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CHEMICAL TECHNOLOGY DIVISION

UNIT OPERATIONS SECTION

MONTHLY PROGRESS REPORT

JUNE 1959

NOTICE

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ORNL CF 59-6-63

UNIT OPERATIONS SECTION MONTHLY PROGRESS REPORT

June 1959

CHEMICAL TECHNOLOGY DIVISION

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

Date Issued

SEP 4 1959

ABSTRACT

The addition of a surface active agent to an aqueous-organic interface produced a resistance to mass transfer equivalent to slightly more than 1 cm of water. Five semicontinuous Druhm runs were made with 1/2-in. thick MgO liners and terminated due to either failures of the UF_6 nozzle or a top gasket leak. In preliminary scale-up tests of the flame calcination equipment, a maximum feed rate equivalent to 720 g oxides/hr was achieved using a 3-in. i.d. magnesia reflector with an outside wall temperature of 1500°C. In a test with a light water feed, 99% Cu, 25% Ni, and 0% Mn were removed from a UO_2SO_4 solution by electrolysis with a mercury cathode in 7800 ampere hours. The effect of varying the total sulfate concentration on the kinetics of the absorption of uranyl sulfate on Dowex 21K at a uranium concentration of 0.005779 $\underline{M}$ and a sulfuric acid concentration of 0.020 $\underline{M}$ was studied in a series of runs using a stirred bath containing enriched uranium. Chloride was removed to 64 ppm in Yankee Atomic and to 70 ppm in APPR solvent extraction feeds using a reference Darex flowsheet with air sparging during a two hour reflux period in the 10-in. prototype titanium feed adjustment tank. Soluble uranium contained in a filter cake deposited onto a 20 micron porous metallic star shaped filter from approximately twenty-one liters of Darex solvent extraction feed solution was recovered to 99.9% by a single 5 liter water wash of the cake. An experimental Redox solvent extraction program was completed. Shear blade evaluation tests have begun at Birdsboro and Clearing under subcontract and will be completed by July 1. Tests were made on the separation of water associated with sheared material through porous bottom baskets as would be required in wet shearing concepts. Consolidated Edison prototype elements assembled with ductile Coast Metals 50 brazing metal could not be disassembled with the impact wedge previously successfully used to disassemble elements made up with brittle Nicrobraze 50. A reactor and condenser system designed to sublime ZrF_4 from the hydrofluorinator to a separate receiver at temperatures above 902°C was operated at condensation rates between 150 and 500 g per hour of ZrF_4. The thermal conductivities of granular Darex, Purex, and TBP-25 calcined solids were in the range of 0.043 to 0.097 Btu/hr sq ft (°F/ft) at room temperature.

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SUMMARY

1.0 CHEMICAL ENGINEERING RESEARCH

The diffusivity of uranyl nitrate was measured by a diffusion experiment using a 5-cm long capillary tube containing 0.2 $\underline{M}$ $UO_2(NO_3)_2$ immersed in a bath of 30% TBP in Amsco. When 10 ppm "Tide" was added to the bath, the apparent intergal diffusivity of the uranyl ion decreased from 0.67 to 0.44 x 10^{-6} sq cm/sec. The surface active agent at the aqueous-organic interface produced a resistance to mass transfer equivalent to slightly more than 1 cm of water.

2.0 DRUHM

Five semicontinuous runs made with 1/2-in. thick MgO liners were terminated due to either failures of the UF_6 nozzle or a top gasket leak. Although massive uranium metal was not obtained, there was evidence of appreciable quantities of finely divided uranium metal and the MgO liners were not badly damaged.

3.0 HR FUEL AND BLANKET PREPARATION AND PROCESSING

3.1 Flame Calcining

In order to evaluate the stability and erosion characteristics of thoria-urania-alumina slurries in a pump loop, a 50 to 100-lb sample is required. In preliminary scale-up tests, a maximum feed rate equivalent to 720 g oxides/hr was achieved using a 3-in. i.d. magnesia reflector with an outside wall temperature of $1500^\circ C$.

3.2 Electrolytic Nickel Removal

The electrolytic test cell was modified so that the recirculating uranyl sulfate solution containing copper, nickel, and maganese ions entered under the surface of the mercury cathode to provide agitation. The combined liquid and gas phases from the cell were discharged through a single line. In a test with a light water feed, 99% Cu, 25% Ni, and 0% Mn were removed from solution in 7800 ampere hours. Current reversal removed 90% of the copper and 99% of the nickel from the mercury.

3.3 HRT - Multiple Hydroclone Test

Room temperature calibration and efficiency tests were made for a multiple hydroclone which was installed across the HRT heat exchanger with the underflow as feed to the original chemical processing system. This unit with thirteen 0.60-in. dia hydroclones in parallel should have a 50% efficiency for two-micron particles and should result in corrosion product collection rates of 3-6 times those of the original processing system.

4.0 ION EXCHANGE

The effect of varying the total sulfate concentration on the kinetics of the absorption of uranyl sulfate on Dowex 21 K at a uranium concentration of 0.005779 $\underline{M}$ and a sulfuric acid concentration of 0.020 $\underline{M}$ was studied in a series of runs using a stirred bath containing enriched uranium. The apparent diffusion coefficient calculated from a simple diffusion model remained within the range 1.25 to 1.3 x 10^{-7} sq cm/sec over a range of total sulfate concentrations from 0.0258 to 0.201 $\underline{M}$, with the exception of one run (D = 1.0 x 10^{-7} sq cm/sec) which may have been in error. The data indicate that the simple diffusion model probably is inadequate at small values of contact time. A test varying stirrer speed showed that the liquid film resistance to diffusion could be safely disregarded in this series of experiments.

5.0 POWER REACTOR FUEL REPROCESSING

5.1 Darex

Chloride was removed to 64 ppm in Yankee Atomic and to 70 ppm in APPR solvent extraction feeds using a reference flowsheet with air sparging during a two hour reflux period in the 10-in. prototype titanium feed adjustment tank. Two identical runs in the 4-in. glass equipment showed that the presence of Ti in the vapor phase had no adverse effect on chloride removal. In glassware, chloride was removed to less than 23 ppm in a solution of Al dissolved to 45 g/liter in 5 $\underline{M}$ HNO$_3$ - 2 $\underline{M}$ HCl. Loadings of 1 $\underline{M}$ stainless steel were achieved when dissolving Yankee Atomic prototype fuel with either 6 or 5 $\underline{M}$ HNO$_3$ - 2 $\underline{M}$ HCl. The initial dissolution rate of 2S Al in 5 $\underline{M}$ HNO$_3$ - 2 $\underline{M}$ HCl was about 40% that of Hg^{++} catalyzed (0.005 $\underline{M}$) nitric acid. Overall heat transfer coefficients in the titanium feed adjustment tank of 170-320 Btu/hr-sq ft-°F were measured for Δ T = 22 - 64°F with both APPR and Yankee Atomic dissolver product solutions.

5.2 Feed Clarification

Soluble uranium contained in a filter cake deposited onto a 20 micron porous metallic star shaped filter from approximately twenty-one liters of Darex solvent extraction feed solution was recovered to 99.9% by a single 5 liter water wash of the cake. Centrifugation test data with a 5-in. dia solid bowl centrifuge indicated the particle size distribution of the siliceous solids contained in Darex (APPR) solutions to be in the 1-15 micron range after passage through an intense shear field. Comparison tests between filtration and centrifugation showed that filtration would maintain agglomerated and easily settled silica particles produced by feed adjustment of APPR Darex dissolver product.

5.3 Solvent Extraction Studies

An experimental Redox solvent extraction program was completed. The purpose of the program was to assist the Hanford Atomic Products Operation in adapting the Redox process to the reprocessing of spent stainless steel power reactor fuels.

Although much of the analytical data from the final efficiency runs is not yet available, the following tentative conclusions can be made regarding packed extraction column capacity:

(1) Acidifying the feed or solvent increased capacity.

(2) Increasing silicon content of the feed decreased capacity.

(3) The addition of Mistron (an insoluble calcium-magnesium silicate powder) to the feed increased capacity for feeds containing silicon.

(4) Molybdenum in the feed column also increased for a feed containing silicon, perhaps due to the formation of a silicomolybdic acid complex.

5.4 Mechanical Processing

Shearing. Shear blade evaluation tests have begun at Birdsboro and Clearing under subcontract and will be completed by July 1. The fabrication was completed of eight pairs of blades and two die sets for the experimental program at ORNL.

The bulk density of sheared lengths of a Mark I prototype fuel assembly varied from 120 lb/cu ft for 0.5-in. lengths of 80 lb/cu ft for 3-in. lengths after a 2-ft fall into a leaching vessel. The per cent separation of UO_2 from sheared stainless tubes could be correlated by: $P = 13/L^{1.2}$, where $P =$ per cent separation and $L =$ length of sheared tube in inches. The particle size distribution of fines produced from shearing porcelain-filled stainless tubes varied with the length of sheared piece, from $95\% < 1230\mu$, $d_{50} = 230\mu$ to $95\% < 1600\mu$, $d_{50} = 270\mu$ for 0.5 and 2-in. lengths, respectively.

Leaching. Tests were made on the separation of water associated with sheared material through porous bottom baskets as would be required in wet shearing concepts. The flowrates of water under a 15-in. head through beds made up of pieces of stainless steel clad porcelain rods sheared at both 1/2-in. and 1-1/8-in. lengths supported on a 10 sq in. porous metal (Poromesh, nominal 150 micron pore size) decreased to less than 8 cc/min sq in. as the amount of material placed on the filter increased to 1/10 of a Mark I prototype.

In 13 M HNO_3, stainless tubing was leached free of UO_2 in 20 to 85 minutes for 0.5 to 2.75-in. sheared lengths while the acidity decreased to 11 M.

Fuel Disassembly. Consolidated Edison prototype elements assembled with ductile Coast Metals 50 brazing metal could not be disassembled with the impact wedge previously successfully used to disassemble elements made up with brittle Nicrobraze 50. However, since Coast Metals 50 contains 1.9% boron, it probably would not be used for power reactor fuel assembly.

The SRE decladding equipment was received from Southern Machine Co., Chattanooga, Tennessee and was installed for preliminary testing. Laboratory

tests show that steam at rates up to 0.4 lbs/hr and possibly higher would be a satisfactory reagent in reacting the NaK for disposal as waste. The reaction proceeded uneventful at a hydrogen evolution of ~1 liter/min for a 35 min period while reacting 98.4 ml of NaK, the total volume contained in a single SRE element.

6.0 VOLATILITY PROCESS

Dry Hydrofluorination

A reactor and condenser system designed to sublime ZrF_4 from the hydrofluorinator to a separate receiver at temperatures above 902^oC was operated at condensation rates between 150 and 500 g per hour of ZrF_4. The corresponding rates of non-condensible gas used as a sweep were 0.23 and 2.1 liters N_2/g ZrF_4. A Dynel filter in the off-gas line satisfactorily removed ZrF_4 fines from the N_2, and no pressure buildup occurred during 3 hours of operation.

7.0 WASTE PROCESSING

The thermal conductivities of granular Darex, Purex, and TBP-25 calcined solids were in the range of 0.043 to 0.097 Btu/hr sq ft (^oF/ft) at room temperature. The thermal conductivity of TBP-25 solids increased to 0.12 Btu/hr sq ft (^oF/ft) at 1600^oF. In preliminary experiments with a packed distillation tower to be used for off-gas treatment studies, the flooding point was estimated at 330 lb/hr/sq ft.

1.0 CHEMICAL ENGINEERING RESEARCH

M. E. Whatley

1.1 Diffusion Measurements - C. V. Chester

The measurement of the diffusivity of uranyl nitrate was continued, using the capillary apparatus described in the March monthly report (CF 59-3-61). The diffusivity was calculated from the equation:

$$D = \frac{F^2/4\pi}{T/L^2}$$

referred to in the May monthly report (CF 59-5-47).

In last month's report, diffusion into 0.1 M HNO_3 and 30% TBP in Amsco was compared and it was concluded that the interface between the aqueous solution in the capillary and the 30% TBP had negligible resistance to mass transfer. Since the long range objective of the present study is to measure this interface resistance, it was decided to modify the interface character- istics substantially in order to determine if the apparatus was sensitive to gross changes in the interface diffusion resistance.

The diffusion experiments with 30% TBP in Amsco were repeated with the addition of a surface active agent. The organic phase contained 10 ppm of the synthetic detergent "Tide." The results are presented in Figure 1.1, and the experimental data from which the results were calculated are in Table 1.1.

From Figure 1.1 it may be seen that a consistant lowering of the apparent diffusivity of the uranyl nitrate occurred when 10 ppm of Tide was added to the Amsco. The apparent diffusivity decreased from 0.67 x 10^{-6} to 0.44 x 10^{-6} sq cm/sec.

According to the previous equation, if the actual length of the capillary had been 6.2 cm instead of 5.0 cm, the same diffusivity would have been measured in each case. Thus the interface resistance was equivalent to slightly more than 1 cm of water.

