MASTER

EXTERNAL TRANSMITTAL AUTHORIZED
~~EXTERNAL DISTRIBUTION LIMITED~~
ORNL
Central Files Number
58-2-139

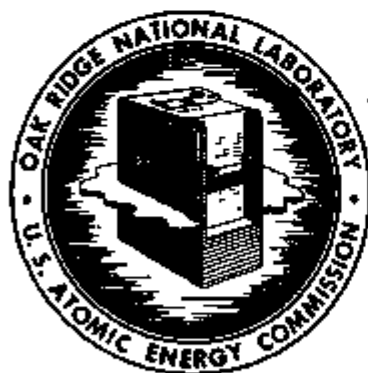CHEMICAL TECHNOLOGY DIVISION

UNIT OPERATIONS SECTION

MONTHLY PROGRESS REPORT

FEBRUARY 1958

<u>NOTICE</u>

This document contains information of a preliminary nature and was prepared primarily for internal use at the Oak Ridge National Laboratory. It is subject to revision or correction and, therefore, does not represent a final report.

OAK RIDGE NATIONAL LABORATORY

operated by

UNION CARBIDE CORPORATION

for the

U.S. ATOMIC ENERGY COMMISSION

RELEASE APPROVED
BY PATENT BRANCH

DISCLAIMER

DISCLAIMER

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

CF-58-2-139

Copy No. 1

Chemical Technology Division

UNIT OPERATIONS SECTION MONTHLY PROGRESS REPORT

February 1958

J. C. Bresee
P. A. Haas
C. D. Watson
M. E. Whatley

Date Issued

JUN 2 7 1958

OAK RIDGE NATIONAL LABORATORY
Operated by
UNION CARBIDE CORPORATION
for the
U. S. Atomic Energy Commission
Post Office Box X
Oak Ridge, Tennessee

ABSTRACT

Calibrations have resulted in conflicting data for the yield of neutrons from a teflon-polonium solution interface. The installation of the continuous DRUHM reaction system is approximately 60% complete. The Fluorox fluidized bed reactor was operated continuously for 12 hr, producing 1.6 kg of UF_6. In homogeneous reactor studies, installation of a mock-up for in-pile slurry bomb heat removal tests has been completed. From material balances, about 2-1/2 g of plutonium remain in loop P-1 after repeated washing and descaling treatments. A Sharples Model P-4 Super-D-Canter was adequate for continuously discharging ThO_2 cake and clarified supernate. In ion exchange studies, data have been obtained on the complex ion equilibria in uranyl sulfate solutions. A continuous self-sustaining Darex dissolution and stripping run of 46 hr duration was made. In a hydrochlorination run of 35 hr duration, 97.4% of a 4.39 kg section of a STR subassembly was reacted with anhydrous HCl gas with a uranium loss to the sublimate of 0.095%. The studies of the dissolution of dummy zirconium fuel elements in fused salt with HF have been continued at increased HF velocities. In waste processing studies, the design of an adiabatic self-sintering experiment is 90% complete and the construction of the field facilities is 50% complete.

TABLE OF CONTENTS

SUMMARY

1.0 CHEMICAL ENGINEERING RESEARCH

Calibrations have resulted in conflicting data for the yield of neutrons from a teflon-polonium solution interface.

2.0 DRUHM

The installation of the continuous reaction system is approximately 60% complete. A second reactor is being fabricated for this system which can be used with a high-fired MgO liner which was obtained from Y-12.

3.0 FLUOROX

The Fluorox fluidized bed reactor was operated continuously for 12 hr, producing 1.6 kg of UF_6. There were some operating difficulties with the UF_4 feed to the fluidized bed reactor.

4.0 HOMOGENEOUS REACTOR PROJECT

4.1 <u>Slurry Irradiation Studies Assistance</u> - Installation of a mock-up for in-pile slurry bomb heat removal tests has been completed. In an initial test, over 99% of the ThO_2 circulating was collected into an underflow receiver by a hydroclone.

4.2 <u>UO_2SO_4 Fuel and Blanket Processing Studies</u> - From material balances, about 2-1/2 g of plutonium remain in loop P-1 after repeated washing and descaling treatments. The loop will be transferred to the burial grounds and disassembled there for examination of components.

4.3 <u>Thorium Oxide Preparation</u> - The 1600°C fired, micropulverized ThO_2 classified by the Sharples Super Classifier has been returned for product evaluation. Results show that the effectiveness of hydroclones for classifying ThO_2 is dependent on the dispersion obtained and that a dependable dispersion method must be developed to assure consistent results. A Sharples Model P-4 Super-D-Canter was adequate for continuously discharging ThO_2 cake and clarified supernate. Final results on the previously reported flame calcination test using a CH_3OH-ThO_2 slurry feed show a 97% ThO_2 recovery, a poor feed dispersion, and a calcination equivalent to 1200°C in a furnace. Design calculations and development tests of a reflective burner show that flame temperatures are increased and that particle temperatures above 1600°C can probably be obtained. Revision of a Schori flame spray pistol, an atomic hydrogen torch, and an ultrasonically agitated feed cup have eliminated initially observed operating problems.

5.0 ION EXCHANGE

The kinetics of transfer of uranium from uranyl sulfate solutions to anion exchange resins is being studied. Data on equilibrium of the complex ions involved in solution has been obtained from the literature.

6.0 POWER REACTOR FUEL REPROCESSING

6.1 Darex

6.1.1 Continuous Dissolution and Stripping Studies

A continuous self-sustaining dissolution and stripping run of 46 hr duration was made. During the run the dissolver discharged its product at a varying rate which flooded the stripper at cyclic intervals and gave varying stripping of chloride (100 ppm - 1500 ppm in the product). An overall material balance based on average values was consistent even though it does not reveal the intermittent upsets of the system.

6.1.2 Feed Adjustment Tank Studies

Preliminary bench scale studies in which dissolver product containing 900 ppm chloride was concentrated continuously show that (a) the chloride remains with the concentrated product, and (b) the concentrated product containing 280 g SS/liter and 2.9 $\underline{M}$ HNO_3 was metastable, requiring as long as 16 hr at room temperature for solids to appear.

6.2 Zircex Engineering Studies

In a hydrochlorination run of 35 hr duration, 97.4% of a 4.39 kg section of a STR subassembly was reacted with anhydrous HCl gas fed at approximately 6 g-moles/hr. The utilization of HCl was 90%. Uranium loss to the $ZrCl_4$ sublimate was 0.095%. Hydrogen evolution was practically constant throughout the run (~2.68 cu ft/hr) indicating that the reaction rate was independent of total area.

6.3 Mechanical Processing

Shearing Studies - Shearings of unirradiated stainless steel clad uranium oxide (Yankee Atomic fuel) gave the following results:

(a) The UO_2 from sheared lengths less than the length (3/8-in.) of a fuel pellet was usually dislodged after shearing.

(b) The UO_2 from sheared lengths greater than the length (3/8-in.) of a full pellet and up to 1/2-in. long was retained ~50% of the time.

(c) The UO_2 from sheared lengths 1/2-in. long and greater, was always retained except at the sheared face.

(d) The air count of air withdrawn near the point of shearing exceeded masking tolerance by a factor of 3×10^3.

6.4 Materials Evaluation

A proposed polyester canal lining (Amercoat 1679) failed from blistering after exposure to 10^9 r, in water at ~ $104°F$.

7.0 VOLATILITY

HF-Fused Salt Dissolution - The studies of the dissolution of dummy zirconium fuel elements in fused salt with HF have been continued at increased HF velocities. The specific dissolution rate increased approximately as the logarithm of the HF velocity.

8.0 WASTE DISPOSAL STUDIES

The design of an adiabatic self-sintering experiment is 90% complete and the construction of the field facilities is 50% complete. A small-scale high level sintering experiment to characterize radioactivity levels in the off-gas has been started.

1.0 CHEMICAL ENGINEERING RESEARCH

P. A. Haas

Interfacial Area Measurements- C. V. Chester

The α,n reaction of fluorine at the interface of an aqueous Po^{210} solution and a liquid fluorocarbon is being developed as a method of measuring interfacial area.

A series of experiments is under way to remeasure the absolute value of neutron yield from a polonium solution-teflon interface. Using teflon plate of 1-in. to 1/4-in. thickness, the yield was 10 ± 2 neutrons/min, cm^2, mc/ml. Using teflon plates of 1/8-in. thickness, the measured yield was 5 ± 2 neutrons/min, cm^2, mc/ml. Several possible reasons for the apparent change in yield with thickness have been disproven experimentally. Surface finish and material composition have been ruled out as causes for the discrepancy by machining plates of the several sizes out of the same piece of stock. Random experimental error has been ruled out by numerous reruns of the experiment. The amount of α contamination on the plates after tests was not sufficient to account for the results.

Effort to resolve the discrepancy is continuing.

2.0 DRUHM

C. D. Scott

The direct reduction of UF_6 to metal by used of sodium is being studied. Work is progressing on the facility for the continuous reaction study.

Continuous Reaction Study

The installation of the continuous reaction system is approximately 60% complete. The anticipated completion date is March 15, 1958. A new reactor is being fabricated for this system which can be used with a high-fired MgO liner which was procured from Y-12. The possibility of flame coating a reactor or liner with MgO is being investigated.

3.0 FLUOROX

M. E. Whatley

3.1 Fluidized Bed Development - C. D. Scott, W. G. Sisson, D. H. Newman

A fluidized bed reactor is being developed to carry out the Fluorox reaction ($2 UF_4 + O_2 \longrightarrow UO_2F_2 + UF_6$). The bed, operating continuously with a UF_4 feed, approaches a steady state composition which is predominately UO_2F_2. The objects of the present studies are to investigate operational and mechanical difficulties and to obtain kinetics information in a continuous system.

Run FBR-16 using a bed temperature of $800^\circ C$ and a UF_4 feed sized between 40 and 200 mesh was completed. The system included a rotary pump feeder which discharged the UF_4 feed to an O_2 stream which carried it into the bottom section of the reactor. The product gas stream was routed through a set of filters to remove the fines and solid intermediate products, through cold traps to collect the UF_6, and finally through chem traps before being exhausted to the hot off-gas system. The solids from the filter housing and the fluidized bed itself were periodically sampled. The bed level was to be maintained by removing solids from a sample line at the bottom of the reactor.

3.2 Experimental Results

The chemical analysis of the samples from run FBR-16 are not yet finished, so complete discussion of the results cannot be made. There were, however, data obtained from the operation itself.

Essentially constant operating conditions were maintained for 9.7 hr out of a total operating time of 12.2 hr. The run was terminated when the bottom solids removal line became plugged and the subsequent addition of feed caused an excessive build-up of the bed. The average UF_4 feed rate was 597 g/hr. Material collected in the cold trap (UF_6) amounted to 1,600 g, and the material collected in the filter housing (including reaction intermediates) amounted to 2,870 g. The overall material balance for the run was complete and consistent.

The rotary feeder, which was a modified rubber impeller pump, did not operate satisfactorily. Initial tests showed it to work well, and it was calibrated between 100 and 2000 g/hr; however, during the run the vibration of the equipment caused the leakage of UF_4 through the feeder even when the rotor was not moving. The source of the difficulty has not yet been located.

There was a tendency for the system to plug at the junction of the off-gas line with the reactor. These plugs were freed periodically by striking the reactor flange with a hammer.

3.3 Equipment Changes

Some necessary equipment changes indicated by this run include: (1) the replacement of the off-gas line from the reactor to the filter housing to increase its diameter from 1/2-in. to 1-in., (2) the installation of a 1-in. overflow line on the reactor to maintain continuously the bed level, (3) the installation of a baffle in the reactor at the off-gas line in an attempt to reduce the solids carry-over.

3.4 UF$_4$ Compacting Studies

There is some indication that the UF$_4$ feed to the fluidized bed should be in the same size range as the initial bed, -40 mesh + 100 mesh. Feed for a possible moving bed test would also be larger than the UF$_4$ feed being used now. As a result of these two facts, studies are being made on particle agglomeration or UF$_4$ compacting as a feed to a granulating machine which would reduce the feed to the proper range.

A compacting machine composed of two corrogated rolls, a "Chilsonator", is being studied for this use. Initial tests made on this machine show that it will compact fine UF$_4$, 90% less than 100 mesh, to material greater than + 4 mesh; however, the yield of this compacted material to date has been less than 5% of the feed material. The machine is evidently very sensitive to roll spacings, feed rates, and to the particle size of the feed material. Further compacting tests will be made.

4.0   HR FUEL AND BLANKET PROCESSING

P. A. Haas

4.1   HRP-Slurry Irradiation Studies Assistance

4.1.1   In-Pile Slurry Bomb Cooling Mockup - J. M. Holmes

Construction of the test mockup to determine heat transfer coefficients for cooling the ORR thorium oxide bomb is complete.

A test program using air and mixed air-water coolants has been started.

4.1.2   Hydroclone Tests for Loop Rinsing - J. W. Snider

A study was initiated of the use of a hydroclone with an induced underflow receiver to remove 1600°C fired ThO_2 from a loop liquid charge. The apparatus used consisted of a feed tank with an agitator, a centrifugal pump, an 0.4-in. dia. hydroclone and an underflow pot, Fig. 4.1. The concentration vs time curve for the feed tank, Fig. 4.2, showed over 90% removal of ThO_2 in 75 min. and 99% in 190 min. The underflow receiver volume to feed tank volume ratio was 4.67. About 99.9% of the ThO_2 was in the underflow pot at the end of the run.

Further studies are to be made with varying concentrations, feed materials, underflow receiver/feed tank ratios, underflow receiver geometries, hydroclone sizes, and hydroclone pressure drops.

4.2   HRP-UO_2SO_4 Fuel and Blanket Processing Studies

4.2.1   Loop P-1 Operation - J. W. Snider

The third descaling run with $CrSO_4$ was completed. From material balances, approximately 2-1/2 g of Pu remained in the loop after this run was completed. Preparations are being made to dismantle the loop for inspection of components. This will be done after transfer to the burial grounds to avoid the necessity of cleaning up any plutonium released.

4.2.2   Hydroclone Development - P. A. Haas

Design of a vaned, axial inlet, axial flow hydroclone has been completed and fabrication is about 20% complete (Drawing D-80). This design does not give the high G centrifugal fields of the conventional conical cyclones, but may be more effective due to lower velocity gradients and shear stresses.
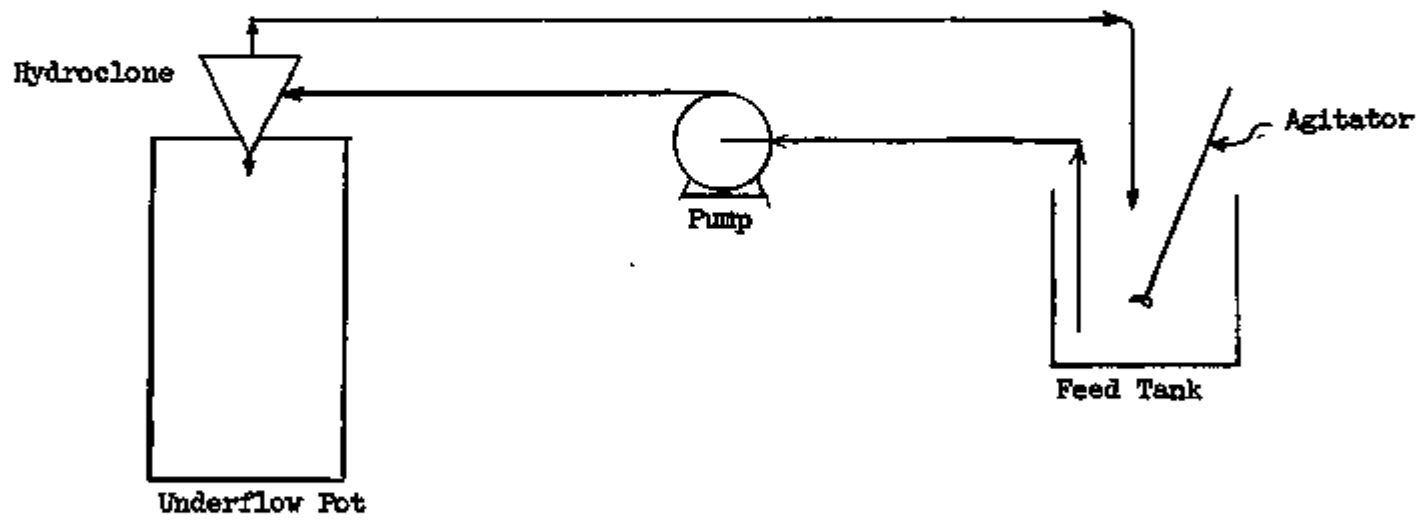
Hydroclone

