-187 blend was not calcined long enough to note any trends. The mole% of Na+K in calcine produced from the blend was 3.8 mole%. Scrubs were not analyzed for Na or K; for calculating Na and K feed concentrations it was assumed that the percent of Na or K in scrub as compared to the concentration of Na or K concentration in feed was equal to the average percent of the concentrations of Al, Fe, B, and Zr in scrub compared respectively to the concentrations of Al, Fe, B, and Zr in the feed. During the calcination of a blend of 9 Vol. WM-187 waste and 1 Vol. WM-184 waste:

MMPD = $0.371^{+0.051}_{-0.045}$ *mm* (average and range of 8 determinations)

Bed bulk density = $1.59^{+0.13}_{-0.10}$ g/cm^3 (average of 8 determinations)

NAR = 584^{+102}_{-36} (average of 10 determinations)

Table 39. Blend of Na Waste (WM-184) and Zirconium waste (WM-187) calcined during NWCF H-1.

	9 Vol. WM-187 Waste – 1 Vol. WM-184 Waste 9/3-9/12/1983
H^+ (M)	1.44
Al (M)	0.50
Zr (M)	0.29
B (M)	0.13
Fe (M)	0.0080
Na (M)	0.223
K (M)	0.018
Hg (M)	0.025
Ca (M)	1.29
Mn (M)	0.0012
Cr (M)	0.00017
Ni (M)	0.00012
F (M)	1.90
NO_3 (M)	5.15
Cl (µg/mL)	1287
SO_4 (M)	0.0065
PO_4 (M)	0.0022
UDS (g/L)	22
Mole% Na+K	3.8
Solid Content (g/L)	221

Rover Waste

Time periods for calcining straight Rover waste varied between one batch and 5 days. These calcination periods were too short to determine the calcination characteristics of Rover waste. If the waste contained only small amounts of Na+K (less than 0.1M), there should have been problems building bed and maintaining bed height when calcining Rover waste for longer periods of time than 5 days (dissolved and undissolved solid content of waste was low). Usually, Rover waste was calcined for short periods of time after a blend contain WM-189 or Na waste to reduce particle size. The composition of Rover waste in making calciner feed calculations for feeds containing Rover waste was obtained mostly from computer print-outs of samples submitted to the Analytical Chemistry Section at various times during the campaign. The composition of Rover waste used in calculations was usually an average of 2 samples taken within a short time of one another; when a constituent was only analyzed for in one of the 2 samples, that one concentration (which was not an average) of the constituent would be used. Of the analyses of Rover waste samples found, only one was analyzed for Nb (Palmer 1983). This one concentration was used for the Nb concentration of all Rover wastes when calculating the compositions of feeds containing Rover waste. Of the analyses of Rover waste found, only one taken July 19, 1985 was analyzed for Na+K. The Na and K concentrations of this sample (0.25 and 0.041 M, respectively) were high. The Na and K concentrations may have been high in the Rover waste batch in NCC-101 (blend tank) from which the sample was taken because Na waste was also stored in NCC-101 for short periods of time and the high Na and K concentration may have been due to a heel from a Na waste previously stored in NCC-101. If 0.25 $\underline{M}$ Na and 0.041 $\underline{M}$ K was the typical concentration in all Rover wastes, then calcine produced would have been 9.4 to 10.5 mole% Na+K from calcining unblended Rover waste and some of the blends containing Rover waste. These solids probably did not clinker because these feeds were not allowed to be calcined for long periods of time (whenever agglomerates were observed in product samples, operating conditions and feeds were changed to reduce particle size). Rover feed compositions were obtained from: 1) composite of information found in Palmer (1983) and an analysis on a computer printout for a sample submitted to the Analytical Chemistry Section on July 9, 1983; 2) composite of analysis on a computer printout for 2 different samples submitted to the Analytical Chemistry Section on January 18, 1984; and 3) composite of analysis on a computer printout for 2 different samples submitted to the Analytical Chemistry Section in April 1984. Scrubs were not analyzed for Na or K; for calculating Na and K feed concentrations, it was assumed that the percent of Na or K in scrub as compared to the concentration of Na or K concentration in feed was equal to the average percent of the concentration of Al, Fe, B, and Zr in scrub compared respectively to the concentrations of Al, Fe, B, and Zr in feed. During the calcination of Rover wastes:

$$\text{MMPD} = 0.367^{+0.075}_{-0.078}\ mm \quad \text{(average and range of 11 determinants)}$$

$$\text{Bed bulk density} = 1.38^{+0.18}_{-0.15}\ \text{g/cm}^3 \quad \text{(average and range of 11 determinants)}$$

$$\text{NAR} = 338^{+288}_{-243} \quad \text{(average and range of 15 determinants)}$$

Due to the short calcination periods of Rover waste and due to the fact that calciner operating conditions while calcining Rover waste were often used to decrease bed particle size, the above NAR, MMPD, and bulk density would not be typical for long term Rover waste calcination.

Table 40. Rover waste blends calcined during NWCF H-1.

	10/6-10/11/1983	4/23/1984 4/30/1984	5/1-5/2/1984 5/3/1984 5/11-5/14/1984	6/4/1984 6/15-6/16/1984
H^+ ($\underline{M}$)	1.04	1.38	1.43	1.42
Al ($\underline{M}$)	0.78	0.51	0.47	0.46
Zr ($\underline{M}$)	0.049	0.038	0.041	0.044
B ($\underline{M}$)	0.13	0.10	0.12	0.11
Fe ($\underline{M}$)	0.025	0.0022	0.0024	0.0026
Na ($\underline{M}$)	0.067-0.23[a]	0.016-0.22[a]	0.035-0.24[a]	0.074-0.266[a]
K ($\underline{M}$)	0.011-0.038[a]	0.0026-0.037[a]	0.0057-0.039[a]	0.012-0.044[a]
Ca ($\underline{M}$)	0.29	0.30	0.33	0.31
Hg ($\underline{M}$)	--	--	--	--
Nb ($\underline{M}$)	0.0089	0.0086	0.010	0.011
F ($\underline{M}$)	0.52	0.54	0.60	0.56
NO_3 ($\underline{M}$)	2.91	2.63	2.56	2.50
Cl (µg/mL)	1,594	245	442	848
UDS (g/L)	16	5.6	5.3	7
Mole% Na+K	2.3-5.4[a]	0.73-8.9[a]	1.5-9.2[a]	3.3-10.5[a]
Solid Content (g/L)	99-115[a]	66-87[a]	69-91[a]	72-93[a]

a. Of analyses found for Rover samples taken only one sample was analyzed for Na and K (submitted July 19, 1983); the lower value assumes no Na or K in Rover waste (Na+K present comes from scrub); the upper value assumes Rover waste had the same concentration as the sample submitted July 19, 1983.

Aluminum Nitrate Waste

The aluminum nitrate waste calcined in NWCF Campaign H-1 (from storage tank WM-182) was somewhat different than aluminum nitrate wastes calcined in WCF Campaigns. The latter wastes were essentially aluminum nitrate (1.3-1.7 *M* Al) containing less than 0.1 *M* sodium, boron (added to prevent formation of alpha alumina during calcination), and mercury; the former waste contained 1.4 *M* aluminum, but also contained 0.24 *M*, 0.06 *M* K, and 0.39 *M* F. Compositions found in Parker (1983c) were used in calculating the composition of aluminum nitrate waste calciner feed. The aluminum nitrate waste calcined in NWCF Campaign H-1, without the fluoride present, would be similar to the blends of 2.2 *M* aluminum nitrate and sodium waste discussed in Newby (1986). WM-182 waste would have the same aluminum to sodium plus potassium mole ratio as a blend of 4 Vol. of 2.2 *M* aluminum nitrate and 1 Vol. of the Na waste used in the studies described in Newby (1986). Both WM-182 wastes calcined in the NWCF and blends of aluminum nitrate and Na wastes calcined in the 30-cm enclosed pilot plant calciner had problems keeping calcined product from becoming too small and in producing copious quantities of fines. The smallest bed particles obtained during NWCF Campaign H-1 (0.197 mm) were obtained during calcination of WM-182 aluminum nitrate waste. WM-182 waste was calcined for 8 days between September 22 and September 30, 1983, 5 days between October 1 and October 6, 1983, and for 1 day on June 15, 1984. These calcination periods were too short to determine the calcination characteristics of aluminum nitrate waste of the WM-182 type. During the calcination of WM-182 type aluminum nitrate waste:

MMPD = $0.30^{+0.191}_{-0.099}\ mm$ (average and range of 22 determinations)

Bed bulk density = $1.47^{+0.24}_{-0.16}$ g/cm^3 (average and range of 22 determinations)

NAR = 211^{+481}_{-108} (average and range of 22 determinations)

Table 41. Aluminum nitrate waste (WM-182) blends calcined during NWCF H-1.

	9/22-9/30/1983	10/1-10/6/1983	6/15/1984
H^+ (*M*)	0.89	0.83	1.04
Al (*M*)	1.24	1.15	1.11
Zr (*M*)	0.055	0.051	0.06
B (*M*)	0.042	0.051	0.039
Fe (*M*)	0.020	0.020	0.017
Na (*M*)	0.25	0.26	0.20
K (*M*)	0.064	0.068	0.052
Ca (*M*)	0.062	0.063	0.061
Hg (*M*)	0.039	0.054	0.016
F (*M*)	0.37	0.38	0.36
NO_3 (*M*)	5.02	4.73	4.65
Cl (µg/mL)	982	1465	1082
UDS (g/L)	55.6	57	45.3
Mole% Na+K	7.5	7.5	6.7
Solid Content (g/L)	157	155	135

NWCF CAMPAIGN H-2

During Campaign H-2 (September 11, 1987 through December 9, 1988), the NWCF calcined 1st cycle Zr waste from tank WM-187, 1st cycle Fluorinel waste from WM-188 and –189 (similar to Zr waste but with about 0.12 molar cadmium), and Na waste from WM-186. The WM-187 waste was mostly calcined unblended, but some was calcined as blends with WM-186 (primarily at a 5:1 volume ratio of 187:186). Fluorinel waste was never successfully calcined straight in calciner pilot plant tests, so during H-2, WM-188 and WM-189 wastes were always blended with sodium waste from WM-186 such that the cadmium content in the calcine was less than 1.55 mole % cadmium. Volume ratios ranged from 4:1 to 9:1 for blends of WM-188 or -189 with WM-186, with a ratio of 5:1 being used for the majority of the campaign. All the wastes were combined with about 5 to 15 volume % acid scrub recycle during calcination. The Zr and Flourinel wastes were blended with the Na waste to obtain from 3 to 6 mole% Na+K in the calcine. Compositions of the waste tanks at the time of operation and the blend ratios used can be found in Staiger (1999). A nominal calcium to flouride ratio of 0.55 was used for unblended WM-187 while a ratio of 0.7 was used for blends of Zr and Flourinel wastes with sodium waste. These blends operated quite well during the campaign and typical blends (not adjusted for scrub recycle) are shown in Table 42. A campaign report is being prepared by M. C. Swenson.

Table 42. Typical Zirconium – sodium blends calcined during NWCF Campaign H-2 (not including scrub recycle).

Constituents[a]	WM-187	5 Vol. WM-187 – 1 Vol. WM-186	5 Vol. WM-189 – 1 Vol. WM-186	5 Vol. WM-188 – 1 Vol. WM-186	5 Vol. WM-189[b] – 1 Vol. WM-186
H^+	1.54	1.59	1.42	2.03	2.13
Al	0.44	0.43	0.39	0.39	0.32
B	0.16	0.13	0.15	0.15	0.17
Ca	1.08	1.15	1.34	1.33	1.26
Cd	0.05	0.04	0.09	0.09	0.09
Cr	0.0126	0.0113	0.0024	0.0024	0.0024
F	1.96	1.64	1.92	1.90	1.80
Fe	0.006	0.009	0.010	0.010	0.011
Hg	0.002	0.002	0.000	0.000	0.000
K	0.004	0.038	0.039	0.037	0.041
Mn	0.0000	0.0023	0.0023	0.0023	0.0023
Na	0.10	0.33	0.29	0.27	0.28
Ni	0.0000	0.0005	0.0010	0.0009	0.0008
SO4	0.073	0.066	0.061	0.037	0.057
Zr	0.32	0.27	0.28	0.26	0.23
NO3	5.08	5.16	5.29	5.19	7.25
Cl	0.0000	0.0052	0.0052	0.0060	0.0068
PO4	0.000	0.000	0.000	0.000	0.006
UDS (g/L)	0.000	1.537	1.537	1.537	1.860
Ca to F mole Ratio	0.55	0.70	0.70	0.70	0.70
Na+K Mol%	1.7%	5.9%	5.0%	4.7%	5.2%
Solid Content g/L	170	181	199	190	184

a. Concentrations are in Molar except where noted and are not corrected for scrub recycle added to the feed.

b. The composition of WM-189 changed for the latter part of the campaign.

NWCF CAMPAIGN H-3

Operating periods for Campaign H-3 were June 18 to 23, 1990 (cold Alumininum Nitrate (ANN) only), December 1, 1990 to January 25, 1991, March 11, 1991 to August 29, 1991, January 10 to 17, 1992 (cold ANN only), and January 8, 1993 to November 1, 1993. The NWCF calcined first cycle Zr waste from tank WM-187 (a mixture of zirconium and Flourinel wastes), first cycle Fluorinel waste from WM-188 (similar to Zr waste but with about 0.12 molar cadmium), Na waste from WM-185, dilute first cycle Aluminum waste from WM-182, and dilute second/third cycle aluminum waste from WM-100 and -102. Compositions of the waste tanks at the time of operation and blend ratios can be found in Staiger (1999) and most of the blend calculations for the campaign can be found in O'Brien (1991). A campaign report has been drafted by T. G. Finup but has not yet been issued.

The WM-188 waste, and part of the WM-187, was calcined as blends with WM-185 producing calcine with 3.5 to 5.3 mole % Na+K and less than 1.55 mole % cadmium. A nominal calcium to flouride ratio of 0.7 was used for blends of Zr and Flourinel wastes with sodium waste. Most of the WM-188 was calcined as a 6:1 blend with WM-185, although the blend ratios varied from 4.2:1 to 7:1. WM-187 to –185 blend ratios varied from 3:1 to 7:1. The WM-188:WM-185 and WM-187:WM-185 blends were similar to the Zr:Na blends calcined during NWCF campaign H-2. Campaign H-3 started on a WM-188:WM-185 blend, which produced agglomerates and did not work as well as similar blends during H-2. This was likely because the fuel nozzles had been eroded. The fuel nozzle caps had not been replaced prior to H-3, and they were found to be badly eroded after a brief shutdown in January, 1991 to dissolve the bed. The Zr/Na blends worked well after the fuel nozzles were replaced.

The WM-182 aluminum waste was quite dilute, which made it difficult to calcine. Most of WM-182 was calcined as 3-way blends with WM-187 Zr waste and WM-185 Na waste. Calcium nitrate was added to a nominal Ca/F ratio of 0.7, and boric acid was added to obtain 0.11 M in the blend. Blend ratios of WM-182:WM-187:WM-185 varied 3.1-6.3:2.1-4:1. These blends built bed poorly or not at all and had a tendency for the particle size to grow. ANN replacing up to ½ of the WM-182 in the 3-way blend was used at times to improve the blend. A blend of 5.4:3.2:1 of WM-182:187:185 which had an alkali metal content of 4 mole % Na+K was used for the majority of the run, but the particle size still tended to grow. Near the end of the run, this 3-way blend was alternated with blends of 0.33 to 1 vol ANN per vol WM-182 containing 0.03 M B for 3-7 days every 2 weeks to bring the particle size back down.

Dilute second/third cycle aluminum wastes from WM-100 and –102 were calcined by blending with ANN to obtain about 1.7 M Al, and adding boric acid to 0.03 M B. More dilute (less ANN) blends were tried but did not build bed.

For a week near the end of the campaign, waste from WM-100 was also blended with WM-185 sodium waste and cold (non-radioactive) ANN. Calcium nitrate was added to obtain 40% excess calcium to chemically combine all the fluoride, chloride, sulfate, and phosphate in the feed. Boric acid was added to the feed based on the amount of sodium plus potassium in the feed according to the relation:
B (M)= 1.1*(0.2149*(Na (M)+K (M)-0.0409) or 0.03 M, whichever was greater

The WM-100:WM-185:ANN blend was followed by a 4:1 volume ratio blend of ANN:WM-185. Both blends produced calcine with about 5 mole % Na+K.

After the difficulties building bed with dilute feeds during H-3, the plant operating data was evaluated by R. J. Rivard (Rivard 1994). He found that during the run, aluminum feeds with less than 84 g/L total solids (total solids = dissolved solids plus undissolved solids) and less than

1.6 M Al did not build bed. For comparison, the cold aluminum nitrate feed consisting of 1.8 M aluminum and 0.02 molar boron which is used for startup produces about 95 g/L total solids. The 3-way Al:Zr:Na feed blends, which were chemically similar to ANN:Na feeds, required more total solids than aluminum blends to build bed.

Table 43. Examples of feed blends calcined during NWCF Campaign H-3 (not including scrub recycle).

Constituents[a]	6 Vol. WM-188 Flourinel – 1 Vol. WM-185 Sodium	4.9 Vol. WM-187 Zirconium – 1 Vol. WM-185 Sodium	3 Vol. ANN – 3.3 Vol. WM-182 Aluminum – 3.8 Vol. WM-187 – 1 Vol. WM-185 Sodium[b]	5.4 Vol. WM-182 Aluminum – 3.2 Vol. WM-187 – 1 Vol. WM-185 Sodium[b,c]	1 Vol. ANN - 1 Vol. WM-182 Aluminum	4 Vol. ANN - 1 Vol. WM-185 Na
H^+	1.33	1.13	0.74	0.88	0.48	0.32
Al	0.27	0.36	0.95	0.72	1.61	1.47
B	0.10	0.08	0.10	0.10	0.02	0.15
Ca	0.98	0.87	0.38	0.39	0.03	0.02
Cd	0.068	0.032	0.014	0.014	0.001	0.000
Cl	0.001	0.001	0.001	0.001	0.000	0.000
Cr	0.003	0.006	0.003	0.003	0.000	0.001
F	1.40	1.24	0.55	0.56	0.04	0.02
Fe	0.007	0.007	0.008	0.013	0.009	0.003
Hg	0.0009	0.0011	0.0005	0.0006	0.0000	0.0005
K	0.022	0.025	0.014	0.017	0.001	0.026
Na	0.15	0.18	0.10	0.12	0.01	0.19
Ni	0.0015	0.0013	0.0006	0.0006	0.0000	0.0002
NO3	3.95	3.96	4.19	4.21	4.92	3.79
Pb	0.0002	0.0002	0.0001	0.0002	0.0000	0.0003
SO4	0.035	0.024	0.018	0.024	0.013	0.007
U	0.003	0.003	0.003	0.003	0.002	0.001
Zr	0.151	0.178	0.078	0.077	0.003	0.002
UDS (g/L)	2.0	2.0	1.1	1.4	0.4	0.7
Ca to F mole Ratio	0.70	0.70	0.70	0.70	0.70	0.70
Na+K Mol%	3.8%	4.6%	2.8%	3.7%	0.2%	4.9%
Solid Content g/L	134	130	103	95	89	98

a. Concentrations are in Molar except where noted and are not corrected for scrub recycle added to the feed.
b. The blend ratios used for 3 and 4-way blends varied considerably during the run due to these blends tendencies to build bed poorly and to cause particle size growth.
c. This blend was alternated with ANN:WM-182 blends to reduce particle size during the latter part of the run.

NWCF CAMPAIGN H-4

Operating periods for NWCF Campaign H-4 were June 5, 1997 to April 12, 1998, January 19, 1999 to June 1, 1999, and March 8, 2000 to May 27, 2000. This campaign was the first long term operation on ANN:Na waste blends at the normal calcination temperature of 500°C, and also included short and long term tests of ANN:Na calcination at 600°C. The feeds calcined were: waste from WM-188, which had a zirconium heel to which was added evaporated blend of WM-183 sodium waste and WM-189 dilute decontamination waste; waste from WM-185, which was a sodium waste; and waste from WM-189, which was a decontamination solution heel to which was added evaporated WM-185 sodium waste and WM-187 mixed zirconium/decontamination/second/third cycle waste. All of the wastes were blended with cold aluminum nitrate (ANN) as a diluent for the sodium and potassium in the wastes, and had calcium nitrate added to provide more calcium than was needed to chemically combine all the fluoride, chloride, sulfate, and phosphate in the feed. When calcining at 500°C, boric acid was added relative to the amount of sodium and potassium in the feed using the same correlation used for ANN:Na blends during campaign H-3. Boric acid was usually not added when calcining blends at 600°C.

An overall Run Report for campaign H-4 has not yet been issued. Feed blend data for 1997 through 1999 are in Staiger (1999). Reportson the high temperature (600°C) trial test in March-May 1999 were issued by Wood (1999) and Nenni et al. (2000). A report on the in March-May 2000 high temperature trial test has been issued by Swenson (2000).

The allowable ranges for ANN to sodium waste blends for each sodium waste (WM-188, WM-185, or WM-189) for the Run Plan were selected to obtain the desired range of Al/Na+K mole ratios in the feed. The upper limit for ANN addition was based on an arbitrary selection of blends which produced 5.5 mole % Na+K calcine or greater (these were greater than the old upper limit of 5.3 mole % Na+K which had been imposed for Zr/Na blends). The lower limit for ANN addition for each blend was selected to obtain the minimum allowable Al/Na+K mole ratio which could be calcined without agglomeration in the Enclosed 15-cm Calciner Pilot Plant (for 500°C calcination: minimum 3.1 mole Al/Na+K for WM-185, 188, or 189; for 600°C calcination: minimum Al/Na+K of 1.5 for WM-185 and 2.5 for WM-189).

Waste from WM-188 was calcined with ANN from June 17, 1997 until the tank was depleted on February 20, 1998. The initial blend was 1.8 vol ANN: 1 vol WM-188 with an Al/Na+K mole ratio of 5.4 and producing calcine with 5.9 mole % Na+K. This was decreased in small steps over the next month down to a blend of 1.2 vol per vol with an Al/Na+K mole ratio of 4.0 and producing calcine with 7.5 mole % Na+K. By that time, the feed NAR had been increased to the maximum of 400 to keep the particle size from growing. The 1.2:1 blend was then calcined successfully until WM-188 depletion. Calcium nitrate was initially added to obtain 40% excess calcium than was needed to chemically combine all the fluoride, chloride, sulfate, and phosphate in the feed. The chloride concentration in the scrub increased over the initial part of the run, and was stabilized at about 3000 to 4000 mg Cl/L by increasing the calcium addition to 90% excess and keeping the scrub acid concentration at 3 to 4 molar acid. Modeling studies had predicted that higher acid concentrations in the scrub would promote chloride from the scrub as hydrogen chloride and reduce chloride buildup.

Waste from WM-185 was calcined with ANN from February 20, 1998 until temporary shutdown in April, 1998. The initial blend was a 2.4 volumes ANN per vol WM-185 which was chemically similar to the successful WM-188 blend (Al/Na+K mole ratio of 4.0, 90% excess calcium) except that it had about ½ the flouride in the blended feed (0.04 M flouride for ANN:WM-185 vs. 0.13 M flouride for ANN:WM-188). It produced calcine with 7.9 mole % Na+K. The blend was lowered to an Al/Na+K mole ratio of 3.6, but the bed particle size tended to increase, and the blend was increased back to 4 mole Al/mole Na+K.

Waste from WM-189 was calcined with ANN from January 23, 1999 to March 23, 1999. The blend was varied from 1.5 to 1.7 vol ANN per vol WM-189 (Al/Na+k mole ratios of 4.0 to 3.6 and producing calcine with 8 to 7 mole % Na+K). Calcium nitrate was added at 60 to 90% excess. The blended WM-189 feed chemical composition was nearly identical to the blended WM-188 feed.

On March, 23, 1999, the feed blend was switched to a 2.4 vol ANN per vol WM-185 blend with an Al/Na+K mole ratio of 4.0. The first high-temperature trial test began when the calciner temperature was increased to 600°C on March 30, 1999, and on April 1, 1999 the blend was changed to a 0.89 vol ANN per vol WM-185 blend having an Al/Na+K mole ratio of 2.0 and no boron added. After an initial stabilization period, the particle size began to grow slowly. Attempts to control the size growth by increasing NAR, O2/fuel ratio, and fluidizing air were too aggressive and caused the blend to stop building bed. The blend was changed back to 4.0 moles Al/mole Na+K on April 14, 2000 without success, and the temperature was decreased back to 500°C on April 17, 1999. Shortly thereafter, the off-gas line downstream of the cyclone began to plug. The restriction was partially cleared by air blasting the off-gas line. The particle size decreased back to desired size of 0.35 mm while the temperature was at 500°C. The temperature was increased back to 600°C on May 6, 1999 while still on the 4.0 Al/Na+K mole ratio blend to observe the effect of high temperature operation on the partially plugged off-gas line. The restriction did not get worse. The bed temperature was decreased to 500°C on May 20, 1999 to change out a fuel nozzle, and the off-gas line plugging subsequently worsened until the calciner had to be shut down on June 1, 1999. The cause of the plugging was later determined to be re-nitration of fines generated at 600°C, which normally deposit in the off-gas line, after the temperature was lowered to 500°C, causing them to swell and become sticky, restricting the off-gas line (Nenni et al. 2000). Sodium and potassium nitrates are molten above 310°C and the equilibrium concentration of sodium and potassium nitrates in the calcine is highly dependent on temperature from 350 to 700°C. Calcination at 500°C denitrates the sodium and potassium nitrates in the feed by about 34%, while calcination at 600°C denitrates them by about 66%.

NWCF operation resumed on March 8, 2000. The initial feed was cold aluminum nitrate and the calcination temperature was 500°C. Feed was switched to a 1.4 vol ANN per vol WM-189 blend with an Al/Na+K mole ratio of 3.9 on March 15, 2000. The temperature was increased to 600°C on March 25, 2000 for the restart of the high temperature trial test. No boron was added to the high temperature feeds, other than that present in the waste. Calcium nitrate addition was reduced to 40% excess because of concern that calcium chloride formation and deposition in the off-gas line might have contributed to the previous off-gas plugging. The blend ratio of ANN to WM-189 was decreased to 1.3, then 1.15, then 1.0 (Al/Na+K mole ratios of 3.7, 3.35, 3.0, respectively) from March 26 through April 21. A blend of 1.2 vol ANN per vol WM-189 (Al/Na+K mole ratio = 3.5, calcine Na+K content = 8.8 mole % Na+K) was calcined until May 12, when the blend was again reduced to 0.9 vol ANN per vol WM-189 (Al/Na+K mole ratio = 2.8, calcine Na+K content = 10.6 mole % Na+K). The blend was again reduced to 0.8:1 ANN:WM-189 on May 18 (11.24 mol% Na+K). During the high temperature test, the particle size grew steadily until it stabilized at a higher than normal value of 0.58 mm in late April. A higher than normal feed NAR of 500 was used to control particle size. Fines carryover to the scrub was quite high during high temperature operation, but the fines were still soluble in the scrub, as indicated by low undissolved solids in the scrub samples. Scrub recycle to the feed was higher normal at about 20 to 25 volume %; however, the chloride concentration in the scrub decreased to 1000 to 2000 mg Cl/L during high temperature operation such that no deep recycles back to the tank farm were required.

Approximate feed compositions for the typical 500C blends and range of 600C blends are provided in Table 44.

Table 44. NWCF Campaign H-4 blended waste feed compositions (not including scrub recycle).

