December 1997

Alternative Calcination Development Status Report

RECEIVED

SEP 15 1998

OSTI

R. D. Boardman

MASTER *JAT*

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

LOCKHEED MARTIN

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Alternative Calcination Development Status Report

R. D. Boardman

Published December 1997

**Idaho National Engineering and Environmental Laboratory
High Level Waste Program
Lockheed Martin Idaho Technologies Company
Idaho Falls, ID 83415**

**Prepared for the
U.S. Department of Energy
Assistant Secretary for
Environmental Management
Under DOE Idaho Operations Office
Contract DE-AC07-94ID13223**

EXECUTIVE SUMMARY

The Programmatic Spent Nuclear Fuel and (INEEL) Environmental Restoration and Waste Management Programs Environmental Impact Statement Record of Decision, dated June 1, 1995, specifies that high-level waste stored in the underground tanks at the ICPP continue to be calcined while other options to treat the waste are studied. The DOE 10-year program plan also indicates that calcination will be employed to stabilize the ICPP high-level liquid wastes. In addition, a Settlement Agreement (Court Order) with the State of Idaho specifies that calcination will be used to process the remaining liquid wastes in the tank farm so that the tanks can be removed from service. This commitment is the most restrictive since it requires calcination of the liquid wastes by December 31, 2012. Projections show that it will be difficult to meet this commitment using the standard practice of adding a large amount of non-radioactive aluminum nitrate solution (ANN) to the feed as it is calcined. Therefore, the High-Level Waste Program has funded a program to develop new flowsheets to increase the liquid waste processing rate. Simultaneously, a radionuclide separation process, as well as other options, are also being developed, which will be compared to the calcination treatment option.

Figure 1 shows the activities that have been completed over the past two years to develop an improved calcination flowsheet. Alternative flowsheets were identified and screened through theoretical and laboratory calcination experiments. Two alternatives emerged as viable candidates; (1) elevated temperature calcination (also referred to as high temperature calcination), and (2) sugar-additive calcination. Both alternatives were determined to be viable through testing performed in a lab-scale calcination mockup. Subsequently, 10-cm Calciner Pilot Plant scoping tests were successfully completed for both flowsheets. The results were compared to the standard 500°C, high-ANN flowsheet (baseline flowsheet). The product and effluent streams were characterized to help elucidate the process chemistry and to investigate potential environmental permitting issues. Several supplementary tests were conducted to gain a better understanding of fine-particles generation, calcine hydration, scrub foaming, feed makeup procedures, sugar/organic elimination, and safety-related issues. Many of the experiments are only considered to be scoping tests, and follow-up experiments will be required to establish a more definitive understanding of the flowsheets. However, the combined results support the general conclusion that flowsheet improvements for the NWCF are technically viable.

A Project Feasibility Study was initiated by the HLW Program in parallel with technology development, and later a Project Conceptual Design was completed on the basis of the experimental results.¹ Interaction between Technology Development and Design personnel helped the HLW Program determine that the high temperature flowsheet would be preferable to implement at the NWCF. Nevertheless, the concepts learned during the development of the sugar-additive flowsheet may have application to other thermal/denitration technologies at the ICPP.

Figure 1. Order of elevated temperature (E.T.) and sugar additive (S.A.) calcination activities (G97001).

The joint development and design studies identified the following major virtues and vices for the alternative flowsheets:

Virtues of the Elevated Temperature Flowsheet

- Calcine denitration is effectively accomplished by increasing the calciner operating temperature to at least 600°C.
- A 75% net increase in the waste processing rate, above the baseline flowsheet, is possible.
- A 33% reduction in the amount of ANN added to the feed is possible.
- Less boron will likely be required to suppress α -alumina formation in the product, compared to the baseline high-ANN flowsheet.
- A 5% decrease in NO_x emissions is projected.
- A slight decrease in CO and unburned hydrocarbon emissions is possible.
- Alkali metals contained in the feed are mainly converted to aluminate salts which are less hygroscopic than the sugar-additive product.

- Product is more soluble in nitric acid solutions than the baseline calcination flowsheet.
- Requires less calcine solids storage space than either the baseline or the sugar additive flowsheet.

Vices of the Elevated Temperature Flowsheet

- Increased flash evaporation of the feed results in the generation of more fines. The impact of this phenomena may not be fully understood until tested in the NWCF.
- Higher temperatures may result in increased corrosion in the fluidized-bed vessel.
- Higher temperatures will increase vessel and piping stresses.
- Increased evolution of volatile species, specifically, chlorides, fluorides, cesium, and technetium, may result.
- Increased halide volatilization may result in higher corrosion rates in the offgas treatment system.
- The calcine product is slightly hygroscopic and may cake upon exposure to a high humidity atmosphere.

Virtues of the Sugar-Additive Flowsheet

- Sugar calcination is effective, and likely a safe method for denitrating the calcine product at 500°C (and perhaps at temperatures as low as 350°C).
- A 68% net increase in the waste processing rate, above the baseline flowsheet, is possible.
- A 64% reduction in the amount of ANN added to the feed is possible, yielding the least total calcine volume.
- Less boron will likely be required to suppress α -alumina formation in the product than is required for the baseline high-ANN flowsheet.
- A significant decrease in NO_x emissions is projected; the majority of the nitrates may be converted to colorless N₂O and/or N₂.
- Less fines are generated, compared to the baseline and high temperature flowsheets.
- Decreased halide volatility was observed during the 10-cm Calciner Pilot Plant runs.
- Product is more soluble in nitric acid solutions than the baseline calcination flowsheet.
- Requires significantly less calcine solids storage space than the baseline calcination flowsheet (but slightly more space than the high temperature flowsheet).

Vices of the Sugar-Additive Flowsheet

- Several safety concerns must be further studied to complete a revision of the NWCF Safety Analysis Report (SAR).
- Feed system modifications would be required.
- Unprocessed feed-sugar mixtures may require a new liquid-phase reactor to reduce the reactivity of the solutions prior to restarting the calciner or before the solutions are returned to the tank farm.
- Increased emissions of CO and unburned hydrocarbons may be outside the safety envelop evaluated in the SAR and allowed by environmental applications. The generation of halogenated organics and other RCRA toxic air pollutants will likely increase.
- Accumulation of unburned hydrocarbons in the scrub system may require a new liquid-phase reactor to eliminate the carbon in the scrub solutions before they can be returned to the tank farm.
- Gradual calcine hydration, and subsequent product deliquescence, is unavoidable at all realistic humidity conditions. Significant changes to the NWCF and CSSF particle collection, transport, and storage system may be necessary.
- NWCF corrosion rates will increase with higher levels of CO in the vessel and offgas system.
- Condensable hydrocarbon emissions may lead to rapid buildup on the NWCF offgas filters, causing filter plugging and safety concerns.

Based on the 10-cm calciner high temperature scoping tests with standard SBW, an operating temperature of 600°C with an aluminum-to-alkali metal ratio of 1.5:1 was recommended for NWCF design modification considerations. Flowsheet optimization and feed composition sensitivity tests are now recommended to determine the optimum amount of boron and calcium nitrate to add to the feed, and to determine the sensitivity of the flowsheet to variations in feed composition, operating temperature, nozzle atomizing air ratio, and other key variables. Efforts need to be made to quantify the extent of fines generation and chloride volatility during these tests. If possible, an on-line monitor needs to be deployed to measure the levels of hazardous air pollutants (HAPs) and criteria pollutants (NO_x, CO, and unburned hydrocarbons) emitted with the calciner offgas. The emissions data will help HLW Projects address design and permitting needs to comply with the proposed MACT (Maximum Achievable Control Technology) rule and other EPA requirements.

The path forward for Alternative Calcination Development is to continue developing the high temperature flowsheet and to investigate the possibility of dissolving boric acid directly in the ANN solution feed-stock. The following tasks are currently planned:

- Conduct 10-cm Calciner Pilot Plant flowsheet refinement and sensitivity tests to determine the optimum amount of feed additives to use (i.e., ANN, $\text{Ca}(\text{NO}_3)_2$, and boron) and to establish a better understanding of high temperature calcination chemistry.
- Conduct tests to quantify corrosion rates in the NWCF fluidized-bed vessel at higher temperatures.
- Conduct tests to quantify corrosion rates in the scrub system with high levels of chloride.
- Determine the feasibility of conducting a short high temperature trial in the NWCF at the end of Campaign H4.
- Conduct calcine hydration tests and calcine retrievability tests to demonstrate product acceptability and possibly to provide NWCF design modifications guidance.
- Conduct baseline flowsheet tests with concentrated feeds obtained by dissolving boric acid in the ANN feed stock.
- Develop and test an offgas monitoring system to help determine the level of criteria pollutants and HAPs that are emitted from the 10-cm calciner and which may be emitted from the NWCF.
- Complete plans for 15-cm Calciner Pilot Plant testing and conduct tests to gain a better understanding of fines generation and fluid-bed dynamics at high temperature.

The knowledge gained from the sugar-additive calcination testing will be incorporated into ongoing studies to identify technologies for conditioning the HLW and LLW that would result if a separation process were implemented to treat the ICPP wastes. Most of the disadvantages of using sugar to denitrate the wastes would be avoided by denitrating the wastes in a rotary kiln or moving bed, with the resulting calcine being directly fed to either a melter, grout mixer, or some other encapsulation process.

ACKNOWLEDGEMENTS

Credit for the accomplishments described in this report is given to group members of the Alternative Calcination Development unit, under supervision of D. V. Croson, with technical lead responsibilities assigned to R. D. Boardman. The results were compiled from several internal letters, laboratory logbooks, and subcontractor reports. The laboratory crucible tests were completed by J. A. Nenni. Lab-scale calcination mockup set up and testing was conducted by J. A. McCray and J. Pao. The calcine volatility tests were carried out by J. A. Del Debbio with assistance from L. G. Olson. Explosion concerns were investigated by D. W. Marshall, who also conducted the mutual solubility studies and sweetened feed sugar-elimination tests. The calcine explosion sensitivity tests were completed with the help of R. C. Green and S. H. Hinckley. The 10-cm calciner upgrade was completed by L. J. Young who also helped secure pilot plant air permits prior to performing the 10-cm calciner scoping tests. The pilot plant runs were carried out by J. A. Nenni and L. J. Young. Modifications for the 30-cm calciner were determined by T. A. Batcheller. The calcine hydration tests were set up by L. G. Olson and L. J. Young. Scrub foaming was investigated by J. Pao. All of the calcination activities and product characterization tests were completed with the aide of four outstanding laboratory technicians, S. H. Hinckley, C. J. Johnson, L. G. Olson, and T. W. Watson. B. H. O'Brien needs to be recognized for providing frequent counsel and advice. His experience and knowledge were extremely valuable to the success of this program. Finally, R. M. Gifford, secretary for the Calcination Unit, made completion of this report possible. Several of the figures and drawings are attributed to her valued skills.

CONTENTS

EXECUTIVE SUMMARY	iii
ACKNOWLEDGEMENTS	ix
ACRONYMS	xiv
INTRODUCTION	1
Alternative Calcination Program Purpose And Scope	2
EXPERIMENTAL PROCEDURES AND RESULTS	4
Thermo-Chemical Studies	4
Thermodynamic Calculations	5
TGA/DSC Analyses	5
Crucible Calcination Study	8
Calcine Volatility Tests	10
Lab-Scale Calcination Mockup Tests	11
General Observations of the LSCM Results	12
Extent of Denitration	14
Particle Size Distribution	14
Safety Analysis Evaluation and Tests	14
Calciner Pilot Plant Tests	17
10-cm Calciner Pilot Plant Upgrade	18
10-cm Calciner Scoping Tests	18
10-cm Scoping Test Observations	18
10-cm Calciner Product Characterization	20
Aerosol-Size Fines Generation	22
Scrub Foaming Tests	22
Calcine Hydration Tests	23
Volatile and Semi-Volatile Analyses	23
30-cm Calciner Upgrade	25
Metal Alloy Corrosion Tests	25
Feed Makeup Studies	26
Sweetened Feed Rheology Measurements	26
Boric Acid Solubility Measurements	28
Sugar Digestion Scoping Tests	29
INTERPRETATION OF THE RESULTS	31
General Reaction Mechanism for High Temperature Flowsheet	31
General Reaction Mechanism for Sugar-Additive Flowsheet	32
Comparison of Flowsheets	33

CONTENTS (Continued)

Pollutant Emissions	36
Feed Make Up.....	36
Sugar/Organic Destruction in Nitric Solutions.....	37
RECOMMENDATIONS AND CONCLUSIONS	38
REFERENCES	41
Appendix A - Calcination History	
Appendix B - Rudiments of Fluidized-Bed Calcination	
Appendix C - Crucible Calcination Data	
Appendix D - Packed-Bed Calcine Volatility Tests	
Appendix E - Laboratory-Scale Calcination Mockup Studies	
Appendix F - 10-cm Calcliner Pilot Plant Scoping Tests	

FIGURES

Figure 1. Order of elevated temperature (E.T.) and sugar additive (S.A.) calcination activities (G97001)	iv
Figure 2. Equilibrium composition of major components in SBW G97002)	6
Figure 3.a. TGA/DSC thermograms for a SBW-type composition (G97003a).....	7
Figure 3.b. TGA/DSC thermograms for an SBW-Al mixture (AAR=1:1) (G97003b)	7
Figure 4. Comparison of TGA for standard SBW and SBW-ANN mixtures G97004)	9
Figure 5. Comparison of TGA for standard SBW and sugar mixtures (G97005)	9
Figure 6. Comparison of nitrate in LSCM calcine product and fines (G97006)	15
Figure 7. Comparison of the ratio of nitrate to alkali metals in LSCM calcine product and fines (G97007)	15
Figure 8. Comparison of nitrate weight percent in 10-cm calciner runs (G97008)	21
Figure 9. Comparison of the ratio of nitrate to alkali metals in product and fines from 10-cm calciner runs (G97009)	21
Figure 10. Matrix of solution mixtures and their measured viscosity (G970010).....	27
Figure 11. Comparison of calcine attrition resistance indexes (G97011).....	35
Figure 12. Comparison of calcine dissolution results in 8 M HNO ₃ (G97012).....	35

TABLES

Table 1.	Average composition of SBW in 2008.	3
Table 2.	Extent of Species Volatilization from heated SBW solids.	10
Table 3.	Distribution of volatiles downstream of heated calcine solids.	11
Table 4.	Summary of operating parameters and results for selected elevated temperature (E.T.) and sugar-additive (S.A.) LSCM runs	13
Table 5.	Sugar-additive safety issues and experimental studies.	16
Table 6.	Summary of operating parameters and measured results for 10-cm calciner high temperature (HT) and sugar-additive (SA) scoping runs.	19
Table 7.	Volatile organic analysis of pilot plant condensate and scrub solutions.	24
Table 8.	Semi-volatile organic analysis of pilot plant condensate and scrub solutions.	24
Table 9.a.	Solubility of boric acid in aluminum nitrate solutions at 25°C.	28
Table 9.b.	Solubility of boric acid in aluminum nitrate solutions at 50°C.	29
Table 10.	Solubility of calcium boride in nitric acid solutions.	29
Table 11.	Physical property data for selected compounds in calcine product.....	32

ACRONYMS

AAR	Aluminum in Alkali-Metal Ratio
ANL	Argonne National Laboratory
ANN	Aluminum Nitrate
ARI	Attrition Resistance Index
CAA	Clean Air Act
CFA	Central Facilities Area
CO	Carbon Monoxide
CSSF	Calcine Solids Storage Facility
DOT	U.S. Department of Transportation
DSC	Differential Scanning Colorimetry
EPA	Environmental Protection Agency
E.T.	Elevated Temperature
HAPs	Hazardous Air Pollutant
HEPA	High Efficient Particle (Filter)
INEEL	Idaho National Engineering and Environmental Laboratory
ICPP	Idaho Chemical Processing Plant
DOE	Department of Energy
HLW	High Level Waste
IR	Infrared
LEL	Lower Explosion Limit
LLW	Low Level Waste
LSCM	Lab-Scale Calcine Mockup
MACT	Maximum Achievable Control Technologies
Na-K	Sodium-Potassium Alloy
NAR	Nozzle Atomizing Air Ratio
NO _x	Nitrogen Oxides (NO ₂ and NO)
NWCF	New Waste Calcination Facility
P/F	Product-to-Fine Ratio
PICs	Products of Incomplete Combustion
S.A.	Sugar-Additive
SAR	Safety Analysis Report
SBW	Sodium-Bearing Waste
TGA	Thermal Gravimetric Analysis
UDS	Undissolved Solids
USQ	Unreviewed Safety Questions
WCF	Waste Calcining Facility

Alternative Calcination Development Status Report

INTRODUCTION

A Settlement Agreement (Court Order) between the State of Idaho and DOE requires that DOE complete calcination of sodium-bearing liquid high-level wastes by December 31, 2012. In order to meet this commitment, several options for treating the intermediate-level radioactive wastes referred to as sodium-bearing waste (SBW) are being considered. Historically, the radioactive liquid wastes have been converted into a free-flowing granular solid oxide (referred to as calcine). In order to calcine the SBW according to proven methods, a large amount of cold aluminum nitrate (ANN) will have to be added to the waste to prevent agglomeration in the bed and calcine storage bins. This practice will draw out the time required to calcine the inventory of SBW, making it difficult to meet the Settlement Agreement. It will also increase the mass of calcine that is generated, requiring significantly larger calcine storage space, and ultimately increasing the volume of waste that will be disposed to an approved long-term radioactive waste storage facility.

Two alternative calcination flowsheet concepts are being investigated by the INEEL High-Level Waste Program to increase the processing rate of SBW. The first concept involves the addition of sugar to the liquid waste as it is fed to the calciner. The sugar and nitrate salts undergo a basic oxidation-reduction reaction and produce a non-agglomerating metal-oxide product at the nominal calciner operating temperature of 500°C. This alternative is aptly named sugar-additive calcination. The second flowsheet concept involves elevating the calciner operating temperature to accelerate the decomposition of sodium and potassium nitrate to their oxide states. This alternative is referred to as elevated-temperature calcination (or high temperature calcination). The object of both flowsheets is simply to reduce the amount of cold chemical additive that must be added to the feed to produce acceptable calcine product. This will expedite calcination of the SBW inventory in compliance with the Settlement Agreement and will reduce the volume of calcine produced.

This report summarizes the progress and results of the activities that have been completed thus far on the development of the two alternative calcination flowsheets. Accomplishments include fundamental and laboratory calcination and volatilization studies, pilot plant calcination flowsheet development tests, and calcine product characterization and testing. An electrically-heated, lab-scale calcination mockup was set up and operated to demonstrate the feasibility of both flowsheets and to help establish the optimum amount of sugar and aluminum nitrate that should be used to calcine the SBW under the new test conditions. The 10-cm Calciner Pilot Plant (which is heated by an in-bed kerosene/oxygen flame in the same manner that the NWCF is heated) was upgraded for high temperature operation. Sugar-additive and high temperature calcination scoping tests were then completed. The results of these tests were compared to the results of a reference (or baseline) flowsheet run which was completed at 500°C with much larger amounts of aluminum nitrate and boron being added to the liquid feed to prevent agglomeration and α -alumina formation, respectively.

In addition to the flowsheet development studies, several supplementary laboratory tests were conducted to support NWCF process design modifications for possible deployment of the new flowsheets. Experiments were conducted to measure the mutual solubility and viscosity of SBW/sugar/aluminum nitrate feed blends. Tests were also completed to address several issues of concern that were identified by the research team and process design engineers, including, explosion

potential, accelerated vessel and offgas system corrosion, increased aerosol-size particulate generation, and increased calcine hygroscopicity. The purpose of these tests, and their results, are presented in this progress report.

Two appendices have been added to provide a broader understanding of waste calcination concepts. Appendix A gives a brief review of previous efforts to develop flowsheets for processing SBW. Appendix B discusses the rudiments of aqueous waste calcination to give better understanding of the physical and chemical mechanisms which govern the fate of the fuel and waste feed during calcination. This discussion is intended to provide a foundation for establishing assumptions to calculate or estimate pollutant emission factors which may be required in present and other potential environmental permitting activities.

Alternative Calcination Program Purpose And Scope

The main goal of the Alternative Calcination Development program is to develop and demonstrate a successful flowsheet that will increase the NWCF throughput in order to safely meet the Court Order Settlement Agreement. With this goal in mind, the following significant objectives also need to be met:

- Develop a flowsheet which requires minimal changes to the NWCF to minimize the process retrofit costs and implementation schedule.
- Minimize the amount of chemical additives required to process the sodium-bearing waste to conserve the calcine solids bin set storage space.
- Demonstrate fluidized-bed calciner operability with respect to bed and system stability and the absence of bed agglomeration.
- Produce a calcine that is pneumatically transportable and retrievable.
- Produce a calcine that is soluble in nitric acid solutions.
- Produce a calcine that is safe to transport, store, and dissolve.
- Control species volatilization and fines generation to an acceptable level.
- Produce a calcine that is chemically compatible with future waste immobilization processes.

The research activities undertaken to develop alternative calcination flowsheets, and also to provide essential process design data, are outlined in Figure 1 (see Executive Summary). Most of the information provided in this report has been documented in internal company letters and reports. The main purpose of this report is to summarize the current accomplishments in a single document which can be more easily tracked and cited. Additional information can be obtained by contacting the experimenters identified in the acknowledgments section of this report and in the accompanying Appendices describing the experimental activities.

The experiments and pilot plant tests were conducted with a standard solution of SBW. The projected composite composition of all SBW in the tank farm in the year 2008 is listed in Table 1. The standard solution was prepared from chemical reagents in a manner that would simulate the complex mixture. It is important to recognize that the results presented herein are for this standard SBW simulant and that the tank farm solutions currently vary widely, although it is anticipated that the compositions in later years will be more uniform.

Table 1. Average composition of SBW in 2008.

Component	Conc. In 2008 Simulated SBW (M)
H	1.59e+00
Al	6.92e-01
B	1.95e-02
Cd	2.99e-03
Ca	5.71e-02
Cl	3.57e-02
Cr	3.87e-03
F	7.64e-02
Fe	2.29e-02
Hg	1.20e-03
Mn	1.28e-02
Mo	6.65e-04
Ni	1.71e-03
NO ₃	5.99e+00
Pb	1.49e-03
PO ₄	14.6e-02
K	2.21e-01
Na	2.049e+00
SO ₄	5.46e-02
Zr	3.24e-03

EXPERIMENTAL PROCEDURES AND RESULTS

Thermo-Chemical Studies

Various chemicals are typically added to the calciner feed to; 1) control agglomeration, 2) suppress the release of volatile species, 3) control attrition, and 4) prevent the formation of hygroscopic^a compounds. A review of the established knowledge base (summarized in Appendix A) was conducted to identify potential flowsheet chemistries which could meet these process objectives. Thermodynamic calculations were completed for the candidate flowsheet systems in conjunction with basic thermogravimetric analyses (TGA), differential scanning calorimetry (DSC), and X-ray diffraction and fluorescence analysis of the calcined product. The chemical thermodynamic calculations were completed using the commercial HSC code for multi-component, multi-phase systems.² The thermograms (TGA and DCS profiles) also provided insight into phase and chemical transformations. The results were interpreted and used to help screen the flowsheets and to help elucidate the calcine product compositions.

The main difficulty to processing the sodium-bearing waste is particle agglomeration due to the persistence of alkali nitrates in the calcine at typical calcination temperatures and residence times. Both the elevated temperature and sugar-additive flowsheet options are intended to improve the waste denitration kinetics. However, it was recognized that the alkali oxide products (Na_2O and K_2O) resulting from complete denitration of the sodium-bearing waste are hygroscopic and are easily converted to alkali hydroxides which are also deliquescent,^b and have low melting points (*viz.*, 318°C for NaOH and 360°C for KOH). Therefore, it was hypothesized that an amphoteric metal,^c such as aluminum, silica, iron, or titanium, could be added to the waste feed to combine with the alkali metals. The anticipated result was the formation of an alkali-aluminate (or silicate, ferrite, titanate, *etc.*) solid that would be less hygroscopic and have a higher melting point.

Calcium nitrate is typically added to the calciner feed to bind up the chloride and fluoride ions. The alkali metals also react with the halide ions to produce low-volatility salts. Based on previous experience, the calcium nitrate was added to the feed to raise the molarity of calcium in the feed to twice the sum of chloride, fluoride, phosphate, and sulfate. Parametric testing on the optimum amount of calcium nitrate to add to the feed still needs to be completed.

The attrition resistance index (ARI) of the calcine is a function of the calcine micro hardness and brittleness, crystalline lattices, and surface irregularities. The formation of crystalline α -alumina has been shown to increase the ARI and erosivity of the calcine. The addition of boron to the feed suppresses the formation of crystalline α -alumina. Initially, the calcination studies were conducted without adding any boron to the mixture. Micrographs of the product revealed that no significant amount of α -alumina was produced in the calcine. While additional tests are needed to confirm this conclusion, this result will be further investigated in future pilot plant calciner tests.

^a A solid (usually a salt compound) which takes up moisture.

^b A solid which dissolves gradually and becomes a liquid by attracting and absorbing moisture.

^c A metal which is capable of reacting either as an acid or a base.

Thermodynamic Calculations

In order to gain an understanding of the potential products formed during calcination of the SBW, a series of equilibrium computations were completed for standard SBW and mixtures of SBW and selective additives. The calculations provided insight into specific metalloids and mole ratios to use to bind up the sodium in more stable components. The additives that were studied were selected on the basis of their ability to combine with the alkali metals. These calculations provided guidance to the laboratory calcination tests which were subsequently completed. The predictions revealed, for instance, that a 1:1 stoichiometric ratio of aluminum to alkali metals would sufficiently bind up all of the sodium and potassium as alkali aluminate compounds at temperatures above 500°C. Similar results were obtained for the other candidate metal additives.

Based on the theoretical and experimental results, aluminum nitrate was selected as the best additive to use in the subsequent pilot plant calcination studies. Aluminum nitrate is commercially available in a ~2.2 *M* solution and it achieves the desired performance objectives; namely, it combines with the sodium and potassium to form an aluminate product which is less deliquescent than sodium and potassium hydroxide, but which is still dissolvable in nitric acid scrub and dissolver solutions.

The results of thermodynamic calculations are tabulated in Appendix C. Figures 2.a and 2.b plot the weight fraction of the major compounds that should exist in the equilibrium product, assuming that the mixture is homogeneous and that intermediate product phases do not occur. Obviously, the assumption of mixture homogeneity is invalid if a secondary phase should form. Under such circumstances, mass diffusion and kinetic limitations can prevent the product from reaching the mixture equilibrium composition. In spite of this shortcoming, it is still instructive to study the equilibrium composition. Some of the important observations of the equilibrium calculations are:

- $\text{Al}(\text{NO}_3)_3$ is quickly hydrolyzed to AlOOH by 200°C.
- AlOOH is gradually converted to Al_2O_3 and NaAlO_2 from 200-500°C.
- NaNO_3 is gradually converted to NaOH and NaAlO_2 from 200-600°C.
- The yield of NaAlO_2 primarily depends on the limiting reactant, either sodium or aluminum, with the excess constituent being converted to other oxides.
- KNO_3 reacts in a similar manner as NaNO_3 to form KOH , KAlO_2 , etc.

TGA/DSC Analyses

Figures 3a and 3b show the TGA and corresponding DSC for standard SBW and an SBW-aluminum nitrate feed mixture.^d While the equilibrium calculations predict complete denitration at around 500°C, the TGA/DSC reveal that the mass loss associated with heating the standard SBW continues up to 900°C while mass evolution is complete at around 650°C for the SBW-aluminum-nitrate mixture. Other observations include:

^d The TGA and DSC shown in this report are actually for a low-level SBW which is chemically similar to the standard 2008 SBW composition.

a. Standard SBW (no additives)

b. Equimolar Al and alkali-metal ratio (AAR=1:1) in the feed.

Figure 2. Equilibrium composition of major components in SBW (G97002).

Figure 3.a. TGA/DSC thermograms for a SBW-type composition (G97003a).

Figure 3.b. TGA/DSC thermograms for an SBW-ANN mixture (AAR=1:1) (G97003b).

- Standard SBW evolves mass at a uniform rate up to around 600°C at which point there is a rapid evolution of mass, subsequently followed by more mass loss up to 850°C.
- The admixture composition shows a sudden mass loss at around 300°C, as well as at around 600°C. The first inflection in the mass curve is likely associated with the conversion of AlOOH to NaAlO and/or Al_2O_3 and possibly the melting of NaNO_3 and KNO_3 .
- The decomposition reactions, as well as phase changes are generally endothermic processes.

Crucible Calcination Study

Laboratory crucible calcination tests were next conducted to investigate the gross behavior of the calcination process and the evolution of volatile species at elevated temperature and mixture conditions. Several additives were studied initially, including activated aluminum (Al_2O_3), amorphous silica (SiO_2), 2.2 M aluminum nitrate nano-hydrate [$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] solution, boric acid (H_3BO_3), iron(III) oxide (Fe_2O_3), and vanadium(V) oxide (V_2O_5). The mixture solutions were dried at low temperature in a beaker and then were placed in 100 ml, inert α -alumina crucibles. The crucibles were placed in a drying oven at 150°C for approximately 24 hours to remove the remainder of the free moisture. The crucibles were then placed in an electric muffle furnace at 200°C for 24 hours. The oven temperature was increased in increments of 50°C every 24 hours after recording the mass loss. The results of the complete battery of crucible calcination tests are shown in Appendix C. Only the results of the SBW-ANN mixture are discussed here.

Figure 4 shows a comparison of the crucible calcination tests completed for standard SBW and SBW-ANN mixtures. The calcine exhibits a monotonic decrease in mass up to at point where mass evolution suddenly increases. The addition of aluminum shifts the temperature at which the sudden decrease in mass is measured. For an Aluminum to Alkali-metal Ratio (AAR) of 1.5:1, mass evolution is complete by 600°C. This is approximately 25°C less than a mixture with a 1:1 AAR and it is approximately 200°C lower than standard SBW calcine. X-ray diffraction analyses of the product are tabulated in Appendix C.

Attempts were made to study the calcination behavior of SBW-sugar mixtures. Gram quantities of standard SBW and sucrose were mixed, dried, and heated in the muffle furnace. As the solutions were heated, the sucrose began reacting with the nitric acid, causing the solution the froth due to the rapid evolution of NO_2 and CO_2 gases. This continued until the solution evaporated to a dry cake. At approximately 300°C the dried mixture ignited and burned as an incendiary mixture. Under these conditions, it was difficult to contain the ash-like product in the aluminum crucible. Figure 5 shows the approximate mass as a function of temperature. Due to the incendiary behavior of the solids, no attempts were made to obtain TGA/DSC thermograms.

Other observations include:

- Some minor differences between the crucible calcination tests and the TGA/DSC thermograms are noticeable. The differences are due to the different sample sizes and heating rates; neither are equilibrium processes.

Figure 4. Comparison of TGA for standard SBW and SBW-ANN mixtures (G97004).

Figure 5. Comparison of TGA for standard SBW and sugar mixtures (G97005).

- The evolution of NO₂ (a brown gas) was observed during at the high temperatures, indicating that component denitration was occurring above 500°C.
- X-ray diffraction analysis of the standard SBW product verified that NaNO₃ was a major component at both 500 and 600°C. NaAlO₂ was not detectable in the 500 or 600°C product.
- X-ray diffraction analysis of the SBW-ANN mixtures showed that the presence of NaNO₃ decreased with temperature while the presence of NaAlO₂ increased with temperature.
- The percentage of NaAlO₂ in the product increased from an estimated 52% to 66% as the amount of aluminum was increased from an AAR of 1:1 to 1.5:1. This indicates that a greater amount of Al is required to bind up a majority of the Na as an aluminate compound.

Calcine Volatility Tests

In parallel with the crucible calcination study, experimental tests were completed to determine the effects of elevated temperature on the volatility of radionuclides and hazardous constituents which may impact the offgas treatment system or environmental operating permits. The major volatile components include Cs, Tc, Hg, Cd, NO_x, Cl, and F. An experimental setup was designed to study the devolatilization of these species from standard SBW over 500-850°C and to determine their potential for accumulation in specific offgas equipment such as the scrub system. Calcine solids were prepared at 60°C with cold chemicals and radioactive tracers. A schematic of the test apparatus and a description of the experimental methods is provided in Appendix D.

The results of the tests are tabulated in Tables 2 and 3. Table 2 lists the percentages of the volatile constituents that were released from the calcine bed as a function of bed temperature. Table 3 lists the distribution of the volatile species in the various parts of the test apparatus representing conditions that exist in the actual NWCF offgas system.

Table 2. Extent of Species Volatilization from heated SBW solids.

Species	% Volatilization ^a at 500°C		% Volatilization ^a at 650°C		% Volatilization ^a at 850°C	
	Run #1	Run #2	Run #1	Run #2	Run #1	Run #2
1E-3M Cs	21±8	29±6	54±5	71±5	100	87±4
1E-5M Cs	9.2 ^b	9.2 ^b	27±6	19±6	nm	nm
⁹⁹ Tc	9±2	8±2	43±5	41±4	nm	nm
Hg	100	100	100	100	100	100
Cd	0	0	0	0	1	0
Cl	98±6	98±6	97±7	97±6	90±4	82±8
F	37±4	43±3	31±5	16±3	89±22	59±23

nm = not measured

a. All data are for 6 hour runs. Tests of 4 hour duration at 500°C and 650°C resulted in 93% and 98% chloride volatilization respectively. A 12 hour run at 650°C resulted in 28±7% Cs volatilization.

b. An estimate based on the 60% reduction in volatilization due to lower concentration observed at 650°C.

Table 3. Distribution of volatiles downstream of heated calcine solids.

Species	Percent Distribution						% Recovered
	Chimney	Transfer Tube	Bubbler #1	Bubbler #2	Condenser	Filter	
Cs	2.3	23	9	14	0.1	2.5	54±10 ^a
⁹⁹ Tc	3.9	50	24	2.7	0	0.5	79 ^b
Hg	0	0	100	5	0	nm	100 ^c
Cl	0.5	0.5	52	40	1.0	0.3	94±4.7 ^d

nm = not measured

a. Average of 4 runs at 650°C.

b. Average of 2 runs at 650°C. Volatilization at 500°C was too small for significant measurements.

c. Average of 6 runs in 500-850°C range.

d. Average of 7 runs from 500-650°C.

The following significant observations were made from the volatility data:

- All of the volatile components, with the exception of Cd and ⁹⁹Tc, exhibited high volatilities at 850°C.
- ¹³⁷Cs, ⁹⁹Tc, and F volatility showed a dependence on temperature and on concentration.
- Mercury is completely volatilized at all calcination temperatures. Mercury is most likely released as HgCl₂, or as nitrate decomposition products (predominately HgO).
- Nearly 100% of the Cl is volatilized, indicating that the Cl is not tied up as a non-volatile salt such as NaCl or CaCl₂. However, this result is contrary to pilot plant test results which showed high amounts of Cl being retained in the product.
- Calcium may not retain Cl as effectively as desired.
- The majority of the ¹³⁷Cs and ⁹⁹Tc accumulated in the apparatus transfer tube and bubblers, indicating that it will likely concentrate in the NWCF scrub solutions. However, a small amount passed through the system and was collected on the filters. A small increase in ⁹⁹Tc stack emissions may result due to the purging of HTcO₄ from the offgas scrub solutions.
- Almost all of the Cl and Hg was captured by the bubblers, indicating that these constituents will accumulate in the NWCF scrub solutions.

Tests with SBW-sugar mixture were not made due to the potential safety risks associated with the ignition and sudden reaction of a large mass of calcine in the packed bed.

Lab-Scale Calcination Mockup Tests

An indirect-heated, lab-scale calcination setup was used to conduct flowsheet "proof-of-concept" and scoping tests. This setup is now called the Lab-Scale Calciner Mockup (LSCM). The primary objective of the LSCM tests was to confirm that high temperature calcination could be successfully controlled in a fluidizing-bed environment where: (1) the residence time is limited and the chemistry may be rate limiting, (2) fresh feed is continuously sprayed on the calcine product, and (3) the contact

between the calcine and oxidizing air is more intimate. Sugar-additive tests were completed to verify the reported results of earlier studies and to establish parameter boundaries for this flowsheet.

A description of the LSCM setup, test methods, and test results is provided in Appendix E. Approximately 30 separate calcination tests were completed with this setup, including several continuous calcination runs lasting up to 60 hours. The effects of calcination temperature, sugar addition, and other chemical additives on the calcine product quality and calcine bed behavior were evaluated. The product was analyzed for nitrate, aluminum, carbon, and crystalline phases. The particle size distribution, densities, attrition indexes, dissolution behavior, and hydration behavior were measured. The offgas was monitored to determine the level of combustible hydrocarbons produced during sugar-additive calcination. Dust explosion and oxidizer classification tests were also completed with the sugar-additive calcine product. With this information, offgas and product explosion concerns for the 10-cm Calciner Pilot Plant tests were allayed.

For convenience, the significant parameters and data of the successful extended-run tests are tabulated in Table 4. Each consecutive tests is identified with a Run number. Run 12 is a baseline (or reference) test where a large amount of aluminum nitrate is added to the feed to allow SBW to be calcined at 500°C. Typically, an aluminum to alkali-metal ratios (AAR) of 3.5:1 is considered adequate to calcine the SBW at the normal operating temperature. However, this depends on the specific tank composition. Recent 15-cm Calciner Pilot Plant flowsheet verification tests for the 1997-98 NWCF campaign demonstrated that the projected feeds could be calcined with slightly less aluminum nitrate additive (i.e., AAR=3.1:1). Nevertheless, the baseline test at an AAR of 3.5:1 provided a consistent comparison of the proposed flowsheets with the accepted practice.

