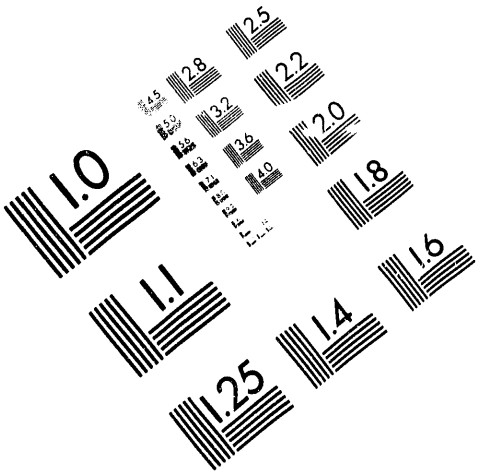
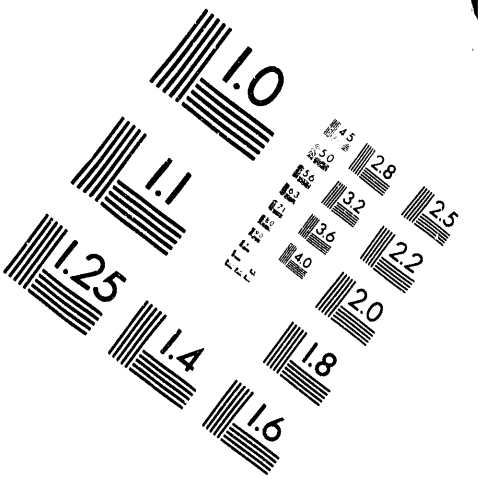


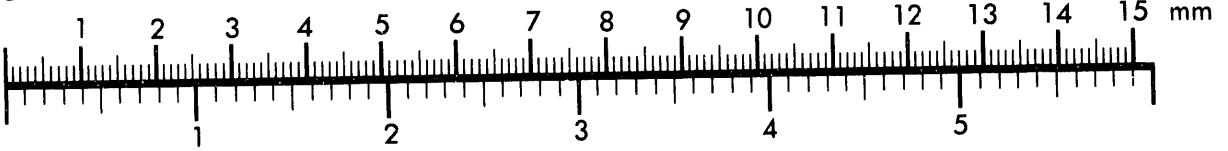
**Association for Information and Image Management**

1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910

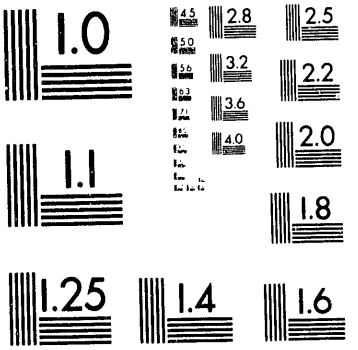
301/587-8202

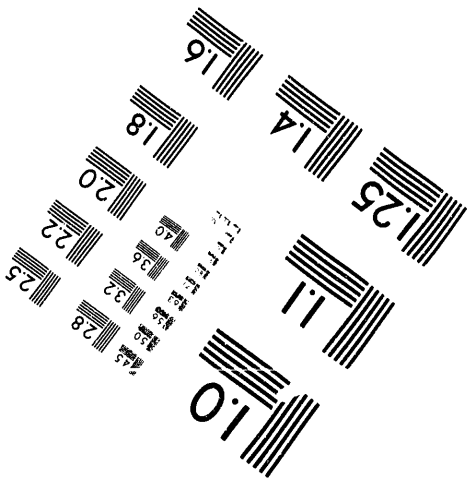


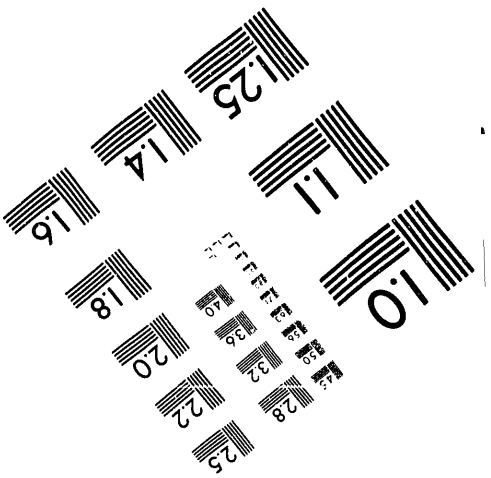
Centimeter



Inches







MANUFACTURED TO AIIM STANDARDS
BY APPLIED IMAGE, INC.

1 of 1

UNCLASSIFIED
(CLASSIFICATION)

GENERAL ELECTRIC

HANFORD ATOMIC PRODUCTS OPERATION – RICHLAND, WASHINGTON

DOCUMENT NO.
HW-65806 RD

COPY NO.

DATE
November 14, 1960

ISSUING FILE

TITLE

# RADIANT-HEAT SPRAY-CALCINATION PROCESS FOR THE SOLID FIXATION OF RADIOACTIVE WASTE, PART I: NON-RADIOACTIVE PILOT UNIT

AUTHOR

R. T. Allemann and B. M. Johnson, Jr.

BATTELLE NORTHWEST
RECEIVED
MAY 16 1969
CIRCULATING COPY
TECHNICAL INFO. SECTION

| ROUTE TO | PAYROLL NO. | LOCATION | FILES ROUTE DATE | SIGNATURE AND DATE |
|---|---|---|---|---|
| ~~V. R. Cooper~~ | | 2704E Bldg | | |
| B. G. Campbell | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |

RECEIVED
JUN 07 1993
OSTI

THIS DOCUMENT HAS BEEN SCANNED
AND IS STORED ON THE OPTICAL DISK DRIVE

THIS DOCUMENT IS PUBLICLY
AVAILABLE

RECEIVED
JAN 27 1994
V. R. COOPER

MASTER

UNCLASSIFIED
(CLASSIFICATION)

54-3000-030 (9-56)
A.E.C.-G.E.-RICHLAND, WASH.

TO BE USED ON UNCLASSIFIED AND OFFICIAL USE ONLY DOCUMENTS

# RADIANT-HEAT SPRAY-CALCINATION PROCESS FOR THE SOLID FIXATION OF RADIOACTIVE WASTE, PART I: NON-RADIOACTIVE PILOT UNIT

by

R. T. Allemann and B. M. Johnson, Jr.

Chemical Research
Hanford Laboratories Operation

November 14, 1960

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

NOTICE!

This report was prepared for use within General Electric Company in the course of work under Atomic Energy Commission Contract AT-(45-1)-1350, and any views or opinions expressed in the report are those of the authors only. This report is subject to revision upon collection of additional data.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission to the extent that such employee or contractor prepares, handles or distributes, or provides access to, any information pursuant to his employment or contract with the Commission.

DISTRIBUTION RESTRICTED TO U.S. ONLY

DISTRIBUTION

1. M. D. Alford - K. J. Schneider
2. G. B. Barton
3. L. P. Bupp - H. M. Parker
4. R. E. Burns
5. E. A. Coppinger
6. V. R. Cooper
7. R. Y. Dean
8. E. Doud
9. J. B. Fecht
10. R. G. Geier -
11. J. M. Gerhart
12. K. M. Harmon
13. M. K. Harmon
14. O. F. Hill
15. J. F. Honstead
16. H. H. Hopkins
17. E. R. Irish
18. B. F. Judson
19. C. E. Linderoth
20. R. L. Moore
21. D. W. Pearce
22. A. M. Platt
23. W. H. Reas
24. C. A. Rohrmann
25. L. C. Schwendimen
26. H. P. Shaw
27. R. J. Sloat
28. R. E. Smith
29. M. J. Szulinski
30. R. E. Tomlinson
31. E. E. Voiland
32. M. T. Walling, Jr.
33. R. T. Allemann
34. B. M. Johnson, Jr.
35. 300 Area Files
36. Record Center

37-50. Extra

TABLE OF CONTENTS

| | | Page |
|---|---|---|
| I. | INTRODUCTION | 5 |
| II. | SUMMARY | 5 |
| III. | CONCLUSIONS AND RECOMMENDATIONS | 7 |
| IV. | PROCESS DESCRIPTION | 8 |
| | A. Atomization | 10 |
| | B. Heat Transfer and Reactor Capacity | 10 |
| | C. Wall Effect | 11 |
| | D. Reaction Rates | 11 |
| V. | EXPERIMENTAL EQUIPMENT AND PROCEDURE | 11 |
| | A. Reactor | 11 |
| | B. Solids Recovery | 15 |
| | C. Off-Gas Treatment | 16 |
| | D. Operating Procedure | 16 |
| VI. | DISCUSSION OF RESULTS | 17 |
| | A. Feed Compositions | 17 |
| | 1. Purex Acidic Waste (1WW) | 17 |
| | 2. Purex Neutralized Waste | 17 |
| | 3. Coating Waste | 17 |
| | 4. Mixed 1WW and Coating Waste | 18 |
| | 5. Mixed 1WW and Organic Wash Waste | 18 |
| | 6. TBP-25 Waste | 18 |
| | 7. Darex Waste | 18 |
| | 8. Zirflex Waste | 18 |
| | B. Product Characteristics | 18 |
| | 1. Particle Size | 21 |
| | 2. Powder Density | 21 |
| | 3. Flow Characteristics | 22 |
| | 4. Caking | 22 |
| | 5. Coagulation | 22 |
| | C. Effect of Additives to Feed | 23 |
| | 1. Phosphate | 23 |
| | 2. Borate | 26 |
| | 3. Sulfate | 26 |
| | 4. Sugar | 26 |
| | D. Thermal Conductivities of Spray Calcined Wastes | 28 |
| | 1. Powders | 28 |
| | 2. Solidified Melts | 28 |

E. Operating Variables 33
1. Extent of Calcination 33
2. Feed Rate 34
3. Atomizing Steam Rate 37
4. Sugar Addition 37
5. Oxygen Addition 40
6. Reactor Temperature 40

F. Wall Deposits 42
1. Effect on Column Operation 42
2. Properties of Wall Powder 43
3. Amount of Wall Powder 43
4. Channel Recycle Studies 43

G. Corrosion 47

H. Separation of Solids From Off-Gas 51
1. Filters 51
a. Micro-metallic Filters 51
b. Ceramic Filters 51
2. Cyclones 52
3. Condenser-Scrubber 52

I. Ruthenium and Cesium Volitilization 52

J. Condensate Characteristics 54

K. Method of Condensation Before Deentrainment of Powder (Slurrying) 55

L. Calcination Profiles in the Spray Calciner Column 57
1. Heat Transfer 57
2. Temperature Profile 57
3. View Factor 59
4. Heat Absorption by Steam 59
5. Spray Turbulence 60

VII. ACKNOWLEDGEMENTS 60

References: 61

APPENDIX I - RADIANT HEAT TRANSFER TO DROPLET 62

APPENDIX II - VIEW FACTOR DETERMINATION 68

APPENDIX III - PARTICLE AND GAS TEMPERATURE DURING PARTICLE IGNITION 72

APPENDIX IV - CALCINER TURBULENCE AS DETERMINED BY EDDY DIFFUSIVITY MEASUREMENTS 78

# RADIANT-HEAT SPRAY-CALCINATION PROCESS FOR THE SOLID FIXATION OF RADIOACTIVE WASTE, PART I: NON RADIOACTIVE PILOT UNIT

by

R. T. Allemann and B. M. Johnson, Jr.

## I. INTRODUCTION

The fixation of radioactive waste in a stable solid media by means of calcination of these aqueous solutions has been the subject of considerable effort throughout the U. S. Atomic Energy Commission and by atomic energy organizations in other countries. Several methods of doing this on a continuous or semi-continuous basis have been devised, and a few have been demonstrated to be feasible for the handling of non-radioactive, or low-activity, simulated wastes. Notable among methods currently under development are: (a) batch-operated pot calcination of waste generated from reprocessing stainless steel clad fuel elements (Darex process) and Purex waste[1,2], (b) combination rotary kiln and ball mill calcination of aluminum nitrate (TBP-25 and Redox process)[3], and (c) fluidized bed calcination of TBP-25 and Purex wastes[4,5,6]. Although a considerable amount of engineering experience has been obtained on the calcination of dissolved salts in a fluidized bed, and the other methods have been the subjects of a great deal of study, none of them have been developed to the extent which would rule out the desirability of further investigation of other possible methods of calcination.

About ten years ago, work was done at the K-25 Plant in Oak Ridge[7] on the spray calcination of uranyl nitrate in which radiant heat directly from the hot walls of the reactor tube was used rather than the sensible heat of hot combustion gases, which are generally used in high-temperature spray drying. A great deal of development work on a similar process for the pyrolysis of sulfite liquors has been done by the Pulp and Paper Research Institute of Canada under the direction of W. H. Gauvin.[8] This process has been designated by him as the "Atomized Suspension Technique". The calcination scheme described herein is an adaptation of these same basic methods. The atomized suspension technique as described by Gauvin consists of atomizing the liquor in the absence of foreign gas, except as required for atomization, into the top of a tower, the walls of which are heated to a high temperature, and of passing the resultant suspension of droplets in the water vapor atmosphere which acts as a carrier, through successive zones of evaporation, drying and chemical treatment as it proceeds down the column. Separation of the solids, noncondensable gases, and steam is then effected by conventional means.

## II. SUMMARY

1. Spray calcination of simulated wastes has been studied in a relatively small scale reactor eight inches in diameter and ten feet tall. A considerable variety of compositions were handled without difficulty,

including wastes generated by TBP-25, Darex, and Zirflex (coating removal of zirconium-clad fuel elements) processes as well as a wide range of possible compositions of acid and neutralized, high-level Purex wastes. Over 130 runs were made in the unit.

2. The product characteristics, such as particle size, density, etc. vary somewhat with the feed composition. In general the powder, made up of flakes of exploded droplets, is rather fine, and as high as ninety-five percent may pass through 325 mesh screen. Density of the powder ranges from 0.12 g/cc, for aluminum nitrate-type waste, to 1.2 g/cc, for Purex waste adjusted in composition by the addition of sugar and phosphoric acid. Powders from many of the unadjusted feeds were of rather low bulk density and not very free flowing.

3. Considerable attention has been given to the use of additives to accomplish one or more of the following: (1) increase the bulk density of the powder product, (2) form a powder which can be subsequently melted into a consolidated solid for final storage, or (3) promote more nearly complete calcinations of the powder during its short residence time in the reactor.

4. The addition of phosphoric acid to simulated Purex waste results in a product which melts in the range 800 C to 900 C. Properties of the calcined powder are also altered; bulk density is increased roughly from 0.5 g/cc to 0.85 g/cc and the surface-average particle size is more than doubled, indicating a less dusty, more free flowing powder.

5. Addition of other anions, such as sulfate and borate, has been studied. High-sulfate Purex waste may contain sufficient sodium sulfate to form a stable solid which melts below 900 C.

6. Boric acid or sodium tetraborate may be added to wastes containing considerable aluminum to produce true glass matrices upon calcination and fusion. Bulk density of the calcined powder from aluminum nitrate-type waste is increased from 0.12 g/cc to 0.7 g/cc by the addition of sodium tetraborate.

7. Sugar is a useful additive for a number of reasons. First used to promote melting of particles of phosphate-treated feed during their residence in the reactor, it has also been used to decompose sodium nitrate and unstable ferric and aluminum sulfates, and to neutralize excess sodium hydroxide in various feed compositions. The burning of the carbonaceous residue of decomposed sugar in oxygen augments particle temperatures and further improves characteristics of phosphate-treated feeds. Neutralized wastes, generally containing considerable sodium nitrate, cannot be calcined without adding sugar (which decomposes the nitrate and converts it to sodium carbonate). High-sulfate Purex waste also cannot be completely spray calcined without the use of a reducing agent to accelerate the decomposition of iron and aluminum sulfates.

8. Thermal conductivity of the powder product is low, ranging from 0.05 to 0.135 Btu/hr, ft,°F over the temperature range 100 to 400 F,

and is primarily dependent upon density rather than composition. Melting and consolidating the product greatly increases the conductivity, to the vicinity of 0.6 But/hr, ft, °F for borate-type glasses, for example.

9. Extent of calcination was not greatly affected by the feed rate up to 4 gal/hr; it generally decreased slightly except with feeds adjusted by the addition of sugar. These showed an increase in extent of calcination at higher feed rates. The quantity of atomizing steam did not consistently affect the calcination so long as the rate was maintained above a certain minimum required to adequately atomize the liquid at a specific feed rate. The addition of 150 to 200 g/l of sugar had the optimum effect on extent of calcination. Decreasing reactor temperature below the usual operating temperature of 800-830°C in the center section reduces the extent of calcination particularly with feeds containing a large amount of sulfates.

10. A considerable quantity of the powder contacts the upper walls of the reactor because of the turbulence induced by the spray jet. Tapping the column periodically prevents any build-up from becoming excessive.

11. Corrosion behavior of the spray calciner is difficult to assess because of the wide variety of feed compositions and operating conditions studied. Short duration corrosion tests with typical Purex calcination conditions indicated good resistance for two possible materials of construction, Inconel and stainless-steel type 446. However, the 1/16-inch thick center section of the reactor failed in the region of a stainless-steel and Inconel weld after 170 total hours of operation. The Inconel, a short distance from the weld, showed little attack at this time.

12. Porous metal filters have been used most successfully for separation of the powder and gas but corrosion may limit their applicability and necessitate use of ceramic elements. Cyclones have not been very successful in the small unit but may be applicable on a larger scale. With porous metal filters, de-entrainment factors of $10^4$ and $10^8$ from the feed to the condensate and off-gases respectively have been measured. Ruthenium and cesium volitalization is less than two percent with both acidic and basic feed liquors, as measured by including augmented quantities of inactive isotopes of each element in the feed.

13. The temperature profile of a radial cross-section of the reactor (below a two-foot nozzle zone) is absolutely flat within limits of measurement. This fact, and measurements of the degree of turbulence within the reactor, indicate scale-up of the unit to a 2 1/2-foot diameter unit, for example, is probably feasible without a marked decrease in volumetric capacity.

## III. CONCLUSIONS AND RECOMMENDATIONS

The application of spray calcination to the continuous calcination of high-level radioactive aqueous wastes has been studied only on

a laboratory scale with simulated feeds. Further development on a larger scale is needed before its full capabilities can be assessed. Nevertheless, these preliminary results lead the writers to believe that the process has several characteristics which make it very attractive for waste calcination, namely: (1) the operation is insensitive to changes in waste composition and is readily adaptable to many different types of feed, (2) remote operation control and maintenance should be simple in comparison to other proposed methods of calcination, (3) initial studies with this unit and the experience of the Canadians indicate that a single unit could handle the present requirements of the Purex plant, (4) the most difficult portion of the operation i.e., the conversion from a fluid to a solid, is accomplished on a continuous basis and avoids the difficulties of foaming, low rate of heat transfer through deposited solids, and widly varying flows through the associated gas clean-up system which are inherent in batch processes.

The laboratory studies have left several questions unanswered, namely: (1) What is the best method of powder melting or coagulation (which is required for final storage because of the characteristics of the powder)? (2) What is the best method of separating the powder from the off-gases in a plant-scale unit? (3) Will corrosion be a serious problem at the operating temperatures of the reactor?

The authors believe that the above questions can be answered in a pilot plant unit and that, with further engineering data, the process will prove to be superior to other proposed methods of waste calcination.

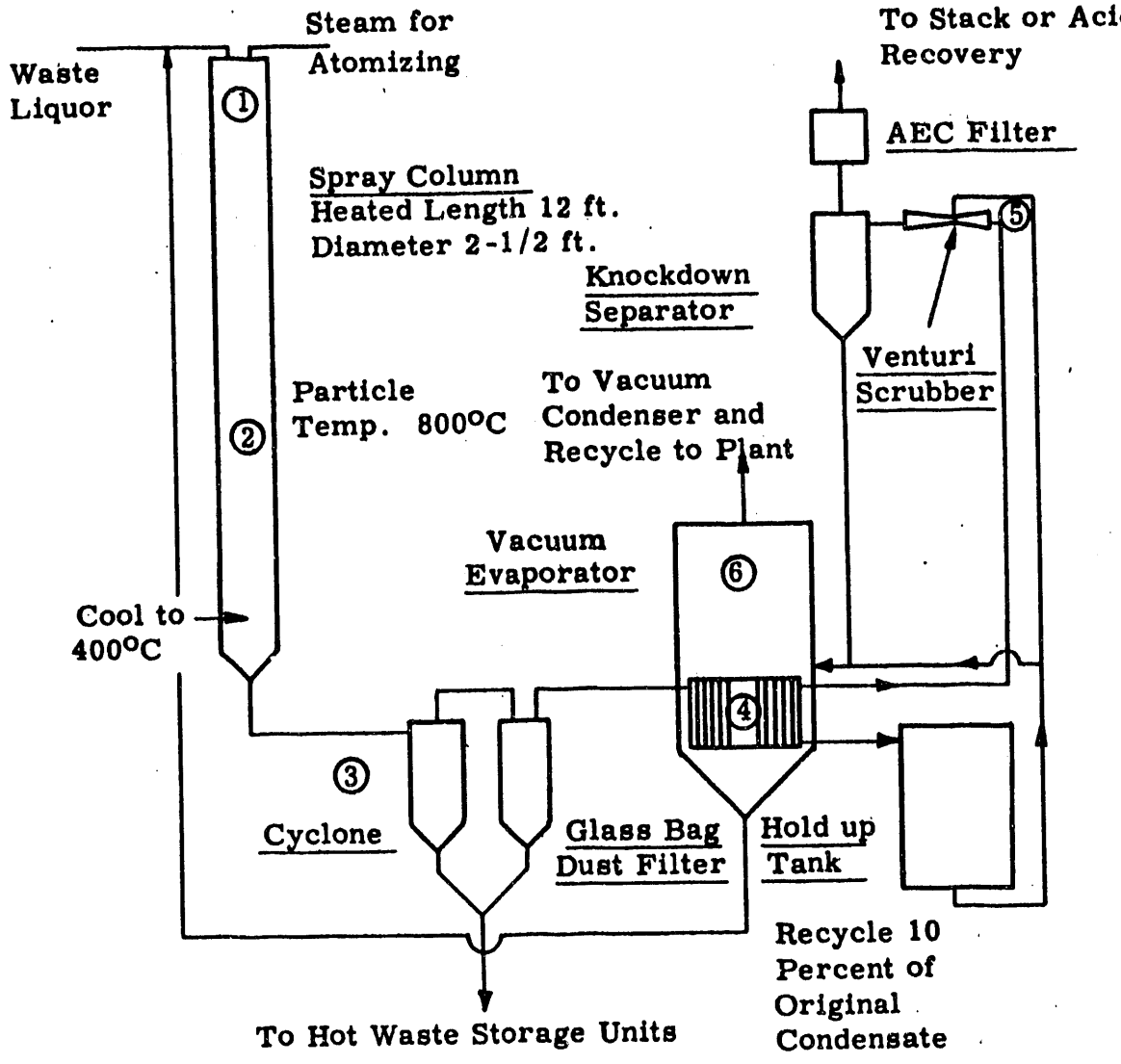
## IV. PROCESS DESCRIPTION

An integrated process for the calcination and disposal of radioactive waste solutions may be envisioned as in Figure 1. The steps involved in the process are as shown in the figure: (1) Waste solution is atomized in a pneumatic nozzle at the top of the radiant-heat calciner. (2) As the droplets pass down through the column, they are first dried and subsequently calcined, that is, the nitrate and some sulfate salts are decomposed during their short ($\sim$15 sec.) residence, (3) the suspension is cooled somewhat in the lowest portion of the column to solidify any partially or completely melted droplets before the solids and gases are separated by means of porous ceramic or porous metal filters or, possibly, by a cyclone separator and high temperature bag filter in series. Solids may be withdrawn as a powder into waste packaging units, or with certain compositions, they may be heated to form a dense clinker or melt. Conceivably, if the solids were sufficiently insoluble, they could be removed as a slurry with the condensed off-gases and could then be thickened and dried to a compact solid.

The treatment of the steam and entrained or volatile fission products is not significantly different than that proposed for other methods of waste calcination. Undoubtedly the condensate will have to be further decontaminated, which will probably involve

FIGURE 1

Spray Calcination Schematic Flowsheet



re-evaporation. This can be accomplished through use of the sensible and latent heats of the off-gases if the smaller operating expense warrants the increased complexity of the equipment and operation. In this situation, the steam and entrained or volatile fission products are condensed (4) in the steam chest of a vacuum evaporator, which could be backed up by a second condenser or subcooler. (5) The condensate, after passing through a hold-up tank, is split into two portions, one of which is pumped through a venturi scrubber where the non-condensables of the off-gas are treated to remove any entrained particles before being sent through the final acid absorber and A.E.C. filter. The other portion of the condensate is sent directly to the vacuum evaporator along with the knockdown liquid from the venturi scrubber (6). Approximately ninety percent of the condensate is evaporated at a sub-atmospheric boiling temperature by the condensation of the hot vapors from the calcining tower in step (4). The overhead material from this operation is reused as plant process water or treated as very low-level waste since a negligible amount of activity will remain. The residue, which will contain fission products entrained past the filters and fission products partially volatilized during the calcination reaction, is recycled to the top of the column.