Species		WM-188 /ANN 500°C	WM-185/ ANN 500°C	WM-189/ ANN 500°C	WM-185/ ANN 600°C	WM-185/ ANN 600°C	WM-189/ ANN 600°C	WM-189/ ANN 600°C	WM-189/ ANN 600°C
Na+K, Calcine	(Mole %)	7.6%	7.9%	7.6%	8.3%	15.1%	8.3%	10.6%	11.24%
Al/Na+K	(Mole Ratio)	3.9	4.0	4.1	4.0	1.8	3.9	2.8	2.5
Ca/($^1/_2$F + $^1/_2$Cl + SO_4 + $^3/_2PO_4$)	(Mole Ratio)	1.87	1.91	1.88	1.91	1.91	1.42	1.42	1.42
Acid	(H+, M)	1.2261	0.5504	1.0603	0.5871	0.9011	1.1526	1.4048	1.47
Nitrate	(NO3, M)	6.1881	5.8372	6.2391	6.2270	5.8980	6.4930	6.4546	6.4
Aluminum	(Al, M)	1.4606	1.5981	1.5461	1.7048	1.3764	1.6043	1.4697	1.44
Boron	(B, M)	0.0432	0.0497	0.0437	0.0056	0.0100	0.0101	0.0128	0.014
Cadmium	(Cd, M)	0.0038	0.0003	0.0018	0.0003	0.0006	0.0019	0.0025	0.0026
Calcium	(Ca, M)	0.1537	0.0688	0.0902	0.0734	0.1320	0.0745	0.0941	0.099
Chloride	(Cl, M)	0.0063	0.0075	0.0089	0.0080	0.0144	0.0097	0.0123	0.013
Chromium	(Cr, M)	0.0054	0.0012	0.0016	0.0013	0.0023	0.0017	0.0022	0.0023
Flouride	(F, M)	0.1281	0.0430	0.0820	0.0459	0.0825	0.0898	0.1134	0.1197
Iron	(Fe, M)	0.0227	0.0066	0.0092	0.0071	0.0127	0.0101	0.0128	0.0135
Lead	(Pb, M)	0.0005	0.0005	0.0004	0.0005	0.0010	0.0004	0.0005	0.0006
Manganese	(Mn, M)		0.0051		0.0054	0.0098			
Mercury	(Hg, M)	0.0031	0.0011	0.0019	0.0012	0.0021	0.0021	0.0026	0.0028
Molybdenum	(Mo, M)		0.0001		0.0001	0.0003			
Nickel	(Ni, M)	0.0022	0.0004	0.0007	0.0004	0.0007	0.0008	0.0010	0.0011
Phosphate	(PO4, M)	0.0001	0.0007	0.0001	0.0007	0.0013	0.0001	0.0001	0.0002
Potassium	(K, M)	0.0602	0.0493	0.0421	0.0526	0.0947	0.0461	0.0583	0.0615
Sodium	(Na, M)	0.3130	0.3514	0.3330	0.3749	0.6744	0.3645	0.4604	0.4860
Sulfate	(SO4, M)	0.0148	0.0097	0.0025	0.0103	0.0186	0.0027	0.0034	0.0036
Zirconium	(Zr, M)	0.0108	0.0029	0.0132	0.0031	0.0055	0.0144	0.0182	0.0193
Uranium	(U, mg/l)	51.9050	20.3729	19.9493	21.7332	39.0968	21.8382	27.5851	29
Undissolved Solids	(UDS, g/l)		1.2849	0.4064	1.3707	2.4658	0.4449	0.5619	0.59
Total Solids	(g/L)	118	119	116	115	121	110	111	111

STUDIES IN A TWO-FOOT SQUARE PILOT-PLANT CALCINER CALCINATION OF AL(NO$_3$)$_3$-NITRIC ACID WASTE

The two-foot-square pilot-plant calciner (heated indirectly by a NaK system similar to that used in the WCF) was used to develop equipment, a flowsheet for calcination of simulated (non-radioactive) $Al(NO_3)_3$-nitrate waste acid waste, techniques, and procedures for use in the WCF. A description of this work can be found in: Brown, Grimmett, and Buckham (1962a); Wheeler, Grimmett, and Buckham (1962); Brown et al. (1964a); and Brown, Legler and Lakey (1964b). The flowsheet development work consisted of determining: whether α or amorphous Al_2O_3 formation during calcination of $Al(NO_3)_3$ waste was the most desirable; what constituents in the waste promoted formation of each type of $Al(NO_3)_3$; and upon finding-out that amorphous Al_2O_3 was the most desirable, what would prevent α- Al_2O_3 formation. Amorphous Al_2O_3 formation was favored over α- Al_2O_3 formation because: 1) amorphous Al_2O_3 is less erosive to equipment than α- Al_2O_3, and will dissolve in a nitric acid scrubbing solution, while α- Al_2O_3 fines do not, and 3) an amorphous, alumina product has a higher attrition resistance. It was found that the presence of sodium nitrate promoted the formation of α- Al_2O_3. The presence of boric acid promoted the formation of amorphous Al_2O_3. Two successful flowsheets for calcining $Al(NO_3)_3$-nitric acid waste are shown in Table 45. It was shown that α- Al_2O_3 would never form if feed Na concentration was 0.03 *M* or less (without H_3BO_3 present); in feeds containing Na concentrations between 0.07 and 0.10 *M* α- Al_2O_3 formation was intermittent; and α- Al_2O_3 always occurred when the feed Na concentration was 0.2 *M*. Since $Al(NO_3)_3$-nitric acid feed would probably contain >0.03 *M* Na, boric acid was added to promote amorphous Al_2O_3 formation. As little as 0.1 *M* H_3BO_3 in feed would prevent α- Al_2O_3 formation in the presence of 0.078 *M* Na, but 0.1 *M* H_3BO_3 was never used with greater Na concentrations than 0.078 *M*. It was also found that α- Al_2O_3 formation was somewhat dependent on temperature (the higher the temperature, the greater the amount of α- Al_2O_3 formed), on residence time in the bed (the longer the run, the more like α- Al_2O_3 would form), and on feed nozzle NAR (high NAR favored α- Al_2O_3 formation (Brown et al. 1964a). It was found that a bed high in α- Al_2O_3 contained less nitrate than a bed low in α- Al_2O_3 (Brown, Grimmett, and Buckham 1962a).

The studies (Wheeler, Grimmett, and Buckham 1962) thought intra-particle porosity was important because the lower the porosity the smaller the storage volume required per unit volumes of liquid Al_3O_3 waste calcined. Intra-particle porosity is highly dependent on calcination temperature and feed concentration (porosity increases as temperature and Al concentration increases). Porosity was found to be slightly dependent on feed Na concentration (increasing feed Na concentrations decreased porosity) and slightly dependent on the presence of α- Al_2O_3, if not generated by adding large amounts of $NaNO_3$ to feed (presence of α- Al_2O_3 slightly increases porosity). Porosity was independent of Hg, H_3BO_3, and HNO_3 fed concentrations, feed nozzle design, NAR when using pneumatic nozzles, feed rate, mode of dry fines return, superficial fluidizing air velocity, location of feed introduction to the calciner, equipment size and equipment configuration.

It was found that a low NAR inhibited α- Al_2O_3 formation, and α- Al_2O_3 formation seemed to be affected differently by nozzles with different atomization characteristics. High elutriation rates of solids from the calciner were associated with: α- Al_2O_3, high feed rates, high or very low nozzle air rates, and with low bed temperature. Only minor amounts of elutriated solids seem to be generated by fluidizing action of the bed and thermal shock of particles (spraying water into bed). High bulk densities were associated with low bed temperatures, high α- Al_2O_3 content, and high NARs. Higher nitrate content in fines than in product suggested fines are freshly generated Al_2O_3 (spray-dryed rather attritted bed particles); however, during a more recent study (Nenni, O'Brien and Schindler 2000), it was found that fines can renitrate at the lower temperatures in the off-gas system. High attrition indices were associated with low bed temperature (Brown, Legler, and Lakey 1964b).

The two-foot-square calciner used a jet grinder in some runs (Brown et al. 1964a) which consisted of five 1/8 inch diameter air orifices discharging horizontally at just about the support plate. The jet grinder did not control MMPD when used on a bed of amorphous Al_2O_3 (has high attrition index) (Brown, Legler, and Lakey 1964b).

STUDIES IN 30-CM CALCINER PILOT PLANTS

Feed and operating data from the 30-cm (12") Calciner Pilot Plant Tests are provided in Appendix A. All pilot plant calciner tests were done using simulated (non-radioactive) feeds and are discussed by feed type in the following sections.

CALCINATION OF ZR WASTE IN 30-CM CALCINER PILOT PLANTS

Unenclosed 30-cm (12-inch) Calciner Runs 7, 11, 13, 14, 18, 21, 22, 23, 51, 53, 63, 65, 66, 69, 73, 74, 76, 80, 83 and Enclosed 30-cm (12-inch) Calciner Run 2 wastes calcined simulated first cycle zirconium.

The beds of early 30-cm fluidized-bed calciners (Unenclosed Calciner Runs 7, 11, 13, 14, 18, and 21) calcining first cycle Zr waste were heated by electric heaters inserted into the bed and usually used calcination temperatures of 400°C; heating beds by in-bed combustion began with Run 22 and calcination temperatures of 500°C were usually used. In Run 14 calcination temperatures of 300°C, 400°C, and 500°C were used; physical constants of calcine and calciner operation seemed to be independent of calciner temperatures, but fluoride volatility seemed to be increase with an increase in calcination temperature. The best method found for controlling particle size was variation of feed NAR; not effective was addition of Al_2O_3 (-48+135 Tyler mesh) added at a rate of 150 g/30 min. (Petrie 1964). NARs of 500-700 were needed to control particle size when the bed was heated with electric heater while NARs of 100-250 were needed to control particle size when the bed was heated by in-bed combustion – apparently the fuel nozzle adds some grinding action. Runs previous to Run 51 used feed prepared by dissolving ZrO_2 in HF; Run 51 and succeeding runs used feed prepared by dissolving Zircaloy in HF – this made a difference in the attrition indexes (AIs) of the calcined solids (in runs dissolving ZrO_2 AI's were 50 to 75%; in runs dissolving Zircaloy, AIs were ~10%). During runs using electric heaters at 400°C, acid did not have to be added to acid scrub because NO_2 generated during calcination made more acid when adsorbed in the acid scrub; when in-bed combustion at 500°C was used, acid had to be added to the scrub solution because during calcination, NO is predominately formed and there was not enough time for NO to oxidize to NO_2 as off-gas passed through the scrub solution. The use of pure O_2 rather than air as kerosene atomizing gas (Run 23) reduced oxygen requirements by 50%. Run 65 showed that Fluorapatite ($Ca_5F(PO_4)_3$) could be coated with Al_2O_3 and Zr waste using the WCF and NWCF startup method; there was not enough PO_4 from Fluorapatite released from calciner and caught in acid scrub to form excessive zirconium phosphate solids in calciner feed when scrub was recycled to feed.

Run 11 used $Al(NO_3)_3$ to suppress fluoride volatility during calcination of Zr waste at 400°C (1 Vol. $Al(NO_3)_3$-Nitric Acid waste – 1 Vol. Zr waste) but corrosion rates on various parts of valves in the acid scrub system were high. Other runs used $Ca(NO_3)_2$ to suppress F volatility. Run 13 used Ca/F mole ratios of 0.06 and 0.28 in the Zr feed; calcination of the former feed resulted in 35% of the fluoride fed to the calciner being volatilized from the calciner vessel; calcination of the latter feed resulted in 10% of the F being volatilized from the calciner vessel. Runs 7, 14, and 18 used a Ca/F mole ratio of 0.50. To prevent accidentally making feed having a Ca/F mole ratio less than 0.50, succeeding runs used a Ca/F mole ratio of 0.55. Runs previous to Run 21 added $Ca(NO_3)_2$ to feed as a 7.6 *M* solution maintained at 90°C but some $Ca(NO_3)_2$ settled out resulting in feeds having a Ca/F mole ratio <0.5. Run 21 added $Ca(NO_3)_2$ as a 3.92 *M* solution and used a Ca/F mole ratio of 0.55. Later runs added $Ca(NO_3)_2$ as a solid. As long as the Ca/F mole ratio remained above 0.5, F volatility (not counting fines entrained in off-gas) from the calciner vessel remained <1.0 wt% of that fed to the calciner. Run 51 used $Ca(NO_3)_2$ coated with hydrocarbon – no problems were attributed to coated $Ca(NO_3)_2$. The last 81.6 hrs of Run 65 supposedly using a Ca/F mole ratio of 0.70 and had a much higher chloride retention in calcined solids (average 61%) (Newby 1978 Nby-15-78) and higher AI (44%) than did Run 74 supposedly using a Ca/F mole ratio of 0.55 (average 27%) (Newby 1979b). The attrition index for these runs was 6-10%.

Table 45. Composition of first cycle zirconium waste calcined in 30-cm calciners.

			Run #13[b]				
	Run #7	Run #11[a]	A	B	Run #14	Run #18	Run #21
H^+ (*M*)	1.03	1.07	1.44	1.33	1.16	$1.11^{+0.21}_{-0.59}$	$1.40^{+0.35}_{-0.05}$
Al (*M*)	0.66	0.82	0.39	0.36	0.39	$0.45^{+0.09}_{-0.15}$	$0.31^{+0.08}_{-0.07}$
Zr (*M*)	0.43	0.24	0.39	0.37	0.30	$0.27^{+0.05}_{-0.10}$	$0.25^{+0.03}_{-0.02}$
B (*M*)	0.17	0.094	0.18	0.10	0.040	$0.036^{+0.005}_{-0.013}$	$0.10^{+0.008}_{-0.007}$
Ca (*M*)	1.21	0.00	0.165	0.62	0.97	$0.96^{+0.31}_{-0.30}$	$0.93^{+0.05}_{-0.08}$
Hg (*M*)	---	0.0045	---	---	----	---	---
Sm (*M*)	0.0057	0.0026	0.0039	0.0000	----	---	<0.13
Na (*M*)	---	0.020	---	---	----	---	---
Cr (*M*)	---	0.0062	0.013	0.012	---	---	$0.0076^{+0.0006}_{-0.0013}$
NH_4 (*M*)	---	0.02	---	---	---	---	---
Ru (g/L)	---	---	---	---	0.01	$0.015^{+0.004}_{-0..008}$	---
F (*M*)	2.45	1.68	2.60	2.23	2.12	$1.81^{+0.22}_{-0..67}$	$1.62^{+0.11}_{-0.35}$
NO_3 (*M*)	4.66	2.69	1.67	2.20	3.37	$3.36^{+0.64}_{-1.22}$	$3.80^{+0.54}_{-0.84}$
UDS (g/L)	---	0.15	35	67	44.92	$56.7^{+34.1}_{-28.2}$	$53.8^{+43.0}_{-17.7}$
Ca/F Mole Ratio	0.49	---	0.06	0.28	0.46	$0.54^{+0.19}_{-0..12}$	~0.57
Total Solid (g/L)	187				131	134	127

Not good flowsheet too corrosive to offgas acid scrub equipment.

Not good flowsheets F volatility from calciner vessel too high

References:

Petrie 1964; Petrie 1965e; Petrie 1966a; Petrie 1966b; Petrie 1966e; and Thompson 1967a.

Table 46. Composition of first cycle zirconium waste calcined in 30-cm calciners.

	Run #22	Run #23	Run #51	Run #57	Run #63	Run #65 (last 81.6 h. of run)
H^+ (M)	$0.83^{+0.17}_{-0.19}$	1.52	1.21	1.27	1.38	1.20
Al (M)	$0.33^{\pm 0.03}$	0.30	0.47	0.51	0.55	0.61
Zr (M)	$0.25^{+0.02}_{-0.01}$	0.22	0.33	0.31	0.37	0.30
B (M)	---	0.18	0.12	0.14	0.20	0.15
Ca (M)	$1.27^{+0.09}_{-0.16}$	0.95	1.22	1.14	1.34	01.81
Hg (M)	0.0031	---	---	---	---	---
Cr (M)	$0.0094^{+0.0017}_{-0.0006}$	0.0087	---	---	---	0.0023
Ce (M)	---	---	---	0.0010	---	---
Na (M)	---	---	---	----	---	0.01
Cs (M)	---	---	---	0.0016	---	---
Sr (M)	---	---	---	0.011	---	---
F (M)	$1.78^{+0.21}_{-0.10}$	1.45	2.17	2.63	2.49	2.23
NO_3 (M)	$3.34^{+0.24}_{-0.28}$	4.13	4.31	6.48	2.93	5.86
SO_4 (M)	---	---	---	---	---	---
PO_4 (M)	---	---	---	---	---	0.0070
Cl (M)	---	---	---	---	---	0.013
UDS (g/L)	$61.6^{+49.4}_{-36.9}$	---	---	---	---	---
Ca/F Mole Ratio	~0.71	0.66	0.56	0.43	0.54	0.81
Total Solid (g/L)	160	131	168	154	188	237

References:
Thompson 1967b; Thompson 1968a; Neuls 1974d; Ahrens 1977; Birrer 1978a; and Newby 1978c.

Table 47. Compositions of first cycle Zirconium waste calcined in 30-cm calciners.

	Run #66, 69, 73, 76, 80 and 83			Enclosed Calciner
	Without Recycle	With Recycle	Run 74	Run 2
H^+ (<u>*M*</u>)	1.37	1.49	0.60	1.13
Al (<u>*M*</u>)	0.63	0.56	0.38	0.58
Zr (<u>*M*</u>)	0.43	0.38	0.20	0.41
B (<u>*M*</u>)	0.23	0.21	0.095	0.19
Ca (<u>*M*</u>)	1.67	1.50	0.80	1.53
Hg (<u>*M*</u>)	0.0017	0.0022	0.0019	---
Ce (<u>*M*</u>)	---	---	---	---
Cs (<u>*M*</u>)	0.008	0.0072	---	---
Sr (<u>*M*</u>)	0.013	0.012	---	---
Rare Earth Carbonates (g/L)	0.52	0.47	---	---
F (<u>*M*</u>)	3.04	2.70	1.14	2.78
NO_3 (<u>*M*</u>)	5.30	5.23	3.04	4.89
SO_4 (<u>*M*</u>)	---	---	0.061	---
Cl (<u>*M*</u>)	---	---	0.0094	---
Ca/F Mole Ratio	0.55	0.56	0.70	0.55
Total Solid (g/L)	231	207	110	211

References:
Newby 1979c; Lamb 1977; Lamb 1978b; Lamb 1978a; Lamb 1979a; Gombert 1980; Lamb 1980; Kirkbride 1980b; Simpson 1983; and Newby 1980b.

In most runs where a mercury material balance was observed, essentially no Hg was found in calcined solids. Where SO_4 material balances were observed essential all of it (~97%) was retained in calcine solids. The fluidized-bed operation and properties of solids generated seemed to be about the same for runs calcining feeds containing the lower concentrations of Al, Zr, and F in the matrix and runs calcining feeds containing higher concentrations of Al, Zr, an F in the matrix.

During runs where feed and scrub were not analyzed, feed compositions were calculated assuming that: a) the composition of the feeds in these runs was close to the theoretical composition, b) addition of solid $Ca(NO_3)_2$ to feed diluted that feed by 15 vol%, c) scrub (when recycled, was recycled at 15 vol% of the gross feed rate), and/or d) the concentration of each constituent in the scrub generated is equal to the same average percent that each constituent in the scrub is to the same constituent in the feed that is found in a number of runs where both feed and scrub were analyzed.

CALCINATION OF MISCELLANEOUS WASTES IN 30-CM CALCINERS PILOT PLANTS

Stainless Steel Sulfate Waste

In unenclosed 30-cm Calciner Run 40, simulated stainless steel sulfate waste was calcined as a blend of 5 Vol. stainless steel sulfate waste – 1 Vol. 2.2 <u>*M*</u> $Al(NO_3)_3$ (Table 48). There was concern that the solid content of this blend was so low that during the blend's calcination: bed particle size would decrease continually; bed wouldn't build; and bed height couldn't be maintained. Even though the product AI was 28%, the product size was controlled using a NAR of 250 to 350 and the product-to-fines ratio was maintained at 1.6. The run was terminated after 109.6 h; there was negligible corrosion in the acid scrub system; particle agglomeration was nil; and practically all SO_4^{-2} was retained in calcined solids. The bed was kept at 500°C (by in-bed combustion of kerosene), and starting bed was dolomite (Taylor 1972).

Table 48. Run 40 feed.

H^+ ($N^{\underline{a}}$)	2.28
Al (<u>*M*</u>)	0.31
Ni (<u>*M*</u>)	0.008
Cr (<u>*M*</u>)	0.012
Fe (<u>*M*</u>)	0.049
NO_3 (<u>*M*</u>)	2.93
SO_4 (<u>*M*</u>)	0.436
Dissolved Content Solids (g/L)	~90

AGNS Commercial Waste

Unenclosed 30-cm Calciner Runs 58 and 60 were made to determine if simulated Allied General Nuclear Services (AGNS) Commercial Waste could be calcined using powdered iron (to complex Na+K) added as the last constituent to the calciner feed. Sufficient iron powder was supposed to be added to the waste to give a Fe:Na mole ratio of 1.0, but in Run 58 the average ratio was 0.63 and in Run 60 the average ratio was 0.84. Run 58 was made to test both Spraying Systems Company (first 124 hours of run) and shrouded Sonicore (last 88 hours of run) fuel nozzle operation. Run 60 was made using a Spraying Systems nozzle to make certain the bed clinker formation in Run 58 was due to use of the Sonicore nozzle. Run 60 was voluntarily terminated after 104 hours without bed clinker formation. In Run 58, the MMPD stayed at about 0.43 mm using a feed NAR of 140 and a Spraying Systems nozzle; the MMPD decreased continually during use of the Sonicore nozzle even though the NAR was decreased to 120.

In Run 58: the AI averaged ~22%; the fluidizing velocity (below nozzle) was 0.3 m/sec; the average product-to-fines ratio was 2.7; and the product bulk density was 2.1 g/cc. The starting bed was 91 kg of Magnorite and 9 kg of Dolomite; the product nitrate concentration was ~2.6 wt%. Feed undissolved solids in both runs was mostly compounds of Zr, Mo, and Fe with Run 60 feed having more solids.

Run 60 used Run 58 product as a starting bed. Whereas the feed for Run 58 was slightly basic, the feed acidity for Run 60 was kept between 2 and 4 $N^{\underline{a}}$. The feed NAR for Run 60 was kept between 150 and 200 which did not control the MMPD; the MMPD continually increased during the run from 0.31 to 0.47 mm and the AI increased from 13 to 52% (probably because HNO_3 being added to keep feed acid increased NO_3 concentration in feed and calcine – NO_3 makes calcine hard). In Run 60: the average product-to-fines ratio was 2.7; the product bulk density leveled out at 2.1 g/cc; the fluidizing velocity (below the nozzle) was ~0.3 m/sec, and the product nitrate concentration was 4.9 wt%. For both runs, bed particles set up while stationary but broke into their original granular state with slight agitation. There was no apparent problem with bed setting up as long as calcine was moving or kept above 300°C (Valentine 1977).

Table 49. AGNS commercial waste calcined in the Unenclosed 30-cm Calciner Pilot Plant.

	Feed for Run 58	Feed For Run 60
H^+ ($N^{\underline{a}}$ or $N^{\underline{b}}$)	0.06 (basic)	2.30 (acidic)
Fe ($\underline{M}$)	0.34	0.27
Na ($\underline{M}$)	0.37	0.33
Ba ($\underline{M}$)	0.016	0.029
Cd ($\underline{M}$)	0.0046	0.0019
Ce ($\underline{M}$)	0.23	0.16
Cs ($\underline{M}$)	0.039	0.037
Gd ($\underline{M}$)	0.19	0.12
La ($\underline{M}$)	0.11	0.064
Mo ($\underline{M}$)	0.053	0.053
Nd ($\underline{M}$)	0.13	0.085
K ($\underline{M}$)	0.019	0.0033
Sr ($\underline{M}$)	0.025	0.014
Te ($\underline{M}$)	0.0074	0.00065
Y ($\underline{M}$)	0.020	0.013
Zr ($\underline{M}$)	0.23	0.10
Cr ($\underline{M}$)	0.0067	0.0070
Ni ($\underline{M}$)	0.045	0.039
Mn ($\underline{M}$)	0.015	0.0069
NO_3 ($\underline{M}$)	2.1	3.52
PO_4 ($\underline{M}$)	0.19	0.19
Cl ($\underline{M}$)	0.0096	0.0096
SO_4 ($\underline{M}$)	0.0036	0.0036
UDS (g/L)	87	134
Mole% Na+K	8.5	10.2
Total Solids (g/L)	314	294

Rover Waste

Unenclosed 30-cm Calciner Runs 59 and 62 calcined simulated Rover waste as blends with simulated Zr waste, while unenclosed 30-cm Calciner Run 95 calcined simulated Rover waste as a blend with simulated Na waste.

Run 59 calcined 1 vol. Rover waste 1 vol. Zr waste; Run 60 calcined 2 vol. Zr waste – 1 vol. Rover waste. Both runs were voluntarily terminated at ~110 hours. The starting bed for Run 59 was zirconia calcine and the Run 59 final bed was used for the starting bed of Run 62. Both runs: were unable to control MMPD (0.35 to 0.40 mm) at NARs between 120 and 200; had AIs of ~10%; used fluidizing velocities (below nozzle) of 0.81-0.89 ft/sec, used calcination temperature of 500°C; and used Spraying Systems nozzles. Product density of Run 59 was ~1.24 g/cm^3 and was 1.29-1.35 g/cm^3 for Run 62. The product-to-fines ratio was 3.7 for Run 59 and 3.0 for Run 62. Neither run used a caustic scrubber to determine F volatility but in both runs there was always enough Al present in the acid scrub to complex fluoride enough to prevent excessive corrosion to the acid scrub system. All F in Run 59 was carried over in fines as CaF_2, but in Run 62 there was always F in the acid scrub in addition to that which would be carried over as CaF_2.

Run 95 calcined Rover waste as a blend of 2.1 vol. Rover waste and 1 vol. Na waste (simulated WM-189 waste calcined in NWCF Run H-1). The run was voluntarily terminated after 100 hours. The feed NAR used (165-202) did not control product size growth (MMPD increased continually throughout the run from 0.38 to 0.48 mm). Agglomeration (based on size of particles in final bed) was low. In Run 95: average bulk density was 1.41 g/cc; AI was 8%, product production rate was low (1.6 kg/h) because feed solid content was low; and product-to-fines ratio was 1.5; Cl retention in calcined solids was only 26 wt%; all F in scrub came over as CaF_2; there was always enough Zr, Al, and B present in the acid scrub to prevent excessive F corrosion to acid scrub system materials of construction; and 0.36 wt% of F fed to the calciner escaped the calciner as volatile F. Starting bed was calcined Al_2O_3.

Table 50. Rover waste blends calcined in the Enclosed 30-cm Calciner Pilot Plant.

	Run 59 1 Vol. Zr Waste – 1 Vol. Rover Waste	Run 62 2 Vol. Zr Waste – 1 Vol. Rover Waste	Run 95 2.1 Vol. Rover Waste – 1 Vol. Na Waste
H^+ (N^a)	2.0	1.89	1.12
Al (*M*)	0.383	0.451	0.56
Zr (*M*)	0.029	0.126	0.032
Nb (*M*)	0.0155	0.013	0.015
B (*M*)	0.13	0.14	0.055
Fe (*M*)	0.0038	0.0028	0.012
NH_4 (*M*)	0.031	0.018	0.086
Na (*M*)	---	---	0.18
K (*M*)	---	---	0.094
Ca (*M*)	1.05	1.01	0.54
NO_3 (*M*)	2.3	2.2	3.8
F (*M*)	0.97	2.24	0.81
Cl (*M*)	---	---	0.0052
UDS (g/L)	49	40	12.9
Total Solids (g/L)	179	161	121
Mole% Na+K	---	---	7.6

Birrer 1978b.

Electrolytic Waste

Simulated electrolytic waste was calcined in Run 68. Run 68 calcined a feed simulating WM-101 waste concentrated to 33% of its original volume for the first 64.3 hours and then used simulated WM-100 waste for the rest of the run. The run was terminated voluntarily after 122.3 hours. A NAR of ~202 controlled the MMPD at ~0.40 mm while calcining WM-101 waste, and a NAR of 145 controlled the MMPD at ~0.40 mm while calcining WM-100 waste. Product bulk density was ~1.46 g/cm^3 for WM-101 waste and ~1.41 for WM-100 waste; an average fluidizing velocity (below nozzle) of 0.24 m/s was used for both WM-101 and 100 waste; the AI was ~40% for WM-101 waste and ~54% for WM-100 waste; and the product-to-fines ratio was 1.1 for WM-101 waste and 1.6 for WM-100 waste. The starting bed was calcined zirconia. No solids were formed by adding $Ca(NO_3)_2$ to the feed. The chloride and fluoride volatized from the calciner vessel during the run was ~100% and 15%, respectively, of that fed to the calciner. Corrosion rates (even with 15% F volatility) were significantly lower than those experienced during calcination of Zr wastes (Birrer 1980).

Table 51. Run 68 feed.

	WM-101 Concentrated 33% of its Original Volume	WM-100 Waste
H^+ (N[a])	3.09	0.74
Al (*M*)	0.98	0.93
Bd (*M*)	0.12	----
Fe (*M*)	0.19	0.065
Cr (*M*)	0.038	0.015
NH_4 (*M*)	0.44	0.35
Ni (*M*)	0.023	0.002
Na (*M*)	0.064	0.024
Ca (*M*)	0.011	0.013
B (*M*)	0.018	0.031
NO_3 (*M*)	5.9	4.1
F^- (*M*)	0.020	0.024
SO_4 (*M*)	0.12	0.04
Cl (*M*)	<0.001	<0.001
Total Solids (g/L)	102	59
Mole% Na	1.8	0.9

CALCINATION OF ALUMINUM WASTE IN 30-CM CALCINERS PILOT PLANTS

Unenclosed Calciner Runs 1, 2, 3, 4, 9, 15, 16, 17, 22, 24, 29, 30, 31, 44, 48, 70, 72 and 77 tested simulated aluminum raffinates. The beds of early 30-cm fluidized-bed calciner tests (Unenclosed Calciner Runs 1, 2, 3, 4, 9, 15, 16, and 17) calcining aluminum waste were heated by electric heaters inserted into the bed and usually used a calcination temperature of 400°C. Calcination temperatures of 500°C were usually used when heating the bed by in-bed combustion. Bed and product attrition indices (AIs) were high (>60% except in run 2 (AI=6%) where bed α-Al_2O_3 content varied between 20 and 61 wt% and Run 77 (AI=6 to 26%) where feed Al concentration was quite high (1.93 $\underline{M}$ and no α-Al_2O_3 detected in solids). Generally, high NAR's (>500) and fluidizing velocities (>1.0 ft/sec.) had to be used (except in Runs 2 and 77) to control particle size; in some early runs particle size control was achieved by adding to bed –80, +115 Tyler mesh sand as 11 g batches every 20 minutes to give a sand addition rate of 20 to 85 g/h. Generally product bulk density ranged between 0.7 to 1.0 g/cm^3, product-to-fines ratio of >3 to 1, and NO_3 content of calcined solids ranged all the way between 1.5 and 11.4 wt%. Much of this variability may have been due to affects of operation at 400°C versus 500°C.