The uranyl ion diffusivity equipment may be used conveniently for comparing the effect of various surface active reagents such as radiolysis products on interface resistance to mass transfer.
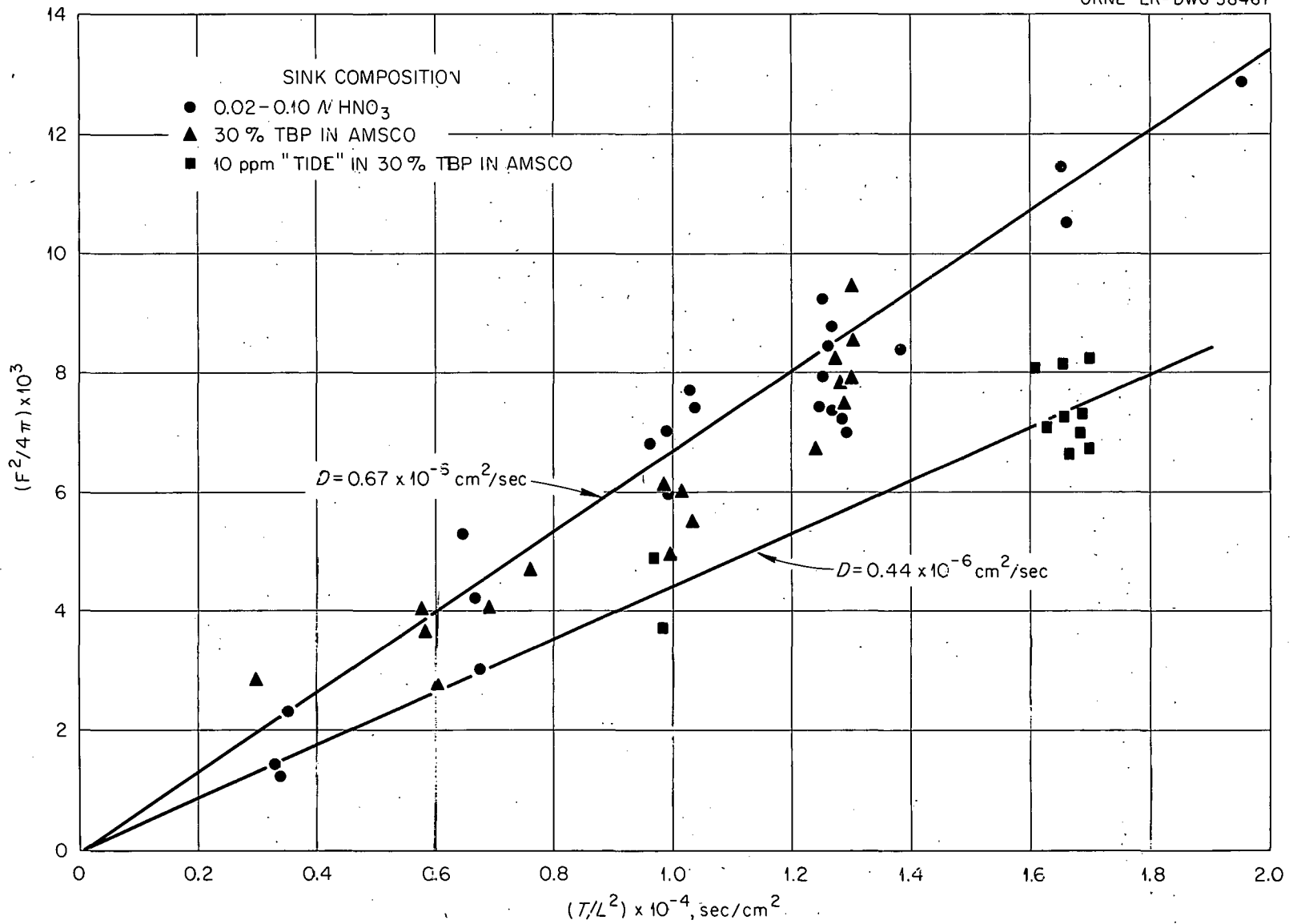
Fig. 1.1. Diffusion of Uranyl Nitrate in Aqueous Solution from Capillary Tubes into Infinite Sink.

Table 1.1. Diffusion of Uranyl Nitrate from Aqueous Solution

into an Infinite Sink of 30% TBP in Amsco Containing 10 ppm Tide

Gamma counts/min			Fraction Diffused	Elapsed Time	Capillary Length	Diffusivity
original	after diffusion	difference		hours	cm	cm^2/sec
1523	1191	332	.218	68.8	5.01	.384 x 10^{-6}
1234	926	308	.250	68.8	5.04	.510
1162	791	371	.319	115.5	5.08	.503
1418	1009	409	.289	117.7	5.04	.398
1650	1148	502	.304	117.8	5.05	.443
1638	1114	524	.320	117.9	5.06	.491
1210	848	362	.299	117.8	5.10	.435
1186	804	382	.322	117.9	4.99	.484
1502	1064	438	.292	117.9	4.99	.398
1204	847	357	.296	118.0	5.03	.413
1213	846	367	.303	117.9	5.01	.432

2.0 DRUHM

P. A. Haas

The direct reduction of uranium hexafluoride to uranium metal by use of sodium, $UF_6 + 6Na = U + 6NaF$, is being investigated. A continuous reaction study is being made with primary emphasis being placed on equipment design and materials of construction.

2.1 Experimental Work - C. D. Scott

Five semi-continuous runs were made in which 1/2-in. MgO liners were used in the 6-in. reactor. The reactor set-up (see Figure 2.1) included separate reactant nozzles with the UF_6 nozzle being made of copper and cooled internally with N_2. The MgO liners which were used were adapted uranium metal pouring crucibles which had been fabricated by pressing and firing to approximately 1800°C. The position of the UF_6 nozzle was changed in some of the runs in an attempt to reduce the possibility of nozzle failure due to rupture in the cooling jacket.

The runs were made with initial induction heating of the reactor to a temperature above the melting point of uranium metal (~1130°C) after which the two reactants were metered into the reactor. The maximum reactor temperature was maintained at 1200°C by adjusting the amount of induction heating used during the run. In all runs there was an initial temperature gradient in the reaction zone up the outside of the reactor of about 300°C which decreased as the run progressed. The temperature measured just above the UF_6 nozzle in the reaction zone was initially less than the melting point of uranium; however, it increased as the run progressed to a maximum at run termination (see Table 2.1).

Table 2.1. Experimental Results of Five Semi-continuous Runs

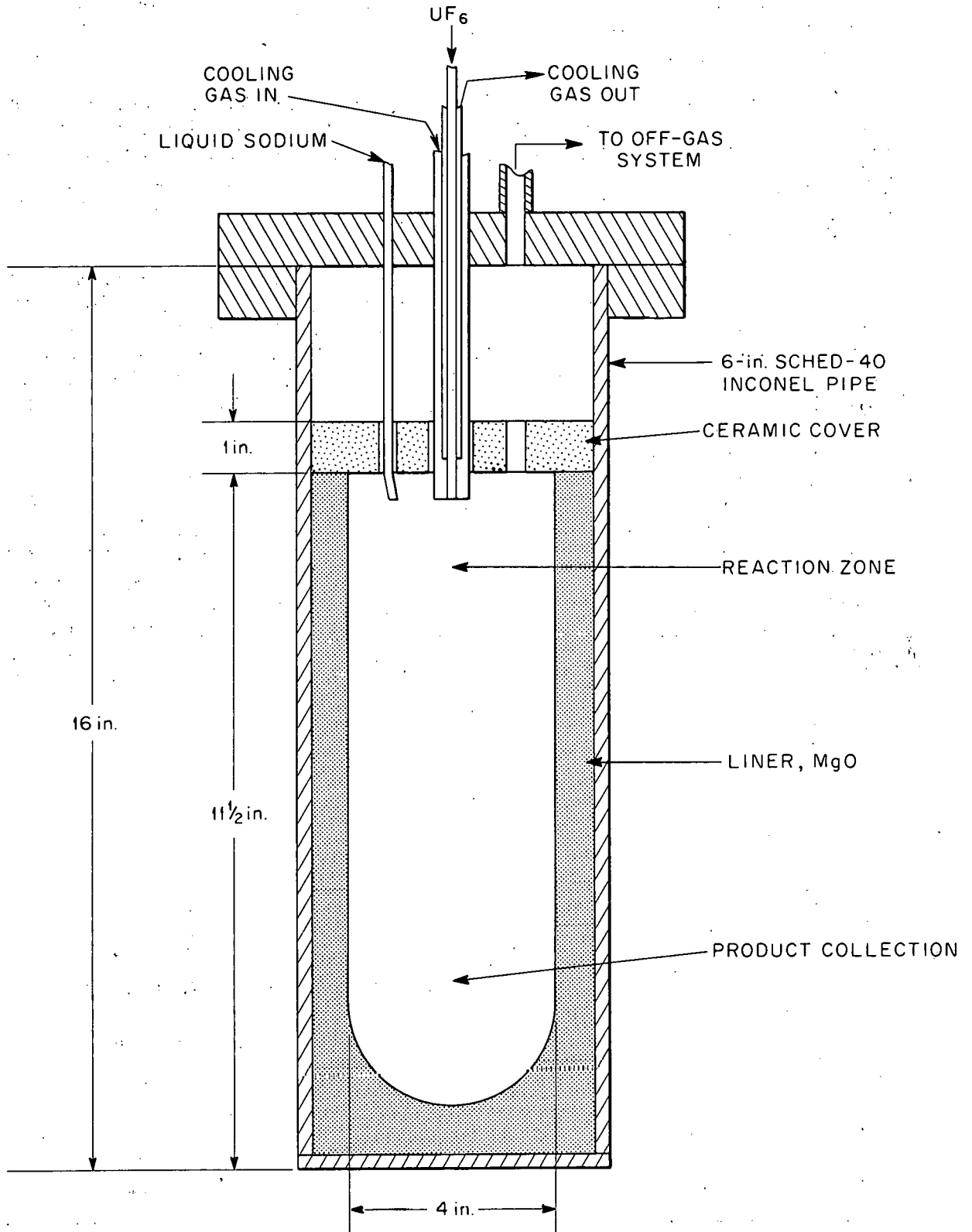| Run No.	Length of run, min	Maximum Reactor Temp. Recorded,°C	Amount of U introduced as UF_6, 2	Reason For Run Termination and Remarks
D-25	10	900	325	Failure of UF_6 nozzle
D-26	30	1200+	1506	Leak developed at top gasket
D-27	7.5	1200+	322	Failure of UF_6 nozzle
D-29	18	1200+	1950	Failure of UF_6 nozzle
D-30	20	1200+	2340	Failure of UF_6 nozzle

Fig. 2.1. Reactor Set-up Used in Runs D-25 Through D-30.

The five runs were terminated because of either mechanical difficulties or failures of the UF_6 nozzle before conditions in the reaction zone approached steady state operation or before the temperature throughout the reaction zone exceeded the melting point of uranium.

In the four cases of nozzle failure (runs D-25, D-27, D-29, and D-30), large quantities of the N_2 cooling gas were released into the reactor when the nozzle cooling jacket was penetrated. This gas caused oxidation and nitriding of the uranium metal due to the N_2 and contained O_2 and H_2O, splattering of the reaction products due to the high velocity of the gas, and immediate cooling and product solidification.

In all runs there was evidence of uranium metal formation by the pyrophoric nature of the reaction products and recovery of many small flakes and beads of metal; however, there was no massive consolidation of uranium metal, and it was impossible to obtain reliable yield data. There was no evidence of damage to the MgO liner other than approximately 1/16-in. penetration of the liner walls by reaction products.

X-ray diffraction analysis of the material removed from the MgO liner walls showed the presence of UO_2, MgO and NaF; however, UF_4 and MgF_2 were not found. Laboratory work by Dr. O. C. Dean of the Chemical Development Section B indicated reaction of UF_4 with MgO to form UO_2 (UF_4 + 2MgO $\rightarrow$ UO_2 + $2MgF_2$); however, this reaction would necessitate the presence of MgF_2 and probably some unreacted UF_4. A possible reaction for obtaining the UO_2 is oxidation of uranium metal by either O_2 or H_2O from the N_2 cooling gas or air. Analysis of the reaction products in the runs in which the nozzle failed and N_2 was released into the hot reactor, showed the presence of uranium nitride.

3.0 HR FUEL AND BLANKET PREPARATION AND PROCESSING

P. A. Haas

The objective of these studies is to develop processing and preparation methods as required for aqueous homogeneous reactor fuel and blanket fluids. A multiple hydroclone and an electrolytic process for removal of nickel were tested for application to HRT fuel processing. A flame denitration process is being developed for production of thoria particles for circulating slurries or fluidized beds.

3.1 Flame Calcining - C. C. Haws, V. L. Fowler

Anticipating production of 50-100 lb of classified, mixed-oxide product, attention was directed toward increasing the production rate of the flame denitration equipment. Stable operation was achieved for the feed conditions of Run 72 (see Table 3.1)(i.e., a feed rate equivalent to 195 g of oxides per hr). This production rate resulted from doubling of the feed concentration.

A further increase during Run 74B in the concentration of the feed (from 408 to 600 g per liter of solution) and an increase in the volume feed rate (to 50 cc/min) achieved a rate equivalent to 720 g (as oxides) per hr. Operation under this latter condition was not as satisfactory as the other tests, since continuous attention to the equipment was required. These production rates were calculated from the material fed to the flame denitration equipment. Actual yields of classified product range from 1/4 to 1/3 of these values.

The properties of the slurries produced in these scale-up tests were essentially the same as those produced in earlier runs. Yield stresses ranged from 0.02 to 0.06 lb per sq ft and surface areas from 1.3 to 2.1 sq meter per g.

3.2 Electrolytic Nickel Removal - E. L. Youngblood, D. H. Newman

The electrolytic test cell for removing nickel from a simulated HRT fuel solution* was modified to reduce the number of solution lines entering the cell. In the revised system, fuel solution from the fuel solution storage tank was pumped into the cell through a pipe extending under the surface of the mercury cathode. The fuel solution and gases from the cell were discharged through the vent line and returned to the fuel storage tank. The fuel exit line was thus eliminated.

Run 5 was made using a light water fuel solution and the modified cell arrangement described above. In 7791 ampere hours of operation during Run 5, approximately 99% of the copper and 25% of the nickel was removed from the fuel solution (Table 3.2). There was no appreciable removal of manganese.

*See flow diagram in ORNL-59-3-61, UNOP Monthly Report, March, 1959.

Table 3.1.

Flame Calcination Experiments

Slurry Characteristics of Flame Denitrated Thorium-Uranium Oxides Containing Alumina

Firing Temperature: 1500°C (outside wall of magnesia reflector)
Volume Feed Rate: 50 (approx.) ml per min for Run 74B
20 (approx.) ml per min for all others

Run No.	Nominal Alumina Conc. wt %	Mean Part. Size micron	Yield Stress lb/sq ft	Surface Area sq m/g	Approx. Feed Rate g oxides / hr	Feed Conc. g nitrates / liter solution
68	2.5	2.9	0.02	1.6	90	188
70	5	1.4	0.02	1.4	95	204
72	5	0.9	0.02	1.7	195	408
73	5	1.1	0.06	2.1	95	204
74B[a]	2.5	2.8	0.02	1.3	720	600

[a] Run 74B was 0.33 hours long; others were 4 hours or longer.

Table 3.2.

Conditions and Analyses for Run 5 Electrolytic Nickel Removal Test

Cathode Current Density - 0.16 amperes/sq cm
Cell Temperature - 25°C
Cell Voltage - ~10 volts
Cell Current - 226 amperes
Volume of Fuel Solution - 22 gallons
Volume of Mercury Cathode - 0.66 gallons

Ampere Hours	Solution Concentrations				
	Cu (g/liter)	Ni (g/liter)	Mn (g/liter)	U (g/liter)	SO_4 (M)
0	17.13	3.04	1.82	82.9	1.02
350	11.63	2.92	--	--	--
740	8.70	2.82	--	--	--
1570	4.50	3.01	1.60	--	--
2471	2.25	2.62	--	--	0.96
3388	1.31	2.62	1.71	--	--
5289	0.46	2.50	1.77	--	--
6429	0.33	2.41	1.77	--	--
7791	0.20	2.29	1.82	85.0	1.01

The amalgam from Run 5 was regenerated in the electrolytic cell by circulating a 1 M HNO_3 and 1.5 percent H_2O_2 solution through the cell while a reverse potential of 1 volt was applied to the cell. Figures 3.1 and 3.2 give the copper and nickel concentration of the regeneration solution as a function of time. In a total 191 hours of contact time between the amalgam and regeneration solution (22 hours of which reverse current was applied), the copper concentration was reduced from about 4% to 0.44% and the nickel was reduced from about 0.2% to 0.002%.