The essential features of the process may be summarized as follows; a more complete discussion is included in the appendices.

A. Atomization

It is quite possible that aqueous wastes solutions will contain varying amounts of suspended solids and may actually be slurries. For such liquors, high pressure atomization would not be feasible; also, one would hesitate handling such highly radioactive materials under high pressure. Pressure-centrifugal nozzles are a possibility for atomization in large equipment, but pneumatic, or two-fluid, nozzles should be used in small installations. Configuration of the spray must be such that it does not contact the walls of the reactor before it has been dried, otherwise a deposit of calcined solids is built up at the point of contact.

B. Heat Transfer and Reactor Capacity

It is very difficult to predict, except from experience, the capacity of such a reactor. A considerable similarity exists between this process and spray drying, and studies by T. W. Hoffman(9) have indicated that although heat is ultimately supplied as radiant energy from the reactor walls, the primary mechanism for heat transfer to the evaporating droplets is by convection from the hot steam within the column because of the high velocity of the droplets and the resultant large convective heat-transfer coefficient. Once the droplets have been decelerated to their terminal velocity, they will be dried before traveling a significant distance further down the column, except for droplets 200 microns or larger in size. When the droplets are dry, the mechanism by which they are then heated to the calcining temperature is probably that of radiant-heat transfer directly to the particles with the vapor being heated by conduction from the particles.

C. Wall Effect

Adherence of the spray and particles to the walls of the reactor does occur with some types of waste compositions, particularly in the region just below the nozzle at the top of the column. This is primarily the result of the highly turbulent flow conditions in this region and may be reduced by several methods. In the lower regions of the column adherence of powder to the walls is slight; this may be due to a thermal repulsive force which exists between the wall and the particles, because of the temperature difference between them. The force can be strong enough to prevent contact if pronounced turbulence is absent.

D. Reaction Rates

Because of the tremendous surface area exposed and the very high rate of heat transfer to each particle, calcination reaction rates are very rapid and complete calcination can often be effected during the very short (usually less than 15 seconds) residence time in the reactor. However, some reactions must be accelerated with chemicals that drive the reaction to completion during the residence time.

## V. EXPERIMENTAL EQUIPMENT AND PROCEDURE

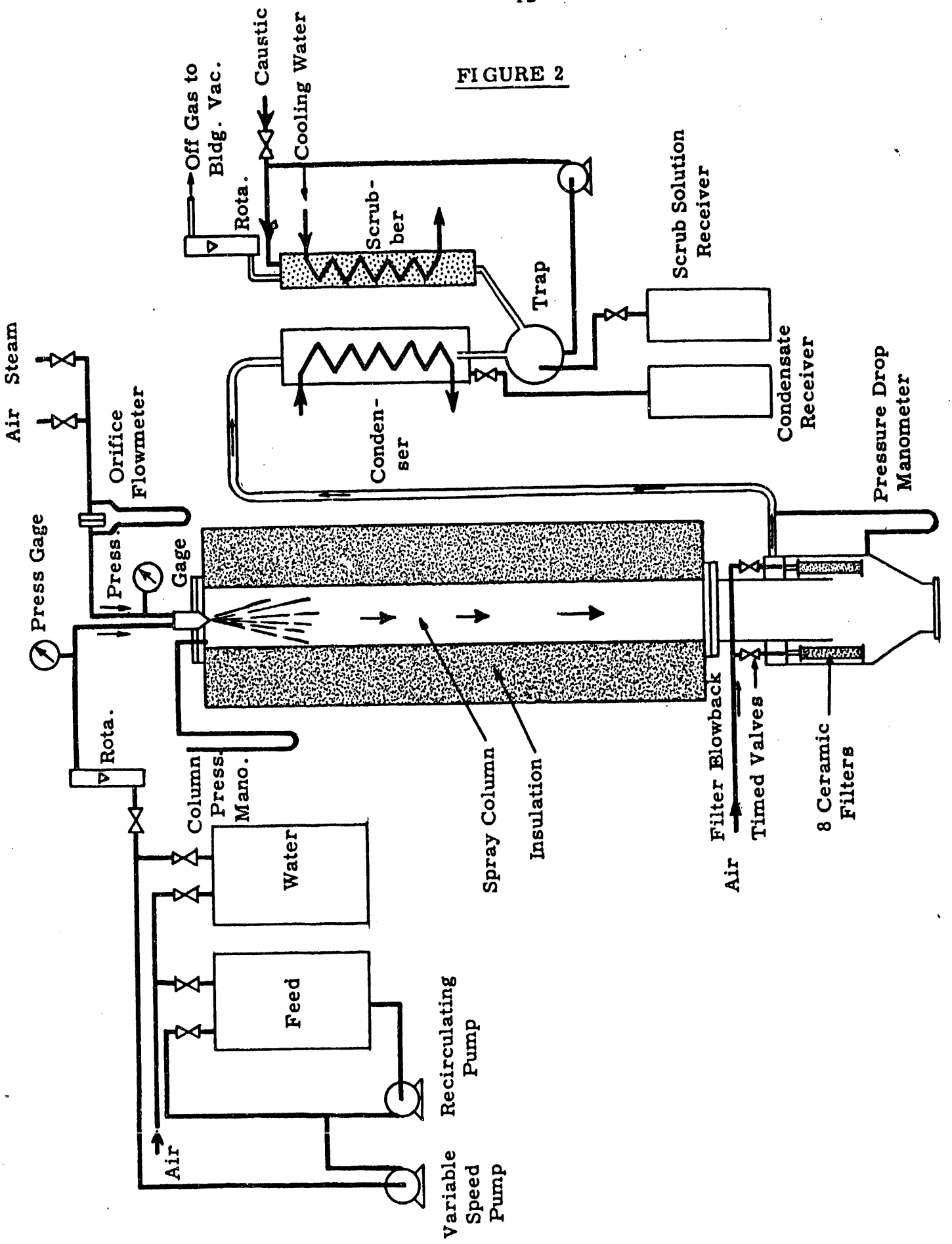
Because of the preliminary nature of the program, the equipment underwent several evolutionary changes during the course of the study. The following description is of the equipment in its present form. Many as yet undeveloped improvements, refinements, and changes could be employed in a plant sized unit.

A. Reactor

The experimental apparatus is shown schematically in Figure 2. Figures 3 and 4 are photographs of the equipment. The reactor is an eight-inch diameter column, ten feet long, constructed in three sections; a 4-1/2 foot top section and a 2-foot bottom section of Schedule 10 stainless-steel pipe, and a 3-1/2 foot center section made from 16 gauge Inconel sheet. Heat is supplied by ten 2000-watt calrod heaters banded to the side of the upper section of the column and by low voltage current passed through the entire column. Seventy-five percent of this latter source of energy is dissipated in the center Inconel section which is heated up to 875 C.

The low voltage current is supplied by a welding transformer equipped to supply secondary voltage in sixteen steps up to 6.4 volts. To date, maximum power generally used from this source has been approximately 3300 amperes at 5.4 volts. Maximum power at 6.4 volts was used for one run at a very high throughput. The calrods which supply a greater portion of heat to the top of the column have been run at approximately 1/2 to 2/3 power and are limited by the allowable sheath temperature of the units.

FIGURE 2


Off Gas to Bldg. Vac.
Caustic
Cooling Water
Rota.
Scrub-ber
Trap
Scrub Solution Receiver
Condensate Receiver
Air
Steam
Orifice Flowmeter
Conden-ser
Pressure Drop Manometer
Press Gage
Press.
Gage
Rota.
Column Press. Mano.
Water
Feed
Recirculating Pump
Variable Speed Pump
Air
Spray Column
Insulation
Filter Blowback
Timed Valves
Air
8 Ceramic Filters

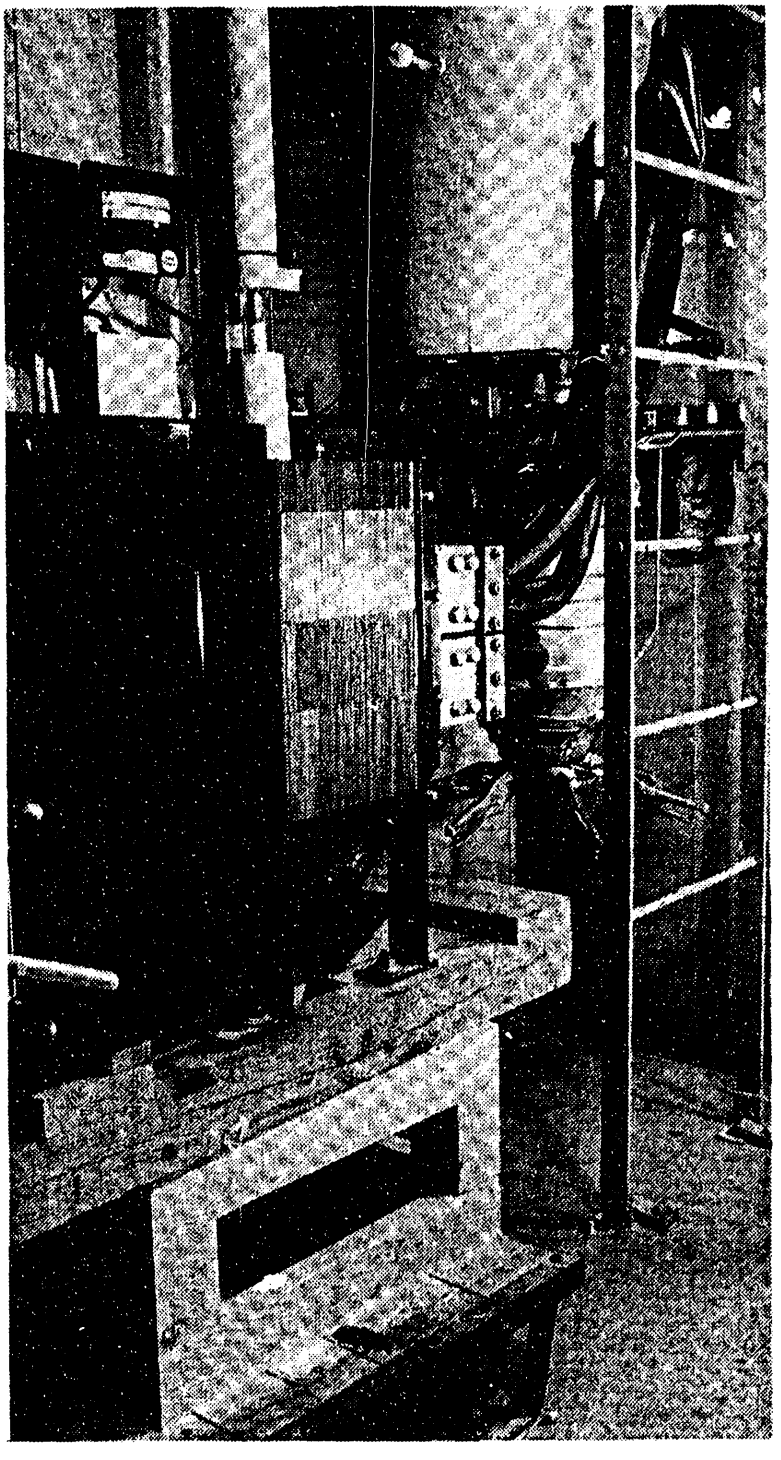


FIGURE 3
SPRAY CALCINATION EQUIPMENT
Power Transformer and Bottom of Calciner

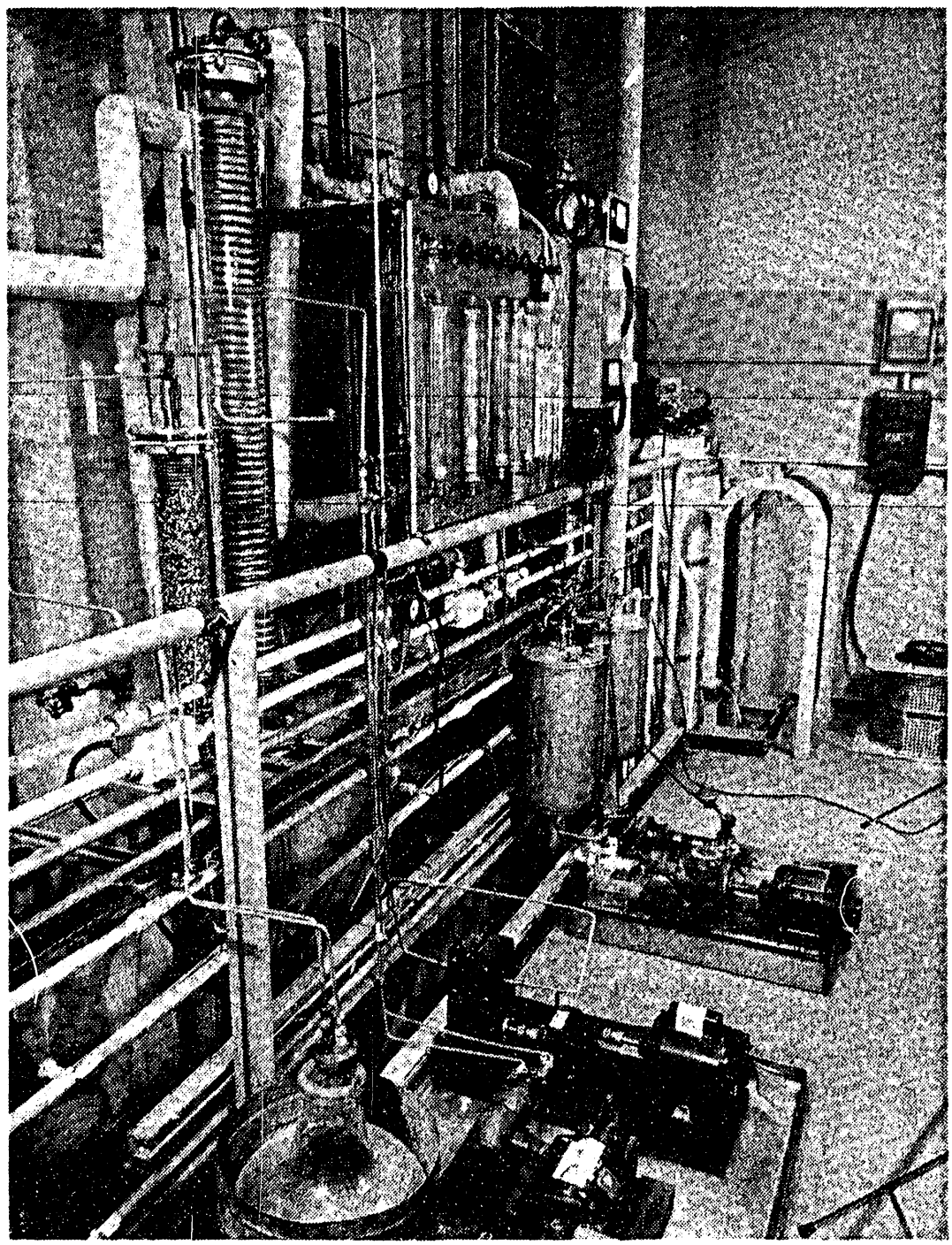


FIGURE 4
SPRAY CALCINATION EQUIPMENT
Operating Gallery

Up to four gallons per hour of simulated waste solution is fed to the top of the unit through a pneumatic atomizing nozzle, using super-heated steam (generally) as the atomizing fluid. The nozzle is located outside the column with the orifice protruding through a water-cooled insert, located at the center of the top cover plate, and is held down and sealed against an asbestos gasket by a toggle clamp. The wall temperature of the reactor is measured at six locations. In addition, two thermocouples inserted into the center of the column, located 50 and 83 inches from the top of the column, serve to indicate off-standard behavior although they do not accurately measure the true temperature of the vapor or solid particles.

Some difficulty has been experienced with a build-up of powder on the walls of the reactor in the nozzle region of the column, i.e., the top portion in which the spray is decelerated to its terminal velocity. As the spray enters the reactor, it behaves as a free-expanding turbulent jet and a great deal of gas is entrained at its boundary. This gas is supplied from the lower section of the column and, consequently, a great deal of back-mixing occurs. Dried particles carried up with this vapor adhere lightly to the wall and with some types of feed solutions, may form a thick, but loose, layer of solids; with other feeds, essentially no deposit is formed. In any event, this build-up can be effectively controlled by vibrating the column. Initially, this was done by means of a Peterson Vibrolator air-driven vibrator, mounted on the top cover of the column. Recently, a pneumatic impactor that periodically strikes the column sharply, has been used. It should be stressed that the design of the atomizing nozzle must be such that the spray does not come in contact with the walls of the column before it has been dried, otherwise a strongly adhering layer of solid would be formed at the area of wet contact.

B. Solids Recovery

The solid particles and vapors are cooled somewhat in the lowest two feet of the column before they pass into the filter section, which is attached to the bottom of the column. This section consists of an inner region, six inches in diameter, partially masked from a three-inch wide concentric annulus which contains eight porous ceramic filter elements. These are rated at five micron retention and have a total surface area of 4.15 square feet. Periodic cleaning of each filter is accomplished by means of a pulse blow-back system, similar to that used by the Argonne National Laboratory on their fluidized-bed calciner. This involves the use of a high pressure pulse of air introduced downstream from the filter through a venturi throat. Duration of the pulse may be as short as 0.2 seconds.

Solids are collected in a receiver sealed to the filter section, or within the section itself during short-duration runs. In some runs the powder receiver was a melt pot in which the product was heated to its sintering or melting point such that a coagulated solid was the ultimate product.

C. Off-Gas Treatment

A down-draft condenser removes steam and other condensables in the column off-gas. Non-condensables are then scrubbed with caustic to remove remaining $NO_2$ and other acidic gases and are then exhausted to the building vacuum system. Provision is made to collect the condensate and the scrub solution for sampling and analysis, and to divert a portion of the non-condensable off-gas for (1) mass spectrometric analysis, (2) analysis for particular components by gas absorption, and (3) analysis for entrained particulate material. The particulate analysis involves passing an isokinetic sample of the gas through a Millipore Filter Corporation, Type AA filter, which is designed to remove all particles which are 0.2 microns and larger in diameter. The filter is then analyzed for iron by a colorimetric method sensitive to one microgram of total iron.

Pressure within the column is maintained at slightly below a atmospheric pressure by manually controlling the flow to the vacuum system.

D. Operating Procedure

Start-up and operation of the spray calciner is very simple. The reactor is preheated to the desired operating temperatures, following which, superheated steam at the desired pressure is introduced into the column through the atomizing nozzle. Since the column pressure is maintained manually, it must be carefully watched during the start-up procedure. After the pressure has stabilized, water and then feed are introduced into the column. Flow rates are controlled manually and indicated by a rotameter. If the feed liquor is a slurry, it is maintained in suspension in the feed tank by a recirculating pump and the flow control is obtained by a variable-speed, back-pressure centrifugal pump. (See Figure 2)

During the time water is fed into the system, the scrubber recirculating pump is started and an appropriate flow of approximately 25 percent caustic is injected into the recirculating scrub stream. Overflow from the trap beneath the scrubber is collected. At the time feed solution is first introduced into the reactor, the condensate is diverted into a 5 gallon sample bottle, to be retained for analysis, as is also the overflow from the scrubber recirculating stream.

High pressure air (90 psig) is supplied to the solenoid valves which control the pulse of air for blow-back of the filters, a system which was developed at Argonne National Laboratory. Timers are generally set to deliver a pulse of 0.2 seconds duration to each filter every four minutes.

During the run, samples can be taken of the non-condensable off-gas for mass-spectrometer analysis and/or two separate portions of the off-gas may be continually withdrawn which

are (1) bubbled through a train of standardized hydrogen peroxide for $SO_2$-$SO_3$ analysis and/or (2) passed through a Millipore filter for analysis of particulate carry-over.

The shut-down procedure involves reverting to water to flush out feed lines and the reactor system, and diverting the condensate and scrub overflow from their respective sample bottles to a common receiver.

Sudden abnormal behavior of the nozzle can be detected by a rapid drop in the temperature indicated by the top probe located 50 inches beneath the nozzle.

## VI. DISCUSSION OF RESULTS

### A. Feed Compositions

The radiant-heat spray calciner has been used to process simulated wastes of many types. The composition of the plant wastes is difficult to determine exactly because it varies from time to time and because of the analytical difficulties associated with extremely radioactive solutions. The compositions of the wastes used for these studies were obtained from the best available data of plant personnel[10] and from unclassified reports[11,12]. The concentrations of fission products are negligible and therefore the compositions given show only the gross constituents. Table I is a compilation of several compositions of simulated Purex waste solutions and slurries processed in the radiant-heat spray calciner. Included is data on the product densities and volume reductions resulting from the reduction to solids.

#### 1. Purex Acidic Waste (1WW)

As presently discharged from the plant, the high-level waste stream is a neutralized slurry of an initially highly acid solution (approximately 6 M $HNO_3$), but in arriving at the compositions listed, it was assumed that future plant practive would include destruction of nitric acid with formaldehyde and possibly neutralization of the resultant low-acid material.

#### 2. Purex Neutralized Waste

This corresponds to the projected composition of a typical formaldehyde-killed Purex waste which has been neutralized with caustic soda. Neutralization is done to minimize the acidic corrosion of underground storage tanks.

#### 3. Coating Waste

The aluminum cladding of Hanford Fuel elements is removed by caustic dissolution. Although not normally considered a high-level waste, coating waste was studied because of possible interest in combining it with Purex acidic waste for reduction to solids. (See below)

4. Mixed 1WW and Coating Waste

Because the coating waste is basic it can be used to neutralize the acidic 1WW. Mixing the two wastes in their plant flow-rate proportions gives a waste slurry of about pH 12.5 which can be calcined in the spray calciner. The composition of this mixture is shown in TABLE I.

5. Mixed 1WW and Organic Wash Waste

In the Purex plant the solvent is reconditioned by contacting it with aqueous sodium carbonate and potassium permanganate. All of these streams are mixed with neutralized 1WW in the underground storage tanks. Some TBP in kerosene was floated on top of the slurry to simulate organic entrainment and the mixture was calcined successfully by adding 100 g/l sugar.

6. TBP-25 Waste

Table I gives the composition of TBP-25 waste which comes from the fuel element processing system used at Idaho Falls. This process utilizes tributylphosphate in kerosene as the extraction solvent similar to the Purex process but aluminum nitrate replaces nitric acid as the salting agent.

7. Darex Waste

Darex waste is expected to result from processing stainless steel clad uranium oxide fuel elements. The process involves dissolution of the element in aqua regia with subsequent removal of the chloride with nitric acid stripping followed by solvent extraction. This waste was calcined both as an acidic solution and a neutralized slurry.

8. Zirflex Waste

Zirflex coating waste results from the dissolution of Zircalloy cladding of a fuel element with ammonium floride and ammonium nitrate and subsequent neutralization. The composition shown is that used in the experiments with the radiant-heat spray calciner, but is believed to be insufficiently neutralized (the $ZrF_6^{=}$ complex should be destroyed).

B. Product Characteristics

Radiant-heat spray calcination has several basic similarities to spray drying, consequently it is not surprising that the powdered product is in some respects similar to spray-dried products. However, whereas spray-dried materials are generally hollow or porous spheres of low density, under the conditions of the studies of radiant-heat spray calcination many of the droplets, originally formed as a spray, shatter during the drying process.