General Observations of the LSCM Results

Several observations were made during the LSCM testing; the most important being the fact that after a system shakedown was completed, both the elevated temperature calcination flowsheet and the sugar-additive flowsheet could be successfully controlled. In spite of problems with achieving significant feed flow (due to electrical heating limitations), and frequent plugging in the sintered metal offgas filter, and also nozzle plugging (due to heat convection to the feed nozzle body), a better understanding of both flowsheets was accomplished. The following observations are derived from the data shown in Table 4.

- The bed turn over is lower than desired to arrive at conclusive observations.
- The amount of nitrate in the final bed decreases with increasing temperatures.
- The product to fines ratio is generally low (i.e., <1.25) for the high temperature runs and decreases as temperature increases (due to increased flash evaporation).
- The product to fines ratio for the sugar-additive flowsheet is acceptable for two of the sugar additive runs (>1.25), with the exception being Run 29.
- The amount of residual organic carbon in the sugar-additive calcine is less than 2% and is less than administrative limits for ensuring the safety of operations.

Table 4. Summary of operating parameters and results for selected elevated temperature (E.T.) and sugar-additive (S.A.) LSCM runs.

Flowsheet Run Number	baseline 12	E.T. 11	E.T. 20	S.A. 28	S.A. 29	S.A. 32
Temperature (°C)	500	600	625	500	500	500
Target AAR	3.5	1.5	1.5	1.0	1.5	SBW
Actual AAR	4.0	1.74	1.44	1.0	1.5	0.31
C:NO ₃ mole ratio ^ψ	na	na	na	1.25	1.25	1.5
Duration (hr)	60	43	40	21.2	28.4	13.2
Feed Rate (L/hr)	0.37	0.47	0.53	0.59	0.55	0.58
Total Feed Calcined (L)	22.2	20.2	21.2	28.6	38.3	15.3
SBW Processed (L)	6.0	10.0	11.3	13.7	14.2	13.2
NAR	1263	724	1188	946	1015	962
•Product/Fines ^ε (weight ratio)	1.23	0.95	0.72	1.5	0.7	3.0
•Bed Turnover %	48	45	39	44.8	48.4	32.1
•wt% NO ₃ in Final Bed	12.3	7.98	4.41	10.7	11.0	6.39
•wt% NO ₃ in ave. Fines	21.6	27.1	25.3	22.9	19.6	19.6
•Mole ratio NO ₃ /Na+K in Final Bed	0.80	0.27	0.15	0.26	0.31	0.13
•Mole ratio NO ₃ /Na+K in ave. Fines	1.1	0.78	0.73	0.50	0.50	0.30
•Mole-ratio Al/Na+K in Final Bed	5.7	3.1	2.8	1.7	2.2	1.3
•Mole-ratio Al/Na+K in ave. Fines	4.0	1.7	1.8	0.94	1.4	0.41
•wt% Organic C in Final Bed	nm	nm	nm	0.03	.030	.03
•wt% Inorganic C in Final Bed	nm	nm	nm	0.20	.44	1.7
•wt% Organic C in ave. Fines	nm	nm	nm	1.1	1.7	0.44
•wt% Inorganic C in ave. Fines	nm	nm	nm	1.3	1.1	4.2
ARI	77	34	49	65.4	82.6	95.6
wt% UDS in 8 M HNO ₃	21.9	na	22	10.8	10.7	11.9
^ψ C:NO ₃ ratio of 1.25 is considered to be approximately stoichiometric. ^ε Does not include the fines lost to the offgas filter.						

- The attrition resistance index for the sugar-additive runs is generally higher than the high temperature runs.
- The dissolution rate of the high temperature fines is equivalent with the baseline run, while the sugar-additive fines are more soluble in acidic solutions.

Extent of Denitration

The chief objective of the alternative flowsheets is to decompose the nitrates which are primarily responsible for agglomeration of SBW calcine. Figure 6 plots the average nitrate content measured in the calcine and fines for each run. Figure 7 plots the mole ratio of nitrate and alkali metals in the product to determine the percentage of alkali nitrates that possibly exist in the solids. The data in these Figures show:

- Significantly high denitration occurs with both the elevated temperature and sugar-additive extended tests.
- The high temperature fines contain higher levels of nitrates due to flash evaporation and rapid elutriation of fine particles. This may lead to fines agglomeration in the fines cyclone separation and fines column if the temperature in these regions exceeds the melting point of NaNO_3 .
- The nitrate concentration in the sugar-additive flowsheet fines and product is low due to rapid chemical denitration.

Particle Size Distribution

A comparison of the particle size distributions for the alternative flowsheets with the baseline run are provided in Appendix E. The sugar additive runs resulted in a relatively low amount of fines. Conversely, the high temperature flowsheet produced more fines. The primary concern is that the high temperature fines may be characteristically smaller, resulting in offgas filtration plugging. Analysis of samples from the sintered metal filter are similar but these may be biased by electrostatic coalescence or chemical interactions of the particles.

Safety Analysis Evaluation and Tests

Safety concerns associated with the sugar-additive flowsheet were identified and a preliminary evaluation of each concern was completed to establish pilot plant operating safety procedures and to provide data to help calculate potential process safety risks. An explosion chemist/consultant was contracted to participate in a safety evaluation of the sugar-additive flowsheet.³ A cross section of personnel in technology development, process design, plant operations, and industrial safety participated in this evaluation.

Figure 6. Comparison of nitrate in LSCM calcine product and fines (G97006).

Figure 7. Comparison of the ratio of nitrate to alkali metals in LSCM calcine product and fines (G97007).

Table 5 lists the categories of safety concerns and the testing that was completed to address each issue. Each credible concern was investigated through laboratory and field tests. A test matrix to study sugar-nitrate interactions in sweetened feeds and in the calcine product was designed to address concerns pertaining to the explosion potential of the sugar additive flowsheet. An internal report is being prepared to document these results.⁴ An offgas monitor was used to verify that the level of combustible hydrocarbons in the offgas remained below the lower explosion limit. The calcine product and calciner effluent solutions were periodically analyzed during the lab-scale and pilot plant calcination tests to

Table 5. Sugar-additive safety issues and experimental studies.

Concern:	Formation of nitro-sugars in SBW-sugar feed and/or nitrated organics in scrub solution mixtures.
Studies:	1. SBW and Scrub sugar-nitrate chemical interaction tests. Solutions aged for 14 days. IR analysis at prescribed intervals to detect the formation of nitro-sugars (~100 ppm lower detection limit). 2. Thermal "cookoff" qualitative observations (noted by INEEL explosion technologist). 3. Thermal sensitivity and shock sensitivity tests. 4. Analysis of spent scrub solution for total organic carbon and nitrated organics.
Results:	1. No physically detectable nor measurable evidence of nitrated sugars in solutions. 2. Solutions offgas NO _x until dry, then burn as an incendiary mixture at ~300°C. 3. No evidence of explosive behavior recorded. Scrub solutions contained less than 1% total organic carbon. Levels of nitrobenzene and other detectable semi-volatile nitrated organics in the scrub were comparable to non-sugar-additive 15-cm calciner tests (See Tables 7 and 8).
Limitation:	The absence of a secondary organic phase (i.e., insoluble nitrated sugars), although unlikely, due to the solubility of partially nitrated sugars, was not proven. Additional tests are recommended prior to large scale, continuous mixing of sugar with SBW.
Concern:	Solid state calcine explosion potential in the calciner bed, or Calcine Solids Storage Facility.
Studies:	Surrogate calcine-sugar (or sugar char) mixtures subjected to friction, spark, impact, thermal, and shock/explosion sensitivity tests, per U.S. Bureau of Mines standard procedures.
Results:	No detectable evidence of explosion behavior exhibited by samples for all tests.
Limitations:	Actual sugar-flowsheet calcine was not tested. The small volumes tested may not bound bin-set storage conditions. Tests for larger geometries should be completed. ⁵
Concern:	Solid state calcine explosion potential in the calciner bed, or Calcine Solids Storage Facility.
Studies:	1. Surrogate calcine-sugar (or sugar char) mixtures subjected to friction, spark, impact, thermal, and shock/explosion sensitivity tests, per U.S. Bureau of Mines standard procedures. 2. Calcine fines tested for classification as a DOT oxidizer (i.e., readily give up oxygen to promote the reaction of a combustible material). ⁶
Results:	1. No detectable evidence of explosion behavior exhibited by samples for all explosion tests. 2. Calcine fines do not behave as DOT-defined oxidizers.
Limitations:	Test with 10-cm calcine fines should be made to strengthen these conclusions.
Concern:	Gas-phase explosion due to the sum of unburned kerosene and sugar pyrolysis products in the calciner vessel and/or offgas treatment system.
Studies:	On-line measurement of the Lower Explosion limit (LEL) during LSCM and 10-cm Calciner Pilot Plant runs.
Results:	Offgas concentration measurements were less than 40% of the LEL.
Limitations:	None
Concern:	Dust explosion of the calcine fines in offgas containing unburned hydrocarbons.
Studies:	Outside consultant subcontracted to study calcine reactivity and to conduct dust explosion tests per U.S. Bureau of Mines standard dust explosion test methods. Sugar-additive fines from the LSCM tested in air and an explosive mixture of propane. ⁷
Results:	The calcine fines are not explosive at any concentration in air. The fines suppress the explosion energy of a propane mixture. ⁷
Limitations:	None. Tests are conservative.

ensure that residual (and potentially reactive) organic carbon levels remained below the levels which were tested in the field and found to be non-explosive.

The results of the nitrate-sugar interaction tests and surrogate calcine explosions sensitivity tests were sufficient to screen unreviewed safety questions (USQ) prior to performing sugar-additive flowsheet tests in the LSCM. Offgas monitoring during the LSCM and dust explosion tests with the fines provided the necessary data to conduct a USQ screening for the 10-cm calciner sugar-additive tests.

Calciner Pilot Plant Tests

Three calciner pilot plants are available for calcination studies at the ICPP; in order of increasing bed diameter, they are the 10-cm, the 15-cm, and the 30-cm Calciner Pilot Plants (see related discussion in Appendix A). All three calciners are heated by in-bed kerosene/oxygen combustion. The 10-cm calciner is primarily used to conduct flowsheet development parametric studies. It is the least expensive to operate and generates the least volume of waste; however, it has limited ability to study particle mechanics because it operates as a slugging bed rather than a bubbling bed. The 15-cm calciner has twice the cross sectional area as the 10-cm calciner but it is uncertain whether it operates in a slugging-bed or bubbling-bed mode. Throughout the course of this research program, the 15-cm calciner was being used to demonstrate standard flowsheets for the 1997/98 NWCF campaign and, therefore, was unavailable for alternative flowsheet development work. The 30-cm calciner operates as a bubbling bed; hence, it is better suited to investigate particle growth, particle attrition, and particle elutriation from the bed. The offgas treatment system of the 30-cm calciner is also similar to the full-scale facility which makes it more suitable for investigating the fate of the gaseous and particulate emissions from the calciner vessel. Unfortunately, the 30-cm calciner requires over 500 person-hours to operate while generating over 1,000 gallons of liquid waste per test. Operating costs for a single test currently can exceed \$100,000.

Plans were made to retrofit both the 10-cm and 30-cm calciners for sugar-additive and high temperature tests. The upgrades to the 10-cm calciner were completed and scoping tests commenced in 1996.

10-cm Calciner Pilot Plant Upgrade

Several modifications were made to the 10-cm calciner to make it possible to conduct the high-temperature tests. A new reactor zone was fabricated and the particle disengaging section was lengthened to reduce fine particulate elutriation. A particle impactor-collector was added to the system to collect aerosol-size fines in the offgas. An on-line monitor was used to draw a sample from the offgas to measure the levels of unburned and burned hydrocarbons in the offgas. An electrical heat tape was added to the primary cyclone separator, under the jacket of insulation, to help alleviate moisture condensation and particle hydration in this piece of equipment.

10-cm Calciner Scoping Tests

A series of five scoping tests were conducted in the 10-cm calciner to evaluate both the elevated-temperature and sugar-additive flowsheets. The first test, SBW-BL-1, was conducted using the baseline flowsheet. This test was completed to serve as a comparative reference for the alternative flowsheets. Two high-temperature calcination tests, SBW-HT-1 and SBW-HT-2, were conducted to compare the effects of temperature and aluminum to alkali-metal ratio (AAR) variations. Two sugar-additive tests, SBW-SA-1 and SBW-SA-2, were completed to compare the effects of varying the AAR. SBW-SA-2 resulted in agglomeration of the bed and was discontinued before the test was completed. An internal report was prepared to document the results of these tests. The body of this report is included as Appendix F. For convenience, a list of the significant test variables and results are compiled in Table 6.

10-cm Scoping Test Observations

Several observations were made during the tests; most of these are summarized in the status report that is appended to this report. Most importantly, the scoping tests show that the alternative flowsheets can accomplish the most important objective of overcoming bed agglomeration by destroying the alkali nitrates in the feed. The results in Table 6 indicate:

- Bed turnover is higher than the LSCM tests due to higher feed rates and longer operating periods.
- The carbon content in the fines is less than the administrative limits set to ensure the safety of operations.
- The products of the alternative flowsheets are more soluble in 2 M HNO_3 (scrub simulant) and 8 M HNO_3 (concentrated dissolver acid) than the baseline flowsheet.
- The high temperature flowsheets resulted in the lowest nitrate content in the product with corresponding higher amounts of nitrate in the fines (compared to the sugar-additive flowsheet).

Table 6. Summary of operating parameters and measured results for 10-cm calciner high temperature (HT) and sugar-additive (SA) scoping runs.

Run Designation	SBW-BL-1	SBW-HT-1	SBW-HT-2	SBW-SA-1	SBW-SA-2
Temperature (°C)	500	650	600	500	500
Target AAR	3.5	1:1	1.5:1	1:1	0.305:1
Actual AAR	3.54:1	0.98:1	1.48:1	1.04:1	-
C:NO ₃ mole ratio ^ψ	na	na	na	1.3	1.4
Kerosene (cm ³ /min)	7.8	10.6	8.2	6	6
Duration (hr)	40	38	58.5	45	14.5
Feed Rate (L/hr)	1.9	2.0	1.5	1.5	1.63
Total Feed Calcined (L)	76	76	88	68	24
SBW Processed (L)	14	33	30	23	-
NAR	1281	995	1047	1189	908
•Product/Fines ^ε (wt. ratio)	1.2	2.6	13.3	2.0	-
•Ave. Product Bulk Density (g/cm ³)	1.1	1.28	1.17	1.22	-
•Ave. Fines Bulk Density (g/cm ³)	0.56	0.65	0.69	0.27	-
•Bed Turnover %	92.9	83.0	92.2	90.3	-
•wt.% NO ₃ in Final Bed	16	4.1	4.2	7.4	-
•wt.% NO ₃ in ave. Fines	15.	13.	13.	10.	-
•mole-ratio NO ₃ /Na+K in Final Bed	0.72	0.077	0.092	0.15	-
•mole-ratio NO ₃ /Na+K in ave. Fines	0.74	0.33	0.42	0.18	-
•wt% Organic C in Fines at COT 2	-	-	-	0.8	-
•wt% Organic C in Fines at COT 5	-	-	-	1.2	-
•ARI	31	60	86	92	-
•wt% UDS in 8 M HNO ₃	8.9	4.5	4.7	6.5	-
•wt% UDS in 2 M HNO ₃	40	2.9	7.6	2.4	-
•% CO in offgas stream	0.7	0.7	0.5	4.8	-
•% CO ₂ in offgas stream	7.8	11.5	22.	15	-
•% LEL of offgas stream	7.8	9.0	9.0	39	-
^ψ Ratio of carbon in the additive sugar to nitrate in the feed. A C:NO ₃ ratio of 1.25 is considered to be stoichiometric. ^ε Average P/F ratio in calcine measured during tests at various times.					

- The feedrate of kerosene required to achieve 600°C is approximately the same as the feedrate to maintain the bed temperature at 500°C. This is attributed to a decrease in the liquid waste feed rate and an increase in combustion efficiencies.
- No specific trends with respect to calcine attrition resistance index are evident.
- The product bulk densities are similar, with the high temperature flowsheet yielding the product with the highest density.
- The density of the sugar additive flowsheet fines is significantly less than the baseline and high temperature runs.
- The product to fines ratio for the alternative flowsheets is higher than the baseline; however, the measurements may not reflect actual conditions due to frequent plugging in the cyclone separator.
- The offgas data show that CO emissions rates decreased at the higher temperatures but increased during sugar-additive calcination.
- The sugar-additive flowsheet results in a significantly higher level of unburned hydrocarbons (generally low molecular weight hydrocarbons) which are presumably the products of sugar-pyrolysis. The LEL of 39% is slightly below the administrative limit of 50% that was set to ensure safe operations.

10-cm Calciner Product Characterization

Analyses of the product and effluent streams lead to several other key observations and conclusions. The following were determined; (1) calcine attrition indexes, (2) calcine dissolution in standard scrub solutions and concentrated nitric acid, (3) calcine hydration properties, (4) bed and fines particle size distributions, and (5) calcine physical and chemical properties, including bulk and true density, carbon content, nitrate content, and crystalline and amorphous phase compositions. In addition, solid and solution analyses were completed for the pilot plant tests to help close the overall and individual component material balances and to help elucidate the process chemistry.

Figure 8 plots the average nitrate measured in the calcine and fines for each 10-cm calciner run. Figure 9 plots the mole ratio of nitrate and alkali metals in the product to determine the percentage of alkali nitrates that exist in the solids.

The results are similar to the LSCM tests. The baseline flowsheet results in a higher level of nitrate in the product, in spite of having 2-3 times the amount diluent mass in the product. The high temperature flowsheet achieves the lowest concentration of nitrate in the product, but has a higher level of nitrate in the fines compared to the sugar-additive flowsheet. Figure 9 indicates that most of the alkali metals in the baseline flowsheet exist as nitrate salts. Conversely, the alkali nitrates are converted to oxide compounds at elevated temperature or by the sugar reducing agent.

Figure 8. Comparison of nitrate weight percent in 10-cm calciner runs (G97008).

Figure 9. Comparison of the ratio of nitrate to alkali metals in product and fines from 10-cm calciner runs (G97009)

Other significant observations from the test results and product analyses include:

- Chloride retention in the product was highest for the sugar-additive flowsheet (79%) compared to the baseline flowsheet (41%) and the high temperature flowsheets (33% and 56%, for SBW-HT-1 and SBW-HT-2, respectively).
- Fluoride volatility generally coincided with the chloride volatility results (52%, 24%, 39%, and 72%, for SBW-BL-1, SBW-HT-1, SBW-HT-2, and SBW-SA-1, respectively).
- The fines for both the high temperature and sugar additive flowsheets resulted in severe plugging of the offgas cyclone (which is cooler than the NWCF cyclone). This was attributed to increased hygroscopicity of the product in the relatively cool cyclone separator and fines collection line.
- Post-run analysis of the fines distribution exhibited small differences in particle size distributions.
- The bed particle size distribution for the tests were within the NWCF acceptance range (0.3 to 0.5 mm); however, the bed had not stabilized by the end of the tests and some large particles, indicative of the onset of particle agglomeration, were observed in the final bed.
- Little or no α -aluminum was detected in the high temperature product even though boron was not added to the standard SBW-ANN feeds. The X-ray diffraction data also confirmed the presence of alkali nitrates in the baseline flowsheet product. Alkali-aluminates were present in the high temperature product, while the amount of alkali-nitrates in the product were very low. The level of alkali nitrates in the sugar-additive product was also low.

Aerosol-Size Fines Generation

On-line measurement of the fines particle distribution was attempted using a particle-cascade impactor. The data obtained from this device are published in the Conceptual Design final report.¹ The generation of fines smaller than 2 μm is a concern during calcination due to the ability of the particles to slip through most of the NWCF offgas system, resulting in HEPA filter plugging. The limited data collected to date do not provide conclusive evidence that either the high temperature or sugar-additive flowsheet results in excessive generation of aerosol-size particles; however, additional sampling has been recommended.

Scrub Foaming Tests

It is imperative that scrub foaming be controllable; otherwise, operational difficulties will occur in the scrub system. The 10-cm calciner effluents were analyzed and tested to help close component material balances and to demonstrate that foaming, as a result of organic accumulation in the scrub, can be controlled during sugar-additive calcination. The temperature of the scrub solutions was raised from 30°C to approximately 60°C during the sugar-additive testing. This resulted in higher scrub evaporation rates but also helped to control scrub foaming. No foaming was observed during the pilot plant runs.

A heated air-agitation apparatus was designed and used to further test the foaming potential of the scrub in the laboratory. Appendix F shows a schematic of the set up that was employed for these tests. The scrub solutions did not exhibit significant foaming, except at extremely high agitation rates

which are uncharacteristic of the NWCF scrub system. The foam quickly dissipated as soon as the air agitation rate was reduced.

Calcine Hydration Tests

Severe agglomeration in the cyclone separator prompted the execution of laboratory studies to determine the hygroscopicity of the calcine product. A simple humidification chamber was designed to expose a packed column of the calcine to a steady stream of moist air. The calcine was periodically removed from the humidification chamber and poured through a small funnel to determine if it remained free flowing and to observe any caking that may have occurred. A schematic of the experimental apparatus used for these tests and the results are summarized in Appendix F, under the 10-cm calciner test report.

Absolute relative humidity frequency distribution data for the ICPP atmospheric conditions were obtained from the Idaho Falls NOAA laboratory⁸ to determine the maximum relative humidity (98% of annual maximum) that the calcine would be exposed to in the transport line to the Calcine Solids Storage Facility (CSSF). Samples of calcine were exposed to the humidified air at various temperatures.

Calcine from Run SBW-SA-1 exhibited severe hygroscopicity at all experimental conditions, including low humidity. At high relative humidities, the sugar-additive calcine was also deliquescent. The high temperature calcine was significantly less hygroscopic than the sugar-additive calcine, but it still took up moisture at high humidity and low temperatures. When exposed to the worst conditions expected in the NWCF-CSSF transport line, however, the high temperature calcine appeared to remain free-flowing. Further testing is recommended to quantify the effects of moisture and temperature on calcine hydration.

Volatile and Semi-Volatile Analyses

The accumulation of unburned hydrocarbons in the 10-cm calciner scrub and condensate solutions prompted an investigation into the possible formation of HAPs in the calciner vessel, with possible synthesis in the heated scrub solutions. Increased concentrations of unburned hydrocarbons (including hydrocarbon radicals), resulting from sugar pyrolysis in the presence of chloride vapors (including HCl, Cl• and possibly Cl₂), suggests that chlorinated hydrocarbons may be formed in the calciner vessel and offgas system. The extent of this phenomena has yet to be determined and will be the subject of future development studies. No attempt has yet been made to directly sample the offgas for chlorinated HAPs. However, there is a strong likelihood of forming HAPs, including dioxins, furans, halogenated hydrocarbons, and products of incomplete combustion (PICs).

Tables 7 and 8 list the results of the EPA volatile and semi-volatile component analysis of samples collected from the combined scrub and condensate solutions collected during the 10-cm calciner sugar-additive runs. The analysis of separate condensate and scrub solutions from a recent 15-cm calciner baseline flowsheet run are also listed. Both flowsheets indicate that the calcination process releases condensable hazardous air pollutants. Caution must be taken when comparing and interpreting these results since the scrub solutions were held at dissimilar temperatures and the samples were not collected for several weeks following the runs. In addition, a number of other factors will affect the sample results, including the vapor space in the waste collection drums, waste transfers, etc.

Table 7. Volatile organic analysis of pilot plant condensate and scrub solutions.

CAS No.	Compound	15-cm Calciner Tests		Sugar-Additive Tests	
		Condensate Conc. (ug/L)	Scrub Conc. (ug/L)	Sample 1 Conc. (ug/L)	Sample 2 Conc. (ug/L)
64	Methylene Chloride	--	--	240	510
67-64-1	Acetone	180	221	4200	5700
91-20-3	Naphthalene	--	--	220	230
97	4-Methyl-2-Pentanone	--	--	--	180
74-87-3	Chloromethane	117	40	--	--
74-83-9	Bromomethane	70	27	--	--
26	Benzene	50	50	--	--
10061-02-6	trans-1,3-Dichloropropene	218	--	--	--

Table 8. Semi-volatile organic analysis of pilot plant condensate and scrub solutions.

CAS No.	Compound	15-cm Calciner		Sugar-Additive Test	
		Condensate (ug/L)	Scrub (ug/L)	Sample 1 (ug/L)	Sample 2 (ug/L)
100-02-7	4-Nitrophenol	458.4	357	--	--
110-86-1	Pyridine	--	932.2	1100	1500
117-81-7	Bis(2-ethylhexyl)phthalate	589.2	4455	1300	1600
121-14-2	(MS) 2,4-Dinitrotoluene	76.8	--	--	--
126-73-8	Tri-n-butyl phosphate	42	203.8	--	--
205-99-2	Benzo(b) fluoranthene	1.2	--	--	--
206-44-0	(CCC) Fluoranthene	2.8	14.2	--	--
207-08-9	Benzo(k) fluoranthene	1.8	--	--	--
51-28-5	2,4-Dinitrophenol	--	--	7200	8400
534-52-1	4,6-Dinitro-2-methylphenol	709.8	482.8	1700	2200
606-20-2	2,6-Dinitrotoluene	--	--	910	1100
65-85-0	Benzoic Acid	--	--	5200	5600
88-74-4	2-Nitroaniline	--	--	--	200
88-75-5	(CCC)2-Nitrophenol	87.8	19.4	--	--
91-20-3	Naphthalene	--	--	170	--
91-57-6	2-Methylnaphthalene	--	6.4	160	--
98-95-3	Nitrobenzene	3551.4	869.4	2100	2500

30-cm Calciner Upgrade

Before high temperature and sugar-additive testing could commence in the 30-cm calciner pilot plant, some modifications were determined to be necessary. An effort was undertaken to decontaminate the 30-cm facility of cadmium-containing dust from previous runs. A stress analysis of the structure was completed and an internal inspection of the facility vessels, piping, and offgas equipment was completed. This work was done in anticipation of conducting a limited number of 30-cm calciner runs in the future. Systems and components requiring modifications or replacement include:

- Fabricate and install a new calciner vessel mounting system.
- Increase the diameter of the expanded freeboard section height so that the ratio of the expanded section to the bed particle transport disengagement height (TDH) is approximately unity.
- Remount the existing cyclone to prevent scrub solution backflow into the cyclone.
- Improve the bed take-off system.
- Increase the demister performance.
- Replace the quench tower spray nozzles.
- Install new mix tanks or add piping to available auxiliary tanks in the CPP-637 building.
- Install new sugar-additive mixing and feed control systems.
- Implement a new RCRA waste collection and storage plan for the condensate and scrub solutions.
- Replace dysfunctional instruments, controllers, pumps, valves, flowmeters, etc.

Although the extent of work required to upgrade this facility is considered modest, it was recognized that the cost and effort may not be justified. Furthermore, the significant volume of waste generated by the facility, coupled with the cost of resources to conduct a single run, prompted development personnel to reconsider plans to use the 30-cm facility. This led to a recommendation that the 15-cm calciner be utilized in the future.

Metal Alloy Corrosion Tests

Both the sugar-additive and high temperature flowsheets have the potential of increasing the corrosion rate in the calciner vessel and the offgas system. The corrosion rate of metal alloys is accelerated at higher temperatures and can be exacerbated by increased levels of CO through a mechanism referred to as carburization. Carburization occurs when the CO reacts with chromium in the metal to form chromium carbide, which reduces the corrosion resistance of the alloy. Severe cases, with alternating reducing/oxidizing environments, can cause metal dusting, where metal oxides spall off the surface. The calcine environment is also rich in acid vapors which can attack the vessel and offgas line walls and cause pitting or crevice corrosion. Thus, it is expected that an increase in the temperature will result in higher corrosion rates. In addition, increased volatilization of Cl and F at higher temperatures

will also result in increased accumulation in the offgas scrub solutions. This will likely cause increased corrosion of the scrub hold tank and scrub recycle appurtenances (pipes, pumps, valves, etc.).

Increased levels of CO are expected to occur during calcination with sugar. This is due to the occurrence of sugar-pyrolysis products which are not completely oxidized in the bed. Except for a minor amount of atomized fuel which is not burned, the kerosene is rapidly combusted with pure oxygen in vicinity of the fuel nozzles where the peak flame temperature is above 2000°C. The sugar, however, enters with the liquid feed and is heated to the mean bed temperature of only 500°C. Both the unburned kerosene and the sugar pyrolysis products undergo partial oxidation in the cooler bed, resulting in significant concentrations of CO in the calciner vessel and offgas. The auto ignition point of CO is 600°C, which indicates that CO will mainly be destroyed by heterogeneous or catalytic reactions in the bed. Therefore, unusually high levels of CO are expected (and have been measured) during calcination, with the highest concentrations occurring during sugar-additive calcination.

A test was completed using simulated scrub solutions and the scrub system metallic alloys to study qualitative corrosion behavior at elevated halide concentrations in the nitric solutions. A second test apparatus was assembled to determine corrosion rates at elevated temperature in the presence of aggressive acid vapors and anticipated CO concentrations (as measured in the pilot plant runs). The latter tests have not been completed. In addition, removable corrosion coupons were fabricated and placed in the 10-cm Calciner Pilot Plant to investigate the severity of corrosion during the pilot plant runs. The in-situ coupons will be examined following each 10-cm calciner test to determine the onset and progression of corrosion in the vessel. Due to the limited time of operation, the 10-cm corrosion results will not provide definitive corrosion rates.

Feed Makeup Studies

Feed makeup for the calciner involves blending the tank farm liquid with stock aluminum nitrate, boric acid solution, and calcium nitrate. With sugar-additive flowsheet, sugar must also be added to the liquid feed. Several methods were evaluated for mixing sugar with the SBW and other necessary feed additives prior to injecting the mixture into the calciner. Either granular sugar or a concentrated syrup can be added directly to the feed or to the aluminum nitrate solution. Mixing can be accomplished by in-line mixers or in a batch mode. In-line mixing would result in the least volume of sugar-feed mixture holdup in the event of an unplanned shutdown; however, it would be the most costly to implement and the most complicated to control. Conversely, batch mixing would be the simplest, and likely the least costly to implement; however, it could result in large volumes of sugar-nitrate mixtures which would have to be deactivated before they could be returned to the tank farm.

Sweetened Feed Rheology Measurements

In order to help the Design team select the best method for adding sugar to the feed, the solubility of sugar in SBW simulant and ANN solutions was verified and viscosity data were determined for the tests. A Rheology International rotary viscometer and Cannon-Fenske capillary viscometer were used to measure the solution viscosities. Figure 10 shows the mixtures of solution mixtures that were systematically combined with their respective property measurements (where the viscosities measured by the rotary instrument and the capillary tube are denoted as μ_R and μ_C , respectively).

Figure 10. Matrix of solution mixtures and their measured viscosity (G970010).

Boric Acid Solubility Measurements

It has been proposed that the boric acid crystals should be dissolved in either the SBW or the ANN solution to reduce the amount of water that is added to the feed tank by adding the boric acid as an independent solution. This action could result in up to a 15% SBW processing rate increase. The solubility of boric acid in SBW was previously measured and found to be sufficient to meet feed blend requirements (personal communication with R. E. Schindler). A recommendation was made to add boric acid to the ICPP High Level Liquid Waste Evaporator which is used to concentrate the tank farm wastes prior to calcination. Because this practice was not adopted, dissolution of boric acid in the aluminum nitrate is now being considered. A limited study of the mutual solubility of boric acid in ANN (initially ranging from 1.8 to 2.26 M) was completed. The results of this test are tabulated in Tables 9.a and 9.b.

A search was made to identify compounds, other than boric acid, which could be used to add boron to the feed. The solubility of calcium boride (CaB_6) in nitric acid was measured to determine whether it would dissolve in the feeds. The measured solubility of CaB_6 is shown in Table 10. The calcium boride is essentially insoluble in 1 M nitric acid solutions and only slightly soluble in higher concentrations. Evolution of brown NO_2 was observed in nitric concentrations above 3.0 M due to the decomposition of the calcium boride. Toxic borane could also be released. As such, calcium boride does not appear to be a suitable alternative to boric acid.

Table 9.a. Solubility of boric acid in aluminum nitrate solutions at 25°C.

ANN Sol'n Volume (mL)	H_3BO_3 (gm)	Initial Al Conc. (M) & Density (gm/mL)	H_3BO_3 Conc. (molal) and Density (gm/mL)*	H_3BO_3 Conc. (gm/L Solv't)
76.7	1.8225	1.77 / 1.267	0.384 / 1.272	23.8
75.6	1.7078	1.97 / 1.294	0.365 / 1.291	22.6
74.3	1.5152	2.17 / 1.324	0.330 / 1.321	20.4
75.0	1.4448	2.36 / 1.357	0.311 / 1.362	19.3

* Measured after a supersaturated solution had cooled to 25°C and excess boric acid had precipitated.

Table 9.b. Solubility of boric acid in aluminum nitrate solutions at 50°C.

ANN Sol'n Volume (mL)	H ₃ BO ₃ (gm)	Initial Al Conc. (M)	H ₃ BO ₃ Conc. (molal) & Density (gm/mL)	H ₃ BO ₃ Conc. (gm/L Solv't)
77.1	3.6941	1.77	0.775 / 1.264	47.9
75.6	3.4741	1.97	0.743 / 1.285	45.9
74.3	3.0860	2.17	0.673 / 1.313	41.6
75.0	2.9263	2.36	0.631 / 1.341	39.0

Table 10. Solubility of calcium boride in nitric acid solutions.

Nitric Acid Molarity	gm CaB ₆ /100 mL
0.00	0.01
0.25	0.02
0.50	0.05
0.95*	0.09*
1.00	0.11
1.50	0.41
2.00	0.69
2.50	1.5
3.00	1.7

* Solution with their dissolved nitrate salts.

Sugar Digestion Scoping Tests

A scoping study was completed to determine feasible methods to eliminate the sugar in unprocessed sugar-SBW feed mixtures in the event of an unplanned shutdown. Unused feed from the 10-cm calciner flowsheet tests was heated in a large "batch" tank as concentrated nitric acid was progressively added to the sweetened feed. The goal was to add enough nitric acid to fully oxidize all of the sugar while maintaining the acid concentration at or above 1 M.

Previous tests have demonstrated that only the nitrates associated with the nitric acid will react with the sugar in solution, giving up gaseous CO₂ and NO_x. Water is also a product of the reaction but it is condensed in the solution and released to the gas by normal evaporation. The nitrate associated with the alkali metals are not affected since the solution charge balance is conserved and the half-cell reactions do not favor reduction nor oxidation of the metal cations in solution. Therefore, excess nitric acid was added to the solution to bring the stoichiometric ratio of carbon and nitric acid to 1.25. Samples were periodically collected and analyzed for pH, organic carbon, and inorganic carbon, to chart the reaction progress.

Once the solution mixture was heated to 90°C, an intense brown NO_x gas began evolving. This continued for approximately 1 hour. The color of the gas gradually decreased during the second hour. Analysis of the solution after 2 hours revealed that 5.7 wt.% organic remained in solution with 2.1 M acid. It was concluded that nitric acid was being vaporized at a significant rate; hence, additional nitric

acid was added to the reaction tank and heating was resumed for 2.5 hours. The results showed high amounts of organic carbon were still present with the acid. Heating was again repeated without a noticeable affect on the organic carbon content. No evidence of a brown gas was observed. It was concluded that the organic carbon had been reduced to refractory compound, such as oxalic acid.

Similar tests are needed to demonstrate that any organics collected in the scrub and condensate solutions can be eliminated; however, authorization to conduct a Waste Treatability Study is needed before these tests can be executed.

INTERPRETATION OF THE RESULTS

The results of the equilibrium calculations and hydration experiments can be put in perspective with the pure compound physical property data for components in the SBW. Table 11 lists some of the physical properties of the major compounds that were observed in the calcine product.

General Reaction Mechanism for High Temperature Flowsheet

Using the data in Table 11, and the information obtained from the equilibrium calculations, the TGA/DSC thermo-grams, and the X-ray diffraction analysis, a general reaction sequence can be hypothesized for the high temperature calcination flowsheet.

- Evaporation of free moisture and nitric acid at low temperatures (@ $T < 150^{\circ}\text{C}$).
- Denitration of $\text{Al}(\text{NO}_3)_3$ to $\text{Al}(\text{OH})_3$ or $\text{AlO}(\text{OH})$ in the solid phase (@ $T < 200^{\circ}\text{C}$).
- $\text{AlO}(\text{OH}) \rightarrow \text{Al}_2\text{O}_3$ (@ $T \approx 150\text{-}250^{\circ}\text{C}$).
- $\text{NaNO}_3 (\text{s}) \rightarrow \text{NaNO}_3 (\text{l})$ (@ $T \approx 300\text{-}320^{\circ}\text{C}$).
- $\text{NaNO}_3 + \text{Al}_2\text{O}_3 \rightarrow \text{NaAlO}_2$ (@ $T \approx 300\text{-}700$).
- $\text{NaNO}_3 (\text{l}) \rightarrow \text{NaO} \rightarrow \text{NaOH}$ or Na_2O_2 (@ $T \approx 400\text{-}850$).
- $\text{NaOH} (\text{s}) \rightarrow (\text{Na}_2\text{O}_2) \rightarrow \text{Na}_2\text{O}$ (@ $T \approx 600\text{-}650$).

Several endotherms are exhibited by the SBW-ANN mixture DSC (Fig. 3). From the heats of formation data listed in Table 11, it can be shown that most of the reactions are endothermic; consequently, heat must be supplied from an external source. For example, the following reaction is correctly balanced as:

In addition, the melting of NaNO_3 is endothermic and occurs just above 300°C .