This regeneration procedure resulted in a 7% mercury loss to the regeneration solution through dissolution by the regeneration solution. This high mercury loss might be reduced by a lower reverse potential during regeneration or could be replaced by mercury additions to the cell.

A platinum plated stainless steel electrode was used in Run 5 to conduct the electric current through the lucite flange to the platinum screen anode. The platinum plating protected the stainless steel from anodic corrosion during the run, but some of the plating peeled off during the regeneration run, leaving the electrode subject to attack in subsequent runs.

3.3 HRT - Multiple Hydroclone Test - E. L. Youngblood

The efficiency of the HRT Multi-Clone[1] for removing suspended particles was measured using a thorium oxide light water slurry at 30°C. The thorium oxide used had a mean particle size of 3.2 microns. Based on the experimental results, the extrapolated value of d_{50} for the Multi-Clone under reactor operating condition is 2.3 microns.

Calculations indicate that installation of the Multi-Clone in the reactor system will result in a solids collection rate three to six times that of the original installation depending on the actual hydroclone efficiencies and the rates of solids deposition and resuspension. Details of the hydroclone efficiency test and the calculated solids removal rate in the reactor system are given in ORNL CF 59-7-49.[2]

[1] See May Unit Operations Monthly for description of Multi-Clone installation.

[2] P. A. Haas and E. L. Youngblood, "HRT-CPP Results to be Expected from Operation of the Multiple Hydroclone with the HRT", ORNL CF-59-7-49, July 1, 1959.
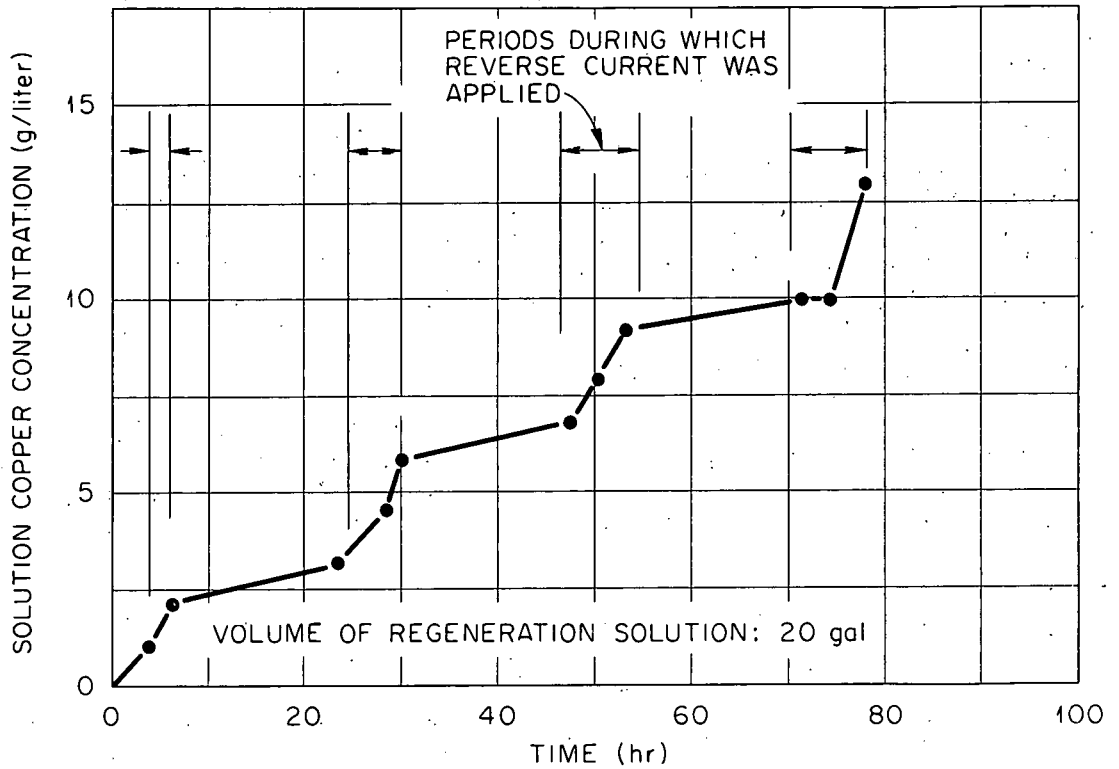
Fig. 3.1. Copper Concentration of Regeneration Solution vs Time.
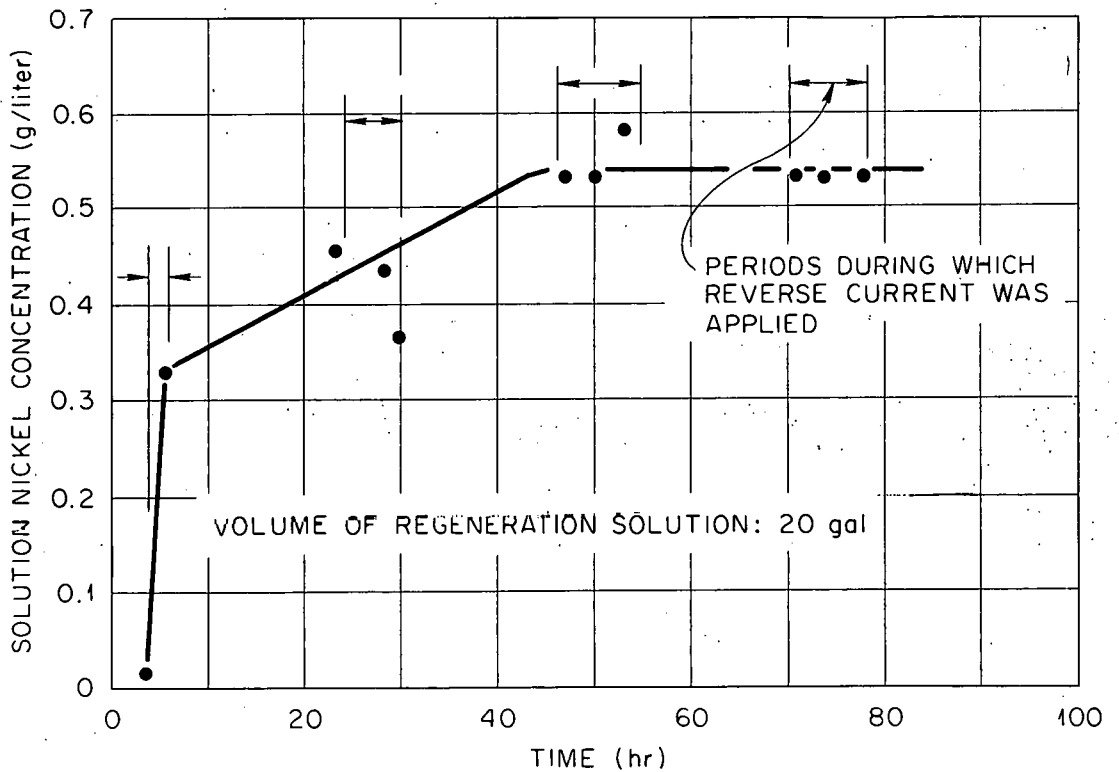
Fig. 3.2. Nickel Concentration of Regeneration Solution vs Time.

4.0 ION EXCHANGE

M. E. Whatley

An understanding of the mechanism and kinetics of anion exchange is necessary in order to make rational predictions of the operating character-istics of uranium anion exchange contactors. Toward this objective the equilibrium sorption isotherms and rates of sorption of uranium on a typical strongly basic anion exchange resin, Dowex 21K, are being determined.

4.1 Mechanism and Kinetic Studies - J. S. Watson

Studies of the rate of sorption of uranium on Dowex 21K are currently being made by determining the loading on beads contacted with a stirred uranium solution bath for different periods of time. The loading on each bead was determined by using enriched uranium and counting the bead in a gamma spectrometer.

This method was used to study the sorption of uranium from solutions with various total sulfate concentrations. The uranium and sulfuric acid concentrations were maintained at 0.0058 M and 0.020 M, respectively, and total sulfate concentration was varied between 0.0258 M and 0.201 M by adding sodium sulfate. Some of the first results of this series of runs were reported earlier,[1] but there was uncertainty because the equilibrium loadings were not accurately known. All of the results of the first series are now available and the values for the equilibrium loadings were determined using independent equilibrium data which had been obtained previously. The results of some of the runs first reported have been corrected with the new equilibrium data.

The results of the kinetics studies are shown in Figures 4.1 through 4.6. The results are correlated with a model for diffusion of a single specie into a sphere with a constant surface concentration.[2] All the runs except the one with the lowest sulfate concentration (0.0258 M) resulted in the same loading curve. The curves correspond to a diffusion coefficient of 1.25 - 1.30 x 10^{-7} sq cm/sec. The one low value (approximately 1.00 x 10^{-7} sq cm/sec) may be due to experimental or calculational error.

There is a notable difference at short contact times in the shape of the experimental curve and that predicted by the simple diffusion model. This difference probably reflects the inadequacy of the simple diffusion model. One possible cause for the difference was the diffusional resistance of the liquid film surrounding the bead. The run with 0.2008 M sulfate concentration was repeated with the stirrer speed reduced from 1650 rpm to 1250 rpm to increase the diffusion resistance of the film (see Figure 4.7).

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[1] UNOP May 1959 Monthly Report, ORNL-CF-59-5-47.

[2] UNOP April 1959 Monthly Report, ORNL-CF-59-4-47.

$D = 1.30 \times 10^{-7} \text{ cm}^2/\text{sec}$

URANIUM CONCENTRATION: 0.005779 M
SULFATE CONCENTRATION: 0.0258 M
SULFURIC ACID CONCENTRATION: 0.020 M
STIRRER SPEED: 1650 rpm

$(1/r^2)^{1/2}$, sec$^{1/2}$/cm

Fig. 4.1. The Rate of Sorption of Uranium on Dowex 21K from 0.026 M Sulfate Solutions.

Fig. 4.2. The Rate of Sorption of Uranium on Uranium on Dowex 21K from 0.0508 M Sulfate Solutions.

Fig. 4 3. The Rate of Sorption of Uranium on Dowex 21K from 0.0758 M Sulfate Solutions.

Fig. 4.4 The Rate of Sorption of Uranium on Dowex 21K from 0.1008 M Sulfate Solutions.
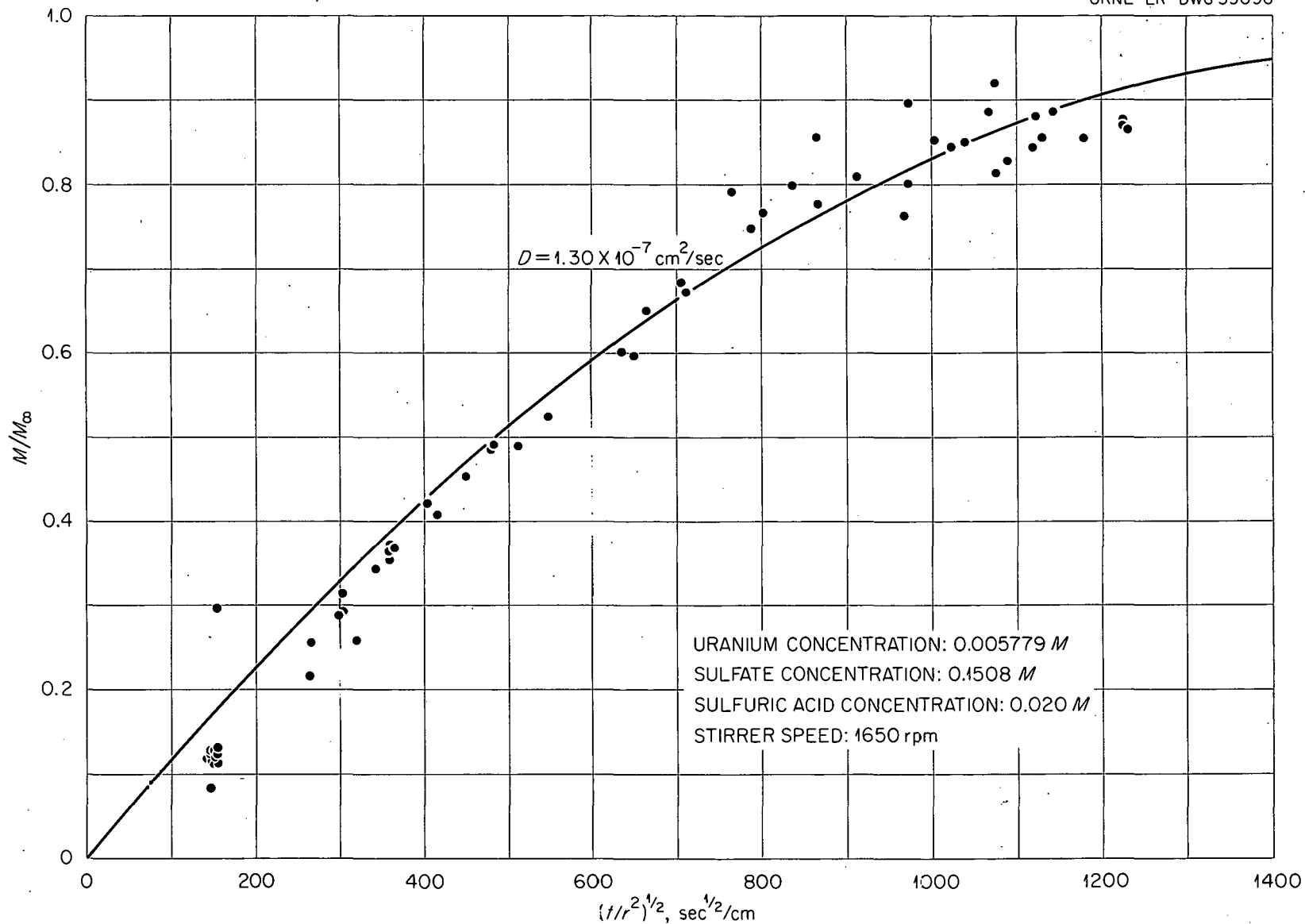
Fig. 4.5. The Rate of Sorption of Uranium on Dowex 21K from 0.1508 M Sulfate Solutions.