Pump

Agitator

Feed Tank

Underflow Pot

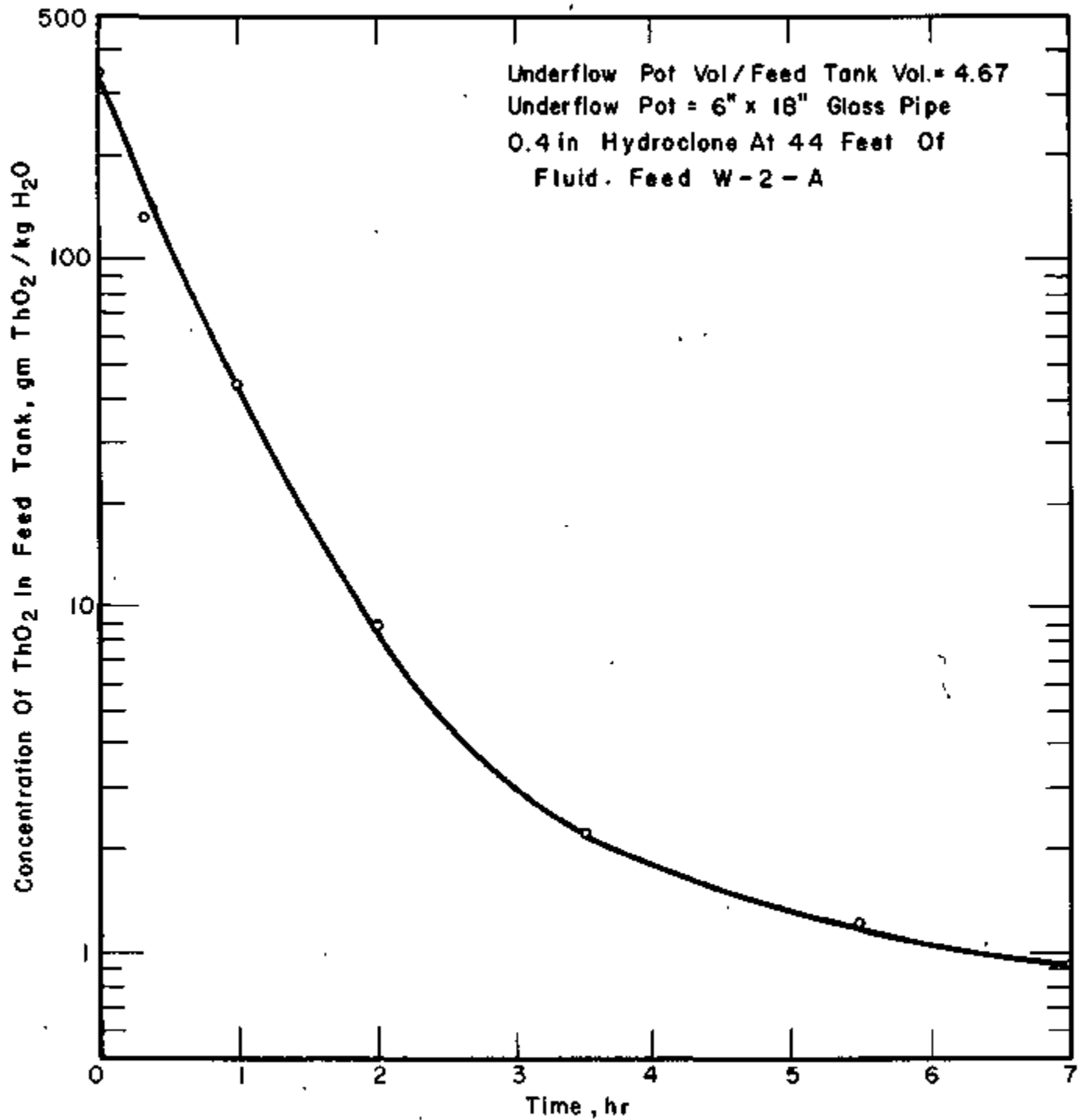Fig. 4.1 Loop Rinsing Apparatus

Fig. 4:2 Concentration Of ThO$_2$ In Feed Tank Versus Time For Run 2

Calibration curves for two Dorr-Oliver Model X-8A high pressure, high temperature hydroclone units, Fig. 4.3, agree with the predicted values, Fig. 4.4. These commercially available units can be altered for induced underflow receiver operation. They may be applicable to HRE No. 3 core processing studies, blanket purge water clarification, or other reactor applications. Each unit has seven 10 mm dia. titanium hydroclones in parallel in a stainless steel case.

4.3 HRP-Thorium Oxide Preparation

4.3.1 Thorium Oxide Size Classification - E. L. Youngblood

4.3.1.1 Sharples Super Classifier

A Sharples Super Classifier located at K-25 has been tested by members of the Barrier Development Section to determine its effectiveness in removing oversize particles from thorium oxide particles in the 1-micron diameter range. In the test two batches of 1600°C fired, micropulverized, thorium oxide (containing different fractions of oversize material) were processed. The fine particle material from both batches was given a second pass through the unit in an attempt to further reduce the fraction of coarse material.

During the first pass, a total of 165 lb of thorium oxide feed yielded 96 lb of fine particle of less than 8 micron diameter. The cutpoint of 8 micron was essentially independent of the particle size distribution of the feed and no additional removal of coarse material was obtained by the second pass of the fine cut through the classifier.

The size distribution curves for the feed, coarse cut, and fine cut from a typical first pass of thorium oxide through the classifier are plotted, Fig. 4.5. The distribution curve for the fine fraction is representative of the fine cuts from the first and second passes of both batches of thorium oxide. The particle size distribution of the coarse fraction varied with the size distribution of the feed.

4.3.1.2 Hydroclone Classification

A series of runs using 10 mm dia. hydroclones have been made to determine their effectiveness in removing oversize particles from thorium oxide in the 1-micron dia. size range. Runs have been made using both single hydroclone systems and a production size TM-3 Dorr Clone which consists of three stages, each of which contains 32 hydroclones in parallel. The flow arrangement of the TM-3 Dorr Clone was modified to permit recycle of both the overflow and underflow streams as shown in Fig. 4.6. The three test runs described below are representative of the separations thus far obtained by hydroclones.
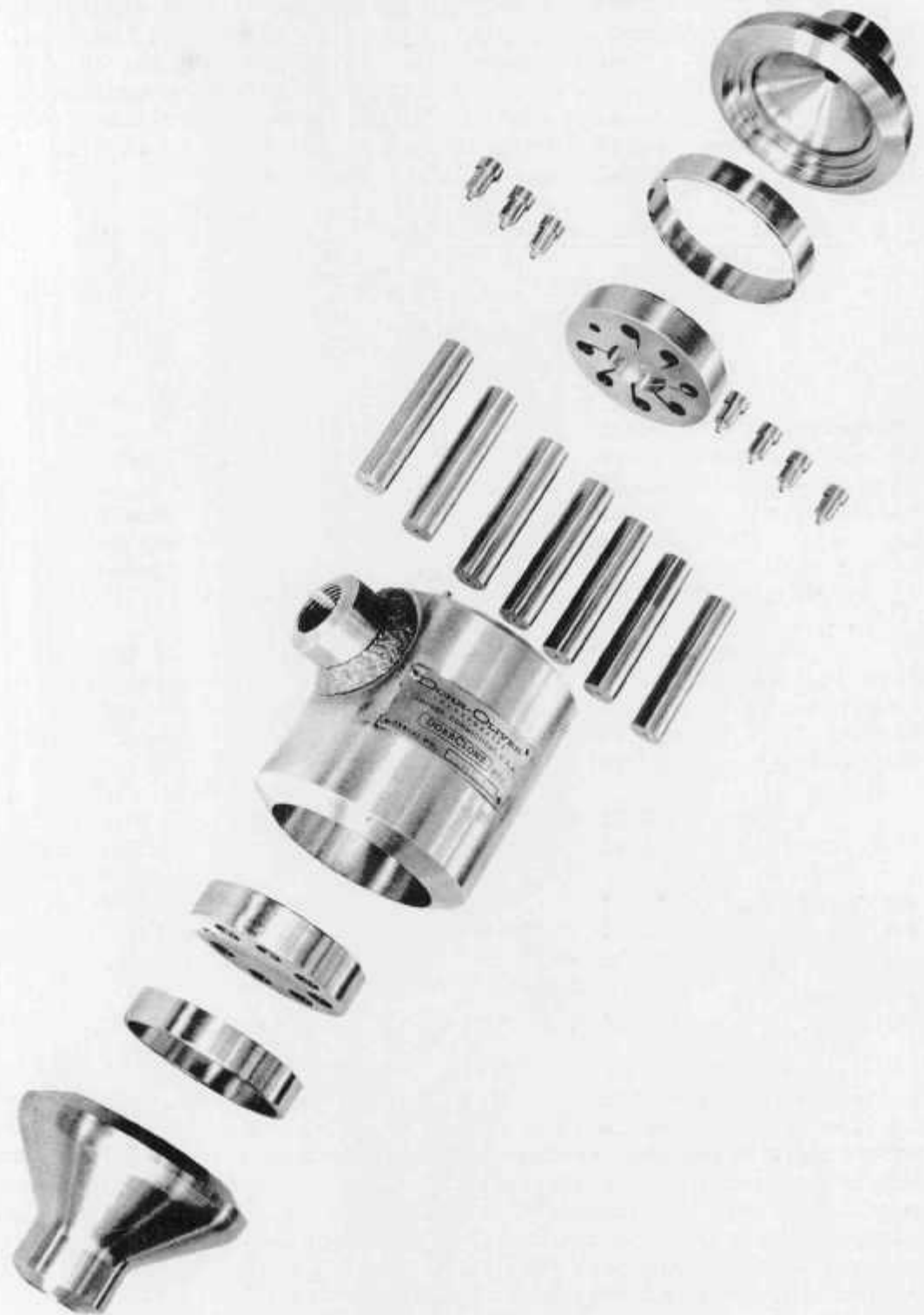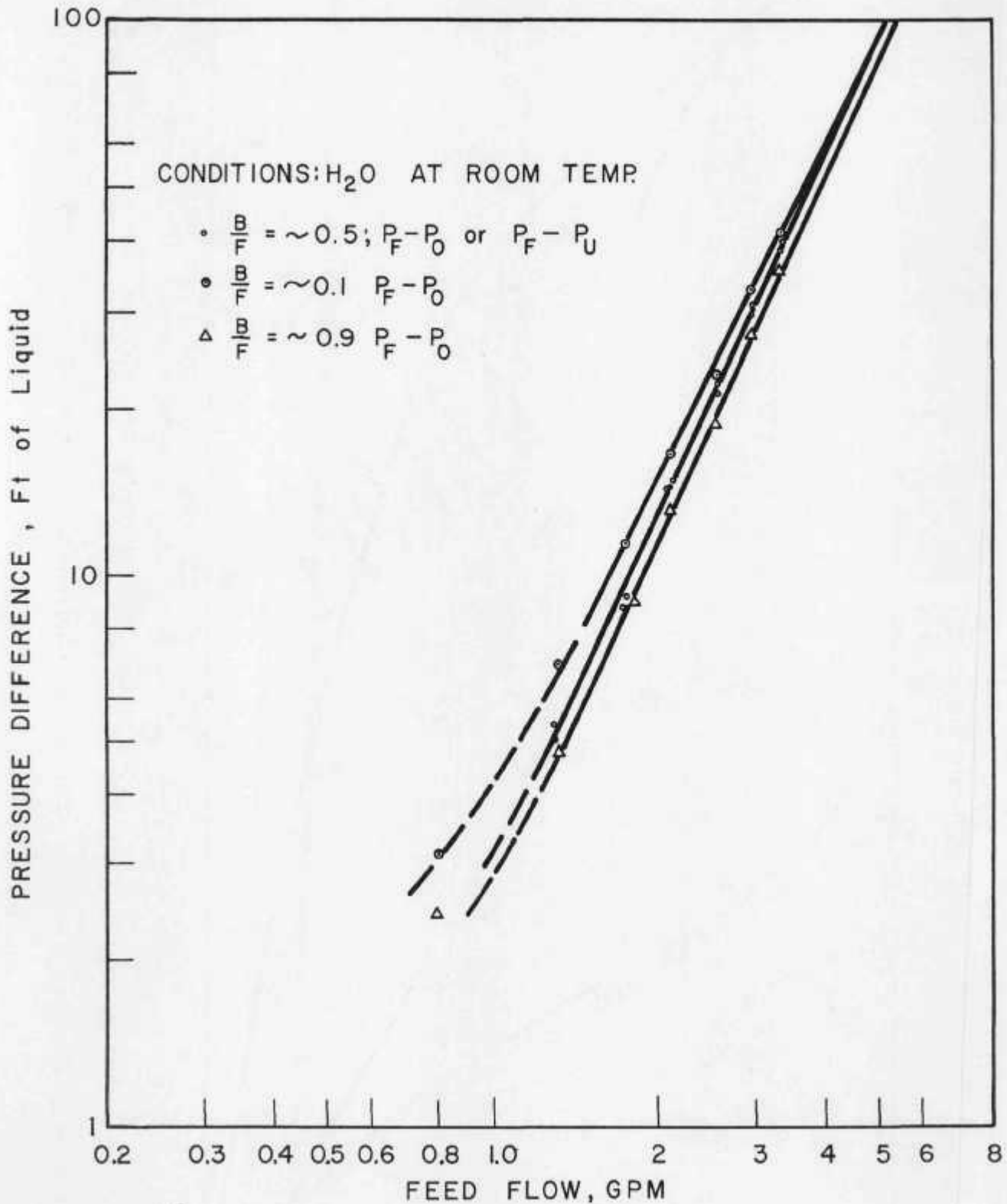
Fig. 4.3   Disassembled View of Dorr-Oliver Model X-8A
Hydroclone (7 (seven) 10 mm units)

Fig. 4.4 Feed Flow Versus Pressure Drops for Dorrclone
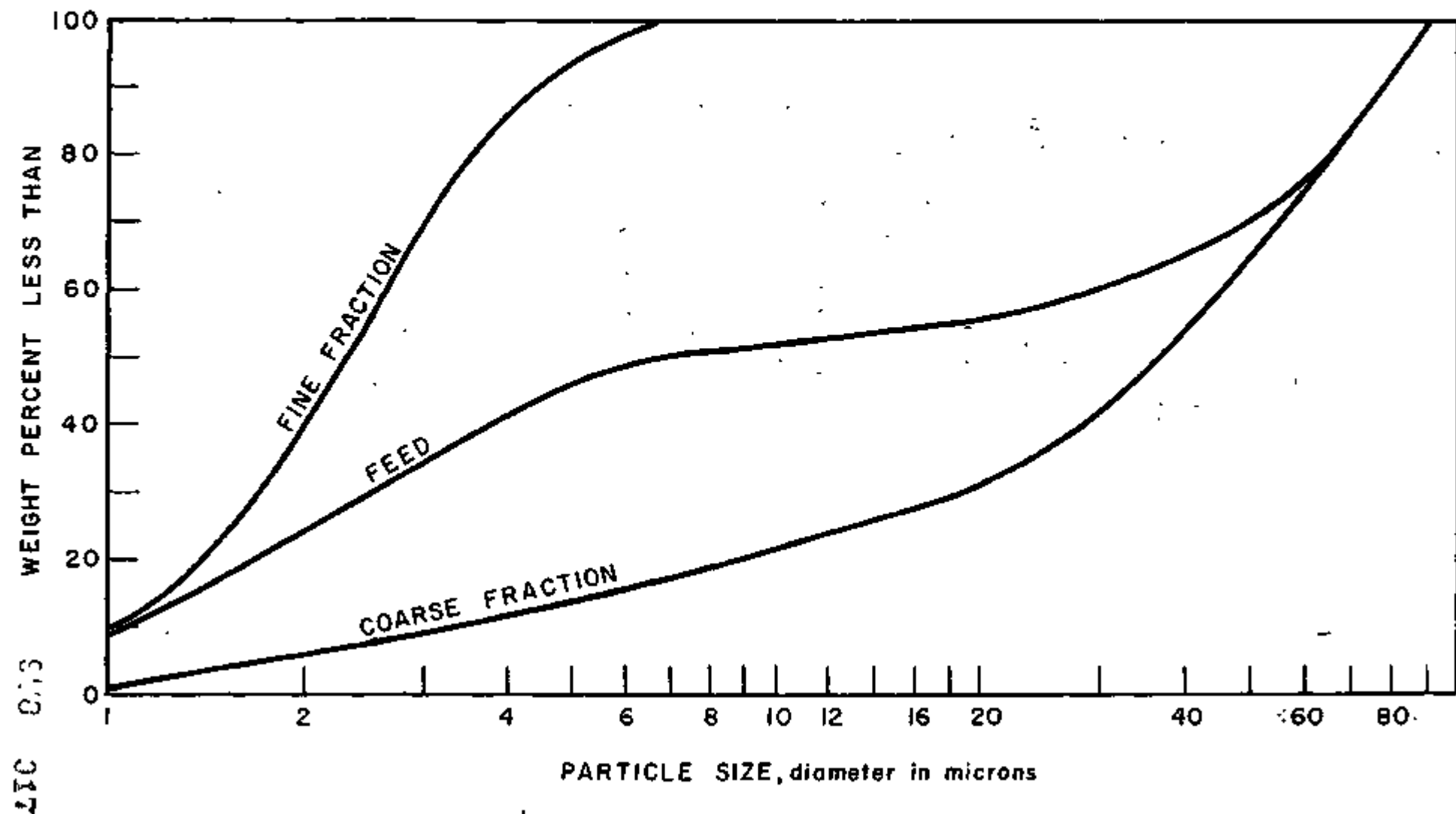Model X-8A, Seven 10mm D unit