Mass evolution occurs gradually until a sudden loss of mass begins at approximately 600°C , corresponding to a steep endotherm well. From experimental observations it appears that this change in the rate of mass loss is the result of a sudden decomposition of NaNO_3 . The standard SBW continues to evolve mass up to 850°C while the SBW-ANN mixture is stable above 625°C .

Table 11. Physical property data for selected compounds in calcine product.^{9,10}

Species (solids)	T _{melt} (°C)	T _{boil} (°C)	T _{decomp} (°C)	T _{sublime} (°C)	$\Delta H_f^{0,K}$ (kcal/gmol)	$C_p^{298,K}(\text{solid})$ (cal/°C-mole)	Solubility 0°C/100°C/ remarks ^λ
Al(NO ₃) ₃ •9H ₂ O	73.5	-	150	-	-897.34	-	63.7/vs,d/ deliq.
Al(OH) ₃	-H ₂ O to yield AlO(OH)				-304.2	-	i
AlO(OH)	-H ₂ O to yield Al ₂ O ₃						i
Al ₂ O ₃	2072	2908	-	-	-384.8	-	i
NaAlO ₂	1800	-	-	-	-273	-	s/vs/hygro
Na ₂ O	-	-	-	1275	-99.4	16.3	d/d/deliq
Na ₂ O ₂ (s)	-	-	657	-	-120.6	-	s/d
NaNO ₃	306.8	-	380	-	-101.5	27.8	92.1/180
NaNO ₂	271	-	320	-	-85.9	-	81.5/163/ hygro
NaOH	318.4	1390	-	-	-101.99	19.2	42/347/ deliq
NO _{2(g)}	-	-	-	-	7.9	-	-
NO _(g)	-	-	-	-	21.6	-	-
H ₂ O _(g)	-	-	-	-	-57.8	-	-

λ: i = insoluble; s = soluble; vs = very soluble; d = decomposes; deliq = deliquescent; hygro = hygroscopic.

Further interpretation of these results will be made after a detailed analysis of the possible reaction sequence is determined. Using the heats of formation, adjusted to the applicable reaction temperatures, a more definitive reaction sequence can be determined. For purposes of flowsheet development, all of the calcination experiments indicate that a slight excess of aluminum to alkali metals (AAR ≥1:1) will promote earlier decomposition of the NaNO₃ to a sodium-aluminate product. Approximately 66% of the sodium combined with aluminum to form NaAlO₂ for a 1.5:1 AAR mixture. When insufficient aluminum is added to the feed, sodium exists primarily as NaNO₃ below 500°C, then it is converted to NaOH (or Na₂O₂) between approximately 500 to 650°C, and subsequently to Na₂O above 650°C.

General Reaction Mechanism for Sugar-Additive Flowsheet

The general reaction sequence for the sugar-additive flowsheet differs from the high temperature flowsheet, in that the alkali metal nitrates are reduced by the sugar. The oxidation-reduction reaction between the nitrates and sugar begins in the liquid phase as the feed droplets are heated up. Rapid evaporation of the moisture and acids infers that the liquid phase reactions are probably insignificant. The sugar in the dried solid undergoes a brief period of pyrolysis, giving up water and light hydrocarbons fragments. Once the temperature of the solid reaches the ignition temperature, at approximately 300°C, a solid-state reaction occurs rapidly. The nitrate salts are reduced to lower oxidation states. This process is summarized by the following steps:

- Evaporation of free moisture and nitric acid at low temperatures (@ T<150°C).

- Denitration of $\text{Al}(\text{NO}_3)_3$ to $\text{Al}(\text{OH})_3$ or $\text{AlO}(\text{OH})$ in the solid phase (@ $T < 200^\circ\text{C}$).
- Redox reaction of the sugar and hydrolizable metals, such as aluminum; e.g.,

$$\text{C}_{12}\text{H}_{22}\text{O}_{11(\text{sol})} + 48\text{HNO}_{3(\text{sol})} \xrightarrow{>50^\circ\text{C}} 12\text{CO}_{2(\text{g})} + 48\text{NO}_{2(\text{g})} + 35\text{H}_2\text{O}_{(\text{l})}$$

$$\text{C}_{12}\text{H}_{22}\text{O}_{11(\text{sol})} + 16\text{Al}(\text{NO}_3)_3 \xrightarrow{<120^\circ\text{C}} 12\text{AlO}(\text{OH})_{(\text{s})} + \{\text{NO}_{2(\text{g})}, \text{CO}_{2(\text{g})}, \text{H}_2\text{O}_{(\text{l})}\}$$
- Partial pyrolysis of the sugar, e.g., $\text{C}_{12}\text{H}_{22}\text{O}_{11} \xrightarrow{>150^\circ\text{C}} \text{sugar char} + \{\text{H}_2\text{O}, \text{C}_x\text{H}_y \text{ etc.}\}$
- Solid-state oxidation of the alkali metals with the sugar char; e.g.,

$$\text{sugar char} + \text{NaNO}_3 \xrightarrow{\geq 300^\circ\text{C}} \text{NaOH} + \{\text{NO}_{2(\text{g})}, \text{CO}_{2(\text{g})}, \text{etc.}\}$$
- $\text{AlO}(\text{OH}) \rightarrow \text{Al}_2\text{O}_3$ (@ $T \approx 150\text{-}250^\circ\text{C}$).

The X-ray diffraction analysis of the LSCM product suggest that NaAlO_2 can also be formed during sugar-additive calcination when excess ANN is added to the SBW; however, these results are currently inconclusive. No significant amount of NaAlO_2 was detected in the 10-cm calciner product. Intuition suggests that several factors limit the conversion of Na to NaAlO_2 during sugar-additive calcination including, direct oxidation of NaNO_3 to stable sodium hydroxide product and the low vessel temperature (i.e., 500°C). The significant differences in hydration properties of the sugar-additive product also infer that sodium is converted to either NaOH or Na_2O , rather than to NaAlO_2 .

Comparison of Flowsheets

The main objective of the LSCM and 10-cm calciner testing was to determine whether the SBW could be calcined with reduced quantities of additives while meeting all other process objectives (produce a retrievable calcine that can be redissolved in nitric acid, etc.). Since sodium and potassium nitrate are responsible for bed agglomeration at typical calcination conditions, the amount of nitrate in the product is a good indicator of the potential for bed agglomeration. The high temperature flowsheet results are slightly better than the sugar-additive flowsheet in terms of decomposing the alkali nitrates, although the high-temperature fines have a higher nitrate content. However, both flowsheets accomplish the desired objective.

The two 10-cm calciner high temperature runs yielded similar nitrate concentrations in the final product, indicating that the calcination temperature only needs to be raised to 600°C (SBW-HT-2 Run) to sufficiently denitrate the calcine. Decreasing the temperature by 50°C had a dramatic effect on the amount of fines that were generated. Even though the product-to-fines ratios reported in Table 6 do not include the fines carried past the cyclone separator, the results show that at the lower calcination temperature significantly fewer fines were generated. This is attributed to a decrease in the rate of flash evaporation of the feed droplets, as well as a reduction of film boiling on the surface of the calcine particles. A test needs to be conducted to determine whether a feed blend with an AAR of 1:1 can be successfully calcined at 600°C .

The calcine hydration results from the preliminary tests demonstrate that there are distinct differences between the baseline, high temperature, and sugar-additive calcine product. A qualitative

comparison of the solubility data provided in Table 11 helps one understand why the sugar-additive product is more deliquescent than the high temperature calcine. Alkali hydroxides in the product are initially more hygroscopic than alkali aluminates. In fact, sodium hydroxide is highly deliquescent and absorbs moisture until a solution is formed which equilibrates with the surrounding atmosphere.

During the hydration experiments, the sugar-additive calcine rapidly took up moisture and formed a moist cake. The high temperature calcines absorbed moisture at a much slower rate and only formed a moist cake at high humidity. By conjecture, the NaAlO_2 product is gradually converted to NaOH and $\text{Al}(\text{OH})_3$. The baseline calcine absorbed only a small amount of moisture. This is consistent with the facts that NaNO_3 is only slightly hygroscopic and that Al_2O_3 is insoluble in water. Additional testing is planned to further elucidate the hydration behavior of the high temperature calcine. For additional discussion, refer to Appendix F which reports the calcine hydration data.

An unexpected result of the high temperature flowsheets is the lack of any evidence to suggest that α -alumina formed in the product. This infers that it may not be necessary to add boron to the feed to suppress the formation of this compound. While further testing is required to arrive at a more definitive conclusion, the results are encouraging. This may allow additional aluminum to be added to the flowsheet, if necessary, to avoid agglomeration while still increasing the calciner throughput significantly. However, this conclusion needs to be qualified. Earlier work suggested that the α -alumina can be undetectable due to its eutectic with sodium.^{11,12}

Figure 11 plots the measured attrition resistance indexes listed in Tables 4 and 6. The sugar-additive flowsheets generally exhibit higher ARIs. The behavior of the LSCM product differs significantly from the 10-cm calciner product. The ARI for the sugar additive flowsheets appears to decrease as increasing amounts of aluminum are added to the feed. The significance of this result is not well understood at the present. No attempt has been made to draw a correlation between ARI and the product-to-fines (P/F) ratio because of uncertainties in the measurements of the latter. Also, fines generation can be caused by flash evaporation and this must be taken into consideration. Further 10-cm calciner testing needs to be conducted to better establish fines generation behavior and to establish a correlation with the ARI.

Comparison of the LSCM and 10-cm calciner product dissolution behavior in 8 M HNO_3 (see Figure 12) shows both the high temperature and sugar additive product generally dissolve more readily than the baseline calcine. This demonstrates that there would be no adverse impact on the dissolution of the calcine in preparation for radionuclide separations.

The sugar-additive flowsheet quite obviously results in higher emissions of unburned hydrocarbons which are carried over into the scrub system. Intuitively, the chances of forming hazardous air pollutants in the offgas, due to the interaction of acid vapors and the products of incomplete combustion (and sugar pyrolysis products) are increased with this flowsheet. However, the alkaline nature of the sugar-additive product is believed to be responsible for greater capture of volatile halides. This provides one possible explanation as to why the sugar-additive product retained higher amounts of chloride than either the baseline or the high temperature flowsheets.

Figure 11. Comparison of calcine attrition resistance indexes (G97011).

Figure 12. Comparison of calcine dissolution results in 8 M HNO₃ (G97012).

The sugar-additive flowsheets results in the accumulation of low, but not insignificant amounts of organic carbon the calciner scrub solutions. From a safety viewpoint, it is not believed that the low amount of carbon will pose any significant risk of an explosion (via rapid reaction of the organics and nitric acid) since most of the carbon appears to be elemental and contained in char particles. All of the safety tests conducted to date with surrogate scrub/sugar-char solutions showed no evidence of nitration nor violent reactivity potential. However, additional safety studies would need to be completed to fully quantify this judgement before this option should be pursued.

Product densities for the 10-cm calciner scoping runs are reported in Appendix F. These data should be viewed as preliminary results; however, the data indicate that the high temperature flowsheet product results in a higher bulk density for both product and fines than the baseline flowsheet. If the data are correct, then the high temperature flowsheet will further decrease the calcine storage requirements by providing a more dense mixture. However, since the bulk density depends on the P/F ratio, additional pilot plant testing will help establish greater confidence in the measured P/F for the high temperature case.

The sugar-additive flowsheet product and fines have a lower bulk density than the baseline flowsheet. This is mainly due to the relatively low density of the sugar-additive fines.

Pollutant Emissions

The results presented in Tables 7 and 8 obviously suggest that interactions between the partially burned fuel (both kerosene and sugar pyrolysis products) and the acidic feed may result in the emissions of regulated PICs and HAPs. These data do not, however, provide a definitive basis for estimating emissions levels from the NWCF. The concentrations of the species identified in the scrub and condensate solutions depend on the temperature and composition of the scrub, as well as the time that the solutions were allowed to stand before the samples were taken. Therefore, the data most likely do not include all volatile and semi-volatile pollutants which may be formed during calcination. It is obvious that the emissions of Clean Air Act (CAA) criteria pollutants decrease with an increase in the calcination temperature. Thus, as the concentration of unburned hydrocarbons decreases in the offgas, so also should the level of HAPs since it is hypothesized that they are formed in the calciner vessel.

Feed Make Up

The results of the mutual solubility studies demonstrate that boric acid crystals can be directly dissolved in either the SBW or ANN feed, rather than being dissolved in a separate boric acid solution before being added to the feed. This change to the current NWCF SBW-feed blending procedure could result in up to a 15% increase in the NWCF throughput without increasing the operating temperature above 500°C. It could also improve the throughput projected for high temperature calcination, although the need to add boron to this flowsheet has not been established.

One concern, however, is that the specific gravity of the feed solutions will increase, which may have an adverse impact on atomization of the feed. Difficulties have been noted in previous 15-cm Calciner Pilot Plant tests when the specific gravity of the feed was increased above $\sim 1.4 \text{ g/cm}^3$. Pilot plant testing is planned to investigate the feasibility of calcining the higher specific gravity mixtures. It should also be noted that the baseline flowsheet will require significantly more calcine storage capacity; in fact, a new bin set would have to be constructed.

Moderate heating may be required ($>50^\circ\text{C}$ solution temperature) to increase the rate of boric acid dissolution in the ANN. Boric acid could be added to the ANN feed stock in this manner by the supplying vendor. Other feed makeup modifications at the ICPP are also possible to accomplish this objective, if elected.

A correlation between the solubility of boric acid in ANN and nitric acid has been noted. Specifically, the activity of boric acid, as a function of solution temperature and in 2.2 M ANN, is similar

to its activity in nitric acid. Aluminum hydrolysis causes an offset in the solubility curve of approximately -0.6 gr-boron/L at 25°C and -1.2 gr-boron/L at 50°C, relative to nitric acid solutions of equivalent nitrate molarities. Thus, it should be possible to use the published data for boric acid-nitric acid solutions to determine solubility requirements/limits. This may be useful for establishing feed makeup procedures.

Sugar/Organic Destruction in Nitric Solutions

Previous development work at Hanford¹³ proved that sugar (sucrose) is very effective at reducing nitric acid, but does not decompose alkali metal-nitrates in solution. It was hoped that the reverse could be demonstrated; i.e., that nitric acid and heat could be used to oxidize the remaining sugar in unused calciner SBW-sugar mixtures, as well as the organics that accumulate in the scrub solutions. Safety Analysis personnel contend that all organics must be eliminated from the plant waste streams before they can be sent (or returned) to the tank farm. The results of the sugar digestion studies with sweetened 10-cm calciner feed were disappointing, but informative. Residual organic persisted in the solution after adding excess amounts of nitric acid and heating the solution up to nearly the boiling temperature. The sugar apparently is converted to oxalic acid (COOH_2) by oxidation of sucrose by nitric acids. Once the sugar is reduced to oxalic acid, it is refractory and does not decompose readily in concentrated nitric acid. Sulfuric acid may attack and destroy oxalic acid, but this would add undesired sulfates to the feed stream and would increase corrosion of stainless steel equipment and piping.

The results of this test indicated that one possible alternative to using sugar to reduce the nitrates would be oxalic acid. Mixtures of oxalic acid and SBW simulant were evaporated and heated in a metal beaker on a hot plate to observe the reactivity of the dried mixtures. The dried mixtures failed to ignite and burn as observed with the dried sugar-SBW mixture. It is presumed that the oxalic acid is vaporized with the moisture during heat up of the sample. Consequently, no further investigations with oxalic acid were made.

RECOMMENDATIONS AND CONCLUSIONS

Both the high temperature and sugar-additive flowsheets were successfully tested in laboratory and pilot plant calcination scoping tests. Both flowsheets effectively denitrate the alkali metals in the calcine to produce a free-flowing product, while significantly reducing the amount of ANN that must be added to the feed. The high temperature flowsheet showed the greatest promise for implementation at the NWCF because of fewer safety and environmental concerns, and also because it would be easier to implement and to operate. However, additional testing needs to be completed to validate the results of the 10-cm calciner scoping tests. Specifically, the amount of fines generated at elevated temperatures needs to be better quantified. The sugar-additive flowsheet also has several merits, but would be more difficult to permit and to operate. Other key conclusions are listed below.

- Aluminum nitrate is the preferred diluent additive for processing SBW. It reacts chemically with the alkali metals to form stable aluminates, it is commercially available, and it can be blended with SBW without causing precipitation in the feed system.
- The LSCM and 10-cm calciner testing corroborated the results of the crucible calcination tests; i.e., an AAR of 1:1 or higher promotes complete product denitration at temperatures of 600°C or higher. NaAlO_2 was a major product in the calcine, rendering the product less hygroscopic than the sugar additive flowsheet. Fines generation, as a result of increased flash evaporation is a concern, but appears to be only moderate at 600°C.
- Equilibrium calculations are helpful in understanding the composition of the calcine product, but they do not predict observed temperature and mass transfer dependence of the calcine product.
- The LSCM and 10-cm calciner testing verified that standard SBW can be nearly completely denitrated at 500°C by adding sugar to the feed in an amount slightly above a carbon to nitrate ratio (molar) of 1.25. The addition of a small amount of ANN helped to prevent agglomeration of the resulting NaOH product in the calcine. Higher emissions of unburned hydrocarbon emissions, accumulation of the hydrocarbons in the scrub system, and calcine hydration are of particular concern to the sugar-additive flowsheet.
- The reaction between sugar and the nitrate salts is rapid but does not exhibit the characteristics of either primary or secondary explosive materials (per semi-quantitative U.S. Bureau of Mines thermal and shock sensitivity tests). The probability of forming nitrated sugars in the feed stream was shown to be low, but cannot be discounted without additional testing.
- Safety-related concerns with the sugar-additive flowsheet were allayed sufficiently to conduct the pilot plant tests; however, additional testing of the 10-cm calciner product is warranted if further flowsheet development is to proceed.
- Scrub foaming did not prove to be a problem during 10-cm calciner testing and was shown to be minimal in laboratory air-agitation tests.

- A possible method of increasing the baseline flowsheet throughput may be possible by dissolving boric acid crystals in the ANN feed-stock rather than adding boric acid as a separate solution.
- A search for other compounds to supply boron to the feed was unfruitful. It was hoped that calcium boride would be sufficiently soluble in nitric acid and could supply both calcium to tie up halides, and boron to prevent α -alumina formation. However, calcium boride is only slightly soluble in nitric acid and causes additional NO_x emissions.
- Analysis of the high temperature and sugar additive product indicate that α -alumina is not produced in detectable quantities. However, previous tests indicate that there may be an induction period before α -alumina is formed, after which the crystalline phase can grow rapidly. Therefore, flowsheet recommendations for the high temperature flowsheet currently include an equivalent amount of boron as the baseline flowsheet. Further pilot plant studies are needed before a confident decision can be made to eliminate boron from the feed blend.
- Hydration of the sugar-additive product can be severe after exposure to high humidity. After only a short duration of time, the hydrated calcine begins to deliquesce. Hydration of the sugar-additive product also occurs at low humidity ($< 5.5 \text{ g H}_2\text{O/m}^3 @ 80^\circ\text{F}$) and can become deliquescent after long exposure times.
- The high temperature calcine takes up a significant amount of moisture at high humidity, but takes up to 100 hours of exposure to begin caking. Hydration of the product at moderate humidity ($< 9.5 \text{ g H}_2\text{O/m}^3 @ 165^\circ\text{F}$) does not appear to affect calcine transportability.
- Both the high temperature and sugar additive calcines have acceptable dissolution characteristics in nitric acid.
- Compared to the baseline flowsheet results, chloride volatility appeared to decrease during sugar-additive calcination, while it increased slightly during the high temperature calcination. These results need to be confirmed by additional flowsheet testing.
- Cesium-137 and Technetium-99, chloride, and fluoride volatility showed dependencies on temperature and on concentration. Mercury is completely volatilized at all calcination temperatures, most likely being released as HgCl_2 , or as nitrate decomposition products (predominately HgO).
- Almost all of the volatile chloride and Mercury can be expected to collect in the NWCF scrub solutions.
- Analysis of the scrub and condensate solutions confirms postulated combustion mechanisms for the formation of PICs and HAPs in the calciner vessel.

The following recommendations are given on the basis of the experimental results and conclusions:

- An operating temperature of 600°C with an aluminum-to-alkali metal ratio of 1.5:1 is recommended for NWCF design modification considerations.

- 10-cm calciner flowsheet refinement and sensitivity runs need to be conducted to determine the optimum amount of additives to use (i.e., ANN, $\text{Ca}(\text{NO}_3)_2$, and boron) and to establish a better understanding of high temperature calcination chemistry. Particular attention needs to be given to fines generation and chloride volatility throughout these tests.
- Additional 10-cm calciner tests of the baseline flowsheet should be made to investigate the possibility of adding boric acid to the ANN feed stock.
- Tests should be conducted to quantify corrosion rates in the NWCF fluidized-bed vessel at higher temperatures. Tests should also need to be completed to quantify corrosion rates in the scrub system with high levels of chloride.
- Cost, time, and waste minimization considerations to upgrade and operate the 30-cm Calciner Pilot Plant warrant looking at alternatives to determining the effects of scale up to the NWCF. Tests in the 15-cm calciner should be pursued in conjunction with attempts to conduct a brief high temperature trial in the NWCF, if feasible, prior to completing major modification to the facility in support of implementing the high temperature flowsheet. If a full-scale demonstration is not feasible, then the 30-cm calciner tests are probably warranted.
- Further calcine hydration tests and calcine retrievability tests need to be completed to demonstrate product acceptability and possibly to provide NWCF design modifications guidance.
- An offgas monitoring system to help determine the level of Criteria Pollutants and Hazardous Air Pollutants that are emitted from the calciner should be used in anticipation of more stringent environmental regulations for the NWCF.

In addition to these recommendations, sugar-additive calcination should be viewed as a prime candidate for denitrating and conditioning the LLW stream and/or the HLW stream that would be derived from a radionuclide separations process. Many of the disadvantages associated with the sugar-additive flowsheet could be avoided if the denitrated product can be directly feed to a glass melter, grout mixer, or some other suitable immobilization process. For example, provisions can be made to recycle all of the scrubber and condensate solutions generated by offgas treatment.

REFERENCES

1. H. Welland, *NWCF Process Modification for Sodium-Bearing Waste Project Conceptual Design*, Final Report, INEL/INT-97-00075, April, 1997.
2. Chemical Reaction and Equilibrium Software and Extended Thermochemical Database, Outokumpu HSC Chemistry for Windows, Version 2.0: Outokumpu Research Oy, Finland.
3. M.T. Abegg, R. C. Green, *Sugar Additive Safety Concerns and Suggested Approaches to the Safe Operation of the 30-cm Calciner pilot Plant*, Subcontract No. C96-175899, January, 1996.
4. D. W. Marshall and R. C. Green, *Sugar-Nitrate Interaction and Sugar-Calcine Reactivity Study*, LMITCO Internal Report, in progress.
5. M. T. Abegg, *Critique of Sugar-Nitrate Interaction and Sugar-Calcine Reactivity Study*, Subcontract No. C96-176083, August, 1996.
6. Safety Consulting Engineers, Inc; *Classification and Packing Group Assignment of Division 5.1 Materials; Test Results*, SCE No. 9688, Subcontract No. C96-530646, October 22, 1996.
7. C. N. Eatough, and L. D. Smoot, L.D., *Calcine Dust Explosion Potential*, Subcontract No. C96-176113 Final Report, September 13, 1996.
8. N. Hukari, personal communication, NOAA Environmental Research Laboratories, Idaho Falls, Idaho, December, 1996.
9. *Handbook of Chemistry and Physics*, Boca Ruton, Florida, 62nd Edition, CRC Press, Inc., 1981-1982.
10. F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, I. Jaffe, *Selected Values of Chemical Thermodynamic Properties, Part I. Tables*, U.S. Department of Commerce, National Bureau of Standards, July 20, 1961.
11. R. F. Murray and D. W. Rhodes, *Low Temperature Polymorphic Transformations of Calcined Alumina*, IDO-14581, September, 1996.
12. H. J. Eding, M. L. Huggins, A. G. Brown, *Phase Transformations in Alumina*, IDO-14580, Standard Research Institute, Subcontract No. AT(10-1)-205, February, 1962.
13. L. A. Bray, *Denitration of PUREX Wastes with Sugar*, HW-76973, Rev, April, 1963.

Appendix A

Calcination History

Calcination History

Acidic aqueous radioactive wastes resulting from fuel reprocessing at the Idaho Chemical Processing Plant (ICPP) have been historically treated in fluidized-bed calciners to convert the liquids into a free-flowing granular solid oxide (referred to as calcine). The ICPP liquid wastes generally fall into one of two separate categories; (1) high-level radioactive wastes which are the raffinate waste stream generated by separating uranium from the fuel dissolver product, and (2) intermediate-level radioactive wastes which are generated by cleaning the uranium extraction solvents and also by facility and equipment decontamination procedures. The intermediate-level wastes are referred to as sodium-bearing wastes (or SBW) because they contain relatively high concentrations of sodium-nitrate. The raffinate wastes can be converted into a relatively high quality calcine without significant operational difficulties. However, the SBW is more difficult to calcine due to the low melting points of sodium-nitrate and potassium-nitrate (also relatively abundant in the SBW) which persist in the calcine product above the nominal operating temperature of 500°C. Until recently, the accepted method for calcining the SBW was to blend a small portion of it with the raffinate wastes, which act as a diluent to the molten alkali-nitrates and prevent them from agglomerating the calciner particulate bed.

With the termination of fuel reprocessing at the ICPP in 1992, the amount of high-level liquid waste has already been reduced to less than 0.3 million gallons. This waste is scheduled to be calcined during the upcoming 1997-1998 calciner campaign with a small portion of the SBW inventory, which currently amounts to over 1 million gallons. Additional SBW will be generated as plant cleanup operations continue into the future, leaving a significant volume of intermediate-activity waste to be processed without the raffinate wastes. As time progresses, the radioactive wastes generated by decontamination activities will become less radioactive due to natural radioactive decay and routine cleaning of the plant facilities. Eventually, the radioactive solutions will be classified as low-level wastes and will not need to be treated prior to being immobilized as a solid.

Calcination Facilities

A concise historical perspective of fuel reprocessing activities at the INEEL, including the dispositioning of the radioactive wastes, has been published in recent conference proceedings.^a Table A1 provides a listing of reports in the external literature on waste calcination development activities at the INEEL, dating back to 1955. Well over 100 man-years of calcination studies are responsible for these reports, as well as other unpublished reports. Through this extended effort, a significant understanding of calcination mechanisms and process performance guidelines has been established.

The concept of calcining radioactive liquid wastes originated at Argonne National Laboratory (ANL). Initially, studies were completed in a 7.5-cm diameter, indirect-heated calciner in the mid 1950's. Later, feasibility tests were conducted in a 15-cm diameter calciner. The first type of waste to be calcined was acidic aluminum-nitrate solutions. Calcination temperatures over the range of 350-550°C were investigated. Eventually tests were conducted with sodium-bearing waste (SBW) liquids. A limited number of calciner tests were completed to investigate the possibility of adding sugar to the feed to help denitrate the waste solids.

^a D. A. Knecht, M. D. Staiger, J. D. Christian, and C. L. Bendixsen, "Historical Reprocessing of Spent Fuel and HLW Management at the Idaho Chemical Processing Plant," *Proceedings of the International Topical Meeting on Nuclear and Hazardous Waste Management, Seattle, Washington, August 18-23, 1996*.

Table A1. Reports in the external literature on INEEL waste calcination studies.*

Author	Date	Title	Source	Reference
A. A. Jonke	1955	A Fluidized Bed Technique for Treatment of Aqueous Nuclear Wastes by Calcination to Oxides	Sanitary Engineering Aspects of the Atomic Energy Industry. A Seminar Sponsored by the AEC and the Public Health Service, Cincinnati Dec 1955 TID-7517 (Pt I), pp 374-383	pp 374-383
C. E. Stevenson	1957	Effluent Disposal Considerations and Summary of Methods Used	Symposium on Reprocessing of Irradiated Fuels, Brussels	TID-7534, Book 1, pp. 351-361
A. A. Jonke, et al	1957	The Use of Fluidized Beds for the Continuous Drying and Calcining of Dissolved Nitrate Salts	Nuclear Science and Engineering	2
E. S. Grimmer	1957	Calcination of Aluminum-Type Reactor Fuel Wastes in a Fluidized Bed	Proceedings: Am. Nuc. Soc. Mtg., Pittsburgh, May	IDO-14416
J. W. Loeding, et al	1958	Fluidized Bed Conversion of Fuel-Processing Wastes to Solids for Disposal	2nd UN Int. Conf. on Peaceful Uses of Atomic Energy, Geneva	Vol. 18, pp 56-67
K. L. Rhode, et al	1959	Fission-Product Ruthenium Volatility at High Temperature	Ind. Eng. Chem.	Vol. 51
G. K. Cederberg, et al	1959	Minimizing Gaseous and Particulate Activity in Idaho Chemical Processing Plant Off-Gas	6th AEC Air Cleaning Conf.	p. 140
B. R. Wheeler	1959	Waste Calcination Off-Gas Studies	6th AEC Air Cleaning Conf.	p. 26
E. F. Edwards	1959	Waste Calciner Off-Gas System	6th AEC Air Cleaning Conf.	p. 55
D. W. Rhodes	1959	Adsorption of Volatile Ruthenium on Silica Gel	6th AEC Air Cleaning Conf.	p. 68
D. W. Rhodes	1960	Fixation of Fission Products in Stable Solid Media and Storage of Calcined Wastes at the ICPP	2nd AEC Symposium on Waste Fixation	TID-7613
A. A. Jonke	1960	Some Recent Developments in Fluid-Bed Calcination Equipment	2nd AEC Symposium on Waste Fixation	
J. I. Stevens	1960	Fluidized Bed Calcining at the ICPP	2nd AEC Symposium on Waste Fixation	BK 1, pp 46-61
J. I. Stevens	1960	Treatment, Processing and Future Disposal of Radioactive Wastes at the Idaho Chemical Processing Plant	Article published in "Disposal of Radioactive Wastes" by IAEA 1960	pp. 481-507
J. I. Stevens	1961	The Fluidized Bed in Radioactive Waste Disposal	AIME Fall Meeting 1961	
J. A. Buckham, et al	1962	The Fluidized Bed Waste Calcination Process	IAEA Symposium, Vienna	Paper 17
J. A. Buckham, et al	1962	Pilot-Plant Studies of the Fluidized-Bed Waste Calcination Process	Proceedings of the Symposium on Treatment and Storage of High Level Radioactive Wastes, IAEA, Vienna, Oct 1962	pp 233 - 254
R. D. Modrow, et al	1963	Removal of Particulates from Waste Calcining Facility Off-Gas	8th AEC Air Cleaning Conf.	p. 280
J. A. Buckham, et al	1963	Development of the Fluidized Bed Waste Calcination Process	AIChE 50th Meeting 1963	No. 53, Vol. 60
J. A. Buckham, et al	1964	Fluidized Bed Calcination of High-Level Radioactive Wastes in a Plant-	AIChE 53th Meeting 1964	

Table A1. Reports in the external literature on INEEL waste calcination studies.*

Author	Date	Title	Source	Reference
		Scale Facility		
E. S. Grimmer	1964	Kinetics of Particle Growth in the Fluidized Bed Calcination Process	AIChE Journal	Vol. 10, No. 5
E. S. Grimmer	1965	Selection and Performance of Sodium-Potassium Heating Systems for a Fluidized Bed Process	CEP Symposium Series	No. 59, Vol. 60
E. D. Cooper	1965	A Performance Comparison of Pilot Plant Scale Fluidized Bed Calciners	CEP	Vol. 61, No. 7
D.F. Bunch, et al	1965	Environmental Effects from Operation of the Waste Calcining Facility	1965 HP Society Meeting, Los Angeles CA, June 14-17	
E. D. Cooper	1965	Pilot-& Plant-Scale Fluidized Bed Calciners	CEP	Vol. 61, No. 7
J. C. Petrie, et al	1966	Improved Air Distributor Caps for Fluidized Beds	CEP	Vol. 62, No. 3
E. J. Bailey, et al	1966	Fluidized Bed Calcination of New Types of High-Level Wastes	Proceedings of the Symposium on the Solidification and Long-Term Storage of Highly Radioactive Wastes, Richland, Wash. Feb 1966	CONF-660208 pp 235-246
G.E. Lohse, et al	1966	Initial Operation of the Idaho Calcining Facility with Radioactive Feed	Proceedings of the Symposium on the Solidification and Long-Term Storage of Highly Radioactive Wastes, Richland, Wash. Feb 14-18, 1966	CONF-660208 pp 388-399
D. W. Rhodes	1966	Storage and Further Treatment of Product from Fluidized Bed Calcination of Radioactive Wastes	Proceedings of the Symposium on the Solidification and Long-Term Storage of Highly Radioactive Wastes, Richland, Wash. Feb 1966	CONF-660208 pp 623-641
J. L. Lockard, et al	1966	Economics of Waste Management Involving Fluidized-Bed Calcination	Proceedings of the Symposium on the Solidification and Long-Term Storage of Highly Radioactive Wastes, Richland, Wash. Feb 1966	CONF-660208 pp 844-857
J. A. Buckham, et al	1966	Fluidized Bed Calcination of High-Level Radioactive Wastes in a Plant-Scale Facility	AIChE Symposium Series	No. 65, Vol. 62, p. 52
B. M. Legler	1967	Feed Injection for Heated Fluidized Beds	CEP	Vol. 63, No. 2
J. C. Petrie, et al	1967	Heat Transfer from Horizontal Tube Bundles to Air-Fluidized Beds	AIChE 60th Meeting 1967	
B. R. Wheeler, et al	1967	Storage of Radioactive Solids in Underground Facility: Current ICPP Practices and Future Concepts	IAEA Symposium, Vienna	SM-93/31
J. A. Buckham, et al	1967	Process Heating of Fluidized Beds by In-Bed Combustion	Joint Mexican and AIChE Mtg. Mexico City Sep 1967	
G. E. Lohse, et al	1968	Calcination of Zirconium Fluoride Wastes in Pilot Scale and Plant Scale Fluidised Beds	The Institution of Chemical Engineers, Proceedings of the Symposium on Fluidization, TriPartie Chemical Engineering Conf., Montreal, Sep 1968	Symposium Series No. 30
J. A. Buckham, et al	1968	Process Heating Via Combustion	CEP	Vol. 64, No. 7
J. C. Petrie,	1968	In-Bed Heat Exchangers	CEP	Vol. 64, No. 7

Table A1. Reports in the external literature on INEEL waste calcination studies.*

Author	Date	Title	Source	Reference
et al				pp 45-51
C. L. Bendixsen, et al	1968	Experience with Non-Mechanical Solids Flow Control Devices in the Waste Calcining Facility	ASME Symposium, Boston	
C. M. Slansky, et al	1969	Ultimate Management of Radioactive Liquid Wastes	CEP Symposium Series	Vol. 65 No. 97
G. E. Lohse, et al	1970	Nuclear-Waste Disposal: Forming Solids Saves Space	Chemical Engineering	Vol. 77 No. 3 p. 94
T. K. Thompson, et al	1972	Fluidized Bed Calcination of Radioactive Waste Using In-Bed Combustion Heating	Nuclear Technology	Vol. 16
F. H. Anderson, et al	1976	Design Criteria for the New Waste Calcining Facility at the Idaho Chemical Processing Plant	IAEA Symposium, Vienna, March 1976	IAEA-SM-207/62
W. A. Freeby	1976	Fluidized-Bed Calcination of Simulated Commercial High Level Radioactive Wastes	AIChE Symposium Series	No. 154, Vol. 72 p.140
G. E. Bingham, et al	1976	The New Waste Calcining Facility	24th Conference on Remote Systems Technology, Wash. DC Nov 14-19	
B. R. Dickey, et al	1978	Calcine Production and Management	Proceedings of the Conf. on High-Level Radioactive Solid Waste Forms, December, Denver	NUREG/CP-0005 pp. 519-558
R. E. Schlindler	1978	Fluidized-Bed Calcination of LWR Fuel- Reprocessing HLLW: Requirements and Potential for Off-Gas Cleanup	15th Air Cleaning Conf.	Vol. 1, p. 82
H.H. Loo, et al	1978	The NWCF Process Off-Gas Filtration System and Remote In-Place DOP Test	15th DOE Air Cleaning Conf.	Vol. 2, p. 806
R.R. Smith, et al	1978	The NWCF Maintenance Features and Capabilities	Proceedings Am. Nuc. Society 26th Mtg.	pp. 230-235
R. T. Jacobs, et al	1978	Remote Process Connectors for the NWCF	Proceedings Am. Nuc. Society 26th Mtg.	pp. 241-249
K. W. May, et al	1978	A Remotely Replaceable and Testable Off-Gas Filter System for the NWCF	Proceedings Am. Nuc. Society 26th Mtg.	pp. 250-254
R. D. Fletcher, et al	1978	Remotely Replaceable Fuel and Feed Nozzles for the NWCF Calciner Vessel	Proceedings Am. Nuc. Society 26th Mtg.	pp. 255-259
M. E. Jacobson, et al	1978	An Integrated Remote Process Sampling System for the NWCF	Proceedings Am. Nuc. Society 26th Mtg.	pp. 260-268
C. M. Cole, et al	1978	The NWCF/ICPP Remote Decontamination Facility	Proceedings Am. Nuc. Society 26th Mtg.	pp. 269-273
M. Fortsch, et al		Process Improvements in the NWCF	Waste Management	
G. E. Bingham, et al	1978	The New Waste Calcining Facility	Basel Switzerland 1978	
D. W. Rhodes, et al	1979	Ruthenium Containment During Fluidized Bed Calcination of Commercial High-Level Waste	AIChE Symposium Series	Vol. 75, No. 191
R. E. Schindler	1980	Incineration of Contaminated Organic Solvents in a Fluidized-Bed	16th Air Cleaning Conf.	Vol. 2, p. 950

Table A1. Reports in the external literature on INEEL waste calcination studies.*

Author	Date	Title	Source	Reference
		Calcliner		
F. C. Olds	1982	Nuclear Waste Calcining at the INEL	Power Engineering April 1982	pp. 76-79
R. R. Smith, et al	1982	The New Waste Calcining Facility at ICPP	Proceedings; Am. Nuc. Soc., April	pp. 445 _ 448
A. P. Hoskins	1984	Processing Experience with the New Waste Calcination Facility	Proceedings; Am. Nuc. Soc., August	Pages 1-87 thru 1-91
R. C Mairson, et al	1986	High-Level Waste Management at the Idaho Chemical Processing Plant	Waste Management 86	
B. R. Wheeler, et al	1986	High-Level Waste Management at the Idaho Chemical Processing Plant	Spectrum 86 - Niagara Falls	Vol. 1 p 779
R. L. Nebecker	1986	Required Development and Installation of NOx Abatement Process at the Idaho Chemical Processing Plant	Waste Management 86	Vol. 1 pp. 287-291
S. S. Bodner	1987	Fines Feeding to a Dilute-Phase Transport System	Pneumatech III, Glasgow Scotland	
H. B. Eldredge, et al	1988	The Effect of Waste Chemistry on the Fluidized Bed Calcination Process for High Level Liquid Waste Disposal	Spectrum 88 - Pasco	pp. 275 - 277
J. A. Gay	1988	A Retrofit design of Remotely Removable Decontamination Spray Nozzles for the New Waste Calcining Facility at the Idaho National Engineering Laboratory	Waste Management 88	
J. D. Christian	1990	Behavior and Control of Ruthenium During Operation of the New Waste Calcining Facility at the Idaho Chemical Processing Plant	21 st DOE Air Cleaning Conf. - August	CONF-90813
J. A. McCray	1990	Description of the NOx Selective Catalytic Reduction Process	Trans. Am. Nuc. Society	Vol.61 pp 59
J. P. Law, et al	1990	Operation of a Dilute-Phase Pneumatic Transport System at the New Waste Calcining Facility	Pneumatech IV, Glasgow	pp. 447- 451
J. A. McCray, et al	1992	The NOx Abatement Program at the Idaho Chemical Processing Plant	Spectrum 92 - Boise	Vol. 1, pp. 174-178
C. J. Herzog, et al	1991	Calcliner Pilot Plant Waste Minimization Practices at the ICPP	Waste Management 91	Vol. 1 pp.799- 802
D.L. Griffith	1994	Retrieval of ICPP Calcine Status of Development Work	Spectrum 94 - Atlanta	Vol. 2 p 1781
D. A. Knecht, et al	1996	HLW Management at the Idaho Chemical Processing Plant Historical Development of Waste Calcination, Vitrification, and Glass Ceramic Waste Form	Waste Management 96	paper
D. A. Knecht, et al	1996	Historical Reprocessing of Spent Fuel and HLW Management at the Idaho Chemical Processing Plant	Spectrum 96 - Seattle	Vol. 3 pp. 2219-2233

* References filed by M. D. Staiger, HLW Plant Engineering, ICPP (526-3122)

After the concept of fluidized-bed calcination gained acceptance, a variety of cylindrical and rectangular pilot plant calciners (most of which were indirectly heated) were built at the INEEL Central Facilities Area (CFA) and the Idaho Chemical Processing Plant (ICPP). It was here that in-bed heating was first investigated, using heat transfer tubes or in-bed combustion to supplement bed heating. Sugar-additive calcination of SBW was again investigated in a 30-cm rectangular calciner. Reports on these tests purport the potential of using sugar as a reductant to promote denitration of alkali nitrates. Stable bed conditions and product acceptability were used as measures for success of the sugar-additive testing.