$D = 1.30 \times 10^{-7} \ cm^2/sec$

URANIUM CONCENTRATION: 0.005779 M

SULFATE CONCENTRATION: 0.2008 M

SULFURIC ACID CONCENTRATION: 0.020 M
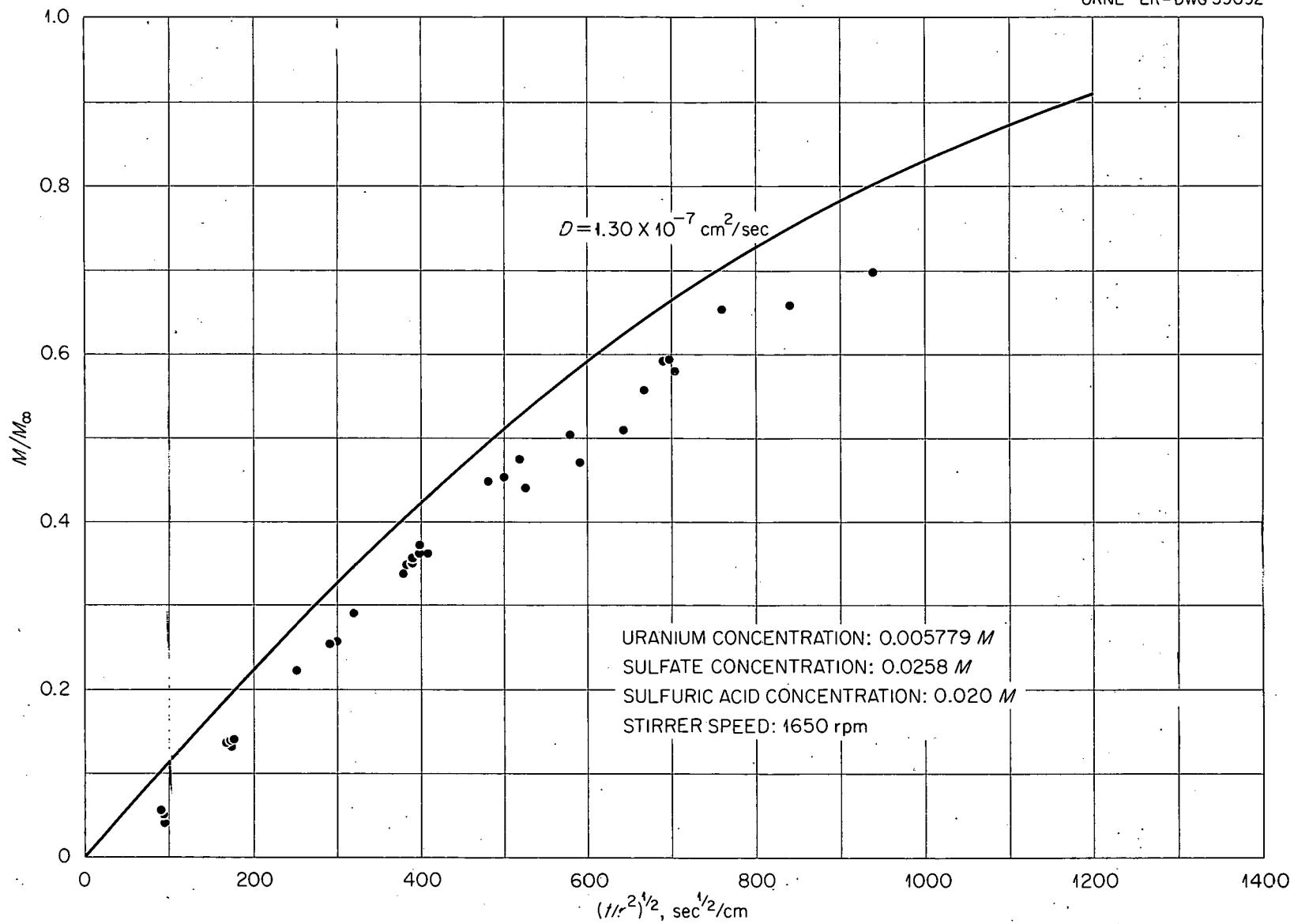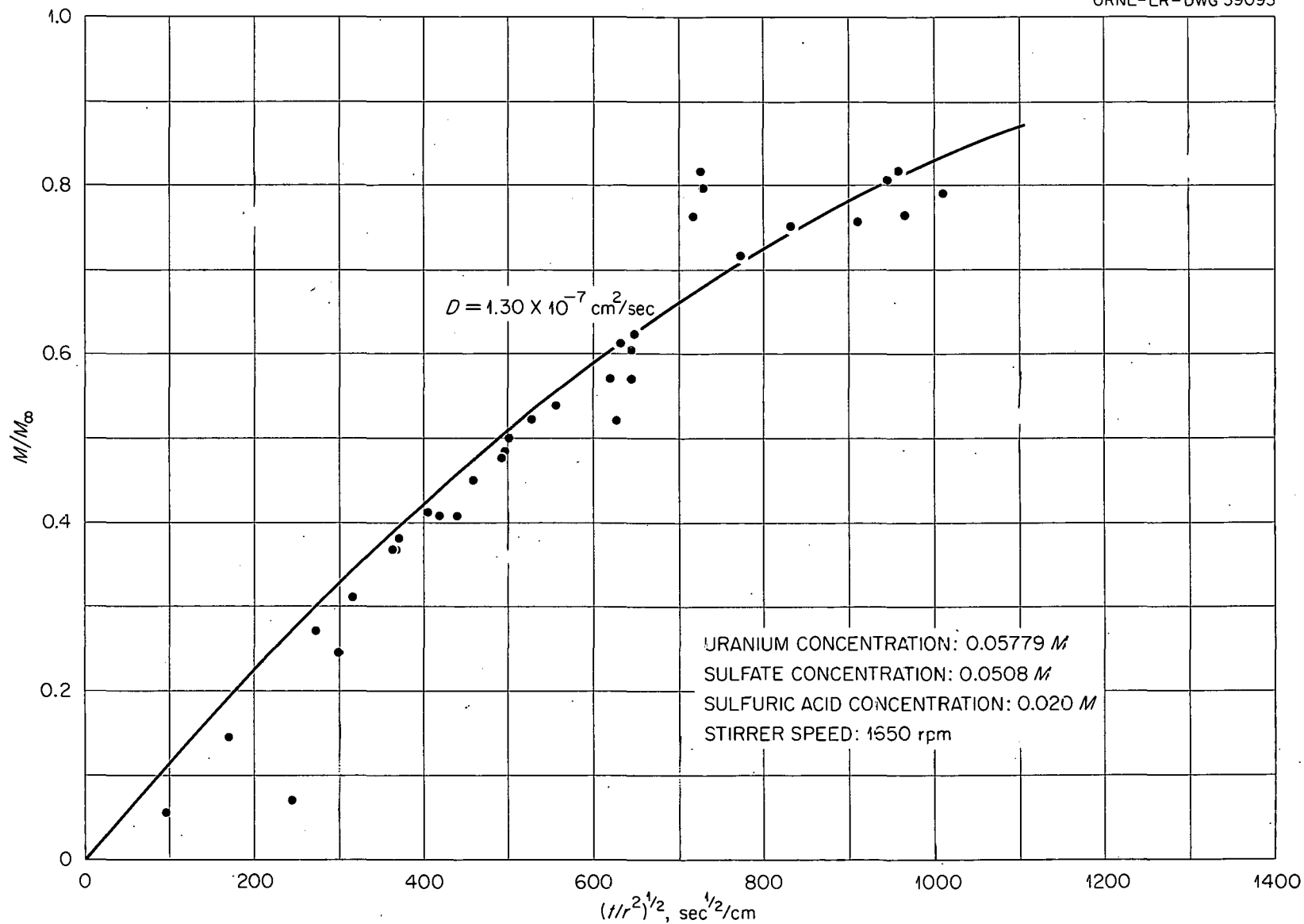
STIRRER SPEED: 1650 rpm

$(t/r^2)^{1/2}$, $sec^{1/2}/cm$
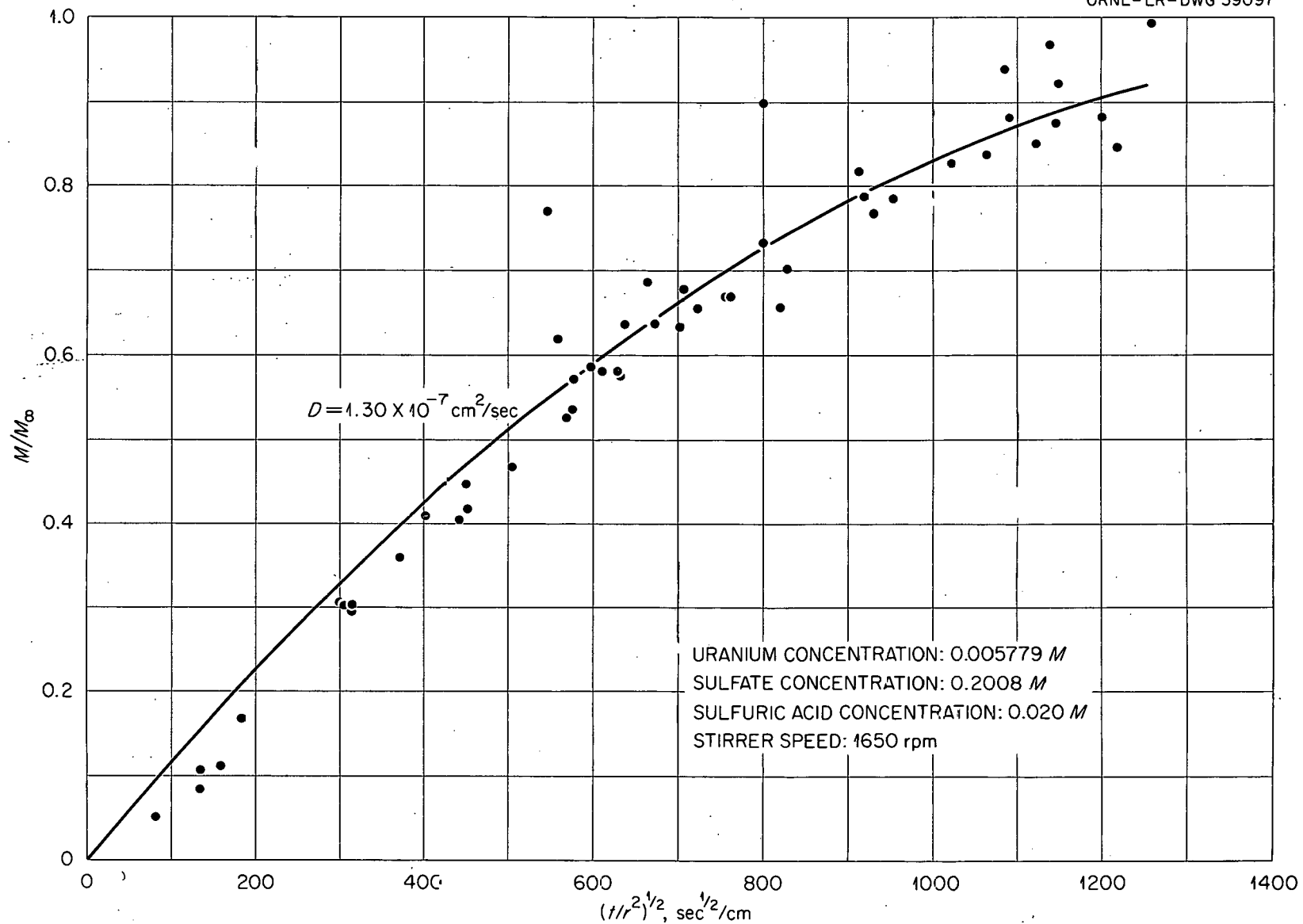
Fig. 4.6. The Rate of Sorption of Uranium on Dowex 21K from 0.2008 M Sulfate Solutions.

