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CALCINATION OF FLUORINEL-SODIUM WASTE BLENDS USING SUGAR AS A FEED ADDITIVE (FORMERLY WINCO-11879)

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Abstract

Methods were studied for using sugar as a feed additive for converting the sodium-bearing wastes stored at the Idaho Chemical Processing Plant into granular, free flowing solids by fluidized-bed calcination at 500°C. All methods studied blended sodium-bearing wastes with Fluorinel wastes but differed in the types of sugar (sucrose or dextrose) that were added to the blend. The most promising sugar additive was determined to be sucrose, since it is converted more completely to inorganic carbon than is dextrose. The effect of the feed aluminum-to-alkali metal mole ratio on calcination of these blends with sugar was also investigated. Increasing the aluminum-to-alkali metal ratio from 0.6 to 1.0 decreased the calcine product-to-fines ratio from 3.0 to 1.0 and the attrition index from 80 to 15%. Further increasing the ratio to 1.25 had no effect.

Summary

One of the major wastes being generated and stored at the Idaho Chemical Processing Plant (ICPP) is sodium-bearing (Na) waste. The waste is difficult to calcine; the sodium nitrate present causes fluidized-bed agglomeration during calcination, and the chloride present can cause excessive corrosion (>51 micrometers/mo or >2 mils/mo) of off-gas scrubbing equipment when volatilized from the calciner vessel and collected by the off-gas scrubbing equipment.

Tests were carried out in the enclosed 10-cm diameter Calciner Pilot-Plant attempting to calcine Fluorinel - Na waste blends, having up to 7.5 mole % sodium plus potassium in the calcined solids, using sugar as a feed additive. Studies in the enclosed 10-cm diameter calciner indicated that the presence of sugar (sucrose or dextrose) in simulated Fluorinel - Na waste blends containing alkali metals (sodium plus potassium) effectively destroys nitrates in the blend during calcination. The studies also showed that, because of the destruction of nitrates, the presence of sugar: a) allows alkali metals present to form compounds stable at calcination temperatures, b) allows the size of the product to be readily controlled using the feed nozzle air-to-feed ratio (NAR), and c) results in high chloride retention in calcined solids.

The tests in this report tried to determine a) which sugar (sucrose or dextrose) was the most effective for calcining Fluorinel - Na waste blends, and b) the effect of the feed aluminum-to-alkali metal mole ratio on the calcination of these blends. The sucrose and dextrose added to the blends were equally effective at destroying nitrates. An average of 45% of the nitrates in the feed for the runs was destroyed during the sugar reactions. Sucrose was determined to be the most promising sugar additive since it was converted more completely to inorganic carbon than was dextrose. When sucrose was used as an additive the wt% of total carbon fed to the calciner that was found in calciner streams as organic (unburned and/or not converted to inorganic carbon) carbon averaged 3 wt%; whereas, when dextrose was used as an additive the average was 34 wt% organic carbon. If dextrose were used in the in the NWCF, the

larger amount of organic carbon would probably plug filters and silica gel beds.

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

The runs also investigated feed aluminum-to-alkali metal (Al/Na+K) mole ratios of 0.6, 1.0 and 1.25. Increasing the feed Al/Na+K mole ratio from 0.6 to 1.0 decreased the calcine product-to-fines ratio from 3.0 to 1.0, the product production rate from 250 to ~175 g/h, and the attrition index from 80 to ~15%. Whereas, increasing the feed Al/Na+K mole ratio from 1.0 to 1.25 had little or no effect on the calcine product-to-fines ratio, product production rate, and attrition indices. Increasing the feed Al/Na+K mole ration from 0.6 to 1.25 had little or no effect on the behavior of chloride, fluoride, carbon, or cadmium during calcination.

CONTENTS

	PAGE
ABSTRACT	i
SUMMARY	ii
1. INTRODUCTION	1
2. EXPERIMENTAL EQUIPMENT AND PROCEDURES	5
3. RESULTS	12
3.1 Calciner Operations	12
3.2 Characteristics of Fluidized-Bed and Solids Produced	13
3.3 Behavior of Volatiles	20
3.4 Miscellaneous Calcination Chemistry	24
4. CONCLUSIONS AND RECOMMENDATIONS	27
4.1 Conclusions	27
4.2 Recommendations	28
5. LITERATURE CITED	29
APPENDIX A	A-1
APPENDIX B	B-1
APPENDIX C	C-1
APPENDIX D	D-1

FIGURES

1. Enclosed 10-cm Diameter Calciner	6
2. Variation of MMPD with Waste NAR During Runs FlNaS-1 and -2	14
3. Variation of MMPD with Waste NAR During Runs FlNaS-3 and -4	15
4. Variation of MMPD with Waste NAR During Runs FlNaS-5 and -6	16

TABLES

1. Parameters Adjusted During Enclosed 10-cm Calciner Runs Using Sugar 2

2. Compositions of Fluorinel and Sodium Wastes Used for Test Blends 3

3. Feed Nitrate Destruction During Sugar Treatment 8

4. Compositions of Wastes And Blends Prior to Calcium Nitrate and Sugar Treatment 9

5. Compositions of Blends After Calcium Nitrate and Sugar Treatment 11

6. Average Characteristics of Fluidized-Bed and Solids Produces During Calcination of Fluorinel-Na Waste-Sugar Blends 17

7. Pneumatic Retrieval Rates Using a Vibrator-Assisted Vacuum Nozzle 20

8. Chloride Behavior in Calciner Off-Gas During Runs FlNas-1, -2, -3, -4, -5, and -6 22

9. Carbon Behavior During Runs FlNaS-1, -2, -3, -4, -5, and -6 . . 23

10. Carbon Monoxide in Off-Gas During 10cm Calciner Run FlNaS-4 . . 25

A-1 Operating Conditions for Runs FlNaS-1 and -2 . . . . A-2

A-2 Characteristics of Fluidized-Bed and Solids Produced During Runs FlNaS-1 and -2 . . . . A-3

B-1 Operating Conditions for Runs FlNaS-3 and -4 . . . . B-2

B-2 Characteristics of Fluidized-Bed and Solids Produced During Runs FlNaS-3 and -4 . . . . B-3

C-1 Operating Conditions for Runs FlNaS-5 and -6 . . . . C-2

C-2 Operating Conditions for Runs FlNaS-5 and -6 (continued) . . . C-3

C-3 Characteristics of Fluidized-Bed and Solids Produced During Runs FlNaS-5 and -6 . . . . C-4

C-4 Characteristics of Fluidized-Bed and Solids Produced During Runs FlNaS-5 and -6 (continued) C-5

D-1 20X Magnification Photographs of Final Bed Calcine Particles D-2

1. INTRODUCTION

Sodium-bearing (Na) waste now occupies six of the ten 300,000 gallon storage tanks in the Idaho Chemical Processing Plant (ICPP) tank farm. Though effective for disposing of the Na wastes, calcination of Na wastes as a zirconium-fluoride-Na waste blend has not kept up with the generation of Na wastes. Therefore, necessary development is underway to modify the Na-Fluorinel waste blend chemistry such that blends containing more Na waste can be calcined.

Enclosed 10-cm diameter Calciner Pilot-Plant studies have shown that the presence of sucrose or dextrose (sugars) in simulated Na-Fluorinel waste blends containing alkali metals (sodium plus potassium) effectively destroys nitrates in the blend during calcination.[1] The destruction of nitrates is desirable since it reduces calcine particle agglomeration to form stable sodium compounds. The same studies have shown that, because of this nitrate destruction, the presence of sugar: a) allows alkali metals present to form compounds stable at calcination temperatures, b) allows the size of the product to be readily controlled using the feed nozzle air to feed ratio (NAR), and c) results in high chloride retention in calcined solids. This may allow the New Waste Calcining Facility (NWCF) to calcine a blend of less than 5:1 volume Fluorinel to Na waste, which would produce calcine containing greater then 5.3 mole% alkali metal (a technical specification limit), without product particle size control problems. The Na waste inventory could then be depleted at a faster rate. Such calcine would also have to have an acceptably high caking temperature to be retrievable from the storage bins.

The greatest disadvantage of using sugar when calcining blends of Na waste and aluminum nitrate in a 10-cm calciner was that incomplete combustion of the sugar produced large amounts of unburned carbon which could plug up silica gel beds and filters.[2] Batch calcination showed that roughly 34.5g of sugar per mole of nitrate in the feed blend would effectively destroy nitrates in Fluorinel-Na waste blends regardless of whether the sugar had 5, 6, or 12 carbons, the sugar was an aldehyde or ketone, or the sugar was a reducing or nonreducing sugar. Two of the cheaper sugars (sucrose and dextrose) were selected for further 10-cm fluidized-bed calciner studies.

A series of six pilot-plant calciner runs were made in the Enclosed 10-cm Calciner Pilot-Plant to test the use of sugar as a feed additive to reduce alkali metal nitrate formation when Fluorinel/Sodium Blends were calcined. The type of sugar (sucrose or dextrose), theoretical alkali metal content of the calcined solids, and aluminum-to-alkali-metal mole ratio were varied during the test series to assess their effects on calcination (Table 1). The compositions of simulated Fluorinel and Sodium Waste used in the tests are given in Table 2.

Table 1. Parameters Adjusted During Enclosed 10-cm Calciner Tests Using Sugar As A Feed Additive with Fluorinel-Sodium Blends.

Run No.	Type of Sugar	Alkali Metal (Sodium plus Potassium) Content of Calcine (Mole %)	Aluminum-to-Alkali Metal Mole Ratio	Fluorinel-to-Sodium Volume Ratio
1	Sucrose	5.3	1.0	4.5
2	Dextrose	5.3	1.0	4.5
3	Sucrose	7.5	1.0	2.8
4	Dextrose	7.5	1.0	2.8
5	Sucrose	7.5	0.60	3.15
6	Sucrose	7.5	1.25	2.63
Note:	All runs used a calcium-to-fluoride mole ratio of 0.7 and 34.5g of sugar adder per mole of feed nitrate.			

Runs FlNaS-1 and -2 were the first in the test series and were designed to evaluate the effectiveness of sugar as a feed additive for calcining blends of Fluorinel and Sodium wastes at an alkali metal content which is calcinable without sugar (5.3 mole %). Both runs used an aluminum-to-alkali metal mole ratio of 1.0, a calcium-to-fluoride mole ratio of 0.7, and produced calcine containing 5.3 mole% alkali metal.