Eventually a full-scale demonstration facility, now referred to as the Waste Calcining Facility (WCF), was built and operated in the early 1960's. Heat to the WCF was initially supplied by an in-bed heat exchanger bundle using sodium-potassium alloy (Na-K) to maintain the bed at approximately 400°C. Then, in order to allow increased WCF capacity and reliability, in-bed combustion heating, using atomized kerosene and oxygen was installed. This allowed the bed temperature to be increased to 500°C, which became the standard operating temperature.

As the WCF began to age, and as new fuel shipments increased at the ICPP, the need to construct a new, remote-maintenance calcination facility became imperative. The New Waste Calcining Facility (NWCF) design began in 1974 and construction began in 1976. It incorporated a significantly larger calciner bed and improved on the offgas treatment system. An exotic metal alloy (Nitronic 50) was used to fabricate the corrosion-susceptible process components in order to protect them against high fluoride concentrations that would be present in the offgas when calcining zirconium-type wastes.

Radioactive feed was first introduced to the NWCF in September, 1982, after extensive system operability and non-radioactive feed testing. Operations continued until March, 1984, when all of the available radioactive liquid feed had been processed. The second NWCF campaign commenced in September, 1987, with the processing of zirconium-type wastes. Sodium-bearing wastes were coprocessed with the zirconium wastes since it was recognized that SBW was difficult to process without adding a diluent. A third NWCF campaign started in December 1991, and ended November, 1993, including some down periods to perform system maintenance. Currently, a fourth campaign is scheduled to startup in May, 1997 to calcine the remaining 300,000 gallons of fuel reprocessing raffinates.

Calciner Flowsheet Development

Wastes that have been calcined at the ICPP include aluminum nitrate - nitric acid, aluminum nitrate - ammonium nitrate, stainless steel sulfate, stainless steel nitrate, zirconium fluoride, Rover waste, and sodium-bearing wastes. Literally hundreds of pilot plant tests have been completed to develop successful calcination chemistries. A comprehensive review of pre-1980 calcination flowsheet development work was published by Newby, et. al.^{b1} This report describes the systematic development and testing that was routinely completed to ensure problem-free operation of the WCF.

Three pilot plants were constructed at the ICPP to develop flowsheets for the process wastes. These pilot plants are, in order of increasing internal diameter, the 10-cm, 15-cm, and 30-cm Calciner Pilot Plants. The 30-cm calciner was designed to help scale-up the calcination flowsheets to the NWCF. It has a similar offgas treatment system and operates at over 10-times the capacity as the 10-cm calciner. The 10-cm calciner, because of its small capacity, is used to perform parametric and flowsheet sensitivity tests. However, it operates as a slugging bed and does not model the fluid-bed dynamics. The 15-cm calciner is more useful for studying flowsheet gross behavior, although, it too does not possess dynamic

^{b1} B. J. Newby, J. H. Valentine, G. L. Cogburn, and C. M. Slansky, *Calcination Flowsheet Development*, ICP-1163, UC-70, Allied Chemical Corporation, October, 1978.

similitude with the NWCF. It is mainly used to boost confidence in the 10-cm calciner results, at 3-times the feedrate. It is not certain whether the 15-cm calciner operates in a bubbling or slugging bed regime.

During the 1980's, and up to the present, the chief objective of calcination development has been continued flowsheet development for the NWCF. As SBW has accumulated in the tank farm, the focus was on the development of flowsheets to process SBW by blending it with the zirconium raffinate waste and other diluents. The flowsheets were mainly developed for calcination at the normal operating temperature of the NWCF. Out of these efforts, the standard practice of calcining the sodium-bearing waste with aluminum nitrate feed stock was established.^c

The results of the numerous calciner runs helped established a data base of artificial intelligence (also referred to as the calcine advisor expert system)^d to predict flowsheet chemistries. Interpolation of the results of the data base helps to predict the amount of chemicals to blend with the feed to avoid bed agglomeration, to chemically bind up chloride and fluoride in the product, and to prevent the formation of α -aluminum in the product. Through the use of this system, subjective calcination characteristics are related to objective flowsheet performance criteria. This in turn helps guide flowsheet development and ultimately helps ensure successful calcine production in the NWCF.

Interest in the high-temperature and sugar-additive flowsheet was renewed by incentive to eliminate the significant amount of aluminum nitrate that is required to calcine SBW at 500°C. From crucible calcination tests designed to denitrate sodium-bearing LLW for grouting, insight was gained on the kinetics of sodium and potassium nitrate decomposition. It was shown that the wastes were not completely denitrated until temperatures as high as 850°C. The recommendation to investigate the sugar-additive flowsheet was based on previous attempts at ANL, CFA, and later at the ICPP, to use sugar to promote product denitration.

^c B. J. Newby, *Calcination of Sodium-Bearing Waste Using Aluminum Nitrate*, WINCO-1026, 1985.

^d B. H. O'Brien, *Calciner Pilot Plant Database and Calcination Advisor*, WINCO Internal Letter Report, December, 1989.

Appendix B

Rudiments of Fluidized-Bed Calcination

Rudiments Of Fluidized-Bed Calcination

The four decades of calcination development described in Appendix A has provided a fundamental understanding of calcination chemistry for several unique types of fuel reprocessing wastes and decontamination solutions. However, there is still much to be learned about waste spray deposition behavior and chemical conversion into calcine product, about combustion of kerosene fuel in the bed, and also about interactions of the burned and unburned fuel with the calcine product and volatile waste vapors. Up until the present, it has been sufficient to operate the calciner with only a stochastic understanding of the chemical processes. However, in order to improve upon established SBW calcination flowsheets, and to provide information appertaining to environmental permits, a mechanistic understanding of the chemical and physical processes is necessary.

This appendix is broken into four sections: (1) Overall Calcination Process Description; (2) SBW Waste Calcination Chemistry; (3) Particle Growth and Attrition; and (4) Kerosene Combustion Chemistry. The discussion will perhaps bring up more questions that it will answer. Indeed, there is much to be learned before an accurate molecular understanding of the chemistry will be achieved. Nevertheless, the information provided herein provides a basis for discussing what is known, and what is not known, about the calcination process.

The gross behavior of fluidized-beds is not addressed herein; this discussion is left to the legion of texts and reports which have been published on fluidized beds. A good review on the design of the ICPP fluidized beds and bulk behavior of the bed is given by Eldredge^a who developed correlations for predicting particle recirculation, feed deposition, and particle growth rates as a function of empirically-derived fitting parameters. However, parts of the discussion that follows are taken from Eldredge.

Calcination Process Description

The ICPP fluidized-bed calciner is a complex process involving particle fluidizing mechanics and multiple physical-chemical transformations of the feed into a solid, granular product. The liquid feed (comprised mainly of nitric acid and nitrate salts) is sprayed onto a bed of hot fluidized particles using air to atomize the feed as depicted in Figure B.1. The water and acids in the feed are vaporized and the nitrate salt residue remaining on the particles begins to decompose and is eventually converted into an oxide. Uniform feed deposition on the particles causes the particles to grow spherically as a function of residence time in the bed. Decomposition of the nitrates begins to occur as the film covering the hot particles dries and is heated up to the bed temperature. Multiple kinetic steps control the denitration and oxidation of the metal constituents as well as their conversion to crystalline phases and to durable, double-metal oxides such as NaAlO_2 . Constituent volatilization is also controlled by particle residence time, temperature, and chemical specification in the reaction vessel.

The fluidized bed hydrodynamics are controlled by passing a constant stream of preheated air up through a distributor plate at the bottom of the calciner vessel. The bed is further heated by in-bed, kerosene-oxygen, fuel injector nozzles which increase the fluidizing air superficial velocity (i.e., empty vessel linear gas velocity) above the fuel nozzles. The vaporizing feed and the feed atomizing air further affect the bed hydrodynamics above the feed injection level. The fluidizing air is adjusted to approximately twice the minimum velocity required to overcome the pressure drop through the bed. This causes a bubbling bed to exist at all levels in the calciner and helps to prevent serious particle size segregation throughout in the bed. The individual particles circulate randomly throughout the bed under

^a H. B. Eldredge, *The Solids Mixing Model for Scale-Up of the Fluidized Bed Calcination Process*, Ph.D. Dissertation, Department of Chemical Engineering, University of Idaho, 1991.

Figure B1. Schematic "cut-away" of the ICPP fluidized-bed New Waste Calcination Facility.

these conditions. The "well-mixed" conditions ensure uniform feed deposition on all particles. The calciner vessel has an expanded section above the bed to disengage the majority of fine particles which are entrained (elutriated) from the bed. The vessel offgas enters an offgas treatment system where the remaining fine particles are separated from the gas before it is discharged to the atmosphere.

SBW Calcination Chemistry

The history of an individual particle (or an ensemble of particles) in the calciner bed is illustrated in Figure B2. As the particles circulate randomly in the bed, they pass through the feed spray zone where they are coated with fresh feed. The particles are momentarily quenched by the cooler feed droplets and the energy required to vaporize the moisture and acids. Once out of the relatively cool feed spray zone, the particle is rapidly dried and heated by the thermal mass of the bed. As the particles are heated, the metal salts progressively decompose to hydroxides and oxides. Table B1 lists the major species believed to exist as the SBW is converted to metal oxides.

An important consideration in calcining SBW is the relatively high decomposition temperatures of sodium and potassium nitrates, which also have low melting points. Sodium nitrate theoretically decomposes to sodium hydroxide or to the sodium dioxide dimer, Na_2O_2 , between 400-550°C. This is followed by conversion to sodium monoxide at around 650°C. However, experimental evidence shows that some sodium nitrate persists in standard SBW solids up to 850°C. Because the salts are molten at 500°C, this generally leads to particle agglomeration, unless a diluent, such as aluminum nitrate, is added to the feed.

Aluminum nitrate decomposes at a fairly low temperature. It is initially converted to amorphous aluminum, but can be subsequently converted to crystalline phases, such as γ -alumina and α -alumina, at elevated temperature (>900°C). Crystalline phases of aluminum are highly coordinated structures. They are some of the most refractory materials known. With in-bed combustion, crystalline phases of aluminum can be formed in the calcine. Fundamental laboratory studies provide evidence to suggest that sodium nitrate can initiate aluminum crystals, which grow rapidly in the flame region in the calciner bed.^{bc} For this reason, boric acid is usually added batch-wise to the feed to suppress crystallization in the product. This also helps control the particle size and improves the solubility of the product in the scrub system.

Sodium and aluminum can also combine to form a double-metal oxide with a general formula of NaAlO_2 . The formation of this compound appears to depend on temperature and the availability of amorphous, rather than crystalline, aluminum in the calcine. The temperature dependence of this reaction is not well established, but sodium aluminate has been detected in SBW-aluminum calcine product.

Calciner Bed Hydrodynamics

Stable bed hydrodynamics requires a balance on the production of fines and control of particle agglomeration in the bed. The production of particles small enough to be elutriated with the effluent calciner gases must be minimized while producing a sufficient amount of small "seed" particles to provide nuclei for particle growth in order to stabilize the mean diameter of the bed particles. Uniform feed deposition on the particles requires a uniform nozzle spray pattern and thorough mixing of the bed

^b H. J. Eding, M. L. Higgins, and A. G. Brown, "Phase Transformations in Alumina," IDO-14580, February, 1962..

^c R. F. Murray and D. W. Rhodes, "Low Temperature Polymorphic Transformations of Calcined Alumina," IDO-14581, September, 1962.

Figure B2. Particle history in the fluidized bed.

Table B1. Fate of SBW feed components during calcination.

Component	Assumed Oxidation State in Production	Assumed Compounds Formed
Al	+3	Al ₂ O ₃ , Al ₂ O ₃ B ₂ O ₃ , CaO·Al ₂ O ₃ , KAlO ₂ , NaAlO ₂
B	+3	Al ₂ O ₃ B ₂ O ₃ , CaO·B ₂ O ₃ , KBO ₂ , NaBO ₂
Cd	+2	CdO, CdO·Al ₂ O ₃
Ca	+2	CaO, CaO·Al ₂ O ₃ , CaO·B ₂ O ₃ , CaF ₂ Ca ₃ (PO ₄) ₂ , CaS
Cl	-1	KCl, NaCl, volatile
Cr	+6	K ₂ CrO ₄ , Na ₂ CrO ₄
F	-1	CaF ₂ , KF, NaF
Fe	+3	KFeO ₂ , NaFeO ₂
Pb	+2	PbO, PbO·Al ₂ O ₃
Mn	+4	MnO ₂
Hg	-	volatile
Mo	+6	K ₂ MoO ₄ , Na ₂ MoO ₄
Ni	+2	NiO, NiO·Al ₂ O ₃
NO ₃	-1	NO, NO ₃ , NO ₂ ↑
PO ₄	-3	Ca ₃ (PO ₄) ₂ , K ₃ PO ₄ , Na ₃ PO ₄
K	+1	KAlO ₂ , KBO ₂ , KCl, K ₂ CrO ₄ , KF, KFeO ₂ , NaNO ₃ , Na ₃ PO ₄ , Na ₂ SO ₄
Na	+1	NaAlO ₂ , NaBO ₂ , NaCl, Na ₂ CrO ₄ , NaF, NaFeO ₂ , NaNO ₃ , Na ₃ PO ₄ , Na ₂ SO ₄
SO ₄	-2	CaSO ₄ , K ₂ SO ₄ , Na ₂ SO ₄
U	+6	K ₂ UO ₄ , Na ₂ UO ₄
Zr	+4	ZrO ₂ , CaZrO ₃

while the product is continually drawn from the bed to maintain a constant bed height. Buildup of particle agglomerates (caking) in the bed, on the vessel walls, on the calciner appurtenances, or on the feed nozzles must be avoided.

Fine particles are generated by flash evaporation of the liquid droplets prior to and after adhering to the bed particles. The current feed nozzle design intentionally produces a finely divided mist in order to enhance uniform deposition on the bed particles. The atomized feed droplets evaporate according to the d^2 evaporation law:

$$d^2 = d_o^2 - \left[8 \frac{\rho_{air} D_{H_2O,air}}{\rho_l} \ln(1+B) \right] t \quad [m^2]$$

where B is the Spaulding transfer number calculated from the following quantity,

$$B = C_{pl} \frac{(T_\infty - T_s)}{\Delta H_v}$$

(with standard convention for all symbols). These equations show that the droplet life is a direct function of the properties of the gas, the temperature difference between the droplet surface and the surroundings, and most importantly, the initial diameter of the feed droplets size. Hence, the feed droplet size can be increased to offset enhanced flash evaporation at elevated bed temperatures.

Evaporation by film boiling on the surface of the particles will also increase at higher temperatures, resulting in the formation of small satellite particles that can detach from the surface of the

host particles. Film boiling results when the rate of heat transfer from the bed particles is high enough to cause rapid evaporation, which, consequently prevents the droplets from wetting and adhering to the particle surface.

To a lesser degree, the feed atomizing air is also believed to control the particle size through jet grinding. By increasing the velocity of the atomizing air, the momentum of the feed spray is increased. This increases the intensity of the particle-particle collisions in vicinity of the feed nozzle. The collisions result in particle fracturing (attrition). The fluidizing air circulates the bed and causes particle collisions, but the fraction of fines attributed to the fluidizing air is minor compared to the fuel and feed nozzle atomizing air. An exclusive, high intensity, air nozzle is currently not installed in any the ICPP calciners to control the particle size by jet grinding.

The combined processes that affect the particle size distribution are illustrated in Figure B3. In order to maintain steady bed hydrodynamics, a target mean particle diameter must be achieved while the bed is withdrawn at the same rate as it is generated. This requires a balance between building the bed (increasing the particle diameters) and generating seed particles. If an excessive amount of fines are generated, or if the diameters of the fines are too small, then the fines will be elutriated from the bed, causing excessive loading on the offgas cleanup equipment and possibly resulting in a calcine product that is difficult to pneumatically transport.

Figure B3 Processes that affect the particle size distribution during fluidized bed calcination.

The use of sugar to react with the nitrates may also increase the rate of fines generation if the reaction is rapid and leads to material being propelled from the surface of the calcine particles, or if the reaction leads to internal particle pressures that cause the particles to rupture and fragment.

Particle elutriation is affected by the fluidizing air velocity at the top of the bed and by bubble eruption at the bed surface. As the air bubbles burst at the surface, both large and small particles are thrust up into the particle disengaging section. The fines that are entrained in the gas stream can be carried into the offgas system unless they lose momentum and disengage from the offgas in the freeboard section above the calciner bed. Most of the larger particles fall back to the bed; however, some of the fines remain entrained and are carried over into the offgas cleanup train.

Combustion Chemistry

The fluidized bed of the NWCF is heated by an in-bed, oxygen-atomized, kerosene flame. There are four concentrically opposed fuel nozzles (which are not always used at the same time). Pure oxygen is used to provide higher combustion efficiency and to balance the fluidizing air requirements. As the

fuel mist evaporates, it mixes with the atomizing oxygen and is combusted via homogeneous reactions. The length of the flame is affected by the surrounding calcine bed and the fluidizing air which are both cooler and tend to quench the combustion reactions. The partially burned fuel then mixes with the bed and continues to burn, but at a much slower rate.

Fuel Evaporation

The fuel is injected through liquid-air coaxial-stream nozzles. The pressurized oxygen gas impinges on the liquid kerosene to produce a finely divided mist. Standard correlations show that the diameter of the spray droplets ranges from 10-100 μm .

Kerosene consists of the light distillate hydrocarbons with an average molecular formula of *n*-decene ($\text{C}_{10}\text{H}_{20}$) which are collected over the temperature range of approximately 175-315°C.

The rate of droplet evaporation is predicted by the d^2 evaporation law. For example, Sarofim and Bartok^c give measured evaporation constants, λ , that fit the d^2 law for liquid fuels; i.e.,

$$d^2 = d_o^2 - \lambda t \quad [m^2].$$

The constant for kerosene in a surrounding air temperature is 1064°K is 1.47×10^{-6} . For a droplet with an initial diameter of 25 μm , droplet extinction occurs in only 0.4 milli-seconds. A 100 μm droplet would exist for 6.8 milli-seconds. Obviously, higher flame temperatures give rise to more rapid evaporation rates. Since the peak flame temperature for a kerosene liquid-oxygen flame is around 2000°C, there is sufficient heat to completely vaporize most of the droplets before they contact the bed.

There is however, a small fraction of the spray which impinges on the bed particles at the edge of the flame near the nozzle, or as particles penetrate the flame zone near the nozzle. This fuel is also rapidly vaporized. However, the fuel that contacts the bed is broken down and burned differently than the fuel that is vaporized and rapidly burned in the flame zone.

Fuel Combustion

The combustion of hydrocarbons is complex but can be generally explained by the presence of specific radicals that are responsible for hydrogen abstraction, bond cleavage, and oxidation of the fuel. Three unique temperature regimes (low-temperature, intermediate-temperature, and high-temperature) have been distinguished- each characterized by the presence or lack of presence of the radicals and intermediates that control the reaction rates and conversion to end products. For example, at intermediate flame temperatures (approximately 800-1200°K), concentrations of the hydroxide radical ($\dot{\text{O}}\text{H}$) become significant and speed up the rate of fuel oxidation. In the low temperature region, the hydroxide radical is shifted to H_2O_2 , which is stable. In the upper temperature region, concentrations of other radicals, including hydrogen atoms ($\dot{\text{H}}$) and oxygen atoms ($\ddot{\text{O}}$), increase and accelerate the attack and oxidation of the fuel. At very high temperatures ($T > 1800^\circ\text{K}$), the reactions become almost instantaneous, reacting as soon as the fuel and oxidizer are mixed.

^c W. Bartok and A. F. Sarofim, *Fossil Fuel Combustion*, New York, New York: John Wiley and Sons, 1991.

The low temperature combustion regime is characterized by endothermic reactions which tend to extinguish the flame. Hence, this regime is also called the "negative temperature coefficient" regime and produces what some have called "cool" flames. In this regime, the long-chain hydrocarbons are converted to appreciable concentrations of olefins ($\text{RC}=\text{CH}_2$), hydroperoxides (RCH_2OOH), alcohols ($\text{RC}-\text{OH}$), epoxides ($\text{RCH}-\text{CH}_2\text{O}$), aldehydes ($\text{R}-\text{CHO}$), and ketones ($\text{RC}=\text{O}$). The production of CO and CO_2 in this regime occurs through the reaction of the oxygenated compounds; for example,

with some contributions coming from;

This chemistry infers that a certain fraction of the unreacted kerosene which reaches the bed will not be oxidized to end products; rather, it may result in products of incomplete combustion (PICs).

At temperatures beginning about 800°C (527°C), the rate of hydrocarbon combustion increases dramatically and "hot ignition" occurs; that is, the reactions become exothermic and produce enough heat to auto-heat the reacting gases. However, the rate of CO oxidation is still relatively slow, proceeding by the bi-molecular reaction with the hydroxide radical shown above. Thus, the conversion of CO to CO_2 is very slow in the calciner bed, unless it is oxidized by NO_x or via heterogeneous reactions. The reaction of CO with NO_x , as well as the possibility of any number of surface reactions, makes an exact understanding of the calciner combustion kinetics a formidable challenge. Only a general mechanistic understanding is possible. It is also important to understand that the field of kinetics is progressing so rapidly that after first gaining these general insights, one should refer to the most recent literature in forming the basis for estimating the fate of PICs in the calciner.

In the central flame region where the peak temperature exceeds 2000°C , the combustion chemistry is very rapid and leads almost exclusively to end product of CO_2 and H_2O . However, as the kerosene spray approaches the bounding bed particles, the temperature drops and combustion then proceeds by the intermediate temperature, slower reaction rate, regime. In this regime, the end products include light hydrocarbons (via a process called beta-scissioning of the long-chain hydrocarbons), such as ethylene, ethane, and methane. Each of these species, like CO , are oxidized slowly at the bed temperatures and may result in measurable emissions from the calciner.

Pollutant Formation

This brief discussion on pollutant formation is only intended as a primer for understanding the possible formation of pollutants in the calciner. As already discussed, processes of inefficient combustion give rise to potential emissions of unburned hydrocarbons, including some constituents that are considered hazardous air pollutants (HAPs), such as acetone. However, it should be understood that to date, no definitive analysis of the NWCF offgas, except for NO_x , radionuclides, and CO/CO_2 , has been made. Thus, the inferences made in this section are on the basis of conjecture and not a definitive understanding of either the combustion chemistry nor the interactions of the feed and fuel by-products. A more thorough study is needed to estimate the potential emissions levels of all but the NO_x emissions.

The SBW contains several hazardous metals which are potentially volatile, including Cd , Cr , Hg , Pb , and radionuclides. From the calcine volatiles studies, it was concluded that nearly 100% of the Hg is

volatilized in the calciner. A fraction of the cesium may be released as volatile CsCl, but the majority of this compound is also captured in the offgas treatment system. Most all of the Cd, Cr, and Pb, should be retained in the product as oxides or sulfates.

Evaporation of the nitric acid and decomposition of the nitrates leads to high concentrations of NO_x (NO₂ and NO) in the offgas stream. However, because of the lack of any nitrogen in the combustion air and the fuel, the kerosene-oxygen flame does not produce any fuel-NO_x nor thermal-NO_x (nor prompt-NO_x). Thermal NO_x is only produced at high flame temperatures in the presence of molecular nitrogen through the classical Zeldovich mechanism;

where temperatures exceeding 1500°C are required to begin dissociating O₂ to any appreciable extent.

The only significant source of NO_x generated in the calciner is by the conversion of the nitric acid and nitrates to NO₂ and NO. The reaction sequence is simplified by the following reactions and equilibrium expressions;

As shown by these expression, the concentrations of NO₂ and NO are governed by the rate at which the nitrates are converted first to NO₂, which then disassociates to NO, and subsequently to molecular nitrogen and oxygen. The forward and reverse reactions rates for Expression B.6 and B.7 are relatively slow at the conditions in the calciner, therefore, it is inappropriate to estimate the NO_x emissions by an equilibrium composition calculation. The equilibrium composition is only on the order of a few ppm total NO_x. Concentrations as high as 33,000 ppm NO_x were measured at the NO_x Abatement Pilot Plant in 1991, with a time average of around 20,000 ppm.

The split between NO₂ and NO exiting the calciner vessel is approximately 90/10, respectively. However, this depends on the location of the measurement, and the length of the sample line used to measure the concentrations. Kinetic calculations show that NO₂ shifts to NO in the offgas line when the temperature is above 335°C, assuming the partial pressure of oxygen is 15%.^d Below this temperature, and also at higher partial pressures of oxygen, NO is converted to NO₂. Thus, once the offgas is cooled and diluted with air in the main stack, NO is converted back to NO₂. However, given enough residence time in the hot calciner, NO₂ would be driven to NO.

Other than HNO₃, HCl is another acid vapor that is possibly emitted from the calciner. However, calculations indicate that most of the chloride is converted to CaCl₂ or NaCl in the product. It may also be bound up with the volatile mercury, as HgCl₂, which is believed be captured by the offgas scrubber and quench systems.

^d From an internal company letter, BDMN-07-92, "ICPP Plume Visibility Report," dated May 19, 1992.

From the discussion on the fuel combustion chemistry, it is obvious that there are possible interactions between the volatile feed components and the products of incomplete combustion. Emissions may include trace quantities of oxygenated hydrocarbons, halogenated hydrocarbons, and possibly oxy-chloro-cyclic compounds (i.e, dioxins and furans). The 10-cm and 15-cm calciner pilot plant runs already confirm the presence of semi-volatile components, such as acetone, in the offgas. In addition, the simultaneous presence of NO_x , nitric acid vapors, and PICs may lead to the formation of nitrated organics. Nitro-benzene was also detected in the pilot plant scrub and condensate solutions, but this may have been formed by the nitration of organics captured in the acidic solutions.

Appendix C
Crucible Calcination Data

Crucible Calcination Data

Lead Experimenter:
Laboratory Technician:
From Internal Letter:

Joe Nenni (526-3350)
Steve Hinckley (526-1080)
JAN-05-95

Table C1. Thermodynamic equilibrium predictions for SBW with no-additive.

CALC. TEMP. (°C)	200	300	400	500	600	700	800	900
SOLIDS	WEIGHT FRACTION							
Al(OH) ₃	0.00001							
Al ₂ O ₃	0.01250	0.00628	0.00001					
AlOOH	0.15486	0.01320	0.00011	0.00002	0.00001			
CdO•Al ₂ O ₃	0.00001	0.00001						
Cd(OH) ₂	0.00002							
CdO	0.00156	0.00191	0.00223	0.00268	0.00280	0.00282	0.00287	0.00295
CaAl ₂ O ₄		0.00021	0.00001	0.00001	0.00001	0.00001	0.00002	0.00003
CaAl ₄ O ₇		0.00135						
CaB ₂ O ₄	0.00001							
Ca ₂ B ₂ O ₅		0.00014	0.00001	0.00001	0.00001			
Ca ₃ B ₂ O ₆		0.00191	0.00125	0.00134	0.00069	0.00019	0.00006	0.00002
CaF ₂	0.00162	0.00043	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001
Ca ₃ F(PO ₄) ₃	0.01042	0.00591						
Ca(OH) ₂		0.01118	0.02079	0.01499	0.00510	0.00152	0.00054	0.00023
Ca ₃ OH(PO ₄) ₃		0.00017						
CaO		0.00002	0.00116	0.00883	0.01767	0.02092	0.02225	0.02315
CaO ₂			0.00002	0.00013	0.00023	0.00025	0.00025	0.00024
Ca ₃ (PO ₄) ₂		0.00002						
CaSO ₃ •½H ₂ O	0.01430	0.00433	0.00004	0.00002	0.00002	0.00003	0.00003	0.00003
CaZrO ₂		0.00047	0.00243	0.00345	0.00362	0.00349	0.00335	0.00322
PbO		0.00009	0.00191	0.00238	0.00251	0.00254	0.00259	0.00265
PbO ₂	0.00001	0.00003	0.00010	0.00004	0.00002	0.00001		
PbO•Al ₂ O ₃	0.00200	0.00235	0.00001					
PbO•6Al ₂ O ₃	0.00014							
MnO				0.00001	0.00008	0.00042	0.00139	0.00309
MnO ₂	0.00475	0.00577	0.00666	0.00778	0.00738	0.00599	0.00430	0.00272
Mn ₂ O ₃			0.00003	0.00023	0.00085	0.00175	0.00228	0.00199
Mn ₃ O ₄					0.00001	0.00004	0.00011	0.00014
HgO	0.00110	0.00122	0.00016	0.00001				
NiO	0.00047	0.00062	0.00077	0.00092	0.00097	0.00097	0.00099	0.00102
NiO•Al ₂ O ₃	0.00018	0.00010						
KAlO ₂		0.00135	0.00795	0.05230	0.07936	0.08368	0.08357	0.07747
KBO ₂	0.00003	0.00005	0.00024	0.00129	0.00178	0.00173	0.00158	0.00134
KCl	0.00030	0.00054	0.00166	0.00605	0.00692	0.00548		
K ₂ CINO ₃	0.00035	0.00018	0.00016	0.00008				
K ₂ CrO ₄	0.00007	0.00011	0.00060	0.00332	0.00316	0.00217	0.00142	0.00066
KFeO ₂	0.00122	0.00137	0.00302	0.00869	0.00901	0.00752	0.00621	0.00492
KF			0.00002	0.00022	0.00047	0.00063	0.00073	0.00075
KOH			0.00025	0.00725	0.01636	0.02054	0.02302	0.02228
KNO ₃	0.09011	0.10814	0.11446	0.05075	0.00408	0.00035	0.00004	0.00001
KNO ₂			0.00009	0.00056	0.00036	0.00017	0.00009	0.00005
KO ₂				0.00001	0.00002	0.00004	0.00005	0.00006

Table C1. Thermodynamic equilibrium predictions for SBW with no-additive.

CALC. TEMP. (°C)	200	300	400	500	600	700	800	900
SOLIDS	WEIGHT FRACTION							
K ₃ PO ₄			0.00006	0.00540	0.00868	0.00665	0.00444	0.00236
K ₂ SO ₄	0.00167	0.00011	0.00066	0.00796	0.01030	0.00829	0.00614	0.00390
NaAlO ₂	0.00038	0.25141	0.32278	0.35215	0.34777	0.34710	0.35513	0.37079
NaBO ₂	0.00524	0.00522	0.00656	0.00717	0.00755	0.00794	0.00831	0.00871
NaCl	0.00712	0.00860	0.00919	0.00790	0.00775	0.00730		
Na ₂ CrO ₄	0.00262	0.00316	0.00327	0.00177	0.00211	0.00297	0.00368	0.00444
NaFeO ₂	0.00981	0.01202	0.01271	0.01085	0.01142	0.01285	0.01437	0.01599
NaF	0.00997	0.01451	0.01790	0.02143	0.02218	0.02206	0.02181	0.01912
Na ₃ AlF ₆	0.00023							
Na ₃ F(SO ₄)	0.00020	0.00097	0.00125	0.00119	0.00147	0.00188	0.00235	0.00255
NaOH		0.00177	0.08432	0.29720	0.34916	0.35221	0.35483	0.34730
Na ₂ OH(NO ₃)	0.00002	0.00832	0.08257	0.01740	0.00129	0.00016	0.00004	0.00002
Na ₃ OH(SO ₄)	0.00000	0.00058	0.01563	0.02560	0.02298	0.02014	0.01762	0.01458
NaNO ₃	0.64909	0.48304	0.23004	0.02956	0.00254	0.00033	0.00006	0.00002
NaNO ₂		0.00006	0.00070	0.00093	0.00048	0.00025	0.00015	0.00010
NaO ₂				0.00002	0.00004	0.00006	0.00008	0.00011
Na ₂ O							0.00002	0.00007
Na ₂ O ₂					0.00001	0.00002	0.00003	0.00005
Na ₃ PO ₄	0.00004	0.00645	0.01435	0.01312	0.01139	0.01309	0.01514	0.01721
Na ₂ SO ₄	0.01600	0.03274	0.03128	0.02669	0.02909	0.03303	0.03747	0.04295
ZrO ₂	0.00157	0.00158	0.00054	0.00028	0.00029	0.00040	0.00055	0.00071
Total Solids	2.24E+02	1.85E+02	1.59E+0	1.32E+02	1.26E+02	1.26E+0	1.23E+02	1.20E+02
			2			2		
GASES	VOLUME FRACTION							
HF						4.0E-06	0.00002	0.00009
OH							1.2E-06	5.7E-06
Hg		1.4E-06	0.00002	0.00002	0.00002	0.00002	0.00002	0.00002
N ₂	0.02997	0.03510	0.03944	0.04402	0.04495	0.04502	0.04499	0.04494
NO					1.3E-06	4.6E-06	0.00001	0.00003
O ₂	0.07283	0.08562	0.09648	0.10797	0.11030	0.11047	0.11043	0.11032
KCl					1.6E-06	0.00003	0.00018	0.00019
(KCl) ₂						3.8E-06	0.00002	3.9E-06
KF							3.4E-06	0.00003
KOH					1.4E-06	0.00002	0.00012	0.00052
NaBO ₂								1.2E-06
NaCl						0.00002	0.00019	0.00028
(NaCl) ₂						4.9E-06	0.00004	0.00001
NaF							2.5E-06	0.00003
(NaF) ₂							1.3E-06	0.00002
NaOH						0.00001	0.00012	0.00071
(NaOH) ₂							2.0E-06	9.7E-06
H ₂ O	0.89720	0.87927	0.86407	0.84799	0.84472	0.84440	0.84384	0.84280
Total Gases								

Table C2. Thermodynamic equilibrium predictions for SBW with ANN.