TABLE I

COMPOSITIONS OF SIMULATED WASTES CALCINED IN THE RADIANT-HEAT SPRAY CALCINER

| TYPE AND COMPOSITION | ADDITIVES | DENSITY (g/cc) Powder | DENSITY (g/cc) Melt or Sinter | VOLUME REDUCTION FACTOR = Volume of Feed / Volume of Melt or Sinter |
|---|---|---|---|---|
| **Purex:** Acid Killed-High Sodium-Low Sulfate, Volume = 25 gal/T of U | | | | |
| Na 2.50 M, Fe 0.50, Al 0.25, Ni 0.015, Cr 0.025, H 0.50; $NO_3$ 2.86 M, $SO_4$ 1.25 | a) No additive | 0.4 | 2.4 (S) | 12 |
| | b) W/Phosphate $H_3PO_4$ = 1.62 M | 0.8 - 0.9 | 2.8 (M) | 12.5 |
| | c) W/Phosphate and Sugar = 250 g/l | 0.9 - 1.1 | 2.9 (M) | 13 |
| **Purex:** Acid Killed-Low Sodium-High Sulfate, Volume = 25 gal/T of U | | | | |
| Na 1.00 M, Fe 0.60, Al 0.20, Ni 0.01, Cr 0.02, H 2.22; $NO_3$ 0.52 M, $SO_4$ 2.60 | a) No additive | 0.7 - 0.8 | 2.3 (M-2 phase) | 12 |
| | b) W/Sugar = 150 g/l | 0.7 - 0.8 | 2.3 (M-2 phase) | 12 |
| | c) W/Phosphate $H_3PO_4$ = 1.16 M | 0.8 - 0.9 | 2.8 (M) | 12.5 |
| | d) W/Phosphate and Sugar = 250 g/l | 0.9 - 1.1 | 2.9 (M) | 13 |
| | e) W/Calcium $Ca(OH)_2$ = 1.0 M | 0.8 | — | |
| **Purex:** High Acid-Neutralized W/Caustic, Volume = 50 gal/T of U | | | | |
| Supernate: Na 7.65 M; $NO_3$ 7.15 M, $SO_4$ 0.50 | a) No additives | (Cannot be calcined) | | |
| | b) W/Sugar = 200 g/l | 0.85 | 2.3 | 5.5 |
| Solids: $Fe(OH)_3$ 0.2 moles/l; $Al(OH)_3$ 0.1 moles/l; $Ni(OH)_2$ 0.006 moles/l; $Cr(OH)_3$ 0.010 moles/l | | | | |
| **Purex:** High Acid Plus Coating Waste, Volume = 246 gal/T of U | | | | |
| Supernate: Na 2.7 M; $NO_3$ 0.842 M, $NO_2$ 0.835, $SO_4$ 0.203, $AlO_2$ 0.55, $SiO_4$ 0.017 | a) No additive | 0.65 | — | |
| | b) W/Sugar = 150 g/l | 0.64 | — | |
| | c) W/Sugar and *$H_3BO_4$ = 75 g/l *(added to solids) | — | 2.3 (M) | 8.5 |
| Solids: $Fe(OH)_3$ 0.061 moles/l; $Al(OH)_3$ 0.677 moles/l; $Cr(OH)_3$ 0.002 moles/l | | | | |

TABLE I CONTINUED

COMPOSITIONS OF SIMULATED WASTES CALCINED

IN THE RADIANT-HEAT SPRAY CALCINER

| TYPE AND COMPOSITION | | | | | | ADDITIVES | DENSITY (g/cc) Powder | DENSITY (g/cc) Melt or Sinter | VOLUME REDUCTION FACTOR = Volume of Feed / Volume of Melt or Sinter |
|---|---|---|---|---|---|---|---|---|---|
| **Purex:** | | | | | | | | | |
| Mixed Neutralized Waste and Organic Wash Waste | | | | | | | | | |
| Na | 8.00 | M | $NO_2$-$NO_3$ | 2.3 | M | a) No additive | .735 | 2. | 10. |
| K | 0.15 | | $CO_3$ | 1.5 | | b) W/Sugar=100 g/l | .54 | 2.0 | |
| | | | $SO_4$ | 1.00 | | | | | |
| | | | OH | 0.68 | | | | | |
| | | | $PO_4$ | 0.01 | | | | | |
| Solids | | | | | | | | | |
| $MnO_2$ | 0.15 moles/l | | | | | | | | |
| $Fe(OH)_3$ | 0.75 moles/l | | | | | | | | |
| $Cr(OH)_3$ | 0.04 moles/l | | | | | | | | |
| $Ni(OH)_2$ | 0.02 moles/l | | | | | | | | |
| **Purex:** | | | | | | | | | |
| Coating Waste Volume = 209 gal/T of U | | | | | | | | | |
| Na | 3.43 | M | $AlO_2$ | 1.44 | M | a) No additive | 0.57 | — | |
| | | | OH | 0.57 | | b) W/Sugar = 150 g/l | 0.20 | — | |
| | | | $NO_3$ | 0.31 | | c) W/Sugar and *$H_3BO_4$ = 75 g/l *(added to solids) | — | 2.3 (M) | 10 |
| **TBP - 25** Volume = 0.11 - 0.22 gal/g-U 235 | | | | | | | | | |
| Al | 1.6 | M | $NO_3$ | 5.5 | M | a) No additive | 0.18 | — | |
| $NH_4$ | 0.05 | | $SO_4$ | 0.02 | | b) W/Borate $Na_2B_4O_7$ = 1.22 M | 0.70 | 2.3 (M) | 37 |
| Hg | 0.01 | | | | | | | | |
| Fe | 0.002 | | | | | | | | |
| H | 0.5 | | | | | | | | |
| **Darex:** Volume = 0.5 gal/g U-235 | | | | | | | | | |
| Fe | 0.68 | M | $NO_3$ | 6.1 | M | a) No additive | 0.81 | — | 7 |
| Cr | 0.16 | | | | | | | | |
| Al | 0.123 | | | | | b) Neutralized W/$NH_4OH$ | 1.30 | — | 11 |
| Ni | 0.075 | | | | | | | | |
| H | 2.94 | | | | | | | | |
| **Zirflex:** (Neutralized) | | | | | | | | | |
| $NH_4$ | 1.9 | M | $ZrF_6^{=}$ | 0.6 | M | a) No additive | 0.67 | 3 | 85 |
| | | | F | 0.6 | | | | | |
| | | | $NO_3$ | 0.08 | | | | | |

1. Particle Size

The average particle size of the product varies considerably with the feed composition and, to a lesser extent, with the temperature maintained in the top of the column. The mean diameter of the spray droplets is roughly 25 microns whereas the surface-average particle size was from 1.6 to 12.6 microns as measured by air permeability. The latter method is derived from measurements of the surface area and represents the uniform particle size of a powder containing perfect spheres which would have the same surface area as the sample. Hence, non-spherical particles which have high specific surface areas appear as smaller spherical particles having the same specific surface area, and consequently this is not a realistic estimate of particle size. Viewed under a microscope, many of the particles appear to be shattered remnants of larger drops and the powder, particularly that formed from relatively low sulfate feed, is rather dusty and not particularly free flowing.

Despite the fine solid particles formed, de-entrainment of the solids from the off-gas appears to be handled adequately by porous metal filters, as will be discussed subsequently. One possible explanation for this effective removal was brought to light by the particle size analyses, by sedimentation, of the -325 mesh fractions from three different runs with straight Purex feed. These indicated that there were no particles less than two microns in diameter which might pass through the filter despite the formation of fine particles by shattering of the droplets. One might postulate that this lower size limit reflects the limiting thickness of the shell of a droplet before shattering and that, since there is no attrition within the column, no finer particles are formed.

2. Powder Density

Like spray-dried materials, spray-calcined powders are of low density compared with a coagulated solid of the same material. The combined internal (particle) and external (powder) porosity generally ranged from about 50 percent to 85 percent; one feed composition resulted in a product containing over 97 percent void space. These figures correspond to densities ranging from 0.40 to 1.4 g/cc. Simulated acidic Purex waste calcined to a fine, light powder with a bulk density varying from 0.4 to 0.8 g/cc depending primarily upon the initial composition of the feed; a higher sulfate content resulted in a more dense powder. Addition of fluxing agents, such as borate and phosphate, and the use of sugar as an additive generally increased the bulk density somewhat. These effects will be discussed subsequently.

3. Powder Flow Characteristics

Because spray calcined powders are largely made up of shattered remnants of large spherical particles, they are generally not very free flowing. A considerable range in this characteristic was noted but no attempt was made to measure it quantitatively. The dustiness of the powder affects the free flowing behavior of the powder because the fine dust particles fill the interstices between the larger particles and cause a "binding" action. The powder as a whole then flows like a fine particle mass since the large particles are subdued. As mentioned, the lack of sphericity of the particles also contributes to the non-flowing behavior of the powder. Again, the use of additives generally improved these characteristics of the powders by increasing their average particle size and enhancing their sphericity.

4. Caking

Incompletely calcined powders, notably the product from high-sulfate Purex waste, were difficult to handle because of their tendency to cake. They form a hard compact layer on the filter surfaces, which is not easily removed by the blow-back pulse, and in the off-gas line when the cyclone was used instead of the filter. This difficulty was experienced principally with the acidic waste but also to a lesser extent with the neutralized waste. The addition of sugar to the feed solution was effective in overcoming the caking of the acidic waste product; the neutralized waste calcined with sugar still exhibited a slight tendency to form lumps in the cyclone.

5. Coagulation

With all but a few waste compositions studied, the powder could be coagulated by melting or sintering into a massive solid for final storage. As with any method of calcination, the final product in this form will be more dense, and consequently will have the advantages of reduced storage volumne per unit of production, higher thermal conductivity to aid in dissipating heat of radioactive decay, and lower solubility with less danger of spreading contamination if the disposal container fails. Because of these advantages, the characteristics of the melted or sintered solids were also studied for various feed compositions. To form the melt the powder was allowed to fall into a ceramic-lined pot which was heated to approximately 900 C by an electric clam-shell furnace. At this temperature the powders melted or sintered to compact solids ranging in density from 2.25 to 3.0 g/cc. In general, the low solubilities of these products still are too high to be considered for other than contained storage. The volume reduction factor from liquid to a massive solid form ranges from about 8 to 12 depending on the feed composition and the initial concentration of the waste.

The advantage in mounting a spray calciner over the melting pot, which must be disposed of as a batch-operated unit, is that it avoids many of the difficulties inherent with direct batch calcination from the original feed solution, such as entrainment, foam formation, and low rate of heat transfer.

C. Effect of Additives to the Feed

Because of the low bulk density inherent with solids produced from solutions by means of spray drying, consideration was given to the possibility of increasing bulk density through use of additives which allow the solid to melt during its residence time in the reactor. Generally, the particles formed by spray drying are hollow or porous as the result of gas escaping through the semi-solid droplet during the last stages of drying. If the droplet can be heated sufficiently to melt the solid, its surface tension would possibly be sufficient to consolidate the droplet into a relatively dense particle. Of course, provision must be made to subsequently cool the particle below the melting point before attempting to separate it from the off-gases.

Although the initial interest in additives was to increase bulk density of the powder, their continued use has been mostly on the basis of forming a powdered product which can subsequently be melted into a consolidated solid, or on the basis of promoting more nearly complete calcination of the particles during their short residence time in the reactor.

1. Phosphate

Work on the formation of melts or glasses from the aqueous wastes, carried on apart from the spray calcination program[13], had indicated that the addition of sufficient phosphoric acid to the feed liquor to form orthophosphates of all cations results in the formation, upon drying and calcination, of a solid with a low melting point in the range of 800 C to 900 C. The exact temperature depends upon the initial composition of the feed. The product is undoubtedly not simply the orthophosphate of each of the cations present but more closely approximates the metaphosphate of sodium with the remainder of the phosphate distributed as the pyrophosphates of the other metallic constituents.

The effects of phosphate addition are summarized in Table II. Also included are the effects of sugar addition with and without phosphate. The effect of sugar will be discussed shortly.

TABLE II

EFFECT OF SUGAR AND PHOSPHATE ON PRODUCT CHARACTERISTICS

| Feed Composition | Density g/cc | Surface-Average Particle Size, Microns | Total Sulfate Lost, Percent |
|---|---|---|---|
| Low-sulfate Acidic Purex Waste | 0.4-0.5 | 1.6-2.5 | 0 |
| Above plus phosphate | 0.8-0.9 | 3.9-4.2 | 24 |
| Above plus phosphate and sugar (200 g/l) | 0.9-1.1 | 5.6-12.4 | 70-90 |
| High-sulfate Acidic Purex Waste | 0.5-0.75 | | 13 |
| Above plus sugar (50 g/l) | 0.9-1.3 | | 25 |
| Above plus sugar (150 g/l) | 0.5-0.7 | | 75 |

The addition of phosphoric acid to the simulated Purex waste altered the properties of the calcined powder considerably and resulted in a more dense, less dusty powder. Bulk density of the product was improved to the range of 0.8 to 0.9 g/cc and the surface-average particle size was increased to 4 microns.

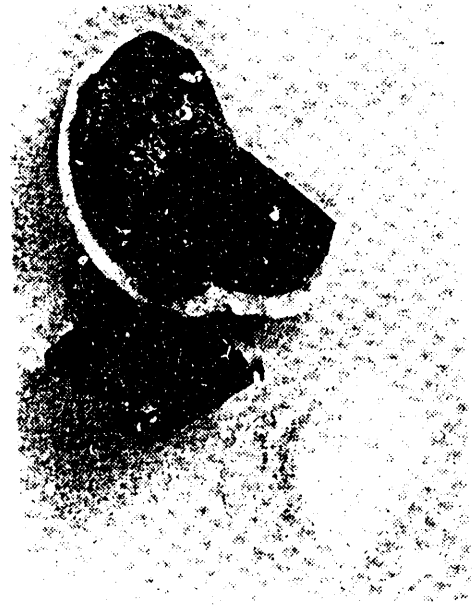
It is not known with certainty whether or not the individual particles are completely melted during their short residence within the reactor. The increase in density and particle size lead one to believe they are, since shrinking of the porous particles would result in higher density and lower specific surface area. However, both of these effects could be the result of basic differences in feed characteristics (such as higher viscosity) and, hence, larger initial droplets and the formation of a mastic stage during drying which retards the shattering of the droplets. X-ray diffraction patterns of the product powder and finely ground samples of melted and quenched product indicated essentially the same amorphous structure.

With the use of the melt-pot arrangement on several of the runs, the final product was an agglomerate solid with a melt density of about 2.8 g/cc. Shrinkage on freezing resulted in a void at the center as seen in Figure 5. The volume reduction factor from liquid to the melt was approximately 14. Melting point of the product was approximately 820 C though at 900 C, the average temperature of the pot, it was still a rather viscous fluid.

a
Purex Waste-No Additives

b
Purex Waste-w/Phosphate

c
Purex Waste-w/Phosphate & Sugar



d
TBP-25 Waste-w/Borate

FIGURE 5
SPRAY CALCINATION PRODUCTS

2. Borate

The use of other anions, such as sulfate, borate, and silicate were also considered as fluxing agents. The use of boric acid with feed liquors containing a considerable amount of sodium results in the formation of a soluble glass while with waste containing a great deal of aluminum the use of sodium tetraborate produces an inert glass upon calcination. With forty weight percent boric acid added, the product from the calcination of the combined high-acid Purex waste and the coating removal waste can be melted to form a clear amber glass. This corresponds to ratio of $B_2O_3$: $M_{2/n}O$ = 0.405, where M stands for metallic cation and n for its charge. (This system of nomenclature comes from the mineralogy-ceramic fields.) The ratio of sodium to all other cations, expressed as $Na_2O/M_{2/n}O$, is 0.415. With the TBP-25 waste, which contains a neglible amount of sodium, sodium tetraborate ($B_2O_3$: $Na_2O$ = 2) is added to the feed such that ratio $B_2O_3$: $M_{2/n}O$ = 0.667 which includes the sodium introduced with the additive. The resultant ratio of sodium to all cations is $Na_2O/M_n$ O = 0.335. These represent the lower limits of boric acid and sodium tetraborate addition that will result in melting points below 900 C with these particular waste compositions.(14)

3. Sulfate

The addition of sodium sulfate will result in a product which is fusible at 900 C, as is evident from experience with products which contain a large amount of this constiuent. No specific study was made to define the required amount of sodium sulfate; however, it has been noted that if the ratio $Na_2SO_4$: $M_{2/n}O$ is greater than 0.44 for either acid or basic Purex-type waste, within a narrow range of compositions listed in Table I, the powder will melt to a consolidated two-phase solid at 900 C. Systems containing slightly lower ratios (ca. 0.41) behave somewhat unpredictably with some samples appearing to melt and others simply sintering with an approximately two-fold reduction in volume. If the ratio is reduced to 0.39 sintering, but no melting, occurs.

No runs were made during which silicates were added, for although the resultant solids would generally be much more insoluble than those considered theretofore, the melting points of such systems would generally be in the 1100 C to 1300 C range unless the sodium content were very high. In any event they are characterized by very high viscosities which was thought to be a distinct disadvantage in considering them for remote operation.

4. Sugar

Because the melting point of the product from the phosphate-treated feed was very nearly equal to the maximum temperature obtained in the column, a means of producing an exothermic

reaction within, or on the surface of, the particle was studied. Sugar, added to the feed in concentrations up to 250 g/l, decomposes in the reactor to a carbonaceous residue which ignites in the hottest section of the column if oxygen is introduced into the column. Improvement in powder characteristics was very marked (both with feed to which phosphate had been added and with high-sulfate Purex acidic waste without phosphate) if the amount of oxygen introduced was properly controlled as discussed subsequently. Sugar addition decreases the sulfate content of the product as the result of three factors: (1) the reduction of iron and consequently the displacement of a greater quantity of sulfate, (2) direct reduction of sulfate, and (3) thermal decomposition of iron and aluminum sulfate because of higher particle temperature. Approximately 75 percent of the sulfate is removed from the original feed liquor by the addition of phosphate plus sugar as compared with 20 percent by the addition of phosphate alone.

As shown in Table II, the addition of both sugar (250 g/l) and phosphate increased the bulk density of the powder to the range of 0.9 to 1.1 g/cc and markedly increased the surface-average particle size. The melting point of powder produced from liquor containing sugar and phosphate is somewhat lower (about 50 C) than that from liquor to which only phosphate is added. Densities of the resulting melts are about equal, 2.8 to 3.0 grams/cc.

The addition of sugar plus oxygen greatly reduced the heat load on the column. Measurement of the heat load can be done only approximately by noting power required to maintain a set temperature distribution with no feed and subtracting this from that required while processing feed. Such measurements have indicated that the power requirement with feed containing sugar at 250 g/l, plus a stoichiometric amount of oxygen, was less than twenty percent that for straight Purex waste. The cloud temperature in the hottest section of the calciner also reflects the exothermic reaction between oxygen and the decomposition products of sugar. Figure 15 shows that cloud temperatures may exceed the measured wall temperature by as much as 50 C and individual particle temperatures are probably considerably above that. Appendix III contains a theoretical discussion of possible ignition temperatures.

Neutralized Purex waste which contains a high concentration of sodium nitrate in the supernate cannot be calcined in the spray calciner without the addition of sugar. The sodium nitrate is liquid over the range in temperature from 310 C to greater than 900 C and coats the walls of the reactor and the filters as a molten salt. Sugar serves as a reductant which reacts almost explosively with the

nitrate as the solution is dried and heated to 220 C. The presence of very small amounts of material at any one time makes the reaction safe in the spray calciner. Nevertheless, as a liquid mixture the system is completely stable and safe to handle. The product is predominantly sodium carbonate and one possible equation for the reaction is:

$$4NaNO_3 + 5C \rightarrow 2Na_2CO_3 + 3CO_2 + 2N_2.$$

However, a considerable quantity of ammonia is present in the condensate which indicates that at least a portion of the nitrate is reduced beyond elemental nitrogen as in the equation:

$$2NaNO_3 + 4C \rightarrow Na_2CO_3 + 2NH_3 + CO_2.$$

D. Thermal Conductivities of Spray Calcined Wastes

1. Powders

Thermal conductivities of spray calcined simulated wastes range from 0.05 to 0.135 Btu/hr, ft$^2$,°F/ft. over the temperature range, 100 to 400 F. Figure 6 shows that variation of thermal conductivity with temperature is quite linear and experimental results at higher temperatures indicate extrapolations may be made at least to 1100 F. Extrapolations of the data in Figure 6 is valid except for some powders which decomposed upon further heating, such as a high-sulfate Purex waste.

The thermal conductivities of spray calcined powders are more strongly dependent on powder density than composition. This is shown in Figure 7 in which the thermal conductivities of various spray calcined powders are plotted versus their densities. Any method of increasing the density will also increase the conductivity of the powder. In storage of radioactive wastes the heat generation rate also goes up linearly with density. Therefore an increase in the density, and hence conductivity, of a powder is offset by an increase in the volumetric heating rate and the steady state internal temperature of a stored waste powder would not be changed. Therefore the main advantage of increased density is the decrease in required storage space.

2. Solidified Melts

Melting and resolidifying the waste powders results in a marked increase in thermal conductivity as well as density. Thermal conductivity of solidified melts range from 0.3 to 0.85 Btu/hr ft$^2$ °F/ft at about 250 F. Melting increases the thermal conductivity by a factor of 3 to 10 while the density is increased by a factor of 3 to 4 over the powder.

The thermal conductivities of two types of simulated waste melts (Purex with phosphate added and Redox-aluminum nitrate with Borax added) versus temperature[13] are shown in Figure 8. An extrapolation of the powder thermal conductivities is also shown in Figure 8. It can be seen that melting offers considerable advantage in reducing the internal waste temperature as well as storage space.

## LEGEND

Figures 6 and 7

Note: The densities of powders used in these thermal conductivity tests are not necessarily representative of the particular feed. The bulk density is also a function of other variables such as feed rate, atomizing fluid, column temperature, and oxygen addition. The data merely inidcate the independence of thermal conductivity on feed composition.

- ▽ Simulated acid killed Purex waste with phosphate and borate added.
- △ Simulated neutralized Purex waste with 250 g sugar added per liter.
- ○ Simulated acid killed Purex waste with phosphate and 250 g sugar added per liter.
- ◇ Simulated TBP-25 waste with 1.2 moles of boron per mole of aluminum added as tetraborate.
- ⬡ Simulated Acid killed Purex waste.
- □ Simulated acid killed Purex waste with phosphate and 250 g sugar added per liter.