The purpose of Runs FlNaS-3 and -4 was to test the calcinability of feed which produced calcine containing 7.5 mole % alkali metal, an alkali metal content higher than that calcinable for Fluorinel/Na blends without sugar. Being able to calcine and retrieve solids from blends producing calcine containing 7.5 mole% alkali metal rather than containing 5.3

mole% would reduce the Fluorinel-to-Na waste volume ratio in Fluorinel-Na waste blends by about 38 vol %. This would increase the Na waste calcination rate by a corresponding percentage. Both runs used an aluminum-to-alkali metal mole ration of 1.0 and a calcium-to-fluoride mole ratio of 0.7.

The purpose of Runs FlNaS-5 and -6 was to test how calcination characteristics of Fluorinel-Na waste blends containing sucrose are affected by changes of the aluminum-to-alkali metal mole ratio in the feed. The feed for Run FlNaS-5 was a blend of 3.15 vol Fluorinel to 1.0 vol Na waste containing an aluminum-to-alkali metal mole ratio of 0.60. The feed for Run FlNaS-6 was a blend of 2.63 vol Fluorinel to 1.0 vol Na waste containing an aluminum-to-alkali metal mole ratio of 1.25. Both runs used feed that contained a calcium-to-fluoride mole ratio of 0.7 and produced calcine containing 7.5 mole % alkali metal.

One disadvantage in using sugar when calcining blends of Fluorinel and Na wastes is that more calcine fines are produced than desired because the calcine product is soft.[2] Runs FlNaS-1, -2, -3, and -4 calcined blends of Fluorinel and Na wastes with sugar using feeds that

Table 2. Compositions of Fluorinel and Sodium Wastes Used for Sugar Tests

Constituent	Fluorinel Waste	Sodium Waste
H^+ (N̲ᵃ)	1.91	1.6
Al (M̲)	0.233	0.7
Zr (M̲)	0.431	
B (M̲)	0.22	
Na (M̲)		2.1
K (M̲)		0.3
Cd (M̲)	0.14	
NH_4^+ (M̲)	0.052	
F (M̲)	3.03	
NO_3 (M̲)	2.26	6.0
SO_4 (M̲)	0.080	0.07
Cl (μg/ml)		1,775

contained an aluminum-to-alkali metal mole ratio of 1.0. It was thought that feeds with aluminum-to-alkali metal mole ratios of 0.60 or 1.25 might enhance production of alkali metal-alumina compounds during calcination that would reduce fines production. Increasing aluminum nitrate concentrations of a waste feed prior to calcination will most likely increase the hardness of the calcine produced. However, not having to add cold aluminum nitrate to the feed to obtain an aluminum-to-alkali metal mole ratio of 1.0 would: 1) decrease the amount of sugar that needed to be added to the feed (which in turn would cause the feed to produce less unburned sugar when calcined), and 2) increase the calcination volume reduction factor.

2. EXPERIMENTAL EQUIPMENT AND PROCEDURES

A schematic diagram of the enclosed 10-cm-diameter Calciner Pilot-Plant used in the runs described in this report is shown in Figure 1. The feed was sprayed into the calciner under the surface of a fluidized-bed of particles and removed from the calciner as particles (product) and fines.

The calciner's fluidized-bed was heated by in-bed combustion of kerosene. A propane torch was used to raise the temperature inside the calciner above the autoignition temperature of a kerosene-oxygen mixture in the bed (340°C). The calcination temperature was 500°C. The feed nozzle used during every run was a Spraying Systems Co. 40100 liquid, 120 air. The fuel nozzle used for Runs FlNaS-1, -2, -3, -4, and -6 was a Spraying System Co. 2050 liquid, 67-6-20-70° air; whereas, the fuel nozzle used for Run FlNaS-5 was a Spraying Systems Co. 1650 Liquid, 67-6-20-70° air. The size of the calcine particles was controlled by varying the feed nozzle air ratio (NAR).

Off-gas leaving the enclosed 10-cm-diameter Calciner Pilot-Plant passed through (in the order named): a primary cyclone to remove fines, a venturi scrubber (containing nitric acid) for further fines removal, a secondary cyclone, and finally through two water cooled condensers. About 3.0 vol % (4 sLpm) of the total off-gas was pulled through a caustic scrubber (to analytically determine chloride, carbon, cadmium, and fluoride volatility) from a point located between the secondary cyclone and the primary condenser.

If the temperature of the acid solution in the off-gas scrub tank was kept at ~70°C (the off-gas acid scrub solution of the NWCF is kept at ~70°C), the scrub did not foam due to the scrubbing of unburned sugar (as the acid was depleted) within the 8 hour operating period (initial scrub acid concentration was 4.0 M). It is convenient to operate the enclosed 10-cm Calciner Pilot-Plant with the acid scrub tank at ~30°C, but at this temperature 4 M acid scrub foams in less than 4 hours when sugar is used as an additive. If allowed to foam too vigorously for too long, the scrub will solidify. To prevent foaming in Runs FlNaS-1, -2, -3, -4, -5,

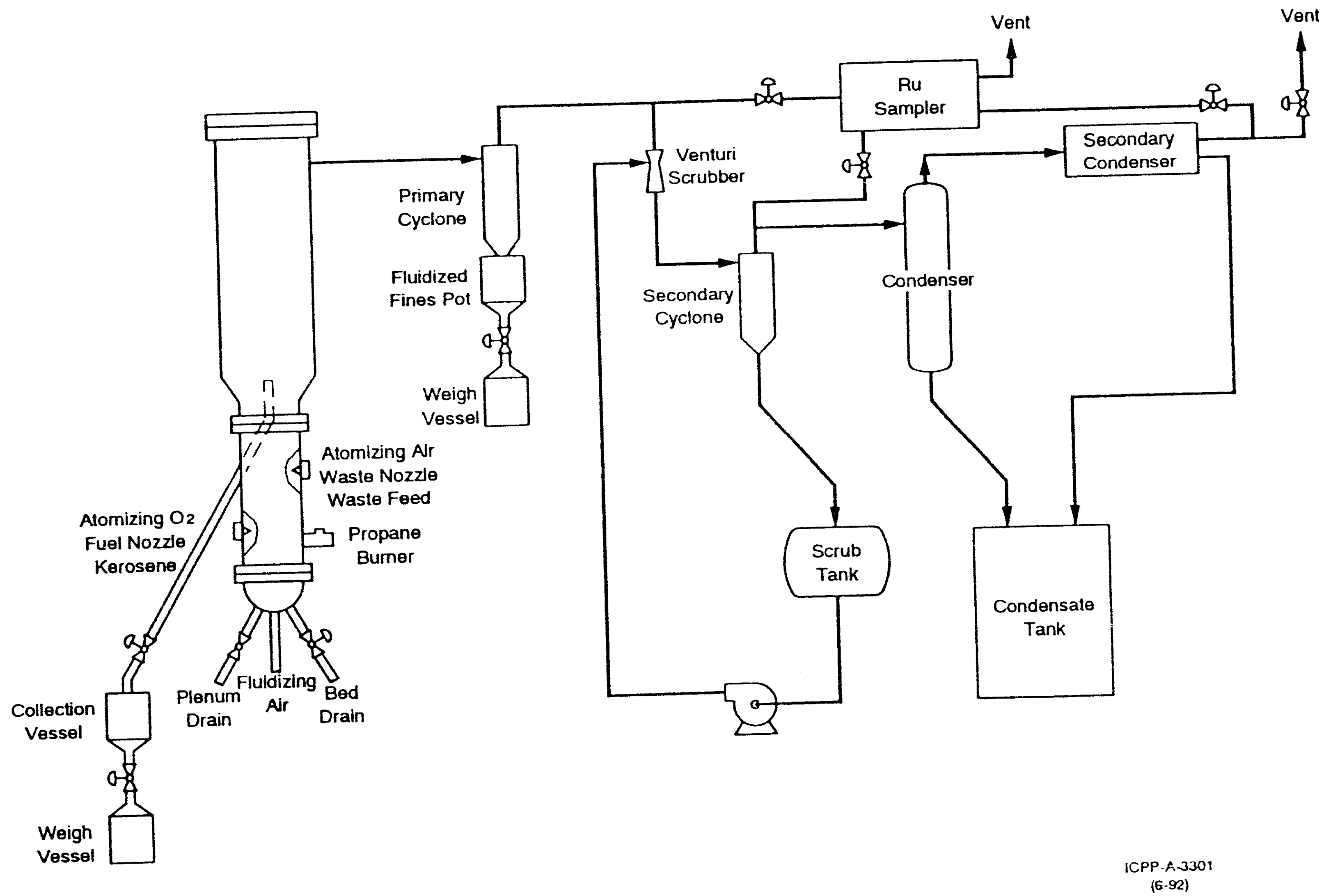

Figure 1. Enclosed Ten-Centimetre Diameter Calciner

and -6, the initial scrub solution in the venturi scrubber was 13 M nitric acid; whenever the scrub foamed, the solution was removed from the scrubber system and replaced with new 13 M nitric acid. Acid scrub solution generated during a run was put in a carboy and a homogeneous sample was taken at the end of the run. Solution from the acid scrub system was not recycled to the calciner feed.

The caustic scrubber was operated, usually for 8 hour periods, at various times throughout the runs. One liter of 6 M sodium hydroxide was added to the scrubber at the beginning of each operating period, and samples of caustic scrub were taken from the scrubber at the end of each operating period.

The feed containing calcium nitrate was sampled prior to being fed to the calciner. Samples of product and fines were taken every 8 hours.

In preparing feed for the runs, sugar was added slowly over a period of 30 minutes to a solution containing calcium nitrate at 80°C. The reaction releasing NO_x typically occurred after a 1 to 2 hour induction period. The temperature of the feed was kept below 90°C using a cooling coil. Adding water to keep the volume constant, the feed was kept between 80 and 90°C for 2 hours, to make certain any reaction taking place between the sugar and the nitrates was completed and as much excess sugar as possible was destroyed. An average of 45% of the nitrates in the fuel for the runs was destroyed during the sugar reactions . Nitrate destruction for each feed is given in Table 3.