CALC. TEMP. (°C)	200	300	400	500	600	700	800	
SOLIDS	WEIGHT FRACTION							
2Al ₂ O ₃ •B ₂ O ₃	0.00007							
Al(OH) ₃	0.00002							
Al ₂ O ₃	0.05479	0.07143	0.03442	0.03311	0.03583	0.03719	0.03466	0.03411
AlOOH	0.33837	0.04206	0.00665	0.00203	0.00082	0.00038	0.00019	0.00010
CdO•Al ₂ O ₃	0.00002	0.00008	0.00008	0.00011	0.00017	0.00022	0.00024	0.00028
Cd(OH) ₂	0.00001							
CdO	0.00113	0.00148	0.00180	0.00180	0.00178	0.00175	0.00175	0.00174
CaAl ₂ O ₄		0.00043	0.00287	0.00543	0.00755	0.00973	0.01256	0.01463
CaAl ₄ O ₇		0.03476	0.04839	0.04868	0.04613	0.04217	0.03638	0.03171
Ca ₂ B ₂ O ₅		0.00002	0.00007	0.00006	0.00004	0.00003	0.00002	0.00002
Ca ₃ B ₂ O ₆		0.00006	0.00065	0.00038	0.00014	0.00006	0.00005	0.00003
CaF ₂	0.00107	0.00031	0.00048	0.00065	0.00072	0.00069	0.00034	
Ca ₃ F(PO ₄) ₃	0.00755	0.00365	0.00023	0.00002				
Ca(OH) ₂		0.00179	0.00181	0.00052	0.00016	0.00007	0.00004	0.00002
Ca ₃ OH(PO ₄) ₃		0.00005	0.00001					
CaO			0.00010	0.00030	0.00054	0.00089	0.00158	0.00231
CaO ₂					0.00001	0.00001	0.00002	0.00002
Ca ₃ (PO ₄) ₂		0.00002	0.00001	0.00001				
CaSO ₃ •½H ₂ O	0.01058	0.00308	0.00285	0.00326	0.00323	0.00304	0.00293	0.00258
CaZrO ₂		0.00008	0.00061	0.00076	0.00073	0.00073	0.00082	0.00083
PbO			0.00008	0.00027	0.00052	0.00081	0.00111	0.00130
PbO•Al ₂ O ₃	0.00005	0.00024	0.00228	0.00206	0.00169	0.00128	0.00087	0.00058
PbO•6Al ₂ O ₃	0.00375	0.00452	0.00004					
MnO•Al ₂ O ₃			0.00001	0.00008	0.00042	0.00121	0.00210	0.00279
MnO				0.00001	0.00005	0.00026	0.00080	0.00163
MnO ₂	0.00345	0.00458	0.00550	0.00539	0.00477	0.00363	0.00243	0.00141
Mn ₂ O ₃			0.00002	0.00015	0.00052	0.00094	0.00106	0.00076
Mn ₃ O ₄						0.00002	0.00004	0.00004
HgO	0.00080	0.00098	0.00014	0.00001				
NiO	0.00024	0.00028	0.00048	0.00051	0.00052	0.00052	0.00055	0.00056
NiO•Al ₂ O ₃	0.00038	0.00058	0.00036	0.00031	0.00030	0.00029	0.00025	0.00023
KAlO ₂		0.00259	0.06244	0.08367	0.08985	0.09335	0.09583	0.09687
KAl ₉ O ₁₄	0.00006	0.05238	0.00531	0.00110	0.00042	0.00017	0.00005	0.00002
K ₂ Al ₁₂ O ₁₉		0.02314	0.00431	0.00032	0.00005	0.00001		
KBO ₂	0.00002	0.00007	0.00069	0.00077	0.00073	0.00068	0.00062	0.00057
KCl	0.00022	0.00057	0.00377	0.00364	0.00315	0.00238		
K ₂ CINO ₃	0.00017	0.00013	0.00005					
K ₂ CrO ₄	0.00005	0.00015	0.00251	0.00188	0.00107	0.00059	0.00036	0.00019
KFeO ₂	0.00088	0.00143	0.00624	0.00526	0.00410	0.00324	0.00263	0.00219
KF			0.00006	0.00011	0.00016	0.00018	0.00010	
KOH			0.00003	0.00007	0.00012	0.00018	0.00027	0.00038
KNO ₃	0.06554	0.06660	0.01504	0.00047	0.00003			
KNO ₂			0.00001	0.00001				
K ₃ PO ₄			0.00212	0.00215	0.00146	0.00096	0.00063	0.00043
K ₂ SO ₄	0.00002	0.00017	0.00750	0.00538	0.00334	0.00237	0.00172	0.00127
NaAlO ₂	0.00058	0.35735	0.69523	0.70796	0.70307	0.70284	0.71815	0.72346
NaAl ₉ O ₁₄	0.00003	0.02655	0.00060	0.00021	0.00013	0.00008	0.00004	0.00002
Na ₂ Al ₁₂ O ₁₉		0.00610	0.00006	0.00001	0.00001			
NaBO ₂	0.00378	0.00500	0.00519	0.00537	0.00555	0.00565	0.00577	0.00580

Table C2. Thermodynamic equilibrium predictions for SBW with ANN.

CALC. TEMP. (°C)	200	300	400	500	600	700	800	
SOLIDS	WEIGHT FRACTION							
NaCl	0.00520	0.00673	0.00573	0.00597	0.00630	0.00575		
Na ₂ CrO ₄	0.00190	0.00246	0.00102	0.00159	0.00227	0.00267	0.00290	0.00305
NaFeO ₂	0.00713	0.00926	0.00722	0.00825	0.00928	0.01005	0.01071	0.01112
NaF	0.00661	0.01165	0.01423	0.01416	0.01367	0.01176	0.00521	
Na ₃ AlF ₆	0.00080							
Na ₃ F(SO ₄)	0.00009	0.00070	0.00093	0.00114	0.00134	0.00135	0.00069	
NaOH		0.00070	0.00261	0.00360	0.00444	0.00554	0.00738	0.00924
Na ₂ OH(NO ₃)	0.00001	0.00167	0.00010					
Na ₃ OH(SO ₄)		0.00021	0.00045	0.00045	0.00043	0.00043	0.00045	0.00043
NaNO ₃	0.47199	0.21959	0.00829	0.00035	0.00003			
NaNO ₂		0.00003	0.00002	0.00001	0.00001			
Na ₃ PO ₄	0.00004	0.00622	0.01001	0.01036	0.01093	0.01134	0.01172	0.01190
Na ₂ SO ₄	0.01145	0.02659	0.02685	0.02849	0.03007	0.03114	0.03264	0.03404
ZrO ₂	0.00114	0.00146	0.00141	0.00133	0.00135	0.00136	0.00131	0.00131
Total Solids								
GASES	VOLUME FRACTION							
AlOF ₂								2.0E-06
HCl						5.9E-06	0.00002	0.00001
HF				2.6E-06	0.00003	0.00016	0.00065	0.00101
OH							1.1E-06	5.2E-06
Hg		1.1E-06	0.00001	0.00002	0.00002	0.00002	0.00002	0.00002
N ₂	0.06209	0.06839	0.07243	0.07268	0.07269	0.07268	0.07263	0.07260
NO					2.2E-06	8.0E-06	0.00002	0.00005
O ₂	0.15344	0.16913	0.17926	0.17990	0.17992	0.17992	0.17983	0.17979
KCl						0.00002	0.00011	0.00012
(KCl) ₂						1.5E-06	7.9E-06	1.7E-06
KF							1.7E-06	8.4E-06
KOH							1.8E-06	0.00001
NaCl						0.00002	0.00020	0.00027
(NaCl) ₂						6.5E-06	0.00005	0.00001
NaF							2.3E-06	0.00001
(NaF) ₂							1.2E-06	3.9E-06
NaOH							3.1E-06	0.00002
H ₂ O	0.78447	0.76248	0.74829	0.74739	0.74734	0.74716	0.74646	0.74603
Total Gases								

Table C3. Results of X-Ray Diffraction Analyses

Sample #	Al:Na+K Mole Ratio	Calcination Temp. (EC)	Weight Percent of Compound in Sample				
			NaNO ₃	NaAlO ₂	Na ₂ SO ₄	Na ₂ Mo ₄ O ₁₃	K ₃ Na(SO ₄) ₂
1*	straight SBW	500	major				
2*	straight SBW	600	major				
3	straight SBW	700			not completed		
4	1:1	500	100				
5	1:1	600	25	52	13	9	
6	1:1	700		84	9	8	
7	1.5:1	500	100				
8	1.5:1	600		66			34
9	1.5:1	700		77			33
10**	2.5:1	500	100				
11**	2.5:1	600	100				
12**	2.5:1	700		100			

* samples were not complete, previous results are included

** samples were mainly amorphous, therefore, peak identification was very subjective

Figure C1. Mass of calcine vs. Calcination temperature for TGA on 200 ml of liquid SBW with 1:1 mole ratio of additive:Na+K.

Appendix D

Packed-Bed Calcine Volatility Tests

Packed-Bed Calcine Volatility Tests

Lead Experimenter:
Laboratory Technician:
Radio-chemical Analyst:
From Internal Letter:

John A. Del Debbio (526-3429)
Lonnie G. Olson (526-6872)
Robert K Hague (526-1377)
JAD-03-96/LGO-04-96/RKH-23-96,

Experimental Methods

Sodium-bearing waste simulants, prepared according to 2008 calcination flowsheets, were evaporated in an oven at 60°C. The resulting solids were crushed and sieved to produce workable particle sizes in the range of 0.1-0.5 mm. Both cold and tracer studies were conducted. For the tracer studies, three 500 ml batches were separately traced with solutions of $^{137}\text{CsCl}$, $\text{NH}_4^{99}\text{TcO}_4$ and Na^{36}Cl prior to evaporation. Table 1 lists the concentrations of the volatile species in the simulants used for the cold and tracer tests.

Although Cl volatilization was measured during the cold tests, the very small quantities present in the complex matrix of the solids created difficulties for the analytical methods used, resulting in unusually large standard deviations. Consequently, only the results of the tracer measurements are reported.

The test apparatus used for the volatilization measurements is schematically illustrated in Figure D1. A 20 g sample of the SBW solids was placed in the open-bottom alumina crucible on top of ceramic wool, which is 96% Al_2O_3 . The sample was heated at the test temperature while being purged with air at an actual flowrate of 2.5 L/m, and a superficial linear velocity of 0.20 m/s. The linear velocity approximates the velocity just above the distributor plate of the pilot plant calciners and New Waste Calcination Facility (NWCF). The section of the alumina sleeve above the tube furnace and the quartz chimney were heated to simulate the transfer line between the calciner and cyclone. For test temperatures of 500°C, 650°C, and 850°C, temperatures in this region averaged 460°C, 560°C, and 740°C, respectively. The temperature of bubbler #1 was maintained at 70°C to simulate quench tower temperatures. With the exception of a 4 hour run with ^{36}Cl , and a 12 hour cold run, all runs were 6 hours.

The solids before and after heating were analyzed in triplicate to determine the percentages of volatiles lost. After cooldown, all parts of the apparatus, except bubbler #2 and the condenser, were either soaked in, or rinsed with 4M HNO_3 to collect condensed volatiles for analysis. Bubbler #2 and the condenser were rinsed with deionized water. The total mass, or activity collected, expressed as disintegrations/minute, was used to calculate mass balances. For the cold tests, Cs and Cd analyses were done by Inductively Coupled Plasma (ICP) methods. Mercury was determined by Atomic Absorption Spectroscopy (AAS), and F by ion specific electrode techniques. For the tracer studies, ^{137}Cs was gamma-counted, and ^{99}Tc and ^{36}Cl were determined using beta-counting methods.

Table D1. Concentrations of volatile components in SBW simulants tested.

Components	2008 Composite	Molarities Cold Tests	Hot Tests
Cs	1.2E-5	1.1E-3	1.1E-5
⁹⁹ Tc	5.2E-6	na	2.5E-5
Hg	1.2E-3	1.1E-3	5.2E-4
Cd	3.0E-2	2.8E-2	1.3E-3
Cl	3.6E-2	2.9E-2	1.6E-2
F	7.6E-2	6.9E-2	3.3E-3

na = not applicable

Figure D1. High temperature calcination volatiles test apparatus.

Appendix E

**Laboratory-Scale Calcination
Mockup Studies**

Laboratory-Scale Calcination Mockup Studies

Lead Experimenter: John A. McCray (526-3745)
Jenn-Hai Pao (526-0072)
Laboratory Technicians: Cal K. Johnson (526-7376),
Tony Watson (526-3118)
From Internal Letter: JAM-08-96/JHP-06-96

LSCM System Description

The LSCM system is located in the walk-in hood in Laboratory 133 of CPP-637. A schematic of the equipment setup is presented in Figure E1. The system consists of a 3-1/2" diameter fluidized bed calciner. The distributor plate is a bubble cap design with three bubble caps located equidistant from each other, 1.062 inches from the center.

The fluidizing air is pre-heated by a tube furnace, followed by two semi-cylindrical ceramic fiber radiant heaters. The bed temperature is maintained with two additional semi-cylindrical ceramic fiber radiant heaters clamped around the fluidized bed vessel. The tube furnace and the clamp-on preheater provide 1.3 and 0.7 kW, respectively. The bed semi-cylindrical ceramic heaters supply a total of 2 kW to the fluidized bed. In addition, heat tapes are installed between the clamp-on pre-heater and the calciner vessel, on the off-gas line from the calciner vessel to the off-gas filter, and on the filter unit to provide extra heat input. The calciner vessel and all areas with heat tapes are insulated to minimize heat loss. Each heater is equipped with a 0 to 100% power control, which can be adjusted to attain the desired process temperatures.

The fluidizing air is supplied from a low pressure plant air source, and the air flow rate is measured with a rotameter before heating. Block and regulating valves control the fluidizing air flow rate requirements. The heated air enters the calciner plenum and then passes through the distributor plate into the calcine bed.

Calcine bed material is added to the calciner vessel through a feed pot equipped with a block valve. A 25 psig air purge is installed in the feed pot to ensure solids flow into the calciner vessel. The bed material enters the calciner vessel 15 inches above the distributor plate.

Liquid waste simulant feed is sprayed onto the fluidized bed particles 4 inches above the distributor plate, using a pneumatic (air) atomizing nozzle. The average liquid feed flow rate is 6-10 ml/min, and the liquid spray droplet size can be adjusted by varying the atomized air flow rate.

A filter unit equipped with a sintered metal filter is installed in the off-gas line to disengage solids (larger than 0.3 micron) from the off-gas stream. The off-gas is then cooled by a condenser to remove moisture, and then is released to the hood where it is vented through the laboratory ventilation system. As the pressure drop across the filter increases, the particles accumulated on the filter element are periodically removed using a 25 psig air blowback. The fines particles are collected below in a collection pot. The laboratory hood has a minimum 125 fpm air velocity into the hood.

An IBM computer is used to collect operating temperature and pressure data. Thermocouple and pressure transmitter readings can be stored in the computer for future evaluation.

Figure E1. Lab-scale calcination mockup schematic.

Test Feed Solutions

For all LSCM tests conducted, a SBW simulant with the following approximate concentrations was used:

- 1.9 M Sodium Nitrate (NaNO_3)
- 1.6 M Nitric Acid (HNO_3)
- 0.6 M Aluminum Nitrate ($\text{Al}(\text{NO}_3)_3$)
- 0.2 M Potassium Nitrate (KNO_3)

This simulant is absent of toxic metals and other additives that are present in actual SBW to simplify monitoring, product handling, waste disposal, and other safety concerns.

For each test run, additional 2.59 M aluminum nitrate was added to the SBW simulant to attain the desired feed sodium-plus-potassium to aluminum mole ratio.

Baseline Case Extended-Duration Test

A baseline-case extended-duration calcination test (Run 12) was performed with sodium simulant feed for the purpose of comparing results with those of denitration (high-temperature and sugar-additive) calcination tests. Run 12 was conducted using a 3.5:1 Al to Na+K mole ratio flowsheet, and 500°C operating temperature. This flowsheet has been previously proven for SBW calcination in other calciners. The starting bed for Run 12 was aluminum calcine.

Operating conditions and test results from this baseline run are added to the Tables throughout this report to provide a benchmark or reference for the alternative flowsheets. The final bed of this test after 60 hours of operation consisted of a significant percentage as large particles (greater than 595 micron).

High-Temperature Extended-Duration Tests

Operation Description

Four extended-duration LSCM calcination tests, Runs 11, 16, 17 and 18, were conducted at an elevated operating temperature of approximately 600°C. An additional extended-duration test, Run 20, was conducted at an operating temperature of 625°C. Other operating conditions for the five runs are given in Table E1. All five high-temperature runs were conducted using a 1.5:1 Al to Na+K mole ratio feed. The starting bed for the five runs was NWCF aluminum calcine (non-radioactive), with the exceptions of Run 11 which used the final bed from short-duration Run 10 (screened to 250-595 micron size particles) with aluminum calcine added to attain a 2 liter volume, and Run 17 which used approximately 50% aluminum calcine and 50% final bed calcine from Run 16 (screened to 250-595 micron size particles).

Table E1. Average operating conditions for high temperature calcination.

Run No.	12	11	16	17	18	20
	(baseline)					
Calcination Temp (°C)	500	600	600	600	600	625
Total Blend (SBW Simulant+ANN, L)	22.2	20.2	14.1	9.1	17.3	21.2
Calcined Total SBW Simulant	6.0	10.0	7.5	4.9	9.2	11.3
Calcined (L)						
Blend Vol. Ratio (ANN/SBW Simulant)	2.73/1	1.03/1	0.88/1	0.88/1	0.88/1	0.88/1
Feed Al/Na+K Mole Ratio (Desired)	3.5	1.5	1.5	1.5	1.5	1.5
Feed Al/Na+K Mole Ratio (Actual)	4	1.74	1.58	1.41	1.98	1.44
Test Duration (hrs)	60	43	22	24	34	40
Feed Rate (L/hr)	0.37	0.47	0.64	0.38	0.51	0.53
Fluidizing Air Rate (L/min, @12.4 psia, 20°C)	17	13.7	15.6-19.5	19.5	19.5	19.8
Feed Atomizing Air Rate (L/min, @ 1 atm, 20°C)	8	5.7	8	8.8	8.8	10.5
NAR (nozzle air to feed volume ratio)	1263	724	746	1393	1038	1188

Numerous feed nozzle plugging problems were encountered in each of the five high-temperature runs. (Nozzle plugging problems occurred only twice during baseline Run 12). Generally, these were corrected using the nozzle plunger attachment, or by shocking the plug with a quick water flush. (A water supply controlled by a toggle valve is attached to the feed inlet line. Generally, a water flush introduces enough water into the system to drop the calciner temperature by 10-20°C.) Additionally, the system was shut down for approximately 3.5 hours during Run 11 to allow the replacement of a plugged offgas filter, for approximately 5 hours during Run 17 to clear a nozzle plug that could not be otherwise cleared, and for approximately 3 hours during Run 20 to clear a plugged off-gas line. The nozzle plugging problems and subsequent water flushes are believed to have caused some bed agglomeration. All of the runs, including the baseline, exhibited agglomerates in the bed (see discussion on large bed particle problem).

Runs 11 and 16 were terminated after approximately 43 and 22 hours of operation, respectively, both due to bed agglomeration problems. Run 16 had a 36% increased feed rate, 14-42% increased fluidizing air rate, and 41% increased feed atomizing air rate as did Run 11. Run 17 was a continuation of Run 16, using a 41% decreased feed rate, and slightly increased fluidizing and atomizing air rates than those used in Run 16. Run 17 was terminated after approximately 24 hours of operation due to plant problems not related to the test.

Run 18 was conducted using an average feed rate in between those used in Runs 16 and 17, and at the same fluidizing and atomizing air rates as Run 17. Run 18 was terminated after approximately 30 hours of operation, due to bed agglomeration problems.

In addition to Run 20 being performed at an elevated operating temperature (625°C), the atomizing air rate was also slightly increased from those of the other three runs. The feed rate was similar to that of Run 18. Run 20 was terminated after approximately 40 hours of operation due to bed agglomeration problems.

Results and Discussion

Product generated from the five high-temperature tests, as well as the baseline test, was generally acceptable with respect to nitrate concentration. The product and fines from all high-temperature runs did, however, exhibit some degree of caking at the surface when left exposed to room air for an extended period (over night). This indicates that the high-temperature product is somewhat hygroscopic.

Final Bed Composition- The elemental chemical compositions of the feed, initial bed, final bed, and fines for the five high-temperature runs are provided in Table E2. Of particular interest is the significantly lower nitrate content of the final bed for Run 20, as compared with those of the other runs. This strongly indicates that thermal denitration of the alkali metal nitrates is greatly enhanced by the increase in calcination temperature from 600 to 625°C. Further minor increases in the process temperature will likely result in significant additional denitration. This could not be verified in the LSCM because of heating limitations.

Nitrate Mass Balances- Based on nitrate concentrations determined for the starting beds, fines, product samples, and final beds, nitrate mass balances were performed for the baseline test and the five high-temperature tests. This information is presented in Table E3. Of significant note is the decreased $\text{NO}_3/\text{Na}+\text{K}$ mole ratio for each of the high-temperature runs, as compared to that of the baseline run. This indicates that the destruction of alkali nitrates is significantly increased at elevated calcination temperatures.

Fines Generation- Product and fines generation data for the five runs are presented in Table E4. Product-to-fines weight ratios determined for the different runs vary significantly. However, the multiple operational upsets, combined with the forced shut-downs due to bed agglomeration, likely influenced these numbers greatly, making an accurate comparison impossible. As Run 17 was a continuation of Run 16, it is suspected that fines generated during the former were collected in the later. The average of the product-to-fines ratios for the two runs is 1.35, which is very close to the same as for Run 18 (which had the same feed flowsheet and operating temperature as the previous two runs).

The low product-to-fines mass ratio of Run 20 (0.72) indicates that higher fines production will result from calcination at higher temperatures due to either the flash evaporation (drying) of a higher percentage of the atomized feed droplets, or higher product denitration. Since the final product attrition indexes determined for Runs 17 and 20 showed no significant difference, indicating that there should be no difference in fines generation due to the differences in particle composition and hardness, it is believed that flash evaporation is the cause for increased fines generation at higher calcination temperatures. Additional pilot-plant testing will be required to verify this. A reduction in the NAR may be necessary to reduce the extent of rapid droplet evaporation by increasing the atomized feed droplet size.

The bulk density of fines generated during Run 20 was determined to be 0.71 g/cc.

Table E2. Compositions of the feed, starting bed, final bed, and fines for high temperature calcination.

Run No.	Component	Feed Solution (M)	Starting Bed (wt%)	Final Bed (wt%)	Fines (wt%)
12 (baseline)	Na	0.47	3.76	5.2	6.77
	K	0.05	0.006	0.85	0.96
	Al	2.08	39	38.2	34.3
	NO ₃	6.3	6.16	12.3	21.6
	Acid	0.22	----	----	----
11	Na	0.78	4.8	9.6	11.7
	K	0.08	0.6	1.67	2.01
	Al	1.5	40.6	37.9	25.1
	NO ₃	5.68	5.53	7.98	27.1
	Acid	0.53	----	----	----
16	Na	0.97	6.26	8.49	11.2
	K	0.1	0.57	1.23	1.75
	Al	1.69	42	38.0	25.9
	NO ₃	6.08	4.3	6.97	29.7
	Acid	1.72	----	----	----
17	Na	0.96	6.37	7.46	9.51
	K	0.1	0.73	1.03	1.49
	Al	1.49	42.3	39.5	33.1
	NO ₃	5.51	2.69	7.57	25.7
	Acid	0.59	----	----	----
18	Na	0.74	4.2	9.35	11.4
	K	0.1	0.11	1.2	2.58
	Al	1.66	45.6	39.9	28.8
	NO ₃	6.4	0.74	8.	24.5
	Acid	1.2	----	----	----
20	Na	0.84	3.97	10.4	10.8
	K	0.1	0.05	1.34	3.5
	Al	1.35	41.2	37.2	27.3
	NO ₃	6.44	0.92	4.41	25.2
	Acid	1.26	----	----	----

Table E3. Nitrate mass balance for high temperature calcination.

Run No.	12	11	16	17	18	20
	(baseline)					
Total Nitrate in Feed (g)	8671.3	7113.6	5315.1	3108.7	6650.	8464.7
Total Nitrate in Starting Bed (g)	145.6	130.5	102.5	57.5	17.9	21.9
Total Nitrate in Fines (g)	278.2	407.2	177.6	236.3	309.5	339.8
Total Nitrate in Product Samples and Final Bed (g)	601.5	298.7	260.7	159.3	284.3	110.5
% of Nitrate lost to Offgas	91.5	91.9	93.7	89.1	91.3	94.9
Final Bed-Mole Ratio $\text{NO}_3/\text{Na}+\text{K}$	0.8	0.28	0.28	0.35	0.29	0.15

Calcine Dissolution- Calcine dissolution tests were conducted on final bed products from Runs 17 and 20. For comparison purposes, dissolution tests were also conducted on the LSCM baseline product (Run 12). A dissolution procedure used in a previous calcine dissolution study⁴ was used in these tests. Dissolution of each sample was attempted in 8 M nitric acid at 90°C over a 4 hour period. The results are listed in Table E4.

Test results indicate no significant change in product solubility for high-temperature calcines (Runs 17 and 20) as compared to that for the baseline case calcine (Run 12). However, previous dissolution testing of the same calcine products⁵ indicated that high-temperature calcines were slightly more soluble than the baseline calcine. It is also important to note that chemical additives generally used in NWCF calcination to hinder the formation of insoluble crystals were not used in any of the three LSCM tests (Runs 12, 17, and 20).

Table E4. Product and fines generation for high temperature calcination.

Run No.	Starting Bed (g)	Bed Material (g)			Total Fines (g)	Product /Fines (weight ratio)	Bed Turnover %
		Samples	Final Bed	Others*			
12 (baseline)	2363	340	3533	30	1249	1.23	48
11	2330	374	3085	253	1452	0.95	45
16	2383	814	2443	470	585	2.30**	43
17	2139	921	1583	0	883	0.41**	16
18	2417	835	2757	143	1040	1.27	42
20	2161	1212	1714	302	1485	0.72	39

* Agglomerated pieces or residual.

** See text for explanation of disparity.

Large Bed Particle Problem- Final bed particle size distribution information for the five runs is also presented in Table E5. All five runs (as well as the baseline Run 12) exhibited the formation of larger particles (greater than 595 microns), some to a greater extent than others. All of the high-temperature runs resulted in a significantly higher final bed fraction greater than 595 microns than did the baseline Run 12, except for Run 17. Run 17 had, however, a total operating time of only 24 hours, less than one-half that of Run 12. Run 17 was also operated with the highest nozzle air-to-feed ratio (NAR). Although the continued increase of these larger particles always eventually lead to a forced system shutdown due to the loss of the ability to adequately fluidize the bed, evidence suggests that bed agglomeration experienced in these runs was not due to high nitrate and/or alkali metals bed concentrations. For example, the final bed nitrate concentration for Run 17 was as high as that for Run 16, and almost as high as that for Run 18. Unlike the other two runs, however, Run 17 was not

Table E5. Final bed properties for high temperature calcination.

Run No.	Particle Sizes in Microns (%)			Attrition Index	Dissolution Test (wt% UDS)*
	<250	250-595	>595		
12 (baseline)	1.4	73.4	25.2	77.	21.9
11	1.8	47.8	50.4	34.	NA
16	2.7	43.8	53.5	NA	NA
17	0.6	84.4	15.	43.5	24.4
18	1.4	44.6	54.	NA	NA
20	2.8	58.3	38.9	48.6	22.

* 2 g calcine in 50 ml 8 M Nitric acid (90°C for 4 hours)
UDS = undissolved solids

terminated because of agglomeration problems. Similarly, the final bed for Run 20 had a relatively higher percentage of large particles and was terminated because of large particles. However, the nitrate concentration for the Run 20 final bed was significantly lower than that for Run 17. (The alkali metal concentrations for Run 20 were relatively high.) Furthermore, the proven flowsheet tested in the baseline Run 12 also resulted in a forced shutdown due to agglomeration problems.

It is believed that the agglomeration problems which have been responsible for all high-temperature calcination run forced terminations were at least partially due to system problems rather than the melting of alkali metal nitrates. Other possible candidates for the formation of agglomerates include: 1) the sudden introduction of relatively large volumes of feed and water during attempts to clear plugged feed nozzles, and 2) insufficient feed atomization.

A short-duration test was conducted to measure the effects of the sudden introduction of water. The 250-595 micron fraction of Run 12 final bed was fluidized at 600°C. To simulate the effects of clearing a plugged nozzle, water was injected at a high flow rate through the feed nozzle and into the bed, for several seconds at a time. Approximately 20 water injections were performed over a period of approximately 2 hours. For each injection, enough water was used to lower the bed temperature by approximately 30°C. The bed temperature was allowed to return to approximately 600°C between injections. Note that although this liquid injection was representative of nozzle plug clearing efforts performed during test runs with respect to liquid volume used, it was not representative of the type of

liquid that was used. Most nozzle plug clearing efforts resulted in a stream of feed solution entering the calcine bed, rather than water.

After the final water injection, the bed was allowed to cool, and the final bed and fines were screened to obtain a particle size distribution. The weights of the different size fractions are given in Table E6. Note that the water injections did cause some bed carryover into the filter vessel. The different size fractions in the filter vessel were separated and are included in the Table E6 data.

Table E6. Mass balance of water spraying test results.

Materials	Particle Size (microns)	Mass (g)
Starting Bed	250 - 595	2428
	>595	58.3
Final Bed Plus Fines	250 - 595	2202
	<250	160.4
	Total	2421.3

Results from this test do show a small fraction (2.6 wt%) of final bed existing as larger particles (greater than 595 micron), supposedly due to the water injections. However, the larger particle fraction of the bed is small enough to deem the results inconclusive.

X-Ray Diffraction Analysis- X-ray diffraction spectroscopy analytical results for the final bed products of Runs 12 (baseline) and 20 (625°C operation) are presented in Tables E7 and E8, respectively. This analysis allows the identification of crystalline constituents present in the bed material. Due to the lack of reference standards for most of the components, and the complexity of the resulting spectra, only peak heights of the specific species were determined. Thus, the trends (increasing or decreasing) of individual species are only indicated.

Of significant note is that the X-ray diffraction results for Run 20 indicate a downward trend in concentrations of both sodium nitrate and alpha alumina, as opposed to the upward trend in peak intensities for both crystalline species for Run 12. This agrees with previous studies which concluded that the presence of sodium nitrate promotes alpha alumina formation.⁶ Also noted from the Run 20 results is a general increase in concentrations of sodium aluminate crystalline species. (Only two sodium aluminate polymorph phases were detected for Run 12).

Fines Particle Size Distribution (PSD)- Concerns have been identified about the potential for a significantly higher volume of fines generated during high-temperature or sugar-addition calcination of SBW reaching and plugging the HEPA filters, as compared to normal NWCF operation. Of specific concern is the potential for increased production of fines less than 10 microns, which are particularly difficult to remove from the offgas stream with existing equipment upstream of the HEPA filters. Increased filter loading of fines less than 10 microns during SBW calcination could be the result of either a decreased product-to-fines weight ratio (assuming no corrective shift in removal efficiency upstream of the filters), or by a downward shift in the PSD of the fines produced.

Table E7. X-Ray diffraction analysis (peak heights) - Run 12.

COT (hrs)	Species Card # Peak (s)	$\text{Na}_2\text{Al}_2\text{O}_{3x+1}$ 29-1164 5.42+2.22	NaAlO_2 20-1073 2.1	$-\text{Al}_2\text{O}_3$ 19-1179 1.98+1.4	$-\text{Al}_2\text{O}_3$ 10-173 3.47+2.08	NaNO_3 36-1474 3.04	$\text{NaOH}\cdot\text{H}_2\text{O}$ 30-1194 2.7	$\text{Al}(\text{OH})_3$ 15-136 4.38
0	Starting Bed (Al Calcine)	10	5	10	16	10	4	NA
7	Bed 12-1	30	8	62	91	97	16	15
25	Bed 12-3	69	20	61	66	92	5	19
45.6	Bed 12-5	115	18	54	83	106	3	16
55.3	Bed 12-6	122	16	41	60	122	*	13
59.6	Bed 12-7	136	15	51	72	113	24	11
59.6**	Bed 12- 8B	134	16	48	66	120	*	14
59.6**	Bed 12- 8C	95	23	56	91	105	14	12
59.6**	Bed 12- 8D	100	21	48	84	110	19	13

* Peak interference by a nearby peak prevents accurate reading

** Bed 12-8B, particle size 595-1000 microns; Bed 12-8C, particle size 250-595 microns; Bed 12-8D, particle size <250 microns

Table E8. X-Ray diffraction analysis (peak heights) - Run 20.

COT (hrs)	Species Card # Peak (s)	$\text{Na}_2\text{Al}_2\text{O}_{3x+1}$ 29-1164 5.42+2.22	$\text{NaAlO}_2^{(1)}$ 20-1073 2.1	$-\text{NaAlO}_2$ 19-1179 4.2+2.6	$\text{NaAlO}_2^{(2)}$ 33-1200 4.18+2.6	$-\text{Al}_2\text{O}_3$ 10-425 1.98	$-\text{Al}_2\text{O}_3$	NaNO_3
0	Al Calcine	27	35	5	12	21	74	173
0.3	Bed 20-0	27	32	13	9	24	82	64
8	Bed 20-2	21	35	57	11	26	87	1
16	Bed 20-4	27	27	111	16	31	75	7
32	Bed 20-8	54	25	184	28	41	64	25
40	Bed 20-11	44	18	210	40	39	41	25

Note: Only the predominant species are shown here.

(1) Rhombohedral form.

(2) Orthohombic form.

To address the later concern, PSD analysis was performed for the fines produced during three different LSCM test runs; Run 12 (baseline, 500°C), Run 18 (600°C), and Run 20 (625°C).⁷ Results (Figure E2) indicated that the PSDs for the three samples are very similar, and the bulk of the fines from each sample is in the 20-100 micron range. There is no sign of correlation between calcination temperature and mean particle size for the fines produced.

Figure E2. LSCM off-gas fines high temperature testing PSD (G9700E1).

SUGAR-ADDITIVE EXTENDED-DURATION TESTS

Operational Safety

Prior to performing any LSCM tests with sugar added to the feed, extensive investigations and studies were conducted concerning potential dangers that might exist with respect to combining nitrates with carbon (both liquid and solid phases) during the operation of this system.^{8,9,10} Several precautionary system and procedural modifications were made to assure safe operation. The major safety concern of sugar-additive calcination involved the generation of fines with organic carbon concentrations greater than 5 wt%. The highest concentration of organic carbon in fines for any of the tests performed was 1.7 wt% (Run 29). These fines were subjected to dust explosion tests by an outside subcontractor,¹¹ and were determined non-explosive under all conditions tested. In fact, the fines behaved as an explosion inhibitor when added to explosive gas mixtures of propane and air.

Operation Description

A total of five LSCM sugar-additive tests were conducted, Runs 27, 28, 29, 30, and 32. All runs were conducted at an operating temperature of approximately 500°C, with the exception of Run 30 which was conducted at an operating temperature of approximately 575°C. All runs were conducted with feed having approximately the stoichiometric ratio of carbon-to-nitrate (1.25 moles of carbon per 1.0 moles of nitrate), with the exceptions of Run 30 and Run 32. Only enough sugar for approximately 0.6 times the stoichiometric ratio of carbon-to-nitrate was used in Run 30. An excess of sugar (approximately 1.2 times the stoichiometric ratio of carbon-to-nitrate) was used in Run 32.

Feed solutions for Runs 27, 30, and 32 were straight sodium simulant and sugar, and used no additive ANN solution. Aluminum nitrate was added to the feed solutions of Runs 28 and 29 to achieve Al to Na+K mole ratios of 1.0 and 1.5, respectively. The starting beds for the five runs consisted of

NWCF aluminum calcine (non-radioactive). For all runs, except Run 32, the starting bed was heated at temperatures in excess of 600°C for 2-3 hours before operation to denitrate the starting bed. Other operating conditions for the five runs are presented in Table E9.

Table E9. Average operating conditions for sugar-additive calcination.

Run No.	12 (baseline)	27	28	29	30	32
Calcination Temp (°C)	500	500	500	500	575	500
Total Feed (SBW Simulant + ANN + Sugar, L) Calcined	22.2	16.9	28.6	38.3	8.1	15.3
Total Blend (SBW Simulant + ANN, L) Calcined	22.2	12.5	21.2	28.4	6.8	13.2
Total SBW Simulant Calcined (L)	6.0	12.5	13.7	14.2	6.8	13.2
Feed Vol. Ratio (Sugar Solution/ANN + SBW Simulant)	---	0.35/1	0.28/1,(6) ⁽¹⁾ 0.35/1, (10) 0.42/1,(5.2)	0.35/1	0.2/1	250 g per liter simulant ⁽²⁾
Blend Vol. Ratio (ANN/SBW Simulant)	2.73/1	0/1	0.55/1	1/1 ⁽³⁾	0/1	0/1
Feed Al/Na+K Mole Ratio (Desired)	3.5	SBW Simulant	1	1.5	SBW Simulant	SBW Simulant
Feed Al/Na+K Mole Ratio (Actual)	4	0.34	0.94	1.46	0.31	0.31
Feed C/NO ₃ Mole Ratio	---	1.39	1.02/1.27/ 1.53	1.24	0.79	1.65
Test Duration (hrs)	60	34	48.3	69.8	14.8	26.3
Feed Rate (L/hr)	0.37	0.5	0.59	0.55	0.55	0.58
Fluidizing Air Rate (L/min, @12.4 psia, 20°C)	17	21.4	20.5	20.1	19.8	20.8
Feed Atomizing Air Rate (L/min, @ 1 atm, 20°C)	8	9.3	9.3	9.3	9.1	9.3
NAR (nozzle air to feed ratio)	1263	1116	946	1015	993	962
Note:	(1) Used the ratio of sugar solution (50%) as specified, the quantity (in liters) of each blend calcined is shown in parentheses.					
	(2) Added 250 grams of solid sugar per liter of sodium-bearing SBW simulant.					
	(3) Used low concentration aluminum nitrate solution (approximately 2.23 M).					

