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CALCINATION FLOWSHEET DEVELOPMENT

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Abstract

Calcination flowsheets for radioactive liquid wastes generated at the Idaho Chemical Processing Plant are systematically developed using laboratory and pilot-plant equipment and are tested in pilot-plant calciners and the Waste Calcining Facility (WCF) before being routinely utilized in the WCF. Characteristics of the wastes and the flowsheet development effort for each waste including stability studies, DTA-X-ray and TGA studies, pilot-plant and WCF testing are discussed herein.

Summary

High- and intermediate-level radioactive, aqueous wastes are converted to solids for storage at the Idaho Chemical Processing Plant (ICPP) using fluidized-bed calcination in the Waste Calcining Facility (WCF). Wastes that have been or will be calcined at the ICPP are aluminum nitrate-nitric acid, aluminum nitrate-ammonium nitrate, stainless steel sulfate, stainless steel nitrate, zirconium fluoride, sodium-bearing, WM-183, Fluorinel, and Rover wastes. Systematic development and testing of a calcination flowsheet for a waste on a laboratory, pilot-plant, and plant scale is required before that waste can be routinely processed in the WCF. Calcination flowsheet development for the wastes listed above is described in this report.

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I. Introduction

High- and intermediate-level radioactive, aqueous wastes are converted to solids at the ICPP using fluidized-bed calcination in the WCF. The fluidized bed provides high rates of heat transfer and produces particulate solids for storage in underground stainless steel bins. The high-level wastes produced at the ICPP consists of the raffinate from the first-cycle extraction of uranium which contains the cladding and alloying components of nuclear reactor fuel, as well as radionuclides. The solids content of this waste is approximately 99% nonradionuclide material. Intermediate level wastes are those from sources other than the first-cycle extraction columns and include aqueous radioactive wastes from second and third extraction processes, chemical laboratories, the hot pilot plant, the Multicurie Cell, the remote analytical facility, the fuel storage basin, the decontamination facility, waste cell floor drains, and process equipment.

Before a waste is calcined in the WCF, extensive laboratory and pilot-plant development and testing of chemical and equipment flowsheets for the waste are required. This consists of: (1) a literature search, (2) stability studies, (3) differential thermal analyses (DTA) and/or thermal gravimetric analyses (TGA), (4) corrosion studies, (5) testing in 10- and 30-cm-diam. (4 and 12 in.) pilot-plant, fluidized-bed calciners, (6) testing in the WCF, and (7) study on a laboratory and/or pilot-plant scale any problems uncovered during pilot-plant calciner and WCF studies. If time does not permit, some of these steps are carried out simultaneously rather than in sequence.

The initial step in the development of a chemical flowsheet for a waste requires a search of the literature to predict the thermal decomposition and high temperature reactions of a waste's constituents, to predict possible fire, explosion, toxicity, corrosion, and fluidized-bed particle agglomeration problems resulting from these decompositions and reactions, and to obtain possible solutions for these problems. Stability tests are performed if it appears desirable to improve calcination characteristics by adding chemicals to a waste, blend wastes, or reduce the volume of a waste by evaporation. The thermal decomposition and high temperature reactions of the waste's constituents as well as the effectiveness of additives to prevent fluidized-bed particle agglomeration (if such a problem exists) are studied using DTA and/or much less frequently, TGA. Chemical flowsheets showing the most potential in stability studies, DTA, and TGA are tested in pilot-plant, fluidized-bed calciners. Initially, scoping runs are made in a 10-cm-diam. (4 in.) calciner. The most promising flowsheet is then tested in a 30-cm-diam. (12 in.) calciner before a recommendation for WCF operation is made. Corrosion studies are not only performed in the laboratory, but continuous corrosion surveillance is performed on pieces of equipment where corrosion is most likely to occur during operation of the larger pilot-plant calciners and the WCF. This report discusses the flowsheet development for the aqueous radioactive wastes which have been or will be calcined at the ICPP in the near future.

II. Aluminum Nitrate-Nitric Acid Waste

1. Characteristics

Aluminum nitrate-nitric acid waste was the first calcined at the ICPP. This waste was generated during the continuous dissolution of spent, aluminum-containing nuclear reactor fuel in nitric acid catalyzed by mercuric nitrate followed by tributyl phosphate (TBP) extraction. The major constituents and their concentrations are given in Table 1. Radioactive aluminum nitrate-nitric acid waste amounting to about 4,977 m^3 (1,315,000 gal) was calcined as a separate entity during the first six processing campaigns of the WCF.[1-5]

When coprocessing of aluminum and zirconium fuels began in 1970, the aluminum nitrate-nitric acid waste was no longer stored or processed separately. Prior to this time, zirconium fuels were also processed separately. The fuel was dissolved in hydrofluoric acid and the uranium was extracted with TBP. In the coprocessing system, dissolver product from aluminum fuel processing is used as the aluminum nitrate-nitric acid complexing solution for the zirconium fuel process. The combined solutions are then fed to the TBP extraction system. Since the sixth WCF campaign, stainless steel nitrate waste and other nonfluoride wastes have been added to the remaining aluminum nitrate-nitric acid waste in tank WM-183. The calcination of this waste combination will be discussed later in this report.

2. Thermogravimetric Study of Aluminum Nitrate

Since aluminum nitrate is a major constituent of aluminum nitrate-nitric acid waste, the thermal decomposition of aluminum nitrate was investigated using a thermal balance.[6] Aluminum nitrate nonahydrate was heated at rates of 1.0 and 2.6°C/min. The thermal decomposition of aluminum nitrate was investigated over the temperature range of 24-460°C using the lower heating rate with constant weight being attained at 340°C; the final product was amorphous and was not completely converted to alumina as established by an 85.3% weight loss when subsequently fired. The sample, for all practical purposes, attained constant weight at about 530°C when heated at the higher rate; the sample heated to 1035°C formed gamma alumina and underwent an 86.1% weight loss.

3. DTA-X-Ray Examination of Synthetic Waste

The thermal decomposition of synthetic aluminum nitrate-nitric acid waste was examined by differential thermal analyses; X-ray diffraction was used to interpret the DTA curve.[7] The synthetic waste was heated at a rate of 6°C/min. The instruments used in this study only indicate the pyrolysis chemistry of the major constituents, in this case aluminum nitrate. The DTA curve showed melting, dehydration, and decomposition of aluminum nitrate nonahydrate (through possible intermediates) to amorphous alumina between 65 and 392°C; transition of amorphous to gamma alumina started taking place at 880°C. Net reactions taking place in the calcination process at 400°C are:[8]

$2Al(NO_3)_3 \cdot nH_2O \rightarrow Al_2O_3+6NO_2+3/2O_2+2nH_2O$

$2HNO_3 \rightarrow 2NO_2+1/2O_2+H_2O$

$NO_2 \rightleftarrows NO+1/2O_2$

$Hg(NO_3)_2 \rightarrow HgO+ 2NO_2+1/2O_2$

$HgO \rightarrow Hg+1/2O_2$

Fission product nitrates → Fission product nitrates/oxides+NO_2, O_2, NO

$NaNO_3 \rightarrow NaNO_3/Na_2O+NO_2, O_2, NO$

$2H_3BO_3 \rightarrow B_2O_3+3H_2O$

4. Flowsheet Development

Pilot plant work in indirectly-heated 60-cm-sq (2 ft) and 15-cm-diam. (6 in.) fluidized-bed calciners was performed to determine if fluidized-bed calcination could be used to convert highly radioactive, aqueous, processing wastes to a solid.[8-12] Most of the work in the 15-cm-diam. (6 in.) calciner and all the work in the 60-cm-sq (2 ft) calciner was performed using synthetic aluminum nitrate-nitric acid waste. An additional 3,700 h of test operations with simulated aluminum nitrate-nitric acid was made in the WCF before the process was developed sufficiently for use with radioactive wastes.[13]

Table 1

TYPICAL COMPOSITION OF ALUMINUM NITRATE WASTE
(Concentrations in Molarity)

Component	Nitric Acid Type	Ammonium Nitrate Type
H^+	0.8	0.13 acid deficient
Al	1.5	1.65
Fe	0.005	0.004
Na	0.065	0.1
Hg	0.018	0.02
NH_4		1.4
NO_3	5.4	7.1

5. Phase Transformations of Alumina

The properties of calcine product changed markedly (increased hardness, decreased particle size, increased bulk density, increased friability, etc.) over a 24-h period under steady-state calcination conditions during calcination of synthetic waste at 400°C in a 60-cm-sq (2 ft), fluidized-bed calciner.[9] An X-ray diffraction examination of the calcine showed that the property changes had been caused by a change in crystal structure from essentially amorphous alumina to alpha alumina. Studies were carried-out at the Stanford Research Institute and the ICPP to determine what caused the alumina phase transformations and how to prevent them. Pilot plant studies were also performed to determine which alumina phase is the most suitable for the fluidized-bed calcination of aluminum nitrate-nitric acid waste. In the literature, amorphous alumina is not reported to be converted to alpha alumina at temperatures as low as 400°C. Examination at the Stanford Research Institute revealed that this amorphous alumina was different than usual because it contained small crystallites which appear amorphous to electron diffraction as well as X-ray diffraction.[14] Thus, the amorphous alumina product in the 60-cm-sq (2 ft) calciner was structually predisposed to form alpha alumina. Theoretical considerations were applied to the effect of additives on the type of crystal, on the size of crystallite, and on amorphous alumina. Based on these considerations, the Stanford Research Institute predicted that the sodium ion would aid alpha alumina formation and boron or phosphorous would aid amorphous alumina formation. Studies at Stanford Research Institute[15] and at the ICPP[16] showed that the presence of 0.01 to 0.06 moles of boric acid or phosphoric acid per mole or aluminum present in aluminum nitrate-nitric acid waste would prevent formation of alpha alumina during calcination. Pilot plant studies at the ICPP showed that the presence of 0.25 M sodium in aluminum nitrate-nitric acid waste would form alpha alumina during calcination of the waste.[11] Studies at the ICPP[16] showed that: (1) it was necessary to form amorphous alumina under fluidized-bed conditions in order to produce an amorphous alumina that can be converted to alpha alumina at 400°C, (2) an atmosphere containing the oxides of nitrogen and water vapor was necessary to produce alpha alumina from amorphous alumina at 400°C, and (3) sodium must be present in the alumina to produce alpha alumina from amorphous alumina at 400°C. Amorphous alumina is required for WCF operation because: (1) amorphous alumina is less erosive to equipment than alpha alumina and produces less fines, (2) fines from amorphous alumina will dissolve in a nitric acid scrubbing solution, while alpha alumina fines do not, and (3) an amorphous, alumina product has a higher attrition resistance.[13] It is easier to prevent alpha alumina formation by calciner feed additives than by attempting to control the calciner operating conditions. In cold tests at the WCF 0.01 M boric acid prevented alpha alumina formation; higher boric acid concentrations in feed may have caused nozzle caking.[13] A small amount of boric acid (0.01 M) was added to the feed solution during the first and second processing campaigns in the WCF, when aluminum nitrate-nitric acid waste was being calcined. The alpha alumina content was maintained below 5%, the detection limit for X-ray diffraction, throughout both campaigns.[17]

6. Mercury Volatility

In developing the aluminum nitrate-nitric acid waste calcination flowsheet, studies were made concerning the ruthenium and mercury volatility. Volatile ruthenium escaping the fluidized bed and off-gas acid scrubber of the WCF was essentially all removed from the off-gas on silica gel. Ruthenium volatility is discussed in detail in another report.[18]

In the reprocessing of aluminum containing fuel, mercuric nitrate is added to the nitric acid to catalyze the dissolution of aluminum. Hence ionic mercury is present in all aluminum-type raffinates. Because of the low decomposition temperature of the majority of mercury compounds and because of its high toxicity, mercury can present problems during calcination of aluminum nitrate wastes. One percent of the mercury present in aluminum nitrate-nitric acid waste escaped from the bed during calcination of the waste at 400°C in a 15-cm-diam. (6 in.) fluidized bed calciner.[12] During calcination of the same waste at 400°C in a 60-cm-sq (2 ft) fluidized bed calciner, 65% of the mercury stayed in the calciner product.[19] In the WCF mercury presented no problem during calcination of aluminum nitrate-nitric acid waste. About 95% of the mercury in the feed appeared with the product transferred to storage; the wet scrubbing systems removed about 80% of the mercury in the calciner off-gas, and the adsorbers and HEPA filter efficiently trapped the remainder.[1]

7. Calcination History

Aluminum nitrate-nitric acid wastes were the first calcined in the WCF. In the first calciner campaign which started in December 1963, approximately 1,938 m^3 (508,000 gal) of aluminum type wastes were converted to solids.[1] The gross feed to the calciner originated from two sources: the liquid waste tank plus dilution from steam jet transfer (jet dilution averaged about 5%) and the off-gas scrubbing solution. The solutions were transferred batchwise to the calciner waste hold tanks at the approximate ratio of three waste volumes to one volume of scrubbing solution. The waste came from three main tanks of which tank WM-185 (five to seven year aged waste) had higher aluminum-ion and lower acid content than did tanks WM-183 (eight year aged waste) and WM-187 (three year aged waste). The heat generation rate (0.69 BTU/h-gal) from WM-187 was due to the high 144-Ce content. The feed rates were normally maintained within ±10% of the desired value.

There were two occasions when difficulties with feed rate control could be attributed to plugging of the feed nozzles, control valves, or flowmeters. In each case the start of feed control trouble coincided with high solids content in a batch of feed. The high solids content was caused each time by inadvertent agitation of the contents of the underground waste tank just prior to a waste transfer. The solids were apparently picked off the bottom of the tank.

Erratic feed rate control caused by high solids content of the feed continued after a return to normal feed. Gradually, the solids worked through the feed system and control improved. Techniques used to cope with plugging caused by solids were: (1) operation of the nozzle plunger, (2) flushing the nozzle and valve with water, and (3) manipulation of the valve. The last was generally the most successful.

The second WCF campaign began in April 1966, and 2328 m^3 (615,000 gal) of aluminum type waste was converted to solids.[2]

Prior to startup of WCF Run 2, a system for concentrating aluminum feed in an evaporator was designed and installed in a tank previously used for adsorber regeneration, so that increased process throughout could be achieved.[9] Initially, feed control problems originating from insoluble silica gel in the tank were encountered. After cleanout of the system, the evaporator was operated over a 7-month period from May to November 1967. With evaporation the net rate of tank farm depletion averaged 303L/h (80 gal/h) whereas, the net rate over a different 14-month period without evaporation averaged 254 L/h (67 gph). The gross feed rate to the calciner in both cases was essentially the same. Therefore, evaporation of the aluminum waste just prior to calcination in the WCF provided an increase of almost 20% in the net WCF throughput rate.

During the first four months of operation, severe plugging in the feed system continued to plague the process. During one week in July 1966, only one of the three feed nozzles remained operable. Between the dates May 12 and September 12, 1966, the "B" feed nozzle was plugged completely and could not be used. The restrictions were believed to be caused by: (1) solids being recycled to the feed system from the quench system, and (2) solids resulting from concentrating the aluminum nitrate waste from the permanent storage tanks in the newly installed waste evaporator, WC-114. Calciner operation did improve when recycle of the scrubbing solution to the feed system was discontinued. Further improvement was also noted when the raw concentrated feed was processed. Tests were conducted by recycling scrub solution and concentrating the aluminum nitrate-nitric wastes, but plugging in the feed system remained a major problem. The calciner was voluntarily shut down in March 1968.

In the sixth processing campaign 416 m^3 (110,000 gal) of remaining aluminum nitrate-nitric acid waste was processed out of tank WM-183 with no feed problems.