The composition of the Fluorinel and Na wastes used in runs FlNaS-1, -2, -3, -4, -5, and -6 are given in Table 4. The composition of these wastes correspond to those of future wastes predicted by P.A. Anderson[3] and R.I. Donovan.[4] Table 4 also gives the theoretical compositions of blends of 4.5 (Runs FlNaS-1 and -2), 2.8 (Runs FlNaS-3 and -4), 3.15 (Run FlNaS-5), and 2.63 (Run FlNaS-6) vol Fluorinel waste to 1.0 vol Na waste prior to treatment with calcium nitrate and sugar. The composition before calcium nitrate addition and sugar treatment is a theoretical composition, while the composition after calcium nitrate addition and

Table 3. Feed Nitrate Destruction During Sugar Treatment

Run F1NaS-	Feed NO_3 Prior To Sugar Reaction[a] (M)	Feed NO_3 After Sugar Reaction[b] (M)	Nitrate Destroyed (%)
1	5.71	2.67	53%
2	5.71	2.98	48%
3	6.38	3.72	42%
4	6.38	3.56	44%
5	5.25	3.52	33%
6	6.41	3.27	49%
		Average	45 ±7

[a] Calculated from feed makeup chemical additions.

[b] Based on analysis of feed

Table 4. Theoretical Compositions of Wastes and Blends of Fluorinel and Sodium Wastes Prior to Calcium Nitrate and Sugar Treatment

Constituent	Fluorinel Waste	Sodium Waste	4.5:1 Volume Ratio Blend (Runs FlNaS-1 and -2)	2.8:1 Volume Ratio Blend (Runs FlNaS-3 and -4)	3.15:1 Volume Ratio Blend (Run FlNaS-5)	2.63:1 Volume Ratio Blend (Run FlNaS-6)
H^+(N*)	1.91	1.6	1.85	1.83	1.84	1.82
Al(M)	0.233	0.7	0.44	0.632	0.345	0.826
Zr(M)	0.431		0.35	0.32	0.327	0.312
B(M)	0.22		0.18	0.16	0.167	0.159
Na(M)		2.1	0.38	0.55	0.506	0.578
K(M)		0.3	0.055	0.079	0.072	0.083
Cd(M)	0.14		0.11	0.10	0.106	0.101
HN_4^+(M)	0.052		0.043	0.038	0.040	0.038
F(M)	3.03		2.48	2.23	2.30	2.20
NO_3(M)	2.26	6.0	2.94	3.24	3.16	3.29
SO_4(M)	0.080	0.0 7	0.078	0.077	0.078	0.077
Cl (μg/ml)		1,775	500*	500*	500*	500*

* A chloride concentration of 500 μg/ml is used during calciner pilot-plant runs to ensure that the chloride concentrations in the test samples are above detectable limits.

sugar treatment is based on analyses of the calciner feeds. The composition of the feeds after calcium nitrate addition and sugar treatment are given in Table 5.

A sample from the acid scrub solution in each carboy, all caustic scrub samples, and solid samples taken at arbitrary intervals throughout the runs were analyzed for those constituents that would determine the cadmium, carbon, chloride, and fluoride behavior during the runs. Acid scrub was also analyzed for those constituents that would show if fluoride corrosion to materials of construction in the NWCF acid scrub system would be excessive. Some product and fines were analyzed for their nitrate content and were also examined by x-ray diffraction and emission spectroscopy.

The following fluidized-bed characteristics were determined: a) the mass mean particle diameter (MMPD) and bulk density for the product collected every 8 hours; b) the attrition index (a measure of particle hardness), MMPD, weight, and bulk density for the starting and final calcine beds; c) the attrition index for product taken during the middle part of the run; d) bulk densities of fines collected every 8 hours; and e) weights of product and fines removed from the calcine bed. In addition, a photo was taken of particles of the final bed magnified twenty times to determine the appearance of the particle's surfaces. The bed and inside of the calciner were examined after each run.

Table 5. Compositions of Blends After Calcium Nitrate And Sugar Treatment

Constituent	Run FlNaS-1 Feed	Run FlNaS-2 Feed	Run FlNaS-3 Feed	Run FlNaS-4 Feed	Run FlNaS-5 Feed	Run FlNaS-6 Feed
H^+ (N*)	0.84	0.98	1.18	1.25	0.96	0.70
Al(M)	0.38	0.38	0.62	0.54	0.32	0.75
Zr(M)	0.24	0.26	0.24	0.16	0.15	0.14
B(M)	0.13	0.11	0.18	0.11	0.13	0.14
Na(M)	0.28	0.28	0.48	0.44	0.52	0.70
K(M)	0.041	0.042	0.070	0.068	0.061	0.11
Cd(M)	0.078	0.078	0.081	0.079	0.099	0.10
Ca(M)	1.30	1.28	1.24	1.10	1.15	1.18
F(M)	1.79	1.93	1.59	1.46	1.56	1.72
NO_3(M)	2.67	2.98	3.72	3.56	3.52	3.27
SO_4(M)	0.021	0.030	0.048	0.028	0.054	0.065
Cl (μg/ml)	385	425	451	497	508	475
UDS (g/L)	84	87	24	12	40	30
Sp. Gr.	1.3156	1.3187	1.3495	1.3145	1.344	1.350

* Concentrations are based on analyses of the blends.

3. RESULTS

3.1 CALCINER OPERATIONS

Run F1NaS-1 was forced to shut down at a cumulative operating time (COT) of 17.5 h when acid scrub was inadvertently vented into the off-gas system. The run was started again after modifying the acid scrub tank so that it couldn't pressurize. The run was voluntarily terminated after 39.8 h of operation. Run F1NaS-2 was shut down at COT 1.6 h due to excessive above bed burning caused by the plugging of some holes in the fuel nozzle cap. The run was started again after replacing the cap and was voluntarily terminated after 36 h of operation. Runs F1Nas-3 and -4 were both voluntarily terminated after 39.5 h of operation. There was continual above bed burning during Run F1NaS-3. After the run, it was found that the above bed burning was caused by plugged holes in the fuel nozzle cap. The fuel nozzle plugging in Runs F1NaS-2 and -3 were due to calcine getting into the nozzle cap during startup and not due to flowsheets. Run F1NaS-5 was temporarily terminated at COT 7.9 h due to formation of an agglomerate on the fuel nozzle (caused by allowing the calcination temperature to get too low). The bed was sieved, the product collected through COT 7.9 h plus extra material was added to the sieve bed, and the calciner was restarted and operated without further shutdowns until it was voluntarily terminated at COT 39.99 h. Run F1NaS-6 was terminated after 38.95 h of operation due to a loss of inbed-combustion fire. This loss was caused by the fuel nozzle being coated over.

After Runs F1NaS-1, -2, -3, -4, and -6, the inside of the calciner looked relatively good; there was the typical build up on surfaces across from the feed nozzles; other calciner wall surfaces, the distributor plate, propane torch, and thermocouple sheaths were free of agglomerates. Also, in Runs F1NaS-1 and -2, there were small cones on the feed nozzles, while in Run F1NaS-6 the fuel nozzle was coated over. The most consistent equipment problem during these runs was that the metal dip-tube in the calciner feed reservoir (connected to the plastic tubing transporting feed from the reservoir to the calciner feed nozzle) plugged frequently.

During Run FlNaS-5 bed temperatures at different heights diverged throughout the run. Apparently bed temperatures diverged when agglomerates formed on the fuel nozzle and came back together again when the agglomerates fell off the nozzle. This theory was supported by the fact that the final bed contained star-shaped agglomerates whose shape indicated that they had formed on the fuel cap. After the run there was: 1) a 1/2 inch by 2 inches agglomerate on the wall opposite the feed nozzle (larger than normal), and 2) a small amount of agglomerate covering 2 holes on the top side of the oxygen cap. Otherwise, the inside surfaces of the calciner vessel including walls, nozzles, propane torch, and thermocouple sheathes were free of agglomerates.

The bed particle size growth for Runs FlNaS-1, -2, -5, and -6 (Figures 2 and 4) was controlled by varying the feed nozzle air ratio (NAR). In Runs FlNaS-3 and -4, the bed particle size continually decreased due to NAR values that were too high (Figure 3). Both runs should probably have used a NAR of about 700 to control bed particle size. NARs used in 10-cm calciners are higher than those used in larger calciners; NAR ranges of 700 to 1300 are typical in the 10-cm calciner. A NAR of about 1100 is typical for calcining Fluorinel/Sodium Blends without sugar in the 10-cm calciner.

3.2 CHARACTERISTICS OF FLUIDIZED-BED AND SOLIDS PRODUCED

Photos of final bed particles magnified 20 times show that the particles produced in all of the runs were spherical with smooth surfaces. A bed of such particles would give high quality fluidization at the NWCF. These photographs are given in Appendix D.

Table 6 gives the important average data obtained on fluidized-bed operation and properties of solids generated during each run; additional information is given in the Appendices.