Runs using sand or amorphous Al_2O_3 as starting beds (when Na concentration in waste was no greater than 0.04 $\underline{M}$) didn't generate α-Al_2O_3 when boron was not present; when the starting bed contained some α-Al_2O_3, α-Al_2O_3 was generated until boron was added.

In Run 4 NO_3 content of calcined solids was greater when calcining $Al(NO_3)_3$-HNO_3 waste at 300°C than at 400°C; $NaNO_3$ was found in former solids but not in latter solids. Rates of elutriation did not seem to be different whether operating at 300 or 400°C.

Run 16, using electric heaters to heat bed, was made to determine if the presence of 0.0075 $\underline{M}$ Cr in $Al(NO_3)_3$-HNO_3 waste (to be calcined in WCF Run H2) caused processing difficulties; the Cr caused no problems. Run 22 calcined the same waste but used in-bed combustion of kerosene to heat the bed. In Run 16 about 99% of the Hg stayed in calcined solids. In Run 22, the off-gas composition was 3.4 mole% CO, 10.3 mole% CO_2, 0.04 mole% CH_4, 9.3 mole% O_2, and 75.4 mole% N_2; presence of N_2O, NO, or NO_2 was below detection limit of 0.01 mole%. In Run 1, N_2O (<0.1 mole%) was the only NO_x found in the off-gas and there were no α-Al_2O_3 in calcined solids; in Run 2, the bed α-Al_2O_3 concentration was from 20 to 61 wt%, and off-gas contained 1.5 mole% NO_2 and 0.05 mole% N_2O.

Pilot-plant operating conditions were compared with those of the WCF when both calciners were calcining about the same $Al(NO_3)_3$-HNO_3 waste using indirect heating to heat beds (electric heaters for the pilot-plant; the NaK system for the WCF). Relatively more solids were elutriated from the WCF than from the pilot-plant; particle size control was effected at lower NAR values in the WCF than in the pilot-plant.

Runs 24 and 29 were made to compare kerosene and #2 fuel oil as fuels for the in-bed combustion process. Kerosene and #2 fuel oil performed similarly with an external mix nozzle. Bed ignition temperature used for both fuels was 370°C; the lowest oxygen combustion achieved was slightly less for #2 fuel oil (132%) than for kerosene (168%). Run 24 showed that a Dolomite startup bed was compatible with in-bed combustion. Runs 30 and 31 were the first runs to use internal-mix fuel nozzles (former runs used external-mix nozzles). Better combustion was obtained with an internal-mix fuel nozzle than was obtained with an external-mix fuel nozzle. Combustion was more efficient at 500°C than at 450°C and at an O_2/fuel ratio of 1800 than at a ratio of 1400. Use of oversize internal-mix fuel nozzles caused no gross differences in combustion other than lower waste/fuel ratios and thermal efficiencies.

Run 44 compared the operation characteristics of a Sonicore fuel nozzle and Incoloy 825 shroud with those of spraying systems fuel nozzles. The Sonicore fuel nozzle and shroud: a) caused less calcine solid attrition than the spraying systems nozzle, b) produced a CO_2/CO ratio 3.5 times that of a spraying systems nozzle, and c) had an average combustion efficiency of 99.2% compared to 94-95% for spraying systems nozzles. The shroud lost 0.4 g from erosion during the 100 hour run. When a Sonicore nozzle and shroud was used with Zr waste, it caused agglomeration of particles (was too hot for zirconia particles).

Run 48 calcined eurochemic waste which was a dilute $Al(NO_3)_3$-HNO_3 waste (contained 0.85 *M* Al). There was no problem calcining the waste even though it was quite dilute. Feeds this dilute usually had problems building bed. A fluidizing velocity of up to 1.3 ft/s combined with a NAR up to 400 was needed to control particle size.

Runs 9 and 15 calcined $Al(NO_3)_3$-NO_4NH_3 waste which simulated that calcined in WCF Run H-2. The beds in the 30-cm calciner used in Run 9 and 15 and WCF Run H-2 were heated indirectly (by electric heaters and the NaK system, respectively). Calcination of 5000 gallons $Al(NO_3)_3$-NO_4NO_3 waste in WCF Run H-1 showed Millon's base (- Hg – NH – Hg)$^{+2}$ + 20H, an explosive under certain conditions, present in the undissolved solids of the off-gas acid scrub system. The purpose of both Runs 9 and 15 was to verify presence of Millon's base in acid scrub solids, and an addition purpose in Run 15 was to find the base's equilibrium concentration in the scrub. Run 9 found Millon's base in acid scrub solids (as well as mercuric chloride and mercury), but Run 15 did not find the base in acid scrub solution. Runs 9 and 15 had problems controlling product size from becoming too large – it took a NAR of 650 plus adding sand (finer than 35 Tyler mesh) at a rate of 170 (later 85) g/h to control product size growth. Adding scrub to feed in Run 9 had no noticeable effect on the calcination process. The starting bed in Run 9 and the original bed in Run 15 was calcined $Al(NO_3)_3$-NH_4NO_3 waste; the latter bed was contaminated with NaCl so Run 15 was started again with a sand starting bed. No α-Al_2O_3 was ever found in the solids of either run. When calcining all feeds in the two runs: the product bulk density was 1.2 g/cm^3, and the AI was 60-90%. Fines elutriation rate during calcination of $Al(NO_3)_3$-NH_4NO_3 waste was higher than with calcination of $Al(NO_3)_3$-HNO_3 waste. Prior to using the sand bed in Run 15, mercurous chloride was a major constituent in off-gas acid scrub solids; after using the sand bed only trace quantities of mercurous chloride was found in acid scrub solids. Ammonia was not found in Run 9 off-gas; small amounts of ammonia were detected in off-gas of Run 15. Calcination temperatures of both runs were 400°C.

Table 52. Composition of $Al(NO_3)_3$-HNO_3 wastes successfully calcined using indirect heating.

			Run #3				
	Run #1	Run #2	first 173 hours of Run	Last 36 hours of Run	Run #4	Run #16	Run #17
H^+ (N^a)	2.13	1.78	0.62	2.29	2.34	2.08	0.75
Al (*M*)	1.27	1.45	1.75	1.25	1.30	1.38	1.64
Na (*M*)	0.0299	0.0300	0.040	0.076	0.087	0.052	0.065
B (*M*)		0.043		0.0096	0.010	0.0076	0.1
Hg (*M*)	0.0090	0.0092				0.0053	0.012
Cr (*M*)						0.0075	
NO_3 (*M*)	~6.0	~6.2	~5.9	~6.1	~6.3	5.73	5.8

References:
Brown 1961a; Brown 1961b; Brown 1961c; Brown 1962b; Brown 1963; Petrie 1966c; and Petrie1966d.

Table 53. Composition of $Al(NO_3)_3$-HNO_3 waste successfully calcined using in-bed combustion.

	Run #22	Run #24	Run #29, #30, and #31	Run #44	Run #48 Eurochemic Waste	Run #70 and #72	Run #77 (not too successful)
H^+ (N[a])	1.18	0.90	0.58	0.90	>4.0	0.8	1.23
Al ($\underline{M}$)	1.43	1.41	1.74	1.41	0.85	1.5	1.93
Na ($\underline{M}$)					0.03	0.065	0.101
B ($\underline{M}$)	0.049	0.008	0.018	0.043	0.04	0.02	0.026
Hg ($\underline{M}$)	0.0031					0.001	0.0015
Cr ($\underline{M}$)	0.0069						
Fe ($\underline{M}$)						0.005	0.006
NO_3 ($\underline{M}$)	5.24	5.18	6.00	5.13	>6.0	5.4	7.67
Cs_2CO_3 (g/L)						0.60	0.67
$Sr(NO_3)_2$ (g/L)						1.10	1.53
$Ce_2(CO_3)_3 \bullet 5H_2O$ (g/L)							0.22
Rare Earth Carbonates (g/L)						0.40	[a]

a. Other rare earths added but not analyzed for. Ran 204 hours but had too many fines.

References:

Thompson 1967b; Thompson 1968b; Grady 1973; Buckham 1973; Kirkbride 1979; and Kirkbride 1980a.

Table 54. Composition of $Al(NO_3)_3$-NH_4NO_3 wastes successfully calcined using indirect bed heating.

	Run #9		
	1st 132.2 hrs	Last 94.5 hrs (Blended with Scrub)	Run #15
H^+ (N[a])	0.1 Acid Deficient	1.13	0.57
Al ($\underline{M}$)	1.50	1.19	1.60
Na ($\underline{M}$)	0.016	0.013	0.018
B ($\underline{M}$)	0.010	0.0073	0.0054
Hg ($\underline{M}$)	0.012	0.010	0.0083
NH_4 ($\underline{M}$)	0.48	0.92	1.05
NO_3 ($\underline{M}$)	5.24	5.58	5.92

References:

Petrie 1965c and Ballard 1966.

CALCINATION OF NA WASTE IN 30-CM CALCINERS

Unenclosed Calciner Runs 8, 10, 12, 35, 38, 39, 49, 50, 52, 53, 61, 64, 67, 71, 75, 78, 79, 81, 91, 92, 93, 94, 96, 97 and Enclosed Calciner Runs 3 and 4 tested simulated sodium wastes, usually as blends with other wastes. The beds of early 30-cm fluidized bed calciners tests (Unenclosed Calciner Runs 8, 10, and 12) calcining Na waste were heated by electric heaters inserted into the bed and used calcination temperatures of 400 or 500°C. In 30-cm calciner scoping runs (Run 8) of 12 hours or less it was found that addition of 2 lb/gal. sugar to Na waste calcined at 500°C shows promise but use of less sugar at lower calcination temperatures did not. Blending 1 vol. Na waste with 1 vol. Zr waste at 400°C also showed promise as a method for calcining Na waste. Methods that showed no promise were: 1) no additive(s), 2) boric acid as an additive (Na/B mole ratio in feed 24:1) at 400 and 500°C, 3) feed made 1.53 $\underline{M}$ in phosphate at 400°C, and 5) feed made 1.2 $\underline{M}$ in oxalic acid at 400°C. A longer run calcining a blend of 1 vol. Na waste and 1 vol. Zr waste terminated after 32 ½ hours due to caking and bed agglomeration (Run 10).

The most successful method for calcining Na waste consisted of blending Na waste with Zr waste and adding sufficient $Ca(NO_3)_2$ to the blend to give a Ca/F mole ration of 0.70 (0.75 when calcining a blend of Zr waste and WM-183 waste). WM-183 was a mixture of aluminum nitrate, electrolytic first-cycle extraction, and Na wastes during the period (1976-1978) when this waste was being studied by pilot-plant calciner test personnel. The use of $Ca(NO_3)_2$ allowed only 1 wt% or less of total fluoride to escape the calciner vessel and retained 67-81% of the Cl in calcined solids. Calcination of these blends using a Ca/F mole ratio of 0.50 to 0.53 allowed bed agglomeration and agglomerates to form around the fuel nozzle. Bed particles formed at the lower $Ca(NO_3)_2$ concentration contained nodules on their surfaces, which possibly contributed to bed agglomeration because the particle could not slide by each other freely. Run 52 successfully calcined a Zr-Na waste blend containing a Ca/F mole ratio of 0.50 by alternately calcining the Zr-Na waste blend until nodules began forming on product followed by calcining Zr waste for ~11 hours. Preventing particle size from becoming too large was the greatest disadvantage of this method. Particle size was controlled by using a high NAR (300-400), an oxygen-to-fuel ratio of at least 2000, and a high fluidizing velocity below the fuel nozzle of 0.79-1.28 ft/s (0.24-0.39 m/s). The product-to-fines ratio was usually >2.0, product bulk density 1.25-1.38 g/cm^3, attrition index 43-58%, and the one time SO_4 retention was measured, 97 wt% was found in calcined solids. Kerosene was usually used as the fuel, but it was also found that 5 vol. % tributyl phosphate (TBP) in tetradecane, 1% TBP in AMSCO, and 5% TBP in AMSCO could be burned without operational difficulties. In runs using TBP mixtures: only 0.086% of the PO_4 entering the calciner was found in the off-gas; increasing TBP concentration from 1 to 5% only negligibly increased mass loading of off-gas and did not increase UDS in scrub or PO_4 in the UDS; larger TBP concentration in the fuel (1 vs. 5%) did increase PO_4 in the scrub supernate; P_2O_5 did not plug HEPA filters. To prevent bed from setting up into a fragile agglomerate when shutting down, the bed had to be kept fluidized until cooled below 150^{o}C. It was found that when feeding a Zr-Na waste blend (Ca/F mole ratio of 0.7) was interrupted routinely by water flushes at high rates, agglomerates would form around the feed nozzle. It was recommended that air or small amounts of acid or water presssurized by air should be used in place of water flushes.

Na waste was also successfully calcined at 500^{o}C by adding 2 lb. sugar per gallon of Na waste (Run 12A) or by adding 1.36 lb sugar per gallon of 1 to 1 blend of Na and Zr waste (same sugar-to-Na weight ratio as in part A) for Run 12B. These runs were made using a bed heated by electrical heaters; different results could be obtained using in-bed combustion. In both runs: a NAR of 600 controlled MMPD; all of the Hg and part of the Al precipitated from the solution; calcined solids were grey to black. Run 12A was plagued by frequent off-gas system plugging and pressure imbalances and had a product bulk density = 1.1 g/cm^3, fines bulk density = 0.5 g/cc, attrition index = 62.68%, product-to-fines ratio = 10. The off-gas contained 2 mole % CO_2, 0.1 mole % Hg, 0.1 mole N_2O, and 0.03 mole% NO_2. Run 12B had few operational problems. Five percent of the total fluoride was found in the acid scrub (much too high if not enough Al+B+Zr present in scrub to complex fluoride). The run had a product bulk density = 1.25 g/cc, fines bulk density = 0.3 g/cc, AI = 30%, and product-to-fines = ~10.

Three runs (35, 38 and 39 all using in-bed combustion) calcined a blend of 1 vol. Na waste and 1.5 vol. Zr waste without addition of $Ca(NO_3)_2$. High fluoride volatility caused excessive corrosion in the acid scrub system. Aluminum nitrate was added to the acid scrub to reduce the corrosion to acceptable levels, but $AlF_3{}^\bullet xH_2O$ (from acid scrub system) caused plugging in the off-gas system. A ZrO_2-CaF_2 starting bed seemed to cause bed agglomeration while alumina starting bed did not. All runs were forced to terminate due to excessive acid scrub corrosion or bed agglomeration, but ran from 3 ½ to 103 hrs. Chloride in the feed was not held in calcined solids but concentrated in the acid scrub. Product MMPD's were controlled using NAR's between 162 and 487; making the blend 0.11 _M_ in boron increased the attrition index (AI) from 3 (without B present) to 58%; product-to-fines ratio varied between 1.9 to 41.1; product bulk density ~1.22 g/cm^3; fines bulk density ~0.71 g/cm^3.

Six runs (86, 87, 91, 96, 93, and Enclosed Calciner Run 3 calcined Na waste as a blend with 2.2 M $Al(NO_3)_3$ (Newby 1986). In 3 of the runs Na was waste was represented by $NaNO_3$ equal to the concentration of Na+K nitrates in a typical Na waste plus aluminum nitrate (these feeds were also used during cold tests at NWCF); the other runs used Na waste containing all major and minor constituents. One run calcined a blend of 6 vol. 2.2 M $Al(NO_3)_3$ and 1 vol. Na waste; the others calcined a blend of 2 vol. 2.2 M $Al(NO_3)_3$ and 1 vol. Na waste. All runs calcining the abbreviated Na waste were voluntarily terminated; the other runs were forced to terminate early due to equipment problems (off-gas plugging, feed running into the bed from a pressure probe, high fuel nozzle pressure and some equipment problems possibly caused by the flowsheet). In runs calcining the abbreviated Na waste, Spraying Systems Co. 60100 feed nozzles successfully used 120, 140, and 150 caps; it seemed important in the other runs that a 120 cap rather than a 140 cap be used to prevent extremely high feed nozzle pressure readings. The product-to-fines ratio for the 6 to 1 blend was 1.2, but less than 1.0 for the 2 to 1 blend. Preventing the particle size from becoming too small was much more of a problem in runs calcining non-abbreviated Na waste than in those calcining abbreviated Na waste. Two drums of product that had been allowed to sit at <35°C (from 2 runs calcining blend containing non-abbreviated Na waste) were examined after 1 years; one drum was caked on the surface of the material, but the product in the other drum was caked throughout its entirety. All runs had: excessive fines; no agglomeration problems; smooth surface calcine product; crystalline alumina present in solids; product bulk density = 1.0 g/cm^3; fines bulk density = 0.47 to 0.86 g/cm^3, and AI = 43-57% Cl retention in calcined solids was ~32 wt%. Five runs used kerosene as a fuel; one used a mixture of 70 volume % hexone, 24% AMSCO, and 6% TBP. The only difference found between using kerosene and the hexone-AMSCO-TBP mixture was that the autoignition temperatures were higher for hexone mixtures. Hexone fuel should be injected into the calciner only when the bed is 475°C or greater. Also in a run using unabbreviated Na waste, it was shown that 1.1 moles of bismuth nitrate per mole of Cl present plus 1.5 moles borium nitrate per mole of sulfate plus phosphate present was not effective in suppressing chloride volatility. Although these tests of Na waste blended with 2.2 M simulated ANN were not completely sucessful, additional tests of ANN-Na blends was conducted in the 1990-1997 in 10-cm (4") and 15-cm (6") calciner pilot plants (Nenni 1998 and Thomson 1997). These were more successful with the result that blends of ANN-Na which contained a Na+K/Al mole ratio of 0.25 and about 0.05 M B were calcined successfully during NWCF Campaign H-4. Higher sodium content ANN-Na blends were also calcined successfully at 600°C (Swenson 2000).

Two runs attempted to calcine Na waste using iron powder as an additive. In Run 61 enough iron powder was added to simulated WM-183 waste to make the waste 0.85 M in iron. The run had to be terminated 3 different times with in 45.5 hours due to bed clinker formation. Chloride retention in calcined solids during the run was excellent (~96 wt%). The surface of the calcined product was very rough. In Run 4 (using an enclosed calciner) enough iron powder was added to a blend of 2 vol. 2.2 M $Al(NO_3)_3$ and 1 vol. of Na waste to make the blend 0.52 M in iron. The run was terminated after 54.1 hours because product MMPD dropped below 0.13 mm. A drum of Run 4 product stored at <35°C for less than 1 year was caked throughout its entirety. Chloride retention in calcined solids was good (78 wt%).

Two runs attempted to calcine Na waste by adding $Al(NO_3)_3$ to blends of Zr and Na waste to which $Ca(NO_3)_2$ had been added to suppress F volatility. Run 93 calcined a blend of 2 vol. Zr waste – 1 vol. Na waste – 1.6 vol. 2.2 M $Al(NO_3)_3$ containing a Ca/F mole ratio of 0.55. Even though a high NAR (372) and high air fluidizing velocity (>0.30 m/s or >1.0 ft/s) was required to control product size, the run had a product-to-fines ratio of 0.95. Since the AI was 76%, the product must be a hard, brittle material. The chloride retention in calcined solids was only 29.4 wt%. Run 94 calcined a blend of 3 vol. Zr waste -

1 vol. Na waste – 1.3 vol. 2.2 *M* $Al(NO_3)_3$ containing a Ca/F mole ratio of 0.70. Again it was rather hard to control product size (used a NAR of ~300, a high air fluidizing velocity of >0.30 m/s) and the product-to-fines ratio was low (0.80). The chloride retention in calcined solids was very high (99%); apparently the increasing calcium concentration in the blend increased chloride volatility suppression. Corrosion in acid scrub was not a problem since there was adequate Al, B, and Zr in the scrub to complex Al. Less than 1% of the total fluoride escaped the calciner vessel. In both runs: there was little agglomeration; A.I. = 76%; final bed bulk density = 1.54-1.67 g/cm^3; and final fines bulk density = 0.92-1.43 g/cm^3.

Table 55. Composition of Zr-Na waste blends successfully calcined containing $Ca(NO_3)_2$ to suppress F volatility (used in-bed combustion).

			Run #64[b] (WM-183 Wastes)		Run #67[b]			
	Run #52[a]	Run #53[b]	1st 68 hrs	Last 34 hrs	1st 40 hrs	Last 72 hrs	Run #71[b]	Run #75[b]
H^+ (N[a])	1.59	1.59	1.38	1.28	1.07	1.16	0.56	1.4
Al (*M*)	0.58	0.58	0.79	0.66	0.46	0.56	0.34	0.48
Zr (*M*)	0.31	0.31	0.33	0.35	0.26	0.26	0.24	0.19
B (*M*)	0.14	0.14	0.17	0.23	0.12	0.11	0.087	0.08
Na (*M*)	0.40	0.40	0.25	0.18	0.38	0.25	0.32	0.28
K (*M*)	0.061	0.061	NA	NA	0.042	0.028	0.036	0.03
Fe (*M*)	0.0057	0.0057	0.0029	0.023	NA	NA	NA	0.010
Ca (*M*)	1.06	1.48	1.64	1.28	1.30	1.60	0.59	0.84
Cr (*M*)	NA	NA	NA	NA	NA	NA	NA	0.0050
Cu (*M*)	NA	NA	NA	NA	NA	NA	NA	NA
Mg (*M*)	NA	NA	NA	NA	NA	NA	NA	0.011
Mn (*M*)	NA	NA	NA	NA	NA	NA	NA	0.0035
Ni (*M*)	NA	NA	NA	NA	NA	NA	NA	0.0017
Pb (*M*)	NA	NA	NA	NA	NA	NA	NA	NA
Hg (*M*)	NA	NA	NA	NA	0.0018	0.0018	0.0026	0.0026
F (*M*)	2.12	2.12	1.78	1.78	1.69	1.73	0.94	1.2
NO_3 (*M*)	4.98	5.82	6.13	5.00	5.32	5.66	3.22	1.4
SO_4 (*M*)	NA	NA	0.042	0.020	NA	NA	0.065	0.06
Cl (*M*)	0.0077	0.0077	0.0029	0.0022	0.0081	0.0080	0.013	0.014
Mole% Na+K	7.0	6.2	3.1	2.6	6.7	4.0	8.6	6.6
Total Solids (g/L)	196	242	267	216	212	237	138	158

a. Alternated calcining blend of Zr and Na wastes until nodules formed on product followed by calcining Zr waste for ~11 hours.

b. Difficult to control product size, had to use high NAR and air fluidizing velocity.

NA = Not analyzed or not present.

References:

Petrie 1965a; Petrie 1965b; Neuls 1973b; Buckham 1974; Newby 1978a; Newby 1979b; and Lamb 1979b.

Table 56. Composition of Zr-Na blends with $Ca(NO_3)_2$ (used in-bed combustion).

	Composition of Zr-Na Waste Blends Successfully Calcined Containing $Ca(NO_3)_2$ to Suppress F Volatility		Composition of Zr-Na Waste Blends Unsuccessfully Calcined Containing $Ca(NO_3)_2$ to Suppress F Volatility[c]	
	Run #78[a]	Run #79[b]	Run #49	Run #50
H^+ (N^{a})	1.45	1.39	1.43	1.22
Al (*M*)	0.41	0.42	0.57	0.53
Zr (*M*)	0.18	0.18	0.28	0.35
B (*M*)	0.09	0.21	0.13	0.14
Na (*M*)	0.21	0.029	0.48	0.29
K (*M*)	0.029	0.014	0.051	0.046
Fe (*M*)	0.014	1.20	0.0076	0.0062
Ca (*M*)	0.91	NA	1.04	1.12
Cr (*M*)	0.010	NA	NA	NA
Cu (*M*)	NA	NA	NA	NA
Mg (*M*)	0.0063	NA	NA	NA
Mn (*M*)	0.0027	NA	NA	NA
Ni (*M*)	0.0018	NA	NA	NA
Pb (*M*)	0.00036	NA	NA	NA
Hg (*M*)	0.0027	NA	NA	NA
F (*M*)	1.30	1.72	2.04	2.11
NO_3 (*M*)	3.40	4.44	4.92	4.75
SO_4 (*M*)	0.045	0.048	NA	NA
Cl (*M*)	0.0072	0.010	0.011	0.0070
PO_4 (*M*)	0.0027		NA	NA
Mole% Na+K	5.2	5.0	8.2	5.2
Total Solids (g/L)	152	141	196	194

a. Difficult to control particle size, had to use high NAR and fluidizing velocity.

b. Used as fuel 1% and 5% TBP in AMSCO and 5% TBP in tetradecane; these fuels had no adverse effects on run.

c. Formed noduled particles, runs terminated early due to clinker formation around fuel nozzle.

NA = Not analyzed or not present.

References:

Petrie 1965a; Petrie 1965b; Kilian 1973; Neuls 1974c; Staiger 1980; Ramer 1980; and Ramer 1982.

Table 57. Composition of sodium waste successfully calcined – using sugar and heating bed with electric heaters.

	Run 12A[a]	Run 12B[b]
H^+ (N[a])	0.91	0.68
Al (*M*)	0.68	0.84
Zr (*M*)	None	0.43
B (*M*)	None	0.23
Na (*M*)	1.74	1.57
Hg (*M*)	0.00095	0.00055
NH_4 (*M*)	0.053	None
Sucrose (*M*)	0.70	0.48
F (*M*)	None	2.13
NO_3 (*M*)	4.63	3.42
SO_4 (*M*)	0.076	None
PO_4 (*M*)	0.026	None
Mole% Na	34	21
Total Solids (g/L)	191	203

a. Plagued by off-system plugging and pressure imbalances; essentially no $NaNO_3$ in calcined solids; calcined solids colored grey to black; no caking problems.

b. Few operational problems; no $NaNO_3$ in calcined solids; no caking problems; calcined colored grey to black.

References:
Petrie 1965a; Petrie 1965b; and Petrie 1965d

Table 58. Composition of Zr-Na waste blends unsuccessfully calcined not containing $Ca(NO_3)_2$ to suppress volatility (used in-bed combustion).

	Run #35[a]	Run #38[b]	Run #39[c]
H^+ (N[a])	0.9	Not analyzed	Not analyzed
Al (*M*)	0.50	0.57	0.56
Zr (*M*)	0.16	0.16	0.21
B (*M*)	None	0.046	0.11
Na (*M*)	0.73	0.87	0.75
Fe (*M*)	None	None	0.009
Hg (*M*)	None	None	0.0022
F (*M*)	1.42	1.47	1.65
NO_3 (*M*)	2.97	Not analyzed	2.82
SO_4 (*M*)	0.087	0.143	0.12
Cl (*M*)	None	0.021	0.018
PO_4 (*M*)	0.0013	None	0.0013
Undissolved Solids (g/L)	2.6	Not analyzed	3.0
Mole% Na	20	21	18
Total Solids (g/L)	97	118	112

a. No bed caking; run terminated after 97.5 hours due to leak in acid scrub system, probably F corrosion; starting bed was Al_2O_3.

b. Run terminated after 3 ½ hours due to bed clinkering believed to be caused by reaction between SO_4 and ZrO_2-CaF_2 starting bed – was not the case when calcining Na-Zr waste blends containing Ca/F mole ratio of 0.70.

c. Added $Al(NO_3)_2$ to scrub to prevent excessive F corrosion; run terminated after 103 hours due to poor fluidization caused by too many agglomerates; off-gas equipment plugging problems from Al in scrub; Cl not held in solids; Al_2O_3 starting bed used.

References:
Petrie 1965a; Petrie 1965b; Thompson 1971; and Taylor 1972a.

Table 59. Composition of Na waste blends unsuccessfully calcined used iron powder or iron powder plus 2.2 M $Al(NO_3)_3$ – in bed combustion.

	Run #61[a] (WM-183 Waste)	Run #4[b] (Enclosed Calciner)
H^+ (N[a])	2.23	0.78
Al (M)	0.97	1.14
B (M)	0.0043	0.0034
Na (M)	1.00	0.79
K (M)	0.15	0.084
Fe (M)	0.80	0.44
Ca (M)	0.11	None
Cr (M)	0.13	None
Cu (M)	0.0011	None
Mg (M)	0.031	None
Mn (M)	0.013	0.0072
Ni (M)	0.0054	None
Pb (M)	None	0.0013
F (M)	0.024	None
NO_3 (M)	7.3	5.12
SO_4 (M)	0.10	0.025
Cl (M)	0.011	0.0152
PO_4 (M)	0.0010	0.0080
Mole % Na+K	18	16.6
Total Solids (g/L)	227	172

a. Terminated 3 times within 45.5 hours due to bed clinker formation; chloride retention in calcined solids ~96 wt%.

b. Terminated after 54.1 hours because product MMPD fell below 0.13 mm; Cl retention in calcined solids was 78 wt%.