III. Aluminum Nitrate-Ammonium Nitrate Waste

1. Characteristics

Spent aluminum-containing nuclear fuel elements were dissolved in nitric acid with a mercuric nitrate catalyst in a batch process at the ICPP. Hexone (methyl isobutyl ketone) was then used for the first-cycle solvent extraction process. Because of the chemical attack of nitric acid on Hexone, the residual nitric acid in the dissolver product was neutralized with ammonium hydroxide. Approximately 1005 m^3 (265,000 gal) of this waste was generated. The concentrations of the major constituents in this waste are given in Table 1. Upon changing to a continuous dissolution process, TBP (tributyl phosphate) was substituted for Hexone as the first-cycle extractant. TBP is not attacked by acid so neutralization was no longer necessary before extraction; therefore, aluminum nitrate-ammonium nitrate waste was no longer generated at the ICPP.

2. Flowsheet Development

The major problem anticipated for calcination of the waste containing high concentrations of ammonium nitrate was the potential for explosive decomposition of the ammonium nitrate. An extensive literature search indicated that aluminum nitrate-ammonium nitrate waste could be decomposed by fluidized-bed calcination at 400°C without hazard.[17]

The possible formation of mercury fulminate, an explosive, was also anticipated during calcination of aluminum nitrate wastes. However, an extensive literature survey indicated that the formation of mercury fulminate before or during calcination was improbable as neither the initial nor intermediate organic compounds necessary for the formation of mercury fulminate from mercury and nitric acid were present in ICPP wastes.

Laboratory studies demonstrated that ammonium nitrate would deposit on a cold section of the off-gas line during calcination of aluminum nitrate-ammonium nitrate waste.[17] The following reactions were thought to take place:

1. $NH_4NO_3 \rightarrow N_2O + 2H_2O$

2. $NH_4NO_3 \rightarrow NO + 1/2N_2 + 2H_2O$

3. $NH_4NO_3 \rightarrow NH_3 + HNO_3$

Reaction 3 is reversible and probably accounts for the solid ammonium nitrate addition in the off-gas line. Blending the aluminum nitrate-ammonium nitrate waste with aluminum nitrate-nitric acid waste diluted the concentration of the ammonium ion, but at the same time maintained the concentration of aluminum nitrate at approximately the same level, thus producing during calcination an oxidizing atmosphere conducive to complete decomposition of the ammonium ion.

Calcination of 19 m^3 (5000 gal) of aluminum nitrate-ammonium nitrate waste in the first WCF processing campaign revealed an unexpected problem.[1] Mercuric ion formed an insoluble mercury-hydroxamine-type solid similar to Millon's base in the undissolved solids of the scrubbing system. Since Millon's base is explosive under certain conditions, the compound that formed in the scrubbing system was synthesized in the laboratory for additional study. This synthetic amidonitrate-mercury compound was found to be stable at calcination and calcine storage temperatures.[17] Blending of the aluminum nitrate-ammonium nitrate waste with aluminum nitrate-nitric acid waste during the second WCF processing campaign prevented any significant buildup of the insoluble amidonitrate-mercury compound in the scrubbing system.[2]

During this time, a high pressure drop across the HEPA final filters was observed. Below 85°C, ammonium nitrate is in the rhombic form; above 85°C, the crystals convert to the tetragonal form. Transition from the rhombic to the tetragonal form is accompanied by expansion. Apparently, rhombic crystals were deposited on the filter when the off-gas entering the filters was below 85°C; when the off-gas entering the filters was allowed to rise above 85°C, the tetragonal crystals were formed, the expansion plugged the filters. To solve this problem, the temperature of the off-gas entering the filters was maintained at 80°C and the aluminum nitrate-ammonium nitrate waste was alternately batched with aluminum nitrate-nitric acid waste to prevent buildup of ammonium nitrate crystals on the filters. When the volume in the two tanks (WM-180, ammonium, and WM-182, $Al(NO_3)_3$-HNO_3) were sufficiently lowered, 350 m^3 (92,600 gal) from WM-180 was transferred to WM-182, and the resulting blend calcined without difficulty.

IV. Zirconium Fluoride-Aluminum Nitrate Waste

1. Characteristics

Zirconium fluoride-aluminum nitrate waste is a combination of wastes generated from two separate dissolution processes. An aluminum nitrate-nitric acid solution originates from the continuous dissolution of spent aluminum-containing nuclear reactor fuel in nitric acid catalyzed by mercuric nitrate. A zirconium solution is generated by dissolving spent zirconium clad nuclear fuel in hydrofluoric acid. The two process streams are combined before extraction. The volume of waste generated is reduced because the alumina complexes the fluorides and additional additives are not needed. This prevents excessive corrosion to the stainless steel in the extraction columns. The major constituents and their concentrations are shown in Table 2.

Zirconium fluoride-aluminum nitrate waste (subsequently will be called zirconium waste) is the major waste generated at the ICPP, and since the third processing campaign, has been the major waste calcined in the WCF. A total of 5216 m^3 (1,368,000 gal) has been calcined through Run 7 in the WCF.

TABLE 2

TYPICAL COMPOSITION OF ZIRCONIUM FLUORIDE-ALUMINUM NITRATE WASTE

Constituent	Concentration (M)
H^+	1.4
Al	0.68
Zr	0.41
Cr	0.015
Fe	0.0076
B	0.19
Sn	0.0047
NH_4^+	0.02
F^-	3.24
NO_3^-	2.28

2. Stability Studies

Zirconium fluoride waste has relatively narrow regions of long-term stability. O. W. Parrett studied these stability regions as a function of zirconium, fluoride, aluminum, and acid concentrations as well as of aging and temperature.[20] Figure 1 is a stability curve from Parrett's report simulating closest the zirconium fluoride wastes presently stored at the ICPP. At a concentration of 0.75 M aluminum in zirconium fluoride waste, the highest stable zirconium concentration is about 0.6 M in a system composed of 3.2 M fluoride, 1.05 M hydrogen ion, and 2.56 M nitrate. A hydrogen ion concentration above 1.5 M causes aluminum compound precipitation; a hydrogen ion concentration much below 1 M causes zirconium compound precipitation. A limited number of blends of aluminum nitrate-nitric acid waste and WM-183 waste with zirconium fluoride waste were stable for greater than 6 months and 1 month, respectively. Blends of zirconium waste with other wastes studied were unstable within a short time. Other wastes studied included stainless steel sulfate, stainless steel nitrate, Rover waste, and sodium-bearing wastes.

The WCF initially calcined aluminum process raffinates, emptying several of the 1135.5 m^3 (300,000 gal) storage tanks. These tanks were then used for storing zirconium fluoride wastes. Since the storage tanks can never be emptied completely of their former contents, some blending of aluminum and zirconium process raffinates were inevitable. Since it is the policy at the ICPP to store only stable solutions in waste storage tanks and precipitation of the hydrolytic products of zirconium fluoride was well known, it was necessary to study the stability of aluminum nitrate-nitirc acid waste blended with zirconium fluoride waste. At 35°C blends containing 20% by volume or less zirconium fluoride waste and 90% or more zirconium fluoride waste, both with aluminum nitrate-nitric acid waste, were found to be stable for greater than 54 weeks.[21] Wastes are routinely stored at 35°C in ICPP waste storage tanks.

3. Flowsheet Development

In the waste calcination process, if the fluoride is not further complexed, enough fluoride will be released to excessively corrode the calciner and off-gas system as well as harming plant and animal life when released to the environment. Therefore, the major development work has been associated with finding an additive that will effectively suppress fluoride volatility during calcination of the waste.

In 1959, work was initiated to study the feasibility of calcining zirconium wastes containing fluoride and nitrate. The first process investigated involved evaporation to dryness and calcination in the presence of silica.[22] With this additive, silica tetrafluoride would have to be absorbed from the off-gas stream before release. Addition of calcium oxide to the waste was a more attractive method because it kept the major portion of the fluoride in the bed.[23] Pilot-plant runs were then tried with calcium nitrate. By addition of stoichiometric amounts of calcium nitrate to the waste, greater than 99% of the fluoride was retained as solids.[24] Adding calcium nitrate ($Ca(NO_3)_2$) to the simulated waste produced an easy-to-handle flocculent precipitate. Dolomite (a calcium magnesium carbonate) dissolved in nitric acid was used to suppress fluoride volatility during laboratory calcination of zirconium waste but offered no advantage over $Ca(NO_3)_2$ except for possibly being a cheaper source of calcium.[25] Laboratory scoping studies

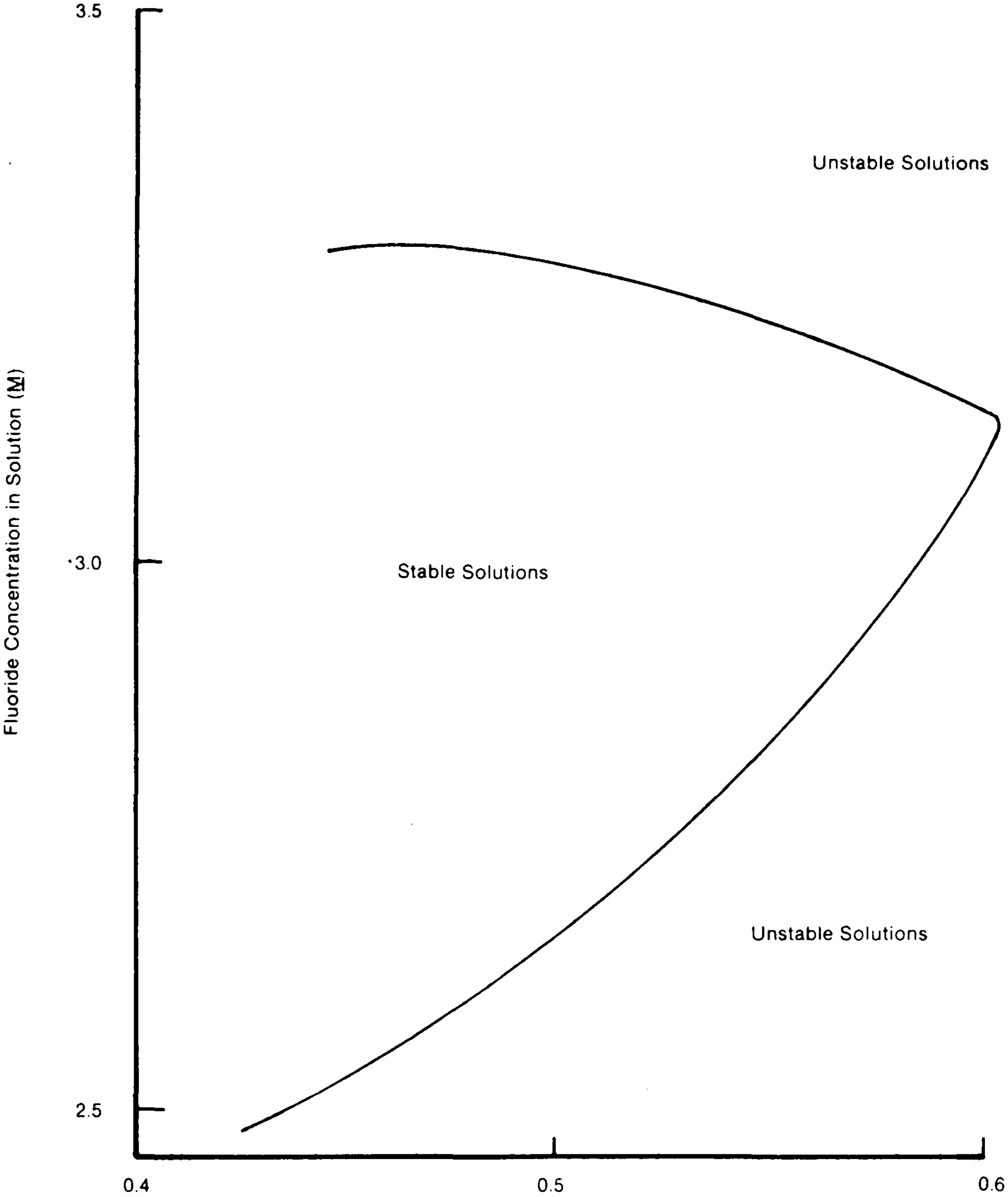

Figure 1. Regions of Long-term Stability for Zirconium Fluoride Waste (0.75 M Aluminum at 25°C)

ACC-A-3293

were made to see if magnesium sulfate could be substituted for $Ca(NO_3)_2$ because the magnesium compound would form less solids in calciner feed.[26] However, 2-6% of the fluoride in the calciner feed volatilized during laboratory static calcination tests at 500°C. Fluoride volatility adding sufficient $Ca(NO_3)_2$ to calciner feed to give a calcium to fluoride (Ca/F) mole ratio of 0.55 would be 0.7% or less.

The thermal decomposition of synthetic zirconium waste containing enough $Ca(NO_3)_2$ to give a calcium to fluoride mole ratio of 0.55 (mole ratio actually used during calcination of the waste) was studied by DTA-X-ray techniques.[7] The DTA curve for zirconium waste containing $Ca(NO_3)_2$ shows that aluminum nitrate decomposes to form Al_2O_3 and $Ca(NO_3)_2$ dehydrates between 57 and 152°C; the calcium fluozirconate formed when $Ca(NO_3)_2$ is first added to zirconium waste decomposes between 352 and 590°C during calcination to form CaF_2 and ZrO_2; excess $Ca(NO_3)_2$ also decomposes between 352 and 590°C.

4. Fluoride Volatility Suppression

Calcium nitrate is currently added to zirconium waste prior to calcination to suppress fluoride volatility during calcination. Calcium nitrate added to zirconium waste forms calcium fluozirconate which can be relatively gelatinous and voluminous and tends to plug calciner feed control valves, flowmeters, and nozzles. Laboratory studies were made to find a method that would form less gelatinous solids in the zirconium waste while effectively suppressing fluoride volatility. Attempts were made to effectively suppress fluoride volatility while minimizing solid formation in calciner feed by finding a substitute for $Ca(NO_3)_2$ or by using $Ca(NO_3)_2$ and altering the concentrations of the calciner feed constituents.

4.1 Use of Calcium Nitrate

Calcium nitrate was added to zirconium waste as a saturated solution during the first five processing campaigns of the WCF. In laboratory waste work, it was determined that $Ca(NO_3)_2$ could be added to zirconium waste as a solid rather than a solution, thus reducing the volume of waste by 17.5% as opposed to liquid addition.[27] Calcium nitrate was routinely added to zirconium waste as a solid beginning in the sixth processing campaign of the WCF.