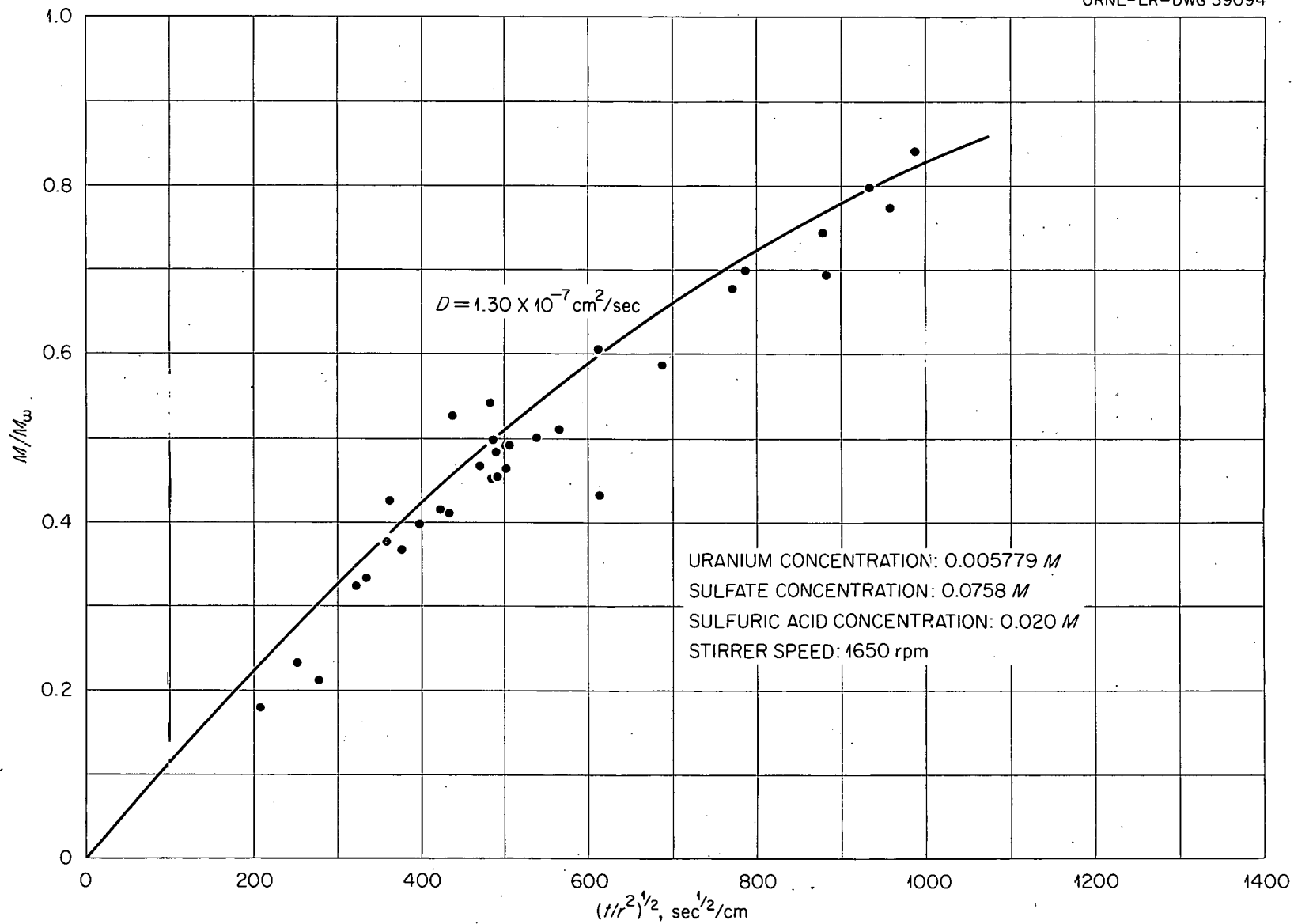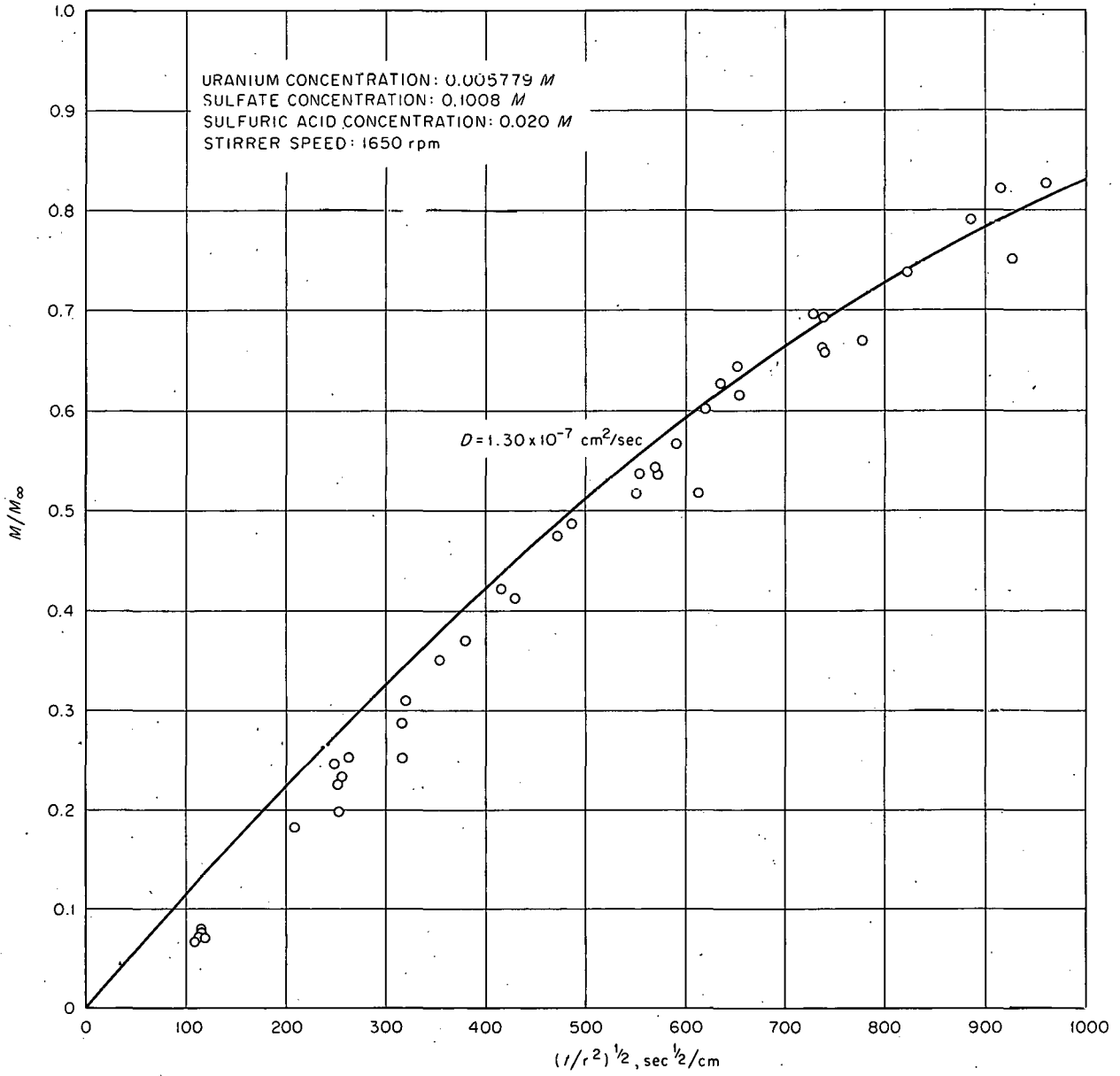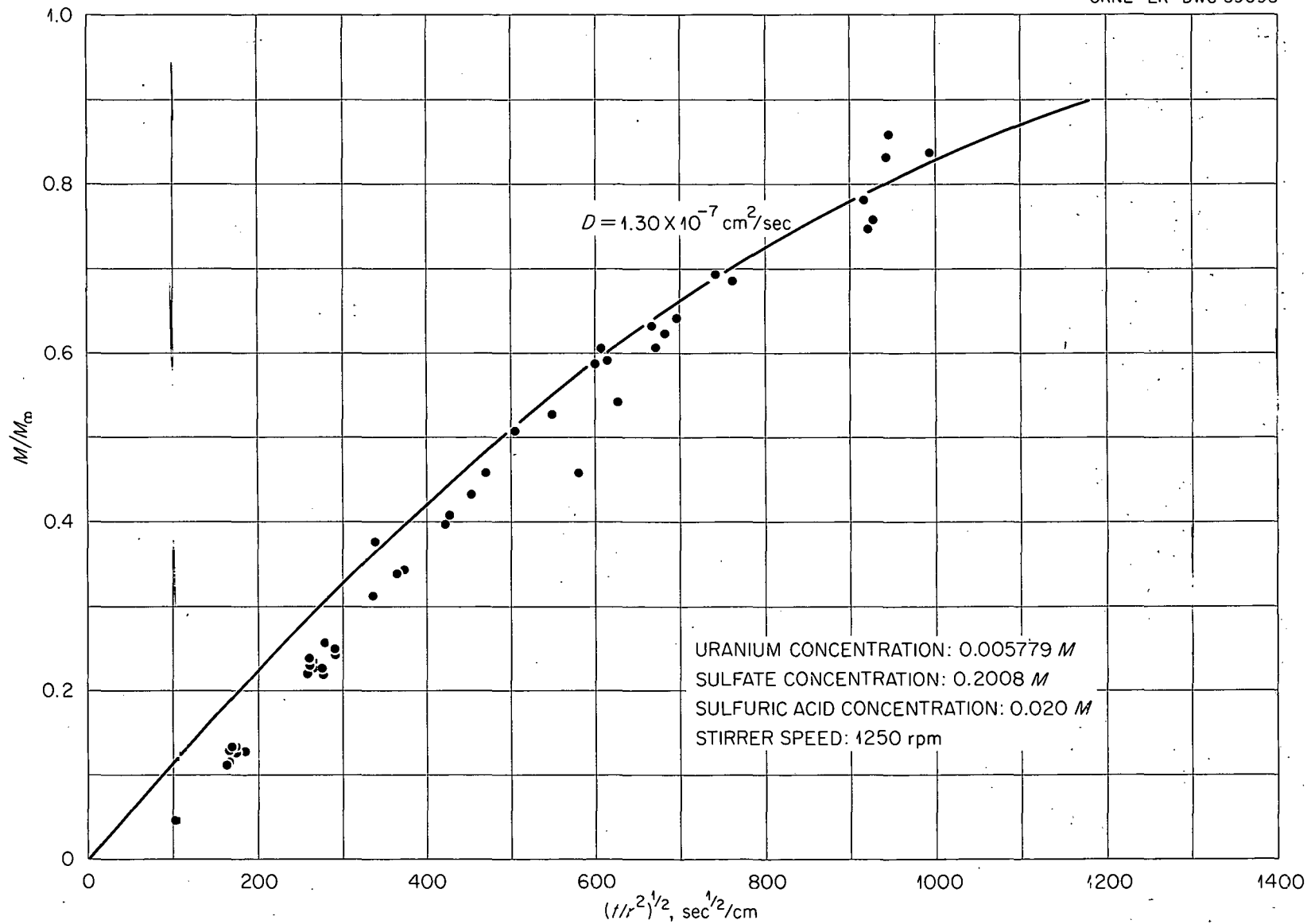Fig. 4.7. The Rate of Sorption of Uranium on Dowex 21K from 0.2008 M Sulfate Solutions.

No difference in the loading curves for the two runs (Figures 4.6 and 4.7) could be found. These results show that both curves are quite close to the curve corresponding to a diffusion coefficient of 1.30×10^{-7} sq cm/sec.

These data also suggest the variation in capacity or structure of individual resin beads. The scatter of the data increased as the contact time increased. This result would be expected if either the diffusion coefficient or the capacity of the individual beads differed. Also, the rather large variations in the equilibrium loadings of individual beads made it necessary to make measurements on several beads to obtain a representative value for the average loading.

5.0 POWER REACTOR FUEL REPROCESSING

C. D. Watson

5.1 Darex - F. G. Kitts, B. C. Finney, R. C. Early

The purpose of the Darex process is to convert SS-U and SS-UO$_2$ fuels into chloride-free nitrate solutions suitable for processing in existing stainless steel solvent extraction equipment. Chloride is necessary for dissolution of stainless steel in HNO$_3$ contained in titanium process equipment, but it must be removed to avoid corrosion of stainless steel process equipment. In the present investigation, a batch flowsheet is being studied in which dissolution product is treated with 61 wt % HNO$_3$ to produce solvent extraction feed containing 2-3 M HNO$_3$ and less than 350 ppm chloride.

5.1.1 Flowsheet Development

Five chloride removal and feed adjustment runs were made in the 10-in. titanium feed adjustment tank (FAT) using the ORNL reference flowsheet; three runs were made with APPR material and two with Yankee Atomic. Two APPR runs were also made in the 4-in. glass equipment, containing Ti metal in the vapor phase during one run. Laboratory runs included two runs with Yankee Atomic fuel and one with aluminum foreign research fuel. Dissolutions of these latter fuels in aqua regia were also studied in the laboratory.

Run YA-62 (see Table 5.1) was made with no reflux or sparging using dissolver product (DP) produced from prototype fuel. A high boil-up rate (resulting in low residence time) which was used to obtain heat transfer data at high temperature differences resulted in chloride removal only to 1410 ppm in the solvent extraction feed, a factor of 4 above specifications. A later run, YA-68, using a 2 hr reflux period with air sparging at 1.6 liters/min during reflux and recycle acid recovery, resulted in 64 ppm chloride in the solvent extraction feed. After one and two hours refluxing the acidified concentrate contained 325 and 184 ppm chloride, respectively.

Run APPR-63 was a reduced volume run with only 8.7 liters of dissolver product feed to eliminate entrainment from the FAT tank. The run was made at high boil-up rates and gave chloride removal to only 730 ppm even though two hours of reflux were employed. Very little chloride reduction was accomplished during the second hour of refluxing. The next run, APPR-64, was a duplication of the last successful run (APPR-59 reported last month) except an attempt was made to hold $\Delta T \cong 15°C$ throughout the run; chloride was removed to 306 ppm in the solvent extraction feed. Since chloride removal to < 200 ppm had not been accomplished in the 10-in. Ti equipment, run APPR-65 was made in the 4-in. glass equipment to evaluate the effect of aging on chloride removal from a batch of DP. A chloride concentration of 154 was produced in the solvent extraction feed, compared with ~50 ppm achieved in earlier runs.

Table 5 1. Darex Chloride Removal and Feed Adjustment Runs

| Run No. | Equipment | Dissolution Product | | | | | Acid Waste | | | At Constant Level | | | | Add 13.3 M HNO$_3$ (l) | Acidified Concentrate | | | Reflux Time (hr) | Recycle HNO$_3$ (Trace Cl$^-$) | | Solvent Extraction Feed | | |
| | | | | | | | | | | Add 12 M HNO$_3$ (l)[3] | Aqua Regia Recycle | | | | | | | | | | | | |
		Vol. (l)	H$^+$ (M)	Cl$^-$ (M)	U (g/l)	SS (g/l)	Vol. (l)	HNO$_3$ (M)	Cl$^-$ (M)		Vol. (l)	HNO$_3$ (M)	Cl$^-$ (M)		Vol. (l)	HNO$_3$ (M)	Cl$^-$ (M)		Vol. (l)	HNO$_3$ (M)	Vol. (l)	HNO$_3$ (M)	Cl$^-$ (ppm)
YA-62	10 in. Ti	10.8	3.07	1.25	149	40	3.0	0.75	0.25	9.4	9.4	6.55	0.55	5.45	~13.25	11.0	0.076	None	9.4	12.3	10.8	2.02	1410
YA-68	10 in. Ti	10.8	4.35	1.54	211	58	3.0	1.85	0.60	8.0	8.0	7.15	0.55	5.5	~13.3	10.26	0.185	2[1]	9.4	12.15	10.8	1.15	64
APPR-63	10 in. Ti	8.7	2.92	1.75	5½	55	2.4	0.55	0.20	7.5	7.5	5.9	0.65	5.3	~11.6	11.44	0.18	2	7.5	11.9	9.8	4.04	730
APPR-64	10 in. Ti	10.8	2.92	1.75	5½	55	3.0	0.55	0.25	9.4	9.4	5.65	0.65	6.6	~14.4	11.28	0.16	None	9.4	12.0	12.4	3.18	306
APPR-65	4 in. glass	5.4	2.92	1.75	5½	55	1.5	0.35	0.25	4.7	4.7	5.35	1.05	3.3	~7.2	11.12	0.12	None	4.7	11.6	6.2	3.52	154
APPR-66	10 in. Ti	8.7	2.92	1.75	5½	55	2.4	0.40	0.20	7.5	7.5	5.35	0.70	5.3	~11.6	11.02	0.22	2[1]	7.5	11.6	9.8	3.27	70
APPR-67	4 in. glass[2]	5.4	2.92	1.75	5½	55	1.5	0.37	0.23	4.7	4.7	5.55	1.10	3.3	~7.2	11.3	0.062	None	4.7	11.7	6.2	3.93	70
BYA-5	Lab glass	1.08	1.60	1.55	211	60	0.30	0.18	0.05	0.94	0.94	6.28	0.62	0.545	~1.32	9.34	0.40	None	0.94	12.1	1.08	1.10	7450
BYA-6	Lab glass	1.08	1.11	1.66	199	56	0.30	0.01	0.00	0.94	0.94	5.65	0.60	0.60	~1.38	9.81	0.39	None	0.94	12.15	1.08	1.51	4600
AI-2	Lab glass	0.42	1.04	1.35		45[3]	None			0.21[4]	0.315	3.45	1.15	None	~0.31	5.5	0.001	None	None		0.35	4.7	23

[1] 1.6 l/min air sparge during reflux and recycle acid removal.

[2] Ti present in vapor phase.

[3] 45 g/l aluminum rather than SS.

[4] 13.3 M HNO$_3$.

The 4-in. glass equipment has a Ti bottom flange and heating coil but no Ti is exposed in the vapor phase. Another run (APPR-67) was made in the 4-in. glass equipment with 132 sq in. of 20 mesh Ti screen made of 0.010-in. wire and 122 sq in. of 0.010-in. Ti sheet inserted in the unheated vapor-space above the boiling liquid. Chloride removal was to 70 ppm in the solvent extraction feed.