References:

Petrie 1965a; Petrie 1965b; Hoskins 1977; and Newby 1983c.

Table 60. Composition of Na waste blends unsuccessfully calcined using 2.2 M $Al(NO_3)_3$ and using in-bed combustion to heat bed.

	Run #86[a]	Run #87[b]	Run #91[c]	Run #96[d]
H^+ (N[a])	0.60	0.60	0.63	0.54
Al (M)	1.95	1.65	1.58	1.41
B (M)	0.02	0.20	0.21	0.15
Na (M)	0.29	0.67	0.68	0.54
K (M)	None	None	None	0.057
Fe (M)	None	None	None	0.0049
Mn (M)	None	None	None	0.0049
Pb (M)	None	None	None	0.00086
NO_3 (M)	6.74	6.22	6.05	5.47
SO_4 (M)	None	None	None	0.017
Cl (M)	None	None	None	0.011
PO_4 (M)	None	None	None	0.0055
Mole % Na+K	5.4	11.9	12.4	12.5
Total Solids (g/L)	125	148	146	131

a. Few agglomerates, lots of fines, difficult to control size – used NAR of ~360; feed nozzle cap of 120 used; prod./fines ratio = 1.2.

b. Feed nozzle pressure high several times; prod./fines ratio = 0.84; controlled MMPD at NAR 200-250; feed nozzle cap of 120 used.

c. Used feed nozzle caps of 140 and 150; prod./fines ratio = 0.2; very little agglomeration.

d. Terminated 5 times within 3 days due to high feed nozzle pressure – seemed to be caused by use of a 140 rather than 120 nozzle cap.

References:

Petrie 1965a; Petrie 1965b; Newby 1981a; McDonald 1982; Newby 1985; Eldredge 1986; and Newby 1986.

Table 61. Composition of Na waste blends unsuccessfully calcined (in-bed combustion).

	Using $Al(NO_3)_3$		Adding Al $(NO_3)_3$ to Zr-Na Waste Blend Plus $Ca(NO_3)_2$	
	Run #97[a]	Run #3[b] (Enclosed Calciner)	Run #93[c]	Run #94[d]
H^+ ($N^{\underline{a}}$)	0.56	0.40	0.76	1.17
Al (*M*)	1.41	1.64	0.87	0.79
Zr (*M*)	None	None	0.14	0.19
B (*M*)	0.087	0.15	0.097	0.087
Na (*M*)	0.54	0.62	0.30	0.27
K (*M*)	0.057	0.067	0.032	0.029
Fe (*M*)	0.0049	0.0057	0.0027	0.0024
Ca (*M*)	None	None	0.58	0.98
Mn (*M*)	0.0049	0.0057	None	None
Pb (*M*)	0.00086	0.0010	None	None
F (*M*)	None	None	1.06	1.30
NO_3 (*M*)	5.47	6.03	5.21	5.12
SO_4 (*M*)	0.017	0.02	0.0096	0.0083
Cl (*M*)	0.011	0.012	0.010	0.0058
PO_4 (*M*)	0.0055	0.0063	None	None
Mole % Na+K	12.5	12.5	6.6	5.1
Total Solids (g/L)	131	151	142	180

a. Used as fuel 70% Hexone, 24% AMSCO, and 6% TBP-used autoignition temperature of 475°C other wise no different than kerosene; controlled MMPD at NAR of 300; used feed nozzle cap of 120; prod./fines ratio = 0.77; little agglomeration; terminated at COT 80.5 hours due to fines plugging off-gas system; Cl retention in calcined solids = 32 wt%; product caked on surface after standing 1 year.

b. Product-to-fines ratio <1.0; drum of product caked through-out after 1 year; 32% of Cl retained in calcined solids.

c. Took a NAR of 372 to control MMPD; product-to-fines ratio was 0.95; very few agglomerates; Cl retention in calcined solids ~29.4 wt%.

d. Took a NAR of ~300 to control MMPD; prod./fines ratio = 0.80 very few agglomerates; chloride retention in calcined solids ~98.9%; <1.0% of total F escaped uncomplexed from calciner.

References:

Petrie 1965a; Petrie 1965b; Eldredge 1986; and Newby 1986.

STUDIES IN 10-CM (4") and 15-CM (6") CALCINER PILOT PLANTS

4" CALCINER PILOT PLANT RUNS CALCINING ZR AND NA WASTE BLENDS

Runs Sodium-Bearing Waste (SBW)-4-8, 9, 10, 11, 12, and 13 tested simulated zirconcium-sodium waste blends in a 4" (10-cm) calciner pilot plant using in-bed combustion. Runs SBW4-8, -9, -10, -11, -12 and –13 were all calcined at 500°C and had a Ca/F mole ratio of 0.70. The simulated Zr and Na wastes were blended together in ratios varying from 2:1 to 8:1. All runs were voluntarily terminated after 40 hours; none of the runs showed a high tendency toward agglomeration. All runs: a) produced product having relatively smooth surfaces; b) realized high retention of Cl in calcined solids (~90% of total) and low F volatility from the calciner vessel (0.81 wt% or less). Fluidized-bed agglomeration, smoothness and nodule content of the product, product density (~1.58 g/cm^3), and chloride and fluoride volatility, were independent of the Zr to Na wastes' blend ratio. Christian (1975) says when using Zr-Na waste blends having Ca/F mole ratios of 0.5 that the attrition indices (AIs) go through a maximum at a Na+K concentration of ~0.34 *M* with blend ratios containing higher and lower Na+K concentrations, having lower AIs. This may also be true in the above runs; the AI of the 3:1 blend (Na+K = ~0.41 *M*) is 80%, but the AIs of blends more and less concentrated than ~ 0.41 *M* Na+K are lower. Run SBW4-1 calcining a 1:1 blend (alkali metal content of calcine = 13.9 mole%) of the same Zr and Na wastes and having a Ca/F mole ratio of 1.0 was voluntarily terminated after 14 hours without clinker formation (AI=68%), but the surface area of the product was very noduled. The difficulty in controlling the product MMPD with feed NARs may have confirmed that the product AI may have gone through a maximum: the 8:1 blend was definitely controlled at NARs ranging between 935 and 994; the 2:1 and 4:1 blends were definitely controlled at a NAR of 1045; the 3:1 blend was definitely not controlled at a NAR of 1020; and it could not be determined whether the MMPDs of the remaining blends could be controlled by NARs for the information obtained. Undissolved solids in feed increased as the Zr-Na waste blend ratio increases due to the higher fluoride concentration in the Zr waste and precipitation of calcium fluoride and calcium fluozirconite solids after calcium nitrate addition to the feed (Newby 1978a, Newby 1974b).

Table 62. Successful 4” calciner runs using Zr-Na waste blends.

	SBW4-8	SBW4-9	SBW4-10	SWB4-11	SBW4-12	SBW4-13
H^+ (N^a)	1.42	1.48	0.46	1.16	1.41	1.38
Al (*M*)	0.59	0.60	0.49	0.53	0.53	0.54
Zr (*M*)	0.33	0.30	0.31	0.33	0.28	0.31
B (*M*)	0.16	0.14	0.14	0.16	0.12	0.13
Na (*M*)	0.28	0.37	0.15	0.20	0.52	0.29
K (*M*)	0.030	0.040	0.015	0.022	0.055	0.031
Mn (*M*)	0.0027	0.0034	0.0013	0.0018	0.0047	0.0026
Hg (*M*)	0.00045	0.00060	0.00023	0.00033	0.00083	0.00046
Fe (*M*)	0.0027	0.0034	0.0013	0.0018	0.0047	0.0026
Ca (*M*)	1.38	1.22	1.66	1.59	1.52	1.61
Mg (*M*)	---	---	---	---	---	---
NO_3 (*M*)	5.83	6.02	5.78	5.97	6.17	6.22
F (*M*)	2.22	2.10	1.90	2.14	1.74	2.00
Cl (*M*)	0.0058	0.0074	0.010	0.011	0.014	0.0072
PO_4 (*M*)	0.0029	0.0038	0.0015	0.021	0.0053	0.0029
SO_4 (*M*)	0.0092	0.012	0.0047	0.0065	0.017	0.0092
Mole % Na+K	4.3	5.9	2.4	3.0	7.9	4.4
Total Solids (g/L)	220	209	235	233	255	243
Ca/F Mole Ratio	0.62	0.58	0.87	0.74	0.87	0.80
Al/Na+K Mole Ratio	1.90	1.94	2.9	2.4	0.92	1.7
Blend Ratio Zr:Na	4 ½:1	3:1	8:1	6:1	2:1	4:1

4" CALCINER RUNS BLENDS OF ZR AND NA WASTES

For Run FV4-4, the bed was heated with in-bed combustion of kerosene at 500°C; feed was a blend of 3 vol. Zr waste – 1 vol. Na waste. Precipitation of calcium fluozirconate can be suppressed by increasing the Al/F ratio to about 0.32 in the ZrF containing waste prior to $Ca(NO_3)_2$ addition. Run FV4-4 was made to determine if increasing the Al concentration of the blend had any detrimental effect on F or Cl volatility, calcine operability, or calcine properties during calcination of the wastes. No detrimental effect was noted. Feed NAR of 1045 possibly controlled MMPD; bulk density = 1.58 g/cm^3; product-to-fines ratio = 2.8; AI = 76%; wt% of bed that is +14 mesh particles = 0.4; F volatility = 0.39 wt% from calciner vessel; Cl volatility = 93% retention in solids (Newby 1980a, Newby 1977).

Table 63. 4" Calcine Pilot Plant Run FV4-4 with increased Al concentration.

	Feed
H^+ (N^{a})	1.32
Al (*M*)	0.59
Zr (*M*)	0.33
B (*M*)	0.13
Na (*M*)	0.38
K (*M*)	0.040
Mn (*M*)	0.0042
Hg (*M*)	0.0008
Fe (*M*)	0.0080
Ca (*M*)	1.42
NO_3 (*M*)	5.71
F (*M*)	1.86
Cl (*M*)	0.0066
PO_4 (*M*)	0.0048
SO_4 (*M*)	0.015
Mole % Na+K	5.8
Total Solids (g/L)	239
Al/Na+K Mole Ratio	1.40

When $Ca(NO_3)_2$ is added to Zr-F containing wastes, copious quantities of a gelatinous precipitate is formed which has a tendency to plug restrictions in lines such as feed nozzles, flowmeters, and valves. In runs FV4-5 through 9, $Mg(NO_3)_2$ was tested as a substitute for $Ca(NO_3)_2$ to suppress F volatility from the calciner vessel because $Mg(NO_3)_2$ forms no precipitate when added to zirconium fluoride containing wastes, and based on batch calcination studies which showed it was as effective as $Ca(NO_3)_2$ in suppressing F volatility during calcination of zirconium fluoride containing wastes at 500°C. Calcination of a blend of Zr-Na waste having a Mg/F mole ratio of 0.7 and an Al/F mole ratio of 0.30: produced a product having an AI of 40% and a bulk density of 1.50 g/cm^3; had a product-to-fines ratio of ~2.0; and had low agglomeration tendencies. $Mg(NO_3)_2$ was as effective as $Ca(NO_3)_2$ in suppressing F volatility but was not as effective in suppressing Cl volatility (66 wt% vs. 90% Cl retention in calcined solids). Decreasing the Mg/F mole ratios from 0.70 to 0.50 for Na-Zr wastes blends having an Al/F mole ratio of

Table 64. Runs FV4-5, -6, -7, -8, -9.

	Run #FV4-5	Run #FV4-6	Run #FV4-7	Run #FV4-8	Run #FV4-9
H^+ (N[a])	1.47	1.44	1.28	1.34	1.22
Al (*M*)	0.48	0.52	0.56	0.59	0.46
Zr (*M*)	0.25	0.28	0.27	0.24	0.25
B (*M*)	0.12	0.16	0.15	0.12	0.12
Na (*M*)	0.35	0.40	0.39	0.35	0.34
K (*M*)	0.038	0.042	0.042	0.037	0.036
Mn (*M*)	0.0032	0.0036	0.0035	0.0031	0.0032
Hg (*M*)	0.0006	0.0007	0.0007	0.0006	0.0034
Fe (*M*)	0.0060	0.0068	0.0068	0.0059	0.0062
Ca (*M*)	---	---	---	---	0.69
Mg (*M*)	1.22	1.21	0.96	1.19	0.82
NO_3 (*M*)	4.80	4.35	4.54	5.09	5.19
F (*M*)	1.72	2.14	1.87	1.83	1.98
Cl (*M*)	0.0058	0.012	0.0089	0.0075	0.0028
PO_4 (*M*)	0.0036	0.0041	0.0040	0.0036	0.0037
SO_4 (*M*)	0.011	0.013	0.012	0.011	0.012
Mole % Na+K	6.3	6.6	7.1	6.1	5.6
Total Solids (g/L)	182	186	166	181	214
Mg or Ca/F Mole Ratio	0.70	0.5	0.6	0.9	0.7
Al/Na+K Mole Ratio	1.23	1.18	1.30	1.51	1.21

0.3 (Run FV4-5 had a Mg/F mole ratio 0.70, FV4-7 had a Mg/F mole ratio of 0.60, and FV4-6 had a Mg/F mole ratio of 0.50) had little effect on calciner operation, product and fines characteristics, or fluoride volatility, but did decrease chloride retention in calcined solids (from 66 wt% to 38%). Increasing the Al/F mole ratio (Mg/F mole ratio being 0.70) from 0.30 to 0.40 (Run FV3-8): increased the AI to 70%, possibly increased the product bulk density (from 1.50 to 1.60 g/cm^3), had no effect on F volatility, and increased Cl retention in calcined solids to 90 wt%. Run FV4-9 using a Ca/F mole ratio of 0.35 and a Mg/F mole ratio of 0.35 and: a) produced a product with an AI of 50% and a bulk density of 1.70 g/cm^3; b) had 0.34 wt% of total F fed to calciner escaping from the calciner; c) had a product-to-fines ratio of 2.4; and d) had 68% of the total Cl retained in calciner product. Except for the run having the high Al concentration, product MMPD seemed to be readily controlled by feed NAR (Newby 1980, Newby 1979a, McCray 1972, Newby 1974).

4” CALCINER BLEND’S OF ZR AND NA WASTES CONTAINING HIGH AL CONCENTRATIONS

It was thought that the Na waste calcination feed rate could be increased without agglomeration problems by decreasing the Zr to Na waste blend ratio to a ratio less than normally used and increasing the Al concentration to a greater value than normally found in such blends. Blends of 2 vol. Zr waste – 1 vol. Na waste – 1.6 vol. 2.2 M $Al(NO_3)_3$ with a Ca/F mole ratio of 0.7 (Run SAL4-1A) or a Ca/F mole ratio of 0.55 (Run SAL4-2A) are shown in Table 65 and were voluntarily terminated after being calcined for 80 and 108 hours, respectively, in a 4” calciner. Both runs had difficulty controlling particle size; Run SAL4-1A used a NAR of 1667 (average NAR = 1364) and a diluted feed with 20 vol. % acid scrub to decrease MMPD; Run SAL4-2A used a NAR of 1625 (average NAR = 1454) and diluted feed with 15 vol. % acid scrub to decrease MMPD. No excessive agglomerate formation inside the calciner was found after either run. In both runs some offgas equipment and line plugging, occured probably due to the relatively high fluidizing velocity used. Pertinent information for Run SAL4-1A was: O_2/fuel ratio = 1972, fluidizing air rate = 1.88 scfm (0.94 ft/sec fluidizing velocity), starting bed was calcined Zr-Na waste (0.4402 mm), product bulk density = 1.70 g/cc, AI = 88%, smooth, uniform product with no nodules present, product-to-fines ratio of 3.71, wt% of final bed +14 mesh particles = 20%, MMPD of final bed = 0.5399 mm, fluoride volatility (other than as CaF_2) = 1.1 wt %, chloride retention in calcined solids = 79.1 wt %. Pertinent information for Run SAL4-2A was: O_2/fuel ratio = 1658, fluidizing air rate = 1.81 scfm (0.91 ft/sec fluidizing velocity), starting bed was calcined Zr-Na waste (0.4437 mm), bulk density = 1.69 g/cc, AI = 86%, rough surfaced product with some nodules, product-to-fines ratio = 3.75, wt % of final bed + 14 mesh particles = 2.6 wt%, MMPD of final bed = 0.5608 mm, fluoride volatility (other than as CaF_2) = 4.2 wt%, chloride retention in calcined solids=37.0 wt% (McCray 1983).

Table 65. 4” calciner pilot plant runs testing blends of Zr and Na wastes with aluminum nitrate.

	Run #SAL4-2A	Run #SAL4-1A
H^+ (N^a)	0.74	0.74
Al (M)	1.18	1.18
Zr (M)	0.20	0.20
B (M)	0.13	0.13
Na (M)	0.41	0.41
K (M)	0.043	0.043
Mn (M)	0.0037	0.0037
Fe (M)	0.0037	0.0037
Ca (M)	0.76	0.96
Pb (M)	0.00065	0.00065
NO_3 (M)	4.60	4.69
F (M)	1.37	1.37
Cl (M)	0.0078	0.0078
PO_4 (M)	0.0041	0.0041
SO_4 (M)	0.013	0.013
Mole % Na+K	6.7	6.3
Total Solids (g/L)	190	212
Ca/F Mole Ratio	0.70	0.55
Al/Na+K Mole Ratio	2.6	2.6
Blend Ratios (Zr:Na: 2.2 M $Al(NO_3)_3$)	2:1:1.6	2:1:1.6

4" CALCINER RUNS WITH ZR AND NA WASTES USING NITROGEN AS FLUIDIZING GAS

It has been found that many of the difficulties in calcining Na-waste (such as agglomeration, chloride volatility, and difficulty in keeping product size from increasing), could be decreased under conditions that would lead to the production of calcine having low nitrate content (<5.0 wt%). An attempt was made to do this using nitrogen gas to fluidize the bed and to atomize the feed. Two runs (Runs N24-1 and –2) were made using the same blend of Na-Zr wastes as feed (see compositions in Table 66), the same starting bed, the same fluidizing velocity (0.28 m/s below nozzle), the same feed rate, and same NAR (1100 for Run N24-1 and 1000 for Run N24-2). Run N24-1 used air and Run N24-2 used nitrogen gas from liquid nitrogen bottles to fluidize the calciner vessel bed and to atomize the feed. Both runs were voluntarily terminated after 40 hours without unusual operating problems. A much higher fuel nozzle O_2/fuel ratio was required for the run using nitrogen.

Table 66. 4" calciner pilot plant runs to compare air versus nitrogen as fluidizing gas.

	Run #N24-1 (Air)	Run #N24-2 (Nitrogen)
Al (*M*)	0.61	0.64
Zr (*M*)	0.34	0.33
B (*M*)	0.16	0.16
Na (*M*)	0.30	0.32
K (*M*)	0.028	0.029
Ca (*M*)	1.60	1.60
NO_3 (*M*)	5.57	6.15
F (*M*)	2.08	2.01
Ca/F Mole Ratio	0.77	0.80
Mole % Na+K	4.3	4.5
Total Solids (g/L)	250	253

Comparison of the calcined solids' nitrate concentrations as well as other calcined solids' properties (see Table 67) showed that the less oxidizing atmosphere of Run N24-2 did not reduce residual nitrates in calcined solids (Spiers 1984).

Table 67. Final properties of calcined solids for Run N24-1 and –2.

	Run #N24-1 (Air)	Run #N24-2 (Nitrogen)
Final Product NO_3 Concentration (wt%)	4.87	5.50
Final Fines NO_3 Concentration (wt%)	5.22	6.09
Final Bed Attrition Index (%)	58	43
Final Bed Bulk Density (g/cm^3)	1.44	1.47
Final Fines Bulk Density (g/cm^3)	0.48	0.45
Product Production Rate (g/h)	347.5	342.5
Fines Production Rate (g/h)	99.2	108.8
Product-to-Fines Ratio	3.4	3.1
Final Bed MMPD (mm)	0.53	0.44

4" CALCINER RUNS BLENDS OF ZR AND WM-183 (Sodium) WASTES

A series of 4" calciner runs (Table 68) was made to determine if a mixture of aluminum nitrate, electrolytic first cycle extraction, and Na wastes stored in tank WM-183 during ~1976-1978 could be calcined as a blend with Zr waste. The runs showed that WM-183 waste could be calcined as a blend of ~2 Vol. Zr waste and 1 Vol. WM-183 waste. Run 183-4-13 showed that a blend of 2 Vol. Zr and 1 Vol. WM-183 waste using a Ca/F mole ratio of 0.63 produced particles having rough surfaces containing some nodules and that chloride in calcined solids is dependent on calcium concentration in a calciner feed (increasing the calcium concentration from a Ca/F mole ratio of 0.63 to 0.77 increased Cl retention in calcined solids from 62 to 100 wt%. Run 183-4-14 showed that substituting $Mg(NO_3)_2$ for $Ca(NO_3)_2$ softened calcine, increased fines production, reduced Cl retention in calcined solids, and produced smooth surfaced spherical particles. Run 183-4-15 using a Ca/F mole ratio of 0.58 produced rough surface calcine but for some reason the Cl retention in calcined solids was high (89%). Run 183-4-16 showed that nodule formation on calcine surfaces could not be prevented by adding powdered iron to feed containing Ca/F mole ratios varying between 0.51 and 0.55, but showed that adding powdered iron to feed increased Cl retention in calcined solids. Runs 183-4-13B and –17 showed that a Ca/F mole ratio of ~0.75 gives excellent retention of chloride in calcined solids. Runs 183-4-13, -14, -15, -16, and –17 calcined WM-183 waste concentrated to 60% of its original volume; Run 183-4-18 calcined unconcentrated WM-183 waste showing that a blend of 2 Vol. Zr waste and 1 Vol. unconcentrated WM-183 waste would build bed (using a zirconia starting bed). Runs 183-4-13, -14, -15, -16, and –17 had used both zirconia and calcined Zr-WM-183 wastes for starting beds; building bed using zirconia starting beds seemed to be more difficult then building beds using calcined blends of Zr waste and WM-183 waste as starting bed (Newby 1983c).

Table 68. 4” calciner pilot plant runs using Zr and WM-183 (Na) blends.

	Run #183-4-13A	Run #183-4-13B	Run #183-4-14A	Run #183-4-14B	Run #183-4-15
Blend	2 Vol. Zr – 1 Vol. Na[a]		2.5 Vol. Zr – 1 Vol. Na[a]	2.2 Vol. Zr – 1 Vol. Na[a]	1.9 Vol. Zr – 1 Vol. Na[a]
H$^+$ (N[a])	1.81	1.81	1.66	1.68	1.78
Al (*M*)	0.81	0.81	0.94	0.94	0.96
Zr (*M*)	0.30	0.30	0.35	0.34	0.34
B (*M*)	0.17	0.17	0.18	0.17	0.16
Na (*M*)	0.37	0.37	0.31	0.34	0.38
K (*M*)	0.053	0.053	0.046	0.050	0.055
Ca (*M*)	1.32	1.62	0.034	0.038	1.20
Fe (*M*)	0.022	0.022	0.019	0.021	0.023
Cr (*M*)	4.7x10^{-3}	4.7x10^{-3}	4.0x10^{-3}	4.4x10^{-3}	4.8x10^{-3}
Cu (*M*)	4.0x10^{-4}	4.0x10^{-4}	3.4x10^{-4}	3.8x10^{-4}	1.0x10^{-3}
Mg (*M*)	0.011	0.011	1.33	1.46	0.015
Mn (*M*)	5.0x10^{-3}	5.0x10^{-3}	4.3x10^{-3}	4.7x10^{-3}	5.2x10^{-3}
Ni (*M*)	2.0x10^{-3}	2.0x10^{-3}	1.7x10^{-3}	1.9x10^{-3}	3.1x10^{-3}
NO$_3$ (*M*)	3.78	3.78	4.04	4.17	4.32
F (*M*)	2.10	2.10	2.14	2.06	2.07
Cl (*M*)	0.0040	0.0040	3.4x10^{-3}	3.8x10^{-3}	4.1x10^{-3}
PO$_4$ (*M*)	4.0x10^{-4}	4.0x10^{-4}	3.4x10^{-4}	3.8x10^{-4}	4.1x10^{-4}
SO$_4$ (*M*)	0.042	0.042	0.036	0.039	0.043
Ca/F Mole Ratio	0.63	0.77	0.016	0.018	0.58
Mole % Na+K	5.4	5.0	4.4	4.6	5.5
Total wt. of Solids (g/L)	240	273	228	244	241
Type of Heat	All In-Bed Combustion at 500°C				
Fluidizing Velocity (m/s)	0.27 (average)	0.31 (average)	0.26 (average)	0.26 (average)	0.30 (average)
Feed NAR	894 (average)	1098 (average)	940 (average)	1012 (average)	1128 (average)
O$_2$/Fuel Ratio	2131 (average)	2203 (average)	1940 (average)	2203 (average)	2281 (average)
Product Production Rate (g/h)	247		164		293 (average)
Bed Turnover (%)	89	97.9 accumulative	82	98.6 accumulative	99
MMPD (mm)	0.59 (Final Bed)		0.50 (Final Bed)		0.60 (final bed)
Product Size Controlled	Product Size Kept Constant at NAR of 1100-1150		Product Size Kept Constant at NAR of 1000		Product Size Kept Constant at NAR of 1100-1150
Product Bulk Density (g/cm^3)	1.64 (average)	1.59 (average)	142 (average)	152 (average)	1.61 (average)
Product/Fines Ratio	1.9	2.8	1.3	1.5	4.3
Wt.% of Total Cl Retained in Calcined Solids	62	100	10-19	26-31	89
Appearance of Product Surface	Surfaces were rough and noduled	Surfaces were relatively smooth	Surfaces smooth; spherical		Surfaces rough, not spherical
Product Attr. Index (%)	71	69	32	61	70

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a. WM-183 waste concentrated to 60% of its original volume.

Other Early 4" Calciner Runs Using Zr-Na Waste Blends

Nineteen runs (SC4-1 through SC4-19) varying in length from 2 to 80 hours were made in an unenclosed (#3) 4-inch calciner varying: a) blend ratios of Na and Zr wastes from 1 to 5 vol. Zr waste per vol. Na waste); b) calcium concentrations (Ca/F mole ratios of 0.50 to 0.70); and calcination temperatures (400-550°C). Also, sugar was used with a 1 vol. Zr waste – 1 vol. Na waste blend, and iron powder used with unblended Na waste. The composition of the Na and Zr wastes used in these runs are shown in Table 71. It was found that blends of 1 to 5 vol. Zr waste and 1 vol. Na waste containing a Ca/F mole ratio of 0.5 formed noduled particles. Since noduled particles don't slide by one another freely during fluidization, fluidizing a bed of noduled particles can eventually lead to bed agglomeration. Calcination of blends using Zr waste-to-Na waste blend ratios of 5 to 1 and 3 to 1 containing Ca/F mole ratios of 0.60 and 0.70 did not produce noduled particles (blend ratios of less than 3 to 1 were not calcined having Ca/F mole ratios of 0.60 to 0.70). Addition of $AgNO_3$ to blends containing a Ca/F mole ratio of 0.50 did not reduce Cl volatilization. Blends using Zr to Na waste blend ratios of 5 to 1 and 3 to 1 containing a Ca/F mole ratio of 0.70 had low (<10% of total) Cl volatilization. Zr-Na blends of 1 to 1 and a 2 ½ to 1 Zr-Na and having a Ca/F mole ratio of 0.5 were terminated at 2 and 20 hours, respectively, due to bed clinkering. The calcine produced during the former run contained 16 mole% Na+K; the calcine of the latter run contained 8.3 mole% Na+K. Calcining Zr waste with a starting bed of noduled particles (bed of calcined Na-Zr wastes blend particles) produced a final bed of non-noduled particles after 8 hours. A run calcining a 1 to 1 blend containing 4 gms of sugar per gm of Na was terminated after 32 hours due to bed clinker formation. A calciner run calcining Na waste using 1.5 moles of powdered iron per mole of Na and 3 moles of solid $Ca(NO_3)_2$ per mole of Cl was terminated after 8 hours due to bed clinker formation. Three successful flowsheets from this series of runs are shown in Table 71. It was difficult to control particle size growth in these runs (Neuls 1973a; Neuls 1974a; Neuls 1974b; Neuls 1975).

Table 69. Simulated Zr and Na waste compositions used for feed blends during 4" calciner runs SC4-1 through SC4-9.

	Zr Waste	Na Waste
H^+ (N[a])	1.60	1.06 or 1.40
Al (*M*)	0.67	0.52 or 0.56
Zr (*M*)	0.45	--
B (*M*)	0.20	--
Na (*M*)	--	1.59 or 1.90
K (*M*)	--	0.20 or 0.24
Fe (*M*)	0.005	0.011 or 0.02
NO_3 (*M*)	2.36	4.38 or 4.61
F (*M*)	3.21	--
Cl (*M*)	--	0.032 or 0.048

Table 70. 4” calciner pilot plant runs using blends of Zr and WM-183 (Na) wastes.