At the time $Ca(NO_3)_2$ was added as a saturated solution, the supplying vendor began adding an organic material to the product to make it less prone to agglomeration. The saturated $Ca(NO_3)_2$ solution was prepared by dissolving $Ca(NO_3)_2$ in an agitated solution at 60 to 80°C, transferring to a hold tank, and allowing to cool to ambient temperature. The organic material in the nonagitated hold tank formed a floating scum or grease that coated the sides and heating coils as the tank was drained. Studies were performed: (1) to find $Ca(NO_3)_2$ without an organic coating that could be used at the ICPP, (2) to find a calcium-containing substitute for $Ca(NO_3)_2$, and (3) to examine the properties of the organic material on the $Ca(NO_3)_2$ now used at the ICPP. The problem was solved by purchasing a $Ca(NO_3)_2$ without an organic coating that could be used at the ICPP.28

Several studies were performed to reduce gelatinous solids formed in the zirconium waste when the $Ca(NO_3)_2$ was added.[29,30] If boron was not in the waste, a gel would form.[26] Attempts were made to reduce the gelatinous solids by using $Ca(NO_2)_2$ and altering the addition conditions and/or altering the concentratons of the waste constituents. The gelatinous nature and amount of solid was not affected by waste calcium concentration between a Ca/F mole ratio of 0.55-0.7, variation of $Ca(NO_3)_2$ addition rate, the waste acid concentration, or whether $Ca(NO_3)_2$ was added as a solid or a solution. The most effective method was to increase the aluminum concentration to an Al/F mole ratio of at least 0.27 (usual ratio is 0.21). Less effective methods are to increase the boron concentration from 1.7 g/L to 3.1 g/L prior to $Ca(NO_3)_2$ addition or to hold the waste temperature at 40°C (instead of ambient) while adding $Ca(NO_3)_2$. If the Ca/F mole ratio is decreased to less than 0.5, the fluoride volatility increased. Fluoride volatility was not affected by the aluminum ratio of the waste between an Al/F mole ratio of 0.21 and 0.4 or by the addition of $Ca(NO_3)_2$ as a solid or solution. Studies in a 10-cm-diam. (4 in.), fluidized-bed, in-bed combustion calciner showed that zirconium waste containing Al/F mole ratios varying between 0.21 and 0.4 to which $Ca(NO_3)_2$ is added to give a Ca/F mole ratio of 0.55 can be calcined without deleterious effect.[31]

4.2 Use of Calcium Nitrate Substitutes

A number of nitrates known to form stable fluorides, costing no more than a factor of 10 greater than $Ca(NO_3)_2$, producing no solids when added to simulated zirconium waste, and commercially available were studied as potential substitutes for $Ca(NO_3)_2$ in suppressing fluoride volatility during calcination of zirconium waste.[29] Batch calcinations at 500°C were made using ferric, chromic, manganese, lead, copper, zinc, magnesium and nickel nitrates to suppress fluoride volatility during calcination of zirconium waste. The fluoride suppressing reagents were present in the waste in quantities twice that needed to stoichiometrically react with all the fluoride present, assuming trivalent ions form simple tri-fluorides ($Fe^{+3} + 3F^- \rightarrow FeF_3$) and bi-valent ions would form simple di-fluorides ($Mg^{+2} + 2F^- \rightarrow MgF_2$). Table 3 shows that of the nitrates tested, only magnesium nitrate ($Mg(NO_3)_2$) suppressed fluoride volatility as effectively as did $Ca(NO_3)_2$ during the batch calcination of zirconium waste. Further batch calcination studies showed that decreasing the magnesium to fluoride (Mg/F) mole ratio in zirconium waste to less than 0.5 increased fluoride volatility, and fluoride volatility is independent of: (1) the Mg/F mole ratio in zirconium waste between 0.5 and 1, or (2) whether $Mg(NO_3)_2$ is added to the waste as a solid or a solution.

Calcination of zirconium waste in a 10-cm-diam. (4 in.), fluidized-bed, in-bed combustion calciner using $Mg(NO_3)_2$ to suppress fluoride volatility showed the use of $Mg(NO_3)_2$ to be undesirable;[31] the calcine product produced was too soft (attrition index of 4) for effective fluidized-bed operation since such a product would produce too many fines.

TABLE 3

USE OF CALCIUM NITRATE SUBSTITUTES TO SUPPRESS FLUORIDE VOLATILITY DURING BATCH CALCINATION

Calcination temperature = approximately 500°C

Fluoride suppressing reagents added as nitrates to zirconium waste.

Fluoride Complexing Ion	Mole Ratio of Complexing Ion to Fluoride Ion	wt% Fluoride Volatilized
Fe^{+3}	0.7	6.5
Mn^{+2}	1.0	5.3
Pb^{+2}	1.0	1.7
Cu^{+2}	1.0	6.0
Cr^{+3}	0.7	10.1
Zn^{+2}	1.0	5.7
Ni^{+2}	1.0	3.6
Mg^{+2}	1.0	0.4

5. Nitrate Chemistry - Indirect Heating vs. In-Bed Combustion

Nitrate calcination chemistry is different when zirconium waste is calcined in a calciner heated indirectly than when calcined in a calciner heated by in-bed combustion. This was noted in pilot-plant fluidized-bed calciner studies as well as during the operation of the WCF.[4,32] Most of the nitrate salts in the waste feed decompose on calcination to metallic oxides and nitrogen oxides; the former become part of the bed particles, while the latter leaves the calciner with the off-gas. During calcination using indirect heating, a portion of the nitrogen oxides is absorbed as nitric acid in the aqueous scrubbing solution which dissolved fines removed from the off-gas. During calcination using in-bed combustion, insufficient acid is formed; consequently, it is necessary to add concentrated nitric acid to the scrubbing system for dissolving fines removed from the off-gas. In the inbed combustion environment at 500°C, the nitrate ion apparently decomposes to nitric oxide (NO) which is not adsorbed, rather than to nitrogen dioxide (NO_2) which adsorbs in water and forms nitric acid. The oxidation of NO to NO_2 is time and temperature dependent, and there is insufficient time for NO to oxidize to NO_2 as the off-gas passes though the scrubbing system; consequently, there is little or no nitric acid adsorbed. In indirect heated calcination, calciner operations were usually at 400°C, and a considerably larger amount of NO_2 was formed on calcination.

6. Chemical Additives to Feeds for Increasing Attrition Resistance of Calcines[30]

Zirconium waste solutions produce a calcine with low attrition-resistance index, and a small product/fines ratio is formed during calcination. A decrease in fines rate would decrease the plugging potential in the off-gas cyclone and the rate of loading of off-gas HEPA filters. The amount of recycling required would be decreased, with a resulting net increase in throughput in the WCF and in the ratio of net gallons of waste per gallon of fuel consumed.

The feasibility of increasing the attrition resistance of calcines by means of chemical additives to the feeds was considered. The compositions of various waste solutions were compared with the attrition-resistance indexes of the product calcines that had been produced in the pilot plant. From the differences in compositions, the following potential additives for the control of attrition rates were suggested: (1) sodium nitrate in concentrations below that which would cause fluidized-bed particle agglomeration, and (2) aluminum nitrate with boric acid.

7. Calcination History

Zirconium waste was first calcined in the second WCF campaign beginning in 1966.[2] It is still the primary waste now calcined and a total of 5216 m^3 (1,368,000 gal) has been calcined up through the seventh campaign. Table 4 shows the campaigns and the amount of zirconium waste calcined for each campaign.

The 416 m^3 (110,000 gal) of zirconium waste calcined in the second campaign was run continuously from November 1966 to March of 1968. During operation 10% excess calcium, i.e., a Ca/F ratio of 0.55, was added to ensure adequate suppression of the fluoride volatility. Although the addition of the calcium nitrate to the zirconium waste feed converted the solution to a thin slurry, no significant feed control problems were encountered during the campaign. The 10% excess calcium has been used for all zirconium feed.

The WCF operation for the third campaign began in August 1968.[3] A total of 1811 m^3 (312,000 gal) of zirconium waste was converted to solids in the 11-month operating period. A 4-week shutdown occurred in November and was caused by excessive calcium nitrate solids in the feed. Normally 3% by weight, the calcium nitrate concentration in the solids had risen to 17% by weight. The high calcium nitrate composition had been caused by excessive addition of aqueous calcium nitrate to the WCF feed. When the addition rate of calcium nitrate was reduced, a reduction in calcium nitrate concentration in the solids followed, and the mass median particle diameter (MMPD) began to grow as observed in a previous shutdown. As before, excessive MMPD growth was halted only when water feed to one nozzle was used for a brief period. To eliminate this occasional need to feed water to the WCF, and to eliminate wide MMPD variations, a 10% water dilution of all waste feed batches introduced to the WCF was begun on February 20. The amount of dilution was reduced to 7.5% on February 27, which appeared to be a sufficient degree of feed dilution. Dilution of each feed batch was eliminated when 30.3 m^3 (8,000 gal) of water were added to the ICPP storage tank containing the zirconium waste (WM-189). This water addition permanently diluted the zirconium waste stored there by approximately 7-1/2%.

TABLE 4

VOLUME OF ZIRCONIUM LIQUID WASTE CALCINED

WCF Run # (Dates)	Volume Zirconium Type Waste Calcined
2 (1966-68)	413 m^3 (109,000 gal)
3 (1968)	1181 m^3 (312,000 gal)
4 (1971)	825 m^3 (218,000 gal)
5 (1971-72)	893 m^3 (236,000 gal)
6 (1973-74)	1030 m^3 (272,000 gal)
7 (1975-77)	874 m^3 (221,000 gal)

The fourth WCF processing campaign began in August 1971 and ran continuously for six months.[4] The efficiency was improved due to the replacement of the NaK tube bundle heat exchanger with the present in-bed combustion system. A 100% onstream time made it possible to calcine 825 m^3 (218,000 gal) of zirconium type waste.

The fifth processing campaign extended from September 1971 through May 1972.[5] During this campaign, approximately 893 m^3 (236,000 gal) of zirconium type waste was converted to a solid. Calcium nitrate normally added as a liquid, was added as a solid on a demonstrational basis during October and November. Based on satisfactory test results, addition of solid calcium nitrate was planned for future campaigns.

The sixth processing campaign operated between May 1973 and May 1974, reducing the amount of zirconium waste by 1030 m^3 (272,000 gal). Except for startups, calcium nitrate was added as a solid. There were no major problems with the feed during the run.

In the Campaign 7, 874 m^3 (221,000 gal) zirconium waste was calcined between June 1975 through March 1977. Calcium nitrate was added as a solution during startups and until the bed was stabilized; the calcium nitrate was then added as a solid. Silica gel from the system was accidently washed into the waste hold tanks. The feed system plugged and the process was shut down. The silica was dissolved with caustic.

V. Stainless Steel Sulfate Waste

1. Characteristics

Spent stainless steel containing nuclear fuel elements were dissolved in the presence of steel wool with sulfuric acid followed by treatment with nitric acid to dissolve the uranium at the ICPP. Approximately 160 m^3 (42,000 gal) of this stainless steel sulfate waste was generated by this process. The concentrations of the major constituents in the waste are given in Table 5. The waste was stored in 115 m^3 (30,000 gal) tanks which do not have a secondary containment shell (WM-104, -105, and -106). Stainless steel fuels are currently dissolved electrolytically in nitric acid, thus no more stainless steel sulfate waste will be generated at the ICPP.

TABLE 5

COMPOSITION OF STAINLESS STEEL SULFATE WASTE

Component	Concentration
H^+, $\underline{M}$	3.15
Cr, $\underline{M}$	0.02
Ni, $\underline{M}$	0.01
NO_3, $\underline{M}$	2.48
SO_4, $\underline{M}$	0.56
Fe, ppm	0.07
SpGr	1.23
Dissolved Solids, g/L	209
Undissolved Solids, g/L	3.5

2. Stability Studies

For improved liquid storage safety, it was desirable to transfer the stainless steel sulfate waste from the 115 m^3 (30,000 gal) single containment tanks to the larger double containment tanks. This means that this waste would have to be added to one of the wastes contained in the larger tanks. Stability studies were made on blends of stainless steel sulfate waste with aluminum nitrate-nitric acid waste and with zirconium fluoride waste. Stability studies showed that blends varying from 10 vol% stainless steel-90% aluminum raffinate to 90 vol% stainless steel-10 vol% aluminum raffinate were stable for greater than 6 months when stored at 35°C.[26] Studies were undertaken to determine the stability of blends containing 5-15 vol of zirconium fluoride waste to 1 vol of stainless steel sulfate waste stored at 24 and 35°C for 6 months.[28] All the blends studied contained a trace of solids within 30 min; no increase in solids content was noted after 8 days of storage. The solids were fine and easily dispersed. The solids content of the blends was independent of blend concentration between 5 to 15 vol of zirconium fluoride waste per volume of stainless steel sulfate waste and storage temperature between 24 and 35°C. The weight of solids in the blends after 6 months of storage was 0.37 g/L; the volume of packed solids was 0.24 cc solid/L of waste. Solids resulting from blending 140 m^3 (37,000 gal) of sulfate waste with 938.7 m^3 (248,000 gal) of zirconium fluoride waste would amount to 0.15 cm (0.06 in.) on the bottom of a 1,135.5 m^3 (300,000 gal) storage tank.

3. Flowsheet Development

In 1961, stainless steel sulfate waste was found to be calcinable in several runs of less than 40-h duration in a 15-cm-diam. (6-in.) indirectly heated, fluidized-bed calciner.

A major problem foreseen in the calcination of the stainless steel sulfate waste in the WCF was sulfate volatility. Sulfuric acid is potentially volatile at calcination temperatures (400-500°C). If the sulfate was not retained in the bed, it could accumulate in the scrubbing system and cause excessive corrosion to the stainless steel equipment. Aluminum sulfate is thermally stable at calcination temperatures; thus, an obvious approach to inhibit sulfate volatility was to blend the stainless steel sufate waste with aluminum nitrate-nitric acid waste. Laboratory studies in which these two wastes were blended in different proportions indicated that a blend in which the aluminum to sulfate mole ratio is 0.73:1 would cause less than 0.8% of the sulfate to be volatilized.[17]

Development work in 10- and 30-cm-diam. (4-and 12-in.) pilot plant calciners heated by in-bed combusion demonstrated that the blend of stainless steel sulfate and aluminum nitrate-nitric acid wastes with an aluminum to sulfate mole ratio of 0.73:1 could be calcined successfully.[26] Low SO_2 concentrations in the off-gas stream and only slight increases in the sulfate concentration in the scrub solution indicated adequate sulfate retention in the calcined solids during these tests. Corrosion of the stainless steel equipment was minimal. However, a high fines rate was experienced in a five day run in the 30-cm-diam. calciner using this feed. Further scoping studies in the 10-cm-diam. calciner demonstrated that the addition of 0.5 g/L of boric acid to the feed increased the particle hardness by approximately 150%, thus eliminating the excessive fines rate problem.

This flowsheet was tested in the WCF twice during the fifth processing campaign.[5] In both cases, there was a rapid buildup of pressure across the final filters in the off-gas system. The cause was thought to be sorption of water by stainless steel sulfate solids entrained in the WCF off-gas and retained on the filters. In laboratory tests, sulfates likely to have been on WCF off-gas filters were found to be hygroscopic and, if present on the filters, could have caused a pressure drop buildup across the filters.[33] Analysis of WCF filters to date have not proven that the sulfates tested were present in significant amounts on the filters.

A flowsheet was successfully developed in the pilot-plant calciners for calcining the stainless steel sulfate waste by blending it with zirconium waste and adding $Ca(NO_3)_2$ to give a 0.55 Ca:F mole ratio for fluoride complexing.[28] The blend ratio chosen was 1 vol of stainless steel sulfate waste to 6.7 vol of zirconium waste as this is the ratio which would result if 140 m^3 (37,00 gal) of stainless steel sulfate waste (the total inventory on January 1, 1974) were blended with 940 m^3 (248,000 gal) of zirconium waste in a single waste storage tank. A depression in the agglomeration temperature of the calcined product resulted when the stainless steel sulfate waste was blended with the zirconium waste. Because of this, a 1:6.7 or more dilute blend was recommended for WCF processing. Stability studies indicated that only a minimal amount of solids would be formed with a 1:6.7 blend ratio.[28] This flowsheet was successfully tested in the WCF between January 16 and February 6, 1974. Approximately 19 m^3 (5000 gal) of the stainless steel sulfate waste was jetted to WC-114 in three different transfers. WC-114 served as a hold tank for the stainless steel sufate waste. It was then blended at an average ratio of 1:6.2 with zirconium waste. Calcium nitrate and scrub recycle were added.

After successful demonstration of the 1:6.2 stainless steel sulfate to zirconium waste flowsheet in the WCF, the stainless steel sulfate waste was transferred to two of the 1136 m^3 (300,000 gal) waste storage tanks (68 m^3 (18,000 gal) to WM-188 and 72 m^3 (19,000 gal) to WM-189) where it was mixed with zirconium waste.