Run 27 (straight sodium simulant with sugar) consisted of 34.0 hours of operation, using a total of 16.9 L of feed solution (12.5 L of sodium simulant processed). This run was subject to numerous operational problems. Three separate system shutdowns were required to replace the offgas filter due to continual filter plugging problems. Two additional system shutdowns (including the final shutdown) were required because of loss of calciner bed temperature control. Significant temperature differences existed throughout the bed, with the highest temperatures generally existing at locations around the feed nozzle. This is usually indicative of bed agglomeration, as a slight temperature depression should occur

in the vicinity of the feed nozzle due to evaporation of the liquid feed. Increases in the fluidizing air rate (velocity) would usually bring the bed temperatures significantly closer together, only to have them separate again, even with the higher fluidizing velocity maintained. This behavior also suggests inadequate or only partial bed fluidization. After the first shutdown due to loss of temperature control, no agglomerates were found in the bed. The plenum (cone shaped calciner section below the distributor plate) was, however, discovered to be filled with calcine. This supports the notion that the distributor plate may have been partially plugged, and the bed was being only partially fluidized. However, the lack of bed temperature control reappeared prior to the final shutdown. A significant amount of calcine was again emptied from the plenum after the final shutdown.

Run 28 (1:1 Al to Na+K mole ratio feed with sugar) consisted of 48.3 hours of operation, using a total of 28.6 L of feed solution (13.7 L of sodium simulant processed). This run was relatively trouble free, with no shutdowns required because of operational problems. One shutdown was required because of an unscheduled loss of power. During this run, on-line nitrate analysis was performed on product and fines samples. Results from early product samples showed significant nitrate concentration increases with time. This finding led to an increase in the amount of sugar solution that was added to the feed (from 0.28 L to 0.35 L of sugar solution per liter of 1:1 Al to Na+K mole ratio feed solution) starting after approximately 12 hours of run time. Nitrate analysis of the feed was performed after continued increases of product nitrate concentrations were discovered. This revealed a higher than anticipated feed nitrate concentration. This finding led to a further increase in sugar solution addition to 0.42 L per liter of feed solution (starting after approximately 35 hours of run time).

Run 29 (1.5:1 Al to Na+K mole ratio feed with sugar) consisted of 69.7 hours of operation, using a total of 38.3 L of feed solution (14.2 L of sodium simulant processed). This Run was completely free of any significant operating problems, with the exception of one shutdown after approximately 34 hours of run time due to a planned power outage.

Run 30 (straight sodium simulant with partial sugar) consisted of 14.8 hours of operation, using a total of 8.1 L of feed solution (6.8 L of sodium simulant processed). Several minor instances of feed nozzle plugging were experienced during this run, twice requiring water flushes to clear the nozzle. The run was terminated due to the significant and continuous increases of product nitrate concentration as it progressed.

Run 32 (straight sodium simulant with solid sugar) consisted of 26.3 hours of operation, using a total of 15.3 L of feed solution (13.2 L of sodium simulant processed). This run was relatively trouble free, with the exception of operation being disrupted twice with feed pump tubing breaks, and the offgas filter requiring frequent blowbacks during the last five hours of operation. One event that took place towards the end of this run was that a few "sparks" were seen in the calcine product when it was being drained from the calciner vessel for sampling purposes. This was reportedly witnessed by an operating Technician. Subsequent attempts to repeat this event failed.

Results and Discussion

Product generated from all five test runs appeared to be of good quality, with no indication of bed agglomeration. Run 30 was, however, terminated to avoid bed agglomeration.

Final Bed Composition- The elemental chemical compositions of the feed, initial bed, and final bed, for the five sugar-additive test runs are provided in Table E10. Although increases in product nitrate concentrations (from the starting beds to the final beds) are seen for Runs 27 through 29, these data have

been determined to be non-representative of the actual extent of denitration that can be achieved through sugar-additive denitration for the following reasons:

1. For these three runs, nitric acid solution (2-3 M) was fed through the feed nozzle into the denitrated calcine bed during the startup and shutdown of the system, and during system upsets. As discovered during on-line nitrate analysis towards the end of Run 29, this practice results in re-nitration of the bed.
2. Although the carbon-to-nitrate feed concentrations were close to the stoichiometric molar ratio (1.25:1), an excess of carbon was determined necessary to optimize the denitration reactions.

Analytical results showed Run 32 final bed nitrate concentration to be 6.39 wt%. Note, however, that in-house nitrate analysis for Run 32 final bed showed the concentration to be 1.5 wt%.

Further investigation will be performed to resolve this discrepancy. Despite the relatively large difference between the two values, the product nitrate concentration is low compared with results from the other tests. Additionally, the Run 32 starting bed nitrate concentration was significantly higher than those for the other sugar-additive runs (pre-operation thermal denitration was not performed for Run 32 starting bed). This verifies that the use of an adequate excess of sugar in the feed (approximately 1.5:1 carbon-to-nitrate mole ratio), and using water to flush the feed line instead of nitric acid, will result in a significant increase in product denitration. Run 32 product nitrate concentration results much more closely represent the denitration capabilities of a sugar-additive calcine flowsheet.

Nitrate Mass Balances- Based on nitrate concentrations determined for the starting beds, fines, product samples and final beds, nitrate mass balances were performed for the five runs. This information is contained in Table E11. Of significant note is again the final bed $\text{NO}_3/\text{Na}+\text{K}$ mole ratio column. This clearly shows the extents of product denitration with respect to the amounts of SBW simulant accumulated on the beds of the different runs. Close to complete product denitration, and a significant increase in fines denitration, is only achieved when an excess of sugar (over the carbon-to-nitrate stoichiometric ratio) is used (Run 32).

Product and Fines Carbon Content- Organic and inorganic carbon analyses results for the starting and final beds and the fines from the five runs are contained in Table E12. The results indicate that only a small fraction of the carbon used is retained in the product and fines. The worst case of carbon retention was Run 32, where a total of 3.5 wt% of the carbon used (introduced in the feed) remained in the product and fines as inorganic and organic carbon. The majority of that was inorganic carbon (likely Na_2CO_3) in the fines. Most of the carbon used (96.5 wt%) went with the offgas.

The analytical results also suggest a trend of increased organic carbon concentrations in the fines with increased aluminum concentration in the feed. They also indicate that significant increases in inorganic carbon concentrations will result, for both the product and the fines, with increased sugar addition to the feed beyond the stoichiometric carbon-to-nitrate ratio. Using the total analytical results of Run 32 fines, a near-complete mass balance is attained when assuming the inorganic carbon exists as sodium carbonate.

Table E10. Compositions of the feed, starting bed, final bed, and fines for sugar-additive calcination.

Run No.	Component	Feed Solution (M)*	Starting Bed (wt%)	Final Bed (wt%)	Fines (wt%)
12 (baseline)	Na	0.47	3.76	5.2	6.77
	K	0.05	0.006	0.85	0.96
	Al	2.08	39	38.2	34.3
	NO ₃	6.3	6.16	12.3	21.6
	Acid	0.22	---	---	---
27	Na	1.52	4.97	15.5	13.1
	K	0.18	0.02	2.25	1.64
	Al	0.57	41.88	22.7	24.5
	NO ₃	5.38	0.93	12.67	23.2
	Acid	1.48	---	---	---
28	Na	1.1	5.64	13.9	15.6
	K	0.11	0.08	2.25	2.54
	Al	1.14	42.1	30.9	19.0
	NO ₃	5.88	1.35	10.71	22.9
	Acid	1.19	---	---	---
29	Na	0.89	5.37	12.04	13.1
	K	0.09	0.03	1.64	2.58
	Al	1.44	41.7	34.3	23.6
	NO ₃	6.04	1.18	11.01	19.6
	Acid	0.71	---	---	---
30	Na	1.73	5.53	12.5	12.6
	K	0.2	0.13	1.63	1.63
	Al	0.6	42.2	30.5	17.6
	NO ₃	5.42	1.63	16.8	29.4
	Acid	1.48	---	---	---
32	Na	1.75	5.53	17.	22.7
	K	0.22	0.06	2.35	2.7
	Al	0.61	39.7	28.7	11.7
	NO ₃	5.31	8.71	6.39	19.6
	Acid	1.48	---	---	---

Note: Sugar not included.

Table E11. Nitrate mass balance for sugar-additive calcination.

Run No.	12 (baseline)	27	28	29	30	32
Total Nitrate in Feed (g)	8671.3	4170	7728.7	10663	2722.	4345.7
Total Nitrate in Starting Bed (g)	145.6	24.6	31.1	27.8	41.7	219.
Total Nitrate in Fines (g)	278.2	26.7	253.8	421.6	69.1	63.5
Total Nitrate in Product Samples and Final Bed (g)	601.5	407	434.6	377.4	464.7	222.1
% of Nitrate lost to offgas	91.5	90.2	91.5	92.8	81.9	98.5
Final Bed-Mole Ratio NO ₃ /Na+K	0.8	0.28	0.26	0.35	0.46	0.13

TABLE E12. Carbon distribution during sugar-additive calcination.

Run No.	27		28		29		30		32	
Type of Carbon	Organic Carbon	Inorganic Carbon	Organic Carbon	Inorganic Carbon	Organic Carbon	Inorganic Carbon	Organic Carbon	Inorganic Carbon	Organic Carbon	Inorganic Carbon
Total Carbon Fed to LSCM during Operation (g)	1131		1902		2544		334		1368	
Total Carbon in Starting Bed (g)	0.6	13.1	0.6	11.8	0.7	14.2	0.5	10.1	0.7	14.6
Total Carbon in Calcine Products (g)	13.2	22.1	0.9	8.2	5.6	20.4	0.7	8.1	2.8	53.7
Total Carbon in Fines (g)	0.2	0.5	6.4	6.0	29.1	18.9	0.2	1.1	0.7	5.9
% Carbon lost to offgas	98.0		99.5		97.6		100.0		96.5	
Content in Starting Bed (mg/g)	0.2	4.7	0.3	4.8	0.3	6.0	0.2	4.0	0.3	5.8
Carbon Content in Final Bed (mg/g)	4.0	6.6	0.3	2.0	0.3	4.4	0.2	2.9	0.3	16.9
Carbon Content in Final Fines	3.8	8.5	11.2	12.5	16.5	10.5	0.8	4.8	4.4	42.1

Fines Generation- Product and fines generation data for the five runs are presented in Table E13. Product-to-fines weight ratios determined for the different runs vary significantly. However, the data do strongly indicate that fines generation increases with the increase of aluminum content in the feed.

Table E13. Product and fines generation for sugar-additive calcination.

Run No	Starting Bed (g)	Bed Material (g)		Total Fines (g)	Product/Fines (weight ratio)	Bed Turnover %
		Samples	Final Bed			
12 (baseline)	2363	340	3563	1249	1.23	48
27	2727	1271	2585	61	18.5	33.9
28	2402	1416	2412	935	1.5	44.8
29	2460	1711	2376	2151	0.7	48.4
30	2450	300	2466	235	1.3	12.1
32	2514	927	2561	324	3.0	32.1

Bulk density determinations made for Runs 29 and 32 were 0.26 g/cc and 0.78 g/cc, respectively. Although the bulk density for Run 32 (straight SBW simulant and sugar) fines is comparable to that of high-temperature Run 20 fines (0.71 g/cc), no explanation is currently available for the extremely low value determined for Run 29 fines. Further pilot plant testing will be required to determine more absolute fine bulk density values for these flowsheets.

Particle size distribution determinations have not yet been made for sugar-additive calcination fines due to uncertainties concerning waste disposal. These determinations will be made at a later date using fines generated in the LSCM or a pilot-plant calciner. No significant increase in sub-micron particles is anticipated.

Calcine Dissolution- The same dissolution procedure used for the high-temperature final bed product was used on final bed product from all five sugar-additive runs. For comparison purposes, dissolution tests were also conducted on the aluminum calcine starting bed (before and after denitration preheating).

Results from this dissolution testing are included in Table E14. In all flowsheet cases tested, the product solubility is significantly increased over that of the starting bed. In fact, assuming 100% solubility of new bed material, these results show that product from sugar-additive calcination is more soluble than allowed for by the calculated extent of bed turnover achieved for each run. This suggests that fresh bed material reacts with the starting bed (including the insoluble fraction), with the resulting product being soluble.

Table E14. Starting and final bed properties for sugar additive calcination.

Run No./Sample	Bulk Density (g/cc)	Particle Density (g/cc)	Attrition Index	Particle Sizes/Microns (%)				Dissolution Test (wt% UDS)*
				<250	250-595	595-1190	>1190	
Al Calcine	1.23-1.27	2.90	85.2	0	100	0	0	26.3
27	Starting Bed	1.22	3.03	NA	0	100	0	31.1
	Final Bed	1.51	2.59	95.4	1.3	98.5	0.2	16.2
28	Starting Bed	1.15	3.02	NA	0	100	0	23.8
	Final Bed	1.17	2.63	65.4	1.9	97.5	0.6	10.8
29	Starting Bed	1.20	3.04	NA	0	100	0	24.6
	Final Bed	0.92	2.70	82.6	1.0	91.0	8.	10.7
30	Starting Bed	1.16	3.00	NA	0	100	0	24.8
	Final Bed	1.52	2.56	97.2	1.2	98.6	0.2	14.5
32	Starting Bed	1.22	2.92	NA	0	100	0	21.1
	Final Bed	1.44	2.63	95.6	1.9	95.6	2.2	11.9

* 2 g calcine in 50 ml 1M Nitric acid (90°C for 4 hours).

X-Ray Diffraction Analysis- Identification of crystalline constituents present in the final bed material was made for all five runs using X-ray diffraction spectroscopy. The peak heights data for Run 32 are summarized in Table E15. Again, due to the lack of reference standards for most of the components, only the trends of individual species are indicated.

Indications of the X-ray diffraction results are:

1. An upward trend in concentration of -NaAlO_2 results in flowsheets where the Al-to-Na mole ratio is less than one.
2. Decrease ANN addition results in minimal $\text{-Al}_2\text{O}_3$ formation.
3. To obtain near-complete product denitration, the carbon concentration must

Product Particle Size Distribution (PSD)- PSD analysis was performed for the starting and final bed calcines of Runs 27 and 28. This information is presented in Figure E3. Results from both runs show a uniform increase in particle size, with the spread of the distribution being unaffected. The larger magnitude of increase for Run 28 particles, as compared to Run 27 particles, can be attributed to the longer test duration and the associated larger volume of total feed for Run 28. Although the particle growth may indicate a requirement for an independent means of particle breakage (e.g., jet grinder), attrition index results (Table E15) do not fully support this. Although the final bed attrition index for

Run 27 increased from that of the starting bed, the attrition index for Run 28 decreased. Further investigation in the pilot plant calciners is required to resolve this issue.

Table E15. X-Ray diffraction analysis (peak heights) - Run 32.

COT (hrs)	Species Card #	$\text{Na}_2\text{Al}_2\text{O}_{3x+1}$ 29-1164	NaAlO_2 20-1073	$-\text{NaAlO}_2$ 20-1073	NaAlO_2 33-1200	$-\text{Al}_2\text{O}_3$ 10-425	$-\text{Al}_2\text{O}_3$ 10-173	NaNO_3 36-1474
	Peak (s)	5.42+2.22	2.1	4.2+2.6	4.18+2.6	1.98	3.47+2.08	3.04
0		63	12	4	3	20	85	184
8.2		37	13	119	44	18	60	28
16.2		17	8	130	82	24	49	55
26.3		11	8	123	66	16	39	24

Figure E3. LSCM sugar flowsheet testing PSD.

NO_x Emissions- Although offgas NO_x concentrations have thus far not been measured, scoping test results indicate that sugar-additive calcination will result in a substantial decrease in offgas NO_x emissions. This potential is strongly suggested by the difference in the acidity of the process condensates between sugar-additive and high-temperature lab-scale calcinations. Sugar-additive calcination offgas condensate has a pH of approximately 6, while high-temperature off-gas condensate is 2-3 M HNO₃. Nitrate analytical results for condensate from Runs 27 and 28 were 0.41 M and 0.68 M respectively. This suggests that sugar-additive calcination results in near-total reduction of the nitrates contained in SBW

simulant to nitrogenous offgas species which are not highly soluble in the condensate; (i.e. N_2O , NO , and N_2). High-temperature calcination, on the other hand, results in minimal NO_x destruction. Off-gas measurements must be taken during t plant testing to determine the actual NO_x emissions rates of the two processes.

Appendix F

10-cm Calciner Pilot Plant Scoping Tests

**Status Report for
Alternative Calcination Scoping Tests**

**J. A. Nenni
L. J. Young**

April 1997

**Idaho National Engineering and Environmental Laboratory
High-Level Waste Program Department
Lockheed Martin Idaho Technologies Company
Idaho Falls, Idaho 83415**

ABSTRACT

A Court-Ordered Settlement Agreement between the State of Idaho and the DOE requires that the current inventory of radioactive liquid waste (sodium-bearing waste) in the ICPP Tank Farm and any additional waste produced be calcined by 2012. According to current projections, the current baseline flowsheet for calcination of this waste will not allow this deadline to be met. Therefore, two alternative calcination flowsheets are being investigated to increase the processing rate. The first alternative, sugar-additive calcination, involves the use of sugar as a feed additive to react with and decompose nitrates in the liquid waste. The second alternative, high-temperature calcination, involves the use of higher calcination temperatures and aluminum nitrate as an additive to preferentially react with sodium and potassium in the liquid waste. The reaction causes the decomposition and release of nitrate from the waste. A series of five scoping tests were completed to evaluate the proposed alternative flowsheets. The tests conducted include a test of the current flowsheet, two variations of the high-temperature flowsheet, and two variations of the sugar-additive flowsheet. The tests were conducted in the 10-cm Calciner Pilot Plant. The tests indicate that high-temperature calcination at 600°C of a feed blend consisting of an aluminum to sodium and potassium mole ratio of 1.5 produces a calcine that met the defined acceptance criteria. Specifically, 1) the process throughput increased significantly over the current flowsheet, 2) no serious particle agglomeration occurred during operation, 3) initial testing indicated that the product would be transportable, 4) an acceptable product to fines ratio was achieved, and 5) an acceptable calcine chemistry and species retention were achieved. The tests also indicated that further flowsheet refinement is required to optimize the high-temperature calcination flowsheet.

CONTENT

ABSTRACT	ii
ACRONYMS	v
INTRODUCTION	1
Purpose and Scope	2
Background	2
SYSTEM DESCRIPTION	4
TEST DESCRIPTIONS	6
General Test Procedure	6
Test Synopses	9
RESULTS AND DISCUSSION	11
Process Throughput	11
Particle Agglomeration	11
Product MMPD	12
Particle Size Distribution	15
Feed Deposition	18
Fines Generation	18
Attrition Resistance Index	18
Particle Growth and Calcination Reactions	18
Chloride, Fluoride, and Undissolved Particulate Buildup in Scrub	19
Bin Set Storage Requirements	19
Product and Fines Transportability and Storability	20
Calcine Hydration Experiments	20
Calcine Solubility	25
Chemical Analyses	26
Overall and Component Mass Balances	26
Nitrate	27
Aluminum	29
Alkali Metals	30
Halides	32
Carbon	33
Scrub Solution Interactions	33
CONCLUSIONS	36
RECOMMENDATIONS	38
REFERENCES	39
Appendix A. Hygroscopicity Test Apparatus	A-1
Appendix B. Component Balances	B-2

FIGURES

Figure 1.	10-cm Calcliner Pilot Plant process flow diagram.	5
Figure 2.	MMPD and NAR versus operating time for SBW-BL-1.	13
Figure 3.	MMPD and NAR versus operating time for SBW-HT-1.	13
Figure 4.	MMPD and NAR versus operating time for SBW-HT-2.	14
Figure 5.	MMPD and NAR versus operating time for SBW-SA-1.	14
Figure 6.	PSD for SBW-BL-1.	16
Figure 7.	PSD for SBW-HT-1.	16
Figure 8.	PSD for SBW-HT-2.	17
Figure 9.	PSD for SBW-SA-1.	17
Figure 10.	Bed height versus adjusted operating time.	19
Figure 11.	Hygroscopicity Test 1 results.	22
Figure 12.	Hygroscopicity Test 2 results.	23
Figure 13.	Hygroscopicity Test 3 results.	23
Figure 14.	Hygroscopicity Test 4 results.	24
Figure 15.	Hygroscopicity Test 5 results.	24
Figure 16.	Nitrate concentration versus time.	28
Figure 17.	Aluminum concentration versus time.	29
Figure 18.	AAR versus adjusted operating time for SBW-BL-1.	30
Figure 19.	AAR versus adjusted operating time for SBW-HT-1.	31
Figure 20.	AAR versus adjusted operating time for SBW-HT-2.	31
Figure 21.	AAR versus adjusted operating time for SBW-SA-1.	32
Figure A.1	Hygroscopicity test apparatus.	A-1

TABLES

Table 1.	Composition of simulated waste and feed blends.	7
Table 2.	Initial parameters.	8
Table 3.	Average operating parameters.	8
Table 4.	Adjusted operating time factors.	11
Table 5.	Volume percent of SBW in test feeds.	11
Table 6.	Bed turnover percentages.	15
Table 7.	ARI of final bed.	18
Table 8.	Concentration and volume of nitric acid added to scrub solutions	19
Table 9.	Calcine storage requirements data.	20
Table 10.	Calcine characteristics.	21
Table 11.	Hydration test conditions.	21
Table 12.	Calcine Pourability Test Results	25
Table 13.	Product and fines dissolution results.	26
Table 14.	Halide volatility results.	33
Table 15.	Off-gas analysis results.	33
Table 16.	Volatile organic analysis.	34
Table 17.	Semi-volatile organic analysis.	35

ACRONYMS

AAR	Aluminum to Alkali-Metal Ratio
ARI	Attrition Resistance Index
COT	Cumulative Operating Time
DOE	Department of Energy
DSC	Differential-Scanning Calorimetry
FB	Final Bed
HMPD	Harmonic Mean Particle Diameter
ICPP	Idaho Chemical Processing Plant
INEL	Idaho National Engineering Laboratory
INEEL	Idaho National Environmental and Engineering Laboratory
LEL	Lower Explosion Limit
MMPD	Mass Mean Particle Diameter
NAR	Nozzle Air Ratio
NO _x	Nitrogen Oxides
NWCF	New Waste Calcine Facility
P/F	Product to Fines Ratio
PSD	Particle Size Distribution
SB	Starting Bed
SBW	Sodium-Bearing Waste
TGA	Thermal-gravimetric analyses
VOG	Vessel Off-Gas
WCF	Waste Calcining Facility

Status Report for Alternative Calcination Scoping Tests

INTRODUCTION

An accumulation of 1.5 million gallons of liquid radioactive waste containing high levels of alkali metal salts is currently stored at the Idaho Chemical Processing Plant (ICPP). This waste was generated as a result of solvent recovery and decontamination activities associated with spent nuclear-reactor fuel reprocessing. The wastes are acidic and contain high concentrations of sodium, potassium, and nitrates and are commonly referred to as sodium-bearing wastes (SBW). A 1995 Court-Order Settlement Agreement requires that the SBW along with any additional waste generated and stored in the ICPP Tank Farm be calcined by 2012.

In the past, SBW was blended with raffinate waste from fuel reprocessing activities and converted to a solid (calcine) by fluidized-bed calcination in the Waste Calcination Facility (WCF) and the New Waste Calcination Facility (NWCF). Termination of reprocessing activities at the ICPP has resulted in an excess of SBW. The remaining 300,000 gallons of raffinate waste (before evaporation) along with a portion of the SBW will be processed in the next NWCF campaign. More than one million gallons of SBW will remain in the ICPP Tank Farm after the raffinate waste has been calcined.

Calcination of SBW without additives cannot be accomplished in the current operating mode of the NWCF due to two factors. First, the melting points of sodium nitrate and potassium nitrate salts ($T_m(\text{NaNO}_3) = 307^\circ\text{C}$ and $T_m(\text{KNO}_3) = 337^\circ\text{C}$)¹ are lower than the typical 500°C operating temperature of the NWCF. Second, mass transfer and kinetic limitations, and the formation of eutectic phases, prevent complete thermal decomposition of the nitrates at 500°C , although the decomposition temperatures ($T_d(\text{NaNO}_3) = 380^\circ\text{C}$ and $T_d(\text{KNO}_3) = 400^\circ\text{C}$) (see Reference 1) are lower than the operating temperature of the calciner. If SBW were processed alone, molten sodium and potassium nitrate salts would cause agglomeration of the bed and thus prevent fluidization.

To overcome this problem, in the absence of raffinate wastes, a non-radioactive diluent (aluminum nitrate) is currently added to the SBW during calcination. This prevents agglomeration and allows for successful calcination. This flowsheet has been successfully tested in the NWCF and is commonly referred to as the baseline flowsheet. The baseline flowsheet produces a calcine with approximately 8.9 mole% sodium plus potassium which is equal to an aluminum to alkali metal mole ratio (AAR) of 3.5.

The large quantity of diluent required for the baseline flowsheet significantly reduces the waste processing throughput and produces a copious amount of calcine. The Settlement Agreement commitment to calcine the waste in the Tank Farm by 2012 cannot be met with this flowsheet, according to current projections. Therefore, to meet the commitment, two alternative calcination schemes are being investigated. Both options involve changing the flowsheet mixture and may require modifications to the existing NWCF system.

The first alternative, sugar-additive calcination, involves the addition of a reducing agent (sucrose) to cause denitration of the sodium and potassium nitrates at temperatures lower than 500°C . The second alternative, high-temperature calcination, involves calcining at a higher temperature to increase the extent of destruction of the sodium and potassium nitrates. Consequently, the amount of additional chemicals required for either alternative can be significantly reduced, enabling the net SBW throughput to be increased.

Sugar-additive calcination is effective because the reduction-oxidation reaction between sucrose and nitrate is very rapid at elevated temperatures. Denitration begins to occur in the aqueous phase, as nitric acid reacts

with the sugar. Sucrose is an advantageous reducing agent since it is inexpensive, easy to handle, dissolves readily in aqueous solutions, and does not completely volatilize before reaction with the nitrates.

High-temperature calcination is effective because nitrate decomposition kinetics are more favorable at higher temperatures and the alkali metals form eutectic oxides with the additives. Aluminum nitrate is used as an additive for its chemical rather than diluent properties. Aluminum nitrate is an advantageous additive for high-temperature calcination since it is readily available, not prohibitively expensive, soluble in process solutions, and produces a calcine that is compatible with the current off-gas scrubber.

Purpose and Scope

Five scoping tests were completed to evaluate the proposed alternative flowsheets. The tests conducted include a test of the baseline flowsheet, two variations of the high-temperature flowsheet, and two variations of the sugar-additive flowsheet. The tests were conducted using the 10-cm Calcliner Pilot Plant. The tests are viewed as scoping tests due to variations in the pilot plant operating performance compared to that of the full-scale calciner system.

Performance objectives were developed to evaluate the alternative flowsheets. The objectives were based on current operational needs for successful implementation in the NWCF and past calcination development experience. The performance objectives are listed below:

- The amount of chemical additives must be minimized to improve the NWCF processing rate and to conserve calcine solids storage space.
- Fluidized-bed calciner operability must be demonstrated with respect to bed and system stability and the absence of bed agglomeration.
- The calciner process must be compatible with the current off-gas treatment system with respect to species volatilization and fines generation.
- The calcine produced must be pneumatically transportable and retrievable and pose no additional safety concerns during transport, storage, or retrieval.
- The calcine produced must be soluble in nitric acid and compatible with the proposed final waste immobilization process.

Seven acceptance criteria were established to provide a quantitative measure of the performance objectives. The criteria include process throughput, particle agglomeration, fines generation, product and fines transportability and storability, calcine solubility, chemical compositions, and scrub solution interactions.

Background

The flowsheets evaluated in these tests were based on previous laboratory and pilot plant tests. As a precursor to the high-temperature tests, bench top temperature and additive variation tests were performed to determine optimum blend ratios and calcination temperatures. Thermal-gravimetric analyses (TGA), theoretical thermodynamic equilibrium calculations, differential-scanning calorimetry (DSC), calcine hydration and x-ray diffraction analyses were completed to define the mixture equilibrium chemistry as a function of calcination temperature.²

The sugar-additive flowsheet tests were based on an extensive amount of previous work using sucrose to enhance the destruction of nitrate salts. Sugar-additive calcination was attempted at Hanford Reservation on a sodium-bearing PUREX process waste stream during the late 1950s.³ At the INEL, sugar-additive calcination was investigated during the early 1960s using indirectly-heated calciners. The results indicated that the sugar caused the calcine to be softer, lighter in color, less dense, and reduced the amount of energy required due to the exothermic reaction between the sugar and nitrates. In 1965, a 12-inch indirectly-heated fluidized bed calciner was used to successfully calcine sodium-bearing solutions similar to SBW with sugar.⁴ No agglomeration was noted during these tests and the tests showed that sugar prevented the formation of sodium nitrate in the product while significantly reducing the calciner energy requirements. Newby *et al.*, also studied the use of sucrose and other additives throughout the 1970s and 1980s.⁵⁻⁷ Newby's tests showed that although there was no bed agglomeration, there were problems with calcination temperature control, above-bed burning, plugging in the off-gas system, caking and agglomeration of the fines, and foaming in the liquid scrub solutions. Laboratory tests were performed to gain information on alleviating these problems. The tests included TGA, DSC, and x-ray diffraction analyses.

A series of high-temperature and sugar-additive tests were conducted in an indirectly heated laboratory-scale calciner, as a part of the alternative flowsheet development.⁸ The lab-scale calciner was used since it minimized chemical use and waste generation. Trends in fines generation, attrition resistance, nitrate destruction, and agglomeration were established in the lab-scale calciner. Flowsheets that were successful in the lab-scale calciner were then tested in the 10-cm Calciner Pilot Plant as discussed in this report.

SYSTEM DESCRIPTION

The 10-cm Calciner Pilot Plant is located in Building CPP-637 at the ICPP. The 10-cm Calciner Pilot Plant was constructed in the early 1980s and was modified prior to these experiments to ensure compatibility with the flowsheets tested. A generalized flow diagram for the system is shown in Figure 1. The pilot plant is housed in a stainless steel enclosure equipped with a ventilation blower. The enclosure prevents the release of toxic chemicals and gases into the surrounding control and work areas. The calciner vessel consists of three sections: the plenum with the distributor plate; the reaction zone; and the disengagement section. The distributor plate is a perforated plate design. The reaction zone is located above the distributor plate and has a 10 cm (4 in.) internal diameter and a height of approximately 38 cm (15 in.). The reaction zone was constructed from 310 stainless steel to withstand elevated temperatures. The feed and fuel atomizing nozzles are located in the reaction zone. Spraying System Co. Nozzle 40100/120 was used on the feed system and Nozzle 2050/67-6-20-70 was used on the fuel system. The feed was atomized with air, and the fuel with oxygen. The disengagement section is located above the reaction zone and is approximately 117 cm (46 in.) in height. The internal diameter of the disengagement section widens from 10 to 15 cm (4 to 6 in.) in the base of the disengagement section. The disengagement section and the plenum were constructed from 304L stainless steel. Product continually overflows from the vessel through the overflow line which extends approximately 8 cm (3 in.) into the disengagement section. The product is collected in the product collection vessel. The vessel off-gas stream (VOG) from the calciner discharges at the top of the disengagement section (approximately 145 cm (57 in.) above the distributor plate) into the off-gas treatment system.

The VOG passes through the primary cyclone where entrained fines are removed from the gas stream and are collected in the fines collection vessel. The VOG is then quenched in the venturi scrubber using nitric acid to cool the stream and remove any remaining entrained fines. Downstream of the scrubber, the secondary cyclone removes acid droplets and fines from the gas stream. The solution from the secondary cyclone drains into the scrub collection vessel. Acid from the scrub collection vessel is continually recycled to the venturi scrubber. The off-gas stream is further cooled upon passing through the main condenser. Condensate is removed from the gas stream by the final cyclone. The off-gas stream then passes through the final condenser before being discharged into the pilot plant enclosure ventilation system.

Two auxiliary sampling systems are connected to the off-gas line and were used intermittently throughout the tests. The off-gas sampling and analysis system provides on-line measurements of carbon monoxide volume percent, carbon dioxide volume percent, and combustible gas concentrations as a percentage of the lower explosion limit in the off-gas stream. The off-gas sample for this system was pulled from the VOG line between the primary cyclone and the venturi scrubber. The second sampling system measured the particle size distribution of the solids exiting the primary cyclone. The particle impactor system was used to determine if submicron particles, that could plug the filter system in NWCF, were generated.

Figure 1. 10-cm Calcliner Pilot Plant Process Flow Diagram

TEST DESCRIPTIONS

A series of five scoping tests were conducted in the 10-cm Calciner Pilot Plant to evaluate the alternative flowsheet chemistries. The first test, SBW-BL-1, was conducted using the baseline flowsheet. This test was completed to serve as a comparative reference for the alternative flowsheets. Two high-temperature calcination tests, SBW-HT-1 and SBW-HT-2, were conducted to compare the effects of temperature and AAR variations. For Tests SBW-HT-1 and SBW-HT-2, respectively, the calcination temperatures were 650 and 600°C and the AARs were 1:1 and 1.5:1. Two sugar-additive calcination tests, SBW-SA-1 and SBW-SA-2, were completed to compare the effects of varying the AAR. For Tests SBW-SA-1 and SBW-SA-2 the AARs tested were 1:1 and 0.305:1, respectively.

General Test Procedure

The calcination tests were begun by preheating the vessel to drive off any moisture that had collected in the system. The preheater on the fluidizing air and a propane torch assembly in the reaction zone were used as heat sources. Starting bed material was then added to the system through the bed addition vessel. Nonradioactive alumina calcine generated during NWCF startup (between 212 and 600 microns in size) was used as starting bed for each of the tests. The vessel and the starting bed were then heated to 340°C, approximately 70°C higher than the auto-ignition temperature of kerosene, prior to starting the kerosene flow. The kerosene flow rate was dependent on the desired operating temperature. The ratio of oxygen to fuel (based on volumetric flows) in the fuel nozzle was set at approximately 2000. The composition of SBW simulant used for these tests was based on the predicted waste composition in the tank farm in the year 2008. The feeds for each test were varying blends of SBW simulant, aluminum nitrate, calcium nitrate, boric acid, and sucrose. The desired feed compositions for each test are listed in Table 1. Feed flow was initiated after the vessel temperature reached the desired operating temperature. The ratio of air to feed (based on volumetric flows) in the feed nozzle was then adjusted to the desired initial value. This ratio is commonly referred to as the nozzle air ratio (NAR). The initial parameters for each test are listed in Table 2.

Temperatures, pressures, and flowrates were recorded periodically throughout the run, and product and fines were collected at regular intervals. Adjustments were made to the various operating parameters as necessary throughout the run. The average operating parameters for each test are given in Table 3. The fluidizing air flow was adjusted to maintain a superficial velocity above the distributor plate at approximately twice the minimum fluidization velocity. The minimum fluidization velocity was calculated periodically throughout the run based on bed temperature, average particle size, and particle density.

Scrub composition and temperature were designated for the tests based on the expected fines loadings and the probability of foaming in the scrub solution. More concentrated nitric acid was used in those tests where high fines loading or foaming were expected. Based on past experiments, the scrub solution temperature was raised to approximately 60°C for the sugar-additive tests to control foaming. (see Reference 6)

Table 1. Composition of simulated waste and feed blends.

Component	2008 SBW (M)	SBW-BL-1 (M)	SBW-HT-1 (M)	SBW-HT-2 (M)	SBW-SA-1 (M)	SBW-SA-2 (M)
H	1.596	1.45e-01	9.20e-01	7.09e-01	7.14e-01	1.228
Al	6.92e-01	1.68	1.31	1.513	1.016	5.33e-01
B	1.95e-02	6.84e-02	1.12e-02	8.66e-03	8.72e-03	1.50e-02
Cd	2.99e-03	6.32e-04	1.72e-03	1.33e-03	1.34e-03	2.30e-03
Ca	5.71e-02	2.80e-02	7.64e-02	5.89e-02	5.93e-02	1.02e-01
Cl	3.57e-02	7.55e-03	2.06e-02	1.59e-02	1.60e-02	2.75e-02
Cr	3.87e-03	8.18e-04	2.23e-03	1.72e-03	1.73e-03	2.98e-03
F	7.64e-02	1.62e-02	4.40e-02	3.39e-02	3.42e-02	5.88e-02
Fe	2.39e-02	5.05e-03	1.38e-02	1.06e-02	1.07e-02	1.83e-02
Hg ¹	1.20e-03	---	---	---	---	---
Pb ¹	1.49e-03	---	---	---	---	---
Mn	1.28e-02	2.71e-03	7.38e-03	5.69e-03	5.73e-03	9.85e-03
Mo	6.65e-04	1.41e-04	3.83e-04	2.96e-04	2.98e-04	5.12e-04
Ni	1.71e-03	3.62e-04	9.86e-04	7.60e-04	7.65e-04	1.32e-03
NO ₃	5.988	5.899	6.267	6.344	4.865	4.723
PO ₄	1.46e-02	3.09e-03	8.42e-03	6.49e-03	6.53e-03	1.12e-02
K	2.21e-01	4.67e-02	1.27e-01	9.82e-02	9.89e-02	1.70e-01
Na	2.049	4.33e-01	1.18	9.10e-01	9.17e-01	1.576
SO ₄	5.46e-02	1.15e-02	3.15e-02	2.43e-02	2.44e-02	4.20e-02
Zr ²	3.24e-03	---	---	1.44e-03	1.45e-03	2.49e-03
Sucrose	NA	NA	NA	NA	5.59e-01	5.43e-01

1. Mercury and lead were not used in the feeds due to air permit restrictions.

2. Approval for using zirconium, based on air emissions, was not obtained until after Test SBW-HT-1

Table 2. Initial parameters.