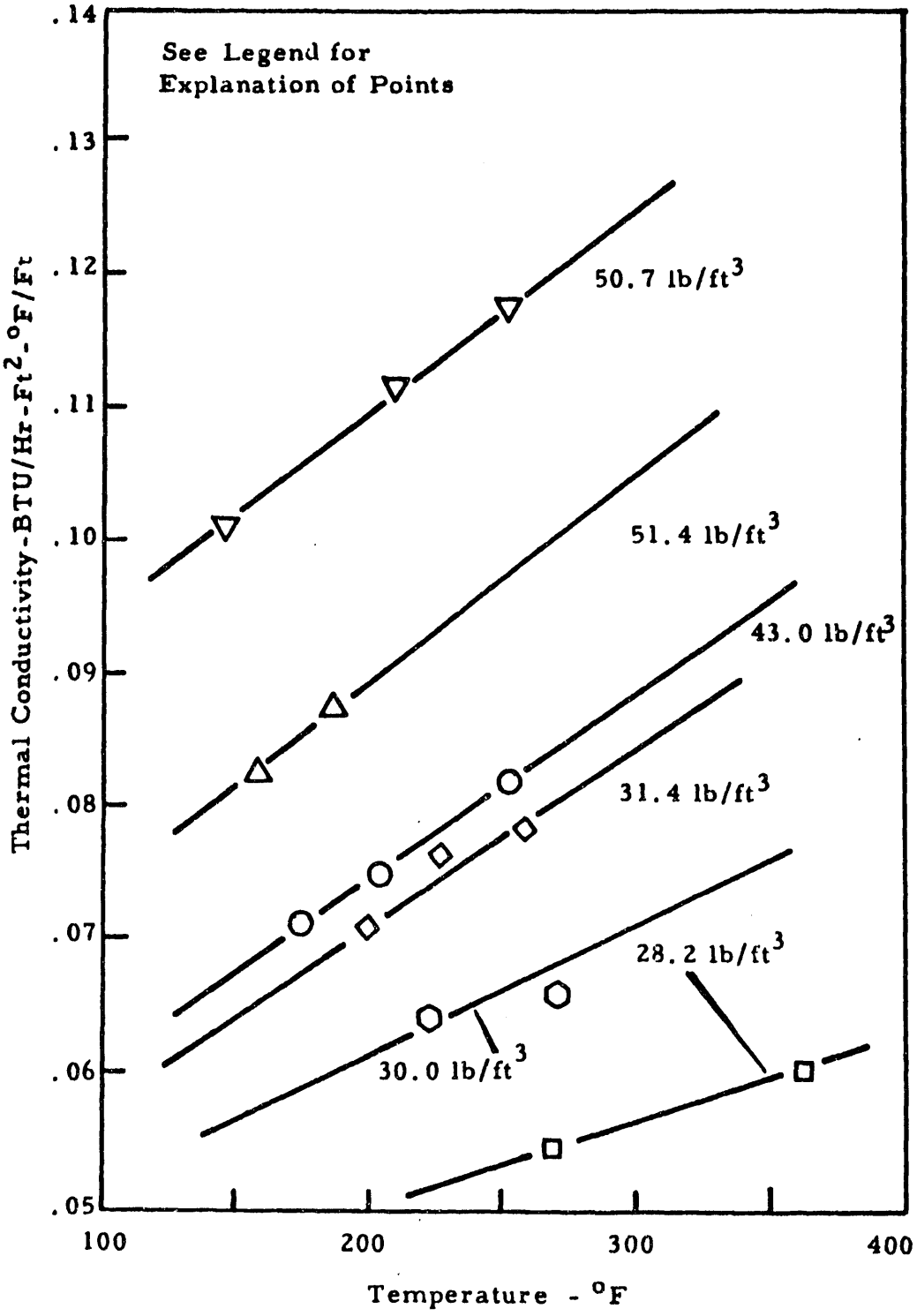



FIGURE 6

Thermal Conductivity of Spray Calcined Powders

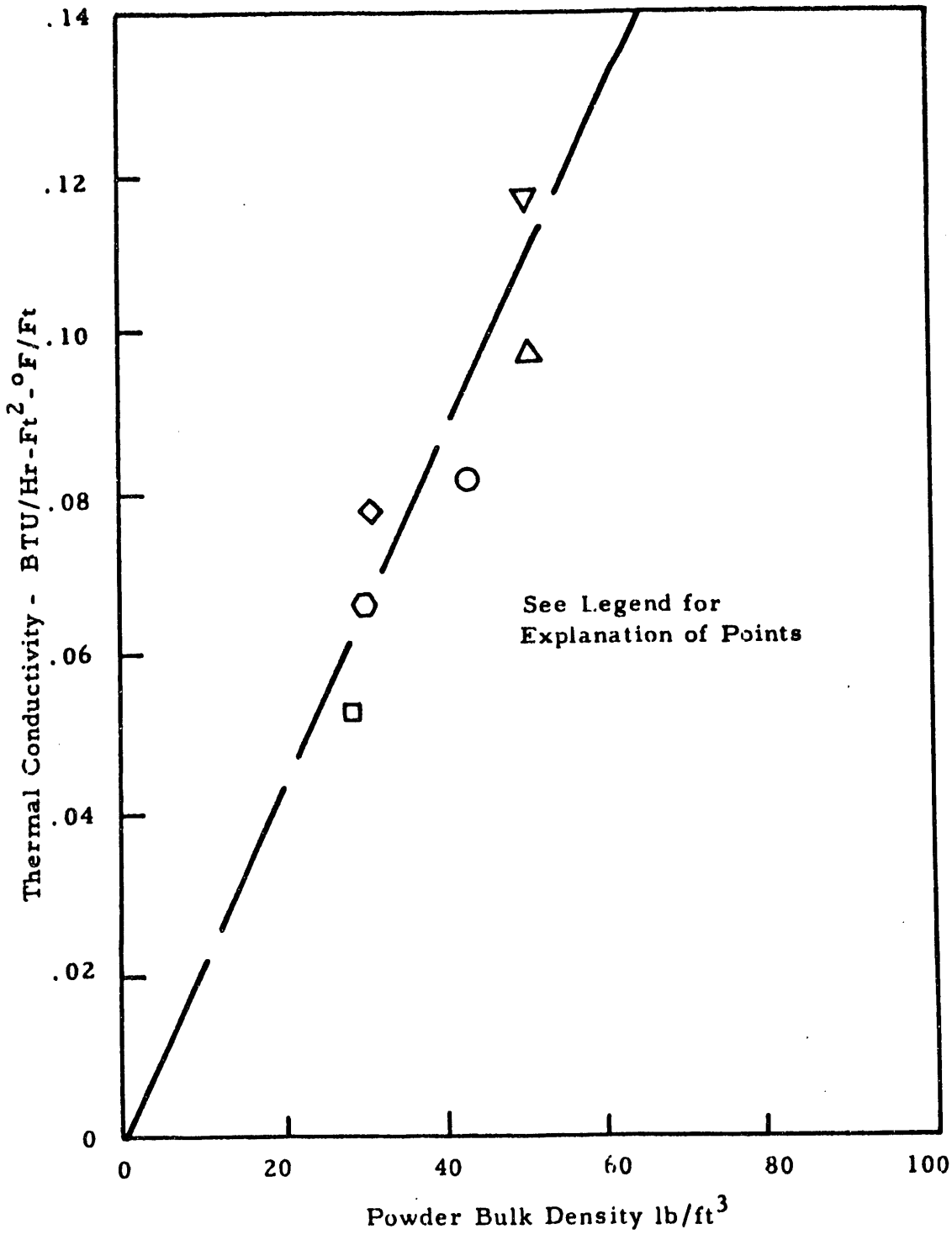



FIGURE 7

Bulk Density Effect on Thermal Conductivity of Spray Calcined Powders at 250 F



AEC-GE RICHLAND, WASH

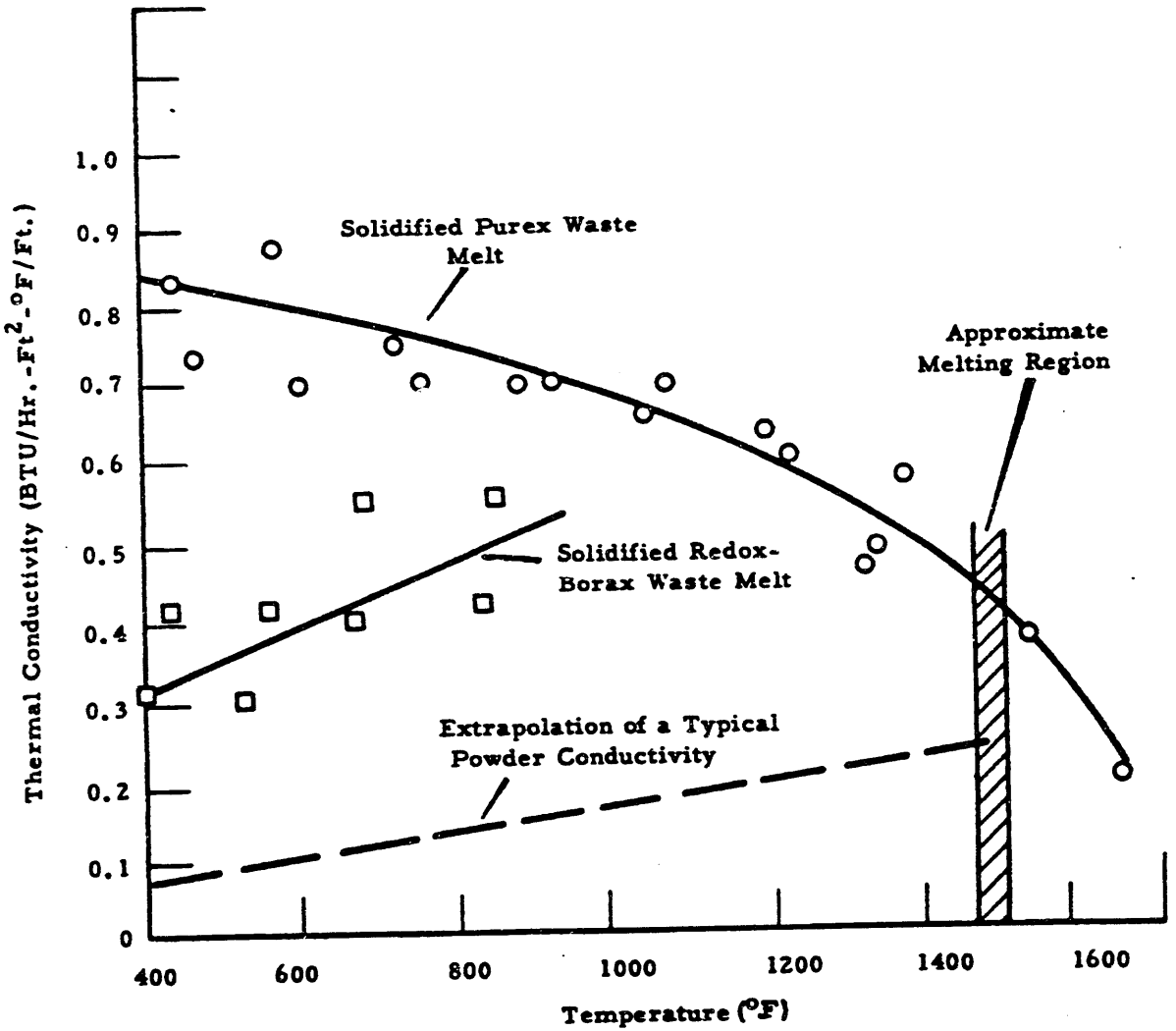



**FIGURE 8**

**Thermal Conductivities of Resolidified Melted Wastes (G. B. Barton)**

ARC-88 SCHUTZ, WASH.

E. Operating Variables

The principal operating variables that may be conveniently adjusted in the spray-calcination process are (1) feed rate, (2) atomizing steam rate, (3) the quantity of additives introduced, (4) the amount of oxygen introduced, if any, to complete the combustion of sugar in the reactor, and (5) reactor wall temperatures. Although the process is generally operable over a wide range of conditions, the product characteristics are affected by the conditions. As noted previously, the emphasis placed upon improving such characteristics as powder density and free flowing character is dependent upon whether the product is to be stored as a powder or a consolidated solid. From the brief study made of the operating variables it was concluded that they could not be adjusted to produce the most favorable condition of all the characteristics for powder disposal. But, with melt disposal, several of the product characteristics, notably powder density and free flowing nature, are of lesser importance and operating conditions can be specified that would result in a product favorable in all other respects.

1. Extent of Calcination

The primary product characteristic used to measure the effect of the operating variables was the extent of calcination. The final products of calcination of the gross chemicals present in high-sulfate Purex waste are sodium sulfate, which is relatively stable up to a temperature of above 900 C, and oxides of iron and aluminum. The sulfates of iron and aluminum are formed first on drying and decompose to the oxides relatively slowly at temperatures below 800 C. Consequently, incompletely calcined powders decompose further on heating, and give off a considerable amount of gas which is accompanied by a loss in weight. The loss of weight on heating the powders for a prolonged period at 900 C was used to indicate the extent of calcination.

G. B. Barton demonstrated the stability of the sodium sulfate and the decomposition of the sulfates of iron and aluminum in a series of experiments in which powders having different ratios of sodium to sulfate were heated to 900 C and measurements made of the volume of gas driven off and loss in weight of the samples. Results are summarized in Table III.

TABLE III

EFFECT OF SODIUM-to-SULFATE RATIO ON

EXTENT OF PRODUCT OFF-GASING

| Equivalents Ratio Na: $SO_4$ | Wt. Loss per cent | Total Acid in Off-Gases m-equivalents/gram |
|---|---|---|
| 0.25 | 40.6 | 8.88 |
| 0.87 | 5.47 | 1.01 |
| 1.0 | 3.39 | .50 |
| 1.14 | 4.39 | .13 |

These results indicate the relative stability of the sulfate tied up as sodium sulfate.

2. Feed Rate

Figure 9 shows the effect of feed rate upon the extent of calcination. One observes that the effect is not consistent. With neutralized feed slurries to which sugar has been added or acid feed solutions with no sugar, the weight loss increased slightly with the feed rate, while with acid feed plus sugar the weight loss decreases with increasing feed rate. The increase in weight loss (less complete calcination) with higher flow rates is the more expected behavior; the lower residence time of the powder within the reactor results in less complete calcination. A possible explanation for the anomolous behavior of the acidic feed with sugar is that all these runs were made with a constant rate of addition of oxygen. As will be pointed out subsequently, sugar appears to be less effective in reducing sulfates in the presence of oxygen, hence this increase in extent of calcination with feed rate may simply reflect the decrease in the stoichiometric quantity of oxygen present in the system as the flow rate is increased.

The variation in the bulk density of the powder with feed rate is summarized in Figure 10. The density increases with the feed rate, with the exception of the series of runs with acidic high-sulfate waste to which 150 grams per liter of sugar had been added. Probably this is the result of the lower temperature in the nozzle zone of the reactor at a higher feed rate. Control of the upper section of the column is from a point 30" below the nozzle. As the drying load is increased, the top of the column operates at a lower temperature and the rate of evaporation for an individual droplet is reduced. As a consequence, less

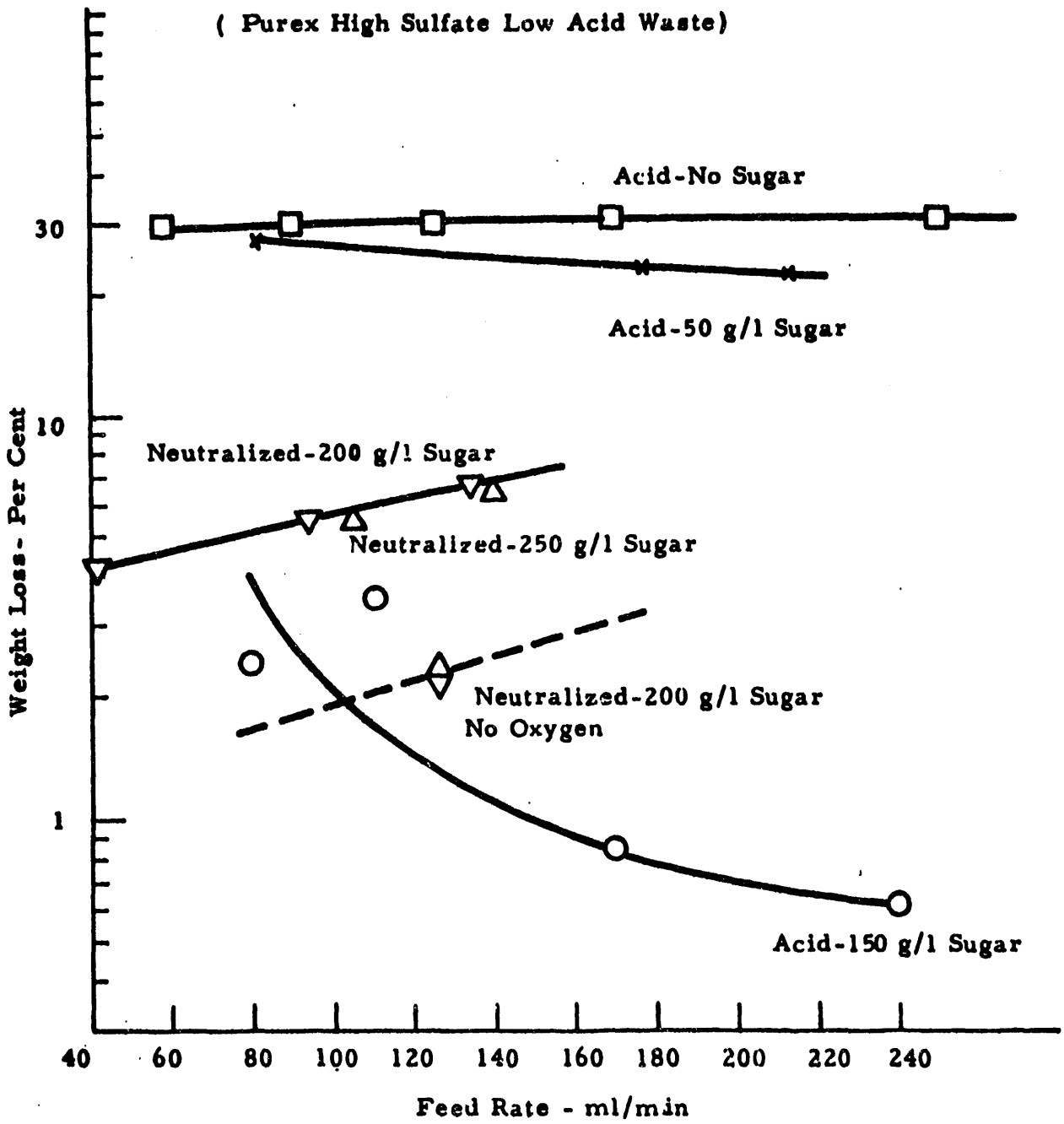



FIGURE 9

Effect of Feed Rate on Degree of Calcination
As determined by powder weight loss upon heating to 900°C

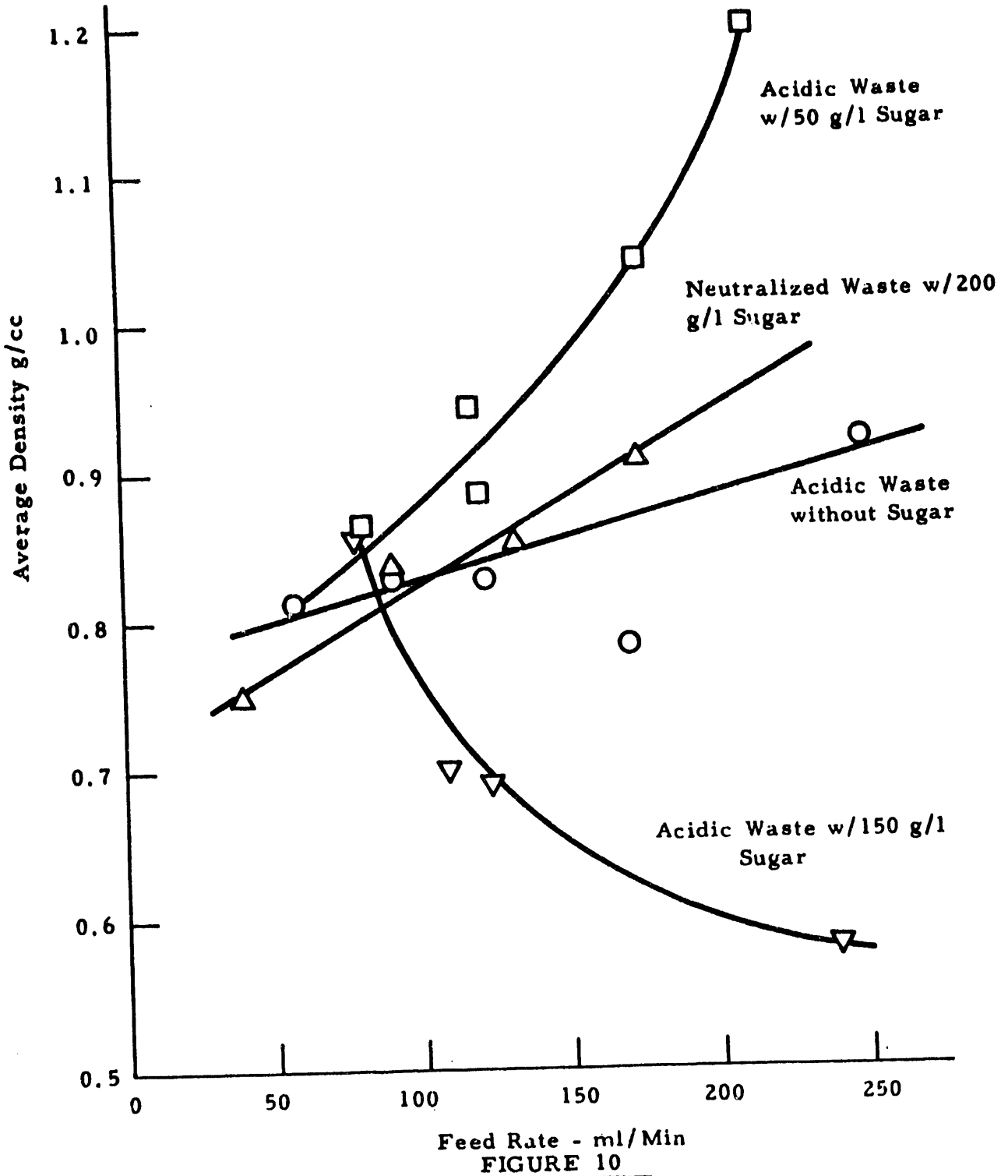



FIGURE 10

Effect of Feed Rate on Product Density in Spray Calciner with Low Acid High Sulfate Purex Waste



ARCHIVES RICHLAND, WASH.

shattering of the particles during the last stages of drying takes place. Possibly other factors contribute to the increase in density; for example, one may observe from Figures 9 and 10 that an increase in density is generally accompanied by a decrease in extent of calcination. This suggests that the decomposition of the insoluble sulfates results in a porous particle of lower density. This effect may be the predominant one in the case of acid waste to which sufficient sugar has been added to remove the preponderant amount of the unstable sulfates.

3. Atomizing Steam Rate

Normally steam was used and preferred as the atomizing fluid in the two-fluid nozzle, although air was also satisfactory, because the volume of off-gas following removal of the condensables is considerably less. Furthermore, under some conditions a reducing atmosphere within the column may be desirable.

Within the normal operating range of the nozzle, the steam pressure, and hence its flow rate, does not strongly effect the degree of calcination of the product. Several runs were made with acidic Purex waste (composition) with 150 g/l sugar added at a feed rate of 120 ml/min during which the atomizing steam pressure was varied between 40 and 75 psig. The weight loss of the products heated to 900 C varied between 0.74 and 2.0 weight percent but showed no consistent trend with increasing steam pressure.

However, a definite lower limit for the steam-to-feed ratio does exist below which the system becomes inoperable. The steam pressure must be sufficiently high to break up the jet of liquid issuing from the center of the nozzle. If it is not, the liquid is atomized to only a small extent and the resultant droplets are too large to be dried before impinging on the walls or falling through the reactor. The flow ratio of steam-to-liquid at which this instability is first noted is dependent on the design of the nozzle and the liquid properties, including viscosity, density, and surface tension. With the particular nozzle used for most of the studies (Spraying Systems Company Set-Up No. 22) the lower limit of the steam-to-liquid flow ratio was approximately 0.5, i.e., the contribution of the atomizing steam to the volume of condensables was about one third the total volume.

4. Sugar Addition

The rate of decomposition in the calciner of iron and aluminum sulfates is enhanced by the addition of sugar, which serves as a reducing agent as well as an additional heat source (by burning) within each particle. The effect

of adding sugar is shown in Figure 11 in which the weight loss resulting from heating the product powders to 900 C is plotted as a function of the sugar added. One may conclude that the residual amount of unstable sulfates is greatly reduced if at least 150 grams per liter of sugar is added to the feed; The high weight loss from the sample containing 250 g/l sugar is probably an error; this run was the first of the series following a run without sugar addition and consequently the samples were probably contaminated by the previous run. Table IV summarizes the results.

TABLE IV

EFFECT OF SUGAR CONTENT ON EXTENT OF CALCINATION

(Simulated Purex High-Sulfate Acidic Waste)

Feed rate - 118 ml/min. Nozzle steam pressure-40 psig.

| Sugar Conc. g/l | Ave. Wt. Loss on Heating of Product Per Cent | Powder Density g/cc | $SO_4^{=}$ Concentration, Wt. Per Cent |
|---|---|---|---|
| 50 | 23.6 | 1.03 | 55.3 |
| 100 | 5.8 | 1.36 | 39.3 |
| 150 | 0.74 | .71 | 33.1 |
| 200 | 0.61 | .81 | 32.6 |
| 250 | 6.1 | 1.05 | 36.6 |

One sees from the tabulated results that the most completely calcined product has also the lowest density. This is of little concern since the powder could be melted to a compact solid before storage so that the final product density is not a function of the bulk density of the powder.

One of the principal advantages of sugar addition (> 100 g/l) to high-sulfate waste is that it overcomes the tendency of the powder to cake on the surfaces of the off-gas filters or within the off-gas lines and the cyclone separator. Operation of the equipment was very poor without the sugar; powder would build up on the filter forming a hard, dense cake that could not be removed by the pulse blow-back arrangement. With the cyclone separator in place of the filters, the powder formed a hard cake along the walls of the off-gas line, building up particularly at pipe elbows and near the inlet of the cyclone. Addition of 150 g/l sugar resulted in a fine, but relatively free flowing product, that could be easily filtered or handled in the cyclone. Incipient melting or a mastic phase resulting from the partial decomposition of the iron and aluminum sulfates is probably the cause of the caking tendency of this powder when calcined without the addition of sugar.

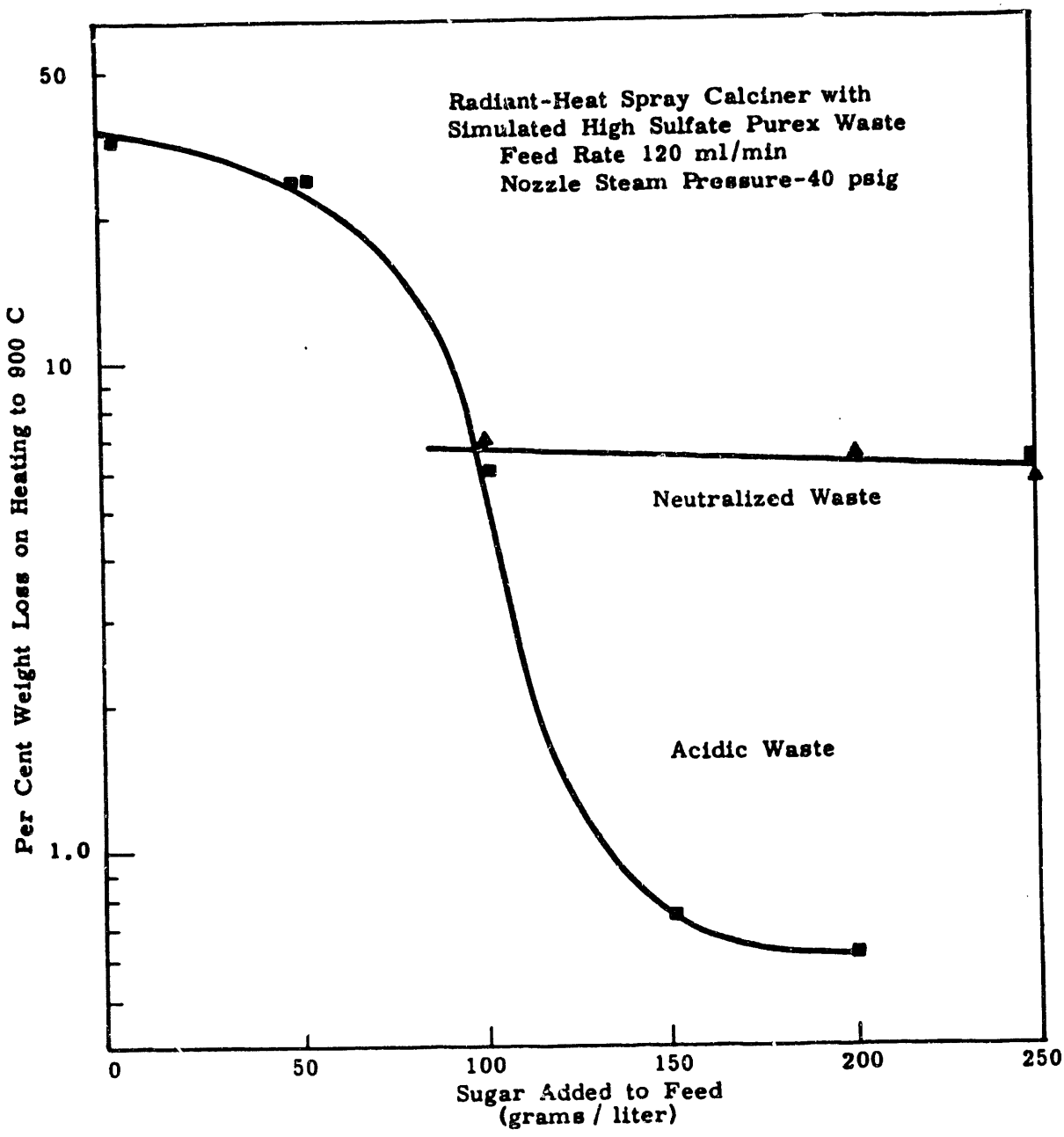



FIGURE 11

Effect of Sugar Addition on Extent of Calcination

5. Oxygen Addition:

As discussed earlier, the introduction of oxygen into the reactor to ignite the carbonaceous residue provides a competing reaction to the reduction of sulfate by the carbon (sugar). A series of runs was made in which the sugar content and feed rate of a high-sulfate, acidic Purex waste was maintained constant while the quantity of oxygen introduced was varied from zero to about 140 percent of the stoichiometric amount required to oxidize all the carbon to carbon dioxide. Results are summarized in Figure 12 in which the sulfate content and the weight loss on heating to 900 C is plotted as a function of the oxygen concentration. One observes that increasing the oxygen above approximately 30 percent stoichiometric does decrease the amount of sulfate removed. The need for a small amount of oxygen for most efficient calcination may reflect the fact that the thermal boost given by the ignition of the carbonaceous residue may be helpful in the removal of the unstable sulfates.