VI. Stainless Steel Nitrate Waste

1. Characteristics

Stainless steel nitrate waste is generated at the ICPP by the electrolytic dissolution of EBR-II (stainless steel) reactor fuel in nitric acid. Table 6 shows the concentration of the major constituents in the four different types of EBR-II first-cycle wastes generated. The stainless steel nitrate waste is currently stored in waste tanks WM-100, WM-101, WM-102, and WM-183. The stainless steel nitrate waste stored in WM-183 has been mixed with aluminum nitrate-nitric acid waste and other non-fluoride wastes. Second- and third-cycle wastes have been mixed with the stainless steel nitrate waste stored in WM-100, WM-101, and WM-102. Compositions of the waste solutions stored in these three tanks are given in Table 7.

TABLE 6

COMPOSITIONS OF EBR-II RAFFINATES

	Stainless Steel g/L	Na M	Gd M	Fissium[a] g/L	Al M	NH_4^+ M	H^+ Na	NO_3 M
Fuel Assemblies Raffinate	6.8	0.007	0.0025	0.37	0.2	0.07	2.2	3.2
Raffinate from Aluminum cans with clad pins	3.0	0.004	0.005	0.4	0.5	0.07	2.2	3.6
Raffinate from Aluminum cans with bare pins or Ingots	---	---	0.005	0.4	0.5	0.07	2.2	3.5
Skull Oxide Raffinate	---	---	0.007	0.23	0.57	0.07	2.2	3.6

(a) Approximately 49% Mo, 39% Ru, 6% Rh, 4% Pd, 2% Zr, and 0.2% Nb.

2. Stability Studies

Stability studies were made of stainless steel nitrate waste blended with aluminum nitrate-nitric acid waste and with zirconium fluoride waste in case it became desirable to blend the stainless steel nitrate waste deliberately with another raffinate to improve the flexibility of tank farm storage. All blends of stainless steel nitrate waste with aluminum nitrate-nitric acid waste studied (10 vol% stainless steel-90% aluminum raffinates to 90 vol% stainless steel-10% aluminum raffinates) were stable for greater than 6 months at 24-35°C.[33] The

TABLE 7

COMPOSITIONS OF WASTES STORED IN WM-100, WM-101, AND WM-102

	WM-100	WM-101	WM-102
Na, ppm	586	510	508
SO_4^{-2}, M	0.04	0.04	0.083
H^+, M	0.66	1.26	1.05
Al^{+3}, M	1.2	0.61	0.65
NH_4^+, M	<0.51	<0.51	<0.51
NO_3^-, M	5.25	3.34	3.68
F^-, ppm	486.1	130.1	49.5
Gd, M	---	0.021	0.0169
Fe, M	0.0733	0.0644	0.0644
Cr, M	0.0035	0.0152	0.0121
Zr, M	0.0083	---	---
Mo, M	---	0.0025	0.0023
Ni, M	0.0017	0.0078	0.0058
Volume, m^3 (gal)	56 (14,800)	69 (18,200)	66 (17,500)

stability of 1 vol of stainless steel nitrate waste blended with 1, 5, and 10 vol of zirconium fluoride waste was studied at 24 and 35°C for 6 months.[30] All blends were unstable within 1 h; the solids content of blends did not appear to increase after 2 days of storage. Solids from all blends were finely divided and easily dispersed in the solution. At the end of 6 months, blends stored at 35°C contained more solids than blends of the same composition stored at 24°C, and the content of solids increased as the volume ratio of zirconium to stainless steel waste increased. After 6 months of storage, solids content of the blends varied from 0.04 g solids/L of waste (1.7 cc solids/L of waste) for a 1 vol stainless steel - 1 vol zirconium wastes blend stored at 24°C, to 0.11 g solids/L of waste (4.2 cc solids/L of waste) for a 1 vol stainless steel - 10 vol zirconium wastes blend stored at 35°C. The quantity of solids on the bottom of an ICPP 1136 m^3 (300,000 gal) tank containing 1080 m^3 (285,000 gal) of zirconium-stainless steel wastes blends would vary from 1 cm (0.4 in.) deep if 1 vol stainless steel - 1 vol zirconium wastes blend was at 24°C, to 2.5 cm (1 in.) deep if 1 vol stainless steel - 10 vol zirconium wastes blend was at 35°C.

3. Flowsheet Development

Transformation studies, including heating of synthetic mixtures at moderate pressure, differential thermal analysis, and calcination in a laboratory scale fluidized-bed calciner indicated that the use of moderate amounts of additives such as boric acid, phosphoric acid, aluminum nitrate, rare earths, and combinations of these would not prevent the formation of alpha-iron-chromium oxide.[15] Of the additives tested, rare earths were the most effective for the suppression of the crystalline species. Similar studies on simulated nichrome solutions indicated that crystalline nickel oxide would be formed despite the use of additives.[15] The effects of these crystalline species on the calcination of this waste were unknown. Vander Wall investigated the thermal decomposition of ferric nitrate nonahydrate, chromium nitrate nonahydrate, aluminum nitrate nonahydrate, and nickel nitrate hexahydrate and mixtures of these compounds with a thermal balance.[6] He concluded that calcination of stainless steel nitrates to the oxides was feasible in the 400-500°C temperature range. DTA-X-ray studies on the thermal decomposition of simulated stainless steel nitrate waste and simulated stainless steel nitrate waste blended with aluminum nitrate-nitric acid waste showed that all nitrates in the wastes would be converted to stable oxides at temperatures below 500°C.[7] These oxides were stable at and above 500°C.

Studies in a 10-cm-diam. (4 in.) fluidized-bed in-bed combustion calciner showed blends of stainless steel nitrate waste with aluminum nitrate-nitric acid waste could be calcined successfully over a wide blend ratio.[33] These studies became academic when sodium containing wastes were added to waste tank WM-183 along with the aluminum nitrate-nitric acid waste and stainless steel nitrate waste already stored in the tank. There was no additional aluminum nitrate-nitric acid waste to blend with new stainless steel nitrate waste being generated.

Flowsheet development studies of blends of various ratios of stainless steel nitrate and zirconium wastes were initiated in 1974.[28] It was found that stainless steel nitrate waste and a 1:1 blend of stainless steel nitrate waste with zirconium waste, when tested in a 10-cm-diam. (4 in.) pilot-plant calciner using in-bed combustion heating produced an excessive amount of fines. Further tests in this pilot-plant calciner demonstrated the feasibility of 1:3, 1:5, and 1:10 blends of stainless steel nitrate and zirconium wastes for use in the WCF.

Processing of a low fluoride waste at the end of a WCF campaign would flush out the system and reduce the amount of decontamination required for a WCF turnaround. Stainless steel nitrate waste was considered for this application and a pilot-plant calcination program for this waste was initiated. Tests in 10- and 30-cm-diam. (4 and 12 in.) pilot-plant calciners demonstrated the calcinability of the waste stored in WM-100 and of the waste stored in WM-101 after being concentrated by a factor of three. The waste stored in WM-102 is similar to that stored in WM-101 and will be processed in the same manner as that waste.

VII. WM-183 Waste

1. Characteristics

Waste storage tank WM-183 contains a mixture of aluminum nitrate-nitric acid waste, evaporator bottoms, stainless steel nitrate waste, and other non-fluoride wastes. The concentrations of the major constituents in WM-183 waste are shown in Table 8.

2. Stability Studies

Waste storage tank WM-183 first contained aluminum nitrate-nitric acid waste. Stainless steel nitrate waste was then added to the aluminum waste since previous results indicated that all blends of the aluminum and stainless steel wastes were stable. When it became necessary to add sodium-bearing waste to the tank containing aluminum and stainless steel wastes, a study was performed to observe the stability characteristics of the resulting aluminum-stainless steel-sodium-bearing wastes blend. A study was made on a blend of 1 vol aluminum waste-1 vol sodium waste-5 vol stainless steel waste stored at 24°C for 196 days. The blend was stable for 57 h, at which time a fine and easily dispersible solid began to form. The solid content did not increase after 88 days of storage. After 196 days of storage, there was 0.3 cc/L (<0.03 g/L) of solids in the blend. The amount of solids on the bottom of an ICPP 1136 m^3 (300,000 gal) tank containing 1080 m^3 (285,000 gal) of this blend at 24°C would be 0.18 cm (0.07 in.) deep.

One month duration stability studies were made on various blends of WM-183 and concentrated WM-183[a] wastes with zirconium fluoride waste (with and without calcium or magnesium nitrate added) at 24 and 35°C to determine the quantity of solids produced.[34] Since the wastes in question would be blended in the calciner hold tanks and calcined within a few days, long-term testing was unnecessary. Blends studies were: (1) 1 vol zirconium waste with 1-3 vol WM-183 waste, (2) 1 vol WM-183 waste with 2 vol zirconium waste, (3) 1 vol zirconium waste with 1 or 2 vol of concentrated WM-183 waste, and (4) 1 vol concentrated WM-183 waste with 1-3 vol zirconium waste. These blends were studied with and without calcium or magnesium nitrate added to give the blend a calcium or magnesium to fluoride mole ratio of 0.7. Zirconium fluoride waste routinely calcined in the WCF with a calcium to fluoride mole ratio of 0.55 contains 70 g/L solids; the maximum amount of solids found in any of the zirconium waste - WM-183 waste blends was 50 g/L. None of the WM-183 - zirconium wastes blends studied should produce enough solids to plug nozzles, valves, and lines in the WCF feed system.

3. Flowsheet Development

Differential thermal analysis[34] indicated that the calcination of WM-183 waste without additives would result in fluidized-bed particle agglomeration. This is probably due to the high sodium content (0.67 M)

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

TABLE 8

COMPOSITION OF WM-183 WASTE

Constituent	Concentration
H^+, N[a]	1.4
Al, M	0.65
Na, M	0.67
K, M	9.7×10^{-2}
Cl^-, ppm	255
F^-, ppm	304
NO_3^-, M	4.4
SO_4^{-2}, M	7.6×10^{-2}
PO_4^{-3}, M	7.0×10^{-4}
Ca, M	7.0×10^{-2}
Cr, M	8.1×10^{-3}
Cu, M	7.1×10^{-4}
Fe, M	3.9×10^{-2}
Mg, M	2.1×10^{-2}
Mn, M	9.1×10^{-3}
Ni, M	3.6×10^{-3}
B, M	2.9×10^{-3}

of the waste. It was hoped that the aluminum in WM-183 waste would react with enough of the sodium nitrate ($NaNO_3$) present to form sodium aluminate below 500°C so that fluidized-bed particle agglomeration would not occur (the melting point of sodium aluminate is 1650°C). The DTA curve for WM-183 waste shows that some of the $NaNO_3$ was converted to the aluminate, but that molten, undecomposed $NaNO_3$ was present up to a temperature of 847°C. Thus, calcination of WM-183 waste would result in fluidized-bed particle agglomeration. Attempts to calcine WM-183 waste without additives in pilot-plant calciners proved unsuccessful due to high fines generation; this was attributed to dilute feed. The fines produced in these tests were sticky. Laboratory studies indicated that WM-183 waste could be concentrated to 60% of its original volume without stability loss.[34] Subsequent pilot-plant studies were conducted using the concentrated WM-183 waste. Calcination of concentrated WM-183 waste in pilot-plant calciners produced sticky calcine.

Experience with simulated Allied General Nuclear Services (commercial) waste showed that the addition of powdered iron to the waste was an effective method for eliminating the stickiness and caking tendency of the bed associated with wastes containing large amounts of sodium.[35] DTA-X-ray diffraction techniques were used to determine if the addition of powdered iron to WM-183 waste might prevent agglomeration during calcination.[34]

A DTA-X-ray analysis was made on simulated WM-183 waste to which sufficient nitric aid and powdered iron were added to give 0.7 mole iron and 3 moles nitric acid present in the waste for every mole of sodium present. Iron decomposes the nitric acid present in the waste, so additional nitric acid must be added to prevent hydroxide precipitation as the waste becomes basic. The DTA curve showed that all the $NaNO_3$ present had been converted to sodium aluminate or ferrate at a temperature of 655°C. Thus, addition of powdered iron to WM-183 waste showed sufficient promise for eliminating agglomeration during calcination to warrant additional studies in a pilot-plant calciner. The fact that the temperature range extended above the normal operating temperature of the WCF (500°C) may indicate that addition of powdered iron to WM-183 waste will not convert enough of the $NaNO_3$ present to ferrate at 500°C to prevent particle agglomeration.

Tests on the calcinability of concentrated WM-183 waste with iron addition were made in the pilot-plant calciners. Gas is vigorously evolved when powdered iron is added to WM-183 waste. A laboratory study showed the approximate composition of the gas to be (% by volume): 0.05% H_2, 20.8% N_2, 0.23% O_2, 0.19% Ar, 0.29% CO_2, and 78.4% NO_x.[36] Thus, hydrogen in the gas that evolved was present in quantities too small to present an explosion hazard. Results of 10-cm-diam. (4 in.) pilot plant tests indicated that calcination of concentrated WM-183 waste waste was possible without significant operating problems by adding 0.5 to 1 mole of iron per mole of sodium to the waste prior to calcination.[36] However, a 10-day run in a 30-cm-diam. (12 in.) pilot plant calciner using 0.75 mole of iron per mole of sodium in simulated concentrated WM-183 waste was terminated due to excessive particle agglomeration in the fluidized bed.

The chloride in the feed volatilizes and accumulates in the scrub system. Attempts to retain the chloride in the bed were made, as volatile chloride would cause excessive corrosion to the off-gas scrubbing system. Studies were conducted in which silver nitrate was added to the feed, and the silver chloride which formed was allowed to remain in the feed during calcination. These studies indicated that the addition of silver nitrate to WM-183 waste that had been treated with iron would retain the chloride in the bed during calcination.[34]

Blending of sodium-bearing waste with zirconium waste showed promise in preventing agglomeration during calcination; thus, blending WM-183 waste with zirconium waste was considered. DTA-X-ray analyses were made on blends of 3 vol zirconium waste - 1 vol WM-183 waste and 1 vol zirconium waste - 1 vol WM-183 waste to determine if this blending would complex the sodium present in WM-183 waste as Na_3AlF_6.[34] The DTA curves for both blends were similar. The DTA curve for the 1 vol zirconium - 1 vol WM-183 wastes blend showed that the $NaNO_3$ in the blend was complexed as Na_3AlF_6 between 474 and 694°C. The Na_3AlF_6 formed at a lower temperature range in the zirconium waste -

WM-183 waste blends studied by DTA-X-ray diffraction than in the zirconium waste - sodium-bearing waste blend studied by the same technique.[37] Thus, blending WM-183 waste with zirconium waste showed promise for eliminating agglomeration during calcination of the waste.

A flowsheet developed for the calcination of intermediate-level sodium-bearing waste recommended a blend with zirconium waste such that the zirconium to sodium (Zr/Na) mole ratio was no less than 0.85. Based on this, a series of tests in a 30-cm-diam. (12 in.) pilot-plant calciner was conducted using a 2:1 blend of zirconium and concentrated WM-183 wastes. This corresponds to a Zr/Na mole ratio of 0.81. Calcium nitrate were used as an additive in these tests. Chloride retention in calcine using blends of zirconium and WM-183 wastes has been excellent probably due to the high aluminum to fluoride (Al/F) mole ratio in the blend. A high Al/F mole ratio was found to aid chloride retention in the bed in tests on blends of sodium-bearing waste with zirconium waste in a 10-cm-diam. (4 in.) pilot-plant calciner. A test was planned in a 30-cm-diam. (12 in.) pilot plant calciner using the most promising of the feed blends tested in the 10-cm-diam. (4 in.) calciner (a 2:1 blend of zirconium and concentrated WM-183 wastes with calcium nitrate added such that the Ca/F mole ratio was 0.75). However, a study revealed that the concentration of WM-183 waste in plant evaporators appeared unfeasible due to the probable corrosive attack by the WM-183 waste on the heat exchanger tube bundles. The 102-h test in the 30-cm-diam. (12 in.) calciner was changed such that the first 68 h was run using concentrated WM-183 waste and the last 34 h was run using unconcentrated WM-183 waste. The test was successful; it was found that the blend was calcineable using either concentrated or unconcentrated WM-183 waste. The flowsheet using the blend with concentrated WM-183 waste and a Ca/F $\underline{M}$ ratio of 0.7 was recommended for use in the WCF. The flowsheet using the blend with unconcentrated WM-183 waste will be used as an alternate.