Fig. 4.5 Particle Size Distribution of Thorium Oxide from Sharples Super Classifier
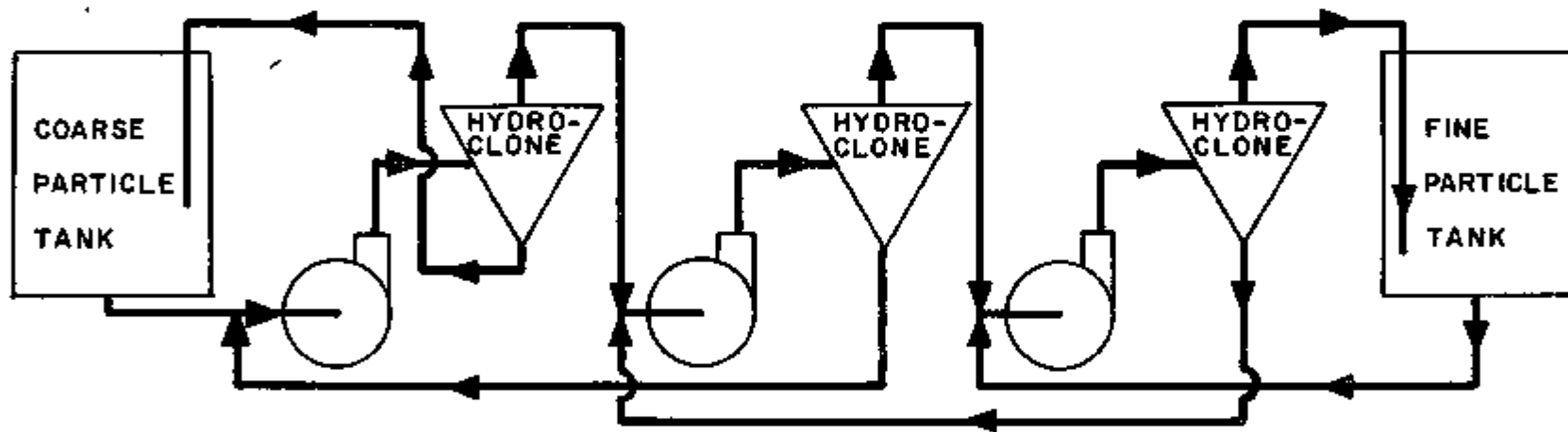
Fig. 4.6 Flow Diagram of A 3 Hydroclone Classification System

The test runs were begun by charging the coarse particle tank with the feed slurry and operating the system at total recycle until equilibrium conditions were reached. Size distribution curves were obtained for thorium oxide in the coarse and fine particle tanks of the TM-3 Dorr Clone system at equilibrium. The feed materials for these runs were 1600°C fired thorium oxide suspended in water which had been adjusted to pH 2.2 with oxalic acid to disperse the oxide. Size distribution curves are shown for a typical test starting with feed concentration of 45 g/liter, Fig. 4.7. Figure 4.8 shows the particle distribution of the fine and coarse fractions based on the percentage material in size groups 0.2 microns wide.
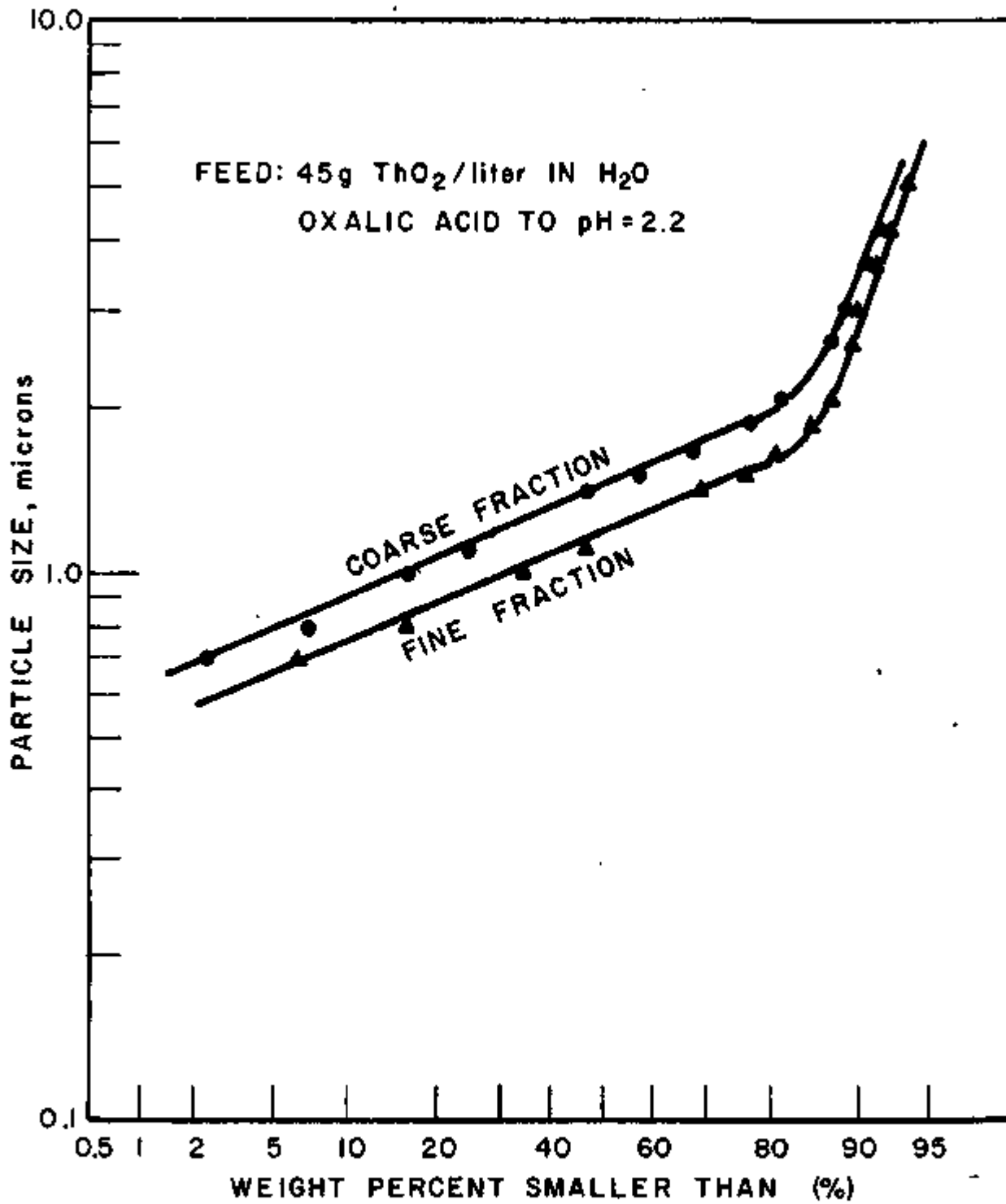
Size distribution curves (based on 0.2 microns size groups) were obtained for the feed, fine fraction and coarse fraction from a two stage single hydroclone system arranged to permit recycle of the overflow and underflow streams are shown, Fig. 4.9. The feed material used in this run was 1600°C fired thorium oxide which had been classified in a Sharples Super Classifier to produce material less than 8 microns in diameter. The feed was suspended in methyl alcohol at a concentration of 10 g/liter.

Size distribution curves were obtained for the feed and fine fraction from a single hydroclone system with no recycle, Fig. 4.10. The feed material used for this run was 1600°C fired thorium oxide from which the particle larger than 8 microns had been removed in a Sharples Super Classifier. The oxide was suspended in demineralized water at a concentration of 10 g/liter.

The work thus far indicates that separation of thorium oxide particles in the 1-micron diameter range is obtainable with 10 mm hydroclones. Future work will be aimed at determining optimum operating conditions and demonstrating continuous hydroclone cascade operation.

4.3.2 Centrifugation of ThO_2 - J. M. Holmes

A test has been completed to determine the efficiency of the Sharples P-4 "Super-D-Canter" for concentrating a thorium oxide slurry. Results show that slurries between 45 and 90 g/liter were concentrated at rates between 375 and 2000 cc/min. with less than 1.1% loss of thorium oxide in the overflow. The underflow stream discharged freely from the machine in the form of a thick paste. Operating data are tabulated in Table 4-1.

FEED: 45g ThO_2/liter IN H_2O

OXALIC ACID TO pH = 2.2

COARSE FRACTION

FINE FRACTION

PARTICLE SIZE, microns

WEIGHT PERCENT SMALLER THAN   (%)

Fig. 4.7 Particle Distribution Curves for ThO_2 from
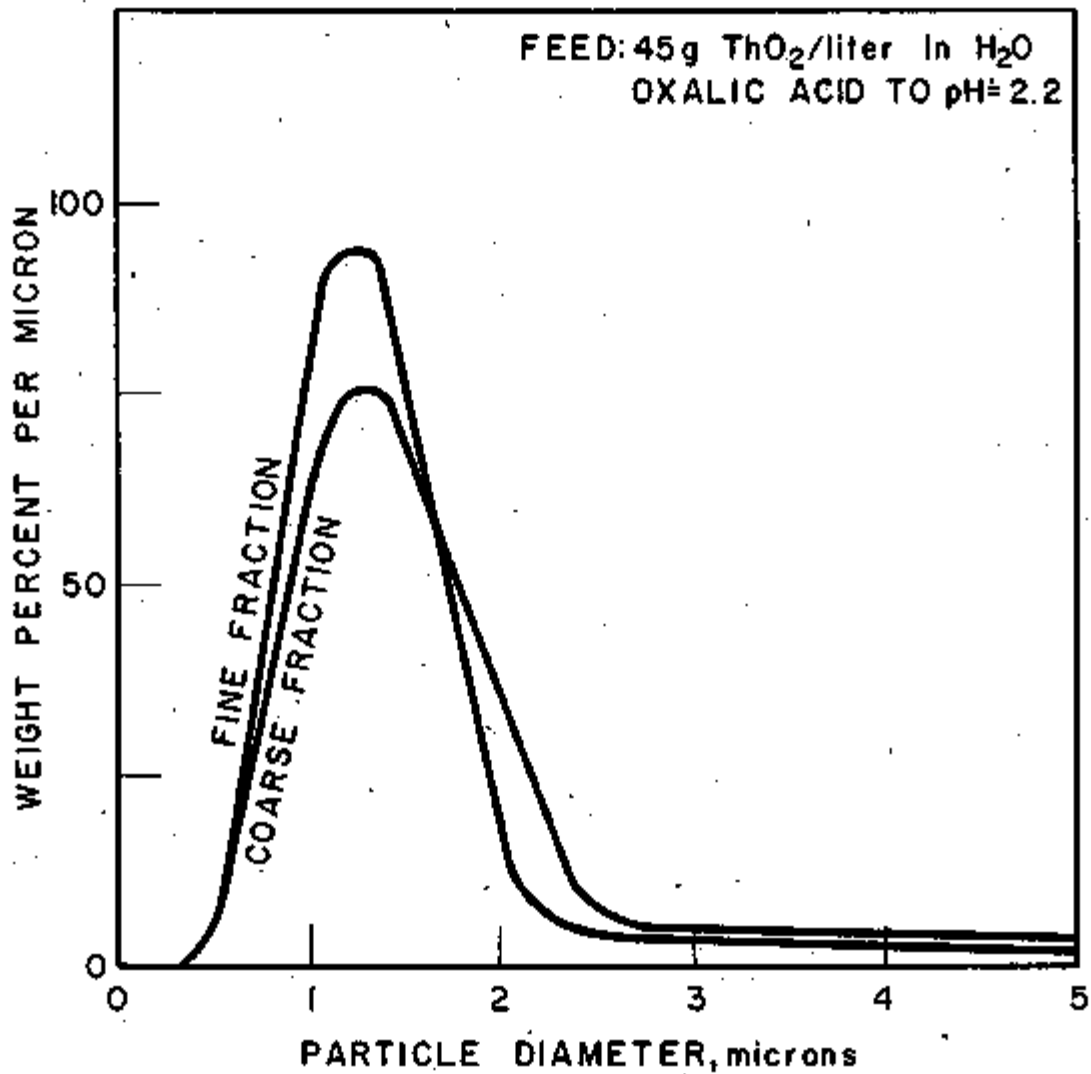TM– 3   Hydroclone Classification System

Fig. 4.8 Particle Size Distribution of ThO$_2$
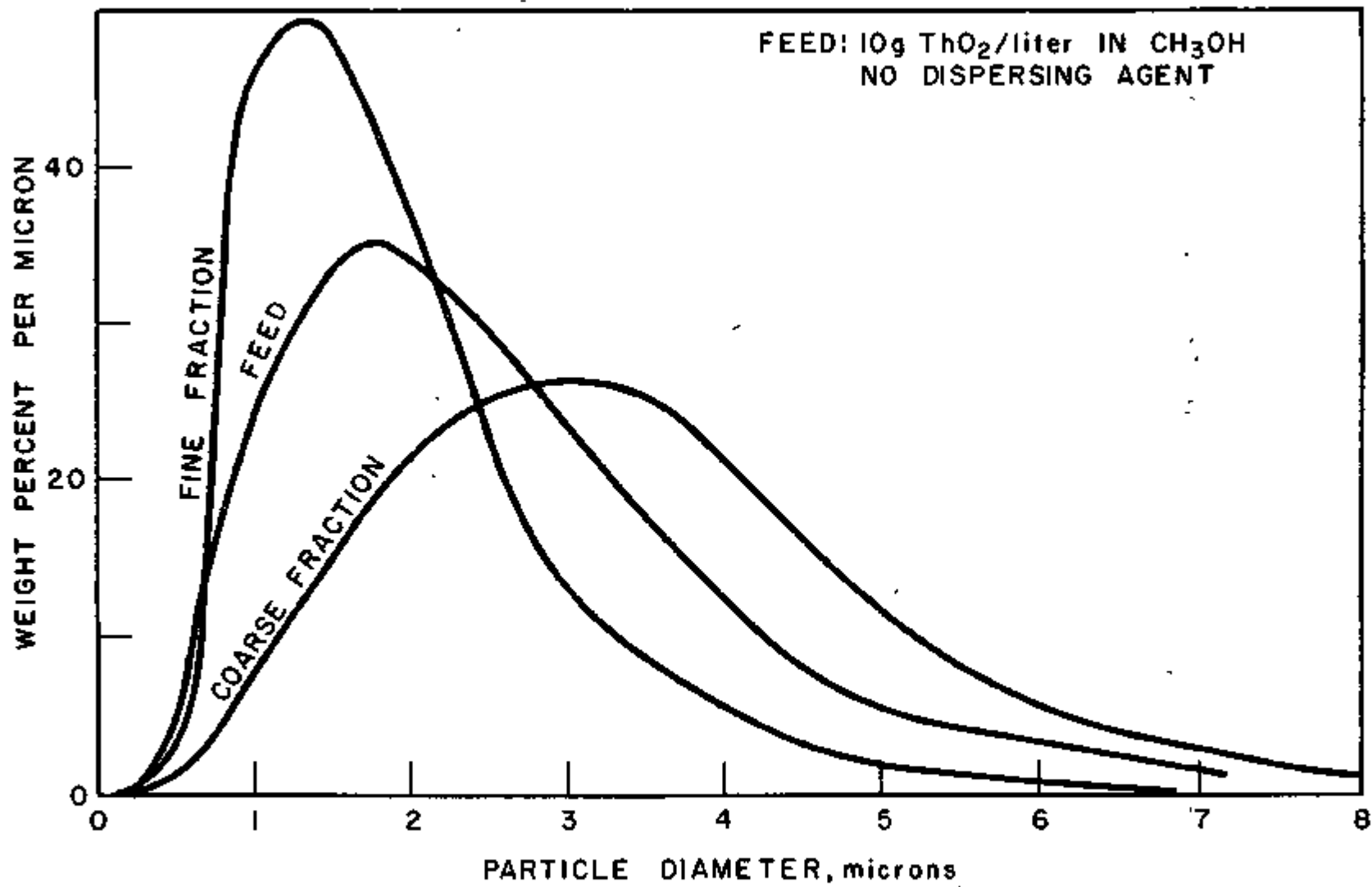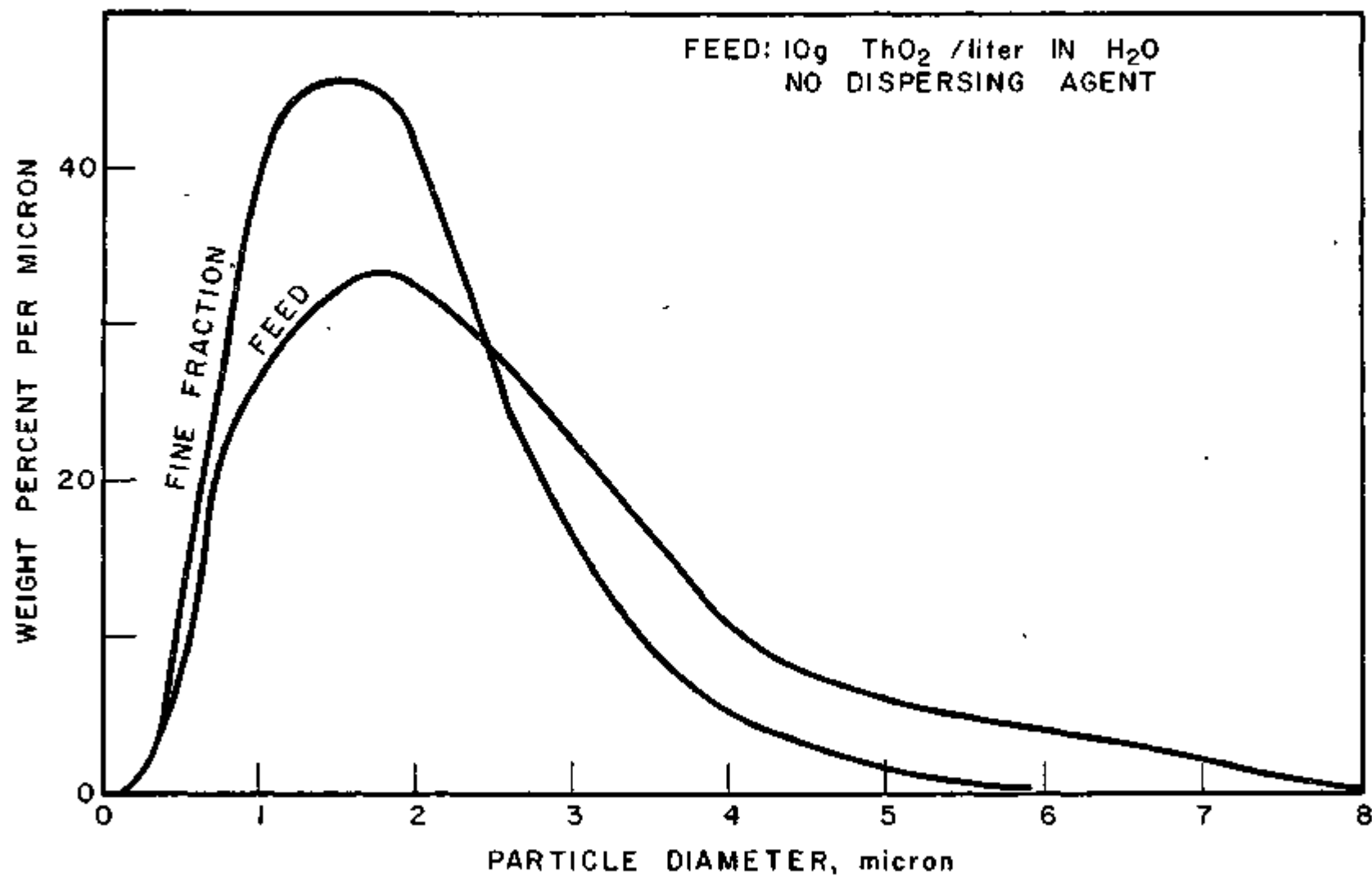from TM-3 Hydroclone Classification System