The low product production rate and low product-to-fines ratio obtained during Runs FlNaS-1, -3, -4, and -6 indicates that there might be difficulty in building bed and maintaining bed height if these flowsheets are used in a large calciner. Run FlNaS-2 had a satisfactory

Figure 2. Variation of MMPD With Waste NAR
During Runs FINaS -1 and -2

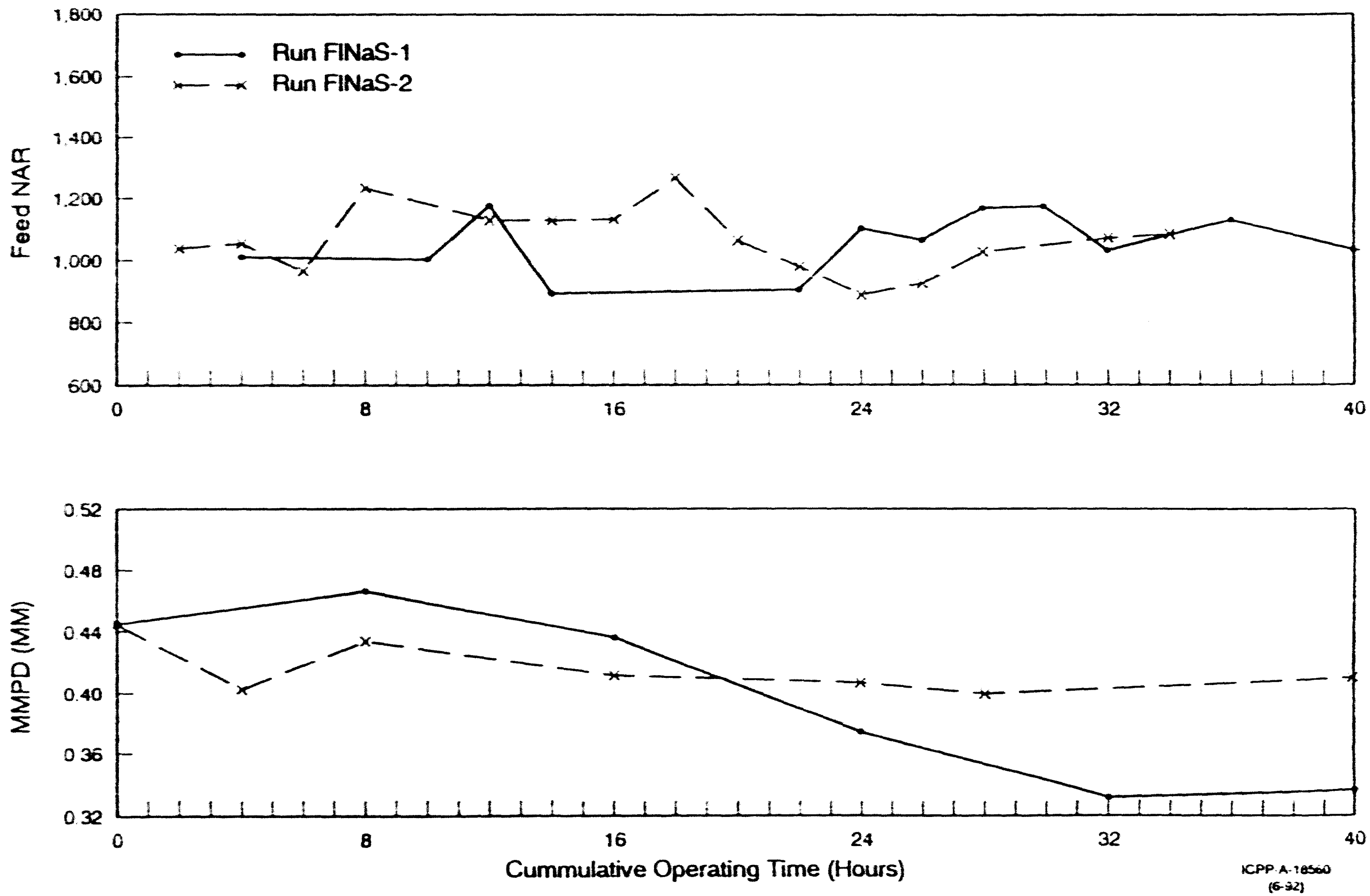

Figure 3. Variation of MMPD with Waste NAR During Runs FINaS-3 and -4

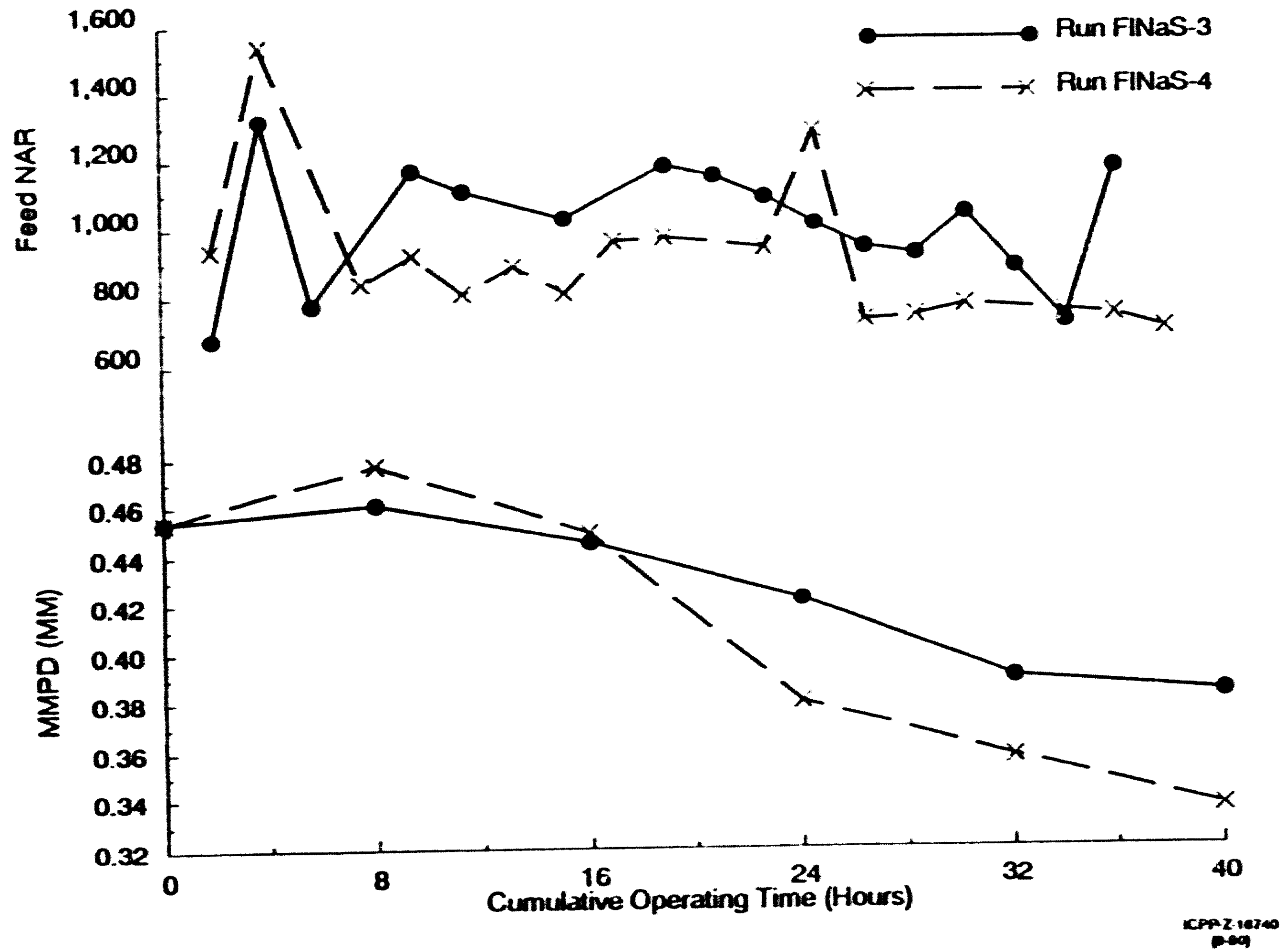

Figure 4. Variation of MMPD With Waste NAR During Runs FINaS-5 and -6

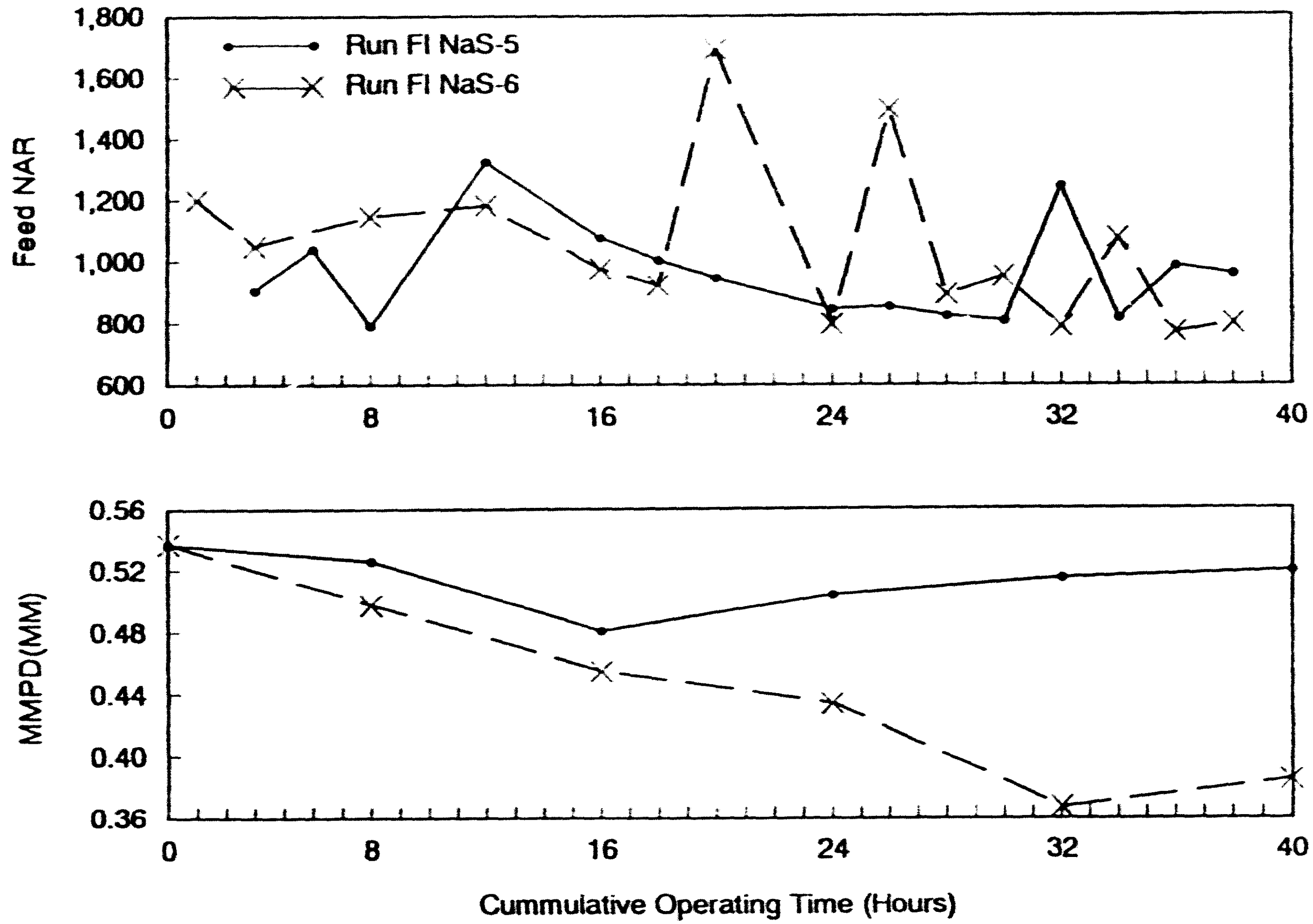

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Table 6. Average Characteristics of Fluidized-Bed and Solids Produced During Calcination of Fluorinel-Na Waste-Sugar Blends[a]