Run APPR-66 was made in the 10-in. Ti equipment utilizing a 2 hour reflux period with an air sparge of 1.6 liter/min; solvent extraction feed containing 70 ppm chloride was produced. After 1 hr reflux the chloride concentration in the acidified concentrate had been reduced to 464 ppm and after 2 hr to 275 ppm.

From this series of runs it was concluded that:

1. Chloride can be reduced to the specified < 350 ppm in both APPR and Yankee Atomic solvent extraction feed solutions by using appropriate periods of reflux and air sparge.

2. The presence of Ti has no adverse effect on chloride removal from the FAT tank.

3. The difficulty of chloride removal encountered when changing from a 4-in. glass tank with an internal heating coil to a 10-in. Ti tank with two external convective boiling loops was attributable to the change in system geometry as it affects internal liquid-vapor contacting, and to shorter residence times when smaller batches and higher boil-up rates were employed.

5.1.2 Dissolution Studies

Approximately 69 g SS and 276g UO_2 (prototype Yankee Atomic fuel) were totally dissolved in 1.2 liters of aqua regia initially 6 $\underline{M}$ HNO_3 - 2 $\underline{M}$ HCl. The final volume after 3 hrs of boiling was 1.15 liters; this produced loadings of 60 g SS and 211 g U/liter. Run BYA-5 (Table 5.1) was an ineffective attempt at removing the chloride from this material using no reflux or air sparge. Approximately the same loadings (56 g SS and 199 g U/liter) were achieved in a total dissolution requiring 3 hrs of boiling in aqua regia originally 5 $\underline{M}$ HNO_3 - 2 $\underline{M}$ HCl. The laboratory feed adjustment run BYA-6 also failed to remove chloride to the desired concentration of < 350 ppm.

The results of run Al-2 (DP made by dissolving 2S Al in 5 $\underline{M}$ HNO_3 - 2 $\underline{M}$ HCl) indicated that chloride removal in the case of Al fuels should be much easier than for those containing Fe (Table 5.1). The results of a preliminary study of initial dissolution rates of 2S Al in aqua regia are shown in Table 5.2.

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Table 5.2

Initial Dissolution Rates of 2S Al in Aqua Regia

Aqua Regia Composition		Dissolution Rate
HNO_3 $\underline{M}$	HCl $\underline{M}$	$\dfrac{Mg}{sq\ cm\text{-}min}$
5	0.5	1.0
5	1	7.1
5	1.5	13.6
5	2	20.5
6	2	13.8
7	2	10.0
5.6	Hg^{++} 0.005	53

These dissolution tests were carried out by immersing aluminum specimens 3/4-in. x 3-in. x 1/4-in. (~42 sq cm) in 500 cc of boiling solution for five minutes; the dissolution rates were calculated from the measured weight loss of the specimens. Dissolution rate increased with increasing chloride (0.5 to 2.0 $\underline{M}$) at 5 $\underline{M}$ HNO_3; increasing HNO_3 above 5 M at 2 $\underline{M}$ chloride gave decreasing rates. The rate for Hg^{++} catalyzed (0.005 $\underline{M}$) HNO_3 (5.6 $\underline{M}$) was faster by a factor of ~2-1/2 than for any of the aqua regia compositions tested. The work was exploratory with no attempt at optimization.

5.1.3 Overall Heat Transfer Coefficients

Overall heat transfer coefficients were determined for the 10-in. diameter titanium chloride removal and feed adjustment tank for runs YA-62 and 68, and APPR-63, 64 and 66. The data were presented in Table 5.3 and Figure 5.1. Also included in Figure 5.1 are the overall coefficients determined for vaporizing water and the coefficients for run YA-61 (ORNL CF-59-5-47).

The overall coefficients based on vaporizing acid (mixed and recycle) from APPR and Yankee Atomic type dissolver products varied from 170-320 Btu/hr-sq ft-$^{\circ}$F over a temperature difference (condensing steam to boiling liquid) range of 25-64°F, whereas the coefficients for vaporizing water increased from 360-460 Btu/hr-sq ft-$^{\circ}$F over the same range. There is considerable scatter in the acid data which may be attributed to the fact that each coefficient was based on the collection of only 1 liter of acid. There was no significant difference noted between vaporizing mixed acid (HNO_3 + HCl) and recycle acid (HNO_3 + trace chloride) from either the APPR

Table 5.3. Heat Transfer Data for 10 In. Diameter Titanium Chloride Removal and Feed Adjustment Tank

2 sq ft heat transfer area

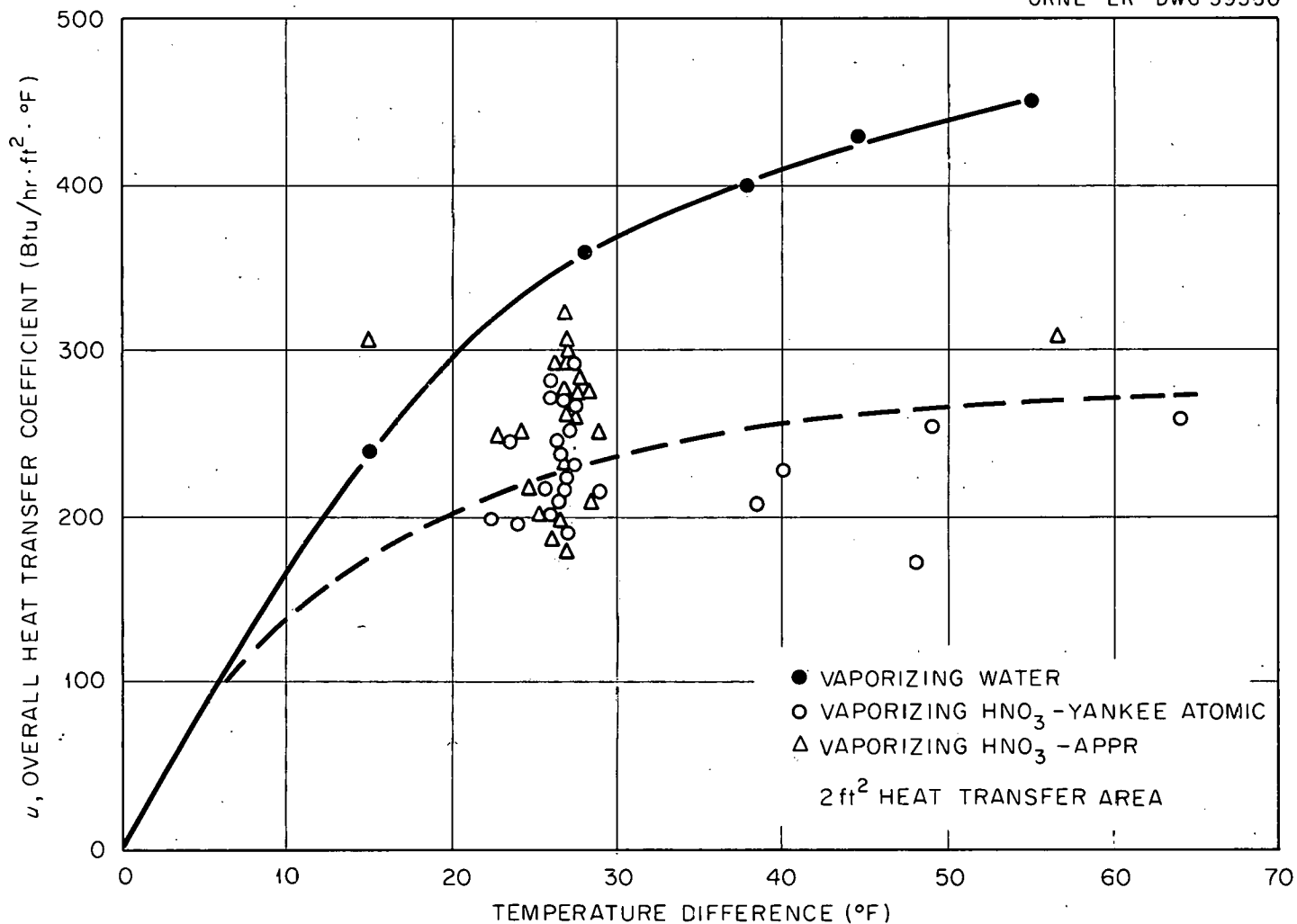| Run No.	Acid Vaporization Rate (lb/hr)	Acid Composition			$L_{v'}$ wt avg (Btu/lb)	Collection Time per Liter of Acid (min)	Liquid Boiling Temperature (°F)	Steam Pressure (psia)	Condensing Steam Temperature (°F)	Temperature Difference (°F)	Over-All Heat Transfer Coefficient, U (Btu/hr·ft^2·°F)
		H^+	Cl^-	NO_3							
YA-62	65.3	12.6		12.6	518	2.75	253.4	87	317.8	64.4	263
APPR-63	58.8	11.6		11.6	548	3.00	251.6	76	308.3	56.7	310
APPR-64	17.2	2.0	0.45	1.55	860	8.30	232	35	259.3	27.3	268
	21.4	3.8	1.13	2.67	800	6.95	234	36	260.6	26.6	323
	21.6	5.0	1.07	3.93	765	7.10	234.5	36.5	261.4	26.9	306
	20.3	6.05	0.90	5.15	725	7.78	236.3	37.5	263	26.7	276
	17.1	7.05	0.52	6.53	697	9.47	241.7	39	265.4	23.7	251
	15.6	7.55	0.47	7.08	690	10.33	244	39.5	266.4	22.7	248
	14.8	8.4	0.42	7.98	650	11.25	247	41.5	269.2	22.2	216
	19.3	9.0	0.25	8.75	635	8.40	247	44.5	273.8	26.8	233
	18.3	12.2	0.05	12.15	535	9.75	249.8	46	275.7	25.9	189
	20.0	12.85	0.05	12.8	508	9.0	251.6	47	277	25.4	202
	20.0	13.65	0.03	13.62	485	9.1	251.6	48	278.4	26.8	182
	22.0	13.95	0.03	13.92	476	8.3	251.6	48	278.4	26.8	196
APPR-66	18.1	4.1	1.2	2.9	790	8.25	234	36	260.6	26.6	270
	20.6	5.4	1.12	4.28	750	7.50	236.3	37	262.2	26.6	292
	21.3	6.15	0.82	5.33	715	7.40	239.0	39	265.4	26.4	290
	21.6	7.05	0.62	6.43	697	7.5	241.7	41.5	269.2	27.5	274
	21.7	7.80	0.42	7.38	665	8.0	242.6	43	271.5	28.9	250
	17.6	8.55	0.35	8.2	650	9.48	245.3	44.5	273.8	28.5	210
	22.2	9.2	0.05	9.15	630	7.6	246.2	44	273	26.8	261
	26.4	10.0	0.02	9.98	590	6.5	248	46	275.7	27.7	283
	27.8	10.65	0.02	10.63	578	6.25	248.9	46	275.7	26.8	300
	28.1	11.4		11.4	552	6.25	248.9	47	277	28.1	276
	28.6	12.15		12.15	516	6.25	249.8	47	277	27.2	271
	28.4	12.7		12.7	504	6.33	250.7	47.5	277.7	27	266
	28.6	13.4		13.4	492	6.33	251.6	48	278.4	26.8	262
YA-68	13.3	1.8	0.4	1.4	870	10.5	232.7	35.5	259.6	26.9	215
	14.7	2.3	0.55	1.75	850	9.67	234.5	36.5	261.2	26.5	236
	15.5	3.3	0.85	2.45	820	9.42	236.3	38	263.7	27.4	232
	13.7	4.9	1.02	3.88	765	10.17	238.2	39	265.3	27.1	193
	14.6	6.35	0.97	5.38	710	10.83	240	39.5	266	26.0	199
	13.6	6.95	0.82	6.13	700	11.83	241.7	39.5	266	24.3	196
	12.8	7.4	0.72	6.68	693	12.75	245.2	40.5	267.5	22.3	199
	16.5	8.15	0.45	7.70	660	10.0	247.1	44	272.7	25.6	213
	19.3	8.7	0.30	8.40	645	8.67	248	47	276.8	28.8	216
	18.8	9.3	0.20	9.10	630	9.0	249.8	47	276.8	27.0	220
	17.5	10.0	0.20	9.80	590	9.83	250.7	47	276.8	26.1	198
	25.2	10.15	0.05	10.1	587	6.83	249	47	276.8	27.8	266
	26.4	10.7	0.04	10.66	578	6.58	249.8	47	276.8	27.0	282
	26.4	11.3	0.04	10.26	556	6.67	250.7	47.5	277.5	26.8	274
	27.2	11.8	0.04	11.76	534	6.50	251.6	47.5	277.5	25.9	280
	27.5	12.4	0.02	12.38	515	6.50	252.5	48.5	278.7	26.2	270
	26.7	12.8		12.8	505	6.75	253.4	50	280.6	27.2	248
	26.5	13.25		13.25	495	6.83	255.2	51	281.8	26.6	237
	23.7	13.50		13.50	490	7.67	257.9	53	284.4	26.5	219
	23.5	13.50		13.50	490	7.75	263.3	55	286.7	23.4	246

Fig. 5.1. 10-inch Diameter Titanium Feed Adjustment Tank Overall Heat Transfer Coefficient as a Function of Temperature Difference (Condensing Steam – Boiling Liquid) Based on Vaporizing Water, and also HNO$_3$ from APPR and Yankee Atomic Type Dissolver Product.

or Yankee Atomic-type dissolver products, although the APPR-type DP had a greater tendency to foam. Note that the coefficients for the recycle acid (9.2 - 14 M HNO_3) recovery step for APPR-66 are significantly higher than for APPR-64 (Table 5.3); air sparging was utilized in this portion of APPR-66 and apparently raised the coefficient due to added turbulence.

It was concluded from the heat transfer studies that an average overall heat transfer coefficient of approximately 250 Btu/hr-sq ft-°F can be expected when vaporizing acid from APPR and Yankee Atomic dissolver products in a titanium vessel utilizing convective circulation with condensing steam as the heat source.

5.2 Feed Clarification - J. B. Adams, B. A. Hannaford, G. B. Dinsmore

Dissolver solutions from fuel reprocessing treatments frequently require clarification because they may contain undesirable precipitates, undissolved fissile or fertile fuel, and emulsion-forming agents (usually silica). An investigation is underway of the clarification of Darex (APPR) solvent extraction feed solutions by filtration and centrifugation and the washing of solids for uranium recovery.

Centrifuge Tests - Centrifuge tests showed that an essentially complete separation of siliceous solids from Darex (APPR) solvent extraction feed solutions could be made in a solid bowl centrifuge. Sufficient data were taken in a 5-in. diameter solid bowl centrifuge to estimate the capacity of larger centrifuges needed on a pilot plant scale.