Fig. 4.9 Particle Distribution of ThO$_2$ from a Two Stage Hydroclone System

Fig. 4.10 Particle Distribution for ThO₂ from Single Hydroclone Classification System

Table 4-1 Results of Centrifugation Tests

Test Unit: Sharples P-4 Super-D-Canter
Speed: 6000 RPM
Centrifugal Force: 2100 g

Feed Rate (cc/min.)	Feed Concentration (g/liter)	Overflow Concentration (g/liter)	Overflow Loss (% of feed)	Overflow Appearance
375	44.9	0.05	0.11	Slight haze
820	89.6	0.13	0.15	Hazy
1460	89.6	0.40	0.44	Milky
2000	47.8	0.52	1.10	Milky

Particle distribution determinations for the feed and overflow streams will be reported when available.

4.4 Flame Calcination - C. C. Haws, K. O. Johnsson

4.4.1 Methanol Alcohol-ThO$_2$ Slurry Results

Complete results are available for the product obtained from the extended thoria firing previously reported (January Unit Operations Monthly Report, CF-58-1-137). The final material balance shows about 97% recovery (Table 4-2).

Table 4-2 ThO$_2$-Methanol Slurry Firing

Run No. 9

Thorium oxide fired (total)	216.9 g
Thorium oxide recovered as product	209.7 g
Material balance	96.7%
Product in filter bag	2%
Product in spray cooler	~73%
Surface area of feed	12.8 sq m/g
Surface area of product	2.9-3.6 sq m/g
Particle size distribution	(Fig. 4.1.1)

Conclusions from these results are:

1. The high recovery of the fired product indicates that product recovery in a bag type vacuum collector is adequate. An uncertainty in this observation is that the particles collected were of relatively large size (see below) and could therefore be collected efficiently by this method.

2. Particulate dispersion in the feed was very poor. The collection efficiency of the spray cooler varies with particle size, being very inefficient for particles below ~ 5 micron. Thus the large fraction of the product caught in the spray cooler (73%) and the small quantity passing through the cooler to be collected in the vacuum cleaner (< 2%) are indications of poor dispersion. A comparison of the particle size distributions between a well dispersed sample of the feed and the product materials effect graphically (see Fig. 4.11). Dispersion was expected to be poor from observation made during the run and the manner in which the feed system was operated.

Preliminary calculation on an idealized flame-ThO_2 particulate system indicate that a bare oxy-acetylene flame cannot heat a 1-micron particle above $1600^{\circ}C$. The surface area of the calcined particles, (2.9-3.6 sq m/g), roughly indicates a $1200^{\circ}C$ firing temperature. For reference, the present $1600^{\circ}C$ pilot plant oxide is ~ 1.8 sq m/g.

Electron micrographs have been received on the vacuum cleaner product in addition to the above data. These micrographs confirm that the particulates are larger than those obtained in previous runs, but it cannot be determined from these prints whether the particulates are simply agglomerated, or fused together. No attempt will be made to degrade any of these product samples.

4.4.2 Dispersion Studies

Fully dispersing the feed material is of primary importance and a considerable effort on this problem is indicated. Current plans include handling thorium bearings particulates using both liquid and gaseous carriers. Use of oxalic acid as a dispersant in the liquid feed was proposed by Chemical Development Section A and it appears to be an efficient system. A firing will be carried out on this system to determine its effectiveness. An investigation of the use of surface agents to reduce the agglomerating tendencies of dried thorium-bearing powders has been started by the Analytical Chemistry Division. A dry dispersion will be required for attaining the highest possible calcination temperatures.

4.4.3 Reflective Burner Development

Previously reported attempts to spheroidize refractory powders in an oxy-acetylene flame; i.e., alundum, zirconia, thoria, as well as the above reported results, have demonstrated a need for achieving higher
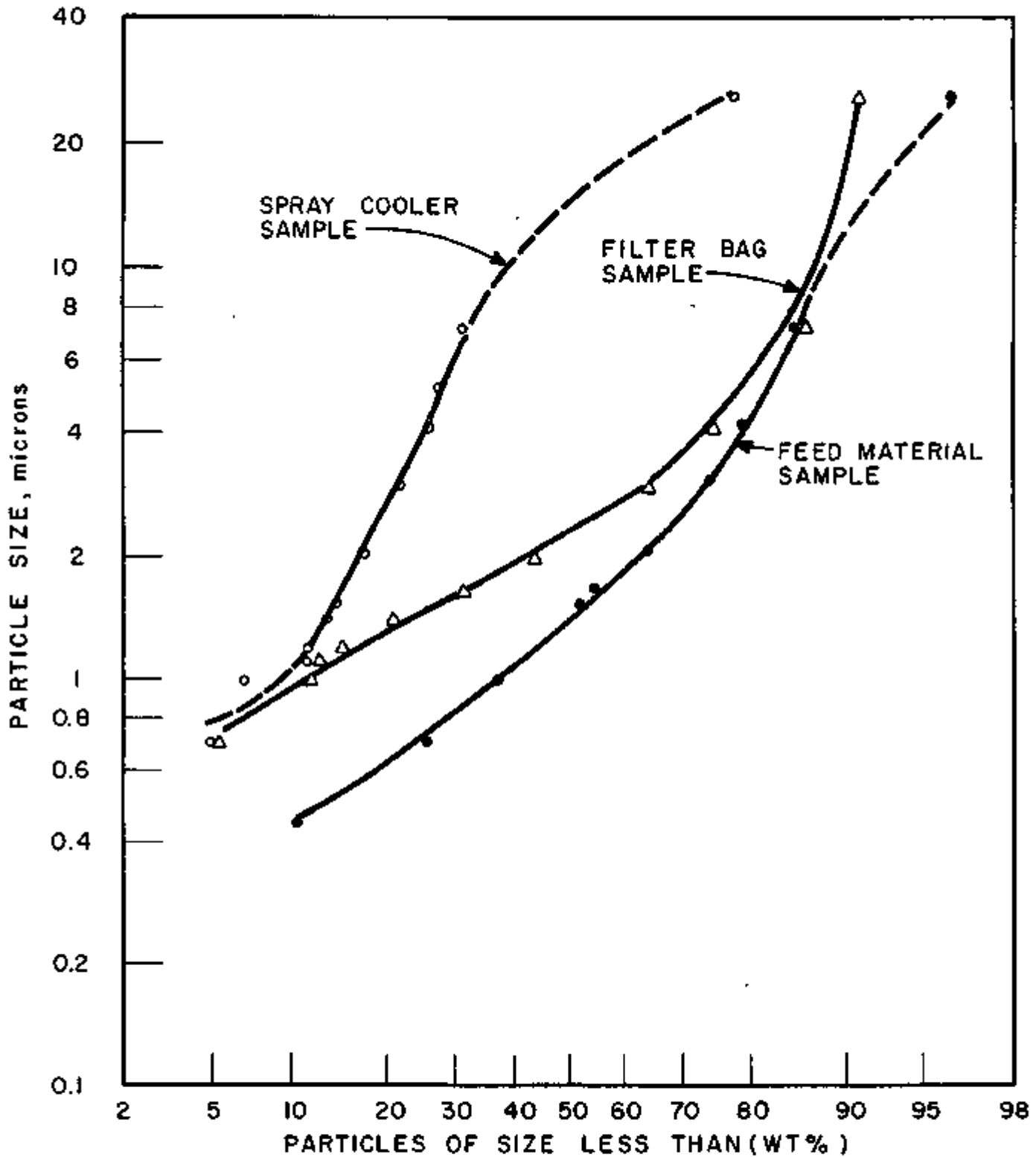
Fig. 4.IJ Flame Calcination Experiments. Comparative
Distribution Data on Feed and Product Samples Run No. 9

particulate temperatures. This higher temperature can be achieved
by extending the length of the flame-atmosphere and by providing a
means of reflecting the heat back onto the particle. A water-cooled
torch was constructed and operated using heavily insulated reflector
tubes of zirconia and graphite. Reflector temperatures above 1800°C
were easily obtained with the zirconia and 1600°C with the graphite
reflectors. Exhaust gas temperatures of over 1600°C were obtained
in all operations. At 0.5 scfm acetylene flow rate, injection of
10 ml/min. of methanol caused no measureable temperature drop in
either the reflector, or the exit gases. Alcohol flow rates in the
15-20 ml/min. range lowered reflector temperatures by ~ 100°C and
brought exit gas temperatures down to 1600°C. Equal slurry feed rates
may therefore be accommodated and still attain the desired calcination
temperature.

Possible weaknesses to present schemes were revealed by the
scouting tests on the reflector burners described above. The zirconia
tubes failed under prolonged heating with the acetylene flame and the
noise produced by the flame during alcohol injection was exceedingly loud.
The zirconia tube failure began by a melting of the refractory insulation
around, and in intimate contact with, the exterior of the tube. The re-
fractory insulating material fused with the zirconia and the resulting
lowering of the zirconia melting point led to failure. This problem can
be met by use of carbon for structural members and loose zirconia as
insulation. Tube diameter will also be increased to lower the heat influx.
The noise problem cannot be effectively met without remote operation and
the elaborate safeguards necessary to such operation. Such a step is not
possible at the present state of development.

4.4.4 Schori Pistol

A Schori flame spray powder pistol was modified for use with ThO$_2$
powder by providing a large and direct connection for the powder (in a
gas stream) to enter the pistol, Fig. 4.1.2. In the first modification
of the pistol, the fuel gas mixture through the injection cone was intended
to aspirate the oxide dust. This proved to be unsuitable since the large
passages in the pistol permitted flash-back of the fuel gas inside the
pistol. Admitting the fuel gas mixture at the regular port and using
oxygen as the aspirating stream appears to be satisfactory.

Feeding to the pistol was done as a batch operation using an
Acoustica ultrasonic generator as a disperser with the transducer connected
to the feed cup, Fig. 4.1.2. Fracture of the feed cup at a weld after about
an hour of operation limited the amount of calcined material produced.
Photomicrographs of the product are not as yet available. A new feed cup
has been fabricated.

4.4.5 Atomic Hydrogen Torch

Two runs were made with an atomic hydrogen flame, one run having
ultrasonically dispersed feed while the other used a simple dusting device.

ThO$_2$ FEED INTO
SIDE OF PISTOL — INJECTION CONE

FUEL MIXTURE — OXYGEN
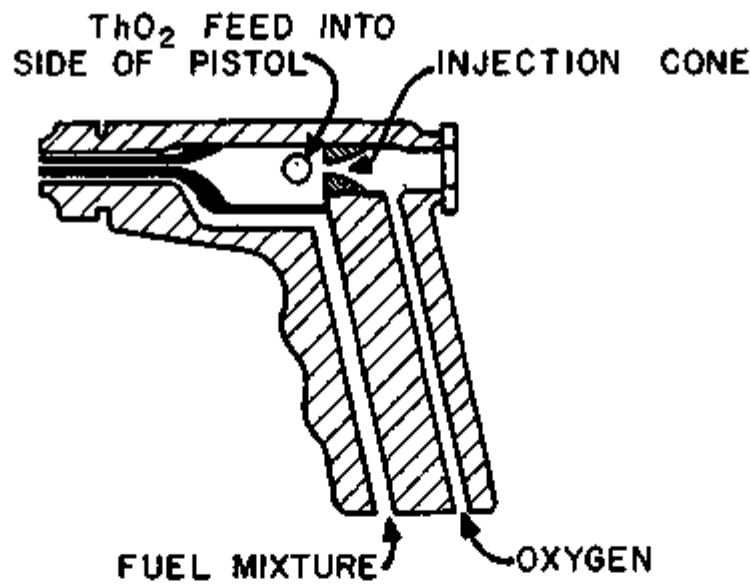
<u>Schori Pistol as Used with ThO$_2$</u>

GLASS   DOME ⟶ TO SCHORIC   PISTOL ⟶

AIR IN LEAKAGE

METAL FEED CUP ⟶

TRANSDUCER

COOLING WATER ⟶

POWER LEAD
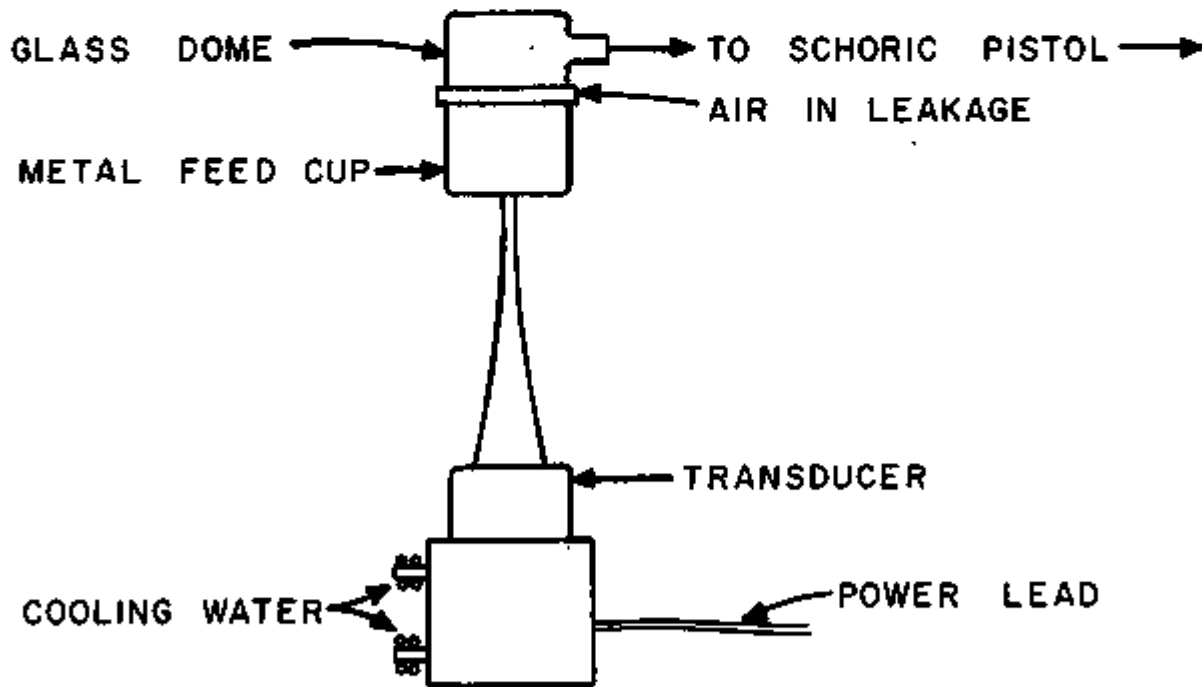
<u>Transducer and Feed Cup for use with Acoustica Generator</u>

948   928

Fig. 4.1.2 Equipment for Flame Calcination of Dry Feed ThO$_2$

The first of these runs was fed with the Acoustica ultrasonic
generator as described above except that it was modified by surrounding
the cup assembly with a gas tight chamber. This chamber was pressurized
with hydrogen and the exit gas containing dispersed ThO_2, was fed to a
1/8-in. dia tube located between the two electrode holders of the
atomic hydrogen welding torch (see Fig. 4.1.3). In this and the following
run the flame was passed through a ZrO_2 tube 3/4-in. in diameter and
6-in. long surrounded by magnesia firebrick, to reduce the radiant
heat loss in the vicinity of the arc and in effect provide a longer
holdup time for a particle at the high temperature. The second run
was made with the hydrogen carrying ThO_2 to the same point between the
electrode holders, but the powder was simply blown from a sealed jar
as indicated in Fig. 4.1.3. Approximately 5 grams of ThO_2 was fed through
the flame in this manner. Samples were taken of the dust in the water
spray cooled exit gas stream.