The series of runs, previously discussed, in which the feed rate was varied while the sugar content and rate of oxygen addition were maintained constant probably also indicates the effect of varying oxygen addition, which ranged from 28 percent stoichiometric at a waste slurry feed rate of 240 ml/min to 85 percent stoichiometric at a feed rate of 80 ml/min (Figure 9). Thus the apparent increase in extent of calcination with feed rate may have been the result of a decrease in the relative rate of oxygen addition to the column.

Oxygen seems to retard the calcination of neutralized wastes also, as well as acidic wastes. A run made without oxygen with a neutralized high-sulfate Purex waste to which 200 g/l sugar had been added gave a product that was more completely calcined than that from a similar run with the addition of 40 percent the stoichiometric quantity of oxygen (i.e., 2.3 versus 6.4 percent weight loss on heating to 900 C).

6. Reactor Temperature:

Because of the very short residence time for the calcination reactions to take place within the reactor, it was concluded that generally the reactor walls should be at the highest temperature commenserate with the corrosion behavior of the materials of construction and their desired service life. However, for optimum powder density, this is not the case. With several different simulated waste compositions, particularly those which undergo melting within the reactor, maintaining the top of the column at a considerably lower temperature than the center section resulted in a higher density product. Operation with a lower temperature at the top reduces the rate of evaporation and therefore the extent of shattering of the droplets,

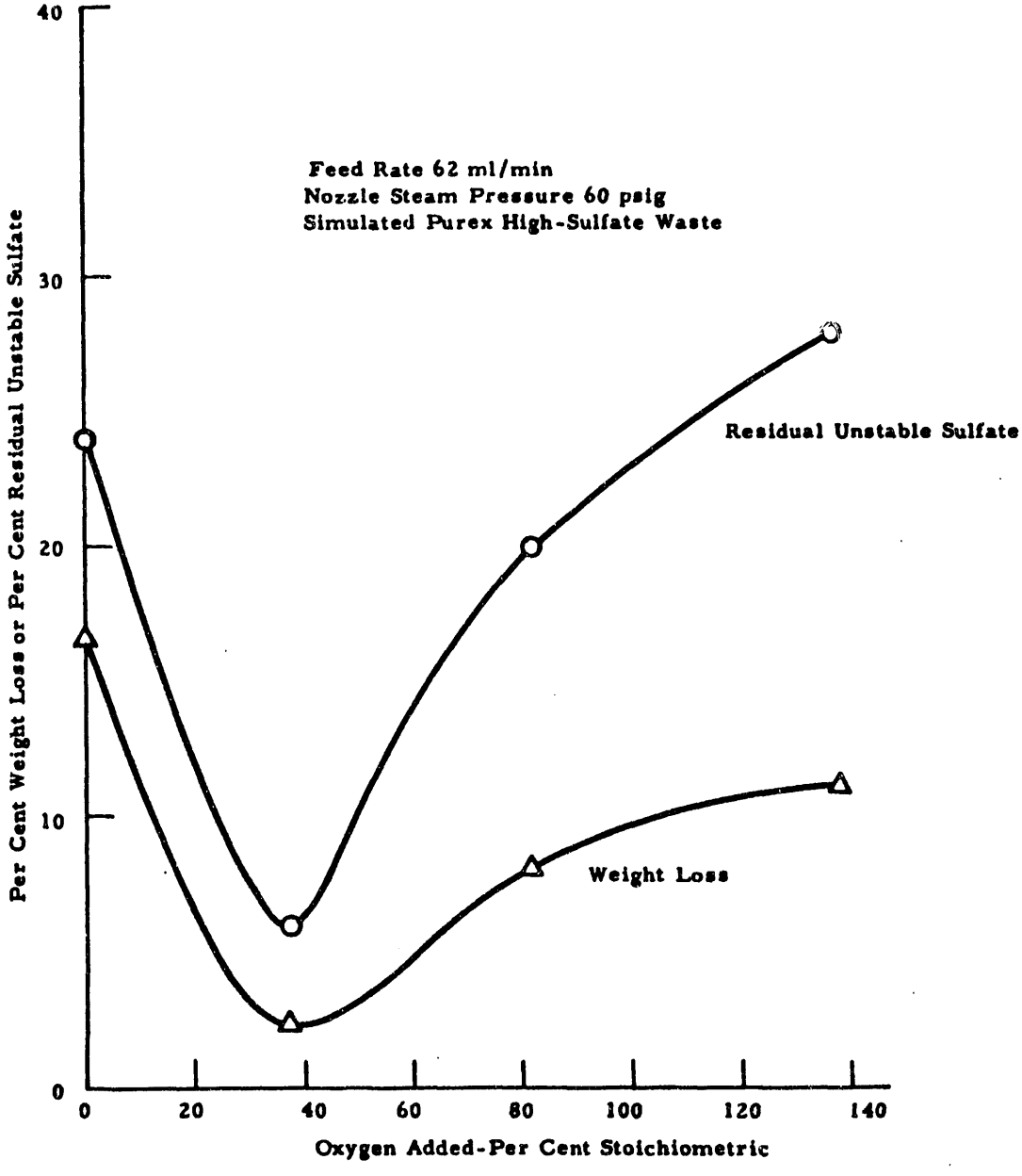



FIGURE 12

Effect of Oxygen Addition on Extent of Calcination



AEC-GE RICHLAND, WASH.

as described previously under the effect of feed rate. Consequently, the average particle size and bulk density of the product are improved. With acidic feed to which phosphate and sugar had been added, a temperature pattern of about 825 C in the center section and as low as 325 C in the top section (measured 15 inches below the nozzle) was found to produce powder of the highest density - up to 1.2 gm/cc.

F. Wall Deposits

As the spray is injected at high velocity into the static gas chamber, it inducts gas into the jet. This gas must be replaced by back mixing of gas from below. Solid powder is also brought back up the column by the turbulent back mixing in the nozzle zone and, upon contact, it adheres to the wall. In general the spray angle is sufficiently small that the particles are dry before they strike the wall.

1. Effect on Column Operation:

The impingement of the particles on the wall causes a build-up to form on the column walls. The build-up may be light and fluffy or flakey, depending on the feed composition. Since the build-up is deposited lightly, it can be knocked off during operation by vibration or by a sharp blow on the column and plugging of the column by this wall build-up does not appear to be a problem. Two runs of 24 hours duration, made with feeds which had the worst tendency to build-up, indicated the thickness of the residue wall powder did not increase beyond 1/4 inch. In these runs a pneumatic vibrator was used to knock down the wall powder. An automatic hammer striking the top of the column occasionally was found to be even more effective.

The column cannot operate with a solution which forms a stable, low-melting solid (upon drying) such as sodium nitrate, which when melted, coats the column walls. Sodium nitrate can be calcined by converting it to sodium carbonate within the reactor through the addition of sugar.

Cleaning the column can be accomplished by one, or a combination, of several methods. Most of the powder is removed by flushing down the cooled walls of the column with water; less than a gallon is generally required. The residue is usually a thin, hard scale which is removed either upon heating as the result of the difference in thermal expansion or by brushing down the sides. Remote cleaning could probably best be accomplished by a small sand-blast lance introduced through the top of the column. Under normal operation no cleaning would be required.

2. Properties of Wall Powder:

Powder which is held up on the wall is not calcined as well as the powder that goes straight through, although changes in column variables as discussed in the last section affect both fractions in a similar manner. The extent of calcination for the two powder fractions, as indicated by the weight loss on prolonged heating at 900 C, agrees generally within 30 percent, with the straight-through powder always the more completely calcined. The explanation for this phenomena is that build-up occurs mostly in the cool upper zone. As the agglomerated particles break off they plummet and do not have sufficient residence time to become completely calcined. Furthermore, the exterior surface of the flake probably shields the interior from the radiant walls.

3. Amount of Wall Powder:

For an acidic Purex waste the indications are that increasing sugar content and increasing nozzle steam pressure and decreasing feed rate reduce the amount of powder which is held up on the walls. The caustic neutralized waste is not as strongly affected by these variables. A high-sulfate Purex waste was used to study the effect of these variables on column hold-up. The results are shown on Table V. The agglomerated wall powder was separated, by means of baffles, from the fine powder which was carried further through the system by the suspending gas.

4. Channel Recycle Studies:

Several methods were tried for reducing back mixing and powder build-up at the top of the column. One possible solution is to use channels along the outside of the column which will allow the needed recycle air to come back to the top after the particles have passed through the hottest zone as small drops. Visual studies of the phenomena were made in a long rectangular box of Lucite (Figure 13) with channels whose entrance and exit could be moved to different heights. The same spray nozzle was used as in the spray calciner with a brightly visible solution of potassium permanganate. With the 20° spray cone angle the wall impingement point was 22" below the top. Recycle through the channels occurred when the port was 24" or more below the nozzle and back mixing in the nozzle zone was almost completely eliminated. Use of the channel recycle principle in the spray calciner would involve a heated interior wall (Figure 14) hung from the top of the column and equipped with ports at the top to provide for recirculation of gases from the annular region.

## TABLE V

## FRACTION OF POWDER HELD UP ON COLUMN WALLS

### ACIDIC FEED

| Feed Rate ml/min | Wall Fraction percent | Sugar Content g/l | Wall Fraction percent | Nozzle Steam Pressure, psig | Wall Fracti percent |
|---|---|---|---|---|---|
| 150 g/l sugar | | 118 ml/min. | | 40 | 35 |
| 80 | 31 | 50 | 47 | 60 | 34 |
| 110 | 34 | 100 | 26 | 75 | 20 |
| 170 | 30 | 150 | 35 | | |
| 240 | 50 | 200 | 20 | | |
| | | 250 | 25 | | |
| No sugar | | | | | |
| 57 | 47 | | | | |
| 92 | 66 | | | | |
| 124 | 59 | | | | |
| 170 | 76 | | | | |
| 250 | 80 | | | | |

### NEUTRALIZED FEED

| | | | | | |
|---|---|---|---|---|---|
| 200 g/l sugar | | 135 ml/min 10 l/min oxygen | | | |
| 93 | 40 | 200 | 40 | | |
| 134 | 40 | 250 | 60 | | |
| No oxygen 200 g/l Sugar | | | | | |
| 125 | 25 | | | | |

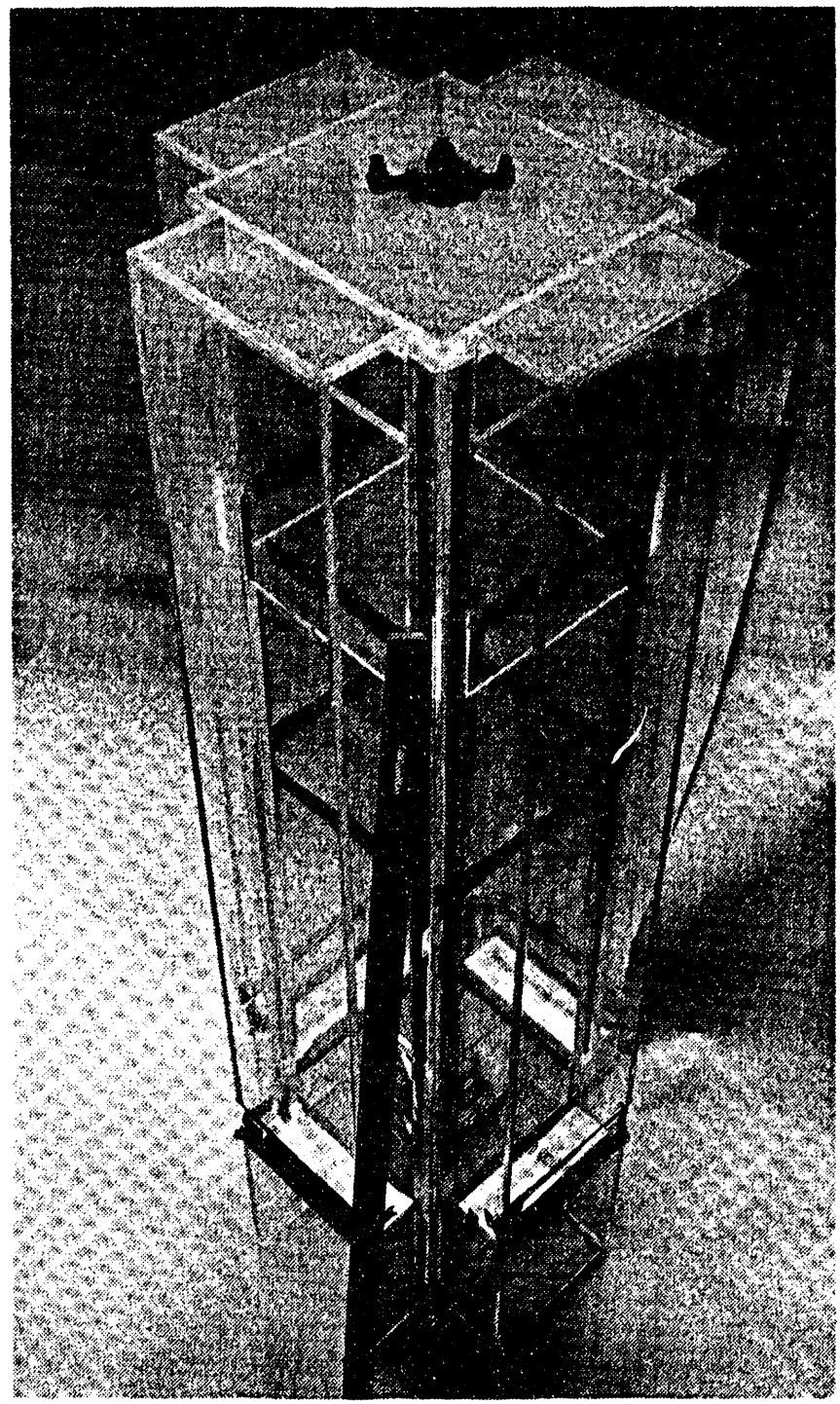


FIGURE 13
Lucite Mock-up of 8 inch Spray Calciner
with Recycle Channels

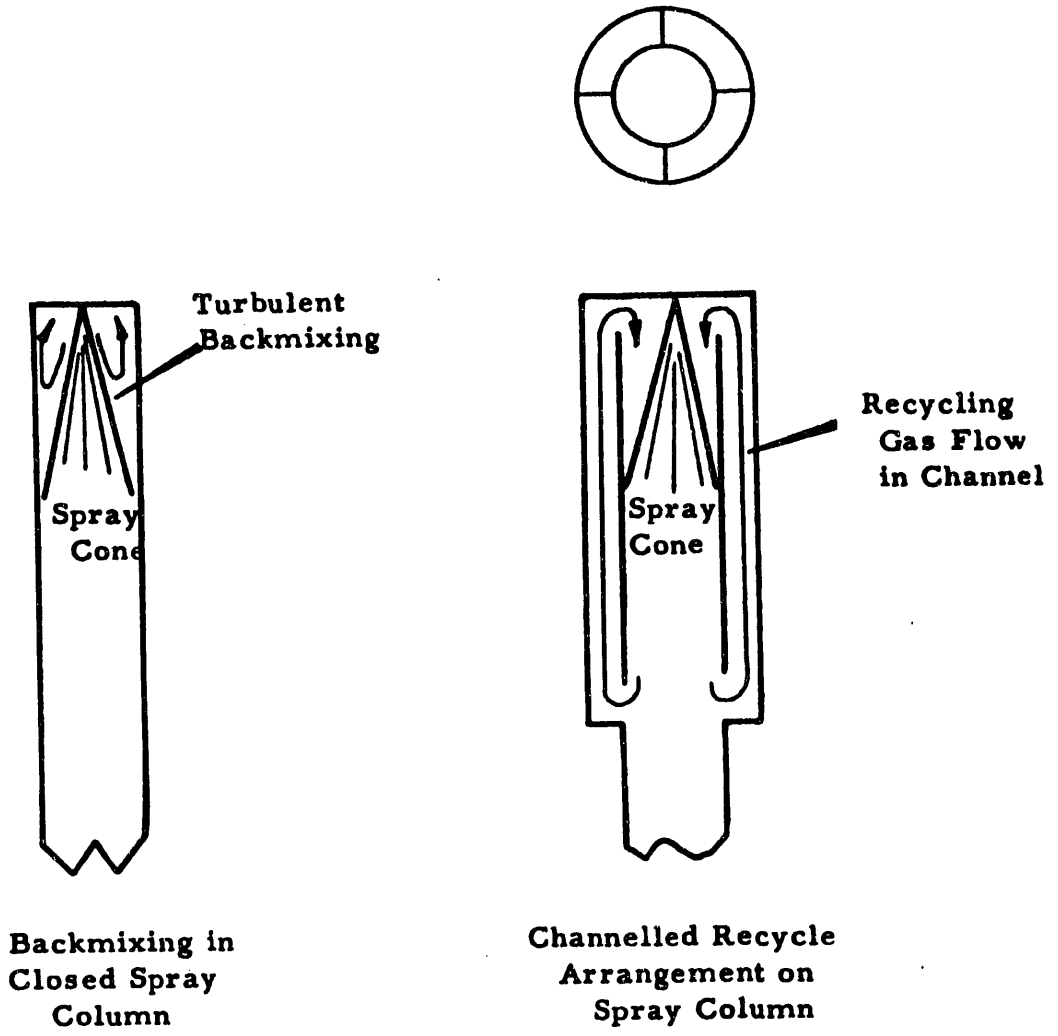



FIGURE 14

Schematic Sketch of Channel Recycle in a Radiant Heat Spray Calciner

The wall would be hollow to allow heating elements to be hung from exterior of the column into the wall. Such an arrangement would provide the extra advantages of nearly twice the effective heating surface of a single column with the same diameter as the inner section of the recycle column (because of the high percentage of back mixing) and a convenient method of heating, from the standpoint of remote maintenance of the heating elements. Figure 15 is a sketch of a spray calciner incorporating channel recycle.

G. Corrosion

Corrosion samples of various metals being considered for materials of construction were held in the calciner column near the hottest (850 C) zone during several hours of operation while simulated wastes were being processed. Corrosion rates for these samples based on actual waste processing time and extrapolated to a monthly rate are shown below for two series of runs.

During the first series several kinds of feeds were used in addition to acidic Purex waste. These included coating waste, and sugar-plus-phosphate added to Purex waste. It is probable that these feeds were more corrosive than the acidic Purex waste which was used exclusively in the second series.

TABLE VI

METAL SAMPLE CORROSION IN SPRAY CALCINER AT 850 C.

| | Corrosion Rate - Mils/Month[a] | |
|---|---|---|
| | 1st Series | 2nd Series |
| Stainless Steel Type 304L | 260 mils/month | - |
| Inconel | 6.3 | 0.4 Mils/month |
| Stainless Steel Type 446 | 48. | .01 |
| Monel | very high - sample almost completely destroyed. | --- |
| Nionel | High - pitting attack | --- |
| Carpenter 20 | Very high | --- |

(a) Assuming 720 operating hours per month

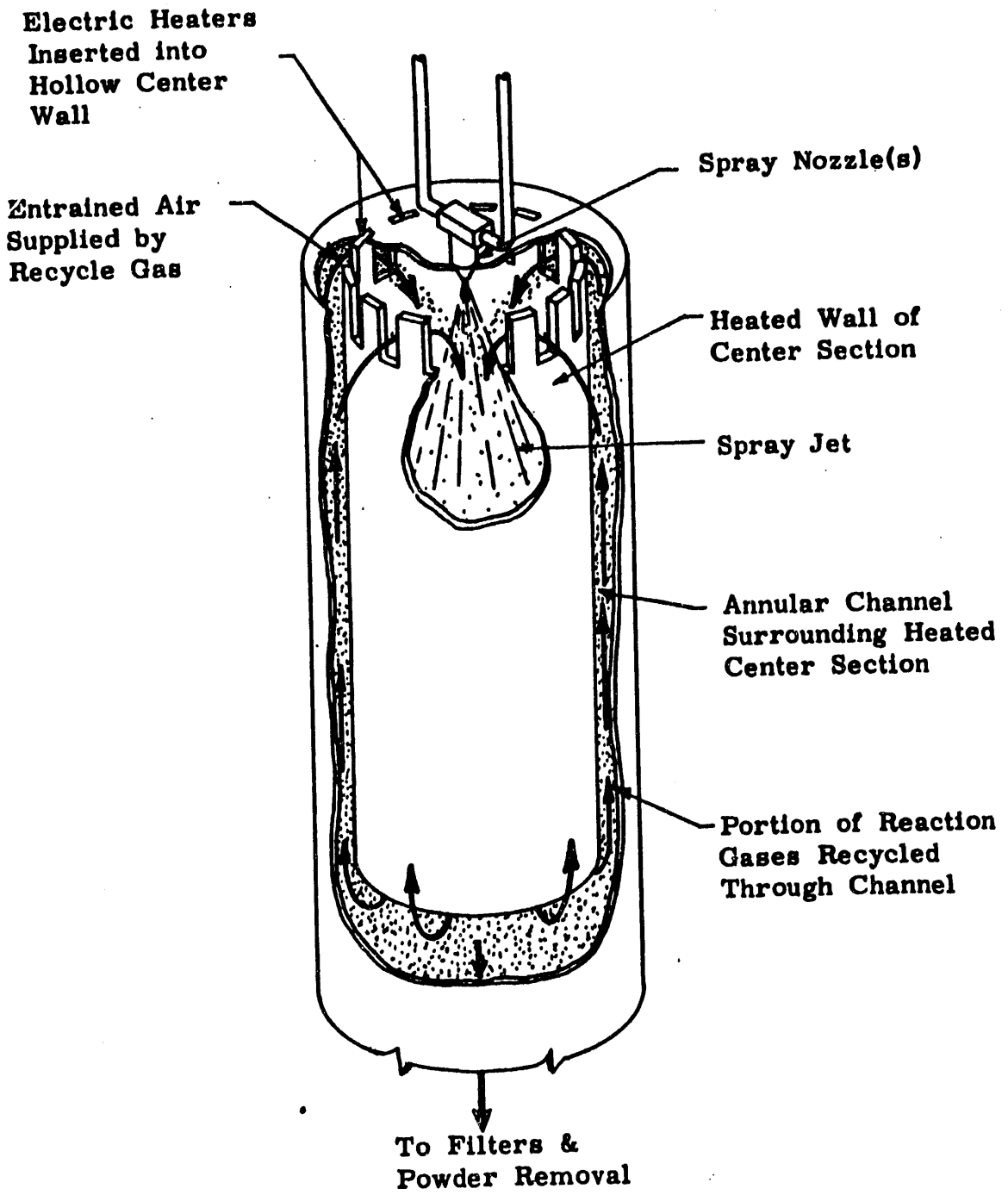



FIGURE 15

Channel Recycle Design

Inconel and stainless steel type 446 formed very stable and strongly adherent oxide films. The second series of runs was made with these two metals at twice the operating time of the first series.