VIII. Sodium-Bearing Waste

1. Characteristics

Aqueous radioactive wastes generated at the ICPP, other than those from first-cycle extraction of uranium, are called sodium-bearing (formerly called second-cycle) wastes. Sodium-bearing wastes include aqueous radioactive wastes from the second and third-cycle extraction processes, several chemical laboratories, the hot pilot-plant, the Multicurie Cell, the remote analytical facility, the decontamination facility, the fuel storage basin, waste cell floor drains, as well as process equipment waste. In addition, sodium-bearing waste includes aqueous radioactive wastes received from other facilities at the Idaho National Engineering Laboratory. The chemical composition of sodium-bearing wastes stored in three different waste storage tanks are given in Table 9.

The synthetic waste used in laboratory and pilot-plant calciner support studies is a composite of the wastes in Table 9.

TABLE 9

CHEMICAL ANALYSES OF ICPP SODIUM-BEARING WASTES

Constituent	Molar Concentration Tank WM-181	 Tank WM-184	 Tank WM-186
H^+	1.4	0.14	1.63
Al	0.56	0.59	0.37
Fe	0.011	0.018	0.022
Na	1.59	2.44	1.59
F^-	0.00065	0.0048	0.0065
NO_3^-	4.38	4.64	5.02
B	0.0057	0.0046	0.015
Cl^-	0.032	0.045	0.020-0.031
PO_4^{-3}	0.020	0.028	0.0099
SO_4^{-2}	0.00036	0.00066	0.00061
Hg	0.0050	0.00073	0.0028
K	0.24	0.13	0.23
Mn	0.023	0.0045	0.023

2. Stability Studies

In the event that the storage tanks designated for interim storage of sodium-bearing waste reach their capacity before a flowsheet is developed for calcining this waste, sodium-bearing waste subsequently generated at the ICPP would be stored in tanks containing other wastes. Studies were initiated to determine the stability characteristics of sodium-bearing waste blended with other wastes. When these studies were initiated, a tank of aluminum nitrate-nitric acid waste was available for blending so stability studies were made on blends of sodium-bearing waste and aluminum nitrate-nitric acid waste. The stability of blends of 1 vol sodium-bearing waste with 1-10 vol of aluminum raffinate and 1 vol aluminum raffinate with 5 and 10 vol sodium-bearing waste were studied at temperatures of 24 and 35°C for 6 months.[28] At the end of 6 months, the blend of 1 vol aluminum with 1 vol sodium-bearing waste stored at 35°C contained only 0.043 g/L (0.4 cc/L) of solids; all other blends of aluminum and sodium-bearing wastes contained only trace amounts of residue. All blends of sodium-bearing and aluminum wastes studied would be suitable for long-term storage with the possible exception of the 1 to 1 vol blend.

Stability studies were then conducted with sodium-bearing-zirconium wastes blends. The stability of 1 vol sodium-bearing waste with 1-100 vol of zirconium fluoride waste was studied at temperatures of 24 and 35°C for 6 months.[28,33] All blends were unstable within 1 day. Blends stored at 35°C contained more solids than those stored at 24°C; the volume of solids in the blends increased as the volume ratio of sodium to zirconium waste decreased. The 1 to 1 and greater than 1 to 10 blends contained fine solids which could be easily dispersed and slurried; the 1 to 2 through 1 to 10 blends produced granular or flakey solids which would be difficult to transport by slurrying. The quantity of solids produced from the blends varied from 3.7 g/L (50 cc/L) produced from the 1 to 1 blend stored at 35°C to 0.17 g/L (1.7 cc/L) produced from the 1 to 100 blend stored at 24°C. The amount of solids on the bottom of an ICPP 1136 m^3 (300,000 gal) tank containing 1080 m^3 (285,000 gal) of zirconium-sodium wastes blends would vary from 30 cm (11.8 in.) deep if the 1 to 1 blend was stored at 35°C, to 1 cm (0.4 in.) deep if the 1 to 100 blend was stored at 24°C. Possibly none of the blends of sodium-bearing and zirconium wastes studied would be suitable for long-term storage.

3. DTA-X-ray Studies

The chemistry during pyrolysis of pure sodium nitrate and sodium nitrate mixed with other compounds which might influence its decomposition must be known to better understand the calcination of wastes containing these chemicals. Thus, DTA curves were studied for sodium nitrate and sodium nitrate ($NaNO_3$) mixed with compounds which might make $NaNO_3$ decompose before it melts or combine with $NaNO_3$ to form a stable compound below 500°C (current calcination temperature of the WCF).[37] Compounds tested with $NaNO_3$ were described in the literature as compounds that decompose $NaNO_3$ or form compounds with $NaNO_3$ that are stable up to 700°C.

The thermogram of $NaNO_3$ shows that it melts at 305°C, but may not be completely decomposed until heated to about 833°C; between 305 and 833°C, the sodium nitrate which remains molten can cause the calciner bed particles to agglomerate. Sodium nitrate decomposes to sodium nitrite; the reaction is reversible, and both sodium nitrate and nitrite are volatile. When sodium nitrite is heated, it acts similarly to the nitrate. Sodium nitrite melts at 260°C and remains in the molten, undecomposed state between 260 and 888°C. No residue was found in the DTA cup after having heated sodium nitrate or nitrite to 1000°C. If the nitrate or nitrite decomposes to the monoxide or peroxide, the nitric oxide released during the decomposition reacts immediatey with either oxide to reform sodium nitrite. Thus, sodium nitrate or nitrite remains in the molten state until they are vaporized.

DTA curves were run on mixtures of sodium and lead nitrates varying from 95% by weight $NaNO_3$ and 5% by weight lead nitrate to 70% $NaNO_3$ and 30% lead nitrate. The thermogram of the 95% $NaNO_3$-5% lead nitrate mixture, which is typical of the other mixtures, shows that sodium nitrate combines with lead monoxide to form sodium plumbate between 650 and 830°C. Thus, mixing lead nitrate with sodium nitrate would not prevent fluidized-bed particle agglomeration.

Sodium nitrate is decomposed by reducing reagents, which, with the exception of weak reducing reagents such as sugar, would not remain in the oxidizing atmosphere of a calciner long enough to be effective. The thermogram for 76% $NaNO_3$-24% sugar shows $NaNO_3$ decomposing between 420 and 773°C which indicates that sugar does lower the decomposition temperature range of $NaNO_3$ slightly.

DTA curves were made for 68% $NaNO_3$-32% SiO_2, 56% $NaNO_3$-44% high-fired alpha Al_2O_3, 84% $NaNO_3$-16% V_2O_5, 62% $NaNO_3$-38% TiO_2, 55% $NaNO_3$-45% Fe_2O_3, and 95.4% $NaNO_3$-4.6% MgO. Sodium silicate was formed between 410 and 750°C, $NaVO_3$ between 448 and 792°C, Na_2TiO_3 between 501 and 741°C, and $Na_2Fe_2O_4$ between 554 and 675°C. Magnesium oxide and high-fired alpha Al_2O_3 catalyzed the decomposition of $NaNO_3$ between 451 and 562°C and between 396 and 694°C, respectively. All of the oxides lowered the temperature range over which $NaNO_3$ exists in the molten undecomposed state, but probably not enough to prevent fluidized-bed particle agglomeration.

Simulated sodium-bearing waste and sodium-bearing waste combined with aluminum nitrate, zirconium waste, boric acid, or magnesium sulfate were examined by DTA-X-ray techniques.[37] The DTA curve for sodium-bearing waste shows that $Al(NO_3)_3 \cdot 9H_2O$ melts and decomposes to the oxide below 165°C; the $NaNO_3$ melts at 305°C and reacts with aluminum oxide to form the aluminate between 640 and 875°C. The aluminate formation can be decreased to between 456 and 703°C by making the aluminum nitrate concentration sufficient to give a sodium/aluminum mole ratio of 0.9. Prior to DTA-X-ray studies, scoping runs in pilot-plant calciners using zirconium waste blended with sodium-bearing waste had shown that such blends could be used to prevent bed agglomeration during calcination of sodium-bearing waste. The thermogram of a blend of 40% by volume sodium-bearing waste and 60% by volume zirconium waste showed that the $NaNO_3$ was converted to Na_3AlF_6 between 446 and 766°C. Ortho boric acid converts the sodium nitrate of sodium-bearing waste to sodium monoxide-boric oxide glasses at 394 to 622°C; magnesium sulfate converts sodium nitrate to sodium sulfate at 352 to 647°C. DTA-X-ray analyses show that aluminum nitrate, zirconium waste, boric acid, or magnesium sulfate added to sodium-bearing waste would lower the temperature range at which $NaNO_3$ exists in the molten, undecomposed state. However, there was a good possibility that this temperature range is not low enough to prevent fluidized-bed particle agglomeraton.

DTA-X-ray examination of wastes containing sodium shows that the sodium in commercial wastes reacts with dissolved powdered iron to form sodium ferrate over a calcination temperature range (301-419°C) 200°C below the temperature where sodium ferrate is formed in ICPP sodium-bearing waste (536-707°C).[38] Sodium ferrate must form at temperatures below 500°C in these wastes to prevent fluidized-bed particle agglomeration during calcination. Further DTA-X-ray studies showed that the temperature at which sodium ferrate forms in ICPP sodium-bearing waste cannot be decreased by adding to the ICPP waste constituents present in commercial wastes, but not in the ICPP waste, prior to iron addition. Aluminum nitrate is present in the ICPP waste but not usually in commercial wastes. The temperature at which sodium ferrate forms in commercial wastes cannot be increased by adding aluminum nitrate to the waste prior to iron addition.

4. Flowsheet Development

Initial attempts to calcine sodium-bearing waste were unsuccessful due to severe fluidized-bed particle agglomeration. Fluidized-bed calcination of sodium nitrate-containing wastes present special problems as the large temperature range over which sodium nitrate exists in the molten, undecomposed state (300-850°C) makes fluidized-bed particles prone to agglomeration. Another problem to be considered in the calcination of sodium-bearing waste is the high concentration of chloride in the waste; approximately 1000 ppm. Volatilized chloride causes excessive corrosion to off-gas cleanup equipment in the fluidized-bed calciner system. Laboratory and pilot-plant studies were conducted to determine the effectiveness of additives for causing sodium nitrate decomposition or conversion to stable compounds within the temperature range of fluidized-bed calcination, and for retention of chloride in the bed. The effectiveness of additives to prevent fluidized-bed particle agglomeration was usually first scoped by DTA-X-ray diffraction techniques and additives showing promise were then studied using pilot-plant calciners. Additives studied in pilot-plant calciners were:[27,28,33,39-41]

zirconium fluoride-aluminum nitrate waste
aluminum nitrate-nitric acid waste
sugar
iron powder
boric acid
phosphoric acid
oxalic acid
sulfuric acid

Boric acid, phosphoric acid, and oxalic acid were all ineffective as additives to the feed in preventing caking in the calciner. Boric acid was added because of its influence on alpha alumina formation. However, based on analysis of calciner cyclone fines, alpha alumina was not present in the calcined product, therefore, the addition of boric acid was not necessary, as it is with first-cycle aluminum waste, to prevent the formation of troublesome alpha alumina during the calcination of second-cycle waste. Phosphoric acid was added to test the effect of its known tendency to form glass-like materials with sodium compounds when calcined. It did indeed form glassy coatings on heat transfer surfaces which interfered with operation before any bed caking became evident. Addition of oxalic acid, known to be the final degradation product in the denitration of acidic waste with sugar, appeared to have no effect on the process of bed caking.[39]

The addition of sugar to the feed in a proportion of 4 g of sucrose/g of sodium proved to be calcinable at 500°C in indirectly heated pilot-plant calciners. In addition, a decided heat benefit was gained during calcination by adding sugar to the feed due to the combustion of the sucrose. However, in subsequent tests using an in-bed combustion pilot-plant calciner, incomplete combustion of the sugar caused severe plugging in the off-gas and scrubbing systems and agglomerates in the fluidized bed were found.

Pilot-plant tests using simulated AGNS (commercial) feeds[35] had indicated that the use of iron powder as an additive to the waste would combine with sodium upon calcination to form sodium ferrate, thus preventing fluidized-bed particle agglomeration associated with sodium nitrate. A pilot-plant test in a 10-cm-diam. (4 in.) calciner using iron powder as an additive to sodium-bearing waste, in which the iron to sodium mole ratio was 1.5, and calcium nitrate as an additive to complex chloride was unsuccessful. Formation of clinkers in the fluidized bed forced termination of the test after 8 h.

Addition of sulfuric acid to sodium-bearing waste was considered as a method of preventing agglomeration in the fluidized bed during calcination. Sulfuric acid added to simulated sodium-bearing waste during pilot-plant studies caused the formation of copious quantities of fine precipitate in the waste after a variable induction period. Since the precipitate caused calciner nozzle plugging problems, laboratory studies were performed to determine the cause of the precipitation and methods of preventing it.[26] Precipitate formation was found to be a solubility problem; if the waste was sufficiently diluted with water prior to sulfuric acid addition, no precipitate would form. However, the waste was too dilute to build bed in tests in a 10-cm-diam. (4 in.) calciner. Adding the sulfate as magnesium sulfate would prevent precipitation in the feed; however, the magnesium concentration caused soft calcine to be formed and an excessive amount of fines was produced.

Several runs of short duration were made in a 10-cm-diam. (4 in.) pilot-plant calciner using blends of aluminum nitrate-nitric acid and sodium-bearing wastes. The runs were successful; however, sodium nitrate was detected in the calcined solids, and it was suspected that runs of longer duration would result in agglomeration of the fluidized-bed particles. Testing of blends with aluminum nitrate-nitric acid waste was discontinued when the last of this waste was blended with stainless steel nitrate waste in the Tank Farm. The aluminum nitrate-nitric acid waste would no longer be available for blending with sodium bearing waste because of mixing with zirconium fluoride in the coprocessing procedure.

Blending zirconium and sodium-bearing wastes was found to be successful as long as the fluoride/sodium mole ratio was greater than 1.0. A blend of 1.5 vol of zirconium waste to 1 vol of sodium-bearing waste produced cryolite (Na_3AlF_6) in the fluidized bed upon calcination at 500°C. Cryolite is a stable species to temperatures up to approximately 1000°C. Feeding the 1.5:1 blend of zironium wastes into a ZrO_2-CaF_2 starting bed caused a reaction which resulted in fluidized-bed particle agglomeration within a very short period of time. Subsequent tests used alumina as the starting bed. Further tests using the so-called cryolite flowsheet revealed that excessive corrosion was occurring in the secondary cyclone downstream of the venturi scrubber in the off-gas cleanup system. Laboratory studies indicated that as the solids that were carried over to the secondary cyclone dissolved in nitric acid, the cryolite would dissolve readily, whereas the Al_2O_3 and ZrO_2 dissolved more slowly. Thus, the fluoride would not be complexed by the zirconium and aluminum and would cause excessive corrosion at this point in the system. Aluminum nitrate was added to the scrub solution in several subsequent tests to complex the fluoride, however, the increased aluminum in the feed due to scrub solution recycle caused fluidized-bed agglomeraton. Excessive chloride volatility also added to the corrosion problem in the off-gas cleanup system. The cryolite flowsheet was then abandoned as a method for calcination of sodium-bearing waste.