	Run #183-4-16A	Run #183-4-16B	Run #183-4-17	Run #183-4-18
Blend	1.9 Vol. Zr – 1 Vol. Na[a]	2.1 Vol. Zr – 1 Vol. Na[a]	1.9 Vol. Zr – 1 Vol. Na[a]	2 Vol. Zr – 1 Vol. Na[b]
H^+ ($N^{\underline{a}}$)	1.78			
Al ($\underline{M}$)	0.96			
Zr ($\underline{M}$)	0.34			
B ($\underline{M}$)	0.16			
Na ($\underline{M}$)	0.38			
K ($\underline{M}$)	0.055			
Ca ($\underline{M}$)	1.14			
Fe ($\underline{M}$)	0.17[c]			
Cr ($\underline{M}$)	4.8×10^{-3}			
Cu ($\underline{M}$)	1.0×10^{-3}			
Mg ($\underline{M}$)	0.015			
Mn ($\underline{M}$)	5.2×10^{-3}			
Ni ($\underline{M}$)	3.1×10^{-3}			
NO_3 ($\underline{M}$)	4.32			
F ($\underline{M}$)	2.07			
Cl ($\underline{M}$)	4.1×10^{-3}			
PO_4 ($\underline{M}$)	4.1×10^{-4}			
SO_4 ($\underline{M}$)	0.043			
Ca/F Mole Ratio	0.55			
Mole % Na+K	5.3			
Total wt. of Solids (g/L)	246			
Type of Heat	In-Bed Combustion at 500°C			
Fluidizing Velocity (m/s)	0.31 (average)	0.32 (average)	0.27 (average)	
Feed NAR	1069 (average)	978 (average)	1000 (average)	
O_2/Fuel Ratio	2177 (average)	2456 (average)	2000 (average_	
Product Production Rate (g/h)	254		302	245
Bed Turnover (%)	87	98.3 accumulative	100	92.4
MMPD (mm)	0.54 (Final Bed		0.57 (Final Bed)	$0.46^{+0.03}_{-0.02}$
Product Size Controlled	Product Size Kept Constant at NAR of 980		Product Size Kept Constant at NAR of 1100-1500	No Information
Product Bulk Density (g/cm^3)	1.61 (average)	1.47 (average)	1.52 (average)	$1.42^{+0.12}_{-0.07}$
Product/Fines Ratio	2.8	1.4	3.0	1.4
Wt.% of Total Cl Retained in Calcined Solids	88	94	100	No Information
Appearance of Product Surface	Non-Spherical with Rough Surfaces		Non-Spherical; had Relatively Smooth Surfaces	No Information
Product Attr. Index (%)	50 (average)	46 (average)	60 (average)	46^{+12}_{-14}
Weight of Final Bed >14 Mesh (Wt%)	3.1		4.8	1.0

a. WM-183 waste concentrated to 60% of its original volume.
b. Unconcentrated WM-183.
c. Iron added as powdered iron.

Table 71. Zr-Na waste blends calcined successfully in a 4" calciner pilot plant.

	Run SC4-12 5:1 Blend with 0.70 Ca/F - 80 hr run	Run SC4-15 3:1 Blend with 0.70 Ca/F – 44 hr Run	Run SC4-16 3:1 Blend with 0.60 Ca/F – 52 hr Run
H^+ (N[a])	1.52	1.55	1.55
Al (*M*)	0.56	0.64	0.64
Zr (*M*)	0.33	0.34	0.34
B (*M*)	0.15	0.15	0.15
Na (*M)*	0.23	0.40	0.40
K (*M*)	0.035	0.060	0.060
Fe (*M)*	0.0052	0.0065	0.0065
Ca (*M)*	1.61	1.69	1.45
NO_3 (*M)*	2.43	2.86	2.86
F (*M)*	2.31	2.41	2.41
Cl (*M*)	0.0049	0.0080	0.0080
Total Solids (g/L)	238	268	241
Mole% Na+K	3.5	5.5	5.9

4" CALCINER PILOT PLANT RUNS WITH NA-WASTE – AL(NO_3)$_3$ BLENDS

Run 32 in a 4" calciner was an early test to demonstrated calcination of a blend of simulated Na waste and simulated Al(NO_3)$_3$ waste(1:4 Na/Al mole ratio) in an in-bed combustion heated, fluidized-bed calciner. The blend ratio was 1 vol. Al(NO_3)$_3$ waste (WM-183 waste) to 0.117 vol. of Na waste. It ran continuously for 110 hours – voluntarily terminated. No nozzle "cake" formation or other problems were encountered during the run. Product AI was 74%; MMPD increased continuously from 0.43 to 0.88 mm during the run even though feed NARs between 980-1300 were used. Bed temperature was 500°C; fluidizing velocity = 0.73 ft/sec (below nozzle) and starting bed was alumina (Holcomb 1971).

Table 72. Feed for 4" calciner Run 32 using simulated Na waste and Al waste.

H^+ ($N^{\underline{a}}$)	0.84
Al (*M*)	1.02
Na (*M*)	0.25
Fl (*M*)	0.0035
NO_3 (*M*)	4.11
SO_4 (*M*)	0.021

The best method for calcining Na waste up to that time was to blend it with Zr or Fluorinel waste and add Ca(NO_3)$_2$ to suppress fluoride volatility. If the constituents of Fluorinel waste that prevent bed agglomeration during calcination of a blend of Na and zirconium fluoride waste could be added to Na waste as cold chemicals, Na waste could be calcined when there wasn't Fluorinel waste available, possibly increasing the rate of calcining Na waste so as to exceed the rate of Na waste generation. It has been suggested that $NaNO_3$ does not cause bed agglomeration during calcination of blends of Na and zirconium fluoride wastes due to the formation of calcium oxide-sodium oxide-aluminum oxide complexes. Thus, sufficient calcium nitrate was added to Na waste-aluminum nitrate blends containing boric acid to form some of these compounds. When it was found that product size was extremely difficult to control during the first run of the series (Run SBW4-31) calcining a blend of 2 vol. 2.2 *M* Al(NO_3)$_3$ - 1 vol. Na waste – 0.15 *M* boric acid (suppresses crystalline alumina formation) – 0.52 *M* Ca(NO_3)$_2$, the feed was modified in the following manner (without success) to make product size control easy: a) 0.15 *M* phosphoric acid (also suppresses crystalline alumina formation) was substituted for 0.15 *M* boric acid (Run SBW4-32); b) boric and phosphoric acids were eliminated and calcium nitrate decreased to 0.24 *M* (Run SBW4-33) and 0.10 *M* (Run SBW4-34), respectively; and c) the blend concentration of aluminum nitrate was decreased from 2 vol. to 1.5 vol. 2.2 *M* aluminum nitrate (Run SBW4-37). Run SBW4-31 was shut down after 28 hours because bed particles were too large to be fluidized properly (didn't try to control particle size soon enough) and Run SBW4-34 was shut down after 33.8 hours due to off-gas line plugging. All other runs were voluntarily terminated after 40 hours. The feeds for these runs are given in Table 73.

Particle size was difficult to control (needed feed NARs > 1000 and/or feed water dilution, in all runs. Also in all runs: a) off-gas equipment continually plugged with fines and product-to-fines ratios were 2.8 or less even through the attrition indices were 48% or greater; b) feed did not contain solids; and c) the surfaces of particles produced were smooth. Decreasing the aluminum nitrate concentration of the blend increased the agglomeration tendency of the bed and decreased chloride retention in calcined solids from ~80 to 32 wt% of total chloride; in all other runs the chloride retention in calcined solids averaged 78 wt% and agglomeration tendency was low. Phosphoric acid was no more effective than boric acid in suppressing formation of crystalline alumina (in Runs SBW4-24 and 32). Nitric acid had to be frequently added to the off-gas acid scrub to prevent the solution from becoming basic in runs SBW4-33, -34, and – 37. Crystalline alumina was not found in calcine produced from runs containing 0.52 *M* Ca(NO_3)$_2$.

Calcine operation, characteristics of the fluidized-bed, and properties of solids produced during calcination of $Al(NO_3)_3$-Na waste blends containing $Ca(NO_3)_2$ and during calcination of Zr-Na waste blends in a 10-cm calciner were not similar. Thus conversion of $NaNO_3$ to sodium-calcium-aluminum oxide complexes during calcination doesn't explain why there is little bed agglomeration during calcination of zirconium waste blends. In the two runs containing phosphate, phosphate retention in calcined solids was ~86 wt% of total; the rest of the phosphate was caught in the acid scrub.

Run SBW4-24 substituted 0.20 M phosphoric acid from 0.20 M boric acid in an $Al(NO_3)_3$-Na waste blend to determine if phosphoric acid had any advantage over boric acid as a crystalline alumina suppressor. The runs were voluntarily terminated after 40 hours. A feed NAR of 1000 was insufficient to control particle size. There were off-gas equipment plugging problems even though the product attrition index was 46% and a product-to-fines ratio of 3.5 was obtained. Surfaces of particles were smooth but particles were irregularly shaped. Chloride retention in calcined solids was only 34 wt% of total; the nitrate content of calcined solids averaged 14.5 wt% (Newby 1980b, Newby 1981b, Newby 1986, Newby 1983a, Newby 1983e).

Table 73. Calcination of Na waste in 4" calciners using calcium nitrate and phosphoric acid.

	Run #SBW4-24	Run #SBW4-32	Run #SBW4-33	Run #SBW4-37
H^+ (N[a])	0.66	0.55	0.50	0.50
Al (M)	1.76	1.64	1.58	1.54
B (M)	0.0025	0.0027	0.0026	0.0025
Na (M)	0.58	0.59	0.62	0.67
K (M)	0.062	0.069	0.069	0.070
Ca (M)	None	0.54	0.18	0.35
Mn (M)	0.0053	0.0057	0.0054	0.0053
Fe (M)	0.0053	0.0057	0.0054	0.0053
NO_3 (M)	6.20	6.76	5.86	6.26
Cl (M)	0.012	0.012	0.014	0.018
PO_4 (M)	0.20	0.14	0.0061	0.0060
SO_4 (M)	0.019	0.020	0.019	0.019
Mole % Na+K	11.7	10.6	12.9	13.1
Total wt. of Solids (g/L)	126	146	115	124

Calcining Na waste using $Al(NO_3)_2$ and boric acid as additive required an Al/Na+K mole ratio of ~2.4 or greater; a run calcining Na waste using $Al(NO_3)_3$ and boric acid as additives having as Al/Na+K mole ratio of 1.3 was terminated after 6.8 hours due to clinker information around the fuel nozzle while a run having an Al/Na+K mole ratio of 1.3 was terminated after 16 hours due to off-gas plugging (the run had continuous feed nozzle plugging). All other runs using the above method had an Al/Na+K mole ratio of ~2.4 in the feed. In runs calcining Na waste using aluminum nitrate plus boric acid as additives, boron was increased from 0.02 to 0.40 M to suppress formation of iota Al_2O_3 (a crystalline Al_2O_3), i.e. to see if fines generation rate could be decreased. Increasing the boron concentration from 0.02 to 0.2 M did decrease iota Al_2O_3, formation by a factor of 3; further increasing boron concentration did not decrease iota Al_2O_3 formation. The x-ray diffraction pattern of iota Al_2O_3 and crystalline sodium aluminate is

Table 74. Calcination of Na waste in 4" calciners using $Al(NO_3)_3$ and boric acid (relatively successful runs).

	Run # SBW4-14b	Run# SBW4-17	Run# SBW4-19	Run# SBW4-30b	Run# SBW4-38
H^+ (N^a)	0.78	0.57	0.51	0.46	0.38
Al (M)	1.70	1.40	1.54	1.60	1.69
B (M)	0.017	0.19	0.020	0.23	0.21
Na (M)	0.61	0.53	0.69	0.51	0.60
K (M)	0.067	0.058	0.080	0.062	0.065
Mn (M)	0.0057	0.0050	0.0052	0.0053	0.0057
Hg (M)	0.0023	0.0056	None	None	None
Fe (M)	0.0057	0.0050	0.0052	0.0059	0.0057
Mg (M)	None	None	None	None	0.20
NO_3 (M)	5.94	5.13	5.84	5.68	5.50
Cl (M)	0.013	0.0042	0.014	0.013	0.015
PO_4 (M)	0.0063	0.0055	0.0057	0.0059	0.0059
SO_4 (M)	0.020	0.017	0.022	0.019	0.020
Al/Na+K Mole Ratio	2.5	2.4	2.0	2.8	2.5
Mole% Na+K	12.8	12.1	15.2	10.5	10.8
Total Wt. of Solids (g/L)	109	97	104	108	123

almost identical so that it is not known whether iota Al_2O_3 and/or sodium aluminate was being formed by this method. Typically all these runs produced smooth surfaced calcine product, large amounts of fines (product-to-fines mole ratio less than 2.0), and attrition indices of greater than 50% with a maximum at ~0.20 M boron. Product size in all runs, except those using 0.02 M B, was very hard to control and required high feed NARs (>1000) plus dilution of the feed with water (adding 200 ml of water or more to 1000 ml of feed). The bed clinkered after 38.3 hours when the feed boron concentration was 0.40 M. Adding 0.2 M Mg $(NO_3)_2$ to feed containing 0.20 M boron did not decrease the difficulty of controlling product size and product attrition index.

Chloride retention in calcine solids was lowest (30 wt% of total) in the run calcining feed containing magnesium and decreased as boron concentration feed increased. Chloride retention in calcined solids was ~70 wt% of total when feed boron concentration was 0.02 M (Newby 1974b, Newby 1974a, Newby 1980b, Newby 1981b, Newby 1980a, Newby 1986).

Sugar (sucrose) added to nitrate wastes doesn't produce as violent of a reaction as other reducing reagents and seems to be effective in destroying nitrates during fluidized calcination of Na wastes. If nitrates in Na waste could be destroyed, Na+K would be free to form compounds stable over calcination temperature ranges; product size should be easy to control, and chloride retention in calcine solids should be high. Six 10-cm calciner runs were made using a feed containing 2 vol. 2.2 M $Al(NO_3)_3$ and 1 vol. Na waste containing 0.2 M boric acid and sugar Table 75. All runs were voluntarily terminated after 40 hours or more run time. In all runs: a) particle size could be controlled using feed NAR alone even though the attrition was high in some runs; b) agglomeration tendencies seemed to be low; c) feed contained no solids; and d) off-gas contained large amounts of unburned carbon (acid and caustic scrubs were black). Color of the calcined solids varied from black when using 1 mole sugar per 10 moles nitrate to tan when using 1 mole sugar per 20 moles nitrate. The attrition index and calcine nitrte content were 28% and 0.2%, respectively at the high sugar concentration (1 mole sugar/10 moles of nitrate) and were 80% and 9wt%, respectively, at the low sugar concentration (1 mole/20 moles of nitrate). The run containing the least feed sugar concentration had the smallest product-to-fines ratio and highest iota alumina and/or crystalline sodium aluminate concentration; thus iota alumina and/or crystalline sodium aluminate concentration may have a greater effect on fines production than attrition index (product brittleness may have influenced production of fines). In order to keep the acid scrub system from vigorously foaming: a) 13 *M* nitric acid was used in the scrub system and as much of the scrub solution as possible was replaced approximately very 2 hours; or b) 4 *M* acid in the acid scrub tank was kept at 70°C and evaporating acid was replaced frequently with 4 *M* acid (solution in the NWCF acid scrubber is kept at ~70°C). Chloride retention averaged 82 wt% of total chloride, and no trend of chloride volatility with feed sugar concentration or length of time feed was heated prior to calcination was observed (Newby 1983d, Newby 1986, Newby 1980b).

Table 75. Calcination of Na waste in 4” calciners using aluminum nitate and sugar.

	Run# SBW4-22	Run# SBW4-23	Run# SBW4-26	Run# SBW4-27	Run# SBW4-28	Run# SBW4-29
Sugar (moles/mole of nitrate)	1/10	1/20	1/15	1/15	1/15	1/15
H^+ (N^a)	<0.00	0.18	0.12	<0.50	<0.50	0.66
Al (*M*)	1.57	1.56	1.50	1.63	1.59	1.47
B (*M*)	0.21	0.20	0.22	0.21	0.18	0.19
Na (*M*)	0.61	0.55	0.58	0.62	0.57	0.61
K (*M*)	0.064	0.059	0.064	0.068	0.061	0.067
Mn (*M*)	0.0052	0.0050	0.0053	0.0057	0.0054	0.0054
Fe (*M*)	0.0052	0.0050	0.0053	0.0057	0.0054	0.0054
NO_3 (*M*)	3.58	4.85	4.53	2.94	5.95	4.38
Cl (*M*)	0.0092	0.0098	0.011	0.011	0.010	0.011
PO_4 (*M*)	0.0060	0.0055	0.0058	0.0063	0.0059	0.0059
SO_4 (*M*)	0.019	0.018	0.018	0.020	0.019	0.019
Al/Na+K Mole Ratio	2.34	2564	2.34	2.36	2.52	2.16
Mole% Na+K	12.3	11.5	12.2	12.2	11.7	13.1
Total Wt. of Solids (g/L)	109	106	105	115	110	105

Higher volume reduction factors were obtained by substituting powdered iron for a part of the aluminum nitrate needed to be added to Na waste prevent agglomeration. Also, powdered iron (not ferric nitrate) added to Na waste prevents agglomeration caused by the presence of alkali metals. Powdered iron added to Na waste causes a vigorous reaction and must be added very slowly and the waste kept at ~72°C to keep the reaction under control. In an attempt to reduce the vigor of this reaction, the iron was added to the feed of one run as iron pieces 1/8 to ¼ inch across their longer dimension; even though the feed was stirred at ~72°C for 1 ½ hours after all the pieces had been added, there were enough undissolved pieces left in the feed to continually plug feed nozzles when the feed was calcined. Also, the undissolved iron kept reacting for several months when the feed was stored at room temperature. This did not happen when feed was stored to which iron powder had been added. The iron, when added to feed, reduced the acidity of the feed and additional nitric acid had to be added to the feed to prevent precipitation from occurring when the acidity became too low.

Table 76. Calcination of Na waste in 4” calciners using $Al(NO_3)_3$ and iron powder (relatively successful runs.

	Run# SBW4-36	Run# SBW4-39	Run# SBW4-42
H^+ (N[a])	0.87	1.05	0.90
Al (*M*)	1.41	0.80	1.10
B (*M*)	0.0034	0.0036	0.0032
Na (*M*)	0.78	0.87	0.74
K (*M*)	0.090	0.090	0.073
Mn (*M*)	0.0072	0.0079	0.0068
Fe (*M*)	0.47[a]	0.52[a]	0.42[a]
NO_3 (*M*)	6.26	6.16	5.97
Cl (*M*)	0.017	0.020	0.019
PO_4 (*M*)	0.0081	0.0088	0.0076
SO_4 (*M*)	0.026	0.028	0.024
Al+Fl/Na+K Mole Ratio	2.2	1.4	1.9
Mole% Na+K	14.5	20.3	16.2
Total Wt. of Solids (g/L)	125	100	104

a. Added as iron powder.

The desired feed (Al+Fe)/(Na+K) mole ratio for runs SBW4-36 and 4-42 was 1.8 and the desired (Al+Fe)/(Na+K) mole ratio of the feed in run SBW4-39 where an attempt was made to increase the volume reduction factor further (by decreasing feed aluminum concentration) was 1.3. Although the latter run was voluntarily terminated after 40 hours, off-gas equipment plugging problems were more severe than in the other 2 runs. Retention of chloride in calciner solids for the run with less feed aluminum concentration was less (68% of total) than in the other 2 runs (86%). The attrition index of runs using $Al(NO_3)_3$ plus iron to calcine Na waste were high varying between 50 and 90%; average nitrate concentration in calcined solids was 15.2 wt% (most of the nitrate was not alkali metal nitrate); crystalline alumina of any type was not detected in calcine solids; and surfaces of particles produced were smooth, and particles were uniformly round. The size of particle formed from calcining Na waste using $Al(NO_3)_3$ and iron as additives was difficult to control; control required high feed NARs plus diluting the feed with water (Newby 1981b, Newby 1986).

Development work in a 4” calciner was done to calcine a mixture of aluminum nitrate, electrolytic first cycle extraction, and sodium-bearing wastes stored in WM-183 during 1976-1978. Short scoping 4” calciner runs showed that one method that had potential for calcining the waste was to concentrate the waste to 60% of its original volume and add enough powdered iron to the waste to give the feed a Fe/Na mole ratio between 0.5 and 1.0. This flowsheet was successfully tested using a Fe/Na mole ratio of 0.75 in a 4” calciner (voluntarily terminated after 120 hours) during Run 183-4-12. Run 183-4-12 feed composition and operating, bed fluidization, and solids’ information are given on the Table 77 (Newby 1983c).

Table 74. Calcination of Na waste in 4" calciners using iron powder.

	Run# 183-4-12
H^+ ($N^{\underline{a}}$)	2.3
Al (*M*)	1.1
B (*M*)	$4.8\text{x}10^{-3}$
Na (*M*)	1.1
K (*M*)	0.16
Ca (*M*)	0.12
Fe (*M*)	0.89
Cr (*M*)	$1.4\text{x}10^{-2}$
Cu (*M*)	$1.2\text{x}10^{-3}$
Mg (*M*)	$3.5\text{x}10^{-2}$
Mn (*M*)	$1.5\text{x}10^{-2}$
Ni (*M*)	$6.0\text{x}10^{-3}$
NO_3 (*M*)	7.3
F (*M*)	$2.7\text{x}10^{-2}$
Cl (*M*)	$1.2\text{x}10^{-2}$
PO_4 (*M*)	$1.2\text{x}10^{-3}$
SO_4 (*M*)	0.13
Mole % Na+K	17.5
Total wt of Solids (g/L)	254
Type of Heat	In-Bed Combustion at 500°C
Fluidizing Velocity (m/s)	$0.28^{+0.02}_{-0.04}$
Feed NAR	963^{+133}_{-147}
O_2 to Fuel Ratio	1488^{+262}_{-120}
Prod. Production Rate (g/h)	270
Bed Turnover (%)	99.8
MMPD (mm)	$0.59^{+0.21}_{-0.13}$
Prod. Size Control	MMPD was decreasing at COT 120 hours using NAR of 850
Prod./Fines Ratio	20
Prod. Bulk Density (g/cm^3)	$1.55^{+0.09}_{-0.19}$
wt% of Total Cl Retained in Calcined Solids	98.3
Appearance of Product Surface	Smooth, contained - no nodules

TESTS OF NA-WASTE/ANN BLENDS IN AN ENCLOSED 10-CM CALCINER PILOT PLANT TO SUPPORT NWCF CAMPAIGN H-4

Test Runs SBW4-45 through SBW4-52 were planned and performed from July 1993 through August 1995 (Marshall 1997). These test runs were made in support of the New Waste Calcining Facility (NWCF) campaign H-4. The feed simulant compositions are provided below. Subsequent testing was performed in the Enclosed 15-cm Calciner Pilot (Thomson 1997; Marshall 1998). Two blends of ANN with WM-185 sodium waste were previously tested during runs SBW4-43 and -44 (Muller 1992).

The objectives of tests SBW4-45 and SBW4-46 were to provide information on the calcinability of aluminum nitrate (ANN)/WM- 180 soduim waste feed blends with high sodium content (11.5 mol% Na+K), to provide calcine for retrieval studies, and to compare chloride volatility with different calcium to volatile species mole ratios (0.41 andl.67 for SBW4-45b and SBW4-46 respectively, desired values were 0.35 and 1.26 respectively).

The objectives of tests SBW4-47 and SBW4-48 were to determine the calcinability of moderately high sodium content (theoretical alkali metals content of 8.4 mol%) blend of ANN and WM-183/189/188 (this waste is based upon a 1.0 to 0.625 voluine rnixture of WM-183 to WM-189 waste evaporated in the High Level Liquid Waste Evaporator (HLLWE) and added to the WM-1 88 tank heel), and to compare the effect of different boric acid concentrations (0.05 molar and 0.10 molar for SBW4-47 and SBW4-48 respectively) on alpha-alumina content of the calcine. Test SBW4-47 used a ratio of 1.21:1 ANN:Waste and an aluminum to alkali metals mole ratio(AAR, moles Al/moles (Na+K)) of 3.60. Test SBW4-48 used a ratio of 1.16:1 ANN:Waste and an AAR of 3.48.

The objectives of tests SBW4-49 through SBW4-51 were to determine the calcinability of high sodium content (10 to 11.5 mole% Na+K) blends of ANN with simulated WM183/189/188 waste, to provide calcine for retrieval studies, and to provide calcine for fliture immobilillation studies. Tests SBW4-49 and -50 also tested the effect of different boron concentrations on alpha-alumina content of the calcine.

The simulated waste feeds used for tests SBW4-49 and -50 had a theoretical alkali metals content of 11.5 mole percent. Run SBW4-49 calcined a 0.629 to 1.0 volume blend of ANN to simulated WM-183/189/188 waste and had a boric acid concentration of 0.08 M and an AAR of 2.3. Run SBW4-50 calcined a 0.563 to 1.0 volume blend of ANN to srmulated WM-183/189/188 waste and had a boric acid concentration of 0.15 M and had an AAR of2.15. Calcium nitrate for both tests was added a in stocbiometric ratio of one mole per mole of volatile species.

Run SBW4-5 I calcined a blend of HLLWE evaporated WM- 183 and WM- 189 waste mixed with WM-188 heel refered to as WM-183E. The simulated WM-183E mixture was blended with ANN to give an AAR of 2.5:1. The boron concentration was 0.10 M to promote amorphous alumina formation rather than alpha alumina. The calcium to flouride ratio was 0.79. The theoretical alkali metals calcine composistion was 10.5 mole percent.

Table 78. ANN/Na waste feed simulant compositions and data for tests SBW4-45 through –52.

Component	SBW4-45b	SBW4-46	SBW4-47	SBW4-48a	SBW4-49	SBW4-50	SBW4-51	SBW4-52
Al (M)	1.935	1.46	1.816	1.39b	1.457	1.045	1.241	1.344
B (M)	0.144	0.104	0.051	0.100b	0.076	0.151	0.109	0.096
Ca (M)	0.011	0.028	0.085	0.082b	0.109	0.106	0.122	0.082
Cd (M)	--	--	0.0031	0.005b	0.0063	0.006	0.0054	0.0032
CI (M)	0.0128	0.0097	0.0175	0.003b	0.0152	0.0142	0.0092	0.0094
Cr (M)	--	--	0.0003	0.000b	0.0014	0.0012	0.0007	0.0009
F (M)	0.038	0.023	0.164	0.117b	0.168	0.153	0.105	0.075
Fe (M)	0.013b	0.013b	0.029	0.027b	0.038	0.036	0.035	0.011
H+ (N[a])	0.108	0.108	0.989	1.164b	1.479	1.237	1.692b	1.186b
K (M)	0.061	0.051	0.054	0.050b	0.06	0.057	0.051	0.053
Na(M)	1.13	0.565	0.306	0.350b	0.496	0.47	0.371	0.396
N03 (M)	6.883	5.565	6.8	6.038b	5.556	4.863	4.93	5.09
P04(M)	--	--	0.003b	0.003b	0.004b	0.003b	0b	0.001b
S04 (M)	0.0012	0.0004	0.0035	0.004b	0.181	0.137	0.031	0.013
Zr (M)	--	--	0.007	0.013b	0.018	0.017	0.022	0.012
A/(Na+K) (desired)	2.48	2.48	3.6	3.5	2.3	2.28	2.5	2.5
A/(Na+K) (actual)	1.62	2.37	5.05	--	2.62	1.99	2.94	3.00
Ca/(F/2+CI/2+SO4+ 3*PO4/2) (desired)	0.351	1.263	1.186	1.197	1.185	1.2	1.004	1.007
Ca/(F/2+CI/2+SO4+ 3*PO4/2) (actual)	0.414	1.674	0.858	--	0.392	0.47	1.382	1.451
Product Bulk Density (g/cc)	1.72	1.66	1.16	1.19	1.56	1.52	1.55	1.60
Product Nitrate (wt%)	13.5	14.8	11.8	--	18.2	19.6	15.8	16.9
Average NAR (sL/L)	1173	1055	1086	1092	1254	1216	1296	1233

a. Run SBW4-48 was involuntarily terminated at COT 8.2, and feed was not analyzed.

b. Not analyzed. Value given is desired value from feed makeup.

SBW4-52 calcined a high sodium/ANN blend of projected WM-1851187/189 waste. It was based on a proposed tank farm transfer scenario that assumed the waste stored in WM- 183 would be transfered to WM- 190 before being blended and HLLWE evaporated with WM-189, leaving a WM-183 heel in WM-190. A volume of 20,000 gallons of decontamination solution (assumed to be 6.0 M nitric acid) would then be sent to tank WM- 187 in order to dilute the flouride content of this tank. A transfer of 20,000 gallons from WM-187 to WM-183 would leave WM-187 at heel level. The waste in WM-185 would then be transferred to WM-187, and this new WM-185/187 solution would be blended with WM-189 and evaporated in the HLLWE. This evaporated mixture would then be added to the WM-190(183) heel. The WM-190(183)/185/187/189 blended and evaporated mixture was refered to as WM-185E. Simulated WM-185E mixture was blended with ANN to produce a feed having an AAR of 2.5:1. The boron concentration was 0.10 M, and the Ca/p ratio was 0.71. The theoretical alkali metals calcine composition was 11.1 mole percent.