After 170 hours of operation, during which feed was actually being processed, a small weld between the Inconel wall and a stainless steel thermocouple tube corroded through. At a distance of approximately one inch from the weld the Inconel wall was in good condition. The circumferential welds to the stainless steel at the top and bottom of the Inconel section showed little or no corrosive attack.

A very corrosive run was then made with caustic neutralized Zirflex waste. The off-gases from this run contained 0.5 percent HF and 0.02 percent $F_2$ which destroyed the temperature controlling thermocouple in the hot zone of the column. Since the arrangement was not fail safe, the column temperature went up to 1000 C at the hottest zone. The Inconel column wall corroded through at several places in the hot zone. Figure 16 is a photograph of the corroded Inconel section. Samples of the wall from this region show sound metal only a short distance up or down from the points of failure. Samples of the wall at the hottest zone show areas of 50 to 70 percent attack, and areas of complete destruction of the metal in close proximity indicating that localized "hot spots" may have accelerated the attack. Photomicrographs of the samples of 50 to 70 percent attack show three definite regions in cross section:

1. The sound crystal grained metal.

2. A region in which some of the grains have a rather amorphous appearance (they do not etch to show crystal planes but show tiny surface pits).

3. The corroded oxide layer interspersed with grains of the amorphous material.

The boundaries of the regions are quite marked.

Although the mechanism is not known, the "hot spot" attack suggests that lower temperatures would be the biggest help in reducing corrosion.

Subsequent to the run, the writers learned that to truly minimize the corrosiveness of Zirflex waste, sufficient caustic must be added to drive off the ammonia as well as to destroy the zirconium fluoride complex. If this is not done, the fluorine is pyrohydrolysed and comes off as HF. With sufficient caustic the fluorine appears as less corrosive NaF. Even so, special materials of construction such as Inconel-X may be required for processing Zirflex waste.

FIGURE 16

CORRODED INCONEL SECTION OF 8" SPRAY CALCINER

Note: Double wall is a temporary patch

## H. Separation of Solids from Off-gas

The near-complete separation or deentrainment of the solid powder from the off-gas is essential to good decontamination performance of a calciner. Any powder that finds its way into the condenser will increase the radioactivity level of the condensate. It is desirable to keep this level as low as possible, but since the condensate can be concentrated and recycled, some contamination is acceptable. Nearly complete decontamination is required of the noncondensable off-gases since it is desirable to release them immediately to the atmosphere. In the case where fission product volitilization occurs, the decontamination of the off-gases will depend upon chemical absorption of the volitilized fission products as well as solid separation.

### 1. Filters:

Separation of the solid from the gas is accomplished most efficiently by filters. At the bottom of the laboratory spray calciner where the filters are located the temperature is about 750 F and special filters were used to resist the temperature and the corrosive atmosphere.

a. Micro-metallic Filters: Sintered type 316 stainless steel filters made by Micro-metallic Company were used successfully to separate the solids. Solid deentrainment factor through the (F-grade, 50 micron poresize) Micrometallic filters was about $1.5 \times 10^4$. A pulse blow-back cleaning system (described on p. 15) was used with the metallic filter and successfully kept the filter pressure drop at 1.8-2.4 inches of Hg for gas flow rates of 13 $ft^3/hr\text{-}ft^2$ for runs of 18-20 hours duration. The stainless-steel micrometallic filter underwent corrosive attack when phosphate was added to the feed.

b. Ceramic Filters: Tubular ceramic filter elements of 5 micron porce size were also used with pulse blow-back cleaning. These elements had to be gasketed at both ends. After trying several gasket materials such as asbestos, polytetrafluoroethylene, silicone rubber, and several fluoro rubbers, it was found that Durabla, made by the Durable Mfg. Co., was able to hold a seal at the operating temperature of the filter section. No deentrainment factors were obtained for the ceramic filters but they did not corrode. When incorrectly mounted they can crack because of differential thermal expansion. With good gaskets they may perform as well as the sintered stainless steel filters. Blow-back cleaning was somewhat less effective with the ceramic filter elements. A hard cake, which could only be removed by scraping, tended to build up on the surface with some waste powders.

2. Cyclones:

Another method which was used to separate the solid from the off-gases before condensing the steam was a cyclone separator. This method is not as effective as the filter for the fine powders produced by the spray calciner. The cyclone was subject to plugging and usually 20 percent of the powder went out the top to the condenser. Nevertheless, a scalping cyclone might still be effective to reduce the powder load on a subsequent filter.

3. Condenser-Scrubber:

A great deal of off-gas clean up occurs in the condenser-scrubber system. It is quite likely that small dust particles which pass through the filter or cyclone, act as condensation nucleii, become wetted, and appear in the condensate. The deentrainment factor between the feed and the off-gas for the metallic filter and condenser-scrubber system was measured to be about $1.8 \times 10^8$. This was determined by filtering all of the off-gas through a 0.5 micron Millipore filter and analyzing the filter paper for iron. This indicated the amount of powder which had passed through the condenser-scrubber. The deentrainment factor between the feed and condensate was about $1.5 \times 10^4$. Therefore, the condenser-scrubber contributed a deentrainment factor of $10^4$ and is quite helpful in reducing the contamination which would go to the atmosphere with the non-condensable off-gases. It should be emphasized that the condenser-scrubber used on this equipment was a simple laboratory arrangement and was not very efficient. A well designed plant unit should improve on deentrainment performance.

I. Ruthenium and Cesium Volatilization:

One of the difficult problems with any radioactive residue treatment process which heats the material to high temperatures is the volatilization of some of the radioactive isotopes. Cesium and ruthenium are both known to volatilize (probably as Cs and $RuO_4$). The volatile radioactive isotopes must be cleaned from the off-gases before release to the atmosphere, and the success of a calcination method may depend on the extent of volatilization which occurs.

Non-radioactive ruthenium ($6.4 \times 10^{-3}$ M) was added to acidic and caustic-neutralized Purex wastes which were then fed at 0.95 gal/hr into the spray calciner column. The column was run at temperatures of 300 C at the top and 820 C in the middle. The results of the ruthenium analysis of the various streams are shown in Table VII.

TABLE VII

NON-RADIOACTIVE RUTHENIUM "SPIKE" DISTRIBUTION IN SPRAY CALCINATION

| | ACIDIC PUREX WASTE | | CAUSTIC NEUTRALIZED PUREX WASTE | |
|---|---|---|---|---|
| Ruthenium in | Analysis | Percent of total | Analysis | Percent of total |
| Feed minus undissolved | 5.1 gms | 100 | 1.33 gms | 100 |
| Ruthenium out | | | | |
| Solid Product | 2.47 gms | 48.5 | 1.69 gms | 98.4 |
| Permanganate wash of off-gas lines | .04 gms | 0.785 | 0.0192 gms | 1.12 |
| Condensate | <0.001 g/ℓ | - | 0.0039 gms | 0.23 |
| Scrub | <0.001 g/ℓ | - | 0.0041 gms | 0.25 |
| | Material Balance $\frac{\text{Ru Out}}{\text{Ru In}} = 0.49^{(a)}$ | | Material Balance $\frac{\text{Ru Out}}{\text{Ru In}} = 1.29^{(b)}$ | |

(a) Much of the ruthenium which was in the product was in an insoluble form which resulted in low analysis values for the product and a poor material balance.

(b) Several possible sources of error exist:

(1) A representative sample of the feed was difficult to obtain because of its form as a heavy slurry.

(2) Analysis of the powder may be in error as a result of non-uniform distribution of Ruthenium.

Segregation of different components in the powder was apparent, as a red powder ($Fe_3O_4$) mixed with a larger quantity of green-brown powder ($Na_2SO_4 + Cr_2O_3$).

Table VII shows that only 2 percent or less of the Ruthenium (when added to feed in gross quantities several times actual level) is volatilized during spray calcination and passes through the filters. A sample of the neutralized waste powder was sintered for one hour at 950 C and 5.4 percent of the ruthenium was lost; therefore, subsequent melting of the powder will require much additional clean-up of ruthenium from the off-gases.

Non-radioactive cesium was also added to the feeds of the runs just described for ruthenium. It was also added to several times its radioactive concentration in the actual Purex waste. In the neutralized waste run, ninety-eight percent of the cesium was found in the solid product collected by the filters. The condensate, scrub and off-gas line wash solution all contained less than 5 ppm, the limit of detection with the technique used. The material balance for cesium was 109 percent, i.e., more cesium was accounted for in the products than in the feed. Sintering the solid powder at 950 C for one hour resulted in no detectable loss of cesium. In the acidic waste run over 99.3 percent of the cesium recovered was found in the solid product collected by the filters. The condensate and scrub solutions contained less than 5 ppm cesium. The cesium in the off-gas line wash solution was 0.3 percent but the material balance was only 95 percent. Further cesium loss upon heating was not determined for the acidic waste powder. It is believed to be low, as with the neutralized waste.

J. Condensate Characteristics

The condensate volume is generally about one and one half that of the feed processed because the steam used to atomize the feed is condensed also. The scrub stream also contributes a little volume but the bulk of the scrub is recycled. The pH of the condensate which results from condensing the off-gases of the spray calciner is most strongly dependent on the type of feed used.

Acidic Purex waste calcines to give off NO and $NO_2$ which are absorbed in the condensate and give it a pH of 2.0 or less.

With coating waste added to the acidic Purex waste in proportion to plant stream flow rates, the pH of the condensate is about 8. Caustic neutralized Purex waste with 200 g/l sugar added calcines to give an ammonical condensate of pH 8-10.

Concentration of the condensate should not be difficult. The dissolved gases would be driven off to the atmosphere and the water evaporated away as with a usual plant dissolver or evaporator. The concentrated condensate would then be recycled to the spray calciner.

It is desirable to have a condenser-scrubber system that can be cleaned in case a faulty filter causes gross contamination with calcined powder.

## K. Condensation Without De-entrainment of Powder (Slurrying)

A method called "slurrying" to separate off-gas from the calcined powder was the subject of several experiments. In this method, (see Tentative Flowsheet - Figure 17) no filter or cyclone is used. The powder goes with the steam directly to the condenser, and becomes a muddy slurry which is removed from the bottom of the condenser. If the powder is sufficiently insoluble, the slurry can be boiled down smoothly and dried to a compact mass. The density of the dried slurry is 1.0-1.5 g/cc or 2 or 3 times that of the freshly calcined powder, probably as a result of breaking down the feathery powder particles. The thermal conductivity is increased by 0.5 Btu/hr, $ft^2$, °F/ft over the unslurried powder. If the powder is soluble, then the boil-down and drying operation is just a repeat of the calcination step and does not proceed so smoothly. For example, products which are high in sodium salts dissolve considerably and do not dry smoothly. Several feeds were tested by this method using a total condenser at the bottom of the spray calciner. The product then came out as a slurry of dilute nitric acid and metal oxides, except in the case of neutralized waste which gave ammonia hydroxide. These slurries were boiled to dryness in a beaker to see how smoothly drying would proceed. The results are shown in Table VIII.

TABLE VIII

PRODUCT-SLURRY BOIL-DOWN RESULTS

| Feed Simulates | Slurry Boil-down Observations |
|---|---|
| 1. Purex-high sulfate low-acid waste | Dried smoothly but a crystalized white crust of the soluble components was left on the surface. |
| 2. Purex + Phosphate + 200 g/l sugar | Dried smoothly to a hard cake. |
| 3. Purex + Phosphate - no sugar | Dried smoothly but not completely. Hygroscopic. A gummy material with a green surface liquid was left in the beaker. |
| 4. Purex waste neutralized with NaOH and 200 g/l sugar | Did not dry smoothly; splattered and left a black cake with a white bubbly crust. |

The high sodium solubility of Run 4 is believed to cause its poor boil-down behavior. Although much work should be done to determine the behavior of volatile radioactive elements under slurry boil-down conditions, the method appears to be feasable for some powders. In addition, the experiments showed that powder which becomes wet can still be processed successfully.

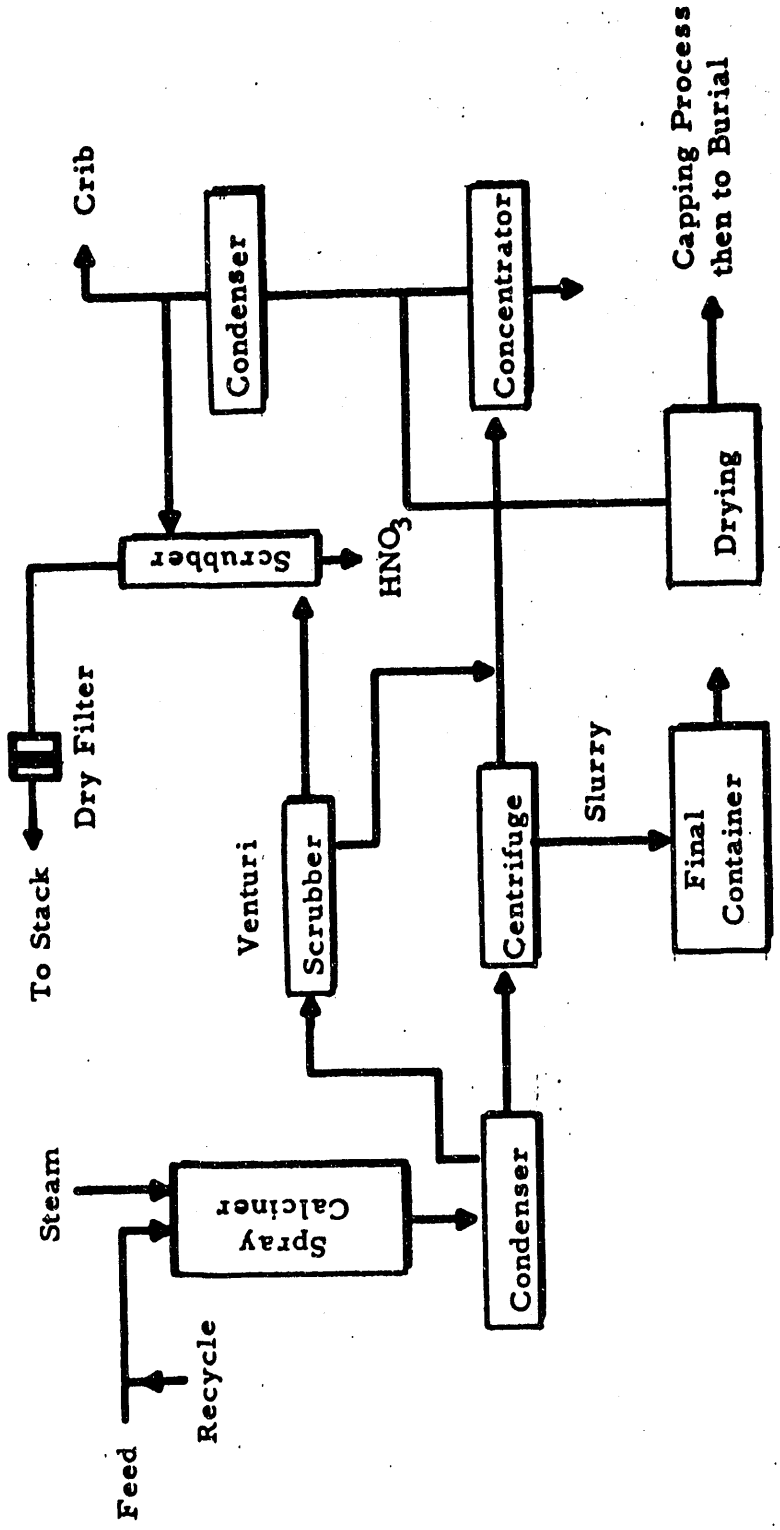



FIGURE 17

Calciner Slurry Flowsheet Acid Waste



ASC-62 RICHLAND, WASH.

Organic liquids such as (alcohol, benzene, or carbon tetrachloride) also increase the density and thermal conductivity of the solid powder. The liquid (thirty to fifty percent of powder volume) is slurried with the powder and then boiled off. The powders are insoluble in organic liquids and therefore the "drying" is very smooth.

## L. Calcination Profiles in the Spray Calciner Column

### 1. Heat Transfer:

The rate of heat transfer to a droplet in the spray calciner during the drying period is controlled by convection in the high velocity region of the spray and the main heat load occurs in this region.(7) Further heating of the dried particle probably occurs by direct radiant-heat transfer to the particle, and the particle temperature rise may be calculated by the equation given in Appendix I.

The results discussed there indicate the particle-gas temperature difference approaches zero very closely and the two phases may be considered as a composite phase for the purpose of calculating their rate of temperature rise. Thus the rate of temperature rise of the particle and its surrounding gas is:

$$\frac{dT}{d\tau} = \frac{3F\epsilon\sigma\,(Tw^4 - T^4)}{S\,\rho_s\left(Cs + \frac{Cp\,\rho g}{\rho c}\right)} \qquad (1)$$

where:

$Cs$ = heat capacity of solid
$Cp$ = heat capacity of gas
$\epsilon$ = emissivity
$F$ = view factor
$\rho c$ = density of particle cloud
$\rho g$ = density of gas
$\rho s$ = density of solid
$S$ = particle radius
$T$ = particle temperature (absolute scale)
$Tw$ = wall temperature (absolute scale).

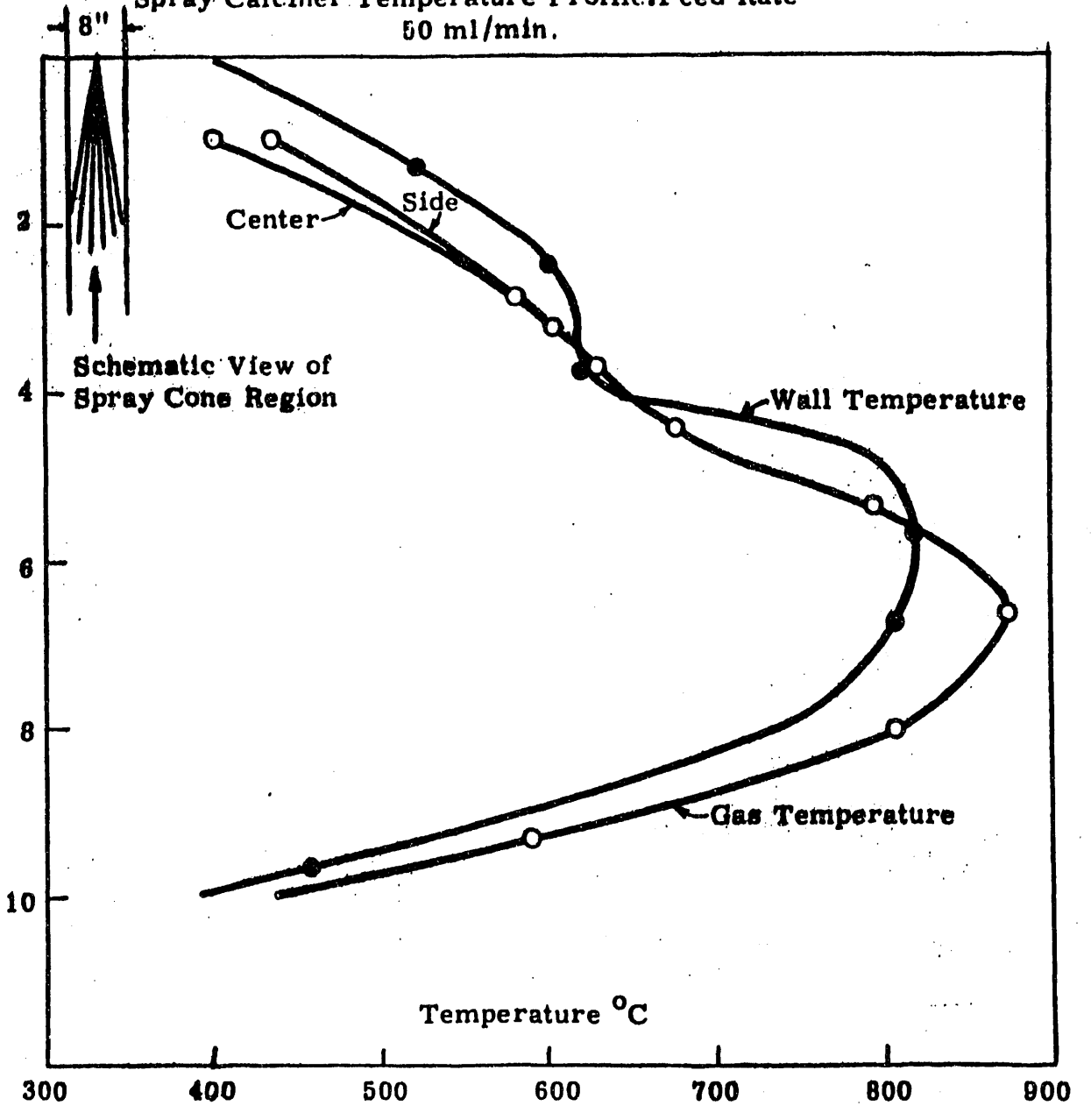
Equation 1 can be used by trial and error to calculate the temperature of a particle in the column if the values of the right-hand side are known. All of the values are dependent on the feed and spray conditions except the wall temperature.

### 2. Temperature Profile:

A typical longitudinal temperature profile of the calciner during operation is shown in Figure 18.

FIGURE 18

Spray Calciner Temperature Profile: Feed Rate - 50 ml/min.



Except for a short distance in the spray cone region the temperatures of the gas, and therefore the particles, is approximately uniform radially across the column. Figure 15 also shows that the gas-particle temperature lags behind the wall temperature somewhat as the material moves down the column. The lag can be predicted by Equation (1) using trial and error methods.

3. View Factor:

The view factor F, appearing in Equation (1) is the ratio of the radiation received by a particle within the gas-solids cloud in the column to that which it would receive if it were the only particle in the column. Thus, if the cloud of suspended solids is very dense and opaque to radiation, very little radiation gets through to a particle in the center of the column, i.e., the view factor, F, is very small. Because of its mathematical complexity (See Appendix II), the view factor can be evaluated only for two special cases, namely, for a particle located at the center of the reactor and at the wall. However, the weighted average view factor throughout the cross-section of the reactor is amenable to solution. These results are shown in Figure 21. The center-line value may be approximated by the equation:

$$F = e^{-1.2R} \frac{3\rho_c}{4S\rho_s} \qquad (2)$$

where:
R = radius of the reactor
$\rho_c$ = density of the solids in the cloud passing down the column
$\rho_s$ = density of the individual particles
S = radius of the particles.

Typical values of the view factor for the center of the 8 inch spray calciner are 0.85 to 0.95 at flow rates of one gallon per hour.

4. Heat Absorption by Steam:

Certain polyatomic gases absorb infrared radiation of specific wave lengths. Steam generated from the drying of the atomized liquid will thus attenuate the radiant energy before it reaches a given particle. An analysis[13] of this effect following the method of Wohlenberg[14] was made for two flat plates at different temperatures, $T_1$ and $T_2$, and separation, L. The results can be expressed by

$$\frac{Ex}{E_o} = \frac{1.20\ T'}{104} - 0.468\ L^{0.47} \qquad (3)$$

where $\frac{Ex}{E_o}$ = ratio of radiation transmitted through the layer of steam to that transmitted through a transparent gas.

$$T' = \sqrt[4]{\frac{T_1^4 + T_2^4}{2}}$$

This result could not be included in the derivations for the analytical solution for the view factor, F, because of its complexity. However, evaluation of Equation (3), as an analogical case of the spray calciner, indicates that heat attenuation by steam will not be too serious a problem even in large columns. For example, two plates at temperatures of 2000°R and 1000°R separated by a steam layer 1.67 feet thick would have about 20 percent of the radiation absorbed by the steam. This corresponds to a situation which would exist in the center of a column more than three feet in diameter. Also, since the particle and the gas in the column closely approach the same temperature anyway, the radiation absorbed by the gas will contribute to rate of heating of the system nearly as effectively as that absorbed by the particles.

5. Spray Turbulence:

Despite the low superficial velocity of the gas in the reactor (Reynolds number of two hundred to three hundred) violent turbulence exists at the top of the column as the result of entrainment at the boundary of the jet as it enters the static gas. The turbulence persists for at least eleven column diameters below the nozzle; measurements of eddy diffusivity in the column at this distance indicated the Reynolds number is in the order of 80,000 to 90,000. (See Appendix IV). Not withstanding this high degree of turbulence and the observation that the gas temperature was approximately constant in a radial cross section, the variation in view factor across the column is apparently significant in its effect on the calcination profile as discussed in Appendix II.

## VII. ACKNOWLEDGEMENTS

The authors are indebted to the personnel of Analytical Laboratories and Technical Shops Operations of HLO for their contributions and work on this research .

Particular thanks go to R. B. Warner, Barbara Van der Cook, Grace Grantham, Anthony Madsen, William Eytcheson, Dennis Getchell, T. R. Cartmell, K. H. Hammill and J. C. Gibson who were especially helpful.