	Run #					
	FlNaS-1	FlNaS-2	FlNaS-3	FlNaS-4	FlNaS-5	FlNaS-6
Feed	4.5 vol Fluorinel Waste - 1.0 vol Sodium Waste	4.5 vol Fluorinel Waste - 1.0 vol Sodium Waste	2.8 vol Fluorinel Waste - 1.0 vol Sodium Waste	2.8 vol Fluorinel Waste - 1.0 vol Sodium Waste	3.16 vol Fluorinel Waste - 1.0 vol Sodium Waste	2.63 vol Fluorinel Waste - 1.0 vol Sodium Waste
Feed Sugar Additive	Sucrose	Dextrose	Sucrose	Dextrose	Sucrose	Sucrose
Feed Sugar Content - grams sugar/mole nitrate	34.5	34.5	34.5	34.5	34.5	34.5
Product Production Rate - g/h	168	276	65.9	182	246	166
Product Bulk Density - g/cm³	1.45	1.38	1.30	1.27	1.46	1.39
Product Attrition Index %	b	b	7.4 at COT 28h	9.2 at COT 20h 2.0 at COT 39.5h	83.6 at COT 24h 83. at COT 38.[illegible]h	24.6 at COT 24h 20.2 at COT 38.86
Nitrate Content of Product - wt %	0.17	0.08	0.048	0.064	0.12	0.061
Fines Bulk Density - g/cm³	0.600	0.606	0.78	0.61	0.54	0.843
Nitrate Content of Fines - wt %	1.02	1.26	0.38	0.45	0.32	0.17
Product-to-Fines Ratio	1.4	1.7	0.34	1.0	3.1	0.82
Weight % of Final Bed + 14 Mesh	18.3	1.3	1.2[c]	0.16[c]	0.88[c]	0.88[c]

[a] The feed for every run was heated at 80 - 90°C for 2 hours before calcination

[b] Not measured

[c] Weight % of bed that is + 16 Mesh Particles

product production rate but a low product-to-fines ratio; thus, if the flowsheet from Run FlNaS-2 were used in a large calciner it would be less likely to have problems building bed and maintaining bed height. Run FlNaS-5 had a sufficiently high product production rate and product-to-fines ration that maintaining bed height and building bed should not be a problem if this flowsheet is run in a larger calciner.

Runs FlNaS-1, -2, -3, and -4 had an Al/Na+K mole ratio of 1.0; whereas, Runs FlNaS-5 and -6 had Al/Na+K mole ratios of 0.6 and 1.25, respectively. The average product-to-fines ratio for runs containing an Al/Na+K mole ratio of 1.0 and 1.25 was 1.0. The product-to-fines ratio for an Al/Na+K mole ratio of 0.6 was 3.1. Thus, the product-to-fines ratio did not change between Al/Na+K mole ratios of 1.0 and 1.25, but decreased between mole ratios of 0.60 to 1.0. These results are exactly opposite of the results seen in previous calciner operations. In previous calciner runs, as the Al/Na+K mole ratio was decreased the amount of fines produced increased. Therefore, the product-to-fines ratio would be expected to decrease (rather than increase as is the case in these tests) as the Al/Na+K mole ratio increases. The tests also show that changing the feed's Al/Na+K mole ratio from 0.6 to 1.25 has little or no effect on the bulk and particle densities of the calcine produced.

There was little tendency for bed particles to agglomerate in any of the runs based on the very small weight percent of particles larger than 14 mesh found in the final bed. Run FlNaS-1 had a large number of particles greater than 14 mesh; however, most of these particles were found on the distributor plate when the calciner was opened after the shut-down at COT 17.5 h. Therefore, there was probably little tendency for bed particle agglomeration during Run FlNaS-1.

The sugars in the feeds of all of the runs did an excellent job of destroying nitrates during calcination (residual nitrates in the product and fines from the runs averaged 0.089 and 0.60 wt%, respectively). In enclosed 30-cm calciner runs calcining blends of Fluorinel and Na wastes without sugar, the nitrate content of fines have varied between 6.9 and 11.1 wt% while the nitrate content of product has varied between 5.7 and 10.3 wt%.

Retrieval tests were performed on homogenous mixtures of product and fines collected during the latter part of Runs FlNaS-1, -2, -3, -4, -5, and -6. The product and fines mixture used for Runs FlNaS-1, -2, -3, -4, -5, and -6 was mixed in the same weight ratio as the run's product-to-fines ration shown in Table 6. The product and fines mixture used for the Run FlNaS-3 retrieval test was a product-to-fines weight ratio of 1.0; it was assumed that a product-to-fines ratio of 1.0 would have been obtained for Run FlNaS-3 if a feed NAR between 700 and 800 had been used. Each retrieval test consisted of attempting (several times) to retrieve a mixture of product and fines that have been subjected to 650°C and a pressure of 8.7 psig (the expected worst case conditions in the bin sets) for three days in a sealed can using a vacuum nozzle with vibrator assistance. During retrieval tests a loading rate of 1.5 kg of calcined solids per kg of vacuum air is considered satisfactory. The fastest loading rate obtained from six attempts to remove Run FlNaS-1 calcined solids from the same can was 2.6 kg of calcined solids per kg of air. Run FlNaS-1 was very similar to Run FlNaS-3 except solids produced had different alkali metal contents. Run FlNaS-1 had an alkali metal content of 5.3 mole % while Run FlNaS-3 had an alkali metal content of 7.5 mole %. The fastest loading rate obtained from three attempts to remove Run FlNaS-3 calcined solids from the same can was 1.4 kg of calcined solids per kg of air. Therefore, even with calcined solids of low nitrate content, increasing the alkali metal content of the solids from 5.3 to 7.5 mole % seems to decrease the loading rate during retrieval.

The fastest loading rate obtained from attempts to remove Run FlNaS-2 (alkali metal content of 5.3 mole %) and Run FlNaS-5 (alkali metal content of 7.5 mole %) calcined solids from their cans were 3.8 and 1.8 kg of calcined solids per kg of air, respectively. Cadmium metal crystals plated-out on the interior surface of the can's lid while the mixture from Run FlNaS-4 was being subjected to heat; the deposited cadmium metal prevented the system that subjects the calcined solids to pressure from working. Perhaps the cadmium metal deposited on equipment during this retrieval test because different final and/or intermediate products were formed during the reduction of nitrates in the different runs. The fastest loading rate obtained from the attempts to remove Run

FlNaS-6 calcined solids from the same can was 3.4 kg of solids per kg of air. Heating Run FlNaS-6 calcined solids at 650°C under a pressure of 8.7 psig for three days rusted parts of the stainless steel retrieval equipment that would be in contact with any gases evolved from the calcine. The inside of the retrieval vessel flaked slightly. In addition, it was extremely difficult to remove the retrieval lid from the vessel. The results of the retrieval tests are summarized in Table 7.

Table 7. Pneumatic Retrieval Rates Using a Vibrator-Assisted Vacuum Nozzle

Run	Retrieval Rate[a,b] (kg calcine per kg air)			Product to Fines Ratio
	Avg	Min	Max	
FlNaS-1	1.7	1.4	2.6	1.4
FlNaS-2	3.3	2.8	3.8	1.7
FlNaS-3	1.1	0.8	1.4	0.34[d]
FlNaS-4	[c]	[c]	[c]	1.0
FlNaS-5	1.4	1.2	1.8	3.1
FlNaS-6	2.6	2.2	3.4	0.92

[a] Prior the retrieval, all calcines were subjected to 8.7 psig and 650°C for three days.

[b] Average of several retrieval attempts.

[c] Cadmium metal crystals formed in the caking can preventing the plunger from applying the desired pressure.

[d] A product-to-fines ratio of 1.0 was used for the caking test.

3.3. BEHAVIOR OF VOLATILES

Fluoride volatility suppression during all of the runs was excellent. Runs FlNaS-5 and -6 had the worst fluoride volatility suppression. During Runs FlNaS-5 and -6, <0.84 and 0.65 wt%, respectively, of the fluoride fed to the calciner was lost from the calciner in a form other than CaF_2 (CaF_2 in off-gas is entrained in the fines). In all of the test runs there was always enough boron, zirconium, and aluminum in the off-gas acid scrub solution to complex the fluoride sufficiently to prevent excessive corrosion to materials that would be in the NWCF off-gas scrub system. Increasing the Al/Na+K mole ratio from 0.60 to 1.25 had no effect on fluoride behavior.

Values summarizing the behavior of chloride in calciner off-gas during the runs are given in Table 8. Chloride retention in calcined solids was excellent, averaging 91 wt% of the chloride found in calciner streams in Run FlNaS-1, 93 wt% in Run FlNaS-2, 92 wt% in Run FlNaS-3, >97 wt% in Run FlNaS-4, 93.8 wt% in Run FlNaS-5, and 95.9 in Run FlNaS-6. Increasing the Al/Na+K ratio from 0.60 to 1.25 had no effect on chloride behavior.