The fluoride volatility for these tests was higher than the 1% or less that is usually achieved in the calciner pilot plants. Although fluoride volatility was above what is normally acceptable for operation at NWCF, the fluoride volatility requirements were based on Fluorinel blends which typically had much higher fluoride concentrations in the feed. Chloride volatility was also higher than the normally acceptable value of 50% for only two runs. This was due to a lack of excess calcium in several of the runs. However, high chloride volatility in several other runs with sufficient calcium content was also experienced. Calcium nitrate addition had been based on a Ca/F ratio of 0.7, as was typically used for Fl/Na blends; however, these blends had much lower fluoride concentrations relative to other volatile species, and thus did not provide enough calcium to stoichiomentrically combine with all the volatile species.

Particle size was successfully controlled by increasing the NAR during tests SBW4-45b, -46, 47, -49, -51, and -52. Tests SBW4-48 was terminated early due to loss of plant oxygen. Test SBW4-5 1 was voluntarily terminated early at COT 32.61 hours to avoid bed agglomeration due to poor fluidization caused by a partially plugged distributor plate. This calcine seemed to be somewhat sticky at calcination temperatures, and would stick together loosely when not fluidized. The bed agglomerated during testSBW4-50.

Calcine product and fines mixtures from SBW4-45b, -46, -49,-51, and -52 were tested for retrievability from simulated worst case bin set conditions of 300°C and 15.3 psig. The tests were all found to retrieve at acceptable rates with vibratory assistance.

Tests Of Na-Waste/ANN Blends in an Enclosed 15-cm (6") Calciner Pilot Plant

Enclosed 15-cm Calciner Pilot Plant Tests EC15-3 through EC15-6 were conducted during fiscal year 1996 (Thomson 1997) in order to verify the calcinability of feed blends planned for processing during the H-4 campaign at the NWCF. Tests EC15-7B (Marshall 1998), EC15-8 (Nenni and Marshall 1998) and EC15-9 (Yoder 1998) also tested feeds for NWCF campaign H-4. The feeds simulated blends of 2.2 molar aluminum nitrate with sodium waste (WM-185) or with evaporated sodium waste/decontamination waste (evaporated WM-183/189 in WM-188 or WM-evaporated 185/187 in WM-189).

Test EC15-3 used a blend with a 0.625 to 1 volume mixture of WM- 189 to WM-183 processed through the HLLWE, had an aluminum to alkali-metal mole ratio of 3.42, and produced a calcine containing 8.61 mole percent sodium plus potassium. Test EC15-4 used a blend with a 0.625 to 1 volume mixture of WM-189 to WM-183 processed through the HLLWE, had an aluminum to alkali-metal mole ratio of 2.9, and produced a calcine containing 9.5 mole percent sodium plus potassium. Tests EC15-5 and -5B used the same blend with a 0.97 to 1 volume mixture of WM- 189 to WM- 183 processed through the HLLWE, had an aluminum to alkali-metal mole ratio of 3.1, and produced a calcine containing 8.9 mole percent sodium plus potassium. Test EC15-6 used a blend with a 0.97 to 1 volume mixture of WM-189 to WM-183 processed through the HLLWE, had an aluminum to alkali-metal mole ratio of 3.28, and produced a calcine containing 8.76 mole percent sodium plus potassium. Tests EC15-7B and EC15-9 used blends of ANN and WM-189 (evaporated WM-185/187) with aluminum-to-alkali-metal mole ratios of 4.7 and 3.6, and produced a calcine containing 6.77 and 8.4 mole percent sodium plus potassium, respectively. Test EC15-8 used a blend of ANN and WM-185 with aluminum-to-alkali-metal mole ratios of 4.7 and 3.6, and produced a calcine containing 6.77 and 8.4 mole percent sodium plus potassium, respectively. The nozzles used for all the tests were a Spraying Systems Co. 60100 liquid/120 gas for the feed and 40100 liquid/140-6-52-70^o gas for the fuel.

Pressure increase across the INTEC plant off-gas HEPA filter resulted in the early termination of Test EC 15-4. Modifications were made to the pilot plant off-gas system and operations were resumed. Tests EC15-5 and -5B were terminated due to excessive agglomeration of the bed. Tests ECl5-3, -6, -7B, -8 and -9 were voluntarily terminated after successful calcination of their respective flowsheets.

The fluoride volatility for tests ECl5-3, -6, 7B, and –8 was higher than is usually seen in the calciner pilot plants, and resulted from inadequate amounts calcium to bind all the fluoride as calcium fluoride.

Although fluoride volatility was above what is normally acceptable for operation at NWCF, the fluoride volatility requirements were based on Zirconium or Fluorinel wastes, which typically had much higher fluoride concentrations in the feed. The ANN/Na waste blends also contain more than enough aluminum than is necessary to complex fluoride in the off-gas and scrub systems.

The chloride volatility was acceptable for tests ECl5-3, -6, 7B, and -8. Fines carry over to the acid scrub system resulted in a high concentration of chloride in the acid scrub system during Test ECl5-3. Modifications to the operation of the fines column in subsequent tests reduced the fines carry over and the chloride concentration in the scrub.

Particle size was successfully controlled by increasing the NAR during tests EC15-3, -6, -7B, -8, and -9. The feed blends for tests ECl5-5 and -5B agglomerated the bed. The feed for test EC15-5B was mostly leftover feed from EC15-4, and it is likely that EC15-4 would have agglomerated if it had not been terminated early.

Calcine product and fines mixtures from tests ECl5-3, -6, 7B, and -8 were tested for retrievability under simulated worst case CSSF 6 and 7 conditions and were found to retrieve at acceptable rates. The calcines from the other tests were not subjected to caking and retrieval tests.

Table 79. ANN/Na waste simulant feed compositions and operating data for 15-cm calciner tests.

Constituent	Test EC15-3 ANN:WM-189/183	Test ECI5-4 ANN:WM-189/183	Test EC15-5B ANN:WM-189/183	Test EC15-6 ANN:WM-189/183	Test EC15-7B ANN:new WM-189	Test EC15-8 ANN:WM-185	Test EC15-9[a] ANN:new WM-189
H+(N[a])	1.31	1.41	1.3	1.1	0.564	0.3	0.946
Al (M)	1.59	1.42	1.35	1.43	1.974	1.457	1.579
B (M)	0.068	0.072	0.075	0.063	0.077	0.072	0.053
Ca (M)	0.108	0.146	0.127	0.117	0.064	0.0624	0.107
Cd (M)	0.006	0.006	0.006	0.006	0.001	0.0003	0.002
Cl (M)	0.01	0.008	0.006	0.009	0.009	0.017	0.1
Cr (M)	--	--	--	--	0.003	0.0015	0.002
F (M)	0.089	0.215	0.22	0.157	0.121	0.0542	0.12
Fe (M)	0.03	--	0.032	0.016	0.002	0.008	0.012
K (M)	0.054	0.052	0.06	0.06	0.049	0.0555	0.051
Ni (M)	--	--	--	--	--	0.00004	--
Na (M)	0.41	0.433	0.375	0.376	0.367	0.4	0.386
NO3$^-$ (M)	5.51	5.6	5.34	5.17	4.996	5.01	6.034
P04^{-3} (M)	--	--	--	--	--	--	--
S04$^{=}$ (M)	0.028	0.026	0.034	0.039	0.003	0.0128	0.011
Zr (M)	0.015	0.017	0.017	0.018	0.015	0.00297	0.011
Al/Na+K	3.42	2.93	3.1	3.28	4.75	3.2	3.6
Ca/ (F/2+CI/2+SO4+3*PO4/2)	1.39		1.04	0.95	0.94	1.29	1.4
Product Bulk Density (g/cc)	1.65	1.59	1.79	1.73	1.69	1.63	1.61
Ave. Product Nitrate (wt%)	12.6	--	11.9	12.6	10.9	12.1	--
Ave. NAR (sL/L)	601	560	560	620	571	573	696

a. Composition from feed makeup rather than chemical analysis.

HIGH TEMPERATURE TESTS OF NA-WASTE/ANN BLENDS IN ENCLOSED 10-CM (4") AND 15-CM (6") CALCINER PILOT PLANTS

A series of tests were completed to verify calcination of ANN/Na blends using 600°C instead of the normal 500°C operating temperature for use at NWCF during campaign H4. The tests used simulated blends of ANN and INTEC Tank Farm tank WM-185 (Nenni and Marshall 1998), WM-180 (Nenni 1999c) or WM-189 (Nenni 1999a, 1999b and 2000) sodium wastes. The WM-185 tests were conducted in the 10-cm and 15-cm Calcine Pilot Plants between December 1997 and July 1998. Tests of WM-180 (SBW-HT-15a/b) and WM-189 blends (SBW-HT-13a, -13b, 14, 16) were conducted in 1999. Additional boron than that in the waste was not added for the high temperature tests, and this did not appear to adversely affect the solubility of the fines or the alpha-alumina content of the fines. Calcium nitrate was added to all the feeds to tie up chloride, fluoride, sulfate, and phosphate in the feed.

The tests were all successful demonstrations of the flowsheets tested except tests SBW-HT-13b and 14, which were terminated early due to bed agglomeration (clinkering). Tests SBWHT-13b, –14, and -16 tested blends of WM-189 which had higher fluoride, zirconium, calcium, and cadmium concentrations than the blends of WM-185 and WM-180 with equivalent Al/Na+K ratios. It is not known for certain which component in theWM-189 caused its greater tendency for agglomeration. Cadmium was associated with agglomeration during Fluorinel tests (see CALCINATION OF FLUORINEL WASTE IN AN ENCLOSED 4" CALCINER), calcium was associated with agglomeration during zirconium/sodium blends (see WCF CAMPAIGN H-7), and fluoride and calcium was associated with agglomeration during ANN/Na blend tests (see Use of Fluorides for Calcination of Na Waste in a 4" Calciner, test SBW4-35); however, much higher concentrations were present in those cases.

The flowsheets were assessed using seven established acceptance criteria: process throughput, particle agglomeration, fines generation, product and fines transportability and ret:rievability, calcine solubility, and scrub solution interactions. These criteria provide quantitative measures to ensure the required performance objectives are met. The tests indicated that high-temperature calcination at 600°C with a feed blend aluminum-to-alkali metal mole ratio (AAR) of 1.7:1 met the defined acceptance criteria, depending on the sodium waste feed. Feeds and selected operating data for the tests are provided in the Table below.

The high-temperature calcination flowsheets successfully demonstrated that SBW throughput could be significantly increased. In the worst case (SBW-HT-10), throughput increased by about 60%. The final test (SBW-HT-12), showed that an increase of greater than 90% could be achieved over the baseline flowsheet. Lowering the quantity of additives in the feed allows significant increases to the SBW throughput This also reduces the calcine storage requirements.

All of the tests except SBW-HT–13b and –14 proved that particle agglomeration was not problematic. During SBW-HT-7, -10, -13a, 15a/b and 16, only very minor changes in NAR were required to keep the MMPD of the bed particles in the acceptable range. During SBW-HT-8 and SBW-HT-12, the MMPD of the bed particles quickly increased outside of the acceptable range; however, significant increases in NAR did provide the means necessary to cause the bed to stabilize by the end of the tests. As stated, it is believed that if the NAR had been increased earlier in the tests, the bed would have stabilized more quickly.

For tests SBW-HT-7 through 12, chloride, fluoride, and undissolved particulate buildup in the scrub was addressed by comparing the concentrations of aluminum, calcium, sodium, and potassium in the composite scrub from the high-temperature tests to that of test EC15-8 (a 500 C test). This showed that only SBW-HT-10 produced a high concentration of those components in the scrub. The reason for this was the cyclone plugging problems that occurred during the entire duration of SBW-HT-10. It was originally believed that fines in the cyclone from previous tests m the 15-cm Calciner Pilot Plant caused the plugging to occur. It was later determined that the equilibrium nitrate content of calcine is highly temperature dependent between 400 and 700^{o}C, and that renitration of high temperature fines at the lower temperatures in the off-gas lines can cause plugging (Nenni, O'Brien, Schindler and Wood 2000). Test SBW-HT-15 simulated conditions that appeared to have plugged the NWCF off-gas line in April-May, 2000, and for this test, the bed temperature was reduced from 600 to 500^{o}C over a 1 hour period midway through in the test. None of the problems experienced by the NWCF were apparent during the transition, probably because the temperature profile in the off-gas line and fines column, and the sodium content of deposited fines in the off-gas lines could not be matched to the conditions at NWCF.

All of the testing performed on the calcine to determine transportability and retrieval acceptability indicated that the high-temperature calcination flowsheets will produce calcine that can be transported to the bin sets and be retrieved in the future.

Table 80. High temperature test ANN/Na waste simulant feed compositions and operating data for 10-cm and 15-cm calciner tests.

Comp.	SBW-HT-7	SBW-HT-8	SBW-HT-10	SBW-HT-11	SBW-HT-12	SBW-HT-13a	SBW-HT-13b	SBW-HT-14	SBW-HT-15a/b	SBW-HT-16
H+ (N[a])	0.883	0.597	0.773	0.965	1.039	1	1.95	1.77	0.135	1.46
Al (M)	1.188	1.442	1.451	1.358	1.321	1.42	1.16	1.26	1.57	1.44
B (M)	--	0.0353	--	--	--	0.064	0.019	0.0173	0.0681	0.0143
Cd (M)	--	--	--	--	--	0.00217	0.0037	0.0033	0.000186	0.00273
Ca (M)	0.0991	0.0662	0.0913	0.0972	0.108	0.112	0.19	0.17	0.0354	0.103
Cl (M)	0.0241	0.0201	0.0203	0.0228	0.0268	0.011	0.018	0.0166	0.0072	0.0137
Cr (M)	--	--	--	--	--	0.002	0.0033	0.00298	0.000883	0.00246
F (M)	0.0927	0.0637	0.0737	0.079	0.0511	0.1	0.17	0.153	0.00976	0.126
Fe (M)	0.0125	0.0094	0.0136	0.0148	0.015	0.012	0.019	0.0175	0.00418	0.0144
Mn (M)	--	0.00753	0.00999	0.0113	0.0102	0	0	0	0.00195	0
Ni (M)	--	--	--	--	--	0	0	0	0.000372	0
NO3 (M)	5.91	5.94	5.96	ND	ND	6.15	6.63	6.53	5.28	6.42
PO4 (M)	--	--	--	--	--	0.00013	0.00022	0.0002	0.00179	0.000165
K (M)	0.0931	0.0645	0.0954	0.103	0.103	0.052	0.087	0.0785	0.0425	0.0648
Na (M)	0.713	0.47	0.679	0.687	0.687	0.41	0.69	0.621	0.465	0.512
SO4 (M)	0.0223	0.0159	0.0221	0.0225	0.0222	0.003	0.0051	0.00459	0.00744	0.00379
Zr (M)	--	--	--	--	--	0.012	0.027	0.0246	0	0.0203
Al/Na+K	1.47	2.70	1.87	1.72	1.67	3.1	1.5	1.8	3.1	2.5
Ca/ (F/2+Cl/2 +SO_4 +3*PO_4/2)	1.23	1.15	1.32	1.32	1.77	1.9	1.9	1.9	1.9	1.4
Pilot Plant	10-cm	10-cm	15-cm	15-cm	15-cm	15-cm	15-cm	15-cm	15-cm	15-cm
Bed Temperature (°C)	600°C	550°C	600°C	600°C	600°C	600°C	600°C	600°C	600°C/500°C	600°C
Product Bulk Density (g/cc)	1.47	1.06	1.63	1.59	1.64	1.63	1.39	1.53	1.03/1.20	1.67

Ave. Product Nitrate (wt%)	6.9	10.3	7.7	11.9	8.9	11.3	(clinkered)	(clinkered)	14.7/17.1	--
NAR (sL/L)	700	1100	750	700	840	521	561	714	607/762	460

Notes: Compositions for SBW-HT-13 through -16 are the desired feed makeup rather than from actual analyses.

CALCINATION OF ROVER WASTE IN A 4" CALCINER

Rover waste was calcined successfully as a blend of 1 vol. Zr waste – 1 vol. Rover waste and 2 vol. Zr waste – 1 vol. Rover waste with both blends having a Ca/F mole ratio of 0.55 (Table 81). Rover waste was also calcined successfully as a blend of 2.1 vol. Rover waste – 1 vol. Na waste and 7.2 vol. Rover waste – 1 vol. Na waste with both blends having a Ca/F mole ratio of 0.70.

A run (RW-4-3) calcining Rover waste using $Ca(NO_3)_2$ as the only additive (using a Ca/F mole ratio of 0.55) was terminated after 9.5 hours because of agglomerate formation in the bed due to poor feed atomization resulting from trying to build bed using very low feed atomizing and fluidizing air flows. Feed composition and operating, bed fluidization, and solids information are shown in Table 81. It was suggested that the flowsheets for the first cycle extraction of uranium from Rover dissolver solution be changed to include chromium nitrate, rather than aluminum nitrate, as a scrubbing reagent to decrease stability problems. The resulting Rover waste when blended with Zr waste as 1 Vol. Zr waste –1 Vol. Rover waste and 2 Vol. Zr waste – 1 Vol. Rover waste (both blends having a Ca/F mole ratio of 0.55) could not be calcined due to clinker formation in-bed within 36.4 hours or less. Information on the runs is shown in Table 82 (Grady 1994, Birrer 1977; Lowe 1979, Newby 1983b).

Table 81. Calcination of Rover waste in a 4" calciner (successful runs).

Blend	Run# RW-4-5 1 Volume Zr – 1 Volume Rover	Run# RW-4-5 2 Volume Zr – 1 Volume Rover	Run# RW-4-5R 1 Volume Zr – 1 Volume Rover	Run# 4-1 2.1 Volume Rover – 1 Volume Na	RW #4-2 7.2 Volume Rover – 1 Volume Na
H^+ ($\underline{N}^a$)	2.12	1.91	2.12	1.17	0.88
Al (*M*)	0.44	0.52	0.44	0.58	0.52
Zr (*M*)	0.06	0.08	0.06	0.037	0.039
B (*M*)	0.13	0.15	0.13	0.056	0.053
Na (*M*)	NP	NP	NP	0.16	0.15
K (*M*)	NP	NP	NP	0.024	0.026
Ca (*M*)	0.62	0.63	0.62	0.66	0.59
Fe (*M*)	0.0038	0.0051	0.0038	0.014	0.007
Cr (*M*)	0.008	0.010	0.008	NP	NP
Nb (*M*)	0.033	0.0022	0.033	0.020	0.025
NH_4 (*M*)	0.031	0.021	0.031	0.088	0.11
Sn (*M*)	0.0010	0.0018	0.0010	0.0007	0.0009
NO_3 (*M*)	2.49	2.42	2.49	3.64	3.20
F (*M*)	1.13	1.15	1.13	0.95	0.89
Cl (*M*)	NP	NP	NP	0.0098	0.011
UDS (g/L)	74	46.8	74	NA	NA
Ca/F Mole Ratio	0.55	0.55	0.55	0.69	0.66
Mole % Na+K	0.0	0.0	0.0	4.80	5.22
Total wt. of Solids	90	97	90	114	103
Type of Heat	In-Bed Combustion at 500°C				
Fluidizing Velocity (m/s)	0.26 ± 0.03	0.26 ± 0.03	0.26 ± 0.03	$0.28^{+0.02}_{-0.07}$	$0.25^{+0.003}_{-0.04}$
Feed NAR	508-748 (only range given)			1000$\pm$0	780^{+120}_{-80}
O_2 to Fuel Ratio	1698-2327 (only range given)			2286$\pm$230	2222^{+185}_{-96}
Prod. Production Rate (g/h)	144	144	123	151	134
Bed Turnover (%)	89.5	99.1 (Accumulative)	95.8	79.0	76.4
MMPD (mm)	$0.42^{+0.05}_{-0.03}$	$0.39^{+0.01}_{-0.00}$	$0.33^{+0.05}_{-0.02}$	$0.57^{+0.11}_{-0.05}$	$0.48^{+0.20}_{-0.10}$
Prod. Size Control	Could be Controlled Using NAR Only			Controlled at NAR of ~1000	
Prod./Fines Ratio	1.8	1.6	1.6	2.3	2.1
% of Final Bed >14 Mesh	Not Given	Not Given	10.1	2.4	2.9
Prod. Bulk Density (g/cm^3)	Not Given	Not Given	1.33	$1.36^{+0.18}_{-0.31}$	$1.33^{+0.15}_{-0.29}$
Attr. Index (%)	26 (Final Bed)	26 (Final Bed)	23 (Final Bed)	58 (Final Bed)	35 (Final Bed)
NO_3 Content of Prod. (wt%)	$0.19^{+0.04}_{-0.04}$	Not Given	0.16$\pm$0.03	$8.9^{+0.5}_{-0.6}$	$8.8^{+0.7}_{-1.1}$
Wt% of Total F Escaping Calciner other than as CaF_2	Value Not Given			0.82	0.64
Wt% of Total Cl Retained	Value Not Given			57	40
Appearance of Prod. Surface	Information Not Given			Smooth, Contained No Nodules	

Note:
NP = Not Present
Values given represent average and range of data.

Table 82. Calcination of Rover waste in a 4" calciner pilot plant (unsuccessful runs).

	Run# RW-4-3	Run# RW10-6A	Run# RW10-6B	Run# RW10-6C	Run# RW10-6D
Blend	Unblended Rover	1 Volume Zr – 1 Volume Rover	1 Volume Zr – 1 Volume Rover	2 Volume Zr – 1 Volume Rover	2 Volume Zr – 1 Volume Rover
H^+ (N^a)	3.17	1.56	1.56	1.44	1.44
Al (*M*)	0.40	0.36	0.36	0.53	0.53
Zr (*M*)	Not Present	0.26	0.26	0.38	0.38
B (*M*)	0.05	0.12	0.12	0.14	0.14
Ca (*M*)	0.66	0.99	0.99	1.22	1.22
Cr (*M*)	Not Present	0.065	0.065	0.053	0.053
Nb (*M*)	0.044	0.013	0.013	0.0097	0.0097
NH_4 (*M*)	0.064	0.195	0.195	0.231	0.231
NO_3 (*M*)	4.61	3.69	3.69	4.37	4.37
F (*M*)	1.20	1.58	1.58	1.97	1.97
Ca/F Mole Ratio	0.55	0.63	0.63	0.62	0.62
Dissolved Solids (g/L)	81	145	145	187	187
Type of Heat	In-bed Combustion at 500°C				
Fluidizing Velocity (m/s)	0.26 (only value given)	0.27 (only value given)	0.27-0.30	0.30	0.30
Waste NAR	460 (only value given)	595-705	510-620	510	510
O_2 to Fuel Ratio	1557	1956-2463	1917-2418	2091-2156	2060-2421
Prod. Production Rate (g/h)	22	170	134	151	229
Bed Turnover (%)	6.0	78	53	17	77
MMPD (mm)	0.48 (Final Bed)	0.34-0.38	0.37-0.45	No Information	0.40-0.41
Prod. Size Control	Controlled with NAR	Information Not Given			
Prod./Fines Ratio	0.78	2.1	2.2	2.5	2.9
% of Final Bed >14 Mesh	6.3	Information Not Given			
Prod. Bulk Density (g/cm^3)	1.13 (Final Bed)	1.30-1.33	1.30-1.32	Not Given	1.28-1.30
Attr. Index (%)	3.8 (Final Bed)	2-14	3	Not Given	5-16

CALCINATION OF FLUORINEL WASTE IN AN ENCLOSED 4" CALCINER

Attempts were made to calcine Fluorinel waste without additives (in the Enclosed 10-cm unless otherwise noted); using sulfuric acid, aluminum nitrate, phosphoric acid, chromic acid, oxalic acid, and acetic acid as additives; and as a blend with Na waste. Calcining Fluorinel waste as a blend with Na waste showed the most promise and was later used successfully in the NWCF. Using sulfuric acid, acetic acid, and phosphoric acid showed less promise. Other alternatives showed little or no promise.

Three runs using blends of Na and Fluorinel lasted greater than 49 hours. Run EM-Fluor-12B used a feed of 3 vol. Fluorinel waste – 1 vol. Na waste, a 1:1 mole ratio of H_2SO_4 to cadmium, and a Ca/F mole ratio of 0.7. The run was terminated after 49.2 hours due to a cake bridge across the calciner at the feed nozzle level probably caused by the calcine having too high of a Na+K mole%. Weitz and Newby (1980) said the cake was caused by off-gas plugging problems, large particle size, and buildup of cake on wall of calciner. Other pertinent information was: O_2/fuel ratio = 1725, fluidizing velocity = 1.1 ft/s, feed NAR= 995, zirconia starting bed (MMPD = 0.597 mm), product bulk-density =1.48 g/cm^3, AI = 58%, angular and regular product, product-to-fines ratio of 3.27, final bed (FB) +14mesh size particles <2 wt% (probably doesn't include wall cake), and product MMPD = 0.5759 mm. Two runs using feeds of 3.5 vol. Fluorinel waste – 1 vol. Na waste and a Ca/F mole ratio of 0.7 were voluntarily terminated after 100 hours or greater. No significant bed agglomeration was present in either run. Sulfuric acid was added to the feed for Run EM-Fluor-15 which resulted in a higher product bulk density and attrition index. Product size seemed to be easier to control in Run EM-Fluor-15 than in –14. Other pertinent information for Run EM-Fluor-14: O_2/fuel ratio = 1946, fluidizing velocity = 1.1 ft/s, NAR 951, zirconia starting bed (MMPD = 0.4173 mm), product bulk density = 1.59 g/cm^3, AI = 62%, smooth rounded product, product-to-fines ratio of 5.3, final bed + 14 mesh size particles (including wall cakes) = 4 wt%, and MMPD of product = 0.6966 mm. Other pertinent information for Run EM-Fluor-15: O_2/fuel ratio = 2241, fluidizing velocity = 1.1 ft/s, NAR= 963, zirconia starting bed (MMPD = 0.4173 mm), product bulk density = 1.67 g/cm^3, AI = 72%, smooth rounded product, product-to-fines ratio 5.6, final bed + 14 mesh size particles including wall agglomerates = 2 wt%, and MMPD of products = 0.5098 mm.

The only run using phosphoric acid (2:1 mole ratio of phosphoric acid to Cd) as an additive (Run EM-Fluor-9a) was forced to terminate after 22.8 hours due to off-gas plugging. The final bed contained relatively small amounts of agglomerates so phosphoric acid was considered a successful additive. The feed had a tendency to coagulate causing feed nozzle plugging problems and excessive fines production caused off-gas equipment plugging. Other pertinent information for Run EM-Fluor-9a: O_2/fuel ratio = 1794, fluidizing velocity = 0.9 ft/s, NAR= 569, calcined Zr-Na waste blend starting bed (MMPD = 0.5383 mm), product bulk-density = 1.35 g/cm^3, AI = 18%, noduled rounded product, product-to-fines ratio = 1.62, final bed + 14 mesh size particles including all agglomerates <5 wt%, and MMPD of product = 0.4630 mm.

Table 83. Calcination of Fluorinel wastes in an enclosed 4" calciner (longer successful calcinations).

	Run# EM-Fluor-1	Run# EM-Fluor-7A	Run# Fluor-9A	Run# Fluor-9C	Run# EM-Fluor-11	Run# EM-Fluor-12B	Run# EM-Fluor-14	Run# EM-Fluor-15
H^+ (N^{a})	1.99	1.17	1.44	1.84	1.40	1.50	1.76	1.29
Al (*M*)	0.42	0.38	0.32	0.19	0.74	0.42	0.33	0.39
Zr (*M*)	0.51	0.37	0.37	0.19	0.27	0.27	0.24	0.31
B (*M*)	--	--	0.10	0.15	0.115	0.122	0.13	0.13
Na (*M*)	--	--	--	--	--	0.47	0.42	0.42
K (*M*)	--	--	--	--	--	0.05	0.044	0.044
Ca (*M*)	1.40	1.19	1.24	1.16	1.67	0.85	1.21	1.21
Mn (*M*)	--	--	--	--	--	0.0042	0.0038	0.0038
Fe (*M*)	--	--	--	--	--	0.0042	0.0038	0.0038
Cd (*M*)	0.21	0.195	0.21	0.16	0.101	0.11	0.15	0.218
NO_3 (*M*)	2.74	4.86	4.34	4.60	5.57	4.92	5.36	5.14
F (*M*)	2.67	2.04	1.67	1.88	1.39	1.32	1.47	1.64
Cl (*M*)	--	--	--	--	--	0.009	0.0080	0.0080
PO_4 (*M*)	--	--	0.42	--	--	0.0048	0.0042	0.0042
SO_4 (*M*)	0.39	0.25	0.022	0.049	0.148	0.21	0.107	0.045
Additive	None	H_2SO_4 (SO_4 usually ~0.05)	H_3PO_4 (0.42 *M*)	Acetic Acid (0.32 *M*)	H_2SO_4 + $Al(NO_3)_2$ (SO_4 usually ~0.05 *M*)	Na waste + H_2SO_4	Na waste + H_2SO_4	Na waste
Run Time	80 hrs	52 hrs	22.8 hrs	50.2	76.4	49.2	104.8 hrs	100 hrs
Mole% Na+K	--	--	--	--	--	9.4	7.6	7.0
Total wt. of Solids (g/L)	244[a]	205[b]	204[c]	160[d]	259[e]	200[e]	229[d]	241[d]

a. Lots of fines.
b. Voluntary shutdown.
c. Offgas problems, little or no agglomerates.
d. Voluntary shutdown, agglomerates.
e. Shutdown caused by agglomerates.