## REFERENCES


1. Shefcik, J. J., HW-66707, August, 1960.
2. Culler, F. L., ORNL-2788, Chemical Technology Division Annual Progress Report, Period Ending August, 1959.
3. Domish, R. F., Tuthill, E. J., and Hatch, L. P., BNL-535 (T-136) (December, 1958).
4. Jonke, A. A., Pelkus, E. J., Loeding, J. W., and Lawroski, S., Nuclear Science and Engineering 2, 303 (1957).
5. Stevenson, C. E., 100 14443, Technical Progress Report for January through March, 1958. Idaho Chemical Processing Plant, September, 1958.
6. Alford, M. D., HW-66384 RD, July, 1960.
7. Allen, A. L., et. al., K-444 (July, 1949).
8. Gauvin, W. H., Tappi 40, 866 (1957).
9. Hoffman, T. W., Ph. D. Thesis, McGill University (April, 1959).
10. Campbell, B. F., HAPO, Private Communication (April, 1960).
11. Empson, F. M., Higgins, I. R., ORNL-2566 (February, 1959).
12. Amos, L. C., HW-60614 (June, 1959).
13. Barton, G. B., HW-66091 (July, 1960).
14. Barton, G. B., HW-63307 (December, 1959).
15. Johnson, B. M., Jr., HW-58641 (February, 1959).
16. Wohlenberg, W. J., Eng. Bul., Purdue University, 24, 4a Eng. Exp. Sta., Res. Ser. No. 75; (August, 1940).
17. Nusselt, W., Z. Ver Deut. Ing. 68, 124 (1924).
18. Dean, R. V., HAPO Private Communication (July, 1958).
19. Dean, R. V., HAPO Private Communication (November, 1958).
20. Towle, W. L., and Sherwood, T. K., Ind. Engr. Chem. 31, 457 (1939).
21. Wilson, H. A., Proc. Cambridge Phil. Soc. 12, 406 (1904).
22. Towle, W. L., Sherwood, T. K., Seder, L. A., Ind. Eng. Chem. 31, 462 (1939).
23. Sherwood, T. K., and Woertz, B. B., Trans. Am. Inst. Chem. Eng. 35, 517 (1939).

## APPENDIX I

## RADIANT HEAT TRANSFER TO DROPLETS

The analysis of radiant heat transfer to a cloud of particles as in spray calcination is similar to a treatment by Nusselt(17) of radiant heat transfer and ignition of pulverized coal in a furnace and follows this treatment with some corrections, as presented in Jakob's "Heat Transfer", Vol. II.

Consider a single spherical particle exposed to the walls of a reactor at a temperature $T_w$ (constant). The rate of radiant-heat exchange between wall and particle is then

$$q_r = F \epsilon \sigma (T_w^4 - T^4) 4 \pi S^2, \tag{4}$$

where: $S$ = particle radius
$T$ = particle temperature
$\epsilon$ = particle emmissivity
$F$ = view factor including radiation decrement from other particles
$\sigma$ = Stephan-Boltzmann constant.

Heat exchange between particle and surrounding gas is

$$q_c = 4 \pi S^2 h (T - T_g), \tag{5}$$

where: $T_g$ = gas temperature
$h$ = particle-to-gas heat-transfer coefficient.

In quiescent gas this may also be written as

$$q_c = 4 \pi \frac{k(T - T_g)}{1/S - 1/r},$$

where: $k$ = thermal conductivity of the gas
$r$ = a radial distance out from the particle, $r > S$.

If one assumes that the temperature $T_g$ exists at $r = \infty$, the result is

$$q_c = 4 \pi k S (T - T_g). \tag{6}$$

The gain in sensible heat of the particle is represented by

$$q_{sh} = 4/3 \pi S^3 \rho_s C_s \frac{dT}{d\tau}, \tag{7}$$

where: $\rho_s$ = particle density
$C_s$ = particle heat capacity
$\tau$ = time.

Energy balances for the particle and the surrounding gas may be written conveniently if the following simplifying assumptions are made: (1) reradiation from the particle to the wall may be neglected, i.e., $T^4 \ll T_w^4$, (2) the gas experiences no radiant heat absorption from either the reactor walls or the particles, and (3) the contribution of heat conducted to the gas from the reactor walls may be neglected. Thus, an energy balance on the particle may be expressed as,

$$q_r = q_c + q_{sh}$$

$$\text{hence, } \frac{dT}{d\tau} + \frac{3\,k}{\rho_s C_s S^2}(T-T_g) - \frac{3\,F\epsilon\sigma}{\rho_s C_s S}(T_w^4 - T^4) = 0 \qquad (8a)$$

$$\text{or, } \frac{dT}{d\tau} + \frac{3\,k}{\rho_s C_s S^2}(T-T_g) - \frac{3\,F\epsilon\sigma}{\rho_s C_s S}T_w^4 = 0 \qquad (8b)$$

if assumption 1 is incorporated. Similarly, an energy balance for the surrounding gas involves equating the heat transferred to the gas with the sensible heat gain of the gas.

The heat transferred to the gas per particle is given by Equation (6) while sensible heat gain of the gas per particle is

$$C_p \text{x(wt. of gas/per particle)} \times \frac{dT_g}{d\tau}$$

$$\text{and} \qquad \text{wt. of gas/per particle} = \frac{4}{3}\pi S^3 \rho_g \frac{\rho_s}{\rho_c}.$$

Thus, the energy balance for the gas may be written

$$4\pi\, k\, S(T-T_g)d\tau = \frac{4}{3}\pi S^3 \frac{\rho_s}{\rho_c} C_p\, \rho_g\, dT_g,$$

where: $\rho_c$ = cloud density of particles
$C_p$ = gas heat capacity
$\rho_g$ = gas density
$T_g$ = gas temperature.

$$\text{Hence,} \qquad \frac{dT_g}{d\tau} = \frac{3\,k(T-T_g)\rho_c}{\rho_s C_p\, \rho_g S^2}. \qquad (9)$$

The two equations (8b) and (9) may be written in terms of dimensionless parameters by substituting

$$T^* = T/T_w, \qquad T_g^* = T_g/T_w,$$

$$\text{and} \quad \tau^* = \frac{3\,k}{\rho_s C_s S^2}$$

with the result

$$\frac{dT^*}{d\tau^*} = \alpha - (T^* - Tg), \quad \alpha = \frac{F\epsilon\sigma\, S T_w^3}{K} \tag{10}$$

$$\frac{dTg^*}{d\tau^*} = \beta(T^* - Tg), \quad \beta = \frac{\rho_c C_s}{C_p \rho_g} \quad . \tag{11}$$

These two equations may be solved simultaneously subject to the initial condition $T = Tg = T_o$ at $\tau = 0$, i.e., initially the gas and solid particles are at the same temperature. The solution results in the following relationships. Particle temperature is,

$$T^* - To^* = \frac{\alpha}{(1+\beta)2} \; 1 + \beta(1+\beta)\tau^* - e^{-(1+\beta)\tau^*} \tag{12}$$

or in terms of the original parameters

$$T - T_o = \frac{F\epsilon\sigma\, S T_w^4}{k\left(\frac{C_s \rho_c}{C_p \rho_g} + 1\right)^2}\left[1 + \frac{3\,k\,\rho_c}{C_p\,\rho_g\,\rho_s S^2}\left\{\frac{C_s\,\rho_c}{C_p\,\rho_g} + 1\right\}\tau - \exp\frac{-3\,k}{C_s\,\rho_s S^2}\left\{\frac{C_s\,\rho_c}{C_p\,\rho_g} + 1\right\}\tau\right].$$

Solving for $Tg^* - To^*$ and subtracting this from Equation (12) to obtain an expression for the particle-gas temperature difference yields

$$T^* \cdot Tg^* = \frac{\alpha}{(1+\beta)}\left[1 - e^{-\tau^*(1+\beta)}\right]. \tag{13}$$

These results are applicable to the situation following the formation of solid particles from the evaporation of the atomized liquid drops. Several points of interest are indicated in the results, Equations 12 and 13. The usual values of the system parameters are such that except at very low values of $\tau$, the exponental term in both equations very nearly approaches zero. Consequently, the temperature difference between the particle and gas rapidly approaches a steady state value, expressed by the first coefficient in Equation (13), and the temperature rise of the particle becomes linear with time.

Equation (12) in its present form is not applicable as T approaches $T_w$ because of the initial assumption that the particle temperatures could be neglected in determining the driving force for radiant heat transfer ($T_w^4 \gg T^4$). The situation in which the reradiation of the particle is not neglected has been solved through the use of a Litton 20 digital differential analyser. Figure 19 represents the time-temperature

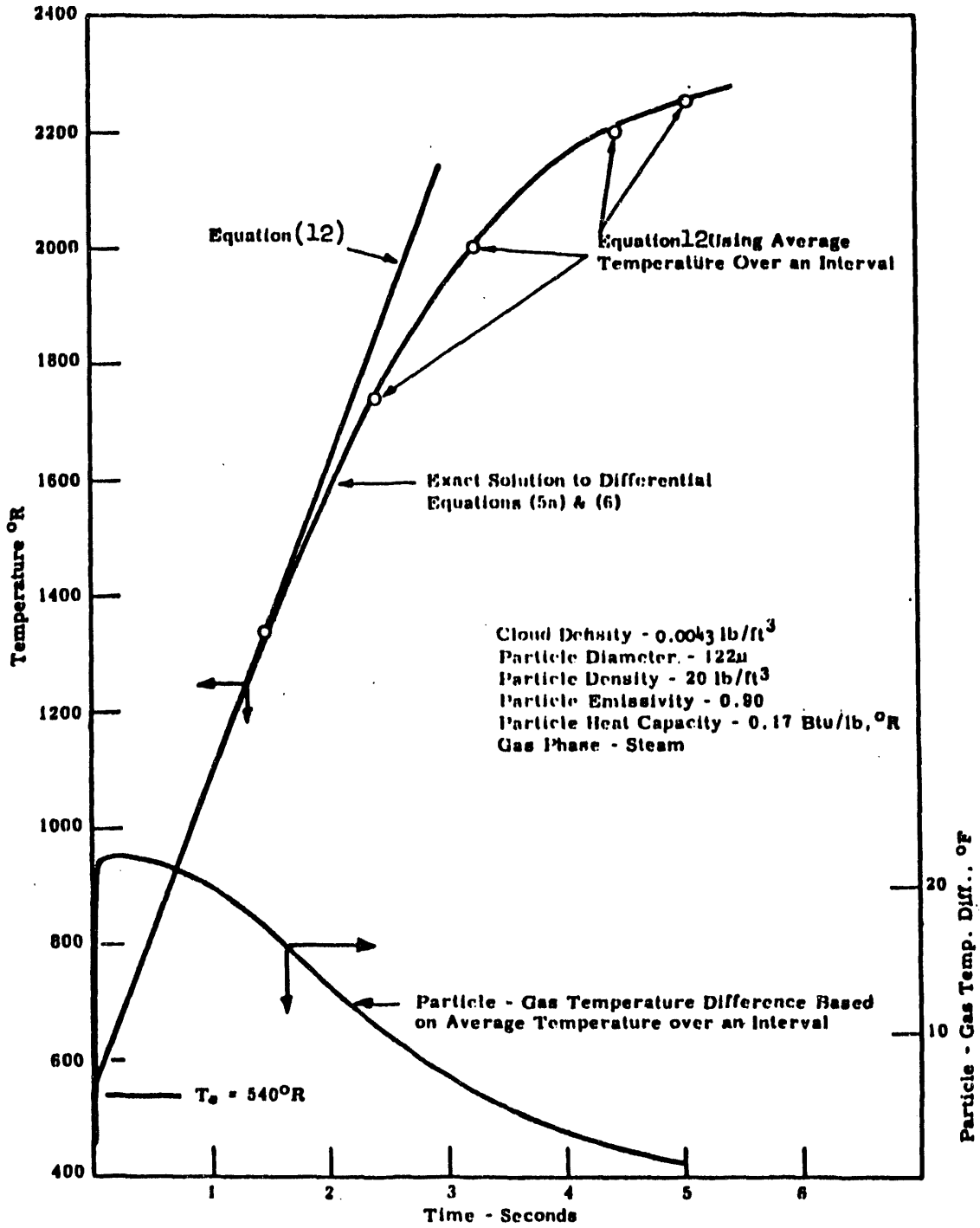



FIGURE 19

Time-Temperature History of a Typical Dry Particle
$T_W$ = 2300°R

history of a typical particle in the center of a cylindrical tube with uniformly heated walls. The computed results may be closely approximated, even in the region in which the particle temperature approaches that of the wall, by calculating the time required to experience a given rise in temperature in a series of steps. In this procedure one neglects the exponential term in all but the initial step and replaces the term $T_w^4$ in the first coefficient with $(T_w^4 - T_{ave}^4)$ where $T_{ave}$ is the average particle temperature over the interval. Also presented in Figure 19 is the particle-gas temperature difference under these same conditions.

Because of the small difference between the particle and the gas temperature, an analytical solution of the temperature history of the particles and gas may be obtained if one assumes that the temperatures of the two phases are equal. The gain in sensible heat of the particle plus associated gas is then represented by

$$q_{sh} = \frac{4}{3}\pi S^3 \rho_s C_c \frac{dT'}{d\tau} \tag{14}$$

where $C_c$ = equivalent heat capacity of cloud relative to the weight of solids present = $C_s + C_p \rho_g / \rho_c$

$T'$ = temperature of gas-solid cloud (assumed to be uniform).

Since the heat capacity of the particles is generally less than the heat capacity of the gas, $T'$ more closely approximates the true gas temperature than the particle temperature.

Thus the two equations, for the gas and for the particles, are replaced by the single equation

$$\frac{dT'}{d\tau} = \frac{3F \epsilon \sigma}{S \rho_s C_c} (T_w^4 - T'^4) . \tag{15}$$

Again, to write this in terms of dimensionless variables one may substitute,

$$T'^* = T'/T_w$$

$$\tau^* = \frac{3F \epsilon \sigma T_w^3}{S \rho_s C_s}$$

with the result

$$\frac{dT'^*}{d\tau^*} = \left[1 - T'^{*4}\right] . \tag{16}$$

The solution to this equation is

$$\tau^* = \frac{1}{2}\left[f(T'^*) - f(T_o'^*)\right] \tag{17}$$

where $f(x) = \left\{\tanh^{-1}(x) + \tan^{-1}(x)\right\}$ which is plotted in Figure 20.

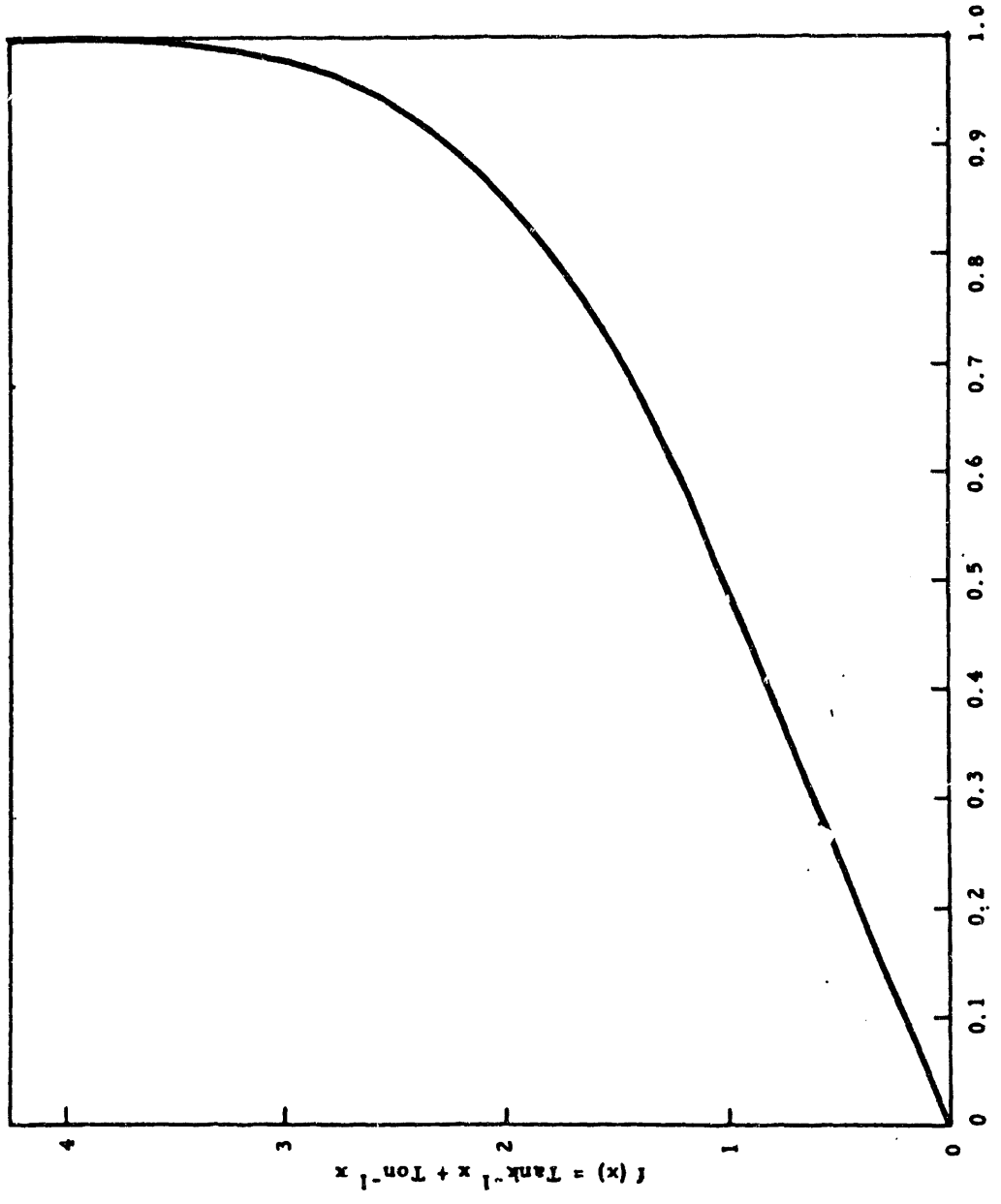



FIGURE 20

F(x) for Calcination of Temperature History Assuming Equal Particle and Gas Temperature

Equation (17) is plotted in Figure 19 for the same condition as that solved on the Litton 20 computer. It predicts temperatures that are very nearly equal to the actual gas temperature.

Equation (1) can be used to calculate the particle temperature rise with a varying column wall temperature by a trial and error method after making assumptions concerning the view factor, particle size, and the particle hold-up time which is affected by the velocity profile in the column.

## APPENDIX II

## VIEW FACTOR DETERMINATION

The utility of equations in Appendix I in calculating quantitative results is limited by the uncertainty in the determination of the factor F, the combination view, or geometric factor, as defined by the Lambert Cosine Law, and logarithmic declination of radiation resulting from shadowing and absorbtion of radiation by intervening particles and gas. If one neglects absorption of radiation by the gas, which is treated in Reference (15), and disregards reradiation of energy absorbed by intervening particles, it is possible to calculate the worst situation with regards to the view factor, i.e., that existing at the center of the column.

In general, the view factor for a single particle may be written

$$F = \frac{1}{4\pi} \int_0^{4\pi} e^{-Mx} \, dw, \qquad (18)$$

where: w = solid angle of the beam
x = distance from particle to element of radiating surface
M = logarithmic decrement of radiation .

An approximate value of M may be obtained from the following probability treatment similar to that suggested by Nusselt. (17)

The number n of particles present in a unit volume of gas is

$$n = \rho_c / (\tfrac{4}{3}\pi s^3 \rho_s).$$

If the cloud of particles is uniformly distributed, one may consider each particle occupying a cube of side length

$$L = (n)^{-1/3},$$

and over a unit length of gas there will be a number of such cubes given by

$$N = 1/L = 1/s \sqrt[3]{\frac{4}{3}\pi \frac{\rho_s}{\rho_c}} .$$

The ratio of the total cross-sectional area of a single cube to the cross-section area of the particle lying in the cube is

$$\gamma = \frac{L^2}{\pi s^2} = \frac{1}{\pi}\left(\frac{4}{3}\pi \frac{\rho_s}{\rho_c}\right)^{2/3} .$$

Thus, a beam of radiant energy on passing through a unit thickness of gas will find free passage over a fraction

$$\psi = \left(1-\frac{1}{\gamma}\right)^N ,$$

which is also given in terms of the logarithmic decrement as

$$e^{-MxL} = \psi ,$$

$$\text{or} \quad M = \ln \frac{1}{\psi} = N \ln\left|\frac{\gamma}{\gamma-1}\right| .$$

Since $\rho_s/\rho_c$ is generally very large, the term $(\gamma/\gamma-1)$ approaches a value of one, and the log is replaced by the first term of the series expansion. Thus,

$$M = -N \ln (1-1/\gamma) \approx \frac{N}{\gamma} = \frac{3\rho_c}{4 s \rho_s} . \qquad (19)$$

The integral over the solid angle can be written in terms of cylindrical coordinates for the situation of a particle located at the axis of an infinitely long cylinder.

$$F = \frac{1}{4\pi} \int_0^{2\pi} \int_{-\infty}^{+\infty} \frac{e^{-M\sqrt{A^2+Z^2}}\, A^2 d\theta dz}{(A^2+Z^2)^{3/2}} , \qquad (20)$$

where: A = radius of the cylinder
Z = distance along cylinder from the normal drawn from the particle to the cylinder wall
$\theta$ = horizontal angle between a line to a particular element of wall area and a fixed line of reference.

This integral was evaluated by R. V. Dean[16]. The results may be expressed in terms of the following definite integrals

$$F(AM) = 1 - AM \left[\pi/2 + K_{j_1}(AM) - K_{j_0}(AM)\right] , \qquad (21)$$

$$\text{where:} \quad K_{j_n}(x) = \frac{1}{x^n} \int_0^x u^n K_0(u)\, du.$$

$K_0$ = modified Bessel function of the second kind of order zero. Figure 21 is a graph of the view factor as a function of the arguement (AM), calculated with the aid of HW-30323, a table of the functions $K_{j_n}(X)$. From the graph

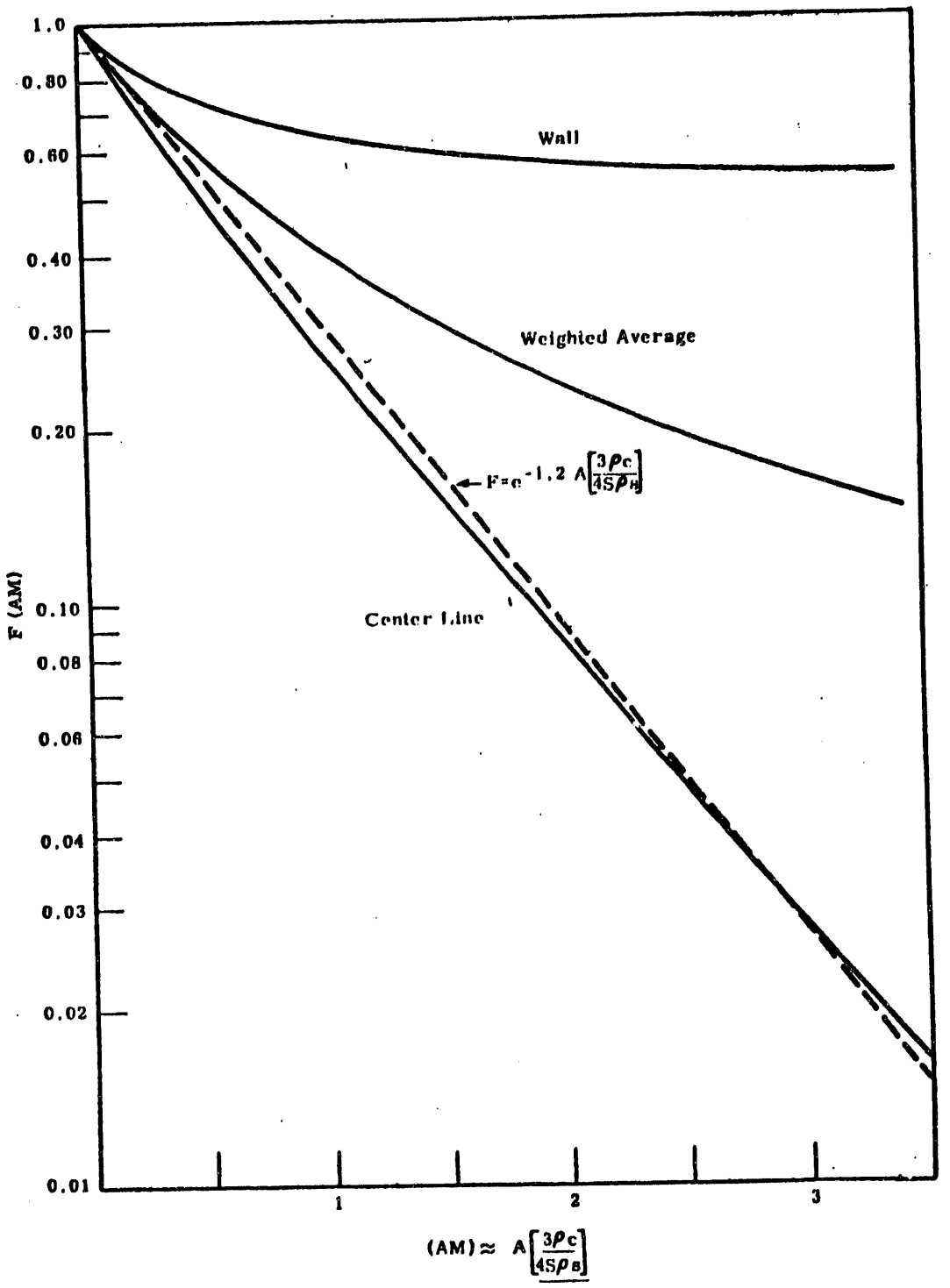



FIGURE 21

View Factor as a Function of Reactor Radius and Log Decrement of Radiation

it is evident that the function may be roughly approximated by the expression

$$F(AM) = e^{-1.2\left(\frac{3A\,\rho_c}{4S\,\rho_s}\right)}, \qquad (22)$$

which was used in the computer solution for droplet temperature shown in Figure 19, Appendix I. This view factor represents the most unfavorable position for radiant heat transfer. The actual condition would probably result in a somewhat better situation as the preponderance of particles are located nearer the walls of the reactor; also there would be some reradiation from those particles located nearer the heat source.