TUNGSTEN
ELECTRODES

TUBE FOR FEEDING
ThO_2 in H_2
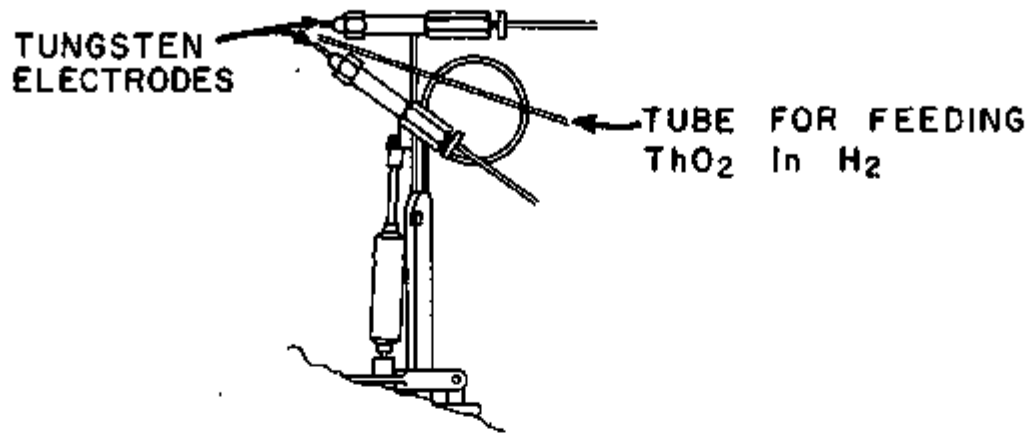
Location of Feed Tube on Atomic Hydrogen Torch

CONTROL VALVES

H_2 →

2oz BOTTLE

ThO_2 POWER
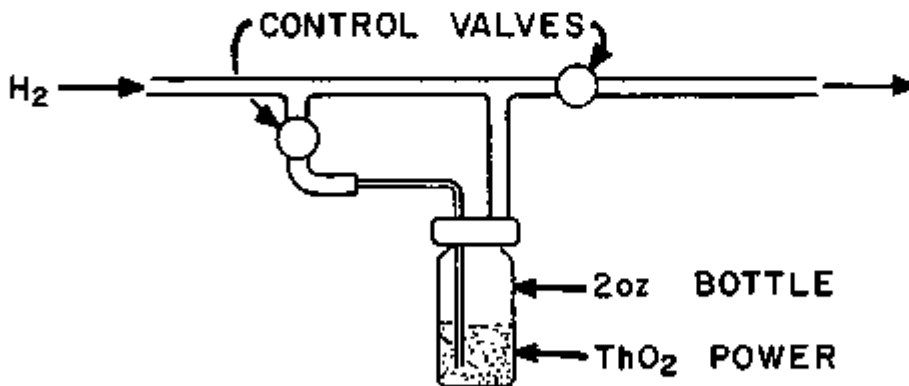
Simple ThO_2 Feeder

Fig. 4.1.3 Equipment for Atomic Hydrogen Experiment

5.0 ION EXCHANGE

J. B. Adams

Some aspects of the ion exchange kinetics of uranyl sulfate solutions with strong base anion exchange resins are being studied. The practical application of anion exchange to recovery of uranium from ore leach liquors is being successfully applied on a large scale. However, quantitative information on equilibrium, rate and mechanism of uranium transfer from solution to resin is scanty. Rational rather than empirical design of various types of ion exchange equipment requires a quantitative knowledge of rate and equilibrium phenomena as functions of solution and resin composition in terms of exchangeable species and requires an understanding of the relative importance of fluid film and solid diffusion mechanisms under various operating conditions. It is believed suitable rate data may be obtained from differential bed experiments with typical solution and resin samples. It is hoped these may be interpreted when accurate equilibrium data is obtained.

In large scale uranium recovery plants common operating procedure involves contacting a uranium-bearing (1/2-2 g U/liter) sulfate (13-35 g/liter) leach slurry, adjusted to pH 1.5 to 2, with a large size (10-20 mesh) strong base anion exchange resin in the nitrate-form (or chloride, depending on the stripping agent used). Most of the presently installed large-scale capacity is in RIP (resin-in-pulp) units. These are similar in concept to a series of fixed-bed units; however, RIP equipment can handle a slime slurry.

The resin is loaded with uranium in a 3-to-1 $SO_4^=$ to UO_2^{++} ratio apparently as the $UO_2(SO_4)_3^{-4}$ ion. The actual mechanism is not clear. In loading the chloride-form of a resin, for instance[2], the transfer appears to require an initial sulfate-chloride exchange. The rate of uranium absorption follows below the sulfate-chloride exchange until most of the chloride has been eliminated, then continues at lower rates by displacing sulfate ions. The equilibrium ratio of sulfate-to-uranium observed could be attained by at least four mechanisms: (1) direct exchange of $UO_2(SO_4)_3^{-4}$ for chloride, (2) exchange of $UO_2(SO_4)_3^{-4}$ for sulfate (and/or bisulfate), (3) absorption of $UO_2(SO_4)_2^{-2}$ on sites occupied by sulfate ions, and (4) absorption of un-ionized UO_2SO_4 on sites occupied by sulfate ions. The observed rates seem to exclude (1), and (2) is doubtful since estimates of $UO_2(SO_4)_3^{-4}$ concentration in solution indicate it to be very small[1][2]; the ion is also relatively large and slow diffusing. Either (3) or (4) seem much more feasible.

[1] Ahrland, S. "On the Complex Chemistry of the Uranyl Ion." Acta Chem. Scand 5, 1151 (1951).

[2] Allen, K. A. "Uranium Extraction by Tri-n-Octylamine Sulfate." Private communication. Oak Ridge National Laboratory.

[3] Arden, T. V. and Rowley, Marion. "Anion Exchange in Uranyl Sulphate Solution. High Concentration Effects and Rate Studies." J. Chem. Soc. p. 1709 (1957).

Both $UO_2(SO_4)_2^{-2}$ and UO_2SO_4 are present in considerably higher concentration than $UO_2(SO_4)_3^{-4}$. Both mechanisms are in accord with the observed effect of the sulfate-chloride exchange on the initial rate of absorption of uranium on resin in the chloride form. In addition, diffusion of UO_2SO_4 is not influenced by ionic charges; i.e., so-called Donnan exclusion wherein the resin excludes ions from the interstitial solution within the resin but not undissociated substances. In fact non-ionized substances may be subject to preferential absorption. Absorption of very large ions, such as hydrated $UO_2(SO_4)_2^{-2}$ and $UO_2(SO_4)_3^{-4}$, tends to be very slow both because of low diffusion rates and possibly, with low porosity resins, due to a physical screening effect.

To simplify the study of the problem both from the experimental and mathematical point of view, it has been decided to study first the transfer of uranium from uranyl sulfate solutions to the sulfate form of strong base resins and consider the sulfate-chloride exchange and the chloride-uranium exchange as a corollary problem. Additional restrictions include a uranium concentration of less than 0.005 molar, a sulfate concentration in the range of 5 to 35 g/liter and a pH close to 2.0. The restriction on pH reduces interference of bisulfate ions to a minimum but requires the presence of large amounts of other cations for electroneutrality. In leach solutions from uranium ores, many impurities are present including some which form complex anions and are absorbed by the resin. This interference is avoided by using pure solutions and supplying sodium ions where cations are required thus avoiding complexing of miscellaneous ions. Above pH 2, complex basic uranyl sulfate ions would start being formed, further complicating the situation. Also above pH 2 the equilibrium ratio of $SO_4^{=}$ to UO_2^{++} on the resin is modified as it is also in solutions above 0.005 M in uranyl ion(3).

An estimate of the concentration of various species: Na^+, H^+, UO_2^{++}, UO_2SO_4, $UO_2(SO_4)_2^{=}$, $UO_2(SO_4)_3^{-4}$, $SO_4^{=}$ and HSO_4^{-} in solutions equilibrated with resin is needed to interpret measured equilibrium resin compositions. Further, data on complexing of $SO_4^{=}$ as HSO_4^{-} in H_2SO_4 solutions is needed. The required data for the estimation of concentrations on complexing constants in solution has been obtained from data in the literature[1],[2], [4],[5]. Independently determined complexing constants for uranium and bisulfate complexes are assumed to be unique functions of the ionic strength of the mixture. Molarities rather than molalities are used for concentration measurements. This results in only a negligible error in very dilute solutions of sulfate salts at room temperature as long as the concentration of sulfuric acid is maintained low (pH $\approx$ 2).

(1) Ibid.

(2) Ibid.

(3) Ibid.

(4) Baes, C. F., Jr. "The Estimation of Bisulfate Ion Dissociation in Sulfuric Acid-Sodium Sulfate Solutions." J. A. Chem. Soc. 79, 5611 (1957).

(5) Sherrill, M. S. and Noyes, A. A. "The Inter-ionic Attraction Theory of Ionized Solutes. VI. The Ionization and Ionization Constants of Moderately Ionized Acids." J. A. Chem. Soc. 48, p. 1861 (1926).

The following set of equations can be written from material balance relationships:

(1) $C_S = (S) + (HS) + (US) + 2 (US_2) + 3 (US_3)$

(2) $C_U = (U) + (US) + (US_2) + (US_3)$

(3) $(US) = K_{US} (U) (S)$

(4) $(US_2) = K_{US_2} (U)(S)^2$

(5) $(US_3) = K_{US_3} (U) (S)^3$

(6) $(HS) = K_{HS} (H) (S)$

(7) $I = 1/2 \left[(H) + (Na) + 4 (U) + 4 (US_2) + 16 (US_3) + 4 (S) + (HS) \right]$

(8) $(Na) + (H) + 2 (U) = 2 (S) + (HS) + 2 (US_2) + 4 (US_3)$

The solution of the system of equations involves extensive trial and error calculations. For even the small range of variables involved, tentatively $0 < C_S < 0.3$, $0 < C_U < 0.005$, $C_S > C_U$, $1.5 \leq pH \leq 2.0$, considerable time is required. Use of a computer for the calculation is contemplated.

Nomenclature

C_S = gross molarity of sulfate

C_U = gross molarity of uranyl

(U) = molarity of UO_2^{++} ion

(US) = molarity of UO_2SO_4 molecule

(US_2) = molarity of $UO_2(SO_4)_2^{-2}$ ion

(US_3) = molarity of $UO_2(SO_4)_3^{-4}$

(Na) = molarity of Na^+ ion

(H) = molarity of H^+ ion

(HS) = molarity of HSO_4^- ion

(S) = molarity of SO_4^{-2} ion

I = ionic strength = $1/2$ $(m_i Z_i^2)$

m_i = molarity of ith ionic species

Z_i = valence of ith ionic species

K_i = complexing constant for formation of ith species

6.0   POWER REACTOR FUEL REPROCESSING

C. D. Watson

6.1   Darex - F. G. Kitts, B. C. Finney, F. L. Rogers, J. Beams,
         G. E. Woodall

The Darex head-end treatment consists in dissolving the fuel in dilute aqua regia and stripping off the chloride before the resultant nitric acid solution is solvent extracted.

6.1.1   Dissolution and Stripping

The Darex experimental equipment was thoroughly checked in preliminary runs after completion of the modifications described last month. Although the dissolver did not flood as before, its operation was still characterized by a cyclic discharge. To remedy this condition it was decided to adjust the recycle aqua regia from the reflux condenser to 5 N HNO_3 - 2 N HCl in a separate vessel rather than in the dissolver. A run, No. 50, of about 46 hr duration, was made operating in this manner. Although aqua regia of a single composition was added at a constant rate and a constant heat input maintained to the dissolver, the dissolver did not deliver product at a uniform rate. This resulted in the chloride strip column alternately running near flooding for a short period of time and then "dry", giving a highly variable V/L and causing poor Cl^- stripping. The material balance for run No. 50, Fig. 6.1, presents experimental data only and contains very few discrepancies of any note; it was based either on composite collections of streams or on an average of 20 samples taken at intervals throughout the run. Thus the average material balance appears favorable without revealing the cyclic upset of the system which caused the poor Cl^- removal, to only 1500 ppm. The losses were similar to those reported previously; all the Cl^- necessary for make-up is due to losses and amounted to 0.276 moles/mole SS dissolved. The HNO_3 loss, by overall material balance, was 0.67 moles/mole SS dissolved which agrees reasonably with the value of one reported from earlier runs.

Several tests have been run to determine the cause of the unstable dissolver operation. Batch dissolutions revealed no significant difference between adjusted condenser product from run No. 50 and freshly mixed 5-2 aqua regia. Different degrees of preheat of the aqua regia feed and heat input to the dissolver itself showed no promising trend. When dissolution is occurring, some foaming is always evident; the present dissolver has overflow delivery and therefore discharges by the height of the variable foam cap and not by the true liquid level. The dissolver is being modified to insure that discharge is from the body of the liquid; an external jack-leg will control level in the dissolver.

OFFGAS
0.276 moles Cl⁻
0.67 moles N

Basis:
1 mole (55.4 g) of
304 SS dissolved in
11.7 minutes

DOWNDRAFT
CONDENSER

CONDENSER PRODUCT
0.852 1, Den = 1.168
1.91 moles HCl (2.24 $\underline{N}$)
3.75 moles HNO₃ (4.4 $\underline{N}$)
$\underline{38.3}$ moles H₂O
43.96 moles total

OVERHEAD M-U
0.23 1, Den= 1.21
1.52 moles HNO₃
0.276 moles HCl
9.6 moles H₂O

ADJUSTED AQUA REGIA
1.08 1, Den= 1.177
5.4 moles HNO₃(5 $\underline{N}$)
2.16 moles HCl (2 $\underline{N}$)
47.5 moles H₂O

$$(V/L)_{top} \quad \frac{43.96}{54.31} = 0.81$$

$$(V/L)_{av} = 0.83$$

$$(V/L)_{bot} = \frac{50.8}{59.5} = 0.85$$

STRIPPER

DISSOLVER

DISSOLVER PRODUCT
1.04 1, Den = 1.25
1 mole SS(NO₃)$_{2.85}$
(53.3 g/1 SS)
2.05 moles HCl (1.97 $\underline{N}$)
1.56 moles HNO₃ (1.50 $\underline{N}$)
$\underline{49.7}$ moles H₂O
54.31 moles total

FUEL ELEMENTS
55.4 g 304 SS

STRIPPED PRODUCT
1.43 1, Den = 1.43
1500 pp, Cl
1 mole SS(HNO₃)$_{2.83}$ (38.7 g/1 SS)
17 moles HNO₃ (11.9 $\underline{N}$)
$\underline{41.5}$ moles H₂O
59.5 moles total