Some Fluorinel waste having sufficient sulfate to react with all the cadmium present ran for 50 hours or longer (Runs EM-Fluor-1, -7A, and –11). Run EM-Fluor-1 used an early composition estimate for the Fluorinel waste. The run was 80 hours long with the greatest disadvantage being generation of excessive fines. Shutdown was caused by fines plugging the off-gas line. There was no operating data or solids characteristics given for the run except <5 wt% of final bed was +14 mesh size particles. Run EM-Fluor-7A contained 1 mole of sulfuric acid for every mole of Cd in its feed. Run EM-Fluor-7A operated for 52 hours before switching to another feed. Pertinent information for Run 7A was: O_2/fuel ratio = 1682, fluidizing velocity 0.9 ft/s, feed NAR = 637, zirconia starting bed (0.4318 mm), product bulk density = 1.28 g/cm^3, AI 8% smooth rounded product, product-to-fines ratio of 5.21, ~11 wt% of final bed was +14 mesh particles including wall agglomerates, and MMPD = 0.4707 mm. The feed of Run EM-Fluor-11 differed from that of the immediately proceeding run in that, in addition to sulfuric acid, it contained 2 mole of Al for each mole of Zr present. Agglomeration forced this run to shutdown after 76.4 hours. Agglomeration was probably caused by too low of a NAR and fluidizing velocity. Pertinent information for Run EM-Fluor-11: O_2/feed ratio = 1774, fluidizing velocity = 0.92 ft/s, feed NAR = 563, zirconia startup bed (MMPD = 0.3300 mm), product bulk density = 1.01 g/cm^3, AI = 48%, smooth rounded product, product-to-fines ratio 2.54, no information for wt% of final bed +14 mesh size particles, and MMPD of product = 0.5326 mm.

Run EM-Fluor-9C was voluntarily shutdown after 50.2 hours and contained a 2:1 mole ratio of acetic acid to Cd in its feed. There were not significant operation problems and the inside of the calciner was relatively clean after the run. Pertinent information for Run EM-Fluor-9C: O_2/fuel ratio = 1688, fluidizing velocity = 0.94 ff/s, feed NAR 562, calcined fluorinel starting bed (MMPD = 0.3894 mm), product bulk-density = 1.43 g/cm^3, AI = 16%, product-to-fine ratio 4.36, <3 wt% of final bed was +14 mesh size particles, and MMPD of product = 0.3848 mm.

Attempts (see Table 84**)** were made to calcine Fluorinel waste feed without additives other than calcium nitrate in 4” (10-cm) calciners. They used an early composition estimate for the Fluorinel waste. All the runs (except for Run EM-Fluor-2C) were terminated due to bed agglomeration or to a cake bridging across the calciner at the feed nozzle level. Zirconium (Zr) waste was calcined successfully for 24 hours during Run EM-Fluor-2C; 0.17 *M* Cd was then added to the Zr waste feed for Run EM-Fluor-2D. After 10 hours, Run EM-Fluor-2D was shutdown due to excessive bed agglomeration. A Fluorinel flowsheet was developed based on a minimum amount of feed Cd concentration. The Cd was replaced by a high boron concentration in Runs EM-Fluor-3A, -3B, -3C, and 3-D. In Run EM-Fluor the boron was reduced to 0.20 *M* and the Al increased to 0.83 *M*. Run Flw4-1 was performed in a unenclosed 10-cm calciner. The purpose of the run was to see if 0.32 *M* B in a Fluorinel waste (calcined with $Ca(NO_3)_3$ as the only additive) would be likely to cause agglomeration (Newby 1980b, Weitz and Newby 1980).

Table 84. Unsuccessful calcination of Fluorinel wastes without additives.

	Run# EM-Fluor-2A&B	Run# EM-Fluor-2C	Run# EM-Fluor-2D	Run# EM-Fluor-3A&B	Run# EM-Fluor-3C&D	Run# EM-Fluor-3E	Run# EM-Fluor-8C	Run# Flw4-1
Feed Type	Fluorinel Waste	Zr Waste	Zr Waste + 0.17 M Cd	Fluorinel Waste with min. Cd	Fluorinel Waste with min. Cd	Fluorinel Waste with min. Cd	Fluorinel Waste	Fluorinel Waste without Cd
H^+ (M)	1.25	1.58	1.58	1.76	1.76	1.76	1.05	2.3
Al (M)	0.43	0.73	0.73	0.64	0.64	0.83	0.34	0.38
Zr (M)	0.43	0.50	0.50	0.52	0.52	0.52	0.49	0.34
B (M)	--	0.22	0.22	0.67	0.67	0.20	0.15	0.32
Ca (M)	1.4	1.7	1.7	2.4	2.4	2.4	1.20	1.78
Cd (M)	0.17	--	0.17	0.062	--	--	0.24	--
NO_3 (M)	2.58	2.14	2.14	2.49	2.49	2.49	4.77	6.40
F (M)	2.29	3.22	3.22	4.35	4.35	4.35	2.16	3.77
SO_4 (M)	0.052	--	--	0.068	0.068	0.068	0.036	--
Run Time (h)	A – 8 hrs B – 8 hrs	24	10	A – 13 hrs B – 2 hrs	C – 3 hrs D – 3.5 hrs	24	21.4	29.1

CALCINATION OF FLUORINEL/SODIUM WASTE WITH SUGAR AS A FEED ADDITIVE IN AN ENCLOSED 4” (10CM) CALCINER

Tests FlNaS-1, -2, -3, -4, -5, and –6 were carried out in the Enclosed 10-cm diameter Calciner Pilot-Plant to test sugar as a feed additive with simulated Fluorinel-Na waste blends producing calcine with 5.3 mole % Na+K (runs FlNaS-1, -2) and 7.5 mole % Na+K (runs FlNaS-3, -4, -5, and –6) (Newby, Thompson and O’Brien 1992). These studies indicated that the presence of sugar (sucrose or dextrose) in simulated Fluorinel – Na waste blends containing alkali metals (sodium plus potassium) effectively destroys nitrates in the blend during feed makeup and calcination. The studies also showed that because of the destruction of nitrates, the presence of sugar: a) allows alkali metals present to form compounds stable at calcination temperatures, b) allows the size of the product to be readily controlled using the feed nozzle air-to-feed ration (NAR), and c) results in high chloride retention in the calcined solids.

Goals of the testing were to determine: a) which sugar (sucrose or dextrose) was the most effective for calcining Fluorinel–Na waste blends, and b) the effect of the feed aluminum-to-alkali metal mole ratio on the calcination of these blends. The sucrose and dextrose added to the blends were equally effective at destroying nitrates. An average of 45% of the nitrates and nitric acid were destroyed by reacting the liquid feed with 35.4 gm sugar per mole of feed nitrate at 80 to 90^{o}C for 2 hours after the 1 to 2 hour induction period for the reaction to begin. Sucrose was determined to be the most promising sugar additive since it was converted more completely to inorganic carbon than was dextrose. When sucrose was used as an additive, the wt% of total carbon fed to the calciner that was found in the calciner streams as organic carbon (unburned and/or not converted to inorganic carbon) averaged 3 wt%; whereas, when dextrose was used as an additive, the average 34 wt% organic carbon. If dextrose were used in the NWCF, the larger amount of organic carbon would probably plug filters and silica gel beds.

The runs also investigated feed aluminum-to-alkali metal mole ratios of 0.6, 1.0, and 1.25. Test FlNaS-5 feed had an Al/Na+K mole ratio of 0.6, test FlNaS-6 feed had an Al/Na+K mole ratio of 1.25, and test FlNaS-3 and –4 feed had an Al/Na+K mole ratio of 1.0. All four feeds produced calcine with 7.5 mole % Na+K. Increasing the feed Al/Na+K mole ratio from 0.6 to 1.0: a) decreased the calcine product-to-fines ratio from 3.0 to 1.0, b) decreased the product production rate from 250 to 175 g/h, c) decreased the attrition index from 80 to 15 %, and d) reduced the formation of fuel nozzle agglomerates. Further increasing the feed Al/Na+K mole ratio from 1.0 to 1.25 had little or no effect on the behavior of chloride, fluoride, carbon, or cadmium during calcination. Feed compositions are shown in the following table.

Table 85. Compositions of Flourinel sodium blends after calcium nitrate and sugar treatment and operating data.

Constituent	Run FlNaS-1 Feed	Run FlNaS-2 Feed	Run FlNaS-3 Feed	Run FlNaS-4 Feed	Run FlNaS-5 Feed	Run FlNaS-6 Feed
H+(Na)	0.84	0.98	1.18	1.25	0.96	0.7
Al (M)	0.38	0.38	0.62	0.54	0.32	0.75
Zr (M)	0.24	0.26	0.24	0.16	0.15	0.14
B (M)	0.13	0.11	0.18	0.11	0.13	0.14
Na (M)	0.28	0.28	0.48	0.44	0.52	0.7
K (M)	0.041	0.042	0.07	0.068	0.061	0.11
Cd (M)	0.078	0.078	0.081	0.079	0.099	0.1
Ca (M)	1.3	1.28	1.24	1.1	1.15	1.18
F (M)	1.79	1.93	1.59	1.46	1.56	1.72
N03 (M)	2.67	2.98	3.72	3.56	3.52	3.27
SO4 (M)	0.021	0.03	0.048	0.028	0.054	0.065
Cl (mg/L)	385	425	451	497	508	475
UDS (g/L)	84	87	24	12	40	30
Feed Sp. Gr. (g/cc)	1.3156	1.3187	1.3495	1.3145	1.344	1.35
Al/Na+K (desired)	1.0	1.0	1.0	1.0	0.6	1.25
Mole% Na+K (desired)	5.3	5.3	7.5	7.5	7.5	7.5
Product Bulk Density (g/cc)	1.45	1.38	1.30	1.27	1.46	1.39
Product Nitrate (wt%)	0.27	0.08	0.049	0.084	0.012	0.051
Average NAR (sL/L)	1129	1067	1196	877	1000	1049

Retrieval tests were performed on homogenous mixtures of product and fines collected following each run. Each retrieval test consisted subjecting a mixture of product and fines to 650°C and 8.7 psig for 3 days in a sealed can, then attempting (several times) to retrieve it from the can using a vacuum nozzle with vibrator assistance. During retrieval tests, a loading rate of 1.5 kg of calcine per kg of vacuum air is ocnsidered satisfactory. Both increasing the feed alkali metal concentration and using sugar as a feed additive seemed to have an adverse effect on calcine retrieval rates. The average retrieval rates for runs FlNaS-1, -2, -3, -5, and –6 were 1.7, 3.3, 1.1, 1.4, and 2.6 kg calcine per kg air, respectively. Cadmium metal crystals plated out on the interior surface of the can lid while calcine from FlNaS-4 was being subjected to heat. This prevented the plunger used to apply pressure to the sample from working. Heating run FlNaS-6 calcine rusted parts of the stainless steel retrieval equipment that was in contact with gases evolved during heating, and flaked the inside of the retrieval can.

CALCINATION OF NA WASTE USING MISCELLANEOUS ADDITIVES

In numerous early short scoping runs for calcining Na waste: two 5 hour runs were successful by adding 113 g of sugar/g mole Na in Na waste calcined at 500°C; a blend of Na and Zr waste having a F/Na mole ratio of 1.25 wase successfully calcined but it generated many fines; a blend of Na+Zr waste having a F/Na mole ratio of 2.59 was successfully calcined without generation of excessive fines; a blend of Na and Zr wastes having a F/Na mole ratio of 1.8 was successfully calcined but generated many fines; a 25 hour run were successfully made calcining Na-Zr waste blend containing a F/Na mole ratio of 1.8 (no $Ca(NO_3)_2$ added); a 29 hour run successful calcined a blend of Na waste and $Al(NO_3)_3$ having a Na/Al mole ratio of 1. In a 5 day run using a blend of Na and Zr waste having a F/Na ratio of 1.8 and 1.73 *M* F; there was a corrosion induced leak in the scrub system after 32.75 hours, a shutdown after another 26.4 hours due to bed agglomeration and too low of a feed NAR; and a third shutdown after another 12.6 hours due to an off-gas plug. Nine-hour tests with blends of Na waste and H_2SO_4 showed that excessive caking occurred only at Na/SO_4 mole ratios above 0.83. In a cryrolite flowsheet (no $Ca(NO_3)_3$) adding $Al(NO_3)_3$ to the acid scrubber reduced corrosion in the acid scrub system by a factor of ~8 over 35 hours of run time, and data making a cryolite feed 0.14 *M* in B increased AI from 3 to 55%. Reaction occurs between (may be from a 12" calciner run) CaF_2-ZrO_2 startup bed and Na-Zr waste blends or Na waste – sulfate blends causing agglomeration. Nozzle caking and bed agglomeration led to termination of a run calcining a blend of 1 vol. Zr waste – 1.17 vol. Na waste (1.8 F/Na mole ratio and Ca/F mole ratio of 0.55) after 32.4 hours. In 3 runs calcining Na waste + H_2SO_4 having SO_4/Na mole ratios from 1.15 to 2.0, runs terminated within 5 hours of operation due to bed agglomeration. Addition of $Mg(NO_3)$ to Zr-Na waste blends (no $Ca(NO_3)_2$) did not increase Cl retention in solids.

Use of Sulfates during 4" Calciner Runs

The addition of sulfuric acid or aluminum sulfate to Na waste has prevented fluidized-bed agglomeration due to formation of Na_2SO_4 or $Na_3Al(SO_4)_3$ which are thermally stable under calcination temperatures used in the NWCF. A number of short-duration (2.5 to 9 hours) fluidized-bed, in-bed combustion 10-cm calciner runs at 500°C with sulfuric acid added to simulated ICPP Na waste suggested that: a) agglomeration always occurred when the Na/SO_4 mole ratio was greater than 1.0; b) a Na/SO_4 mole ratio less than 0.77 would produce excessive fines; c) using a zirconium starting bed would lead to agglomeration but using an alumina starting bed would not lead to agglomeration; and d) soft calcine would be produced. Ten-cm Calciner Run SBW4-15 (Table 86) added sulfate to Na waste as 0.78 *M* aluminum sulfate supposedly to give the waste a Na/SO_4 mole ratio of 0.80 in hopes that increasing the aluminum concentration of the waste would harden the calcine. Sufficient boric acid was added to make the feed 0.20 *M* in boron (to further harden the calcine and prevent crystalline aluminum formation). The starting bed used was from a blend of Na waste and $Al(NO_3)_3$.

Table 86. 4” calciner run using Na waste with aluminum sulfate.

	Run SBW4-15b
H^+ (N[a])	1.40
Al (*M*)	0.67
B (*M*)	0.21
Na (*M)*	0.85
K (*M)*	0.094
Mn (*M)*	0.0077
Hg (*M)*	0.0060
Fe (*M)*	0.0077
NO_3 (*M)*	2.91
Cl (*M)*	0.031
PO_4 (*M)*	0.0086
SO_4 (*M)*	1.23
Na+K/SO_4 Mole Ratio	0.77
Mole% Na+K	21
Total wt. of Solids (g/L)	156

Run SBW4-15 was voluntarily terminated after 40 hours. The calcine was smooth, uniform, and contained no nodules. The tendency of particles not to agglomerate was marginally satisfactory, with 6.6 wt% of final bed being +14 mesh particles. The average bulk density was 1.07 g/cm^3; the product production rate was 193 g/h; and the product-to-fines ratio was 2.6. The run produced wet and sticky fines during the first 36 hours of the run causing flowsheet problems. The fines seemed to dissolve well in the off-gas scrubber solution. Chloride retention in the calcined solids was only 10%. The acid scrub at the end of the run contained 40 g/L of sulfate ion which is considered enough to exessively corrode the stainless steel surface of a scrubber system (Newby 1980c).

Use of Aluminum Nitrate Plus Silica during 4” Calciner Runs

DTA-x-ray studies showed that when a combination of aluminum nitrate and silica or ammonium flowrate were added to synthetic Na waste, the sodium in the waste formed sodium aluminum silicates which are temperature stable over NWCF temperature ranges. Runs were made in 10-cm calciners using a simulated Na waste to which aluminum nitrate, boric acid (to prevent crystalline alumina formation) and a commercial colloidal silica solution (one of Du Pont’s Ludox solutions) or ammonium fluosilicate plus aluminum nitrate, and calcium nitrate (to suppress fluoride volatility) were added to tie up the sodium and potassium of the waste as a sodium aluminum silicate compound.

A series of batch calcinations was made to determine which combination of Na waste, ammonium fluosilicate, and aluminum nitrate would yield the most desirable calcination properties. Runs in an enclosed 10-cm calciner testing two of these combinations were forced to terminate after several hours due to bed clinker formation.

Four calcination runs were made in an unenclosed 10-cm calciner using feed containing roughly ½ mole silicon and 1 mole of aluminum per mole of sodium present after the stability limits of the colloidal silicia, aluminum nitrate, Na waste system had been determined in laboratory studies. Only one of the four runs (SBW4-16D) lasted for 40 hours. Two runs using the same starting bed as Run SBW4-16D (calcined blend of Zr and Na wastes) were terminated early due to equipment problems; the other run using a zirconia bed was terminated early due to bed clinker formation.

Table 87. Na waste calcined with alumina nitrate and silica.

	Run# SBW4-16D
H^+ (N[a])	0.69
Al (*M*)	1.03
B (*M*)	0.26
Na (*M*)	1.11
K (*M*)	0.11
Mn (*M*)	0.010
Hg (*M*)	0.0041
Fl (*M*)	0.010
Si (*M*)	0.44
NO_3 (*M*)	4.89
Cl (*M*)	0.018
PO_4 (*M*)	0.011
SO_4 (*M*)	0.034
Mole Ratio Si:Al:Na	0.40:0.93:1
Mole% Na+K	19
Total wt. of Solids g/L	196

The product produced in Run SBW4-16D was hard (attrition index of 84%) which resulted in a high production rate (310 g/h) and a high product-to-fines ratio (5.7). The product was smooth and free of nodules. An X-ray diffraction examination of calcined solids showed only amorphous alumina. A constant product particle size was maintained using a NAR of approximately 1200 and fluidizing air rate of 2.2 scfm (fluidizing velocity below nozzle of 1.26 ft/s). The tendency of bed particles to agglomerate was high (12 wt% of the final bed was particles larger than 14 mesh in size). Bulk density of the product was 1.10 g/cm^3. The run had off-gas equipment plugging problems, produced damp fines, and had excessive fines in the off-gas acid scrubbing system. The fines would not dissolve in boiling 15.7 *M* nitric acid. Chloride retention in calcined solids was 83 wt%.

The silica flowsheet would not be satisfactory in the NWCF because the fines would not dissolve in the off-gas scrubber, nitric acid could not be used to remove solids from vessels, lines and restricted areas, and bed particles had a strong tendency to agglomerate (Eldredge 1987b; Eldredge 1987a, Newby 1974b, Newby 1974a, Newby 1980c).

Use of Fluorides for Calcination of Na Waste in a 4” Calciner

Table 88. Na waste calcined with aluminum nitrate and fluoride to form alkali metal fluoaluminates.

	Run# SBW4-18	Run# SBW4-35
H^+ (N^a)	3.08	2.35
Al (*M*)	1.23	1.09
B (*M*)	0.17	0.19
Na (*M*)	0.44	0.70
K (*M*)	0.049	0.080
Ca (*M*)	2.03	1.36
Mn (*M*)	0.0042	0.0065
Hg (*M*)	0.0024	--
Fe (*M*)	0.0042	0.0065
NO_3 (*M*)	3.76	7.38
F (*M*)	3.02	1.90
Cl (*M*)	0.0083	0.017
PO_4 (*M*)	0.0047	0.0073
SO_4 (*M*)	0.014	0.023
Mole % of Na+K	5.0	9.7
Total wt. of Solids (g/L)	287	251
Mole ratio Al:F:Ca:Na+K	2.5:6.2:4.2:1	1.4:2.3:1.7:1

Calcining Na wastes as a blend with zirconium fluoride wastes had been the most successful method for calcining Na waste in pilot-plant calciners and the only method proven satisfactorily for calcining Na waste in plant calciners. By assuming the method prevents bed agglomeration by tying up the alkali metals as fluoaluminates such as Na_3AlF_6 (sodium fluoaluminate or Cryolite) and K_3AlF_6 (potassium fluoaluminate), the feed of Run SBW4-18 was selected to simulate the same calcium-to-fluoride-to-Na mole ratio as was in the Na-Zr waste blends successfully calcined in the WCF during Campaign H-8, which had 3 moles of aluminum, 7 moles of fluoride, and 5 moles of calcium per mole of Na. Enough $Al(NO_3)_3$ was added to the feed so that the aluminum and boron (0.17 *M* boron was already present) would complex the fluoride sufficiently to prevent corrosion prior to calcination. The starting bed was a calcined Na waste-Zr waste blend. The run was voluntarily terminated after 40 hours. Calcine produced was smooth and contained only a few nodules. Fines plugging of off-gas lines and equipment was above average. Fines produced were moist at first but became dry as the run progressed. Constant cleaning of product removal line to remove product was required due to above average amounts of small agglomerates in the product. Product size (MMPD between 0.5069 and 0.6254 mm) was controlled using NARs between 1037 and 1190 and a fluidizing air rate of 1.97 scfm (fluidizing velocity below nozzle of 1.1 ft/s). Inside surfaces of the calciner vessel after the run were cleaner than usual. Tendency of the product to agglomerate (5.3 wt% of final bed was larger than 14 mesh particles) was slightly above average. Product production rate was 428 g/h, product bulk density was 1.65 g/cm^3, product-to-fines ratio was 3.4, attrition index was 76%, chloride retention in calcine was 83 wt%, and volatile fluoride (not complexed as CaF_2) was 0.2 wt%. The calculated volume reduction factor was 1.2 volumes of liquid waste per volume calcine.

Run SBW4-35 attempted to increase the volume reduction factor using the same additives that were used in Run SBW4-18. The feed contained 1.3 moles aluminum, 2.4 moles of fluoride, and 1.7 moles of calcium per mole of Na+K present. There was enough boron and aluminum present to prevent excessive corrosion to the stainless steel in the acid scrubber and enough aluminum and fluoride present to form cryolite with the Na+K present. The run used an alumina starting bed. The run was terminated after 25.6 hours because there were about 20 large agglomerates on the distributor plate which caused the bed temperature to diverge. Particle size was controlled with a NAR of 1,100 and a fluidizing air rate of 1.94 scfm (fluidizing velocity below nozzle of 0.98 ft/s). Product production rate was 424 g/h, product bulk density was 1.70 g/cm^3, product attrition index was 80%, product-to-fines ratio was 7.9, and 8.6 wt% of the final bed was particles larger than 14 mesh (Newby 1974a, Newby 1981b, Newby 1980c).

CONCLUSIONS

Acidic aqueous waste feeds with a wide range of compositions have been calcined at INTEC both successfully and unsuccessfully. These have included acidic aluminum nitrate, zirconium fluoride, and sodium nitrate wastes. Limited testing on sulfate wastes has also been done.

The successful calcination of a given feed composition depends on the ability to: minimize agglomerate formation on nozzles, walls and in the bed, control particle size in a desired range, exceed bed attrition with growth (build bed), and control volatilization of undesirable species. The ability to meet these requirements is primarily a function of the chemical composition and concentration (or diluteness) of the calciner feed. It is also affected by the calciner operating parameters and equipment condition. Wastes that have been concentrated by evaporation have generally been easier to calcine than dilute wastes. Waste blending has been used to calcine problematic wastes, such as dilute wastes or sodium nitrate wastes, and a great amount of development work has been done to improve the throughput of sodium nitrate wastes. Chemical feed additives are needed to calcine nearly all the wastes. Boric acid is added to aluminum nitrate wastes to promote amorphous alumina rather than alpha-alumina. Calcium nitrate is added to wastes to control flouride and chloride volatility. Aluminum nitrate has been used as a diluent for sodium-bearing wastes, and to increase the dissolved solids content of dilute feeds. Other feed additives have been tested, but with less success.

The feed compositions, operational information, and feed blending strategies in this report should be used as a starting point for evaluation and selection of calciner feeds. The report also summarizes previous calciner flowsheet development efforts to reduce the potential for future duplication of effort.

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Appendix A
30-cm Calciner Pilot Plant Test Data

Table 1a:
Experimental Test Feed Compositions

Run Number	Record Number	H+ (M)	NH4+ (M)	Al (M)	Zr (M)	B (M)	Na+K (M)	Fe (M)	Ca (M)	Cd (M)	F (M)	NO3- (M)	SO4= (M)	Cl (M)	Na+K (Mole %)	Dissolved Solids (g/L)	CatoF Ratio
52 [illegible]	1	1.59	0.000	0.58	0.31	0.140	0.46	0.006	1.06	0.0000	2.12	4.98	0.000	0.0077	7.0	196	0.50
53	2	1.59	0.000	0.58	0.31	0.140	0.46	0.006	1.48	0.0000	2.12	5.82	0.000	0.0077	6.2	242	0.70
64/hrs1-68	3	1.38	0.000	0.79	0.33	0.170	0.25	0.029	1.64	0.0000	1.78	6.13	0.042	0.0029	3.1	267	0.92
64/hrs68-102	4	1.28	0.000	0.66	0.35	0.230	0.18	0.023	1.28	0.0000	1.78	5.00	0.020	0.0022	2.6	216	0.72
67/hrs1-40	5	1.07	0.000	0.48	0.26	0.120	0.42	*	1.30	0.0000	1.69	5.32	*	0.0081	6.7	212	0.77
67/hrs40-108	6	1.16	0.000	0.56	0.26	0.110	0.28	*	1.60	0.0000	1.73	5.66	*	0.0080	4.0	237	0.92
71	7	0.56	0.000	0.34	0.24	0.087	0.36	*	0.59	0.0000	0.94	3.22	0.065	0.0130	8.6	138	0.63
75	8	1.40	0.000	0.48	0.19	0.080	0.31	0.010	0.84	0.0000	1.20	1.40	0.060	0.0140	6.6	158	0.70
79	9	1.39	0.000	0.42	0.18	0.089	0.24	0.014	1.20	0.0000	1.72	4.44	0.048	0.0100	5.0	141	0.70
49	10	1.43	0.000	0.57	0.28	0.130	0.53	0.008	1.04	0.0000	2.04	4.92	0.000	0.0110	8.2	196	0.51
50	11	1.22	0.000	0.53	0.35	0.140	0.34	0.006	1.12	0.0000	2.11	4.75	0.000	0.0070	5.2	194	0.53
12A [illegible]	12	0.91	0.053	0.68	0.00	0.000	1.74	0.000	0.00	0.0000	0.00	4.63	0.076	0.0000	34.0	191	*
12B " "	13	0.68	0.000	0.84	0.43	0.230	1.57	0.000	0.00	0.0000	2.13	3.42	0.000	0.0000	21.0	203	0.00
35	14	0.90	0.000	0.50	0.16	0.000	0.73	0.000	0.00	0.0000	1.42	2.97	0.087	0.0000	20.0	97	0.00
38	15	*	0.000	0.57	0.16	0.046	0.87	0.000	0.00	0.0000	1.47	*	0.143	0.0210	21.0	118	0.00
39	16	*	0.000	0.56	0.21	0.110	0.75	0.010	0.00	0.0000	1.65	2.82	0.120	0.0180	18.0	112	0.00
61	17	2.23	0.000	0.97	0.00	0.004	1.15	0.800	0.11	0.0000	0.02	7.30	0.100	0.0110	18.0	227	4.58
4E	18	0.78	0.000	1.14	0.00	0.003	0.87	0.440	0.00	0.0000	0.00	5.12	0.025	0.0152	17.0	172	*
86	19	0.60	0.000	1.95	0.00	0.020	0.29	0.000	0.00	0.0000	0.00	6.74	0.000	0.0000	5.4	125	*
87	20	0.60	0.000	1.65	0.00	0.200	0.67	0.000	0.00	0.0000	0.00	6.22	0.000	0.0000	12.0	148	*
91	21	0.63	0.000	1.58	0.00	0.210	0.68	0.000	0.00	0.0000	0.00	6.05	0.000	0.0000	12.0	146	*
22	22	0.54	0.000	1.41	0.00	0.150	0.60	0.005	0.00	0.0000	0.00	5.47	0.017	0.0110	12.0	131	*
97	23	0.56	0.000	1.41	0.00	0.087	0.60	0.005	0.00	0.0000	0.00	5.47	0.017	0.0110	12.0	131	*
3E	24	0.40	0.000	1.64	0.00	0.150	0.69	0.006	0.00	0.0000	0.00	6.03	0.020	0.0120	12.0	151	*
93	25	0.76	0.000	0.87	0.14	0.097	0.33	0.003	0.58	0.0000	1.06	5.21	0.010	0.0100	6.6	142	0.55
94	26	1.17	0.000	0.79	0.19	0.087	0.30	0.002	0.98	0.0000	1.30	5.12	0.008	0.0058	5.1	180	0.75
1 [illegible]	27	2.13	0.000	1.27	0.00	0.800	0.03	0.000	0.00	0.0000	0.00	6.00	0.000	0.0000	0.9	67	*
2 "	28	1.78	0.000	1.45	0.00	0.000	0.03	0.000	0.00	0.0000	0.00	6.20	0.000	0.0000	0.8	76	*
38/hrs1-173 "	29	0.62	0.000	1.75	0.00	0.000	0.04	0.000	0.00	0.0000	0.00	5.90	0.000	0.0000	0.9	93	*
38/hrs173-209 "	30	2.29	0.000	1.25	0.00	0.010	0.08	0.000	0.00	0.0000	0.00	6.10	0.000	0.0000	2.3	70	*
16 "	31	2.08	0.000	1.38	0.00	0.008	0.05	0.000	0.00	0.0000	0.00	5.73	0.000	0.0000	1.5	75	*
17	32	0.17	0.000	1.64	0.00	0.100	0.07	0.000	0.00	0.0000	0.00	5.80	0.000	0.0000	1.5	89	*

Table Ib:
Experimental Test Feed Compositions (cont.)