The size distribution of the solids in two Darex (APPR) solutions was estimated from the recovery data taken and the application of Stoke's law (Table 5.4). From the graph of size distribution (Figure 5.2), it was estimated by extrapolation that ~96% by weight of the solids lay in the 1-15 micron range. This range varied for the two Darex solutions tested from 1-14 microns for one, and from 1.4-6 microns for the other. These size distributions probably approach those of the ultimate particles since the particles had been subjected to intense shear forces in the centrifuge. The original size distribution in the feed probably involved much large particle or agglomerate sizes.

Slurries made from solids taken from the centrifuge bowl were almost unfilterable even with large additions of filter aid. On the other hand, the original feed slurry could be filtered easily without filter aid and much faster when filter aid was used. One obvious inference is that filtration rather than centrifugation would maintain the agglomerated and easily settled silica particles produced by feed adjustment of APPR Darex dissolver product.

Filtration - Washing Tests - Tests were continued on water washing of siliceous filter cakes deposited on porous metal filters by filtration of Darex (APPR) solvent extraction feed solutions. High uranium recovery, 99.9%, was obtained with a small amount of wash water (Table 5.5).

Table 5.4. Data from Centrifugation Tests

Conditions: Darex (APPR) solvent extraction feed solutions

5-in.-dia solid bowl centrifuge (~315 cc volume)

Darex[a] Solution Used	Feed Rate (cc/min)	Centrifuge Speed (rpm)	Centrifugal[b] Force (× gravity)	Nominal Holdup Time in Bowl (min)	Settling[c] Velocity of Smallest Particle Collected (ft/sec)	Volume Solids (cc)	Volume % of Original	Wt Solids (mg)	Wt % of Original	Calculated Separation Size[e] (μ)
						Sample Analysis[d]				
HS-6-A	200	3630	805	1.58	0.000606	0.0	0.0	0.0	0.0	0.92
	300	3560	774	1.06	0.000905	0.0	0.0	0.0	0.0	1.15
	400	3050	569	0.79	0.00121	0.05	5.0	3.0	9.6	1.54
	450	2910	517	0.70	0.00136	0.15	15	3.3	10.5	1.72
	500	2860	500	0.63	0.00151	0.15	15	4.0	12.8	1.84
	1000	2070	262	0.32	0.00301	0.4	40	16.3	52.0	3.59
	Original					1.0	100	31.3	100.0	
HS-6-A	400	2750	462	0.79	0.00121			6.7	18.0	1.71
	800	2360	340	0.39	0.00243			14.1	37.8	2.84
	1200	1940	230	0.26	0.00364			21.0	56.3	4.22
	Original							37.3	100.0	
Mixture of HS-4-A and HS-5-A	400	3050	549	0.79	0.00121			0.0	0.0	1.58
	450	2950	532	0.70	0.00136			0.0	0.0	1.70
	500	2850	496	0.63	0.00152			2.6	8.5	1.86
	600	2640	426	0.52	0.00182			7.6	27.7	2.19
	1000	1950	232	0.32	0.00304			22.1	81.0	3.83
	Original							33.6	100.0	

[a]Feed solutions were essentially the same differing only in having been processed for Cl⁻ removal in different batches.

[b]Average gees = $(2.84/10^5)N^2 r$ with N in rpm and $r = r_{average}$ = 2.15 in. This varies $< \pm 17\%$ over the radius from the lip to the bowl wall.

[c]Distance from lip to wall of bowl ($1\frac{1}{16}$ in.) divided by nominal holdup time of solution in the bowl.

[d]From 12 cc samples taken after reaching steady state; samples were centrifuged ~20 min in a laboratory centrifuge. Solids were washed, dried, and weighed.

[e]From Stokes' law:

$$D_p = \sqrt{\frac{18\mu V}{\Delta\rho a'_g}} = 17.66\sqrt{\frac{3600 V}{a'}}$$

gives equivalent spherical particle diameter in microns, with V, the settling velocity in ft/sec and a', the force, dimensionless, times gravity. Physical properties were taken as $\rho_L = 1.2$ and $\mu_L = 1.9$ cp for the solution and particle density, ρ_S, assumed ~2.2.
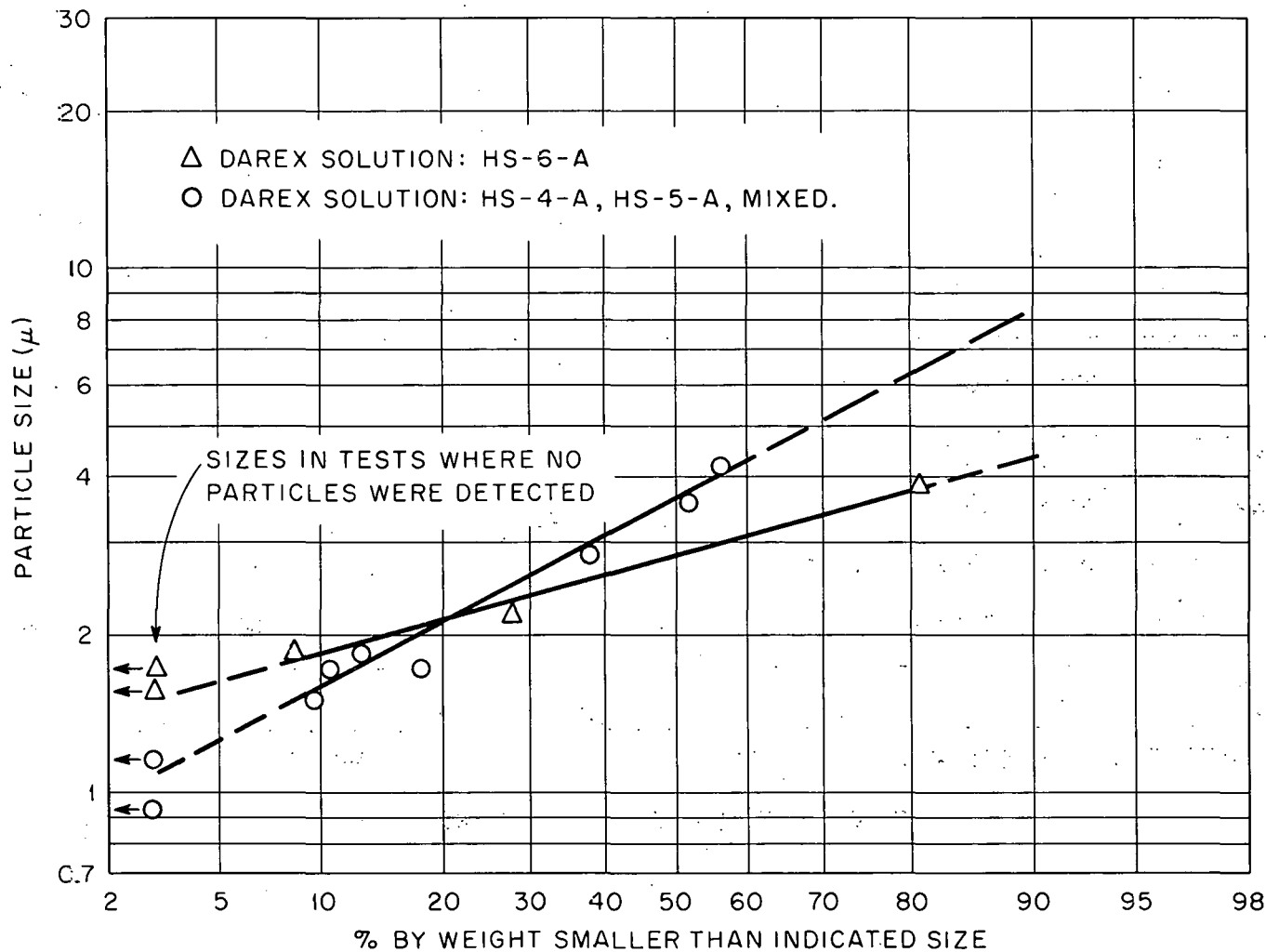
Fig. 5.2 Estimated Particle Size Distribution of Siliceous Solids (Sheared)
From Darex (APPR) Solvent Extraction Feed Solutions.
(Logarithmic Normal Probability Scales)

Table 5.5

Washing Data - Darex (APPR) Filter Cakes

	Amount		Analysis		Distribution of Uranium Values		
	Volume (liter)	Weight (g)	U(g/liter)	U(Wt%)	Wt(g)	Wt%	Cumulative Wt %
Filtrate	20	-	4.68	-	9.36	94.28	94.28
1st Wash	5	-	1.11	-	5.55	5.59	99.87
2nd Wash	5	-	.016	-	0.08	0.08	99.95
3rd Wash	5	-	.001	-	0.005	0.005	99.96
Wet Cake	-	1507	-	.003	0.045	0.045	-

The sludge from 21 liters of Darex (APPR) solution, including 12 g
Celite 545 filter aid per liter that was added, was deposited on a 0.66
sq ft star-shaped porous metal filter.* Three 5-liter batch water washes
were made. The uranium loss after three 5-liter water washes was 0.04%.

5.3 Solvent Extraction Studies - R. J. McNamee, K. Ladd, R. O. Payne,
    F. L. Rogers, G. B. Dinsmore, J. C. Rose, R. C. Early, D. E. Willis

Solvent extraction studies were made in a 2-in. dia packed column to
assist the Hanford Atomic Products Operation in adapting the Redox process
to the reprocessing of spent stainless steel power reactor fuels. During
this report period, 14 runs were made in a 2-in. dia packed column to
investigate the effect of the following conditions on column capacity and/
or efficiency:

(1) Acidification of the Darex feed from 0.2 $\underline{M}$ AD to 0.5 $\underline{M}$ HNO_3.

(2) Silicon addition to the Darex feed.

(3) Mistron addition to the Darex feed.

(4) A Niflex (HNO_3-HF dissolution) type feed.

(5) Molybdenum addition to the Darex feed.

(6) Hexone solvent acidified to 0.15 $\underline{M}$.

Analytical results have not yet been received; however, the experimental
work has been completed, results will be calculated and a final report pre-
pared as soon as the data become available.

Three tentative conclusions can be drawn from the flooding data presented
in Table 5.6:

(1) Acidifying the feed increased the flooding rate. (The flooding
    rate for a previous 0.004 $\underline{M}$ silicon, 0.2 $\underline{M}$ AD flowsheet was 484
    GSFH - see ORNL CF 59-4-47.)

(2) Mistron addition to the feed (100 ppm) increased column capacity
    from 482 to >736 GSFH. However, an addition of only 50 ppm had
    no noticeable effect.

(3) Molybdenum addition to the feed (0.05 $\underline{M}$) increased capacity from
    ~300 GSFH (see Runs 3e and 3h, ORNL CF 58-12-35, and Run 3h-3) to
    556 GSFH. This surprising effect may have been due to the reaction
    of silicon and molybdenum to form a silicomolybdic acid complex[1],
    thereby reducing the effect of the silicon, which has been shown
    to have an adverse effect on column capacity (see ORNL CF 59-4-47).

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* Micrometallic Corp. No. OS-1, 20µ mean porosity.
[1] H. F. Walton, Principles and Methods of Chemical Analysis, p. 125,
    Prentice-Hall, New York, 1952.

Table 5.6

Column Capacity Data for Hanford Assistance Runs

Redox Solvent Extraction for Stainless Steel Fuel Processing

Run	Feed Type	Silicon Conc. M	Mistron Conc. ppm	Molybdenum Conc. M	Feed Acidity M	Flooding Rate GSFH
3h-6A	Darex[1]	0.004	-	-	0.5	778
3h-0A	Darex	-	-	-	0.5	778
3h-0	Darex	-	-	-	-0.2[2]	482
3h-OM₁	Darex	-	50	-	-0.2	482
3h-OM₂	Darex	-	100	-	-0.2	>736
3h-4	Darex	0.015	-	0.05	-0.2	556
3h-3	Darex	0.015	-	-	-0.2[4]	344
8i	Niflex[3]	0.003	-	-	0.2	692

(1) 0.4 $\underline{M}$ U, 0.8 $\underline{M}$ SS, 1.1 $\underline{M}$ NaNO$_3$, 0.2 $\underline{M}$ Na$_2$Cr$_2$O$_7$; Feed/Scrub/Solvent 1/0.24/2.5.

(2) Minus signifies "acid deficient".

(3) 0.14 $\underline{M}$ U, 0.14 $\underline{M}$ SS, 0.7 $\underline{M}$ Al(NO$_3$)$_3$, 0.2 $\underline{M}$ Na$_2$Cr$_2$O$_7$, 0.84 $\underline{M}$ NaNO$_3$, 0.7 $\underline{M}$ NH$_4$F; Feed/Scrub/Solvent = 1/0.14/1.9.

(4) Solvent acidified to 0.15 $\underline{M}$.

5.4 Mechanical Processing - C. D. Watson

Mechanical processing of fuel, if successful, can reduce the quantity of inert structural material processed in a fuel recovery plant resulting in increased plant capacity and a reduction of waste streams. The purpose of this program is to evaluate various mechanical fuel processing methods and to study selected methods with irradiated fuel for: (1) removal of inert end adapters and other structural material; (2) disassembly of fuel assemblies into appropriately sized subassemblies; (3) shearing and leaching of assemblies or subassemblies; (4) dejacketing of individual fuel elements; and (5) disposal of jackets and sheared sections from which fissile and fertile material has been removed.

5.4.1 Shearing - G. K. Ellis, D. E. Willis, F. L. Rogers

Shear Blade Evaluation. The feasibility of shearing and leaching spent power reactor fuel depends largely upon an experimental demonstration of an acceptable shear blade life. An experimental program has been initiated primarily to measure the shear blade life with the Mark I prototype fuel bundle, but also to study the effect of blade shape and velocity on blade life, tube end closure, and material transfer of the assembly through the shear. Research contracts have been let to Birdsboro and Clearing Machine companies for shear blade studies to supplement the ORNL program. For these studies, twenty-five of a lot of fifty Mark I porcelain filled prototypes have been received from Continental Technical Services of Cleveland, Ohio, under an outside contract to ORNL. The remaining twenty-five of the porcelain filled prototypes and an additional twenty-five empty Mark I's to be filled with UO_2 for use in leaching tests, will be received before July 1.

The research subcontracts with Birdsboro and Clearing will end before July 1. The Clearing experimental proposal for blade evaluation was reported in ORNL CF 59-5-47 (May UNOP Monthly Progress Report).

The Birdsboro program will begin June 18. In approximately 21 shearings of a Mark I prototype for each of five blade shapes they propose to select the maximum permissable clearance between blades, measure the increase of clearance between blades with number of cuts, and optimize the velocity for minimum blade wear which will leave the tubes with at least 20% open end areas. They will investigate the degree of clamping required, the power requirements to shear with the different shaped blades and the possible changes in bundle shape which will benefit shearing. For the purpose of determining shear blade life, the blade or blades which give the best performance will be used in making about 300 cuts each of the Mark I prototype.