In all of the runs the product, fines, acid scrub, caustic scrub, and condensate were analyzed for organic and inorganic carbon. Organic carbon getting by the acid scrub system would either go through the off-gas caustic scrubber system (for analyses) or through the condensers. From the information obtained from Runs FlNaS-1 and -2, there was no way to determine how much unburned organic carbon was released from the calciner into the off-gas system. By the time the acid scrub was analyzed for organic carbon much of the initial organic carbon in the acid could have been converted to carbonate, and organic carbon could have gotten by the caustic scrubber or condenser since neither system should be effective for collecting organic carbon. Because of the continual above bed burning experienced during Run FlNaS-3, the concentration of organic carbon in Run FlNaS-3 calciner streams was unrealistically low. Inorganic carbon values for Run FlNaS-3 should also be suspect because of the above bed burning. Table 9 summarizes carbon behavior during all of the runs except Run FlNaS-3 which was omitted for the above mentioned reasons. In calculating percent of total carbon in calcined solids, acid scrub, and caustic scrub; the total is the sum of the carbon in those three media. In calculating percent of total carbon found in condensate; the total is the sum of the carbon concentrations found in the calcined solids, acid scrub, and condensate instead of caustic scrub. In Runs FlNaS-1, -3, -5, and -6, sucrose was used as an additive and the wt% of total carbon fed to the calciner in these runs found in calciner streams as organic (unburned and/or not converted to inorganic carbon) carbon was 7.2, 1.5, 1.3, and 1.5 respectively.[6] In

Table 8. Chloride Behavior in Calciner Off-Gas During Runs FlNas-1, -2, -3, -4, -5, and -6

	Run FlNaS-					
	1	2	3	4	5	6
Calciner Feed	4.5 vol Fluorinel - 1.0 vol Na waste	4.5 vol Fluorinel - 1.0 vol Na waste	2.8 vol Fluorinel - 1.0 vol Na waste	2.8 vol Fluorinel - 1.0 vol Na waste	3.15 vol Fluorinel - 1.0 vol Na waste	2.63 vol Fluorinel - 1.0 vol Na waste
Sugar Type	Sucrose	Dextrose	Sucrose	Dextrose	Sucrose	Sucrose
Al/Na+K mole ratio	1.0	1.0	1.0	1.0	0.60	1.25
% of Total in:[a]						
Calcine Solids	91 $^{+0.0}_{-0.1}$ [b]	92.8 $^{+1.4}_{-1.5}$ [b]	92 $^{+1.6}_{-1.5}$ [c]	>97.1[c]	93.8 $^{+0.5}_{-0.3}$ [c]	95.9 $^{+0.6}_{-0.3}$ [c]
Product	56.0 ±11.0	61.6 ±3.4	28.4 $^{+4.5}_{-4.4}$	>53.2	70.6 $^{+1.3}_{-1.5}$	55.7 $^{+3.9}_{-5.9}$
Fines	35.0 $^{+11.0}_{-11.1}$	31.2 $^{+4.8}_{-4.9}$	63.6 ±6.0	>43.9	23.2 $^{+2.0}_{-1.6}$	40.1 $^{+5.1}_{-3.2}$
Acid Scrub	5.1	4.0 ±0.3	3.0	<0.67	4.2 ±0.4	0.35 $^{+0.04}_{-0.05}$
Off-Gas Leaving Acid Scrub	4.0	3.4	6.8 $^{+0.0}_{-0.1}$	<2.6	2.3 ±0.5	3.8 ±0.2

a The numbers given represent the average, maximum, and minimum values obtained in a run.
b Percent of total found in calcine solids, acid scrub, and condensate. The condensate contained a greater amount of chloride from an 8 h operating period than did the caustic scrub.
c Percent of total found in calcined solids, acid scrub, and caustic scrub.
d Fines plus product
e Based on chloride concentration found in caustic scrubber solution downstream from acid scrubber.

Table 9. Carbon Behavior During Runs FlNaS-1, -2, -4, -5, and -6

Type of Carbon Behavior	Run FlNaS- 1	2	4		5		6	
	Organic	Organic	Organic	Inorganic	Organic	Inorganic	Organic	Inorganic
Grams of Carbon Produced from 8h of Operation, Method a	107^{+58}_{-58}	494 ± 138	679^{+236}_{-167}	$760.8^{+44.7}_{-82.6}$	$9.3^{+0.3}_{-0.6}$	$986.1^{+21.2}_{-22.2}$	14.8 ± 0.1	$1088.6^{+91.9}_{-90.7}$
Grams of Carbon Produced from 8h of Operation, Method b	24^{+2}_{-1}	50^{+3}_{-2}	126^{+8}_{-7}	$16.4^{+2.1}_{-4.1}$	$16.1^{+0.3}_{-0.6}$	$44.7^{+21.2}_{-24.6}$	23.0 ± 0.1	$67.8^{+1.83}_{-1.30}$
Grams Carbon fed in 8h	1,477	1,676	1,628		1,263		1,480	
% of Total in:								
Calcine Solids	$9.8^{+4.2}_{-4.1}$	4.0 ± 1.3	$1.7^{+1.6}_{-0.9}$	$1.97^{+0.67}_{-0.49}$	$41.1^{+1.7}_{-3.2}$	$4.61^{+2.01}_{-2.60}$	4.30 ± 0.4	$0.44^{+0.14}_{-0.16}$
Fines	$9.6^{+4.4}_{-4.3}$	1.7 ± 1.1	$1.6^{+1.3}_{-0.83}$	$0.88^{+0.42}_{-0.47}$	$5.5^{+0.7}_{-0.6}$	$3.58^{+1.98}_{-2.42}$	$0.80^{+0.18}_{-0.08}$	$0.28^{+0.16}_{-0.11}$
Product	0.2 ± 0.2	1.0 ± 0.2	$0.12^{+0.11}_{-0.06}$	$1.09^{+0.13}_{-0.20}$	$36.8^{+2.0}_{-3.0}$	$0.83^{+0.04}_{-0.08}$	$42.2^{+0.6}_{-0.6}$	0.33 ± 0.06
Acid Scrub	$10.8^{+1.9}_{-1.8}$	3.4 ± 0.9	$9.6^{+2.9}_{-3.3}$	0.03	$58.8^{+3.2}_{-1.7}$	0.01	57.0 ± 0.4	0.004
Caustic Scrub	$79.4^{+10.1}_{-10.2}$	$83.8^{+2.3}_{-2.2}$	$88.6^{+0.7}_{-4.2}$	$98.0^{+0.7}_{-0.6}$	0.00	$95.6^{+2.6}_{-2.0}$	0.00	99.4 ± 0.1
Condensate	33.9	48.0	$51.8^{+1.9}_{-1.3}$	$4.8^{+3.0}_{-3.2}$	$42.7^{+1.3}_{-0.7}$	$0.54^{+0.40}_{-0.26}$	$36.8^{+0.2}_{-0.1}$	$5.86^{+1.13}_{-1.41}$

* Total Carbon = carbon in product + in fines + in acid scrub + in caustic scrub
* Total Carbon = carbon in product + in fines + in acid scrub + in condensate
* The numbers given represent the average, maximum, and minimum values obtained during the run
* Fines plus product

Runs FlNaS-2 and -4, dextrose was used as an additive and the wt% of total carbon fed to the calciner in these runs found in calciner streams as organic carbon was 29.5 and 38, respectively.[5] In the NWCF, either 29.5 or 38 wt% of the carbon (in the form of sugar) fed to the calciner escaping the off-gas acid scrubber as unburned carbon would probably plug filters and silica gel beds. Thus, increasing the alkali metal content of calcine solids produced from 5.3 to 7.5 mole % doesn't change the amount of unburned carbon created during calcination of the blends.

Therefore, in runs calcining blends of Fluorinel and Na wastes containing sugar as an additive: a) sucrose burns and/or is converted into inorganic carbon compounds more completely than is dextrose, and b) the low value for wt% of total carbon fed to the calciner found in calciner streams as organic carbon in Run FlNaS-3 was not caused by above bed burning but by the fact that sucrose rather than dextrose was used.[5] The carbon behavior experienced during Runs FlNaS-5 and -6 are similar. Thus, changing the Al/Na+K mole ratio from 0.60 to 1.25 had no effect on carbon behavior.

During Run FlNaS-5, 3.4 wt% of the cadmium fed to the calciner was lost from the calciner. During Run FlNaS-6, 3.6 wt% of the cadmium fed was carried over. Most of the cadmium in the off-gas system was probably carried out of the calciner vessel in the fines.

3.4 MISCELLANEOUS CALCINATION CHEMISTRY

X-ray diffraction examination of the final beds from Runs FlNaS-3 and -4 gave the same results: a) principal crystalline constituents were CaF_2, ZrO_2, and $Ca_{0.15}Zr_{1.85}O_{1.85}$; and b) possible minor crystalline constituents were NaCl, CdO, and an unidentifiable constituent. The presence of NaCl as a minor constituent could explain the excellent chloride retention seen in these runs. The sugar's destruction of nitrates could have left the Na^+ ions free to bind with the Cl^- ions; thereby, retaining the chloride in the calcine. This examination gave no clue as to why cadmium metal plated-out on equipment during retrieval studies on Run FlNaS-4 solids.

There seemed to be more difficulty keeping feed solids in suspension during runs FlNaS-3 and -4 than in previous runs using sugar in the feed. Some of these solids from Run FlNaS-3 were examined by X-ray diffraction and emission spectroscopy. The results of the X-ray diffraction examination showed ammonium citrate to be the principal crystalline constituent and an unidentified, crystalline, minor constituent to be present also. Emission spectroscopic examination of these solids showed zirconium and calcium to be major constituents ($\geq$ 5 wt%); and aluminum, boron, iron, and magnesium to be minor constituents ($\geq$ 1 to <5 wt%).

Run FlNaS-4 off-gas was sampled for its carbon monoxide-carbon dioxide ratio (a measure of combustion efficiency) during the run at cumulative operating times of 19 and 21 hours via a sample bomb installed on the caustic scrubber inlet. Combustion efficiency for these two samples averaged 90%. Two additional samples were taken at the end of the run after operating on nitric acid fuel for approximately 0.5 hours. Combustion efficiency for these two samples averaged 85%. Results of the off-gas samples are listed in Table 10.

Table 10. Carbon Monoxide in Off-gas During 10-cm Calciner Run FlNaS-4

Sample	CO (vol%)	CO_2 (vol%)	CH_4 (vol%)	Combustion Efficiency (1-(CO/CO+CO_2)))	Feedrate (LPH)	O_2/Fuel Ratio (sL/L)
COT_19	1.7	11.3	0.037	86.9	2.1	2230
COT_21	0.85	11.4	0.002	93.1	2.8	2280
AcidFeed-A	1.0*	6.3*	0.050*	86.0	2.8	2040
AcidFeed-B	1.6	7.2	0.049	82.3	2.8	2040

* Replicate agreement was poor.