Run Number	Record Number	H+ (M)	NH4+ (M)	Al (M)	Zr (M)	B (M)	Na+K (M)	Fe (M)	Ca (M)	Cd (M)	F (M)	NO3- (M)	SO4= (M)	Cl (M)	Na+K (Mole %)	Dissolved Solids (g/L)	Catof Ratio
22	33	1.18	0.000	1.43	0.00	0.049	0.00	0.000	0.00	0.0000	0.00	5.24	0.000	0.0000	0.0	73	*
24	34	0.90	0.000	1.41	0.00	0.008	0.00	0.000	0.00	0.0000	0.00	5.18	0.000	0.0000	0.0	72	*
29,30,31	35	0.58	0.000	1.74	0.00	0.018	0.00	0.000	0.00	0.0000	0.00	6.00	0.000	0.0000	0.0	89	*
48	36	4.10	0.000	0.85	0.00	0.040	0.03	0.000	0.00	0.0000	0.00	6.10	0.000	0.0000	1.4	46	*
70,72	37	0.80	0.000	1.50	0.00	0.020	0.07	0.005	0.00	0.0000	0.00	5.40	0.000	0.0000	1.7	82	*
77	38	1.23	0.000	1.93	0.00	0.026	0.10	0.006	0.00	0.0000	0.00	7.67	0.000	0.0000	2.0	107	*
9/hrs1-132.2 4/10/2	39	-0.10	0.980	1.50	0.00	0.010	0.02	0.000	0.00	0.0000	0.00	5.24	0.000	0.0000	0.4	78	*
9/hrs132.2-226 "	40	1.13	0.920	1.19	0.00	0.007	0.01	0.000	0 00	0.0000	0.00	5.58	0.000	0.0000	0.4	62	*
15 "	41	0.57	1.050	1.60	0.00	0.005	0.02	0.000	0.00	0.0000	0.00	5.92	0.000	0.0000	0.5	83	*
7 "	42	1.03	0.000	0.66	0.43	0.170	0.00	0.000	1.21	0.0000	2.45	4.66	0.000	0.0000	0.0	187	0.49
11 "	43	1.07	0.020	0.82	0.24	0.094	0.02	0.000	0.00	0.0000	1.68	2.69	0.000	0.0000	0 5	50	0.00
13A "	44	1.44	0.000	0.39	0.39	0.180	0.00	0.000	0.17	0.0000	2.60	1.67	0.000	0.0000	0.0	51	0.06
13B "	45	1.33	0.000	0.36	0.37	0.100	0.00	0.000	0.62	0.0000	2.23	2.20	0.000	0.0000	0.0	100	0.28
14 "	46	1.16	0.000	0.39	0.30	0.040	0.00	0.000	0.97	0.0000	2.12	3.37	0.000	0.0000	0.0	131	0.46
18 "	47	1.11	0.000	0.45	0.27	0.036	0.00	0.000	0.96	0.0000	1.81	3.36	0.000	0.0000	0.0	134	0.53
21 4/10/2	48	1.40	0.000	0.31	0.25	0.100	0.00	0.000	0.93	0.0000	1.62	3.80	0.000	0.0000	0.0	127	0.57
22	49	0.83	0.000	0.33	0.25	0.000	0.00	0.000	1.27	0.0000	1.78	3.34	0.000	0.0000	0.0	160	0.71
23	50	1.52	0.000	0.30	0.22	0.180	0.00	0.000	0.95	0.0000	1.45	4.13	0.000	0.0000	0.0	131	0.66
51	51	1.21	0.000	0.47	0.33	0.120	0.00	0.000	1.22	0.0000	2.17	4.31	0.000	0.0000	0.0	168	0.56
57	52	1.27	0.000	0.51	0.31	0.140	0.00	0.000	1.14	0.0000	2.63	6.48	0.000	0.0000	0.0	154	0.43
63	53	1.38	0.000	0.55	0.37	0.200	0.00	0.000	1.34	0.0000	2.49	2.93	0.000	0.0000	0.0	188	0.54
65	54	1.20	0.000	0.61	0.30	0.150	0.01	0.000	1.81	0.0000	2.23	5.86	0.000	0.0130	0.1	237	0.81
80/hrs1-36.3	55	1.37	0.000	0.63	0.43	0.230	0.00	0.000	1.67	0.0000	3.04	5.30	0.000	0.0000	0.0	231	0.55
80/hrs36.3-105	56	1.49	0.000	0.56	0.38	0.210	0.00	0.000	1.50	0.0000	2.70	5.23	0.000	0.0000	0.0	207	0.56
74	57	0.60	0.000	0.38	0.20	0.095	0.00	0.000	0.80	0.0000	1.14	3.04	0.061	0.0094	0.0	110	0.70
2E	58	1.13	0.000	0.58	0.41	0.190	0.00	0.000	1.53	0.0000	2.78	4.89	0.000	0.0000	0.0	211	0.55
40	59	2.28	0.000	0.31	0.00	0.000	0.00	0.049	0.00	0.0000	0.00	2.93	0.436	0.0000	0.0	90	*
58	60	-0.06	0.000	0.00	0.23	0.000	0.39	0.340	0.00	0.0046	0.00	2.10	0.004	0.0096	8.5	314	*
60	61	2.30	0.000	0.00	0.10	0.000	0.33	0.270	0.00	0.0019	0.00	3.52	0.004	0.0096	10.2	294	*
59	62	2.00	0.031	0.38	0.03	0.130	0.00	0.004	1.05	0.0000	0.97	2.30	0.000	0.0000	0.0	179	1.08
95	63	1.12	0.086	0.56	0.03	0.055	0.27	0.012	0.54	0.0000	0.81	3.80	0.000	0.0052	7.6	121	0.67
62	64	1.89	0.018	0.45	0.13	0.140	0.00	0.003	1.01	0.0000	2.24	2.20	0.000	0.0000	0.0	161	0.45

Table 1c:
Experimental Test Feed Compositions (cont.)

	Record Number	H+ (M)	NH4+ (M)	Al (M)	Zr (M)	B (M)	Na+K (M)	Fe (M)	Ca (M)	Cd (M)	F (M)	NO3- (M)	SO4= (M)	Cl (M)	Na+K (Mole %)	Dissolved Solids (g/L)	CatoF Ratio
68/hrs1-64.3	65	3.09	0.440	0.98	0.00	0.018	0.06	0.190	0.01	0.0000	0.02	5.90	0.120	0.0009	1.8	102	0.55
68/hrs64.3-112.	66	0.74	0.350	0.93	0.00	0.031	0.02	0.065	0.01	0.0000	0.02	4.10	0.040	0.0009	0.9	59	0.54
Enclosed Run 6	67	1.94	0.000	0.28	0.27	0.140	0.32	0.000	1.41	0.0880	1.78	4.84	0.033	*	5.1	220	0.81
Enclosed Run 10	68	2.62	0.000	0.35	0.26	0.160	0.34	0.000	1.54	0.0960	2.27	6.11	0.024	0.0060	4.9	232	0.68
Enclosed Run 13	69	1.86	0.000	0.28	0.32	0.230	0.31	0.000	1.60	0.0980	2.25	6.19	0.028	0.0090	4.3	243	0.72
Enclosed Run 16	70	1.40	0.000	0.33	0.35	0.180	0.00	0.000	1.17	0.0460	2.17	4.37	0.049	0.0000	0.0	170	0.52
Enclosed Run 17	71	1.65	0.000	0.39	0.23	0.140	0.34	0.000	1.06	0.0810	1.71	4.64	0.046	0.0100	6.0	185	0.62
Enclosed Run 18	72	1.55	0.230	0.33	0.24	0.150	0.27	0.000	1.20	0.0820	1.86	4.75	0.024	0.0080	4.6	189	0.64
Enclosed Run 8	73	0.94	0.043	0.24	0.39	0.260	0.00	0.006	2.07	0.1100	2.96	1.82	0.120	0.0000	0.0	274	0.70
Enclosed Run 19	74	1.01	0.000	1.10	0.01	0.150	0.20	0.003	0.06	0.0000	0.10	4.48	0.007	0.0050	5.5	84	0.59
Enclosed Run 9	75	0.90	0.000	1.60	0.00	0.010	0.00	0.000	0.00	0.0000	0.00	5.70	0.000	0.0000	0.0	82	*
Enclosed Run 14	76	1.32	0.047	0.33	0.40	0.240	0.00	0.000	1.51	0.1400	2.75	2.05	0.091	0.0000	0.0	222	0.55
Enclosed Run 20	77	1.04	0.000	0.87	0.09	0.100	0.22	0.000	0.41	0.0130	0.48	4.47	0.003	0.0097	5.3	117	0.85
	Minimum:	-0.10	0.000	0.00	0.00	0.000	0.00	0.000	0.00	0.0000	0.00	0.00	0.000	0.0000	0.0	46	0.00
	Maximum:	4.10	1.050	1.95	0.43	0.260	1.74	0.800	2.07	0.1400	3.04	7.67	0.436	0.0210	34.0	314	4.58
	Average:	1.23	0.055	0.81	0.17	0.097	0.25	0.030	0.62	0.0099	1.14	4.62	0.025	0.0039	4.8	150	0.41

Table 2a:
Experimental Test Run Parameters

Run Number	Record Number	Bed Heating	Feed Additive	Fluidizing Velocity (m/s)	MMPD (mm)	O2/Fuel Ratio (sL/L)	COT (hrs)	Bed Turnover (%)	Feed Rate (L/hr)
52	1	IBC	none	*	*	*	140.0	*	35.0
53	2	IBC	none	*	*	*	130.0	*	35.0
64/hrs1-68	3	IBC	none	0.23	0.42	1953	68.0	93.80	35.0
64/hrs68-102	4	IBC	none	0.26	0.59	2046	34.0	98.00	35.0
67/hrs1-40	5	IBC	none	0.26	0.38	1942	40.0	85.80	35.0
67/hrs40-108	6	IBC	none	0.26	0.53	2132	68.0	99.60	35.0
71	7	IBC	none	0.27	0.52	1951	*	98.60	35.0
75	8	IBC	none	0.26	0.47	2300	*	99.90	39.1
79	9	IBC	none	0.27	0.51	2115	*	99.00	35.0
49	10	IBC	none	0.19	0.35	2050	90.3	*	35.0
50	11	IBC	none	0.24	0.40	*	70.0	*	35.0
12A	12	elect	sugar	0.34	0.40	*	120.0	*	10.0
12B	13	elect	sugar	0.34	0.33	*	70.0	*	10.0
35	14	IBC	none	0.23	0.39	1514	*	83.00	26.5
38	15	IBC	none	0.27	*	1600	3.5	*	26.5
39	16	IBC	none	0.26	0.50	1760	103.0	88.30	26.5
61	17	IBC	iron	*	*	*	45.5	*	35.0
4E	18	IBC	iron	0.18	0.19	2159	*	87.00	30.0
86	19	IBC	none	0.22	0.64	1974	*	96.10	35.0
87	20	IBC	none	0.18	0.62	1973	*	96.10	35.0
91	21	IBC	none	0.15	0.45	3200	*	60.20	35.0
22	22	IBC	none	*	*	*	*	*	35.0
97	23	IBC	none	0.26	0.52	1529	*	88.60	35.0
3E	24	IBC	none	0.16	0.23	2279	67.4	56.00	22.0
93	25	IBC	none	0.21	0.47	2607	*	86.30	35.0
94	26	IBC	none	0.29	0.49	2552	*	92.30	35.0
1	27	elect	none	0.30	0.60	*	*	92.40	10.0
2	28	elect	none	0.30	0.42	*	*	98.20	10.0
3B/hrs1-173	29	elect	none	0.30	0.62	*	173.0	93.00	10.0
3B/hrs173-209	30	elect	none	0.30	0.50	*	*	94.70	10.0
16	31	elect	none	0.30	0.51	*	*	95.20	10.0
17	32	elect	none	0.30	0.54	*	*	85.00	10.0
22	33	IBC	none	0.30	0.48	2240	*	82.60	15.0
24	34	IBC	none	0.73	0.86	*	*	71.90	28.0
29,30,31	35	IBC	none	0.37	0.78	1459	*	99.00	35.0
48	36	IBC	none	0.33	0.86	1579	*	96.00	35.0
70,72	37	IBC	none	0.25	0.64	1861	*	99.99	46.0
77	38	IBC	none	0.20	0.59	1910	*	99.96	40.0
9/hrs1-132.2	39	elect	none	0.30	0.57	*	132.2	77.50	10.0
9/hrs132.2-226.	40	elect	none	0.30	0.61	*	*	92.50	10.0
15	41	elect	none	0.30	0.36	*	*	84.30	10.0
7	42	elect	none	0.30	0.71	*	*	91.90	10.0
11	43	elect	none	0.30	0.35	*	*	62.50	10.0
13A	44	elect	none	0.34	0.69	*	53.0	25.20	10.0
13B	45	elect	none	0.40	0.75	*	*	87.50	10.0
14	46	elect	none	0.30	0.38	*	*	88.80	10.0
18	47	elect	none	0.30	0.40	*	*	83.60	16.0
21	48	elect	none	0.30	0.64	*	*	99.90	10.0
22	49	IBC	none	0.30	0.55	1750	*	86.50	30.0

Table 2b:
Experimental Test Run Parameters (cont.)

	Record Number	Bed Heating	Feed Additive	Fluidizing Velocity (m/s)	MMPD (mm)	O2/Fuel Ratio (sL/L)	COT (hrs)	Bed Turnover (%)	Feed Rate (L/hr)
23	50	IBC	none	0.61	0.93	*	*	99.99	30.0
51	51	IBC	none	0.24	0.42	*	*	95.00	35.0
57	52	IBC	none	0.24	0.52	*	*	99.80	35.0
63	53	IBC	none	0.25	0.54	1931	*	99.90	35.0
65	54	IBC	none	0.22	0.37	1937	*	99.30	35.0
80/hrs1-36.3	55	IBC	none	0.21	0.35	1988	36.3	93.70	47.0
80/hrs36.3-105	56	IBC	none	0.21	0.43	1836	*	99.99	47.0
74	57	IBC	none	0.25	0.44	1518	*	98.00	47.0
2E	58	IBC	none	*	0.32	2088	*	89.40	35.0
40	59	IBC	none	0.24	0.66	1368	*	70.20	20.0
58	60	IBC	iron	0.29	0.42	1300	*	97.30	35.0
60	61	IBC	iron	0.29	0.41	1800	*	97.90	35.0
59	62	IBC	Nb	0.25	0.43	2175	*	98.40	35.0
95	63	IBC	Nb	*	0.42	*	*	90.00	35.0
62	64	IBC	Nb	0.26	0.36	2110	*	99.00	35.0
68/hrs1-64.3	65	IBC	none	0.24	0.38	1966	64.3	69.60	38.0
68/hrs64.3-112.	66	IBC	none	0.24	0.44	2026	*	86.70	44.0
Enclosed Run 6	67	IBC	none	0.21	0.35	2094	*	95.36	*
Enclosed Run 10	68	IBC	none	0.19	0.36	1987	*	99.99	*
Enclosed Run 13	69	IBC	none	0.22	0.38	2199	*	99.96	*
Enclosed Run 16	70	IBC	none	0.26	0.31	2374	*	99.10	*
Enclosed Run 17	71	IBC	none	0.31	0.41	2081	*	99.81	*
Enclosed Run 18	72	IBC	none	0.31	0.38	2633	*	99.49	*
Enclosed Run 8	73	IBC	none	*	*	*	*	*	*
Enclosed Run 19	74	IBC	none	0.19	0.31	2205	27.3	*	40.0
Enclosed Run 9	75	IBC	none	0.17	0.39	1939	*	*	*
Enclosed Run 14	76	IBC	none	*	0.31	2224	36.6	76.70	*
Enclosed Run 20	77	IBC	none	0.20	0.32	2919	94.0	92.90	* 40
	Minimum:			0.000	0.000	0	0.0	0.00	0.0
	Maximum:			0.730	0.930	3200	173.0	99.99	47.0
	Average:			0.245	0.444	1261	21.6	75.90	24.4

Table 3a:
Experimental Test Notes

Record Number	Run Number	Notes/Source
1	52	Na-Zr blend clinkered due to nodules. Successful by alternating with Zr
2	53	March 1974 Progress Report,BUC-124-74
3	64/hrs1-68	ENICO-1128
4	64/hrs68-102	Size cntrl due to either less Al,Na+K,Ca,Ca/F,NO3 or higher NAR.ENICO
5	67/hrs1-40	Controlled by increasing NAR& O2/Fuel
6	67/hrs40-108	Controlled by increasing NAR& O2/Fuel
7	71	*
8	75	*
9	79	*
10	49	*
11	50	*
12	12A	*
13	12B	*
14	35	*
15	38	*
16	39	*
17	61	*
18	4E	*
19	86	*
20	87	*
21	91	*
22	22	*
23	97	*
24	3E	*
25	93	*
26	94	*
27	1	*
28	2	*
29	3B/hrs1-173	*
30	3B/hrs173-209	*
31	16	*
32	17	*
33	22	*
34	24	*
35	29,30,31	*
36	48	*
37	70,72	*
38	77	*
39	9/hrs1-132.2	*
40	9/hrs132.2-226.7	*
41	15	*
42	7	*
43	11	*
44	13A	*

Table 3b:
Experimental Test Notes (cont.)

Record Number	Run Number	Notes/Source
45	13B	*
46	14	*
47	18	*
48	21	*
49	22	*
50	23	*
51	51	*
52	57	*
53	63	*
54	65	*
55	80/hrs1-36.3	*
56	80/hrs36.3-105	*
57	74	*
58	2E	*
59	40	*
60	58	*
61	60	*
62	59	*
63	95	*
64	62	*
65	68/hrs1-64.3	*
66	68/hrs64.3-112.3	*
67	Enclosed Run 6	*
68	Enclosed Run 10	*
69	Enclosed Run 13	*
70	Enclosed Run 16	*
71	Enclosed Run 17	*
72	Enclosed Run 18	*
73	Enclosed Run 8	Terminated due to plugged pto and kerosene pump failure
74	Enclosed Run 19	Problems:small size, couldn't build bed,nozzle plugging,rupture disk
75	Enclosed Run 9	*
76	Enclosed Run 14	Terminated due to Off-gas plug
77	Enclosed Run 20	Al:Fluor:Na (7:3:1.25) blend

Table 4a:
Experimental Test Results

Run Number	Record Number	Final Bed >14 Mesh (wt %)	Fluoride Volatility (%)	Chloride Retention (%)	Product to Fines Ratio	Product Bulk Dens (g/cc)	Product Rate (Kg/hr)	Attrition Index (%)	Nozzle Air-to-Feed Ratio	Size Control	Product Nitrates (wt%)	Fines Nitrates (wt%)	Particle Surface Appearance	Reason For Shutdown
52 -	1	*	*	*	*	*	*	*	*	*	*	*	nod	bed_clnk
53	2	*	*	*	*	*	*	*	*	incr	*	*	nod	norm
64/hrs1-68	3	0.9	0.2	72	2.4	1.33	3.4	43	380	incr	4.08	*	nod_ir	norm
64/hrs68-102	4	0.9	1	71	3.3	1.34	4.2	43	380	stable	4.14	*	nod_ir	norm
67/hrs1-40	5	*	0.3	75	3.1	1.28	3.6	25	291	incr	9.1	*	nod_ir	norm
67/hrs40-108	6	3.9	0.4	64	2.8	1.34	3.8	43	390	stable	8.81	*	nod_ir	norm
71	7	0.6	0.6	81	4.8	1.3	3.2	50	450	sm_incr	8.54	*	nod_ir	norm
75	8	*	*	*	2.2	1.4	5.1	42	400	incr	*	*	*	norm
79	9	*	*	*	5.9	1.34	3	37	256	sm_incr	6.69	*	*	norm
49	10	*	*	67	2.4	1.65	*	85	*	incr	10.9	*	nod	
	fuel_clnk													
50	11	*	*	50	4.7	1.5	*	*	230	incr	13.9	*	nod	
	fuel_clnk													
12A	12	*	*	*	*	1.3	*	65	600	sm_incr	1.6	*	*	
	norm_ogpl													
12B	13	*	0.9	*	*	1.25	*	45	600	sm_incr	0.45	*	*	norm
35	14	*	39.5	*	1.9	1.06	1.2	3	244	decr	3.8	*	*	og_cor
38	15	6	*	*	*	*	*	*	190	*	*	*	*	bed_clnk
39	16	5	*	*	4.1	0.9	1.4	58.4	370	stable	*	*	*	bed_clnk
61	17	6	*	96	*	*	*	*	*	*	*	*	ir	bed_clnk
4E [illegible]	18	0.76	*	78	0.22	1.42	2.6	44	125	decr	19.8	*	sm	toosmall
86	19	0.52	*	*	1.2	0.92	2	45	380	stable	*	*	sm	norm
87	20	2	*	*	0.84	0.98	2	57	320	sm_incr	*	*	sm	norm
91	21	0.43	*	*	0.16	0.99	0.53	46	199	*	*	*	*	norm
22	22	*	*	*	*	*	*	*	*	*	*	*	*	equip
97	23	*	*	32	0.77	1.03	1.6	43	236	decr	*	*	sm	og_plg
3E [illegible]	24	5.2	*	24	1.5	1.51	0.9	45	150	sm_decr	16.9	*	sm	equip
93	25	0.13	0.68	29	0.95	1.67	1.8	76	372	sm_incr	10.5	*	sm	*
94	26	0.09	0.49	99	0.8	1.54	2.4	76	300	sm_incr	6.5	*	*	*
1	27	*	*	*	*	0.79	1.2	69	300	incr	7	*	*	*
2	28	*	*	*	*	0.9	1.2	50	550	sm_incr	4	*	*	*
3B/hrs1-173	29	*	*	*	4.2	0.8	1	73	650	stable	6.8	*	*	*
3B/hrs173-209	30	*	*	*	4.6	0.9	0.5	74	600	sm_decr	5.5	*	*	*
16	31	*	*	*	11	0.85	0.85	67	700	incr	5	*	*	*
17	[illegible]	*	*	*	7	0.92	0.7	65	650	incr	5.3	*	*	*

Table 4b:

Experimental Test Results (cont.)

Run Number	Record Number	Final Bed >14 Mesh (wt %)	Fluoride Volatility (%)	Chloride Retention (%)	Product to Fines Ratio	Product Bulk Dens (g/cc)	Product Rate (Kg/hr)	Attrition Index (%)	Nozzle Air-to-Feed Ratio	Size Control	Product Nitrates (wt%)	Fines Nitrates (wt%)	Particle Surface Appearance	Reason For Shutdown
22	33	*	*	*	6	0.85	0.82	70	250	stable	3.4	*	*	*
24	34	*	*	*	2.3	*	1.1	*	400	stable	*	*	*	*
29,30,31	35	*	*	*	5.7	*	2.4	*	274	stable	*	*	*	*
48	36	*	*	*	10.7	0.91	1.9	*	285	stable	*	*	*	*
70,72	37	*	*	*	2.7	0.905	3	54	319	stable	0.9	*	*	*
77	38	*	*	*	0.77	0.76	1.9	16	160	stable	1.09	*	*	*
9/hrs1-132.2	39	*	*	*	3	1.2	0.68	83	650	sm_incr	*	*	*	*
9/hrs132.2-226	40	*	*	*	5.1	1.2	0.7	81	650	sm_incr	*	*	*	*
15	41	*	*	*	2.9	1.2	0.75	73	500	sm_incr	*	*	*	*
7	42	*	0.55	*	10	1.1	1.5	82	700	incr	4	*	*	*
11	43	0.1	35	*	1.4	1	0.56	40	500	stable	*	*	*	og_cor
13A	44	*	35	*	6.7	1.2	0.4	60	500	stable	0.24	*	*	og_cor
13B	45	*	10	*	7.7	1.5	1.4	60	500	stable	0.19	*	*	og_cor
14	46	*	1.9	*	8.3	1.5	1.1	55	600	incr	*	*	*	*
18	47	*	0.9	*	4.7	1.4	1.4	9	600	sm_incr	*	*	*	*
21	48	*	0.9	*	12.3	1.38	2	72	700	stable	2.85	*	*	norm
22	49	*	*	*	6.7	1.05	0.91	30	312.5	stable	0.82	*	*	norm
23	50	*	0.9	*	5.8	1.25	2.6	50	550	stable	0.25	*	*	norm
51	51	*	*	*	4.4	1.23	3.6	12	100	stable	0.26	*	*	norm
57	52	*	*	*	3.4	1.18	4.2	*	150	*	0.2	*	*	norm
63	53	*	*	*	4.7	1.17	4.4	10	170	stable	0.27	*	*	norm
65	54	0.8	0.55	61	2.6	1.17	4	10	200	stable	0.81	*	*	norm
80/hrs1-36.3	55	*	*	*	1 3	1.21	4.4	12	140	stable	*	*	*	norm
80/hrs36.3-105	56	*	*	*	3.8	1.21	7.6	11	82	stable	*	*	*	norm
74	57	0.81	1.1	20	2.4	1.39	2.9	16	90	stable	0.23	*	sm	norm
2E [illegible]	58	*	*	*	1.8	1.3	2.2	17	*	stable	*	*	*	*
40	59	*	*	*	1.6	*	2	28	116	decr	*	*	*	norm
58	60	*	*	*	2.1	2.1	5	22	140	stable	2.94	*	nod	norm
60	61	*	*	*	2.4	1.9	7.2	36	200	sm_incr	4.92	*	nod	norm
59	62	0.88	0.34	*	3.7	1.26	3.2	8.6	170	stable	*	*	ir	norm
95	63	1.1	0 32	40	2.8	1.41	1.6	80	165	sm_incr	*	*	sm	norm

Table 4c:

Experimental Test Results (cont.)

	Record Number	Final Bed >14 Mesh (wt %)	Fluoride Volatility (%)	Chloride Retention (%)	Product to Fines Ratio	Product Bulk Dens (g/cc)	Product Rate (Kg/hr)	Attrition Index (%)	Nozzle Air-to-Feed Ratio	Size Control	Product Nitrates (wt%)	Fines Nitrates (wt%)	Particle Surface Appearance	Reason For Shutdown
62	64	*	*	*	.3	1.32	*	10	160	stable	*	*	ir	norm
68/hrs1-64.3	65	*	15	0	1.3	1.37	1.4	19	202	stable	*	*	*	norm
68/hrs64.3-112.3	66	*	15	0	1.5	1.45	1.2	50	145	stable	*	*	*	norm
Enclosed Run 6	67	*	*	*	5.5	1.35	4.33	40	188	sm_incr	5.2	3.4	nod	norm
Enclosed Run 10	68	0.12	*	*	6.5	1.34	5.07	30	194	sm_incr	3.9	8.3	*	norm
Enclosed Run 13	69	0.14	0.11	85.8	3.2	1.59	4.81	37	250	stable	9.2	9.1	*	norm
Enclosed Run 16	70	0.5	0.3	*	3.1	1.48	3.47	17	197	stable	0.52	1.5	ir	norm
Enclosed Run 17	71	0.24	0.41	93.1	4.1	1.6	4.91	56	317	stable	4.8	4.1	nod_ir	norm
Enclosed Run 18	72	0.16	0.37	98.4	2.5	1.75	3.17	75	309	sm_incr	6.1	7.8	nod_ir	norm
Enclosed Run 8	73	*	*	*	*	*	*	*	*	*	*	*	*	equip
Enclosed Run 19	74	*	*	*	0.5	1.35	*	*	174	stable	*	*	*	bedlvl
Enclosed Run 9	75	*	*	*	*	0.9	*	*	109	incr	*	*	*	*
Enclosed Run 14	76	0.2	*	*	1.7	1.49	2.33	39	172	sm_decr	*	*	*	og_plg
Enclosed Run 20	77	0.37	0.5	57	0.69	1.62	1.5	21	*	stable	4.7	5.5	nod	norm
	Minimum:	0.09	0.11	0.00	0.16	0.76	0.40	3.00	82.00		0.19	1.50		
	Maximum:	6.00	39.50	99.00	12.30	2.10	7.60	85.00	700.00		19.80	9.10		
	Average:	1.46	5.83	60.44	3.70	1.26	2.47	44.70	331.93		4.93	5.67		