Parameter	SBW-BL-1	SBW-HT-1	SBW-HT-2	SBW-SA-1	SBW-SA-2
Oper. Temp. (°C)	500	650	600	500	500
Fl. Air Velocity (m/s)	0.33	0.33	0.08	0.09	0.09
Fluidizing Air (sLps)	0.82	0.82	0.25	0.25	0.25
Kerosene (cc/min)	10 - 12	10 - 12	10 - 12	10 - 12	10 - 12
O ₂ to Fuel Ratio	2000	2000	2000	2000	2000
Feed (L/hr)	2	2	1.5	1.5	1.5
NAR	1200	1200	900	1200	1200
Scrub Temp. (°C)	30	30	30	70	70
Duration (hr)	40	40	60	60	60
AAR	3.5:1	1:1	1.5:1	1:1	0.305:1
Sucrose:Nitrate Ratio	NA	NA	NA	0.115	0.115

Table 3. Average operating parameters.

Operating Parameter	SBW-BL-1	SBW-HT-1	SBW-HT-2	SBW-SA-1	SBW-SA-2
Oper. Temp. (°C)	505	647	604	506	502
Fl. Air Velocity (m/s)	0.09	0.06	0.08	0.09	0.09
Fluidizing Air (sLps)	0.25	0.17	0.25	0.26	0.26
Kerosene (cc/min)	7.8	10.6	8.2	6	6
O ₂ to Fuel Ratio	2141	2012	2288	3230	3162
Feed (L/hr)	1.9	1.96	1.5	1.5	1.63
NAR	1281	995	1047	1189	908
Scrub Temp. (°C)	30	31	31	63	63
Duration (hr)	40	38	58.5	45	14.5
AAR	3.54:1	0.981:1	1.48:1	1.04:1	--
Sucrose:Nitrate Ratio	NA	NA	NA	0.108	0.114

The product and fines generated during the calcination tests were characterized using a variety of test methods. The particle size distribution, mass mean particle diameter (MMPD) and harmonic mean particle diameter (HMPD) of the product were determined by sieve screen analysis. An ASTM standard series (12, 16, 20, 30, 40, 50, 70, 100, 140, 200, 270, and 400 mesh US Standard screens) was used in the sieve analysis. The particle size distribution of the fines was determined using a Coulter Counter. The bulk density of the solids was analyzed using a packed-bed mass over volume measurement. The true particle density was determined using a hydrogen pycnometer. The chemical compositions of the solids were analyzed using X-ray diffraction and chemical analysis techniques. A comparative measure of the products' resistance to attrition was also measured. A known mass of solids in the -40 to +50 mesh size range was fluidized in a column at a specified rate and time. The mass percent of particles that were still within the initial size range is the attrition resistance index (ARI). The hygroscopic tendencies of the solids were also measured at varying temperatures and relative humidities. As a final test, the solubility of the solids in varying concentrations of nitric acid was also measured.

Test Synopses

The tests, with the exception of SBW-SA-2, were successful demonstrations of the flowsheets tested. Minor operational difficulties were experienced during each test, with some tests being more problematic than others. Operational difficulties were addressed by changing the operating conditions and in some instances by minor physical modifications to the system between tests. The highlights of each test are discussed below.

The baseline test, SBW-BL-1, had the fewest operating problems. The average operating conditions closely reflected the desired initial operating parameters as expected from the previous tests of the baseline flowsheet. A reduction in the fluidizing air flowrate was required to compensate for using a lighter starting bed material than past tests of the baseline flowsheet. Intermittent problems with plugging in the secondary cyclone and the inlet to the venturi scrubber were experienced during the test. The restrictions were easily cleared by temporarily flooding the secondary cyclone or by routing the scrub flow to the top of the venturi scrubber. Post-test analysis attributed the problems to a low scrub recirculation rate. The recirculation rate was increased during later tests.

Operation of the calciner during test SBW-HT-1 was more difficult. Severe plugging problems in the primary cyclone were experienced throughout the test. The test was halted after six hours of cumulative operating time (COT) and again at a COT of eight hours. The first shutdown was due to a break in a line near the cyclone exit. The break occurred during an attempt to clear a plug in the cyclone. The cyclone was removed for repairs and was found to be packed with fines. The second system shutdown was required when the pressure in the cyclone and vessel reached 20 psi above normal conditions due to plugging. This plug was cleared by rodding out the cyclone and adjacent lines. Plugging in the off-gas system at or near the cyclone continued during the remainder of the test. The plugs were partially cleared by rodding out the cyclone and lines while the system was operating. The test was stopped at a COT of 38 hours when a plug formed in the cyclone that could not be dislodged by rodding out the system. The cyclone was removed after the test and was again found to be packed with fines.

Minor plugging problems in the secondary cyclone, fuel nozzle, and feed nozzle also occurred during Test SBW-HT-1. As in the baseline test, the secondary cyclone was cleared by temporarily flooding it. The plugs in the feed and fuel nozzle were cleared by switching briefly to nitric acid feed and by tapping on the nozzle body, respectively. The NAR was reduced during the test from 1200 to 900 in an attempt to reduce the fines generation rate by increasing the feed droplet size and by reducing attrition of particles within the feed region. Excessive fines were noted in the scrub recycle vessel throughout the test due to the plugging problems in the primary cyclone. During the shut down at COT 6, a heat tape was added to the VOG sampling line to ensure

condensation from this line was not contributing to the plugging problems. The heat tape had no noticeable affect on the plugging problems.

The feed rate for Test SBW-HT-2 and subsequent tests was reduced to 1.5 l/hr to reduce the fines loading in the primary cyclone. Run times were adjusted accordingly to ensure comparable bed turnovers. Cyclone plugging problems also plagued Test SBW-HT-2. The line restrictions were temporarily relieved by rodding out the cyclone during operation. A thermocouple was added to the primary cyclone midway through this test to determine if condensation in the cyclone could be a possible factor in the cyclone plugging. During this test, additional air was added to the calciner in the upper portion of the disengagement section in an attempt to reduce the fines loading and relative humidity in the cyclone. Excessive fines were noted in the scrub collection vessel throughout the test. The plugging problems were manageable throughout the test, and the test was voluntarily terminated at a COT of 58.5 hours due to a feed shortage rather than plugging problems. Visual observation of the cyclone after completion of the test showed the cyclone was again packed with fines. After the test was completed, a heat tape was wrapped around the cyclone to ensure that the wall temperature in the cyclone stayed above the dew point of the off-gas stream.

Off-gas plugging problems were not significant during Test SBW-SA-1. Solids buildup in the plenum during operation caused some operational difficulties with the pressure differential readouts across the distributor plate. The plenum was drained twice during operation to maintain a clear flow through the differential pressure lines. This test was stopped after 45 hours of operation due to problems with the module blower and HEPA filter. Corrective maintenance on the blower remedied several problems with the blower, including the wrong size drive belt, dry bearings, and the belt guard rubbing on the belt. The pressure drop across the module HEPA filter had also risen significantly during this test but returned to normal after shutdown.

Feed nozzle plugging was a major problem during Test SBW-SA-2 and ultimately lead to the agglomeration of the bed that caused the run to be stopped after only 15 hours of operation. The first feed nozzle plug was noticed after approximately five hours of operation. Attempts to clear the nozzle plug with air additions, use of the nozzle plunger, and nitric acid feed were unsatisfactory. Several nozzle cones including one approximately 4 inches long and 1½ inches in diameter, were found in the final bed after the run had been terminated. The cones apparently formed around the feed nozzle and then dropped into the bed. As the cones settled on the distributor plate, the ability to fluidize the bed was rapidly lost and the bed agglomerated.

RESULTS AND DISCUSSION

Seven acceptance criteria have been established to assess the performance of the calcination flowsheet.⁹ These criteria provide quantitative measures to ensure the required performance objectives discussed previously are met. The criteria include process throughput, particle agglomeration, fines generation, product and fines transportability and storability, calcine solubility, chemical compositions, and scrub solution interactions. Each flowsheet is evaluated based on these criteria in the following sections.

A normalized operating time was calculated for each test based on the mean residence time (or space time) of components in the feed with the system. The normalized operating times provide a common basis for comparison of the acceptance criteria. The normalized times compensate for the variation in feed rates between Tests SBW-BL-1 and SBW-HT-1 at approximately 2.0 l/hr and the feed rates for SBW-HT-2, SBW-SA-1 and SBW-SA-2 at approximately 1.5 l/hr. A factor was calculated for each test to use as a multiplier to convert the actual operating time to an adjusted operating time. The factor was calculated by dividing the actual feed rate in l/hr by 1.5 l/hr. The factors calculated for the scoping tests are contained in Table 4. The adjusted operating time is used in the following discussions where applicable.

Table 4. Adjusted operating time factors.

	SBW-BL-1	SBW-HT-1	SBW-HT-2	SBW-SA-1
Adjusted Operating Time Factor	1.29	1.33	1.02	0.989

Process Throughput

A primary objective of the developing alternative calcination flowsheets is to increase the waste processing throughput to meet the terms of the Settlement Agreement. At least a 60% increase in the throughput over the baseline flowsheet is required based on plant waste modeling projections. For the purposes of the scoping tests, throughput was measured by the volume percent of the feed that is SBW. Table 5 contains a list of the volume percent of SBW in the feed for each test. As noted in the table, the feed for SBW-HT-2 contained the least volume percent of SBW for the alternative calcination tests, yet still represents a 90% increase in throughput over the baseline.

Table 5. Volume percent of SBW in test feeds.

	SBW-BL-1	SBW-HT-1	SBW-HT-2	SBW-SA-1
Volume % SBW in Feed	17.9	43.3	34.0	34.2

Particle Agglomeration

Particle agglomeration is the adhesion of individual particles to form larger particles. Three acceptance subcriteria have been linked to particle agglomeration. First, particle agglomeration is considered excessive if the MMPD of the bed increases out of the NWCF design range of 0.3 mm to 0.5 mm. Second, a successful test has less than 1.0 wt% of particles greater than 14 U.S. Standard mesh in the final bed after sufficient operating time to achieve at least a 90% bed turnover. Third, the formation of deposits in the vicinity of the

feed nozzle or on any of the calciner vessel surfaces that are not attributed to system malfunctions will be unacceptable. These subcriteria are discussed in the following sections.

Product MMPD

The MMPD is dependent on the fixed parameters of bed temperature and feed chemistries; it is also dependant on the variable operating parameter of NAR. Therefore, optimization of NAR must be performed for each test. The typical behavior of product MMPD is a slight increase during the first half of the test, followed by leveling off at a constant value as steady state is reached. If the MMPD increases too rapidly, the NAR can be increased slightly to decrease feed droplet size. The NAR is altered by adjusting the atomizing air flow rate rather than the feed flow rate. Decreasing the feed droplet size increases flash vaporization which decreases particle growth rate. Also, higher NAR increases grinding in the bed which causes attrition. Conversely, if the MMPD decreases, the NAR can be decreased. If adjustments to the NAR cannot bring the MMPD within the desired size range, the flowsheet chemistry may not be suitable.

The MMPDs of the product and the NAR, as functions of adjusted operating time for each successful test, are plotted in Figures 2 through 5. The graphs show the inverse relationship between MMPD and NAR. The NAR initially can vary widely due to course adjustment of operating parameters and, therefore, should not be considered when noting trends.

As shown in Figure 2, the NAR during SBW-BL-1 was about 1200 throughout the test. The MMPD increased slightly during the first 24 hours of actual operation (30 hr adjusted time), from 0.34 to 0.47, and leveled off. This trend is indicative of the typical behavior and presents a basis for comparing the remaining tests.

As stated in the test synopsis, SBW-HT-1 was restarted twice during the first eight hours of operation. During the test suspensions, it was noted that the bed particles were shrinking, although no MMPD determination was performed. Also, there were a large amount of fines produced that plugged the cyclone. These were thought to be caused by a higher flash vaporization rate due to the higher temperature. Therefore, when the test was started the third time, NAR was set at 900 rather than 1200. As a result, Figure 3 shows that the MMPDs at 20, 30, and 40 actual cumulative operating hours were constant (≈ 0.395 mm). Plugging problems in the primary cyclone that occurred later during the test may have caused the lower final MMPD due to a diminished flow of smaller particles from the bed.

Figure 4 shows the MMPD and NAR for Test SBW-HT-2. As shown in the plot, the NAR was initially held between 800 - 900. However, the MMPD quickly increased from 0.34 mm to 0.44 mm in the starting bed. This prompted an increase in NAR to 1000. The MMPD continued to increase, therefore, the NAR was continually increased. At the end of the test, the NAR was being held at about 1200, but the MMPD was still increasing. It is difficult to determine if the MMPD increased due to the NAR or if the feed chemistry caused the increase. This test should be repeated with the NAR held at 1200 to determine if the MMPD can be controlled.

The MMPD results of the first sugar-additive test, SBW-SA-1, are presented in Figure 5. The NAR for this test was held at about 1200 for the entire test. It appeared that the test was behaving much like the baseline test in that the MMPD increased slightly from 0.34 mm in the starting bed to 0.39 mm at COT 30 hours. The MMPD increased at COT 40 hours to 0.41 mm and again in the final bed to 0.43 mm where several larger particles formed by smaller particles agglomerating together were noted. As noted in the test synopsis, this test was suspended due to module blower problems, therefore, thorough trending could not be performed. Again, it is not known whether the MMPD increase could have been controlled by adjusting the NAR.

Figure 2. MMPD and NAR versus operating time for SBW-BL-1.

Figure 3. MMPD and NAR versus operating time for SBW-HT-1

Figure 4. MMPD and NAR versus operating time for SBW-HT-2

Figure 5. MMPD and NAR Trends for SBW-SA-1

Particle Size Distribution

The particle size distribution (PSD) is a good indicator as to whether agglomeration of the bed is occurring. PSD, if plotted as the cumulative percent less than a certain particle size as a function of the particle size, usually forms an "S"-shaped curve. A PSD with very little size variation, as with the starting bed for all the tests, is indicated by a very steep center section of the curve. A gradual slope in the center section indicates a wider variation in particle size. Figures 6 through 9 are plots of the PSDs for the tests.

Bed turnover plays a significant role in the PSD. The PSD at less than 90% bed turnover more closely reflects the PSD of the starting bed rather than the changes caused by the flowsheet chemistry. Therefore, the acceptance criteria is based on a 90% bed turnover being achieved. Bed turnover for each test was defined by the following equation:

$$T = (1 - e^{-(P/W)}) * 100$$

where: T = bed turnover percentage

P = total product plus final bed collected (excluding COT 0 product)

W = average bed weight during test (units consistent with P)

Since bed level and product bulk density did not vary significantly during the test, the final bed weight was used as the average bed weight. The bed turnover percentages for the scoping tests are listed in Table 6. As noted in the table, the bed turnover percentages were consistently greater than 90% with the exception of SBW-HT-1. The low bed turnover percentage during this test was most likely due to the high rate of flash evaporation.

Table 6. Bed turnover percentages.

	SBW-BL-1	SBW-HT-1	SBW-HT-2	SBW-SA-1
Bed Turnover (%)	92.9	83.0	92.2	90.3

All of the plots show nearly identical PSD curves for the starting bed. All have very steep center sections which is expected since the starting bed was screened to between 0.212 and 0.600 mm. The PSD plots of the final beds from SBW-BL-1 and SBW-HT-2 (Figures 6 and 7) show good distributions of particles, small percentage of particles greater than 1.7 mm in diameter (1.1% and 0.2%, respectively), and gradual transitions from the center section to the upper section.

The plot from SBW-HT-1 (Figure 8) shows a more steep center section, however, there was a small percentage of particles greater than 1.7 mm in diameter (1.2%). Therefore, it is assumed that no agglomeration was occurring. Also, it should be noted that the center section of the plot exhibits a slight slope change. A greater slope change is characteristic of a bimodal distribution. The slight change in slope may be an indication that this was beginning to occur and could also be attributed to the plugging problems in the primary cyclone.

Figure 9 is the plot of the PSD of the final bed from SBW-SA-1. This plot shows a large percentage of particles greater than 1.7 mm in diameter (4.4%). It was apparent that the early stages of agglomeration were occurring during this test.

Figure 6. PSD for SBW-BL-1

Figure 7. PSD for SBW-HT-1.

Figure 8. PSD for SBW-HT-2.

Figure 9. PSD for SBW-SA-1.

Feed Deposition

Due to the slugging-bed nature and the small size of the 10-cm calciner, feed deposition on the wall opposite of the feed nozzle is inevitable. Therefore, this acceptance criterion will be disregarded for 10-cm Calciner Pilot Plant tests.

Fines Generation

Fines generation is accomplished by two mechanisms: particle attrition and flash vaporization. Several subcriteria have been developed to decide the acceptability of fines generation. All are designed to account for fines generated by either mechanism, with the exception of the ARI, which only accounts for fines generated by attrition. Other acceptance subcriteria state that, first, fines generation is considered excessive if the fluidized bed cannot be maintained during the test as required for particle growth. Second, it is considered excessive if the quantity of fines results in excessive buildup of chloride, fluoride, or undissolved fines in the scrub solution. And third, if it results in high bin set storage requirements. A discussion of the subcriteria with respect to these tests is contained in the following sections.

Attrition Resistance Index

ARI is a measure of fines generation ability due to attrition. Therefore, it should be inversely proportional to the product-to-fines ratio (P/F) if all of the fines were collected and the amount of fines produced by flash vaporization was negligible. However, the chemical analysis results suggest that the formation of fines by flash vaporization is significant. Therefore, the ARI should only be used as a guide for comparing tests and not as a definitive "make-or-break" criterion. The ARI of the final beds from the scoping tests are listed in Table 7. An ARI between 40 and 80 is generally considered acceptable. Although only the final bed from SBW-HT-1 met this criterion, fines generation due to attrition during the other tests was considered neither excessive nor insufficient. The ARI of the starting bed for all the tests, to use as a reference, was 61%.

Table 7. ARI of final bed.

	SBW-BL-1	SBW-HT-1	SBW-HT-2	SBW-SA-1
Attrition Resistance Index (%)	31	60	86	92

Particle Growth and Calcination Reactions

It is difficult to put a definitive quantity on these criteria. However, an increase in MMPD, particularly early in a test, and a steady bed height are good indicators that particle growth is occurring. The plots of MMPD vs. operating time (presented in the previous section) show that particle size did increase during all the tests except SBW-HT-1. Bed height was measured based on differential pressures in the bed. A plot of bed height as a function of operating time for the tests is presented in Figure 10. The figure shows that the bed height remained steady during all the tests.

Figure 10. Bed Height versus Adjusted Operating Time

Chloride, Fluoride, and Undissolved Particulate Buildup in Scrub

Chloride and fluoride retention in the product and carryover to the scrub are discussed in the section on component mass balances. Undissolved solids were not measured for the scrub solutions, however, in general, the scrub solution was partially drained and replenished when it became burdened with solids. Therefore, the volume and concentration of nitric acid added to the scrub system during a test can be used as a guide in determining the acceptability of fines generation with respect to this subcriterion. However, since there was no definite measurement, the use of this as a definitive criterion is unwarranted. Table 8 contains a list of the average nitric acid concentration and the volume added during each test.

Table 8. Concentration and volume of nitric acid added to scrub solutions.

	SBW-BL-1	SBW-HT-1	SBW-HT-2	SBW-SA-1
Avg. Nitric Acid Conc. (M)	4.0	6.1	6.0	13.0
Vol. Nitric Acid Added (L)	20.5	36.5	28.5	20.4

Bin Set Storage Requirements

Bin set storage requirements are determined by the overall bulk density of the solids. That is the bulk density of the product and fines combined in the observed P/F. The product and fines bulk densities, P/F, and the calculated overall bulk density are tabulated in Table 9. Product and fines bulk densities were determined at fixed intervals (either 8 or 10 hours) during each of the tests. Weighted averages of the densities were calculated for each test.

Table 9. Calcine storage requirements data.

	SBW-BL-1	SBW-HT-1	SBW-HT-2	SBW-SA-1
Avg. Product Bulk Den. (g/cm ³)	1.10	1.28	1.17	1.22
Avg. Fines Bulk Den. (g/cm ³)	0.56	0.65	0.69	0.27
Product-to-Fines Ratio - P/F	1.2	2.6	13.3	2.0
Overall Bulk Density (g/cm ³)	0.96	1.47	1.26	0.68

The P/F is a measure of the mass ratio of the product generated during a test to the fines generated during a test. The mass of product includes bed that was built (or lost) during the test, therefore, the P/F was determined by the following equation:

$$P/F = (P + (FB - (SB - COT\ 0\ P+F))) / F$$

where: P/F = product-to-fines ratio

P = mass of product collected during the test (excluding COT 0)

FB = mass of the final bed

SB = mass of the starting bed

$COT\ 0\ P+F$ = mass of product and fines collected at COT 0 hrs

F = mass of fines collected during the test (excluding COT 0)

The calculated values of P/F for the scoping tests are listed in Table 9. It should be noted that these values do not include fines that were carried past the primary cyclone due to plugging. However, these fines would, theoretically, be recycled to the feed, and not collected in the bin sets. All of the calculated values are greater than the acceptable value of 1.5 with the exception of SBW-BL-1.

Product and Fines Transportability and Storability

Product and fine transportability and storability is assessed using standardized retrievability, attrition, hydration, and density tests. Retrievability of the calcines from bin storage is required for future treatment of the calcine to immobilize hazardous and radioactive components. Retrievability tests have not been completed on the calcines from the tests discussed in this report. Calcine attrition resistance affects the erosivity of the solids on the off-gas cyclones and the transport system. The ARIs for the calcines generated in these tests were discussed previously. Calcine hydration impacts both transport and the retrieval of the solids. If the calcines are hygroscopic, caking or fusing of the calcines could adversely impact storage and retrieval. The density of the product and fines impacts the bin-set storage requirements, the lower the bulk density of the solids, the more storage required. Current bin-set capacity is limited and the construction of new storage would be an added expense to the project.

Calcine Hydration Experiments

Calcine hydration tests were conducted to provide a relative measure of how each calcine would perform at representative transport and storage conditions. Observations during the 10-cm Calciner Pilot Plant tests indicated that the calcines formed using both high-temperature and sugar-additive flowsheets were more hygroscopic than the baseline calcine and in some instances were deliquescent. Five hygroscopicity tests

were conducted over a range of expected transport and storage conditions using calcines generated during tests SBW-BL-1, SBW-HT-1, SBW-HT-2, and SBW-SA-1. General characteristics of the calcines which may affect the hygroscopicity of the calcines are listed in Table 10.

Table 10. Calcine characteristics.

Calcine Identifier	Calcination Temp. (°C)	Additives	P/F Ratio in Calcine Tested	AAR in Feed	AAR in Product	AAR in Fines	Nitrate Conc. (Wt%)
SBW-BL-1	500	ANN, HBO ₃ , CaNO ₃	1:1	3.54:1	3.2	5.6	15.92
SBW-HT-1	650	ANN, CaNO ₃	2.6:1	0.98:1	1.13	1.1	4.1
SBW-HT-2	600	ANN, CaNO ₃	2.6:1	1.48:1	1.49	1.7	4.2
SBW-SA-1	500	Sucrose, ANN, CaNO ₃	2.4:1	1:1			7.39

The hygroscopicity tests were conducted using the test apparatus shown in Figure A.1 in Appendix A. For each test, a known mass of calcine (from the final bed) was placed in an open-ended tube equipped with a wire mesh and refractory fiber support and then placed in a laboratory oven. Air passed through a humidification vessel to generate the required humidity, then through an air distribution manifold and the tubes of calcine. To encompass the expected transport and storage conditions, the temperature and relative humidity were varied between the tests as shown in Table 11. A normalized percent mass gain was determined periodically by weighing the samples. The tests were stopped when the mass gain for each sample had stabilized or the sample had visibly agglomerated. A simple pour test was conducted after each test to compare the basic handling characteristics of each sample after exposure to humid conditions.

Table 11. Hydration test conditions.

Test #	Bath Temperature (°C)	Oven Temperature (°C)	Relative Humidity (%)	Air Flow Rate (ml/min)
1	25	30	100	250
2	45	50	100	250
3	70	75	100	250
4	50	75	27	100
5	50	75	27	100

Minor deviations in the general operating procedure were required during some of the tests. During Test 2, testing of SBW-HT-1, SBW-HT-2, and SBW-SA-1 calcines was stopped prior to the testing of the baseline calcine when they had visibly agglomerated. Test 3 was stopped before any of the calcines reached steady state because the conditions exceeded the expected transport and storage conditions. Although Test 3 was halted early, the sugar-additive calcine was visibly deliquescent and the high-temperature calcines were starting to form moist agglomerates. Test 4 was temporarily halted midway during a two week long holiday work curtailment. The samples lost weight during the shut down, but did not regain the mass at the same rate as at the start of the test. Test 5 was a repeat of the conditions used in Test 4, but the pour test was conducted at 50 hour intervals.

Figures 11 through 15 show the percent mass gained for each calcine under the tested conditions while Table 12 gives the results of the pour tests. As initial observations suggested, the baseline calcine was less hygroscopic than the other calcines. The baseline calcine consistently had a lower mass gain and maintained acceptable handling characteristics. Calcine from Test SBW-SA-1 was the most hygroscopic. The sugar-additive calcine rapidly absorbed water during the tests and agglomerated into a moist, sticky mass that failed the pour tests. The sugar-additive calcine was not used in Tests 4 and 5 due to its deliquescent behavior in the previous tests. Calcines from SBW-HT-2 seemed to be slightly less hygroscopic than SBW-HT-1 calcine based on water retention, however both exhibited the same handling characteristics after exposure.

Figure 11. Hygroscopicity Test 1 results.

Figure 12. Hygroscopicity Test 2 results.

Figure 13. Hygroscopicity Test 3 results.

Figure 14. Hygroscopicity Test 4 results.

Figure 15. Hygroscopicity Test 5 results.

Table 12. Calcine Pourability Test Results

Test #	SBW-BL-1	SBW-HT-1	SBW-HT-2	SBW-SA-1
1	No Change	Lightly packed	Lightly packed	Deliquescent
2	Lightly packed	Moist Agglomerate	Moist Agglomerate	Deliquescent
3	Unknown	Moist Agglomerate	Moist Agglomerate	Deliquescent
4	No Change	Hard packed	Hard packed	NA
5a	No change	No change	No change	NA
5b.	No change	No change	No change	NA
5c.	No change	Very light packing	Very light packing	NA

Light Pack-Solid cake of calcine easily broke by tapping on container
Hard Pack-Solid cake of calcine require direct crushing to break

The overall test results indicate that the hygroscopicity of the calcines is not dependent on the nitrate concentration in the solids. Calcine from SBW-BL-1 had the highest nitrate concentration but was the least hygroscopic. Calcine from SBW-SA-1 had the second highest nitrate concentration yet was the most hygroscopic. Hygroscopicity of the calcine does appear to be related to the AAR of the solids. The higher the AAR, the lower the hygroscopicity, as demonstrated by calcine from SBW-BL-1 at an AAR of 3.5:1 and SBW-HT-1 at an AAR of 1:1. The AAR influences the chemical composition with more sodium aluminates being formed at higher AAR and more sodium oxide at lower AAR. This variation in composition may also account for the poorer performance of the sugar-additive calcine over the high-temperature calcines.

Based on the five tests completed in this study, the sugar-additive and high-temperature calcine flowsheets do not meet the hygroscopic characteristics of the baseline flowsheet. Special handling would probably be required to transport and store sugar-additive calcines. The high hygroscopicity and deliquescent nature of the sugar-additive calcines would not be acceptable for the current transport and storage systems. Standard handling methods may be suitable for the high-temperature calcines. Some precautions might be required to ensure that the high-temperature calcines were not subjected to excessively high relative humidities. Based on the limited testing completed, humidities at or below 27% relative humidity at 75°C would be acceptable for the high-temperature calcines. Short duration exposures to 100% relative humidity at 30°C might also be acceptable.

Refinement of both the sugar-additive and high-temperature flowsheets must be completed in order to make a recommendation for the NWCF. Once the flowsheets have been refined, the resulting calcines should be retested to determine their hygroscopic characteristics. Future studies would benefit from a more complete definition of the conditions expected in the transport and storage systems during average and worse case operating conditions.

Calcine Solubility

Product and fines dissolution data provides a measure of the ease or difficulty of dissolving the bed during an upset condition (bed agglomeration) and eventually redissolving the calcine for separations of radionuclides,

if necessary. Fines dissolution data also provides a measure of the extent that the fines dissolve in the acid scrub. An acceptance criterion has been established that calcine solubility is acceptable if the solubility in nitric acid is equal to or greater than that of the baseline calcine. Product and fines dissolution data for the scoping tests are listed in Table 13. Observation of the data suggests that both alternative flowsheets produce calcine that is more easily dissolved than the baseline flowsheet and are therefore acceptable.

Table 13. Product and fines dissolution results.

	SBW-BL-1	SBW-HT-1	SBW-HT-2	SBW-SA-1
% Product Undissolved in 8 M HNO ₃	8.9	4.5	4.7	6.5
% Fines Undissolved in 2 M HNO ₃	40.0	2.9	7.6	2.4

Chemical Analyses

Overall and Component Mass Balances

Material balances were performed for all the tests because certain acceptance criteria address the fate of specific components. For example, in the Fines Generation section, it states the fines generation will be considered excessive if the quantity of fines resulted in an excessive buildup of chloride or fluoride in the scrub solution. Also, material balances provide information that can help quantify other acceptance criteria. In general, material balances for the alternative calcination tests will be compared to the baseline test. The material balances are contained in tables in Appendix B.

The overall mass balances were performed on a dry weight basis. The mass of water was excluded to prevent it from masking the importance of the other components. The system inputs for the baseline and high-temperature tests were: starting bed, feed (excluding water), and acid scrub (excluding water). For the sugar-additive flowsheet test, kerosene was also included in order to perform a carbon balance. Kerosene was not included in the high-temperature flowsheet tests because very little carbon (< 1%) remained in the system during these tests (99% or more was released in the off-gas stream as CO and CO₂). The acid scrub was designated either initial acid scrub or additional acid scrub since the initial acid scrub usually cleans the system of particulate that remains after completion of previous tests. The outputs from the system were: final bed, product, fines, spent acid scrub, condensate, and the off-gas stream. The product and fines collected at COT 0 hr were reported separately from the remainder of the product and fines since the composition was assumed to be identical to that of the starting bed and they were not included in the product-to-fines ratio calculation. The final entry in each of the balances is the mass that was lost which is the difference between the input and the output. The major contributor to the mass that was lost was the nitrate that was decomposed and released as NO_x. However, during some of the tests, a small amount of fines remained in the primary cyclone and was unaccountable, and therefore was assumed to be lost. Since the balance for SBW-SA-1 includes the carbon from the kerosene, comparison to the other overall balances is not possible because most of the carbon is released as carbon dioxide and carbon monoxide.

Comparison of the overall balances reveals that the mass lost is the largest difference between the tests. Test SBW-BL-1 had the least mass lost for two reasons. First, the destruction of nitrate was not as complete (this is discussed in the component balances). Second, after both of the high-temperature flowsheet tests, the primary cyclone was packed with fines.

Other differences between the different flowsheet mass balances are:

- Feed input (excluding water) for SBW-BL-1 is less than that for SBW-HT-1 and SBW-HT-2 because the feed for SBW-BL-1 included boric acid and the water required to dissolve it prior to blending with SBW. Feed input for SBW-HT-1 is less than that for SBW-HT-2 because the latter required more feed for the longer operating time. Feed for SBW-SA-1 includes sugar, however, the water in the sugar was not included, only the carbon.
- The initial acid scrub inputs for the tests were nearly the same, differing only in the amount of solids remaining in the system from the previous tests. The additional acid scrub inputs differed because SBW-HT-1 and SBW-HT-2 required more scrub to keep the greater amount of fines that were carried over in solution. Test SBW-SA-1 required more additional scrub because the higher scrub temperature caused more of the scrub to evaporate.
- The COT 0 product and fines from SBW-SA-1 was lower than the other tests because the product removal line was plugged at the beginning of the test.
- Several factors controlled the amount of product and fines that were removed during each of the tests. First, the amount of feed fed during the test was greatest for SBW-HT-2, therefore, the amount of product removed during that test was greatest. Second, the amount of fines produced by flash evaporation was greatest during SBW-HT-1, however, the fines were not removed due to the plugged primary cyclone. Third, the higher the AAR of the feed (for SBW-BL-1, $AAR \approx 3.5$) the greater the tendency to produce fines by attrition. The fines produced during SBW-BL-1, however, were removed by the primary cyclone.
- Performing a mass balance around the venturi scrubber and condenser for the baseline and high-temperature flowsheet tests shows that the input (Initial Acid Scrub + Additional Acid Scrub) during SBW-BL-1 was much less than the other tests (6.05 kg for SBW-BL-1, 13.25 kg for SBW-HT-1, and 10.71 kg for SBW-HT-2). The output (Spent Acid Scrub + Condensate), however, was greater during SBW-BL-1 (17.36 kg during SBW-BL-1, 13.44 kg during SBW-HT-1, and 15.73 kg during SBW-HT-2). This shows the influence of the elevated temperature on the scrub solution. The increased temperature caused more of the nitric acid in the scrub to decompose and/or volatilize.

The component mass balances were used in conjunction with thermodynamic analyses and x-ray diffraction analyses (contained in Appendix B) to determine component retention in the solids and the compounds that were possibly formed. The fate of the individual components is discussed in the following sections.

Nitrate

Nitrate is the most concentrated component in the SBW and, as noted in the mass balances, represents the majority of the mass lost during calcination, with the exception of water. As stated in the Introduction, nitrate that remains in the bed during calcination as sodium and potassium nitrates can cause agglomeration of the bed if the concentration is too high. Therefore, it is desirable to destroy the nitrate and allow it to be removed from the bed in the off-gas stream. The ability of a flowsheet to allow this to occur is one of the major factors in deciding the effectiveness of the flowsheet. Figure 16 contains plots of nitrate concentration in the bed (product) versus adjusted operating time for the scoping tests.

Figure 16. Nitrate concentration versus time.

From the plots, nitrate concentration trends can be easily noted. For SBW-BL-1, nitrate concentration increased moderately during the first 20 hours of adjusted operating time from 10.2 wt% to 14.3 wt%. For the remainder of the test, nitrate concentration increased slightly from 14.3 wt% to 15.9 wt%. This slight increase is expected since bed turnover was only about 93%. Thermodynamic equilibrium and x-ray diffraction analyses suggest that the nitrate that remained in the bed was in the form of sodium and potassium nitrates. The baseline test shows that, although nitrate concentration was significant, bed agglomeration did not occur because of the alumina diluent. Past experience has shown that the nitrate that was destroyed was released as NO_x .

For SBW-HT-1 and SBW-HT-2, the plots show sharp decreases in nitrate concentration during the first 20 hours of adjusted operating time (10.4 to 1.5 wt% for SBW-HT-1 and 10.3 to 3.3 wt% for SBW-HT-2). During the remainder of both tests, the nitrate concentration remained constant (with the exception of the final bed from SBW-HT-1) even though the bed turnover was not complete for either test. The notable increase in nitrate concentration for the final bed from SBW-HT-1 may have been caused by the plugging of the primary cyclone. As stated in previous sections, plugging may have prevented the removal of fines from the bed. The fines produced during SBW-HT-1 contained a high concentration of nitrate (12.8 wt% average) because flash vaporization produces low density fines that are readily elutriated from the bed which does not allow sufficient residence time for denitration. Since more fines were retained in the bed, the nitrate concentration of the final bed was elevated. Although thermodynamic equilibrium analyses suggest that the nitrate was released as nitrogen and oxygen, observation of the brownish color of the off-gas plume indicated that, for both tests, the nitrate was released as NO_x .

During SBW-SA-1, the nitrate concentration appears to increase from about 0 wt% in the starting bed to 5.7 wt% at about 20 hours of adjusted operating time. The starting bed was not sampled during this test to reduce analytical costs, but instead the trend of the concentration was used to determine the starting bed concentration. This method was used for all of the components. The nitrate concentration continued to increase slightly for the remainder of the test (from 5.7 wt% to 7.4 wt%), again, likely due to the incomplete

bed turnover. Thermodynamic equilibrium analyses suggest that the destroyed nitrate and sugar were released as nitrogen, carbon dioxide, and water. The lack of a brownish colored off-gas plume indicates that this may be true. The following is a possible mechanism for the reaction:

Where M is either sodium or potassium.

Aluminum

For all the scoping tests, aluminum was the most concentrated, non-volatile component. Therefore, aluminum (along with other highly concentrated components such as sodium and potassium) is a good indicator of bed retention ability of the volatile components. That is, comparison of aluminum retention to chloride retention, for example, will indicate whether chloride was volatilized from the bed or if it was removed in the fines and not recovered (*e.g.*, remained in the primary cyclone). The aluminum concentration data of the product for the scoping tests are plotted in Figure 17. In general, the aluminum concentration tended to decrease during all of the scoping tests. The negative slope of the trend became more steep as the aluminum concentration in the feed decreased.

Figure 17. Aluminum concentration versus time.

The fate of aluminum during calcination, as suggested by thermodynamic equilibrium calculations, is to form alkali-metal aluminates with the alkali metals from alkali-metal nitrates that were destroyed. The remaining aluminum forms alumina. This was confirmed by x-ray diffraction analyses of the final bed from SBW-BL-1, SBW-HT-1, and SBW-HT-2. Both of the x-ray diffraction prints from the high-temperature flowsheet tests showed distinct sodium aluminate peaks; however, the print from the baseline test showed a large amount of amorphous material with slight sodium nitrate and sodium aluminate peaks.