The final bed and agglomerates produced in Runs FlNaS-5 were examined by X-ray diffraction and by emission spectroscopy. X-ray diffraction showed: a) CaF_2 and $Ca_{0.15}Zr_{0.85}O_{1.85}$ to be major constituents of both agglomerates and non-agglomerated particles; b) $Ca_2Al_3O_6F$ to be a major constituent of agglomerates and a minor constituent of non-agglomerated particles; c) $CaZrO_3$ to be a minor constituent of agglomerates; and d) $Ca_3ZrSi_2O_9$, CdO, $ZrSiO_4$, and NaCl to be possible minors of non-agglomerated particles. Emission spectroscopy showed agglomerates contained: Cd, Al, and Ca as major constituents ($\geq$5 wt%), and Na, Zr, Cr, Mg, and Fe as minor constituents ($\geq$ 1 to <5 wt%). The spectrochemical examination for non-agglomerated particles was the same as for agglomerates except iron was not present.

The final product produced during Run FlNaS-6 was examined by X-ray diffraction and emission spectroscopy. The X-ray diffraction examination showed that: CaF_2 and $Ca_{0.15}Zr_{0.85}O_{1.85}$ were major crystalline constituents, and CdO and NaCl were possible minor crystalline constituents. X-ray diffraction did not find $Ca_3ZrSi_2O_9$, $Ca_2Al_3O_6F$, and $ZrSiO_4$ in the final product produced from Run FlNaS-6 as it did in the final product from Run FlNaS-5. The emission spectroscopy examination of Run FlNaS-6 final product showed: Zr, Cd, Al, and Ca as major constituents; and Mg, Cr, and Na as minor constituents. This spectrochemical examination is similar to that obtained on Run FlNaS-5 final product except Zr is a major constituent of Run FlNaS-6 final product and a minor constituent of Run FlNaS-5 final product.

4. CONCLUSIONS AND RECOMMENDATIONS

4.1 CONCLUSIONS

The following conclusions were reached based on results presented in this report.

A. Sucrose and dextrose were both effective at destroying nitrate in the feed solutions. The amount of nitrate reduction in feed solutions ranged from 33 mole % to 53 mole %, with 45 mole % being the average amount of nitrate reduced.

B. Sucrose is a more desirable nitrate reductant than dextrose because the unreacted sucrose is consumed in the calciner to a greater extent than the unreacted dextrose. Therefore, using sucrose as a feed additive would probably prevent the NWCF silica gel beds from plugging.

C. Runs FlNaS-3, -4, -5, and -6 successfully produced calcined solids with a Na+K mole % of 7.5.

D. Product-to-fines ratios were low for all runs except for Run FlNaS-5.

E. As the Al/Na+K mole ratio increased the product-to-fines ratio decreased. This unexpected result cannot, at this time, be explained.

F. None of the calcine produced, except Runs FlNaS-2 and -6, had a favorable retrievability.

G. Very few 10-cm Calciner Pilot Plant operational difficulties occurred with the sucrose or dextrose flowsheets.

4.2 RECOMMENDATIONS

The following recommendations were reached based on information presented in this report:

A. Further testing should be conducted on catalysts that could shorten the induction period of the sugar reactions. Laboratory studies have shown that the initiation period required for sucrose reaction with nitrates during feed make up and the amount of sucrose required for efficient reduction of nitrate during calcination can be reduced by using vanadium pentoxide or ferric nitrate as additives[8].

B. An evaluation of the NO_x emissions due to the destruction of nitrates by sugars should be conducted to determine if NO_x abatement will be capable of handling the large releases (an average of 45 mole % reduction of nitrates) of NO_x produced by the sugar reaction.

C. The amount of sugar that must be added to the feed to start a deflagration under typical calciner operating conditions (temperature and pressure) should be determined before calcining blends of Fluorinel and sodium wastes containing sucrose in the NWCF.

D. Liquid or granulated sugar should be used to prevent sugar dust explosions.

5. LITERATURE CITED

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APPENDIX A

RUNS FlNaS-1 and -2

Table A-1 Operating Conditions for Runs FlNaS-1 and -2

Common Operating Conditions

Acid Scrub Recycle to Feed: None
Startup Bed: Calcined Zr/Na Waste Blend
Feed Nozzle: Spraying System Co. 40100 Liquid, 120 Air
Fuel (Kerosene) Nozzle: Spraying System Co. 2050 Liquid, 67-6-20-70' Air

Common Feed Characteristics

Blend Ratio: 4.5 vol Fluorinel Waste/1 vol Na Waste
Ca/F mole Ratio: 0.7
Feed Sugar Conc.: 34.5 g Sugar/Mole of NO_3
Al/Na+K mole Ratio: 1.0
Na+K mole % in Calcined Solids: 5.3

Run No. Feed Sugar Additive	FlNaS-1 Sucrose	FlNaS-2 Dextrose
Specific Run Conditions*		
Calcination Temperature- °C	503±8	501^{+10}_{-7}
Waste Feed Rate-L/h	$2.1^{+0.8}_{-1.0}$	2.5±0.06
Fluidizing Air Rate-L/s	$0.85^{+0.12}_{-0.18}$	$0.78^{+0.08}_{-0.12}$
Fluidizing Velocity (below nozzle)-m/s	0.27 ±0.05	0.25 ±0.03
Feed Atomizing Air Nozzle Pressure-psig	20 ±2	21^{+5}_{-3}
Feed Atomizing Air Rate-L/s	$0.63^{+0.02}_{-0.03}$	$0.63^{+0.02}_{-0.01}$
Fuel Nozzle O_2 Rate-L/s	0.35 ± 0.05	$0.40^{+0.05}_{-0.02}$
Kerosene Feed Rate-L/h	$0.70^{+0.12}_{-0.08}$	$0.72^{+0.04}_{-0.05}$
Fuel Nozzle O_2/Fuel Ratio	2095^{+424}_{-615}	2040^{+206}_{-99}
NAR	1129^{+804}_{-230}	1067^{+214}_{-174}
Bed Turnover-%	83.4	95.0
Run Duration-h	39.8	38

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

Table A-2 Characteristics of Fluidized-Bed and Solids Produced During Runs FlNaS-1 and -2

Common Feed Characteristics

Blend Ratio: 4.5 vol Fluorinel Waste/1 vol Na Waste
Ca/F mole Ratio: 0.7
Feed Sugar Conc.: 34.5 g Sugar/Mole of NO_3
Al/Na+K mole Ratio: 1.0
Na+K mole % in Calcined Solids: 5.3

Specific Propertieis of Fluidized Bed and Produced Solids*

Run No.	FlNaS-1	FlNaS-2
Feed Sugar Additive	Sucrose	Dextrose
Product:		
Production Rate (g/h)	159	278
Bulk Density (g/cm^3)	1.45 +0.23 -0.10	1.38 +0.11 -0.07
MMPD (mm)	0.3824 +0.0701 -0.0498	0.4107 +0.0249 -0.0109
Particle Density (g/cm^3)	2.20 ±0.05	2.00 +0.05 -0.08
Nitrate Content (wt%)	0.17 +0.02 -0.04	0.08 +0.02 -0.03
Fines:		
Production Rate (g/h)	115	162
Bulk Density of Final Fines collected (g/cm^3)	0.600	0.605
Nitrate Content (wt%)	1.02 +0.19 -0.24	1.28 +0.58 -0.31
Product-to-Fines Ratio	1.4	1.7
Starting Bed:		
MMPD (mm)	0.4423	0.4423
Bulk Density (g/cm^3)	1.54	1.54
Attirtion Index of -30+40 Mesh Fraction (%)	77	77
Final Bed:		
MMPD (mm)	0.2995	0.4257
Bulk Density (g/cm^3)	1.45	1.34
Attrition Index of -30+40 Mesh Fraction (%)	44	57
Wt % of Bed that is +14 Mesh Particles	18.3	1.3
Wt % of Bed that is +1/2 inch Diameter Agglomerates	15.1	0.5

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

APPENDIX B

RUNS FlNaS-3 and -4

Table B-1 Operating Conditions for Runs FlNaS-3 and -4

Common Operating Conditions

Acid Scrub Recycle to Feed: None
Startup Bed: Calcined Zr/Na Waste Blend
Feed Nozzle: Spraying System Co. 40100 Liquid, 120 Air
Fuel (Kerosene) Nozzle: Spraying System Co. 2050 Liquid, 67-6-20-70° Air

Common Feed Characteristics

Blend Ratio: 2.8 vol Fluorinel Waste/1 vol Na Waste
Ca/F mole Ratio: 0.70
Feed Sugar Conc.: 34.5 g Sugar/Mole of NO_3
Al/Na+K mole Ratio: 1.0
Na+K mole % in Calcined Solids: 7.5

Run No.	FlNaS-3	FlNaS-4
Feed Sugar Additive	Sucrose	Dextrose
Specific Run Conditions*		
Calcination Temperature- °C	503 +17 -12	501 +18 -21
Waste Feed Rate-L/h	1.8 ±0.5	2.4 +1.2 -0.9
Fluidizing Air Rate-L/s	0.72 +0.06 -0.07	0.72 +0.06 -0.09
Fluidizing Velocity (below nozzle)-m/s	0.23 +0.03 -0.02	0.23 +0.03 -0.02
Feed Atomizing Air Nozzle Pressure-psig	18.2 +11.8 -4.7	14.5 +9.5 -2.5
Feed Atomizing Air Rate-L/s	0.57 +0.30 -0.12	0.50 +0.05 -0.03
Fuel Nozzle Atomizing O_2 Rate-L/s	0.53 +0.02 -0.06	0.40 +0.00 -0.02
Kerosene Feed Rate-L/h	0.70 +0.04 -0.03	0.71 ±0.05
Fuel Nozzle O_2/Fuel Ratio	2494 +609 -488	2148 +352 -348
NAR	1196 ±277	877 +623 -361
Bed Turnover-%	90.7**	88.3
Run Duration-h	39.5	39.5

* The numbers given represent the average, maximum, and minimum values.