Expressions have also been developed for the weighted average view factor throughout the cross-section of the reactor and the view factor for a particle located at the wall of the reactor.

For the situation of a particle located at any point in the cylindrical reactor, the integral of the view factor may be written as a double integral similar to Equation (20).

$$F(A,M,r) = \frac{1}{4\pi}\int_0^{2\pi}\int_{-\infty}^{+\infty} \frac{e^{-M\sqrt{r^2+A^2-2rA\cos\theta+Z^2}}\,(A^2-Ar\cos\theta)\,d\theta\,dZ}{(r^2+A^2-2rA\cos\theta+Z^2)^{3/2}}, \qquad (23)$$

where: r = distance between the particle and the axis of the cylinder.

This integral cannot be evaluated; however, R. V. Dean[19] was able to solve two special cases of particular interest. For a particle located at the wall of the reactor r = A, i.e., the distance from the particle to the axis of the cylinder is equal to the radius of the cylinder, the solution is

$$F(M,\ r = A) = 1-AM + \sum_{n=0}^{\infty} \frac{1}{2^{2n+1}\,n!(n+1)!}\,x^{2n+1}K_{j_{2n}}(AM), \qquad (24)$$

where: $K_{j_n}(x)$ is as defined in Equation 11.

This result is plotted in Figure 21 along with Equation (21).

The weighted average value of the view factor defined in Equation (23) may be evaluated by the expression

$$F(AM) = \frac{1}{\pi A^2}\int_0^{2\pi}\int_0^{A} r\,F(A,M,r)\,dr\,d\theta = \frac{2}{A^2}\int_0^{A} r\,F(A,M,r)\,dr.$$

This integral is amenable to solution and results in the expression

$$F(AM) = 2\, I_1(AM)K_1(AM) + 2\, I_2(AM)K_0(AM) - \frac{4}{3}(AM) + \frac{3}{2} \sum_{n=0}^{\infty} \frac{1}{2^{2n} n!(n+2)!}\, x^{2n+1} K_{J_{2n}}(AM), \quad (25)$$

where $I_1$ and $I_2$ are the modified Bessel function of the first kind of order one and two respectively. This result is also plotted in Figure 22. Figure 21 can be used to find the view factor values needed to solve equations (1), (12), or (15).

A series of experiments were made to show the effect of the view factor by measuring the radial calcination profile in the spray calciner column. The view factor was varied by changing the concentration of the feed* solution and the degree of calcination was measured by chemical analysis of samples of the powder drawn from the column during operation. The results of these experiments are shown in Figure 22, where the degree of calcination points are plotted along with residence-time and view-factor profiles normalized to the values of these quantities in the center of the column. The actual calcination points seem to agree best with a profile of the product of the view factor and the turbulent residence time in accordance with Equation (15). The turbulent profile is realistic since the Reynold's numbers determined by eddy diffusivity measurements were in the neighborhood of 80,000 to 90,000. Without the view factor effect the calcination profile should have the same profile for both feed concentrations studied; all the experimental points would fall on the same line and coincide with the residence time profile. The view factor causes a slight difference in slope which shows qualitatively in the experimental points. Although the experimental results do not agree exactly with the theoretical profile, they do indicate that the view factor has an effect, and that the turbulent residence-time profile is dominant in determining the calcination profile.

## APPENDIX III

## PARTICLE AND GAS TEMPERATURE DURING PARTICLE IGNITION

The analysis of particle temperature within the radiant-heat spray calciner as it is affected by an exothermic reaction (i.e., when sugar is burned) on its surface may be treated in a manner analogous to the radiant-heat transfer to droplets (Appendix I). During the reaction the particle temperature increases as a result of the heat of reaction. Heat is lost to the carrier vapor by conduction-convection and to the wall of the reactor by radiation. Under certain conditions, determined herein, the complex equations for the temperature rise of both the particles and the gas may be simplified and solved. However, under the conditions studied, i.e., the case of carbon combustion at 800 C, it is necessary to make the assumption of equal particle and gas temperature in order to obtain an analytic solution. The temperature difference between particles and gas can then be closely approximated by making use of the form of the simplified equations.

*The feed used was a slurry of ammonium manganese pyrophosphate which calcines by liberating ammonia. The degree of calcination was measured as the change in ammonia to manganese ratio.

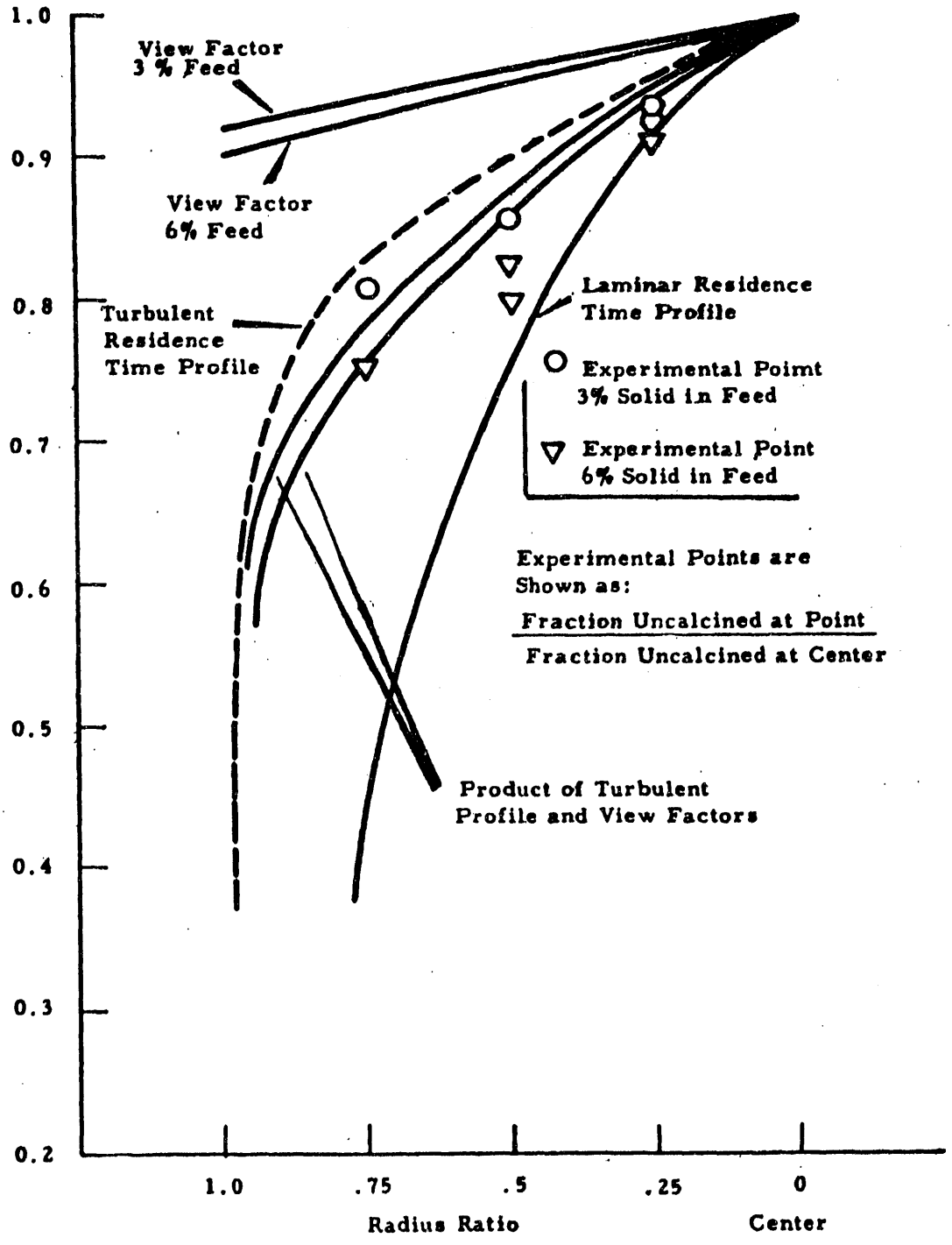



FIGURE 22

Calcination and Residence Time Profiles



AEC-GE RICHLAND, WASH.

The following assumptions are made in this treatment: (1) particle temperature is constant throughout its volume, (2) heat release (rate of reaction) is independent of temperature above ignition temperature and zero order with respect to the solid reactant, (3) particle radius is constant i.e., percentage of reactant is fairly small, (4) heat loss is by conduction to the surrounding gas and by radiation to the reactor walls.

Consider a single spherical particle in which the carbon, or other reactant, has ignited and is burning at a rate proportional to the surface area. Then the heat release is

$$q \text{ react.} = 4\pi S^2 Q \tag{26}$$

where: $S$ = particle radius

$Q$ = rate of heat release per unit area.

Heat loss by conduction to the gas is

$$qc = 4\pi S^2 h (T-Tg) = 4\pi k S (T-Tg), \tag{27}$$

if one assumes a quiescent gas surrounds the particle as in Appendix I.

Heat loss by radiation is

$$qr = F\epsilon\sigma (T^4 - T_w^4) 4\pi S^2 , \tag{28}$$

where the terms are as defined in Appendix I.

The gain in sensible heat of the particle is

$$qsh = 4/3\pi S^3 \rho_s C_s dT/d\tau . \tag{29}$$

The energy balance on the particle may be expressed as

$$q \text{ react.} = qsh - qc - qr, \tag{30}$$

hence,

$$\frac{dT}{d\tau} = \frac{3Q}{\rho_s C_s S} - \frac{3K}{S^2 \rho_s C_s} (T-Tg) - \frac{3 F\epsilon\sigma}{\rho_s C_s S} (T^4 - T_w^4). \tag{31}$$

Similarly for the gas one may write

$$\frac{dTg}{d\tau} = \frac{3k \rho_c}{C_p S^2 \rho_s \rho_g} (T-Tg). \tag{32}$$

These equations may be simplified by expressing the variables in dimensionless form:

$$T^* = T/T_f$$

$$\tau^* = \frac{3k\rho c}{Cs\rho s^2}$$

$$Tg^* = Tg/T_f$$

where $T_f = \sqrt[4]{T_w^4 + \frac{Q}{F\epsilon\sigma}}$, the final particle temperature, assuming the reaction continued indefinitely.

Hence,

$$\frac{dT^*}{d\tau^*} = \frac{QS}{kT_f} - (T^*-Tg^*) - \frac{F\epsilon\sigma ST_f^3}{k}\left(T^{*4} - \frac{T_w^4}{T_f^4}\right) \quad (34)$$

$$= \frac{F\epsilon\sigma ST_f^3}{k}(1-T^{*4}) - (T^* - Tg^*) \quad \text{and}$$

$$\frac{dTg^*}{d\tau^*} = \frac{\rho_c Cs}{\rho g C_p}(T^*-Tg^*). \quad (35)$$

If the amount of reactant present in the particle is sufficiently small, and hence the reaction time is sufficiently short that the particle temperature is not raised beyond the point $T = 0.6\ T_f$, i.e., $T^* < 0.6$, one may neglect the term $T^{*4}$. This is equivalent to saying that the reaction is sufficiently short and the temperature sufficiently low that we may neglect the loss of heat by radiation to the reactor wall. Thus we may write:

$$\frac{dT^*}{d\tau^*} = A-(T^*-Tg^*), \quad A = \frac{F\epsilon\sigma ST_f^3}{k} \quad (36)$$

and

$$\frac{dTg^*}{d\tau^*} = B(T^*-Tg^*), \quad B = \frac{\rho_c\ C_s}{\rho g\ C_p}\ . \quad (37)$$

The solution to this set of linear equations may be written

$$T^*-T_w^* = \frac{A}{(1+B)^2}\left[B(1+B)\tau^* + 1-e^{-(1+B)\tau^*}\right] \quad (38)$$

$$T^*-Tg^* = \frac{A}{(1+B)}\left[1 - e^{-(1+B)\tau^*}\right]. \quad (39)$$

If conditions during the reaction are such that radiation to the reactor cannot be neglected, an approximate solution may be obtained, based upon the assumption of equal gas and particle temperature. Thus, the terms for heat release and heat lost by radiation are the same as before, but the expression for the gain in sensible heat is that used in Equation (14) Appendix I:

$$q_{sh} = \frac{4}{3}\pi S^3 \rho_s Cc \frac{dT}{d\tau} \tag{40}$$

where Cc = equivalent heat capacity of cloud relative to the weight of solids present = $Cs + Cp \frac{\rho_g}{\rho_c}$.

The single differential equation that must now be solved is

$$\frac{dT}{d\tau} = \frac{3Q}{\rho_s CcS} - \frac{3F}{\rho_s CcS}(T^4 - T_w^4) . \tag{41}$$

Again, to write this in terms of dimensionless variables one may substitute

$$T^* = T/Tf$$

$$\tau^* = \frac{3Q\tau}{\rho_s CcST_f}$$

$$\text{where } Tf = \sqrt[4]{T_w^4 + \frac{Q}{F\epsilon\sigma}}$$

with the result,

$$\frac{dT^*}{d\tau^*} = \left[1 + \frac{F\epsilon\sigma T_w^4}{Q}\right]\left[1-T^{*4}\right] = \alpha'\left[1-T^{*4}\right]; \tag{42}$$

the solution to which is

$$T^* = \frac{1}{2\alpha'^2}\left[f(T^*) - f(T_w^*)\right] \tag{43}$$

where $T_w^* = T_w/T_f$

$f(x) = \left\{\tanh^{-1}(x) + \tan^{-1}(x)\right\}$ which may be obtained from Figure 18, Appendix I.

In low density sprays with small particles, T* (the reduced temperature of the gas and particle considered as a unit) is nearly the same as the gas temperature. Therefore, the particle temperature may be obtained from the particle-gas temperature difference equation below, which is adapted from equation (34).

$$T^*_{particle} - T_g^* \simeq \frac{F\epsilon\sigma S T_f^3 (1 - T^{*4})}{k\left(1 + \frac{\rho_c C_s}{\rho_g C_p}\right)} \tag{44}$$

Calculation of Rate of Heat Release

If the rate of reaction is assumed to be limited by the rate of diffusion of the gaseous component to the surface of the particle, the reaction rate is given by the equation

$$4\pi S^2 \quad N_A = \frac{4\pi S\ p\ D\ X_o}{RT} \tag{45}$$

where $N_A$ = rate of reaction, moles/sec, unit area

$D$ = diffusivity of reactant gas through inert gas

$p$ = column pressure

$X_o$ = mole fraction of reactant gas within the reactor.

The rate of heat release Q is determined by

$$Q = N_A H_R$$

where $H_R$ = heat of reaction per mole of reactant.

Based on the assumption of a diffusion-controlled rate of reaction, a reaction time of $2.9 \times 10^{-3}$ seconds was calculated using Equation (45) Then, using Equation (38), the approach which neglects heat loss to the wall one calculates a particle temperature rise of 3425°C. However, in its reduced form this temperature is greater than 0.6 the limiting value for which the approach is valid (see page 54). Equation (43), which assumes equal particle and gas temperature, gives a temperature rise of 3200°C, which is also unreasonable; the maximum temperature rise was about 60°C. Thus it is seen that this particular reaction is not diffusion controlled at this temperature, however, these equations may apply to other more rapid reactions which may be made to take place in the spray calciner.

In preliminary experiments using a glass column, the particles containing carbon were seen to glow for more than a second which indicate that some phenomena at the surface is limiting the kinetics. If two seconds is used as a rough estimate of the reaction time, the second treatment (Equation 43), indicates a temperature rise of 114°C for both gas and particle and a negligible temperature difference between them.

## APPENDIX IV

## CALCINER TURBULENCE AS DETERMINED BY EDDY DIFFUSIVITY MEASUREMENTS

The violence with which the fast-moving spray enters the spray column creates turbulence which persists far down the column. This was proved by measurements of eddy diffusivity which is an indication of the degree of turbulence in a disturbed fluid. Molecular diffusivities of gases are in the order of 0.1-0.2 $cm^2/sec$, whereas the eddy diffusivity of carbon dioxide in air at a turbulent Reynolds number of 91,000 was measured by Towle and Sherwood[20] to be about 23.5 $cm^2/sec$. For the spray calciner, it was thought to be easier to determine the eddy diffusivity than to find the turbulence by velocity measurements. Argon was used as the diffusing gas.

Towle and Sherwood[20] used an equation developed by Wilson[21] in order to determine eddy diffusivities in a moving gas stream. The modified Wilson equation:

$$C = \frac{Q}{4\pi ER} e^{-\frac{U}{2E}(R-x)}, \qquad (48)$$

where C = Concentration and volume fraction,

E = Eddy diffusivity-$cm^2/sec$,

R = Direct distance from injector tube to sampling point-cm,

U = Velocity of gas stream-cm/sec,

Q = Rate of gas injection-cc/sec,

x = Vertical distance from injector to sampling plane-cm,

gives the concentration of a substance which has been injected axially in a moving stream of fluid. It assumes an infinite media, a zero velocity gradient across the duct, and that the mean molar velocity is not affected by the addition of the diffusing gas. The experimental results of Towle and Sherwood[20] were in close agreement with the Wilson equation so a method similar to theirs was chosen to determine the eddy diffusivity in the spray calciner. The method involves injecting a known amount of a gas in the center of the gas stream at about the same velocity. Down stream, samples are taken to determine the concentration profile. Since the Wilson equation can be rewritten as:

$$\ln CR - \ln \frac{Q}{4\pi E} = -\frac{U}{2E}(R-x), \qquad (49)$$

a plot of lnCR vs (R-x) will yield a straight line of slope U/2E. Its intercept at (R-x) = o will give the value of $\frac{Q}{4\pi E}$ which is then solved for E, the eddy diffusivity. The value should also be obtained by inserting the peak profile concentration near the center of the duct in the equation: $E = \frac{Q}{4\pi CR}$ (i.e., the Wilson equation at R-x = o). (50)

Gas Sampler Apparatus

The gas sampler used in the determination of eddy diffusivity consisted of seven 1/16" stainless steel tubes which extended into the column where they were bent upwards one inch against the direction of gas flow. The tips were spaced one inch apart and thus gave a cross section of the gas within the column. The lines were sealed onto the column by passing through a tapered Teflon plug in a 1" pipe side tap.

The stainless steel lines were connected with 1/8" Tygon tubing to a bank of seven 185 ml glass sample bulbs filled with water. The sample was taken by letting the water bleed out through a stop cock into a collecting bottle. Gas analysis was done by Hanford Laboratory personnel with a mass spectrometer. The argon used as a tracer was injected from a 1/2" tube located up the column from the sampler.

Eddy Diffusivity During Spraying

The column was heated to normal operating temperature of 1015 F and argon was injected axially through a stainless steel tube injector 33.6 cm above the samplers at a rate ratio to the steam-air mixture equal to the tube area to column area ratio. Water was sprayed into the column at 58 ml/min through an air atomizing nozzle with air rate of 44,800 ml/min at STP.

The diffusing argon profile obtained is shown as a semi-logarithmic plot of the data in Figure 23. The slope gives a value of 19.6 $cm^2$/sec. The peak value of argon concentration was somewhat below the mean concentration which should have resulted from the flow rate. This is a result of misalignment of the sampling probe such that the concentration peak was not sampled. A material balance by integration of the concentration profile yields only 60 percent. For this reason the Wilson equation (50) involving the peak concentration cannot be used, and only the semi-logarithmic plot is valid for computing the eddy diffusivity. Towle and Sherwood[20] were confronted with the same difficulty when measuring eddy diffusivity with carbon dioxide. A material balance in one profile direction yielded 66 percent and in the other, 130 percent, yet the semi-logarithmic plot method for the two profiles gave them diffusivity values which agreed within 5 percent. Therefore, it seems justified to use the value indicated by Figure 23.

The molecular diffusivity of argon calculated for these conditions is 0.784 $cm^2$/sec. Thus the large value (19.6 $cm^2$/sec) of eddy diffusivity (25 times the molecular diffusivity) indicates that a high degree of turbulence exists at eleven column diameters below the nozzle even at a superficial Reynolds number of 256 for this run. Towle, Sherwood and Seder[22] measured eddy diffusivity of this magnitude at a Reynold's number of about 86,000. A correlation between eddy diffusivity and Rey Reynold's number by Sherwood and Woertz[23] yields a Reynold's number of 90,000 for these run conditions. It is seen from these results that the nozzle greatly affects gas flow in the column by causing considerable turbulence which extends at least eleven column diameters below the nozzle. Thus, small particles which would be affected by the gas turbulence cannot be assumed to stay at the same radius within the column while being calcined.

12-7-60
RT Allemann:pct

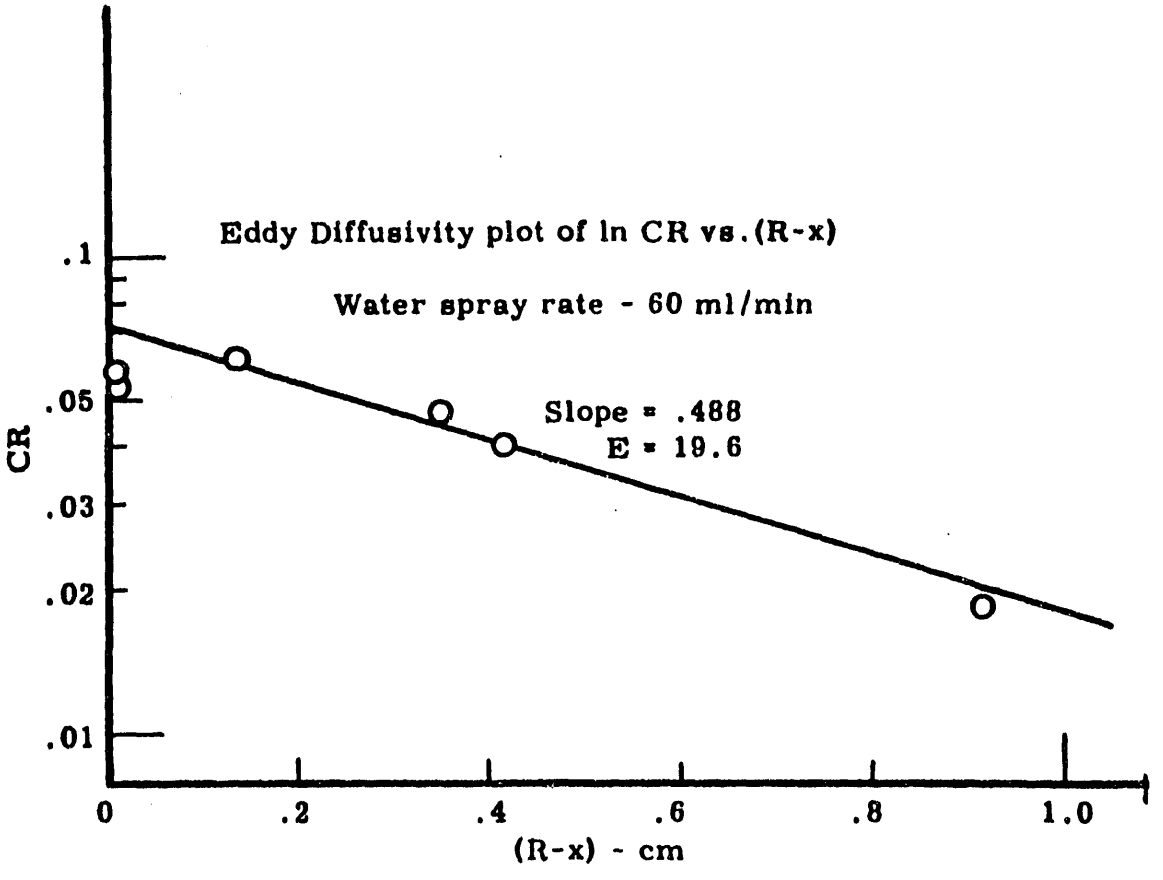



FIGURE 23

Argon Profile with Spray Nozzle - Semi-Logarithmic Plot

DATE
FILMED
8/5/93

END