STRIPPING VAPOR
1.26 1, Den = 1.4
19.0 moles HNO₃(15 $\underline{N}$)
$\underline{31.8}$ moles H₂O
50.8 moles total
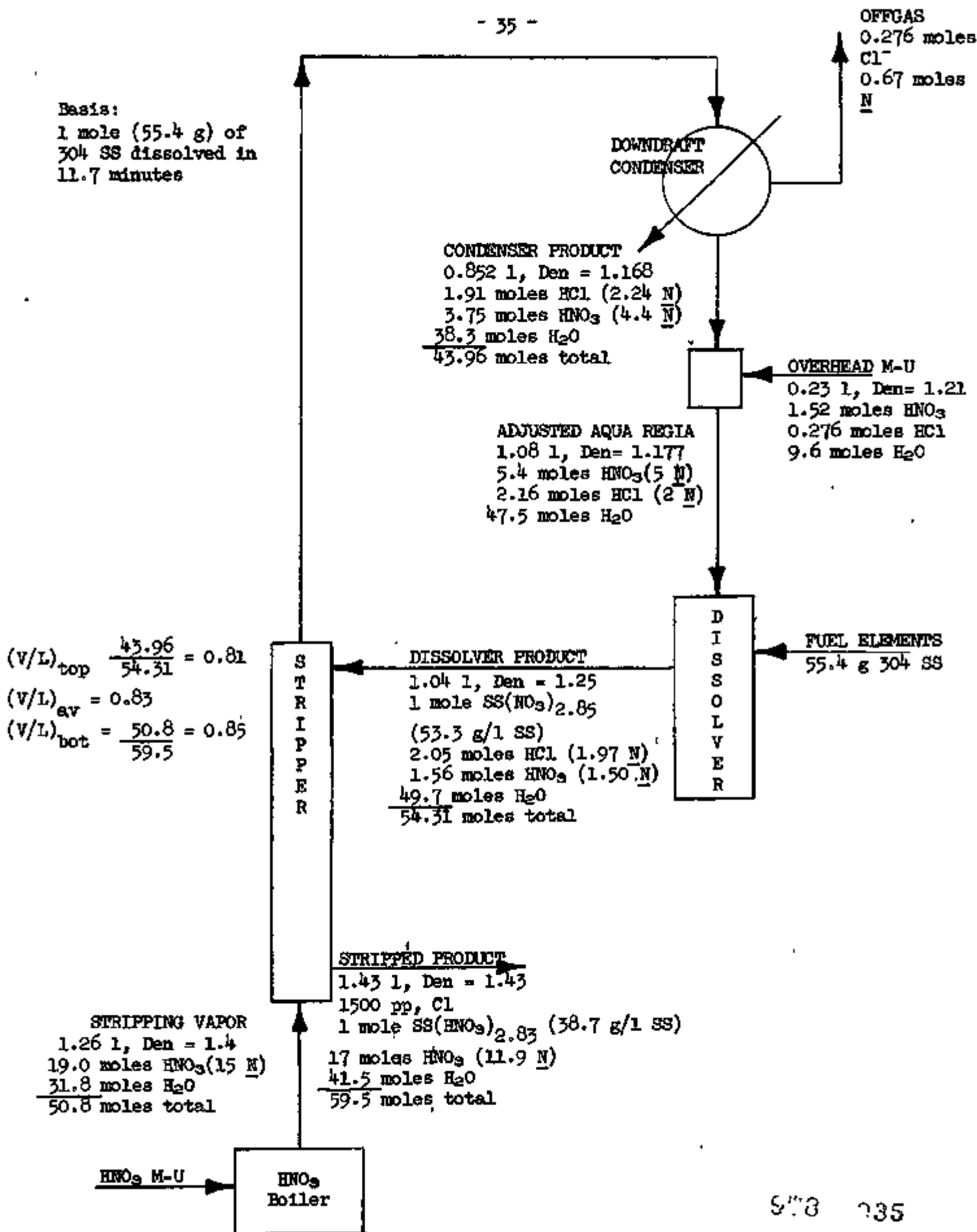
HNO₃ M-U → HNO₃ Boiler

Fig. 6.1 Material Balance Run 50

6.1.2   Feed Adjustment Studies

Three continuous feed adjustment runs of 7, 6, and 7 hr duration were made in laboratory scale glassware equipment. The purpose of these runs was to obtain data toward establishing operating conditions for a feed adjustment tank which could ultimately be tied into the present Darex loop. The equipment consisted of a one liter-3 opening flask with a side arm overflow to control the liquid level, down draft condenser, and a rotameter to control the feed flow. A heating mantle was used as the heat source and 1/2-in. porcelain Berl saddles were added to the flask to smooth out the boiling and to adjust the liquid volume to 500 ml (approximately 4.5 hr hold-up).

The first two runs were exploratory to determine the operability of the equipment and establish which of the operating conditions should be controlling. The results of these runs indicated that temperature should be the independent variable. A material balance for the third run in which feed containing 29 g SS/liter, 900 ppm Cl$^-$ and 12.6 M in nitric acid was concentrated by a factor of 3.8 is presented in Fig. 6.2. Calculations were based on analytical results and the assumption that densities and volumes were additive. The accuracy of the material balance (in/out) for HNO$_3$, H$_2$O, and SS(NO$_3$)$_{2.85}$ was 102%, 109%, and 99.6% and an overall balance $\frac{\text{(total volume in)}}{\text{(total volume out)}}$ for the entire run was 101%. In another run in which stripped product was concentrated to 280 g SS/liter, solids appeared in the concentrated product after sitting for 16 hr at room temperature.

Even though the laboratory investigation was not too extensive, these rough data indicate that continuous feed adjustment is feasible. There is some concentration of the Cl$^-$ in the product and further investigation will be required to determine to what extent this does take place. Of course the Cl$^-$ concentration is directly dependent on the efficiency of the stripping column and can be decreased somewhat by the addition of the diluent in the final adjustment prior to solvent extraction.

6.2 Zircex Engineering Studies -J.J. Perona, G. B. Dinsmore

In a gas-phase run of 35 hr duration, 97.4% of a 4.39 kg section of an STR sub-assembly (unirradiated) was reacted by feeding in hydrogen chloride at a constant rate of about 6 g-moles/hr. The temperature of the reaction was not measured. The uranium loss to the sublimate was 0.095%, corroborating the previous run (see January issue of this report) in which a loss of less than 0.1% to the sublimate was also achieved. Of the uranium reacted, 0.33% was collected by a glass wool filter in the line to the ZrCl$_4$ condenser. The utilization of HCl gas was ~88%.

The unreacted hydrogen chloride leaving the hydrochlorinator, along with the hydrogen produced by the reaction, were passed through a caustic scrubber packed with Berl saddles, where the HCl was absorbed. The rate of hydrogen evolution was then measured by a wet test meter. The rate of

Basis: 1 liter of Feed

FEED

1 liter Den = 1.42
12.59 moles HNO$_3$
0.518 moles SS(HNO$_3$)
2.85 (28.7 g/1 SS)
30.1 moles H$_2$O
898 ppm Cl$^-$

CONDENSER
DOWNDRAFT

OVERHEAD

0.835 liter,
Den = 1.38
11.56 moles HNO$_3$
(13.85 $\underline{N}$)
23.6 moles H$_2$O

FEED ADJUSTMENT TANK

125.5 $\pm$ 1.5^{o}C

DILUENT

0.104 liter
5.78 moles H$_2$O

PRODUCT
0.154 liter, Den = 1.60
0.518 moles SS(HNO$_3$)
2.85 (187 g/1 SS)
0.775 moles HNO$_3$(5.04 $\underline{N}$)
4.0 moles H$_2$O
1850 ppm Cl$^-$

FEED FOR SOLVENT EXTRACTION
0.258 liter, Den = 1.36
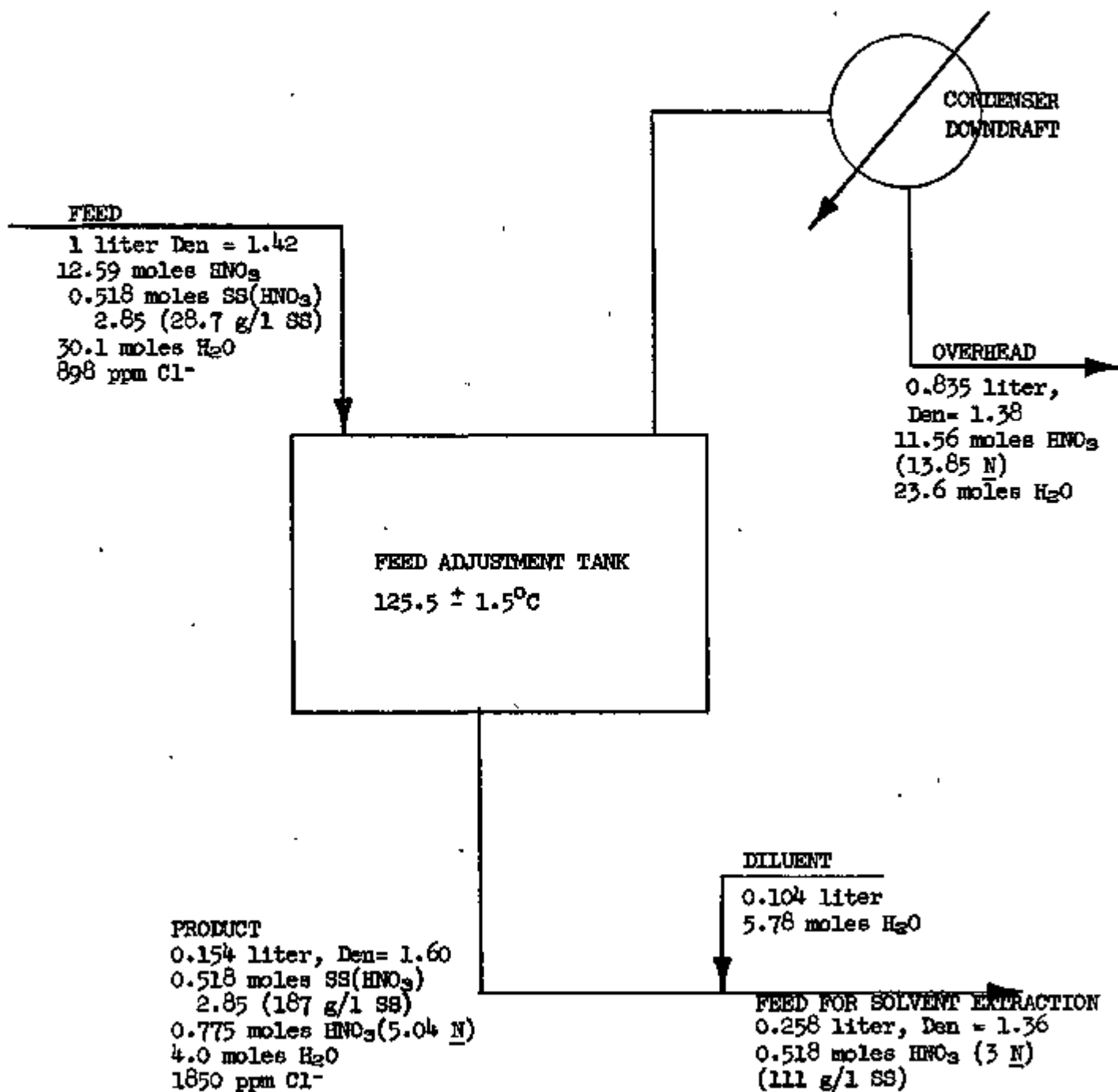0.518 moles HNO$_3$ (3 $\underline{N}$)
(111 g/1 SS)

Fig. 6.2   Run No. 3 Material Balance

hydrogen evolution was very nearly constant, at 2.68 cu ft /hr
(see Fig. 6.3). Thus it is very apparent that the reaction rate was
independent of surface area, which varied from 700 sq in. at the start
of the run to about 22 sq in. at the end. This phenomenon is easily
explained by the great affinity of the zirconium for the hydrogen
chloride, which causes preferential attack of the sub-assembly near the
HCl inlet and sharp concentration gradients in the reaction vessel.
Photographs of partially reacted STR sub-assemblies, showing that only
a small fraction of the area is attacked even at the start of a run,
may be found in ORNL-2416.

6.3 Mechanical Processing

Shearing Studies - G. A. West, J. C. Rose, J. S. Taylor

Studies have been carried out of the shearing of unirradiated Yankee
Atomic fuel elements (stainless steel-clad UO_2). The purpose of the tests
was to determine the oxide losses and air contamination resulting from
the element shearing.

Losses from the shearing of 584 g of UO_2-SS clad fuels, 0.40-in. o.d.
x 16-in. long, were 2.27% UO_2. The powdered UO_2 fell into the crevices
of the machine, and more than 90% of the loss was probably recoverable.
From a total of 55 cuts it was observed that the UO_2 was usually retained
(except for the loss previously stated) when the distance between cuts
exceeded the length of pellet (3/8-in.). When the sheared length was
less than the pellet length, the core was almost completely dislodged.

The sheared pieces were collected in a box from which was withdrawn
1-cfm of air. The air was passed through a paper filter to collect air-
borne particulates and measure contamination. After the shearing test
the filter was counted. The activity on the filter was: 6530 counts/min.α
and 5650 counts/min.β,γ. The indicated air contamination was 1.8×10^{-8} μ
curies/cc, which is 360 times masking tolerance.

6.4 Materials Evaluation - G. A. West

Radiation Damage - A protective coating, Amercoat No. 1679 polyester
base, is not recommended for use after cumulative dosages of 10^9r. Two
panels were irradiated in water to 10^9r by a Cobalt-60 source. The activity
of the source was 2.2×10^6r/hr and the temperature ranged from 102° to 108°F.
The entire coating (on 2-1/2 sq in. x 16 gauge steel panel) was blistered
when removed from the source and random cracking appeared around these
blisters after about 1-week out of the source. The use contemplated for
this material was as a lining for water filled canals with high β,γ back-
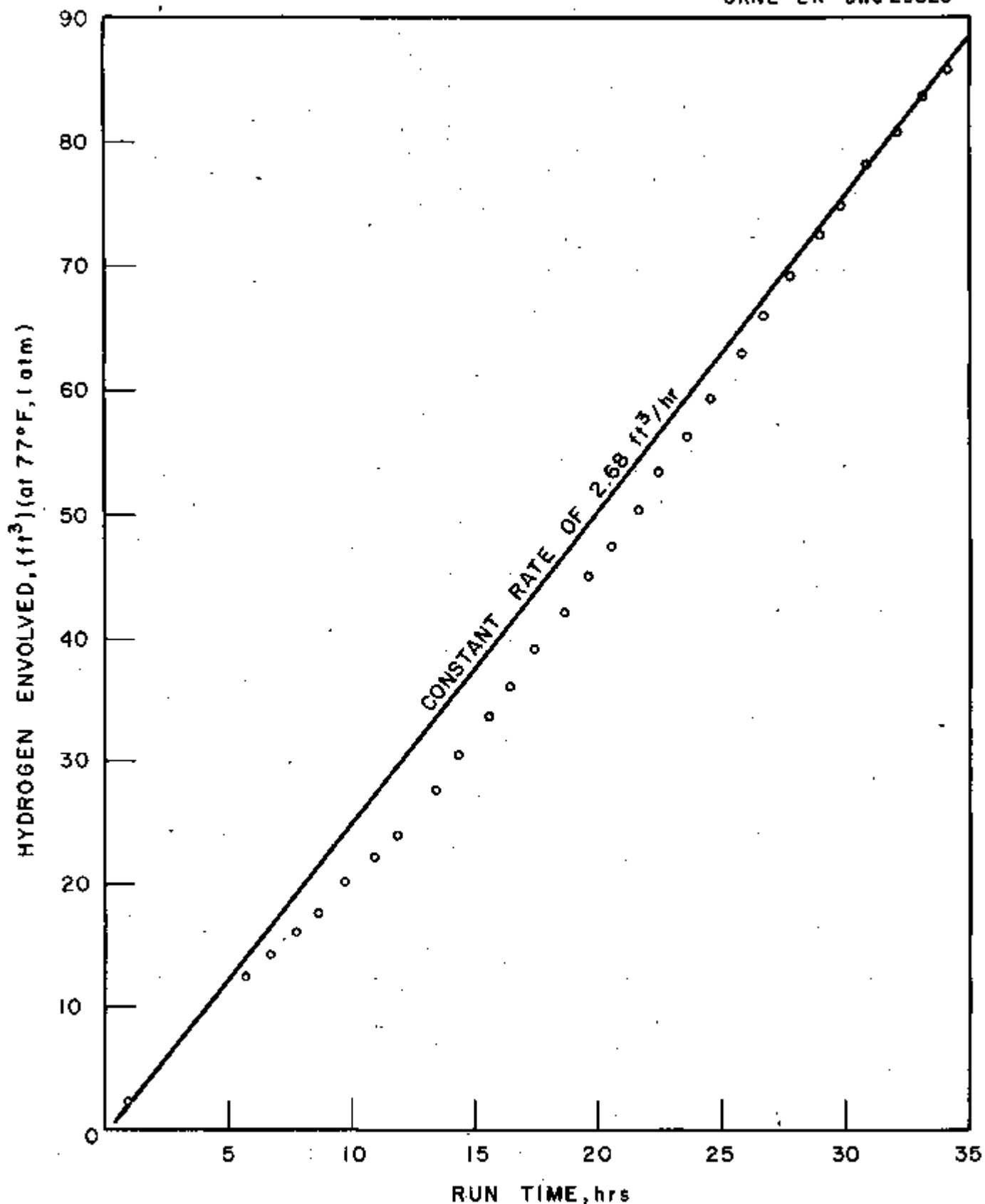grounds.

Fig. 6.3 Hydrogen Evolution from the Hydrochlorination of a Portion of an STR Subassembly

7.0 VOLATILITY

M. E. Whatley

<u>HF-Fused Salt Dissolution of Zirconium</u> - R. W. Horton, L. E. McNeese, M. E. Whatley, G. Jones, Jr., C. C. Nance, D. H. Newman, J. D. Phillips

Three dissolution tests at 650°C in the modified dissolver vessel resulted in dissolution rates of 4.4×10^{-4}, and 5.4×10^{-4} lb/(hr)(sq in.) (equivalent to 0.52, 0.53, and 0.63 mg/sq(cm min.). These rates were achieved with HF velocities 2 to 5 times greater than previously used. A plot of the data indicates that the specific dissolution rate increases as the logarithm of the HF velocity (Fig. 7.1).