Other blends of zirconium and sodium-bearing wastes were tested in which, unlike the cryolite flowsheet, calcium nitrate was used to complex the fluoride during calcination. Calcium nitrate also helps control chloride volatility. A number of tests were conducted using various blend ratios of zirconium and sodium-bearing wastes with calium nitrate and silver nitrate as additives to suppress chloride volatility. Results of these tests indicated that silver-nitrate was ineffective to control chloride volatilization. Tests continued, using several blend ratios of the two wastes with calcium nitrate added for a Ca/F mole ratio of 0.5 at calcination temperatures between 400 and 550°C. Chloride volatilization continued to be a problem, and noduled calcine was produced causing poor fluidization and resultant clinker formation around the fuel nozzle. One method to overcome this problem was to alternately calcine the blend of zirconium and sodium-bearing waste with straight zirconium waste. However, this provided a very low depletion rate for the sodium-bearing waste. A 5:1 blend of zirconium and sodium-bearing wastes with calcium nitrate added for a Ca/F mole ratio of 0.7 was tested successfully in a 10-cm-diam. (4 in.) pilot-plant calciner at 500°C. The calcine produced in this test was not noduled. Further testing proved that a 3:1 blend of zirconium and sodium-bearing wastes with calcium nitrate added for a Ca/F mole ratio of 0.7 could be successfully calcined in a 30-cm-diam. (12 in.) pilot-plant calciner at 500°C. Approximately 70% of the chloride in the feed could be retained in the bed. This flowsheet was recommended for WCF operation.

A significant amount of gelatinous solids are formed when calcium nitrate is added to zirconium waste. It was found that less solids were formed when the calcium nitrate was added to the blend of zirconium and sodium-bearing wastes recommended for WCF operation. It was thought that the higher Al/F mole ratio in the blend was responsible for this effect. Studies were undertaken to further reduce the amount of solids in the feed solution and preserve the calcinability of the blend. Methods considered were: (1) substituting magnesium nitrate for calcium nitrate as an additive for fluoride complexing, and (2) using calcium nitrate as the fluoride complexing additive and increasing the aluminum concentration. Magnesium and calcium nitrates are roughly equivalent in their effect on chloride and fluoride volatility, calciner operability, and properties of calcine produced when used during the calcination of zirconium fluoride-sodium-bearing wastes blends. Two differences are: (1) more chloride is in the fines than in the product when magnesium nitrate is used, while the reverse is true when calcium nitrate is used, and (2) calcine produced with mangesium is softer than with calcium nitrate.[29,31,38,42] Increasing the aluminum concentration in the feed blend from a 0.28 to 0.32 Al/F mole ratio using calcium nitrate as the fluoride complexing agent was found to eliminate the gelatinous behavior of the residue and reduce the amount of solids from 42 to 17 g/L in the solution.[30]

Laboratory experiments were conducted to test methods for decreasing the concentration of chloride in sodium-bearing waste prior to calcination.[43] During calcination of sodium-bearing waste in the WCF, a high concentration of chloride in the off-gas scrubbing solution would cause significant corrosion of the off-gas equipment. The objective of the laboratory studies were: (1) to evaluate candidate processes selected from the literature for reducing the concentration of chloride to 50 ppm or less, (2) to obtain a preliminary evaluation of the complexity of the removal process, the type of equipment required, and the compatibility of the processes with present ICPP facilities, and (3) to obtain a preliminary estimate of the cost of the chemicals that are required for a given process. Of eight candidate methods selected from the literature, four appeared to be suitable for plant installation. Two of these methods, potassium permanganate treatment and nitric acid boildown, oxidize the chloride to a volatile form; the other two methods, treatment with mercurous nitrate or silver nitrate, precipiate the chloride as insoluble compounds. Four other methods were eliminated as candidate processes because of inadequate chloride removal or high capital costs estimated for equipment. The more convenient method for avoiding the corrosion problem in the scrubbing system is to develop a process which will retain the chloride in the calcined solids. Pilot-plant studies indicated this could be done; thus, the methods analyzed for decreasing the chloride concentration in the feed solution prior to calcination were not enacted.

The sodium-bearing waste flowsheet consisting of a 3:1 blend of zirconium and sodium-bearing wastes with calcium nitrate added for a Ca/F mole ratio of 0.7 was tested in the WCF near the end of its seventh processing campaign, in January 1977. High chloride concentrations in the scrub and possible fluidized-bed particle agglomeration after six days caused discontinuation of the test. A total of 86 m^3 (2275 gal) of sodium-bearing waste were calcined during the test.

Flowsheets which appeared feasible for the calcination of sodium-bearing wastes from past studies were again scoped in pilot-plant calciners, and again blends with zirconium waste appeared to be the most promising.[38,44] Tests were again conducted using zirconium waste to sodium-bearing waste blend ratios between two and eight in 10- and 30-cm-diam. (4 and 12 in.) pilot-plant calciners. Blend ratios greater than 2:1 were found to be successful in these tests using a Ca/F mole ratio of 0.7. The 3.5:1 flowsheet was recommended for WCF operation.

During April 1978, a 3.5:1 zirconium/sodium-bearing waste blend with a Ca/F mole ratio of 0.7 was successfully calcined in the WCF for 10 days. A mechanical failure in the off-gas scrubbing system forced a shutdown; however, operation using this flowsheet will continue after repairs are made.

IX. Rover Waste

1. Characteristics

The process developed for recovering uranium from nuclear rocket (Rover) fuels required high concentrations of hydrofluoric acid and nitric acid in the dissolver solution to dissolve the uranium and niobium. The resulting dissolver solution is highly corrosive and the fluoride must be complexed by the addition of aluminum nitrate to prevent corrosion of the stainless steel processing equipment downstream of the dissolver. The concentrations of the major constituents expected in Rover waste is given in Table 10. Current plans call for approximately 470 m^3 (125,000 gal) of Rover waste to be generated at the ICPP beginning in July 1979.

TABLE 10

MAJOR CONSTITUENTS OF ROVER WASTE

Constituent	Concentration
Nb, $\underline{M}$	0 - 0.066
U, g/L	2×10^{-4}
NO_3^-, $\underline{M}$	2.7
H^+, $\underline{M}$	2.5
F^-, $\underline{M}$	0.85
Al, $\underline{M}$	0.17
B, $\underline{M}$	0.069

2. Stability Studies

Stability of the Rover dissolver solution depends on precise addition of the aluminum nitrate complexing solution, as the stability range of the complexed solution is narrow. Overcomplexing the fluoride precipitates Nb_2O_5; undercomplexing causes AlF_3 precipitation.

Sufficient tank storage is not available to devote an entire 1136 m^3 (300,000 gal) tank to storage of Rover waste. One alternate is to blend the Rover waste with zirconium fluoride waste. Stability studies were made of blends of 1 vol Rover waste with 1 to 10 vol zirconium fluoride waste at 24 and 35°C for 6 months.[28] All blends were unstable within 20 days. The quantity of solids separating after 6 months was affected only slightly by storage temperature between 24 and 35°C but increased as the ratio of zirconium waste to Rover waste decreased. None of the blends studied were suitable for long-range storage. A 1:1, zirconium/Rover wastes blend at 24°C formed 3 g/L of solids while a 10 to 1 zirconium-Rover wastes blend at 24°C formed 0.39 g/L of solids. Storing the 470 m^3 (125,000 gal) of Rover waste in 3 different tanks each containing 919.8 m^3 (243,000 gal) of zirconium waste, would produce 4.1 cm (1.6 in.) of solids on the bottom of the 3 tanks. The unblended Rover waste was only slightly unstable after 186 days of storage and would be suitable for long-term storage. The unblended Rover waste will be stored in unused 140 m^3 (37,000 gal) storage tanks WM-103, -104, -105, and -106.

3. Flowsheet Development

Attempts to calcine unblended, simulated Rover waste with calcium nitrate added to complex fluoride (0.55 calcium to fluoride mole ratio) in a 10-cm-diam. (4 in.) pilot-plant calciner were unsuccessful due to the production of very soft calcine and agglomeration of the fluidized-bed particles.[28] A blend of two volumes of zirconium waste and one volume of Rover waste with calcium nitrate added for a 0.55 calcium to fluoride mole ratio was successfully demonstrated in a 10-cm-diam. (4 in.) pilot-plant calciner. A 1:1 blend of zirconium and Rover wastes with calcium nitrate added for a 0.55 calcium to fluoride mole ratio was then attempted and found to be calcinable with no apparent problems. Tests of the 1:1 and 1:2 blends of zirconium and Rover wastes were conducted in a 30-cm-diam. (12 in.) pilot-plant calciner.[36,44] Small fragile agglomerates were found in the bed early in the runs; however, they did not increase in size or quantity throughout the remainder of the runs. Due to the fragility of the agglomerates, WCF operation should not be adversely affected. A 1:1 blend of zironium and Rover wastes with calcium nitrate added for a 0.55 calcium to fluoride mole ratio was the flowsheet recommended for WCF operation.

X. Fluorinel Waste

1. Characteristics

Fluorinel waste will be generated at the ICPP during the dissolution of Fluorinel-PWR, zirconium oxide-uranium oxide fuel in hydrofluoric acid-nitric acid solutions complexed with aluminum nitrate. A typical composition predicted for the waste is shown in Table 11.

TABLE 11

EXPECTED COMPOSITION OF FLUORINEL WASTE

Constituent	Concentration
Zr	0.5 $\underline{M}$
F	2.54 $\underline{M}$
Al	0.42 $\underline{M}$
H^+	2.35 $\underline{M}$
NO_3^-	2.28 $\underline{M}$
Cd	0.214 $\underline{M}$
SO_4^{-2}	0.048 $\underline{M}$
Misc. Dissolved Solids	2.09 g/L
Fission Products	0.72 g/L

2. Flowsheet Development

As of May 19, 1978, 6 calciner runs on flowsheet development for Fluorinel waste calcination were completed. All runs were made using the enclosed 10-cm-diam. (4-in.) calciner, because of the inhalation hazards associated with cadmium.

An 80-h run (Run 1) was completed in October 1977, using a design basis waste with a high sulfate concentration (0.39 $\underline{M}$). A higher than normal amount of fines was generated during the run. No significant bed agglomeration occurred.

The composition of the design basis feed was revised and Run 2 was scheduled for November 1977. The major difference in feed composition consisted of lowering the sulfate to 0.048 $\underline{M}$ and the cadmium to 0.17 $\underline{M}$. Two consecutive 8-h runs resulted in forced shutdown due to excessive agglomeration in the bed. Zirconium-type waste was successfully calcined for 24 h during segment 2C; cadmium (0.17 $\underline{M}$) was then added to the zirconium waste feed. After 10 h the run was ended due to excessive agglomerates. From this run, it was postulated that low-melting (approximately 350°C) cadmium nitrate caused the bed agglomeration; this was later confirmed through DTA studies.

Because of bed agglomeration, a new dissolution flowsheet was developed based on a minimum amount of cadmium (0.062 M). A high concentration of boron (0.672 M) was also used in lieu of the cadmium as the nuclear poison during fuel reprocessing. This waste composition also contained a high fluoride concentration (4.35 M). Run 3 consisted of five segments with variation on the minimum cadmium flowsheet. The first segment operated for 13 h before agglomeration forced a shutdown. The next three segments were also ended by agglomeration. Prior to the last segment, the cadmium was removed, the boron was reduced to 0.2 M, and 8% excess aluminum nitrate was added to simulate zirconium waste with a high F^- concentration. This waste was calcined successfully for 24 h.

Run 4 and the first two segments of Run 5 were again made with zirconium-type waste to verify zirconium waste calcination in the enclosed 10-cm-diam. (4 in.) calciner. Off-gas plugging and extreme variations in the 50 psi air supply caused shutdowns after 29 and 53 h in Run 4. After 29 h of Run 5, off-gas restrictions again forced a shutdown. Both off-gas plugging and fluidizing air supply variations were not related to flowsheet development for Fluorinel waste. Zirconium waste was then successfully calcined for 34 h; the equipment was purposely shut down before switching to Fluorinel Alternative 2 waste to define the degree of bed agglomeration. The Alternative 2 waste would be a mixture of boron and cadmium between the design basis feed (0.214 M cadmium) and the minimum cadmium case (0.062 M). In this run, extra sulfate and aluminum were added to prevent cadmium melting. Operation was successful for 29 h; equipment malfunctions not related to the Fluorinel flowsheet caused a shutdown. The amount of agglomeration was normal for a 10-cm-diam. calciner.

Instead of substituting boron for part of the cadmium during Fluorinel reprocessing to make the waste calcinable, the desired approach is to use only cadmium. Chemical additives would be required to form high melting cadmium compounds during calcination. A literature survey showed that sulfuric acid, aluminum sulfate, oxalic acid, chromic acid, phosphoric acid, and acetic acid could react with the cadmium at calcination temperature to produce high-melting compounds. Each of these potential additives was mixed with simulated Fluorinel waste and the mixture was dried. Each of the six candidate additives prevented cadmium melting based on the DTA test; thus, pilot-plant tests based on chemical additives to prevent bed agglomeration are warranted.

In Run 6, a 1:1 mole ratio of sulfate and cadmium with a high concentration of aluminum (2:1 Al/Zr mole ratio) was the first additive tested. This composition was comparable to earlier zirconium runs. The second part of Run 6 consisted of the sulfate additive with a low aluminum concentration. This waste did not calcine as well, but because of short run times (11 and 12 h) this composition will be tried again.

Future plans call for short run additive testing followed by long-term verification tests. The 15-cm-diam. (6 in.) calciner is presently being enclosed to handle the Fluorinel waste and a new enclosed 30-cm-diam. (12 in.) calciner is planned for operation in 1980.

XI. Recommendations

1. Calcination Chemistry

Pilot-plant and laboratory results were translated to the design of the WCF which has been singularly successful in demonstrating the solidification of high-level wastes on a routine basis for 14 years. However, particle size--at least for zirconium and stainless steel wastes--of the calcine is not adequately controlled. The reason may be in the detailed chemistry taking place in the bed or in the vicinity of the in-bed burners. If a model were to be developed for the unit operation of calcination, it would be necessary to provide the various reactions involved and their rates of reaction.

Needed for a thorough understanding of the thermal decomposition of radioactive wastes, eventually applicable to a fluidized bed, is a chemical kinetic study. The kinetic data could help:

1. Improve equipment design.
2. Reduce corrosion of equipment.
3. Give more efficient calcination.
4. Reduce dusting.
5. Produce a leach resistant product.
6. Reduce the volatile content in calcine product.
7. Provide a material for post calcination treatment and storage.

The unit operations model of a calciner may need the following chemical information:

1. A list of the various reactions involved in calcination. For co-processed waste these might be:
    a. Evaporation of liquid (H_2O and HNO_3) from waste.
    b. Decomposition of HNO_3.
    c. Decomposition of $Al(NO_3)_3$.
    d. Combustion of kerosene (90% complete).
    e. Steam hydrolysis of fluorides of Al, Zr, Ca, etc., (in presence and absence of HNO_3).
    f. HF(g) reaction with Ca compounds.

   g. Conversion of $Ca(NO_3)_2$ to CaO and to $CaCO_3$.

   h. Dehydration of H_3BO_3.

   i. Decomposition of mercury compounds.

   j. Fluxing of oxides by B_2O_3.

   k. Behavior by chloride compounds.

   l. Formation of $CaZrF_6$ and decomposition.