One concern with the formation of alumina is the formation of *alpha*-alumina. *Alpha*-alumina is an insoluble, crystalline form of alumina that can erode the liquid scrub system. Past experimentation suggested that boric acid be added to the feed to cause the formation of aluminum borate rather than alumina. Boric acid was used for this purpose during the baseline test; however, during the high-temperature and sugar-additive flowsheet tests, it was believed that the absence of excess aluminum would preclude the formation of *alpha*-alumina. Therefore, no additional boric acid was included in the feed. Comparison of the x-ray diffraction prints for the starting bed and the final bed confirm that very little, if any, *alpha*-alumina was formed.

Alkali Metals

As stated in the previous section, the high concentration of sodium and potassium in the feed provides a good indication as to the fate of volatile components. In addition, the AAR of the product, as compared to the AAR of the feed, provides an indicator of bed turnover. Figures 18 through 21 contain plots of AAR versus adjusted operating time. The horizontal line in the plots is the AAR of the feed. Complete bed turnover would be indicated by the product AAR being equal to the feed AAR as noted in Figures 18 and 20 for SBW-BL-1 and SBW-HT-2.

Figure 18. AAR versus adjusted operating time for SBW-BL-1.

Figure 19. AAR versus adjusted operating time for SBW-HT-1.

Figure 20. AAR versus adjusted operating time for SBW-HT-2.

Figure 21. AAR versus adjusted operating time for SBW-SA-1.

Halides

The accumulation of halides (*viz.*, chloride and fluoride) is the main cause of corrosion in the scrub system. For comparison between the pilot plant and the NWCF, the scrub system for the 10-cm Calciner Pilot Plant included the condensate tank. Halide ions can enter the scrub system via two mechanisms. The first is carryover with the fines that are not removed by the primary cyclone. The second is volatilization from the calciner bed followed by condensation in the scrub solution. The first mechanism can be controlled by reducing fines generation and by improving the efficiency of the primary cyclone. The second mechanism can be controlled by reducing the operating temperature or by adding chemicals to the feed that reduce volatilization. For example, calcium nitrate is added to the feed to cause the formation of calcium fluoride which is non-volatile. For the scoping tests, the mass percent of chloride and fluoride, that was captured in the scrub system by each mechanism of release from the bed, was calculated. The mass percent captured by the first release mechanism was calculated by summing the mass of aluminum, sodium, and potassium that was carried over to the scrub system divided by the total mass of aluminum, sodium, and potassium that was removed from the calciner (product and final bed), primary cyclone (fines), and scrub system (scrub and condensate). The mass percent of calcine that was not recovered was subtracted from this value. The mass percent captured by the second release mechanism was calculated by the difference between the total mass percent of the halide that was carried over and the mass percent that was carried over as fines. Table 14 contains the halide volatility results from the scoping tests. The percent "Retained in Solids Collected" includes that retained in the product, fines, and final bed that was collected. The percent "Retained in Solids Not Collected" includes that retained in the solids that were not collected; this was determined by the material balance on aluminum, sodium, and potassium. The percent "Contained in Fines Carryover" includes that contained in the fines that were captured in the scrub system. The percent "Volatilized" is that percent that left the calciner in the off-gas stream.

Table 14. Halide volatility results.

	SBW-BL-1	SBW-HT-1	SBW-HT-2	SBW-SA-1
Chloride				
Retained in Solids	40.9%	32.6%	55.8%	78.6%
Retained in Solids Not Collected	12.7%	34.3%	13.8%	10.3%
Contained in Fines Carryover	8.4%	21.9%	25.3%	11.1%
Volatilized	38.0%	11.2%	5.1%	0.0%
Fluoride				
Retained in Solids	51.9%	24.2%	38.8%	71.8%
Retained in Solids Not Collected	12.7%	34.3%	13.8%	10.3%
Contained in Fines Carryover	8.4%	21.9%	25.3%	11.1%
Volatilized	27.0%	19.6%	22.1%	6.8%

Carbon

A complete carbon balance was performed only for SBW-SA-1 because during the baseline and high-temperature calcination tests nearly all of the carbon was released to the off-gas stream as carbon dioxide and carbon monoxide. An average of the analyses from SBW-BL-1, SBW-HT-1, and SBW-HT-2 showed that the solids produced contained less than 0.5 wt% carbon, the scrub contained 360 $\mu\text{g/ml}$ carbon, and the condensate contained 234 $\mu\text{g/ml}$ carbon. By difference, greater than 98% of the carbon was released. For SBW-SA-1, the carbon balance is contained in Appendix B.

Table 15 contains the average off-gas analysis data that was obtained during the scoping tests. The table also contains the percent unburned hydrocarbons in the off-gas stream. This was measured as the percent lower explosion limit (%LEL) of the off-gas stream. For SBW-BL-1, SBW-HT-1, and SBW-HT-2, the %LEL was controlled by the carbon monoxide in the off-gas stream. It is listed here to compare with the sugar-additive flowsheet test.

Table 15. Off-gas analysis results.

	SBW-BL-1	SBW-HT-1	SBW-HT-2	SBW-SA-1
% CO in Off-gas Stream	0.7	0.7	0.5	4.8
% CO ₂ in Off-gas Stream	7.8	11.5	22.0	15.0
% LEL of Off-gas Stream	7.8	9.0	9.0	39.0

Scrub Solution Interactions

Scrub solution interactions are assessed on the extent of foaming, the rate of solids buildup in solution, and the chemical composition. Past tests have shown that the presence of unreacted sugar or carbon in the scrub

solution can cause excessive levels of foaming that adversely impact operation of the scrub recycle system. Foaming was therefore not a concern for the high-temperature or baseline flowsheets. Previous tests have also shown that foaming can be controlled by maintaining a temperature of 60°C or higher in the scrub recirculation (see Reference 6). The scrub solution temperature was maintained at the recommended level during Tests SBW-SA-1 and SBW-SA-2, therefore, foaming was not a problem in either test.

The rate of solids buildup in the scrub solution affects the need for replenishing the scrub solution. Spent scrub solutions must either be added to the feed solutions and processed or recycled to the tank farm for processing at a later date. An increased need to replenish the scrub solutions would decrease the overall waste throughput for the calciner system and is therefore undesirable. Solids buildup in the scrub solution is proportional to the fines generation rate and the efficiency of the primary cyclone. No quantitative measures are available to determine the solids buildup rate. Visual observations however suggest that the solids buildup rate in the scrub solution for the high-temperature tests exceeded those for both the baseline and sugar-additive flowsheets.

Chemical analysis of the scrub and condensate solutions from the sugar-additive tests indicate that there is an interaction between the unburned sugar and the nitric acid. Higher levels of volatile and semivolatile organics were found in the combined scrub and condensate solutions from the sugar additive tests than those found during a test of the baseline flowsheet in the 15-cm Calciner Pilot Plant. The results of the organic analysis are given in Tables 16 and 17.

Table 16. Volatile organic analysis.

CAS No.	Compound	15-cm Calciner Tests		Sugar-Additive Tests	
		Condensate Conc. (ug/L)	Scrub Conc. (ug/L)	Sample 1 Conc. (ug/L)	Sample 2 Conc. (ug/L)
64	Methylene Chloride	--	--	240	510
67-64-1	Acetone	180	221	4200	5700
91-20-3	Naphthalene	--	--	220	230
97	4-Methyl-2-Pentanone	--	--	--	180
74-87-3	Chloromethane	117	40	--	--
74-83-9	Bromomethane	70	27	--	--
26	Benzene	50	50	--	--
10061-02-6	trans-1,3-Dichloropropene	218	--	--	--

Table 17. Semi-volatile organic analysis.

CAS No.	Compound	15-cm Calciner		Sugar-Additive Test	
		Condensate (ug/L)	Scrub (ug/L)	Sample 1 (ug/L)	Sample 2 (ug/L)
100-02-7	4-Nitrophenol	458.4	357	--	--
110-86-1	Pyridine	--	932.2	1100	1500
117-81-7	Bis(2-ethylhexyl)phthalate	589.2	4455	1300	1600
121-14-2	(MS) 2,4-Dinitrotoluene	76.8	--	--	--
126-73-8	Tri-n-butyl phosphate	42	203.8	--	--
205-99-2	Benzo(b) fluoranthene	1.2	--	--	--
206-44-0	(CCC) Fluoranthene	2.8	14.2	--	--
207-08-9	Benzo(k) fluoranthene	1.8	--	--	--
51-28-5	2,4-Dinitrophenol	--	--	7200	8400
534-52-1	4,6-Dinitro-2-methylphenol	709.8	482.8	1700	2200
606-20-2	2,6-Dinitrotoluene	--	--	910	1100
65-85-0	Benzoic Acid	--	--	5200	5600
88-74-4	2-Nitroaniline	--	--	--	200
88-75-5	(CCC)2-Nitrophenol	87.8	19.4	--	--
91-20-3	Naphthalene	--	--	170	--
91-57-6	2-Methylnaphthalene	--	6.4	160	--
98-95-3	Nitrobenzene	3551.4	869.4	2100	2500

CONCLUSIONS

The major performance objectives that must be satisfied for successful implementation of a calcination flowsheet in NWCF are listed in the Introduction. Each of the acceptance criteria discussed in the previous sections provided a quantitative measure by which these objectives were assessed. The baseline flowsheet test provided a reference for comparison of these objectives in the 10-cm Calciner Pilot Plant system.

The high-temperature and sugar-additive flowsheet tests successfully demonstrated that these flowsheets minimize the amount of chemical additives required to process SBW. Approximately twice the net volume of simulant was processed with both the high-temperature and sugar-additive flowsheets compared to the baseline flowsheet. Lowering the amount of required additives reduces the calcine storage requirements. The overall calcine bulk density for either flowsheet will not adversely impact the calcine storage requirements.

The tests, with the exception of SBW-SA-2, demonstrated that stable fluidized-bed calcination is achievable with any of the flowsheets. Agglomeration however, may still be of some concern for both alternative flowsheets. The MMPDs for the calcine generated throughout the tests were within the NWCF acceptance range (0.3 to 0.5 mm), but had not stabilized by the end of the tests. The larger fraction of particles greater than 1.7 mm in diameter in the final bed for Test SBW-SA-1 may indicate the onset of agglomeration during this test. The data on agglomeration are inconclusive since the tests had only achieved approximately 90% bed turnover when they were terminated. Additional longer term testing is required to verify if agglomeration is a concern with these flowsheets. Adjustments to the flowsheet chemistry may also be required to alleviate agglomeration concerns.

Evaluation of the transportability and retrievability of the calcines generated during these flowsheet tests is incomplete since retrieval tests were not performed. The ARI tests show that only the calcine from SBW-HT-1 was within the designated acceptance range for ARIs of 40 to 80%. The baseline calcine was below the range at 30% and may experience size reduction due to fracturing during transport. The calcines from SBW-HT-2 and SBW-SA-1 were above the acceptable range at 86% and 97% respectively. This higher attrition resistance may cause an increase in erosion in the cyclone and transport systems. The baseline calcine outperformed the other calcines in the hydration tests. The calcine from SBW-SA-1 was highly hygroscopic and would be unacceptable for storage and transport unless measures were taken to control the humidity in those systems. The calcines from SBW-HT-1 and SBW-HT-2 were slightly hygroscopic. The exposure of these calcines to high relative humidity should be minimized to ensure their retrievability. As discussed previously, the storage requirements for either flowsheet will be significantly less than that for the baseline flowsheet due to the reduction in chemical additives. Safety concerns regarding the potential for fire or explosion hazards arising from the carbon content in the calcine from the sugar-additive tests were eliminated by rigorous testing.¹⁰ Based on the information available the baseline and high-temperature calcines have acceptable transport and storage properties.

Solubility tests indicate that the calcines from each of the flowsheets have acceptable dissolution characteristics in nitric acid. The lower levels of *alpha*-alumina in the sugar-additive and high-temperature calcines should reduce the quantities of undissolved solids that will be encountered in subsequent treatment processes requiring dissolution of the calcine. Independent testing of the calcines as feed stock for the proposed separations process is required to thoroughly evaluate each flowsheet's performance.

Several serious operational difficulties were experienced with the 10-cm Calciner Pilot Plant off-gas treatment system. Future tests are required to determine if these difficulties arose from system limitations in the 10-cm Calciner Pilot Plant or from the flowsheet chemistries. The large quantity of fines generated during the high-temperature tests are believed to be responsible for plugging the primary cyclone. Fines buildup in the scrub recirculation vessel was high during the high-temperature tests but may be directly

related to the poor performance of the primary cyclone. Problems were experienced with increased pressure drop across the system HEPA filter during the sugar-additive tests. Operational difficulties with the system blower or plugging due to smoke or submicron particles may have caused this increase. Definitive conclusions about the compatibility of the proposed flowsheets with the current off-gas treatment system are not possible based on the information currently available since the 10-cm Calciner Pilot Plant varies significantly from the full-scale system.

Chloride and fluoride volatility for both flowsheets appear acceptable. However, buildup in the scrub system was very high during the high-temperature flowsheet tests. This was likely due to the cyclone plugging problem. As stated previously, more testing should be performed to completely evaluate this criterion.

Scrub solution interaction posed no operational difficulties with either the high-temperature or the sugar-additive flowsheet tests. Deep recycle requirements for the scrub solution cannot be evaluated until the questions regarding excessive fines accumulation in the scrub have been resolved. Successful control of scrub foaming was demonstrated in both sugar-additive flowsheet tests.

RECOMMENDATIONS

Based on the scoping test results presented in this report, both the high-temperature and the sugar-additive options are technically viable. However, programmatic funding limitations, that apply to both development and design efforts, preclude pursuing work on both alternative flowsheets. A decision analysis meeting was conducted to select between the high-temperature and sugar-additive flowsheet options.¹¹ The high-temperature flowsheet was selected for continued development. The major drivers for the selection were safety analysis concerns, compliance with air permits and RCRA, and operational impacts.

In light of the decision to focus development efforts on the high-temperature flowsheet, the following research and development efforts are recommended:

- Determine the optimum flowsheet temperature and chemistry in the 10-cm Calciner Pilot Plant.
 - Complete temperature optimization tests.
 - Determine appropriate AAR.
 - Evaluate the need for boric acid additions.
- Investigate fines generation control.
 - Optimize feed droplet size versus attrition via NAR control.
 - Resolve cyclone plugging concerns and reevaluate P/F ratio.
- Complete retrievability tests.
- Continue calcine hygroscopicity tests.
 - Determine and test conditions that adequately encompass expected conditions in the transport and storage systems.
- Continue corrosion tests within the 10-cm Calciner Pilot Plant vessel and independent of the pilot plant.
- Provide thorough characterization of off-gas stream and scrub/condensate solutions.
 - Emphasize air permitting, safety analysis, and return of solutions to the tank farm (deep recycle).
- Continue evaluation of calcine performance in proposed separation processes.
- Demonstrate and optimize flowsheet on larger scale (15-cm Calciner, 30-cm Calciner or NWCF trial run).

REFERENCES

1. D. R. Lide (ed.), *CRC Handbook of Chemistry and Physics*, 77th Edition, Boca Raton, FL: CRC Press, Inc., 1996.
2. J. A. Nenni letter to D. V. Croson, JAN-05-95, "Status of Alternative Calcination Development Laboratory Tests," December 21, 1995.
3. D. W. Pearce, *Quarterly Progress Report*, HW-60584, April 1958.
4. J. C. Petrie letter to E. J. Bailey, Petr-13-65A, "Report on Run 12 - Twelve-Inch-Diameter Calciner," December 30, 1965.
5. B. J. Newby, *Calcination of Sodium-Bearing Waste Using Non-Radioactive Additives*, ENICO-1043, October 1980.
6. B. J. Newby, *Calcination of Sodium-Bearing Waste Using Aluminum Nitrate*, WINCO-1026, 1985.
7. B. J. Newby, T. D. Thomson, and B. H. O'Brien, *Calcination of Fluorinel-Sodium Feed Blends Using Sugar as a Feed Additive*, WINCO-1130, June 1993.
8. J. Pao and J. A. McCray letter to D. V. Croson, JHP-06-96/JAM-08-96, "Laboratory-Scale Sugar-Additive and High-Temperature Denitration Calcination Test Results," September 30, 1996.
9. R. D. Boardman letter to D. V. Croson, RDB-21-96, "Draft Report on Alternative Calcination Development Research and Development Activities," November 13, 1996.
10. D. W. Marshall letter to D. V. Croson, DWM-03-96, "Report on the Sugar-Nitrate Interaction and Sugar-Calcine Reactivity Study," September 11, 1996.
11. J. A. Nonte and L. C. Seward letter to Distribution, JAN-1-96/LCS-24-96, "Summary of the Decision Analysis Meeting, Alternative Selection between Elevated Temperature and Sugar Added," November 25, 1996.

Appendix A. Hygroscopicity Test Apparatus

Figure A.1 Hygroscopicity test apparatus.

Appendix B. Component Balances

Test SBW-BL-1 Overall and Component Balances

	OVERALL	Al	B	Cd	Ca	Cl	Cr	F	H	Fe	Mn	NO ₃	PO ₄	K	Na	O
MASS INPUT FROM:	(kg)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)
Starting Bed	3.91E+00	1.33E+03	9.77E+00	0.00E+00	7.07E+01	3.12E-01	1.77E-01	0.00E+00	0.00E+00	6.80E+00	8.87E-02	3.98E+02	3.44E+00	6.33E-01	2.62E+02	1.27E+03
Feed	3.01E+01	3.48E+03	5.67E+01	5.02E+00	6.88E+01	3.21E+01	3.37E+00	2.17E+01	2.61E+01	2.33E+01	1.21E+01	2.54E+04	2.49E+01	1.54E+02	7.48E+02	0.00E+00
Initial Scrub	2.27E+00	8.64E+00	4.25E-01	2.52E-02	3.89E-01	0.00E+00	1.33E-01	2.37E-01	3.49E+01	7.15E-01	1.66E-02	2.22E+03	4.37E-02	1.65E-01	1.55E+00	0.00E+00
Additional Scrub	3.78E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	6.05E+01	0.00E+00	0.00E+00	3.72E+03	0.00E+00	0.00E+00	0.00E+00	0.00E+00
MASS OUTPUT TO:																
COT O P + F	8.08E-01	2.76E+02	2.02E+00	0.00E+00	1.46E+01	6.46E-02	3.66E-02	0.00E+00	0.00E+00	1.41E+00	1.83E-02	8.24E+01	7.11E-01	1.31E-01	5.43E+01	2.63E+02
Product	4.60E+00	1.52E+03	2.43E+01	1.70E+00	5.86E+01	3.94E+00	1.56E+00	6.03E+00	0.00E+00	1.08E+01	3.39E+00	6.47E+02	1.09E+01	3.51E+01	3.42E+02	1.47E+03
Fines	3.62E+00	1.18E+03	1.87E+01	1.92E+00	4.34E+01	6.85E+00	1.48E+00	1.08E+01	0.00E+00	1.01E+01	3.75E+00	5.35E+02	1.03E+01	2.91E+01	2.50E+02	1.12E+03
Final Bed	2.79E+00	8.57E+02	1.39E+01	1.36E+00	2.39E+01	2.85E+00	1.03E+00	3.44E+00	0.00E+00	7.54E+00	2.93E+00	4.45E+02	8.99E+00	9.97E+00	2.23E+02	8.27E+02
Acid Scrub	8.43E+00	2.91E+02	5.75E+00	5.39E-01	1.14E+01	1.13E+01	8.31E-01	1.17E+01	1.12E+02	4.16E+00	1.04E+00	7.86E+03	2.21E+00	1.64E+01	8.93E+01	0.00E+00
Condensate	8.93E+00	4.67E+01	9.12E-01	8.48E-02	1.64E+00	4.05E+00	1.19E-01	2.49E+00	1.48E+02	5.20E-01	1.40E-01	8.71E+03	2.62E-01	2.22E+00	1.21E+01	0.00E+00
INPUT - OUTPUT	-1.09E+01	-6.58E+02	-1.14E+00	5.62E-01	1.37E+01	-3.33E+00	1.37E+00	1.25E+01	1.38E+02	3.68E+00	-9.25E-01	-1.34E+04	5.01E+00	-6.17E+01	-4.09E+01	2.41E+03
% OF INPUT FROM:																
Starting Bed	9.8	27.6	14.6	0.0	50.5	1.0	4.8	0.0	0.0	22.0	0.7	1.3	12.1	0.4	25.9	100.0
Feed	75.1	72.2	84.8	99.5	49.2	99.0	91.6	98.9	21.5	75.7	99.1	80.0	87.7	99.5	73.9	0.0
Initial Scrub	5.7	0.2	0.6	0.5	0.3	0.0	3.6	1.1	28.7	2.3	0.1	7.0	0.2	0.1	0.2	0.0
Additional Scrub	9.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	49.8	0.0	0.0	11.7	0.0	0.0	0.0	0.0
% OF INPUT TO:																
COT O P + F	2.0	5.7	3.0	0.0	10.5	0.2	1.0	0.0	0.0	4.6	0.2	0.3	2.5	0.1	5.4	20.7
Product	11.5	31.5	36.4	33.7	41.9	12.1	42.3	27.5	0.0	35.1	27.8	2.0	38.3	22.7	33.8	115.3
Fines	9.0	24.4	28.0	38.1	31.0	21.1	40.2	49.1	0.0	32.7	30.8	1.7	36.4	18.8	24.7	88.3
Final Bed	7.0	17.8	20.9	27.0	17.0	8.8	27.9	15.6	0.0	24.4	24.0	1.4	31.7	6.5	22.1	65.0
Acid Scrub	21.0	6.0	8.6	10.7	8.2	35.0	22.6	53.4	91.8	13.5	8.6	24.8	7.8	10.6	8.8	0.0
Condensate	22.3	1.0	1.4	1.7	1.2	12.5	3.2	11.3	121.8	1.7	1.2	27.5	0.9	1.4	1.2	0.0
Lost	27.1	13.6	1.7	-11.1	-9.8	10.3	-37.3	-57.0	-113.6	-11.9	7.6	42.3	-17.7	39.9	4.0	-189.3

Test SBW-HT-1 Overall and Component Balances

	OVERALL	Al	B	Cd	Ca	Cl	Cr	F	H	Fe	Mn	NO ₃	PO ₄	K	Na	O
MASS INPUT FROM:	(kg)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)
Starting Bed	3.91E+00	1.31E+03	9.77E+00	0.00E+00	7.54E+01	3.12E-01	1.87E-01	0.00E+00	0.00E+00	7.27E+00	7.93E-02	4.05E+02	3.12E+00	7.21E-01	2.66E+02	1.26E+03
Feed	3.19E+01	2.51E+03	9.72E+00	1.30E+01	1.95E+02	7.93E+01	8.99E+00	6.60E+01	7.08E+01	6.12E+01	3.24E+01	2.62E+04	6.16E+01	3.87E+02	1.96E+03	0.00E+00
Initial Scrub	1.35E+00	4.41E+00	8.03E-02	7.76E-03	1.49E-01	0.00E+00	1.53E-02	0.00E+00	2.09E+01	1.18E-01	1.56E-02	1.32E+03	4.15E-02	1.42E-01	1.24E+00	0.00E+00
Additional Scrub	1.19E+01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.91E+02	0.00E+00	0.00E+00	1.17E+04	0.00E+00	0.00E+00	0.00E+00	0.00E+00
MASS OUTPUT TO:																
COT 0 P + F	5.90E-01	1.98E+02	1.48E+00	0.00E+00	1.14E+01	4.72E-02	2.82E-02	0.00E+00	0.00E+00	1.10E+00	1.20E-02	6.12E+01	4.72E-01	1.09E-01	4.02E+01	1.91E+02
Product	2.16E+00	6.37E+02	2.60E+00	2.18E+00	4.19E+01	1.25E+01	1.45E+00	4.89E+00	0.00E+00	9.27E+00	3.96E+00	4.91E+01	1.12E+01	4.47E+01	3.52E+02	7.14E+02
Fines	6.30E-01	1.58E+02	7.15E-01	4.66E-01	1.35E+01	3.85E+00	4.02E-01	3.59E+00	0.00E+00	3.42E+00	1.31E+00	7.88E+01	2.11E+00	1.29E+01	8.05E+01	1.68E+02
Final Bed	2.79E+00	7.29E+02	2.82E+00	3.74E+00	5.08E+01	1.56E+01	2.09E+00	7.29E+00	0.00E+00	1.64E+01	7.79E+00	1.15E+02	2.08E+01	5.69E+01	5.18E+02	8.53E+02
Acid Scrub	1.00E+01	7.31E+02	5.43E+00	2.56E+00	5.62E+01	2.77E+01	2.66E+00	2.46E+01	6.68E+01	1.77E+01	7.36E+00	8.47E+03	1.28E+01	1.31E+02	4.74E+02	0.00E+00
Condensate	3.44E+00	3.76E+01	3.81E-01	1.72E-01	2.97E+00	4.76E+00	1.74E-01	2.15E+00	4.62E+01	9.63E-01	3.85E-01	3.31E+03	8.58E-01	8.86E+00	2.00E+01	0.00E+00
INPUT - OUTPUT	-2.94E+01	-1.34E+03	-6.14E+00	-3.89E+00	-9.34E+01	-1.51E+01	-2.38E+00	-2.35E+01	-1.69E+02	-1.97E+01	-1.17E+01	-2.76E+04	-1.65E+01	-1.33E+02	-7.39E+02	6.63E+02
% OF INPUT FROM:																
Starting Bed	8.0	34.3	49.9	0.0	27.9	0.4	2.0	0.0	0.0	10.6	0.2	1.0	4.8	0.2	12.0	100.0
Feed	65.0	65.6	49.7	99.9	72.0	99.6	97.8	100.0	25.1	89.2	99.7	66.1	95.1	99.8	88.0	0.0
Initial Scrub	2.8	0.1	0.4	0.1	0.1	0.0	0.2	0.0	7.4	0.2	0.0	3.3	0.1	0.0	0.1	0.0
Additional Scrub	24.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	67.5	0.0	0.0	29.6	0.0	0.0	0.0	0.0
% OF INPUT TO:																
COT 0 P + F	1.2	5.2	7.5	0.0	4.2	0.1	0.3	0.0	0.0	1.6	0.0	0.2	0.7	0.0	1.8	15.1
Product	4.4	16.6	13.3	16.8	15.5	15.7	15.8	7.4	0.0	13.5	12.2	0.1	17.3	11.5	15.8	56.6
Fines	1.3	4.1	3.7	3.6	5.0	4.8	4.4	5.4	0.0	5.0	4.0	0.2	3.3	3.3	3.6	13.3
Final Bed	5.7	19.0	14.4	28.8	18.8	19.6	22.8	11.0	0.0	23.9	24.0	0.3	32.1	14.7	23.3	67.6
Acid Scrub	20.5	19.1	27.8	19.7	20.8	34.8	29.0	37.3	23.6	25.8	22.7	21.4	19.8	33.8	21.3	0.0
Condensate	7.0	1.0	1.9	1.3	1.1	6.0	1.9	3.3	16.4	1.4	1.2	8.4	1.3	2.3	0.9	0.0
Lost	59.9	35.0	31.4	29.9	34.6	19.0	25.9	35.6	60.0	28.8	35.9	69.5	25.5	34.3	33.2	-52.6

Test SBW-HT-2 Overall and Component Balances

	OVERALL	Al	B	Cd	Ca	Cl	Cr	F	H	Fe	Mn	NO ₃	PO ₄	K	Na	O
MASS INPUT FROM:	(kg)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)
Starting Bed	3.74E+00	1.29E+03	9.36E+00	2.86E-02	7.60E+01	2.62E-01	1.74E-01	0.00E+00	0.00E+00	5.95E+00	9.84E-02	3.85E+02	4.38E+00	4.25E-01	2.23E+02	1.23E+03
Feed	4.03E+01	3.71E+03	9.66E+00	1.12E+01	1.70E+02	6.29E+01	7.79E+00	5.26E+01	5.48E+01	5.91E+01	2.85E+01	3.38E+04	6.94E+01	3.52E+02	1.93E+03	0.00E+00
Initial Scrub	2.01E+00	1.63E+01	6.93E-02	1.68E-02	5.89E-01	0.00E+00	2.63E-02	0.00E+00	2.91E+01	2.31E-01	6.93E-02	1.96E+03	8.64E-02	3.89E-01	3.53E+00	0.00E+00
Additional Scrub	8.70E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.39E+02	0.00E+00	0.00E+00	8.56E+03	0.00E+00	0.00E+00	0.00E+00	0.00E+00
MASS OUTPUT TO:																
COT O P + F	7.40E-01	2.56E+02	1.85E+00	5.65E-03	1.50E+01	5.18E-02	3.43E-02	0.00E+00	0.00E+00	1.18E+00	1.95E-02	7.61E+01	8.66E-01	8.41E-02	4.41E+01	2.44E+02
Product	5.41E+00	1.69E+03	4.94E+00	3.77E+00	1.11E+02	2.64E+01	3.04E+00	1.28E+01	0.00E+00	2.01E+01	9.05E+00	2.66E+02	1.83E+01	8.64E+01	6.74E+02	1.78E+03
Fines	4.44E-01	1.11E+02	3.08E-01	3.31E-01	7.87E+00	3.03E+00	2.89E-01	2.85E+00	0.00E+00	2.18E+00	7.41E-01	5.75E+01	1.59E+00	8.94E+00	4.56E+01	1.12E+02
Final Bed	3.49E+00	1.03E+03	2.68E+00	3.88E+00	6.70E+01	2.23E+01	2.07E+00	7.93E+00	0.00E+00	1.53E+01	8.49E+00	1.47E+02	1.52E+01	7.41E+01	5.45E+02	1.14E+03
Acid Scrub	1.29E+01	1.13E+03	4.69E+00	2.83E+00	4.61E+01	2.52E+01	3.15E+00	2.73E+01	1.54E+01	1.79E+01	6.70E+00	1.09E+04	1.41E+01	1.32E+02	6.05E+02	0.00E+00
Condensate	2.83E+00	3.77E+01	2.06E-01	9.96E-02	1.83E+00	3.02E+00	1.42E-01	1.59E+00	3.92E+01	6.42E-01	2.10E-01	2.73E+03	4.42E-01	5.12E+00	1.66E+01	0.00E+00
INPUT - OUTPUT	-2.89E+01	-7.67E+02	-4.42E+00	-3.20E-01	2.07E+00	1.68E+01	7.34E-01	-5.10E-02	-1.68E+02	-8.03E+00	-3.46E+00	-3.05E+04	-2.33E+01	-4.65E+01	-2.22E+02	2.04E+03
% OF INPUT FROM:																
Starting Bed	6.8	25.8	49.0	0.3	30.8	0.4	2.2	0.0	0.0	9.1	0.3	0.9	5.9	0.1	10.4	100.0
Feed	73.6	73.9	50.6	99.6	68.9	99.6	97.5	100.0	24.6	90.5	99.4	75.6	94.0	99.8	89.5	0.0
Initial Scrub	3.7	0.3	0.4	0.1	0.2	0.0	0.3	0.0	13.0	0.4	0.2	4.4	0.1	0.1	0.2	0.0
Additional Scrub	15.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	62.4	0.0	0.0	19.1	0.0	0.0	0.0	0.0
% OF INPUT TO:																
COT O P + F	1.4	5.1	9.7	0.1	6.1	0.1	0.4	0.0	0.0	1.8	0.1	0.2	1.2	0.0	2.0	19.8
Product	9.9	33.7	25.9	33.6	44.9	41.7	38.0	24.4	0.0	30.8	31.6	0.6	24.8	24.5	31.3	144.2
Fines	0.8	2.2	1.6	2.9	3.2	4.8	3.6	5.4	0.0	3.3	2.6	0.1	2.2	2.5	2.1	9.1
Final Bed	6.4	20.5	14.1	34.5	27.2	35.3	25.9	15.1	0.0	23.4	29.6	0.3	20.6	21.0	25.3	92.1
Acid Scrub	23.6	22.5	24.6	25.2	18.7	39.9	39.4	52.0	6.9	27.4	23.4	24.4	19.1	37.4	28.1	0.0
Condensate	5.2	0.8	1.1	0.9	0.7	4.8	1.8	3.0	17.6	1.0	0.7	6.1	0.6	1.5	0.8	0.0
Lost	52.8	15.3	23.1	2.9	-0.8	-26.6	-9.2	0.1	75.5	12.3	12.1	68.3	31.6	13.2	10.3	-165.2

Test SBW-SA-1 Overall and Component Balances

	OVERALL	Al	B	Cd	Ca	C	Cl	Cr	F	H	Fe	Mn	NO ₃	PO ₄	K	Na	O
MASS INPUT FROM:	(kg)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)
Starting Bed	3.71E+00	1.44E+03	9.27E+00	9.46E-03	1.10E+02	5.08E+01	2.78E-01	1.72E-01	0.00E+00	0.00E+00	6.41E+00	8.57E-02	1.85E+01	3.52E+00	5.67E-01	2.41E+02	1.56E+03
Feed	3.07E+01	1.84E+03	7.66E+00	9.86E+00	1.37E+02	5.37E+03	6.21E+01	6.61E+00	4.13E+01	4.82E+01	4.45E+01	2.24E+01	2.13E+04	3.04E+01	2.33E+02	1.37E+03	0.00E+00
Kerosene	9.33E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	9.33E+03	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Initial Scrub	2.90E+00	1.19E+01	2.48E-02	7.15E-03	1.57E-01	0.00E+00	0.00E+00	2.37E-02	0.00E+00	4.55E+01	1.41E-01	2.78E+00	2.83E+03	0.00E+00	1.65E-01	1.32E+00	0.00E+00
Additional Scrub	1.22E+01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.95E+02	0.00E+00	0.00E+00	1.20E+04	0.00E+00	0.00E+00	0.00E+00	0.00E+00
MASS OUTPUT TO:																	
COT O P + F	4.10E-02	1.59E+01	1.03E-01	1.05E-04	1.22E+00	5.62E-01	3.08E-03	1.91E-03	0.00E+00	0.00E+00	7.09E-02	9.47E-04	2.05E-01	3.90E-02	6.27E-03	2.67E+00	1.73E+01
Product	3.90E+00	1.29E+03	5.73E+00	2.78E+00	1.01E+02	2.02E+01	1.93E+01	1.79E+00	1.43E+01	0.00E+00	1.27E+01	4.98E+00	2.09E+02	1.41E+01	8.18E+01	4.59E+02	1.36E+03
Fines	1.58E+00	4.11E+02	2.52E+00	8.19E-01	2.37E+01	2.23E+01	2.15E+01	1.10E+00	7.62E+00	0.00E+00	8.01E+00	4.32E+00	1.58E+02	6.93E+00	3.67E+01	3.13E+02	4.78E+02
Final Bed	2.92E+00	8.58E+02	3.57E+00	3.50E+00	7.00E+01	3.08E+00	2.11E+01	1.98E+00	3.65E+00	0.00E+00	1.40E+01	6.42E+00	2.16E+02	1.87E+01	9.01E+01	4.71E+02	9.53E+02
Acid Scrub	1.06E+01	3.58E+02	2.00E+00	9.78E-01	1.41E+01	1.05E+03	2.20E+00	1.07E+00	6.32E+00	8.07E+01	7.93E+00	3.35E+00	8.89E+03	4.38E+00	3.88E+01	1.45E+02	0.00E+00
Condensate	3.39E+00	1.91E+01	1.31E-01	1.20E-01	1.03E+00	1.98E+02	3.15E+00	8.87E-02	0.00E+00	4.41E+01	5.43E-01	1.62E-01	3.11E+03	3.71E-01	3.01E+00	1.33E+01	0.00E+00
INPUT - OUTPUT	-3.64E+01	-3.36E+02	-2.90E+00	-1.67E+00	-3.72E+01	-1.34E+04	4.89E+00	-7.68E-01	-9.45E+00	-1.64E+02	-7.76E+00	-6.01E+00	-2.36E+04	1.05E+01	1.62E+01	-2.12E+02	1.25E+03
% OF INPUT FROM:																	
Starting Bed	6.3	43.7	54.7	0.1	44.6	0.3	0.4	2.5	0.0	0.0	12.6	0.3	0.1	10.4	0.2	14.9	100.0
Feed	52.2	55.9	45.2	99.8	55.4	36.4	99.6	97.1	100.0	16.7	87.2	88.7	58.9	89.6	99.7	85.0	0.0
Kerosene	15.9	0.0	0.0	0.0	0.0	63.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Initial Scrub	4.9	0.4	0.1	0.1	0.1	0.0	0.0	0.3	0.0	15.7	0.3	11.0	7.8	0.0	0.1	0.1	0.0
Additional Scrub	20.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	67.6	0.0	0.0	33.2	0.0	0.0	0.0	0.0
% OF INPUT TO:																	
COT O P + F	0.1	0.5	0.6	0.0	0.5	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.2	1.1
Product	6.6	39.3	33.8	28.2	40.6	0.1	31.0	26.3	34.5	0.0	24.9	19.7	0.6	41.5	34.9	28.4	87.0
Fines	2.7	12.5	14.9	8.3	9.6	0.2	34.4	16.1	18.5	0.0	15.7	17.1	0.4	20.4	15.7	19.4	30.6
Final Bed	5.0	26.1	21.1	35.5	28.2	0.0	33.9	29.1	8.8	0.0	27.4	25.4	0.6	55.0	38.5	29.2	61.0
Acid Scrub	18.1	10.9	11.8	9.9	5.7	7.1	3.5	15.8	15.3	27.9	15.5	13.3	24.6	12.9	16.6	9.0	0.0
Condensate	5.8	0.6	0.8	1.2	0.4	1.3	5.0	1.3	0.0	15.3	1.1	0.6	8.6	1.1	1.3	0.8	0.0
Lost	61.8	10.2	17.1	17.0	15.0	91.2	-7.8	11.3	22.9	56.8	15.2	23.8	65.2	-31.0	-6.9	13.1	-79.7