The dissolver vessel was modified by the insertion of an annular filler ring which reduced the cross sectional area of the dissolver to approximately half of the original. The reduced area section extends to 11-in. above the bottom of the vessel. The upper 20-in. were left at the original area, allowing a large volume for splash of fused salt and for reduction in velocity of the off-gas stream. The depth of salt charge used and the length of element used were also reduced. A comparison of original and modified dissolver dimensions is shown in Table 7-1. Dimensions of the dummy fuel elements used in the two series of tests are shown in Table 7-2.

The reduced cross sectional area allows greater gas velocity past the fuel element for a given mass flow than was previously obtained. The three tests in this series were run at mass rates of 2 lb/hr, 3 lb/hr, and 6 lb/hr of HF. The record of these tests is shown as Table 7-3, 7-4, and 7-5. Zirconium dissolution rates and HF utilization rates were both computed from the hydrogen evolution rate.

Table 7-1   Dissolver Constants

Dissolver Used	Cross Sectional Area (without element) (sq in.)	Volume of Salt Charge (cu in.)	Depth of Salt Charge (in.)	HF Velocity for 1 lb/hr at 650°C, fps	
				13 plate element	11 plate element
Original	25.8	273	12.5	0.111	0.106
Modified	13.45	154	11.0	0.255	0.232

Table 7-2 Element Constants

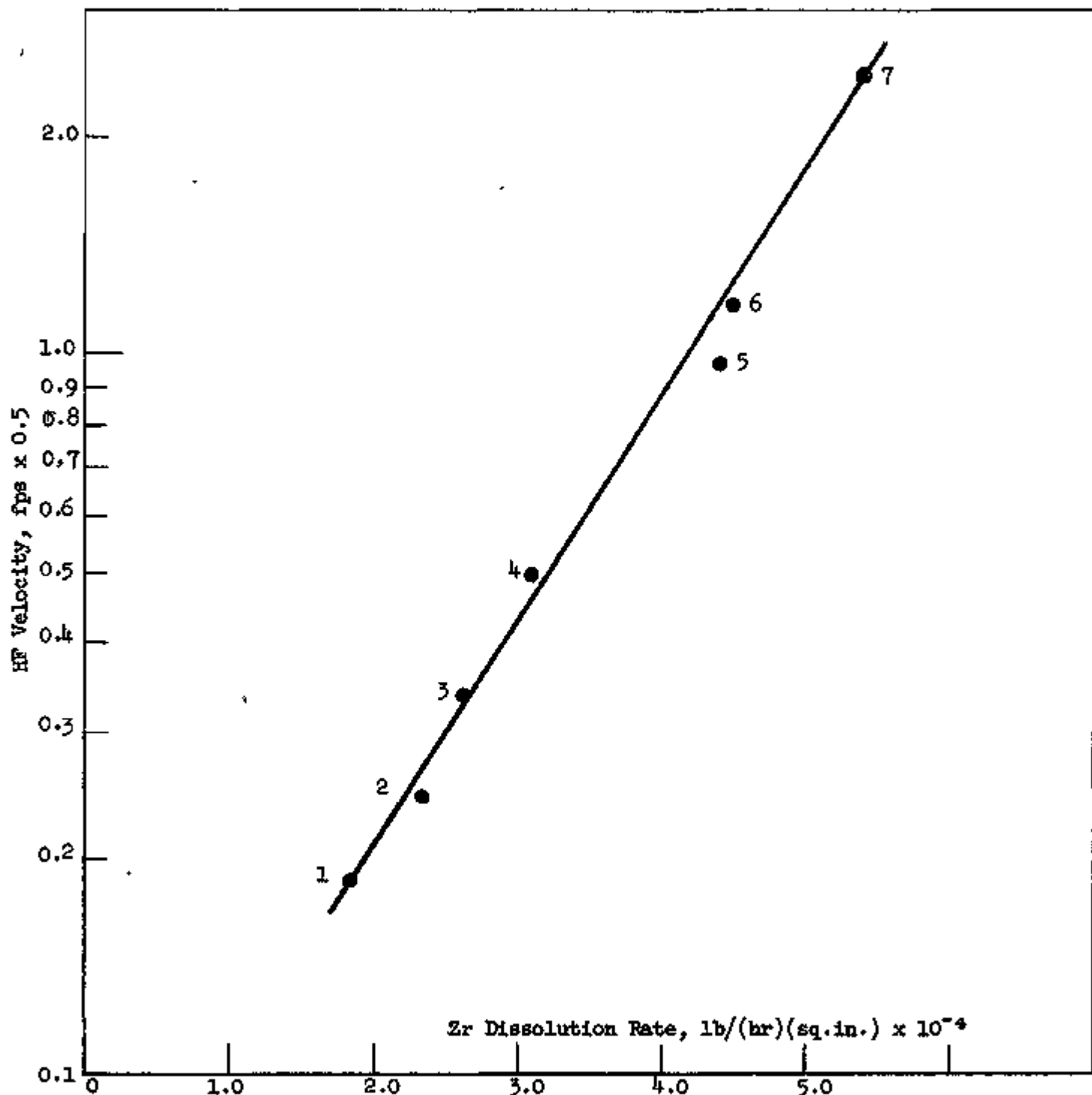| Fuel Element	Outside Dimension (in.)	No. of Plates (incl. ends)	Length (in.)	Cross Sect. Area (sq in.)	Total Surface Area (sq in.)	Weight (lb)
No. 1	2.5 x 2.625	13	11.0	3.95	854.0	10.8
No. 2	2.5 x 2.1	11	5.4	3.0	367.0	4.4

Fig. 7.1 Zr Dissolution Rate vs HF Velocity (at 650°C)
(Points 1 through 4- Original Dissolver Element No. 1)
(Points 5 through 7- Modified Dissolver Element No. 2)

Table 7-3 HF-Fused Salt Dissolution of Zircalloy 3

Run No. ___D-4___ Date ___2-5-58___

Temperature ___650°C___ Salt Composition ___45 mole % ZrF$_4$ 55 mole NaF___

N$_2$ Purge Rate ___0.1 cu ft/hr___ Element Area ___367 sq in.___

Time	HF Feed Cylinder Weight (lb)	HF Rate (lb/hr)	HF Velocity (ft/sec)	Off-gas Rate Standard (cu ft/hr)	Hydrogen in Off-gas (%)	Hydrogen Evolution Rate (lb/hr)	Zirconium Dissolution Rate (lb/hr/sq in.)	HF Utilization (%)
1750	44.06	--	--	--	--	--	--	--
1800	43.63	3.42	0.7934	1.84	--	0.01028	6.3×10^{-4}	6.3
1830	42.81	1.64	0.3805	1.36	--	0.00758	4.7×10^{-4}	9.2
1900	41.69	2.24	0.5197	1.14	53.6	0.00634	3.9×10^{-4}	5.6
1930	40.75	1.88	0.4362	1.08	--	0.00600	3.7×10^{-4}	6.3
2000	39.63	2.24	0.5197	1.14	--	0.00634	3.9×10^{-4}	5.6
2030	38.63	2.00	0.4640	1.25	89.90	0.00695	4.3×10^{-4}	6.9
2100	37.59	2.08	0.4826	--	--	--	--	--
2130	36.56	2.06	0.4779	1.46	85.30	0.00814	5.0×10^{-4}	7.8
2200	35.53	2.06	0.4779	1.25	--	0.00695	4.3×10^{-4}	6.7
2230	34.59	1.88	0.4362	1.18	85.60	0.00656	4.1×10^{-4}	7.0
2250	33.90	2.07	0.4802	1.08	--	0.00600	3.7×10^{-4}	5.8
Average	2.08 lb/hr	2.14	0.4965	1.28	--	0.00712	4.4×10^{-4}	6.80
Totals	10.16 lb	--	--	6.40	--	0.03560	--	6.95

Table 7-4   HF-Fused Salt Dissolution of Zircalloy 3

Run No. D-5

Temperature 650°C

N₂ Purge Rate 0.1 cu ft/hr

Date 2-6-58

Salt Composition 45 mol % ZrF₄
                  55 mol % NaF

Element Area 367 sq in.

Time	HF Feed Cylinder Weight (lb)	HF Rate (lb/hr)	HF Velocity (ft/sec)	Off-gas Rate Standard (cu ft/hr)	Hydrogen in Off-gas (%)	Hydrogen Evolution Rate (lb/hr)	Zirconium Dissolution Rate (lb/hr/sq in.)	HF Utilization (%)
1400	34.19	--	--	--	--	--	--	--
1430	32.69	3.00	0.6960	1.62	--	0.00871	5.4×10^{-4}	5.8
1500	31.13	3.12	0.7238	1.78	--	0.00963	6.0×10^{-4}	6.1
1530	27.88	6.50	1.5080	1.68	--	0.00909	5.6×10^{-4}	2.8
1600	24.94	5.88	1.364	1.51	--	0.00816	5.0×10^{-4}	2.8
1630	22.22	5.44	1.262	1.57	90.5	0.00850	5.2×10^{-4}	3.1
1700	19.03	6.38	1.480	1.60	--	0.00866	5.3×10^{-4}	2.7
1730	16.03	6.00	1.392	1.57	94.9	0.00850	5.2×10^{-4}	2.8
1805	13.00	5.20	1.206	0.86	--	0.00465	2.9×10^{-4}	17.5
Average	5.19 lb/hr	5.19	1.204	1.52	--	0.00817	5.0×10^{-4}	3.1
Totals	21.19 lb	--	--	6.20	--	0.0333	--	3.1

Table 7-5 HF-Fused Salt Dissolution of Zircalloy 3

Run No. D-6

Date 2-6-58

Temperature 650°C

Salt Composition 45 mol % ZrF$_4$ 55 mol % NaF

N$_2$ Purge Rate 0.1 cu ft/hr

Element Area 367 sq in

Time	HF Feed Cylinder Weight (lb)	HF Rate (lb/hr)	HF Velocity (ft/sec)	Off-gas Rate, Standard (cu ft/hr)	Hydrogen in Off-gas (%)	Hydrogen Evolution Rate (lb/hr)	Zirconium Dissolution Rate (lb/hr/sq in.)	HF Utilization (%)
1915	81.06	--	--	--	--	--	--	--
1930	80.41	2.60	0.6032	1.12	--	0.00600	3.7×10^{-4}	4.6
2000	78.88	3.06	0.7099	1.55	83.1	0.00833	5.1×10^{-4}	5.4
2030	78.06	1.64	0.3805	1.26	--	0.00678	4.2×10^{-4}	8.2
2100	76.50	3.12	0.7238	1.18	--	0.00633	3.9×10^{-4}	4.0
2130	74.91	3.18	0.7378	1.20	61.0	0.00645	4.0×10^{-4}	4.0
2200	73.25	3.32	0.7702	1.39	--	0.00747	4.6×10^{-4}	4.5
2230	71.72	3.06	0.7099	1.37	--	0.00736	4.55×10^{-4}	4.8
2250	71.00	2.16	0.5011	1.77	88.5	0.00952	5.9×10^{-4}	8.8
Average	2.81 lb/hr	2.77	0.6426	1.355	--	0.00728	4.5×10^{-4}	5.1
Totals	10.06 lb	--	--	4.85	--	0.02608	--	5.1

The data from the current series and also tests at 650°C from the previous series (reported in Unit Operations Monthly Progress Report January 1958, CF-58-1-137) were compiled to show the dissolution rate per unit area (called specific dissolution rate) and the HF velocity in the dissolver. These results are shown in Table 7-6 and are shown graphically in Fig. 7.1. In calculating these values, the original cross sectional and total surface areas of the element were used throughout the series, although the actual values were changing. Similarly, the hydrogen fluoride velocities were calculated on the basis of the mass of acid fed to the system, ignoring volume changes due to reaction.

Table 7-6   Zirconium Dissolution Rates and HF Velocity
(from all tests at 650°C)

| Run No. | Zirconium Dissolution Rate | | HF Velocity |
	lb/(hr)(sq in.)	mg/min.(sq cm)	(fps)
D-2, P-3	1.8×10^{-4}	0.21	0.093
D-2, P-4	2.3	0.27	0.118
D-2, P-5	2.6	0.30	0.168
D-2, P-8	3.1	0.36	0.250
D-4	4.4	0.51	0.496
D-5	5.4	0.63	1.203
D-6	4.5	0.525	0.642

8.0 WASTE DISPOSAL

C. W. Hancher and W. J. Boegly, Jr.

8.1 Adiabatic Self-Sintering Experiment

The radioactive waste disposal program is a joint function of Chemical Technology Division and Health Physics Division. The adiabatic self-sintering experiment is under the supervision of W. J. Boegly of the ORNL Health Physics Division. The adiabatic self-sintering method of fixing fission products in a ceramic sinter may be a method of ultimate disposal of high level radioactive waste.

The self-sintering disposal method for wastes resulting from the reprocessing of spent reactor fuel utilizes the energy liberated during the decay of the waste fission products to provide the heat necessary to sinter the waste-clay-flux mixture and to fix the fission products. One of the most difficult problems encountered in the laboratory and field experiments has been the simulation of fission product heating using immersion heaters. This was due to the low thermal conductivity of the sinter and the resulting large number and intricate arrangment of heaters required to provide a uniform heat source. It was concluded that the best method of evaluating self-sintering would be to conduct a small experiment using an actual high-level waste solution as the heat source.

The proposed experiment will use a dissolved 90-day cooled MTR fuel assembly irradiated in a monitored thermal neutron flux of $2 \text{-} 3 \times 10^{-14}$ neutrons/sq cm/sec for a period of 42 days (~30% burn-up). No attempt will be made to recover the non-fissioned U^{235}. The 30 gal solution resulting from dissolution of the MTR assembly in the ORNL Thorex facility, will contain approximately 100,000 curies and will be transferred in a carrier to the experimental facility and discharged to an underground mixer where the solid ingredients will be added and mixed. When mixing is complete the slurry will be transferred to a furnace where the material will be sintered. A heat barrier, completely surrounding the furnace, will be used to balance the heat losses from the furnace and reduce the total fission product heat required in the waste solution. The proposed experimental facility will be completely contained in a shielded, underground concrete liner and is vented to an off-gas system for decontamination of the gases, vapors, and aerosols released during the sintering process. Provisions will be made to allow remote disassembly of the facility after thermal and radioactive cooling and removal of the 24-in. dia by 8-in. high sinter for leach testing.

The final disposition of the sinter has not yet been determined. Removal of the uranium from the cooled sinter would be very difficult and is not planned.

The present schedule for the experiment is based on charging the mixer and the furnace on September 1, 1958, with 90-day cooled waste which means the fuel element must be removed from the reactor on June 15.

8.2 Design of the Adiabatic Self-Sintering Experiment

The design of the adiabatic self-sintering experiment was conceived by the Health Physics Waste Disposal Section. The experiment has two main physical sections: the mixer-furnace assembly (Fig. 8.1) and the off-gas processing area (Fig. 8.2). Assistance was given to the group from W. R. Winsbro, (CTD-Design Section) in the design and detailing of the off-gas system.

The design is 90% complete. The details of liquid and gas sampling stations are still to be completed. Completion is estimated February 15, 1958.

8.3 Field Construction of the Adiabatic Self-Sintering Experiment

The adiabatic self-sintering experimental site is south of the present burial ground. The construction was 50% complete on February 1, 1958. The system is to be housed in three sections: (1) control building, (2) six ft dia x 10 ft deep concrete pit for mixer and furnace assembly, to be topped by a 5 ft thick concrete shield block, and (3) two, 7 ft dia by 10 ft deep concrete pits for the off-gas system.

The control building is 100% complete. The power control wiring in the control building has been 40% complete. The instruments for power and heat control and recording are 30% complete. The component parts of mixer and furnace are 100% complete, installation will start in March (Figs. 8.3, 8.4). The four off-gas vessels are fabricated and installed. The off-gas piping has been 20% completed (Fig. 8.5).

A series of pre-tests will be run after the construction has been completed, using artificial heat to simulate fission product heat.