2. The kinetics of the above reactions, particularly in the 300-700°C range.

3. Effect of the substrate on the rates of the above reactions--diffusion through fused solid calcine.

4. Can the rates of the above reactions be affected by additives or other reactions in the series.

5. What effect will these reactions, particularly combustion of kerosene, have on the decomposition or volatility of fission products, and leachability of incorporated fission products in solid phases.

6. Measure the properties of the reacting systems that might be important to fluidized-bed operation:

   a. Melting range, rate, stickiness.

   b. Density of particle, bulk density.

   c. Phase crystallinity, stability, and seeding.

   d. Attrition index of solid.

7. Determine the nature of solid phase in mixtures of the various reactions.

8. If any reactions are extremely slow and lead to either high off-gas losses or long residence time, determine alternate treatment, e.g., a second fluidized bed in series operating with additives or at other temperatues, or possible spray calcination vs. fluidized-bed calcination.

9. Recycle off-gas may furnish $H_2O(g)$ for hydrolysis.

10. Define product properties for choice in making a solid form for post treatment and/or storage.

11. Other effects of direct vs. indirect heating on reactions.

There are many intermediate reactions in the calcination of salts of Al^{+3} or Zr^{+4}. The identification of these intermediate reactions is necessary before making a detailed kinetic study. Calcination is initially a rapid operation and anything which slows the reaction should be evaluated. Gas-solid reactions are involved and diffusion in solids is slow. Furthermore, the contact of a given bed particle by incoming sprayed feed is intermittent and a layered, onion-skin deposition on bed granules has been observed at the ICPP. The completion of the decomposition of waste in a given layer which may be covered by several later layers may be very slow. If HF(g) is released, it must be absorbed by Ca^{++} either in the vicinity of release or elsewhere in the bed; this constitutes a series of reactions whose kinetics are important to design and operation.

The kinetics of the decomposition of major components will have an impact on the behavior of minor components, particularly the fission products. Although the chemistry of ruthenium and other fission products is discussed elsewhere, the chemistry and kinetics begin in the calciner. A survey of the literature shows no rate or mechanism studies except preliminary studies on ruthenium by J. D. Christian. Interaction of fission products with other bed material may affect their part in calcination. For example, radioiodine might react with mercury or cesium to produce a nonvolatile compound which remains in the calcine.

The behavior of residual volatile components, either radioactive or non-radioactive, may indicate the use of a second fluidized bed in series to complete the calcination reaction or off-gas cleanup. In fact, glass-making additives also could be incorporated in the calcine in the second bed.

Another objective of calcination chemistry is the tailoring of the calcine to any post-calcination treatment prior to long-term storage or disposal. Only tentative criteria have been proposed for the final form of the solid waste. Eventually, these criteria must be factored into the product of the calcination process. Furthermore, special requirements for the properties of the calcine may be required for interim storage of the calcine itself.

Of course, in the kinetic studies, one should obtain all properties of the system which might impact fluidized-bed operation and performance. It is apparent that phase composition and crystal structure can be important. Long-term phase changes must be recognized as well as ultimate stability of phases. Other properties include solid-liquid transformations, density of particles, leachability of components, etc.

The most difficult chemical problem will be in extrapolating the performance of the individual reactions to the usual mixture of components in actual radiactive waste. However, the reactions should be useful in any detailed engineering model of the calcination process. Although the above discussion is based primarily on co-processing waste (Zr and Al fuels), the studies might be extended to stainless steel nitrate wastes or even to commercial Purex process HLW calcination.

2. Pilot-Plant Development

1. Baseline studies should be made in the 10-cm-diam. (4 in.) calciners to improve calcination with the smaller diameter vessels. This would be to reduce agglomerate buildups resulting from the feed nozzle cones that build on the opposite wall of the vessel.

2. All analyses on filled waste tanks should be checked for any significant composition changes from previously known flowsheets. If significant changes are evident, then the waste composition should be checked for calcinability in the pilot plant.

3. Additional studies could be made to correlate the pilot-plant operation with the WCF. This information could range from product characteristics to a comparative analysis of the off-gas systems.

4. The new 30-cm-diam. (12 in.) calciner system to be built and located in the High-Bay Extension Building should be enclosed and ventilated to handle cadmium containing Fluorinel Waste. This enclosure should be on a modular basis to allow isolation of certain sections of the system. The new calciner should include features that will allow testing fundamental calciner components, feed systems, flow meters, valves, venturi scrubbers, and properties such as particle growth and chemical volatility.

5. A satisfactory Fluorinel flowsheet should be developed using the enclosed 10-cm-diam. (4 in.) calciner. A flowsheet using a sodium blend with Fluorinel waste should then be developed to provide a means of calcining sodium-bearing wastes in the future.

6. New fluidization concepts such as "fast-fluidization" should possibly be studied to eliminate agglomeration of bed materials such as sodium.

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Appendix

Pilot-Plant Calciners

This section contains a general description of the pilot-plant calciners used in flowsheet development. Since these calciners are experimental, changes are frequently made in the systems to improve the process or to test equipment performance. The schematics and descriptions are generalized. The equipment characteristics are shown in Figure 2 to compare each facility.

The initial development work took place in the 15-cm-diam. (6-in.) calciner (Figure 3) and the 60-cm-sq (2-ft-sq) calciner (Figure 4). Both were located at the Central Facilities Area (CFA). The 30-cm-diam. (12-in.) calciner (Figure 5) was initially located at CFA but was later modified and transferred to CPP-627 where it is used in the present flowsheet development work (Figure 6). The two 10-cm-diam. (4-in.) calciners are located in CPP-637 Low-Bay. The enclosed 10-cm-diam. (4 in.) calciner (Figure 7) is used when hazardous chemicals are being tested. All of the Fluorinel flowsheet work has been done in this facility. Figure 8 shows the schematic of the #3 10-cm-diam. (4-in.) calciner which has been used extensively throughout the flowsheet development work. A brief description of the use of these calciners in developing flowsheets is given in the introduction.

	Heating System	Fines System	Quench Tower	Venturi Scrubber	De-entrainment System	Condenser	Separator	Secondary Condenser	Off-Gas Recycle	Off-Gas Superheater Silica Gel Absorber	Presently In Use
Fifteen-Centimetre (Six-In.)	NAK	Cyclone Fines Recycle	NO	YES	Demister	YES	NO	NO	NO	NO	NO
Sixty-Centimetre (Twenty-four In.)	NAK	Cyclone Fines Recycle	NO	YES	Scrubber Cyclone	York Mesh Tower & Condenser	NO	NO	NO	NO	NO
Thirty-Centimetre (Twelve-In.)	Calrod Heaters	Cyclone Fines Recycle	NO	YES	Scrubber Cyclone	YES	YES	NO	YES	NO	NO
#3 Ten-Centimetre (Four-In.)	In-Bed Combustion	Cyclone	NO	YES	Scrubber Cyclone	YES	NO	NO	NO	NO	YES
Enclosed Ten-Centimetre (Four-In.)	In-Bed Combustion	Cyclone	NO	YES	Scrubber Cyclone	YES	YES	YES	NO	NO	YES
Thirty-Centimetre (Twelve-In.)	In-Bed Combustion	Cyclone	YES	YES	Knock-out Pot	YES	Demister	YES	NO	YES (with by-pass)	YES

Figure 2. Pilot-Plant Calciners Summary Chart

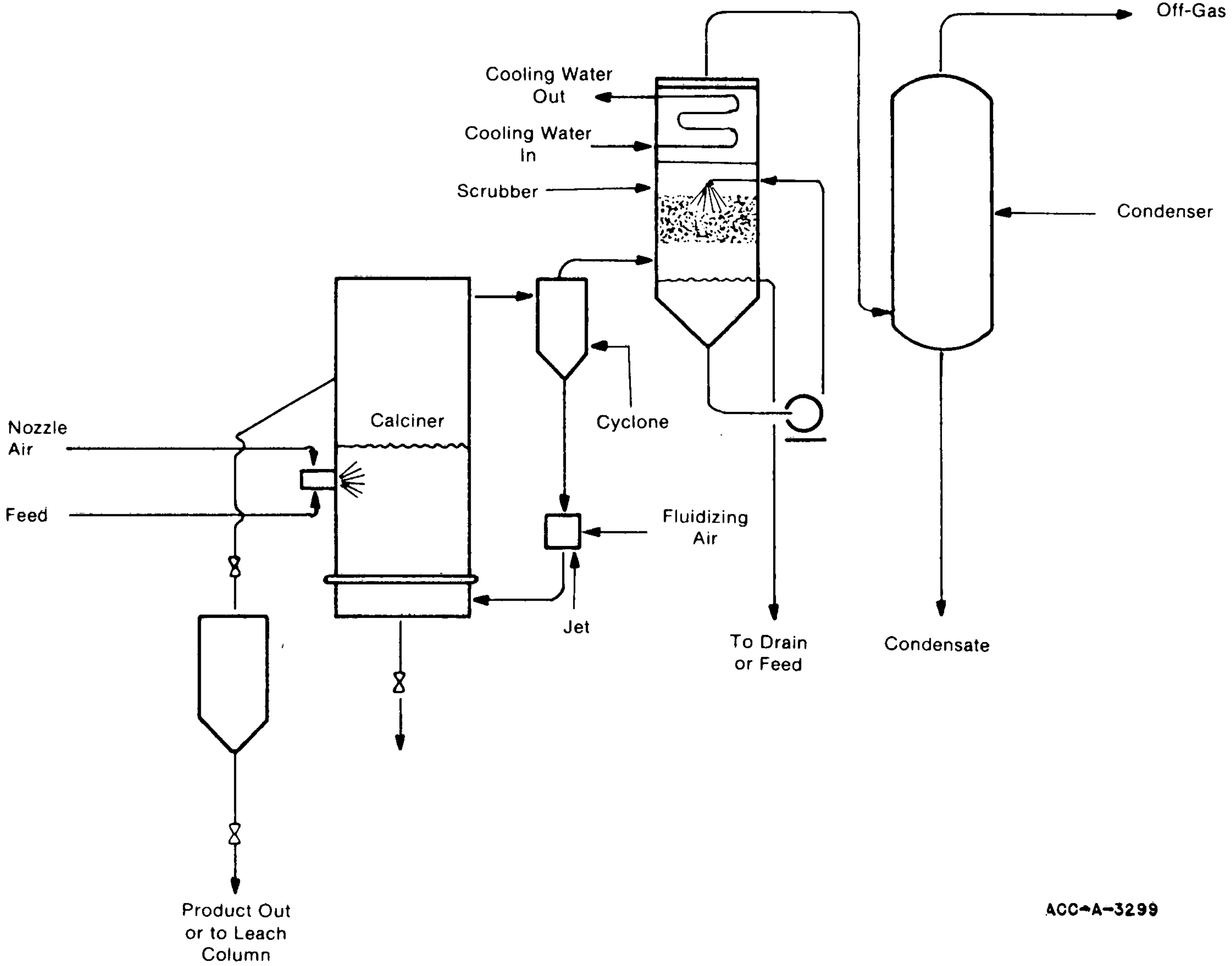

Figure 3. Schematic Diagram of the Fifteen-Centimetre-Diameter (Six-Inch) Fluidized Bed Calciner System

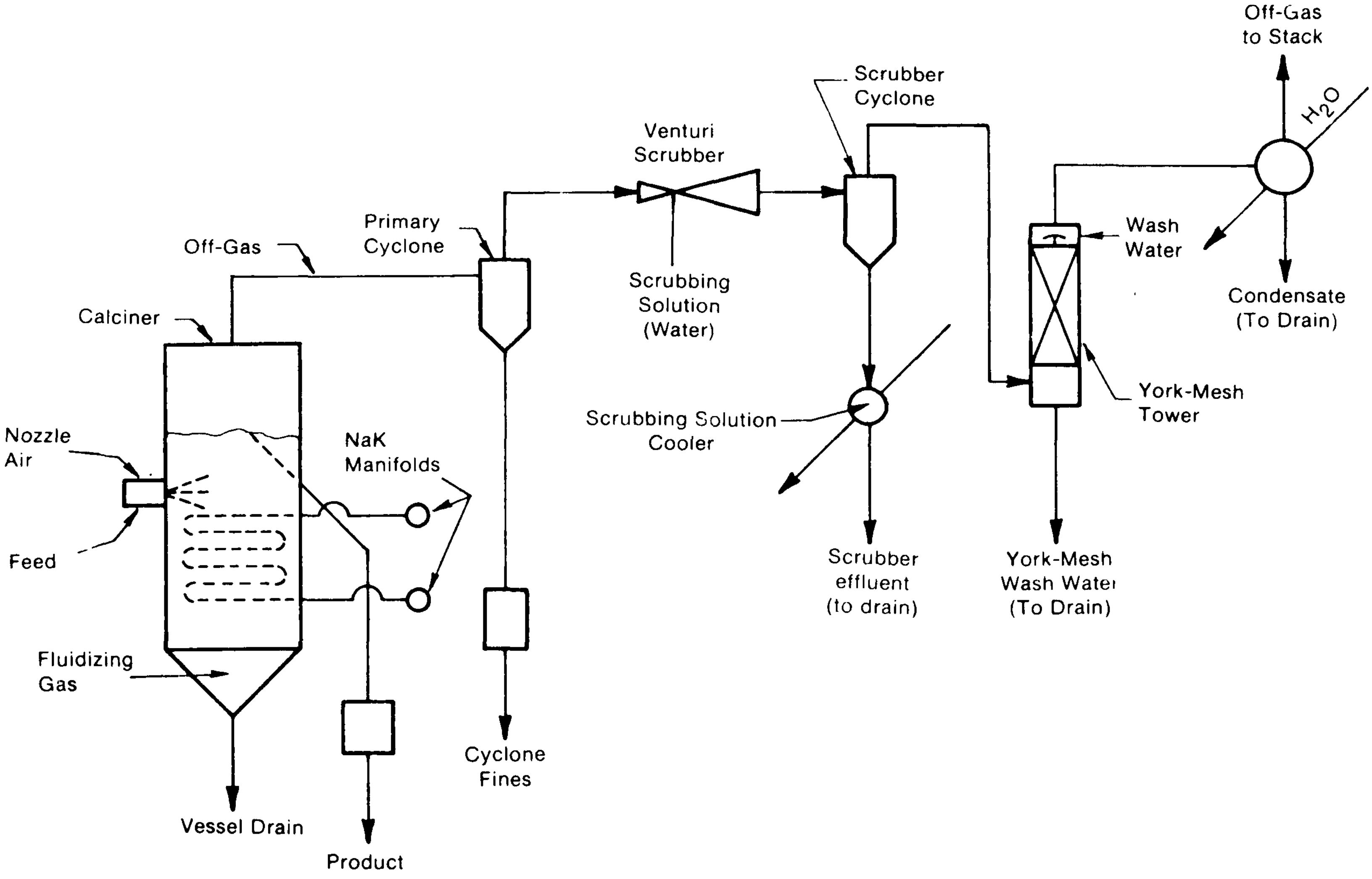

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Figure 4. Schematic Diagram of the Sixty-Centimetre-Square (Twenty-four Inch) Fluidized Bed Calciner System