** Used product plus fines to calculate bed turnover rather than product only.

Table B-2 Characteristics of Fluidized-Bed and Solids Produced During Runs FlNaS-3 and -4

<u>Common Feed Characteristics</u>

Blend Ratio: 2.8 vol Fluorinel Waste/1 vol Na Waste
Ca/F mole Ratio: 0.70
Feed Sugar Conc.: 34.5 g Sugar/Mole of NO_3
Al/Na+K mole Ratio: 1.0
Na+K mole % in Calcined Solids: 7.5

<u>Specific Properties of Fluidized Bed and Produced Solids*</u>

Run No.	FlNaS-3	FlNaS-4
Feed Sugar Additive	Sucrose	Dextrose
Product:		
Production Rate (g/h)	65.9	182
Bulk Density (g/cm^3)	1.30 +0.02 -0.03	1.27 ±0.03
MMPD (mm)*	0.4200 +0.0407 -0.0367	0.3999 +0.0775 -0.0635
Particle Density (g/cm^3)	2.02 +0.04 -0.03	2.01 +0.06 -0.05
Attrition Index of -40+50 Mesh Fraction (%)	7.4 at COT 28h	9.2 at COT 20h; 2.0 at COT 39.5 h
Nitrate Content (wt%)	0.049 ±0.002	0.064 ±0.09
Fines:		
Production Rate (g/h)	192	181
Bulk Density (g/cm^3)	0.78 +0.10 -0.04	0.61 +0.05 -0.07
Nitrate Content (wt%)	0.38 +0.15 -0.16	0.45 +0.19 -0.18
Product-to-Fines Ratio	0.34	1.0
Starting Bed:		
MMPD (mm)	0.4544	0.4544
Bulk Density (g/cm^3)	1.47	1.47
Attrition Index of -30+40 Mesh Fraction (%)	71	71
Final Bed:		
MMPD (mm)	0.3218	0.2979
Bulk Density (g/cm^3)	1.36	1.30
Attrition Index of -30+40 Mesh Fraction (%)	16.2	3.4
Wt % of Bed that is +14 Mesh Particles	1.2	0.15
Wt % of Bed that is +1/2 inch Diameter Agglomerates	0.30	0.00

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

APPENDIX C

RUNS F1NaS-5 and -6

Table C-1 Operating Conditions for Runs FlNaS-5 and -6

Common Operating Conditions

Acid Scrub Recycle to Feed:	None
Startup Bed:	Calcined Zr/Na Waste Blend
Feed Nozzle:	Spraying Systems Co. 40100 liquid, 120 air
Fuel (kerosene) Nozzle:	Spraying Systems Co. 67-6-20-70° air

Common Feed Conditions

Na+K Mole% in Calcine Solids:	7.5
Ca/F Mole Ratio:	0.70
Feed Sugar Conc:	34.5 g sugar/mole of NO_3
Feed Sugar Additive:	Sucrose

Table C-2 Operating Conditions for Runs FlNaS-5 and -6 (continued)

Specific Conditions*

Run No	FlNaS-5	FlNaS-6
Blend Ratio - Vol Fl Waste/Vol Na Waste	3.15/1.0	2.63/1.0
Fuel Nozzle Liquid (Spraying Systems Co.)	1650	2050
Al/Na+K Mole Ratio	0.80	1.25
Calcination Temperature - °C	498 +11 -9	498 ±7
Waste Feed Rate - L/h	2.09 +0.43 -0.64	2.13 +0.97 -0.83
Fluidizing Air Rate - L/s	0.75 +0.05 -0.12	0.78 +0.02 -0.00
Fluidizing Velocity (below nozzle) - m/s	0.23 +0.03 -0.02	0.25 +0.01 -0.00
Feed Atomizing Air Nozzle Pressure - psig	16.4 +2.6 -3.4	18.5 +2.5 -1.5
Feed Atomizing Air Rate - L/s	0.66 +0.04 -0.03	0.62 +0.08 -0.12
Feed Nozzle Atomizing O_2 Rate - L/s	0.38 ±0.05	0.38 +0.08 -0.01
Fuel Nozzle O_2/Fuel Ratio	2319 +548 -519	2280 +469 -166
Kerosene Feed Rate - L/h	0.59 +0.07 -0.05	0.60 +0.03 -0.05
NAK	1000 +479 -209	1049 +639 -279
Bed Turnover - %	91.2	82.5
Run Duration - h	39.99	38.95

* The numbers given represent the average, maximum, and minimum values.

Table C-3 Characteristics of Fluidized-Bed and Solids Produced During Runs FlNaS-5 and -6

<u>Feed Characteristics</u>

Blend Ratio (Vol Fl Waste/Vol Na Waste):	3.15/1.0 for Run FlNaS-5; 2.63/1.0 for Run FlNaS-6
Ca/F Mole Ratio:	0.70
Feed Sugar Concentration:	34.5 g of sugar/mole of NO_3
Al/Na+K Mole Ratio:	0.60 for Run FlNaS-5; 1.25 for Run FlNaS-6
Na+K Mole% in Calcine Solids:	7.5
Feed Sugar Additive:	Sucrose

Table C-4 Characteristics of Fluidized Bed and Solids Produced During Runs FINaS-5 and -6 (continued)

Properties of Fluidized Bed and Produced Solids

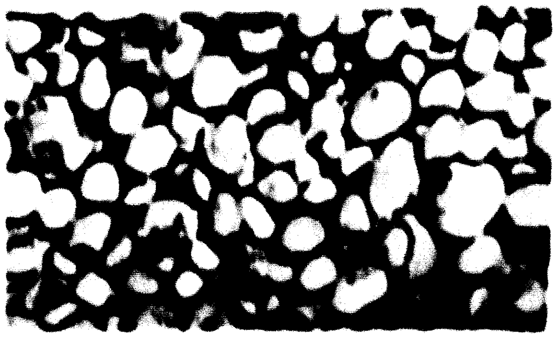
Run No	FINaS-5	FINaS-6
Product		
Production Rate (g/h)	245	166
Bulk Density (g/cm³)*	1.462 +0.051 / −0.054	1.393 +0.062 / −0.101
MMPD (mm)*	0.5047 +0.0141 / −0.0219	0.4278 +0.0704 / −0.0607
Particle Density (g/cm³)*	2.29 ±0.03	2.17 +0.04 / −0.05
Attrition Index of -40+50 Mesh Fraction (%)	83.6 at COT 24 h 83.0 at COT 39.99 h	24.8 at COT 24 h 20.2 at COT 38.95 h
Nitrate Content (wt%)*	0.12 +0.13 / −0.083	0.051 +0.029 / −0.015
Organic Carbon Content(wt%)	<0.010	<0.010
Fines		
Production Rate (g/h)	79	181
Bulk Density (g/cm³)*	0.540 +0.327 / −0.120	0.643 +0.038 / −0.022
Nitrate Content (wt%)*	0.32 +0.15 / −0.09	0.17 ±0.02
Organic Carbon (wt%)*	0.48 +0.03 / −0.06	0.52 +0.06 / −0.02
Product to Fines Ratio	3.1	0.92
Starting Bed		
MMPD (mm)	0.5349	0.5367
Bulk Density (g/cm³)	1.442	1.520
Attrition Index of -40+50 Mesh Fraction (%)	73	73
Final Bed		
MMPD (mm)	0.5028	0.3443
Bulk Density (g/cm³)	1.442	1.520
Attrition Index of -40+50 Mesh Fraction (%)	82.5	48
wt% of Bed that is +16 Mesh Particles	0.89	0.88
wt% of Bed that is +1/2-inch Diameter Agglomerates	0.54	0.79

* The numbers given represent the average, maximum, and minimum values

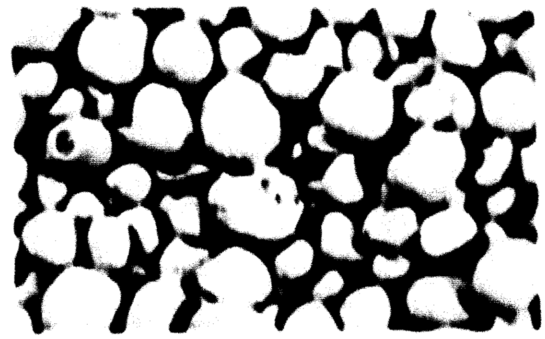
APPENDIX D

20X Magnification Photographs of Final Bed Calcine Particles

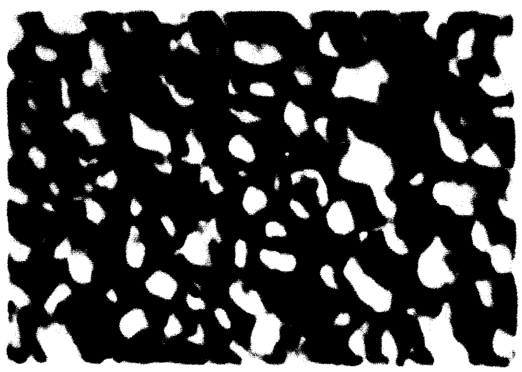
Table D-1
20X Magnification Photographs of Final Bed
Calcine Particles



Run FINaS 1

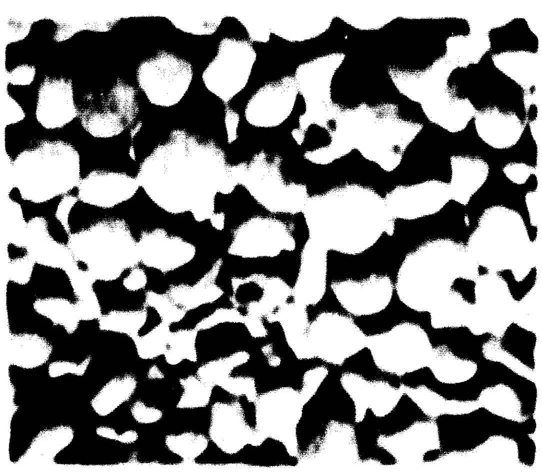


Run FINaS 2

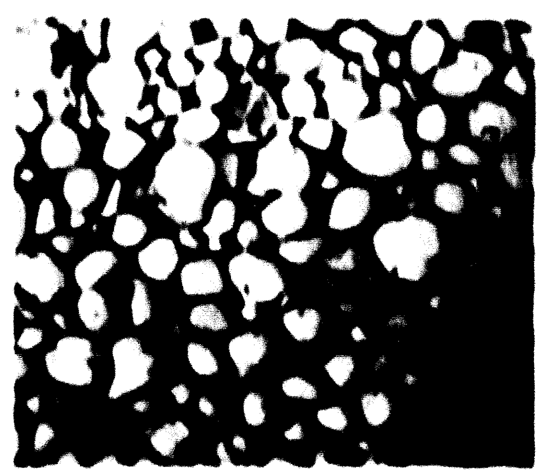


Run FINaS 3

Run FINaS 4



Run FINaS 5



Run FINaS 6

END

DATE FILMED

11/22/93