8.4 High-Level Cell Experiment

A group of three high-level cell runs have been proposed to characterize the amount and level of radioactivity to expect in the off-gas. The experiment will consist of using 12 cc of Purex waste solution, which has been converted to $Al_2(NO_3)_3$ (Hope) type waste. The Hope waste will be mixed with clay solids to form a gel which will be heated in a tube furnace. The furnace off-gas will be treated with the proposed off-gas chemical system.
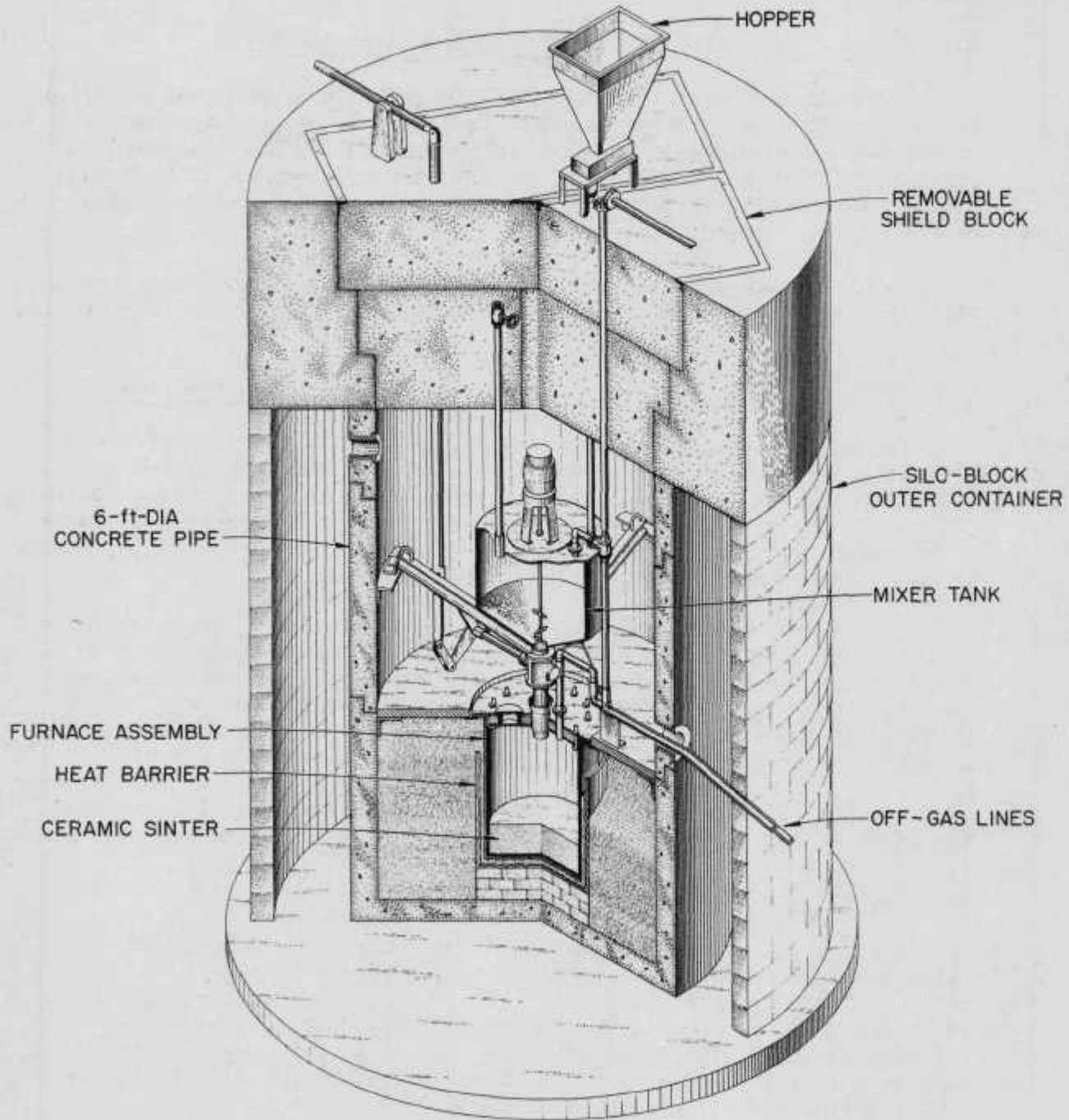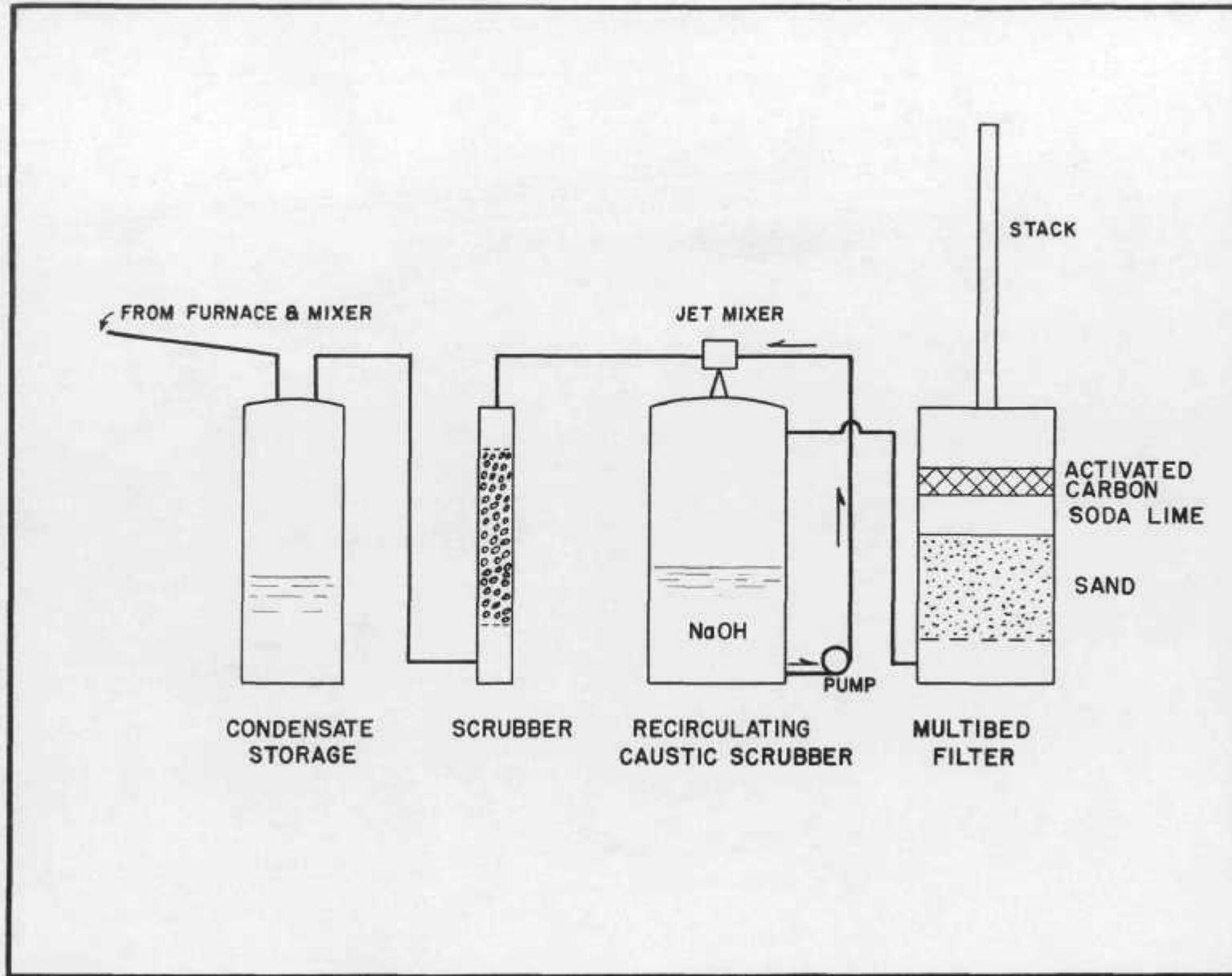
HOPPER

REMOVABLE
SHIELD BLOCK

SILO-BLOCK
OUTER CONTAINER

6-ft-DIA
CONCRETE PIPE

MIXER TANK

FURNACE ASSEMBLY

HEAT BARRIER

CERAMIC SINTER

OFF-GAS LINES

Fig. 8.1   Mixer Furnace Assembly

Fig. 8.2 Schematic of Off-Gas System
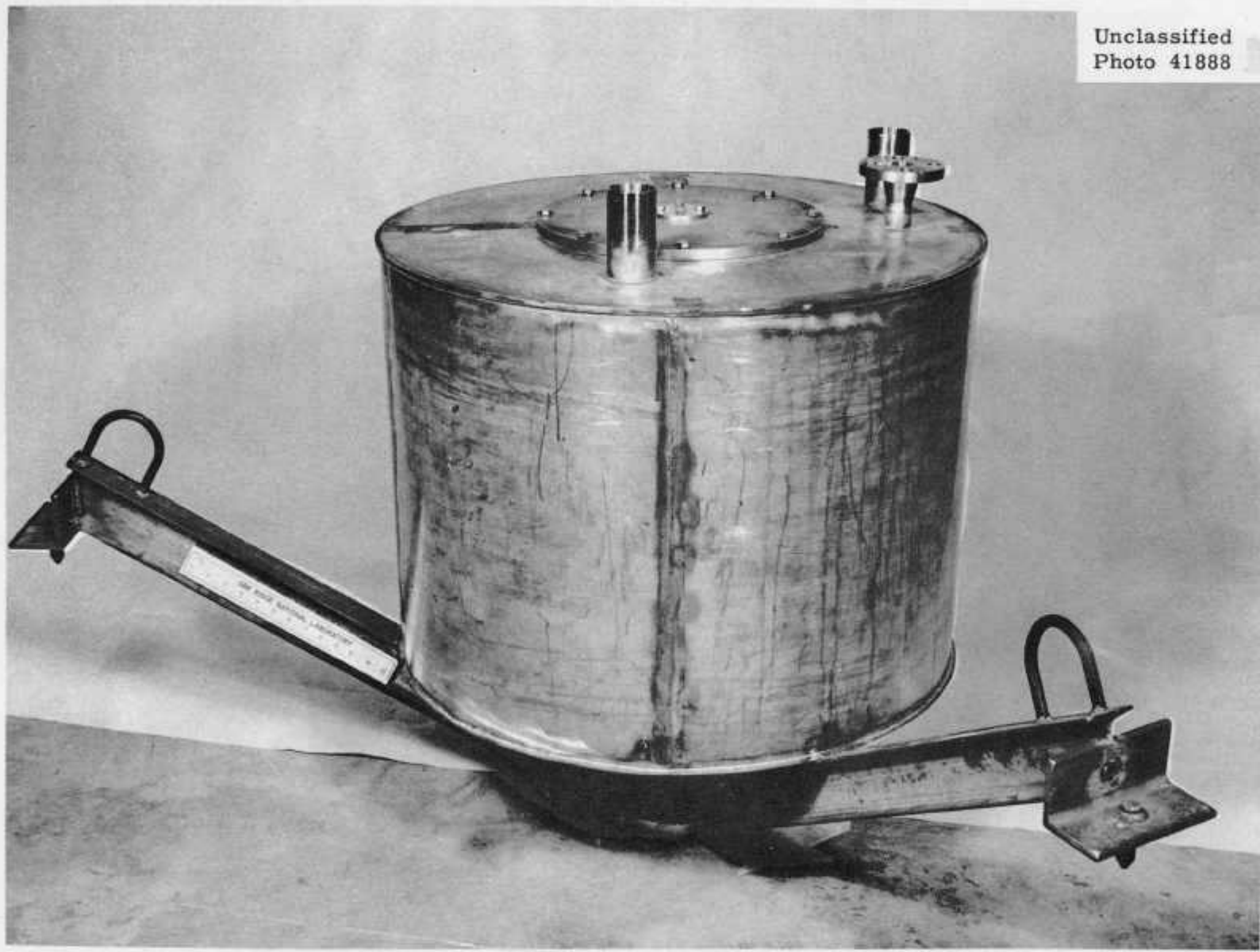
Fig. 8.3   Mixer for Self-Sintering Experiment
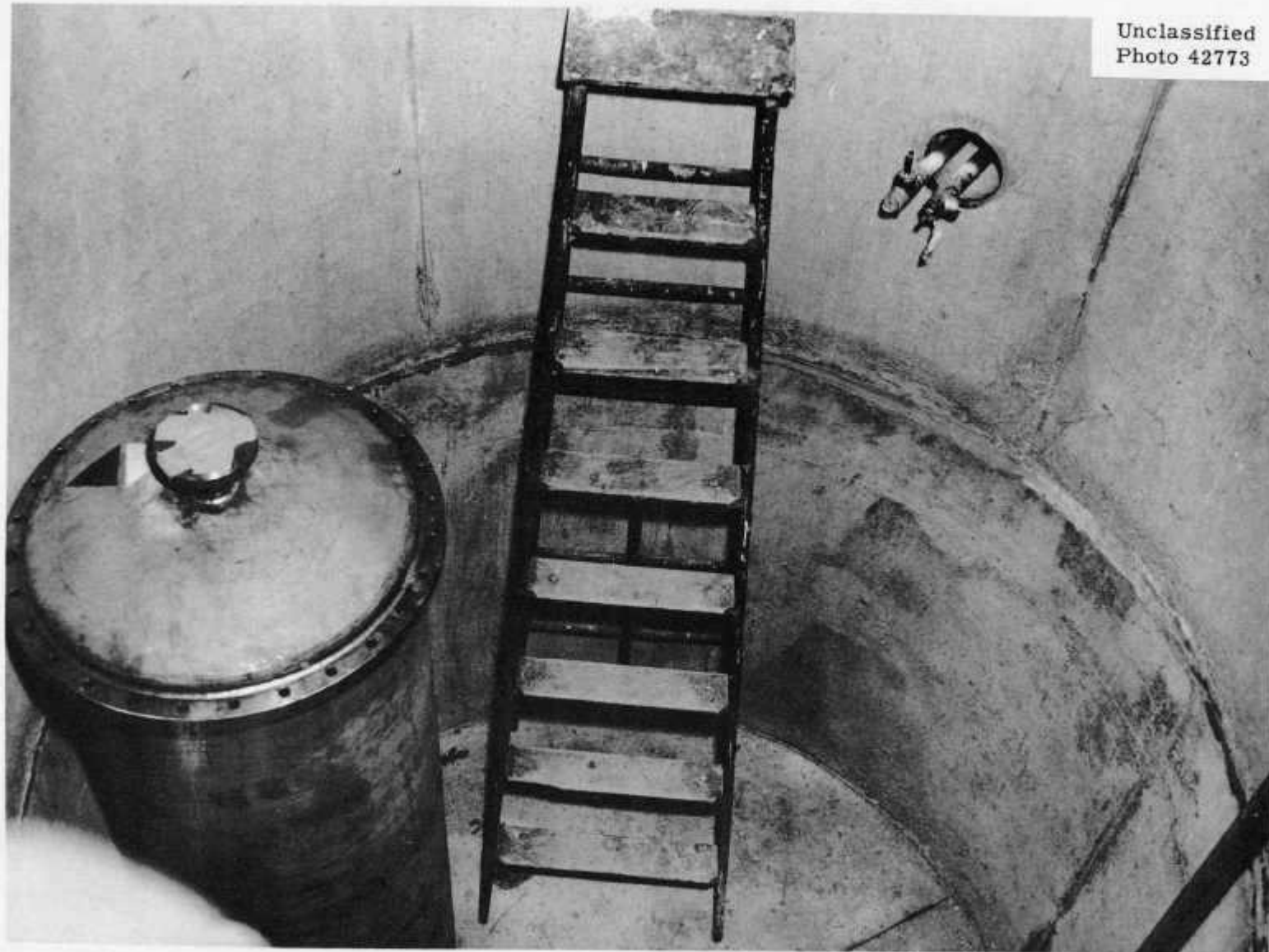
OAK RIDGE NATIONAL LABORATORY

Fig 8.5   Multibed Filter for Off-Gas System in its
Housing for Self-Sintering Experiment.

8.4.1 <u>Reduction of Liquid Wastes to Solids</u> - J. J. Perona, R. J. McNamee

A literature survey is being carried out as the first step in
a program to develop a safe and economical method of the reduction of liquid
wastes to solids preparatory to waste storage. Major problems among the
processes studied are: (1) production of off-gases, (2) loss of volatile
ruthenium with the off-gases, (3) fixation of fission products, and
(4) dissipation of decay heat in product solids.

It is probable that the waste should be allowed to decay as long
as possible prior to treatment. A decay time of 10 yr would give a decon-
tamination factor of 10^3 for Ru 106 and 10^{26} for Ru 103, greatly reducing
the problem of activity in the off-gases. A decay time in excess of 3 yr
does much to relieve the problem of decay heat in product solids.

Considerable development effort has been made on electrolytic
cells for nitrate destruction and ruthenium plating*. The use of one of
these cells prior to a sintering or fusing step would greatly reduce the
off-gas problem by virtually eliminating the production of oxides of nitrogen
at high temperatures where they tend to carry the volatile ruthenium. In
addition a ruthenium decontamination factor of about 10 might be achieved
by electro plating.

A decision as to the necessity of fixation of the fission
products will be the major factor in orienting the study program. If fixation
is necessary, alumina and silica would be used to prepare ceramics or
glasses, with essentially no volume reduction in passing from the liquid
to the solid state. If fixation is not necessary, various calcination
schemes would be investigated with a volume reduction factor of approximately 5.

---

* Higgins, I. R. "Proposal for Installation of Equipment for Treatment
of Oak Ridge National Laboratory High Level Waste." October 24, 1957.
CF-57-10-129. Unclassified.

DISTRIBUTION

1. R. E. Blanco
2. J. C. Bresee
3. K. B. Brown (Y-12)
4. F. R. Bruce
5. L. P. Bupp (HW)
6. F. L. Culler
7. W. K. Eister
8. D. E. Ferguson
9. H. E. Goeller
10. A. T. Gresky
11. P. A. Haas
12. H. F. Johnson
13. S. H. Jury
14. S. Lawroski (ANL)
15. R. B. Lindauer
16. J. T. Long
17. B. Manowitz (BNL)
18. J. W. Morris (SRP)
19. F. S. Patton, Jr. (Y-12)
20. M. J. Skinner
21. S. H. Smiley (ORGDP)
22. C. E. Stevenson (ICPP)
23. C. D. Watson
24. M. E. Whatley
25. C. E. Winters
26-28. E. J. Murphy
29. Laboratory Records (RC)
30-33. Laboratory Records (4)
34-35. Central Research Library
36. Document Reference Section