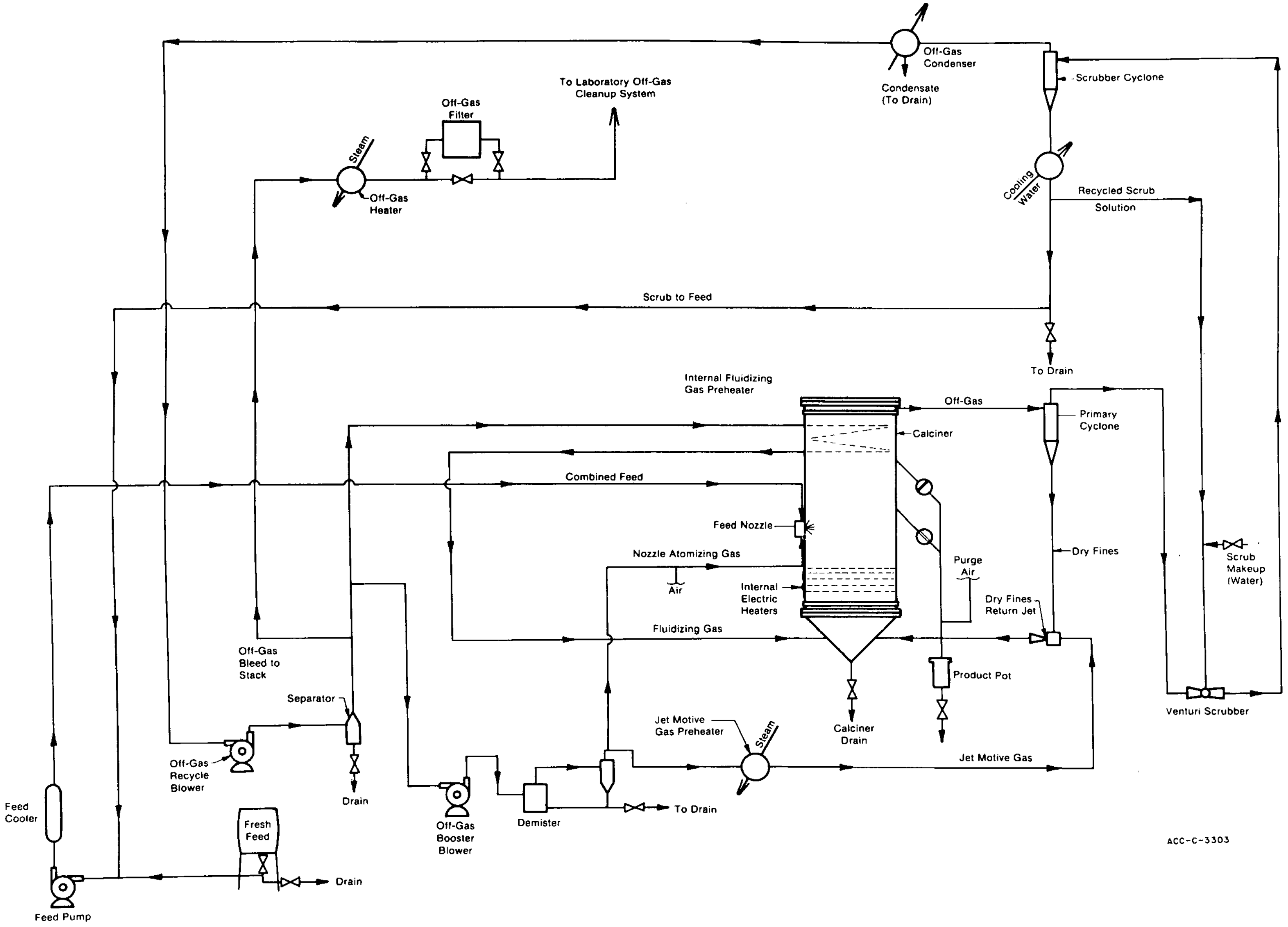
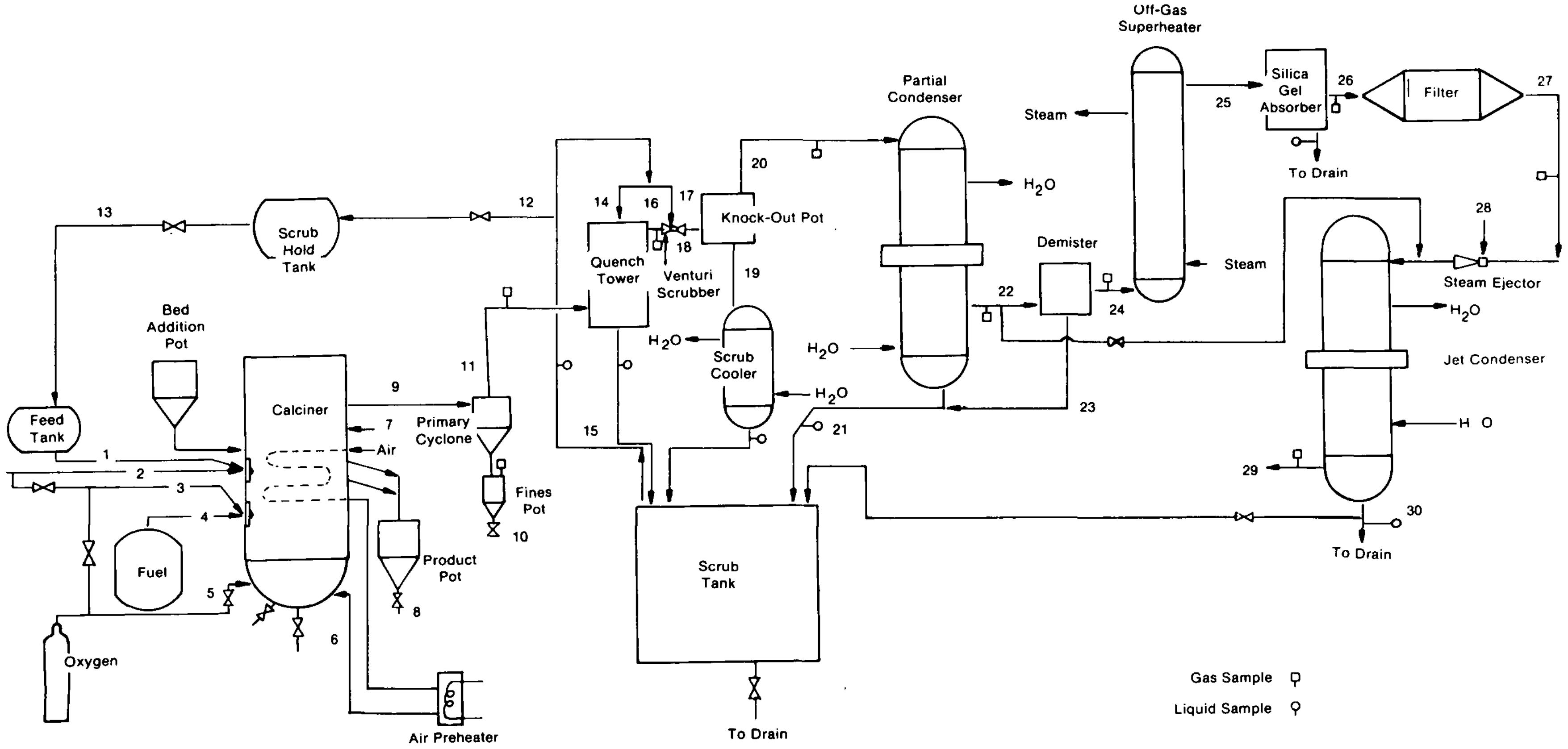


Figure 5. Thirty-Centimetre Diameter (Twelve-Inch) System Cold Pilot Plant



1	Feed	11	Cyclone Off-Gas	21	Partial condenser condensate
2	Feed atomizing air	12	Scrub to hold tank	22	Partial condenser off-gas
3	Fuel atomizing gas	13	Scrub recyle to feed	23	Demister drain
4	Fuel	14	Scrub to quench	24	Demister off-gas
5	Fluidizing oxygen	15	Quench recycle	25	Superheater off-gas
6	Heated fluidizing air	16	Quench off-gas	26	Absorber off-gas
7	Miscellaneous purges	17	Scrub to venturi	27	Filter off-gas
8	Calcine product	18	Venturi off-gas	28	Steam
9	Calciner off-gas	19	Scrub recycle	29	Off-gas to stack
10	Calcine fines	20	Knockout pot off-gas	30	Jet condensate

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Figure 6. Schematic Diagram of Thirty-Centimetre-Diameter (Twelve-Inch) Calciner

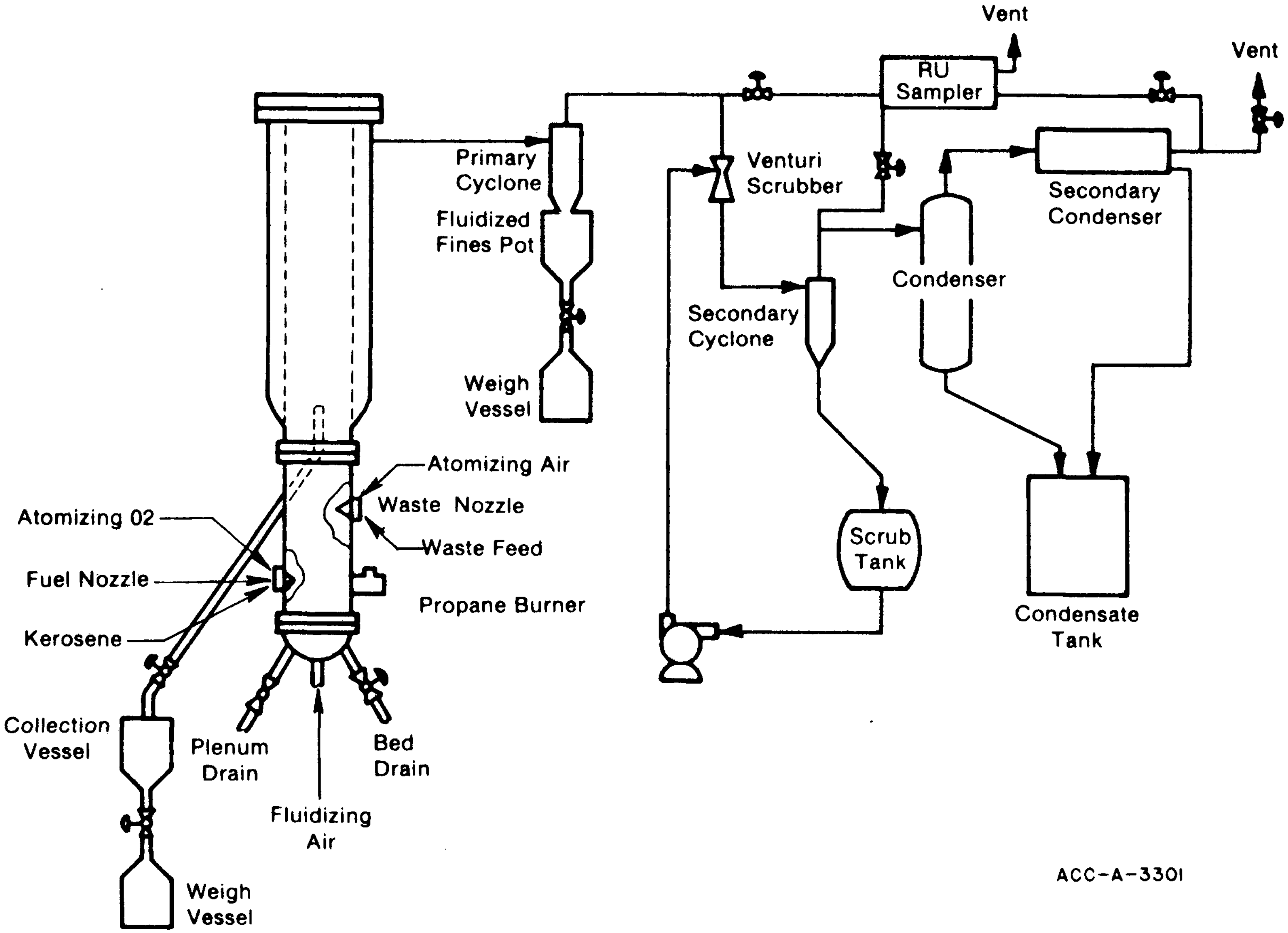

Figure 7. Enclosed Ten-Centimetre-Diameter (Four-Inch) Calciner

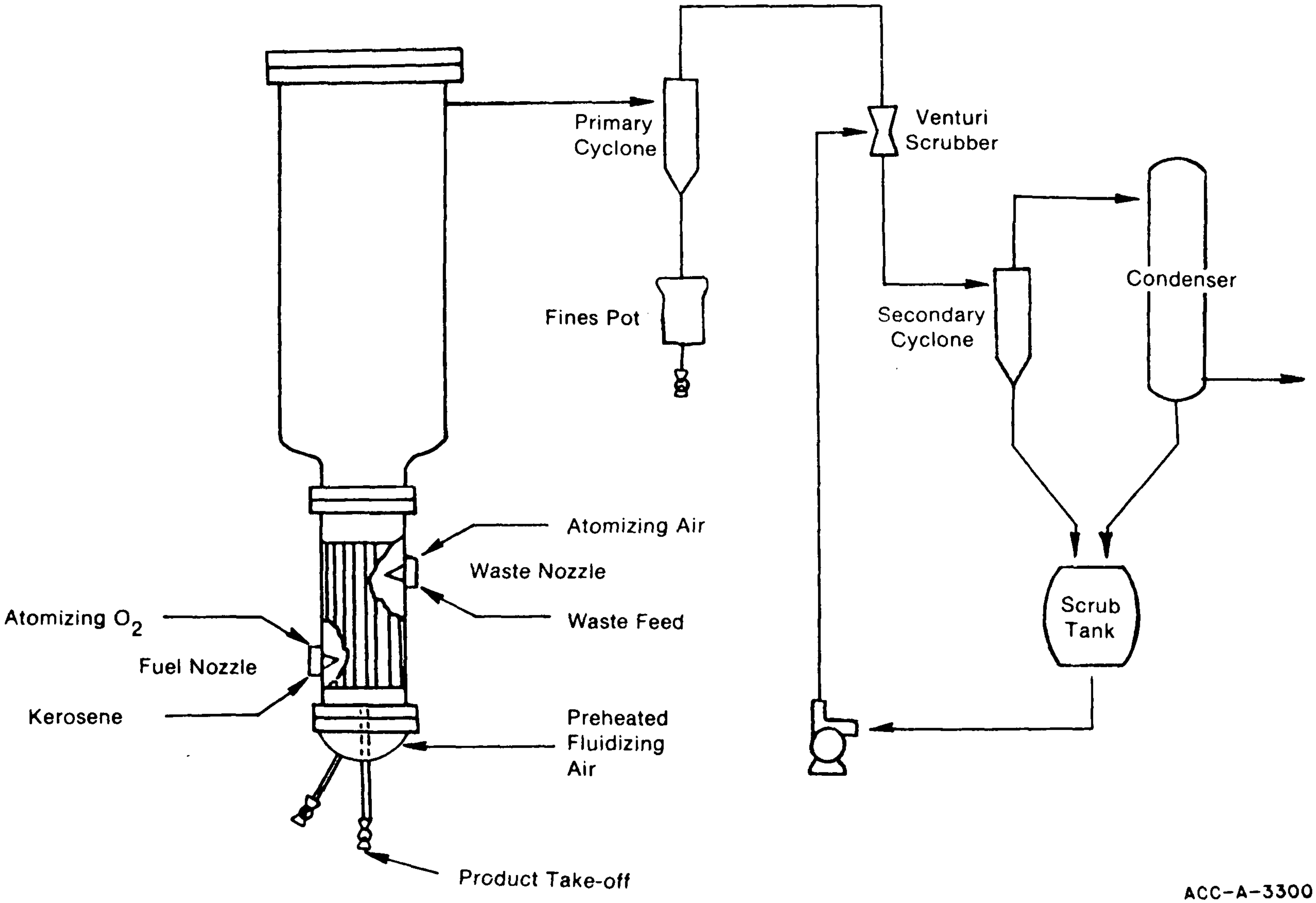

Figure 8. Schematic Diagram of #3 Ten-Centimetre-Diameter (Four-Inch) Calciner