Eight pairs of different shaped blades and two die sets have been completed for the ORNL experimental blade evaluation program. Each pair of blades consist of a punch and anvil, and there is provision for interchange in the die sets of most blade shapes.

Experimental Results of Shearing Tests. Experimental shearings were made with two slow speed (0.3 to 3 in/sec) shears of 125 T and 60 T capacity using Mark I prototype fuel bundles and single stainless steel UO_2-filled tubes. Basic information was obtained for size distributions, densities and the percent ceramic separated for various lengths of sheared porcelain and UO_2-filled stainless tubing.

The approximate bulk density versus length of sheared piece (Figure 5.3) for 4 cuts at each specified length of sheared piece of a Mark I porcelain filled assembly varied from approximately 120 lb/ft^3 at 1/2-in. to 1-in. lengths, to 82 lb per cu. ft. for 3-in. lengths.

It was possible to obtain a range of densities depending upon the extent of packing. For example, a density of 135 lb per cu. ft. was obtained for 1-in. pieces after thorough packing. For purposes of this experiment, packing of the sheared pieces was obtained by free fall from a 2-ft height. The density of loosely packed porcelain fines was about 73 lb/per cu. ft.

The percent UO_2 separated from 15 cuts of each specified sheared length varied from 30% for 0.5-in. sheared lengths to 2% for 5-in. lengths when single 0.4-in. dia stainless clad UO_2 (simulating single Yankee Atomic elements) were sheared with a 60 T "line of contact" blade. The percent UO_2 separated may be expressed as a function of the length in inches of sheared piece, L, by the following equation (Figure 5.4):

$$P = 13/L^{1.2}$$

The size distribution of the separated UO_2 from shearing 150 0.5-in. lengths of prototype Yankee element with the 60 T Manco is shown in Figure 5.5. Ten percent of the separated UO_2 was less than 1 micron size and all the separated UO_2 was less than 2000 micron size except an occasional piece which fell from the open tube after shearing. Figure 5.5 shows a small but definite variation in the size distribution of porcelain fines for various lengths of cuts of a Mark I prototype assembly.

A redesigned "plane of contact" shear blade was tested with the Mark I prototype fuel bundle and produced the least amount of tube closure of any of the blades tested. The new blade is shown in Figure 5.6. Note the sharp blade with an increased blade length (1-5/16-in. compared to 3/4-in. for the original plane of contact blade). The original blade design is shown in Figure 5.7 for comparison.

The results of shearing two Mark I prototype fuel bundles with the original and new plane of contact blades are shown in Figure 5.8. The maximum tube closures are indicated in the photograph. The reduction in tube opening was greatly reduced with the new blade. Note also the much greater cleaness of the cut with the new blade. Very few scrap pieces of stainless tube wall were produced and remained on the bundle after shearing with the new blade. The new blade was dulled by the first 50-75 cuts which may seriously reduce its effective life.
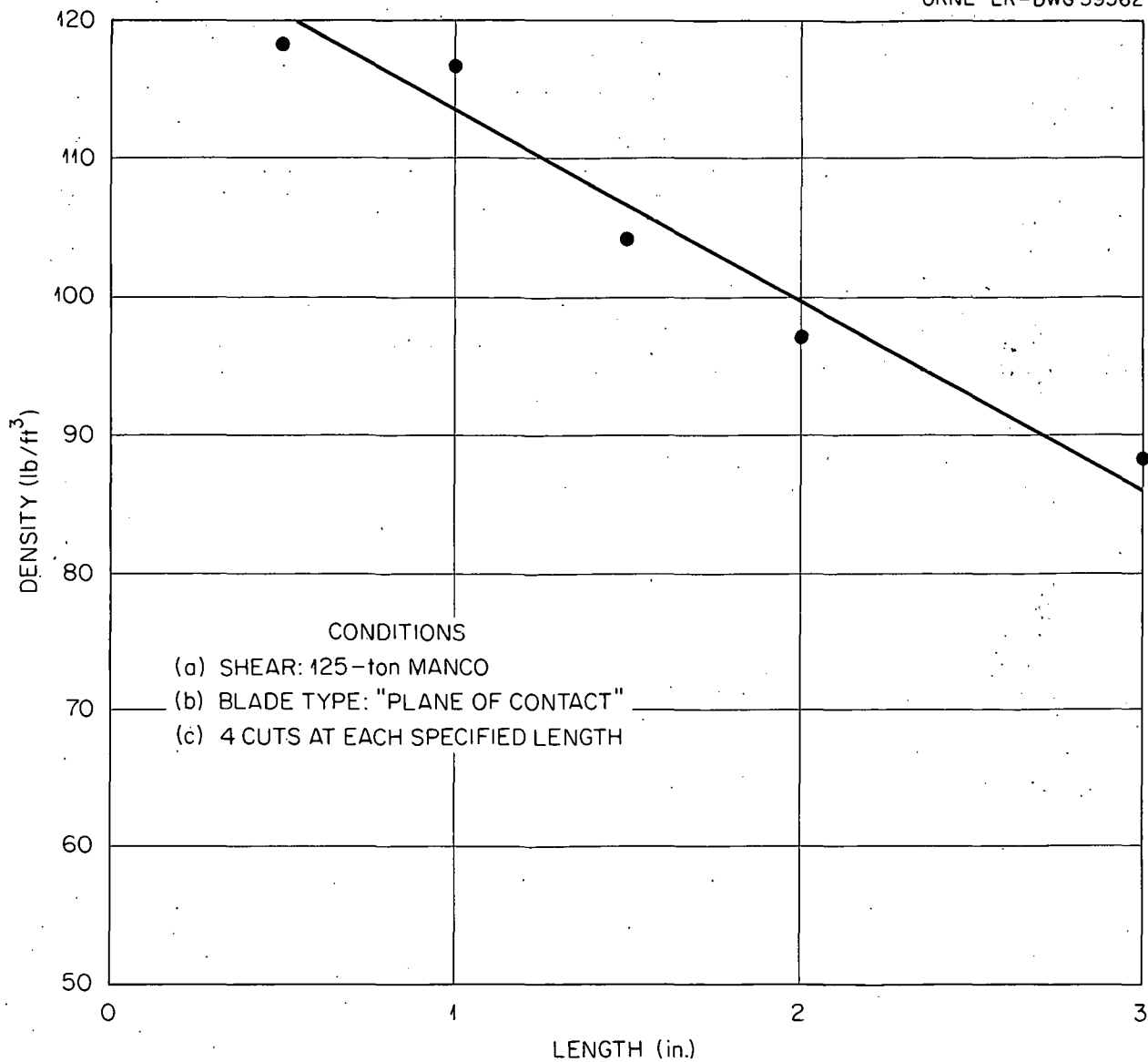
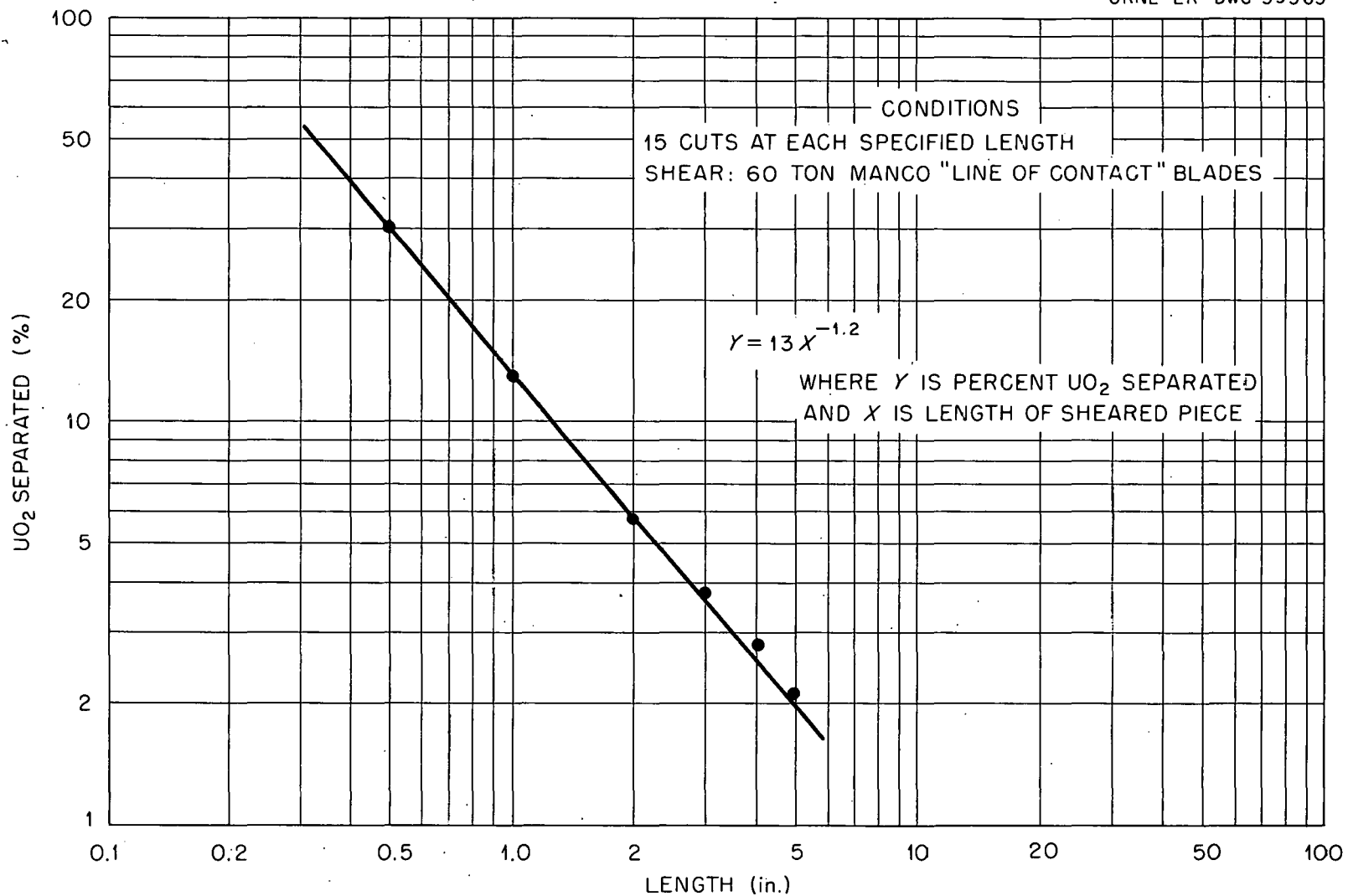Fig. 5.3. Approximate Bulk Density for Various Lengths of a Mark I Porcelain Filled Prototype Assembly.

Fig. 5.4. Percent of UO_2 Separated From Single 0.4-in.-dia Stainless Steel Clad UO_2 Rods vs. Length of Sheared Piece.
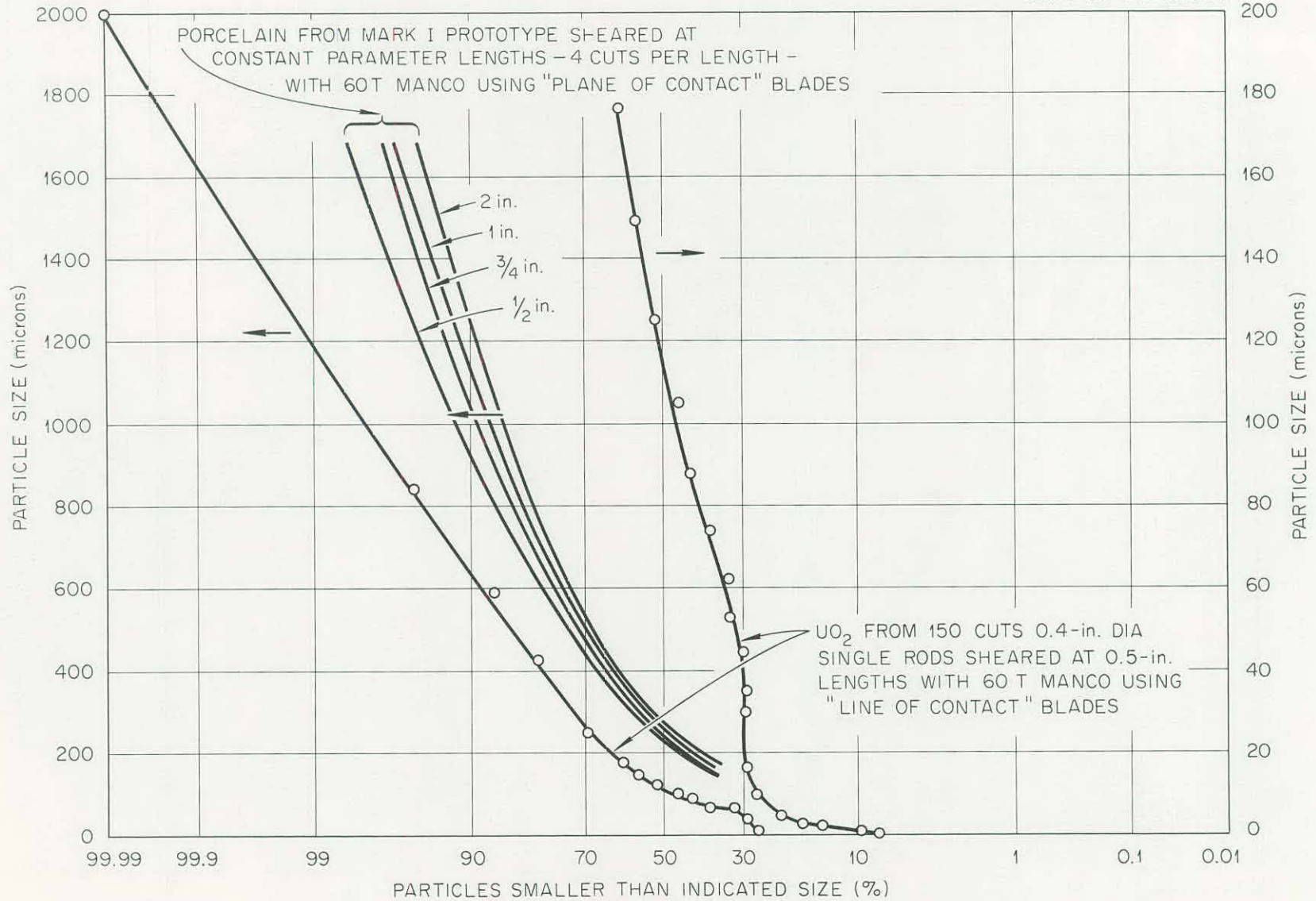
Fig. 5.5. UO_2 and Porcelain Size Distribution from Shearing Metal Clad Ceramic Filled Tubes.
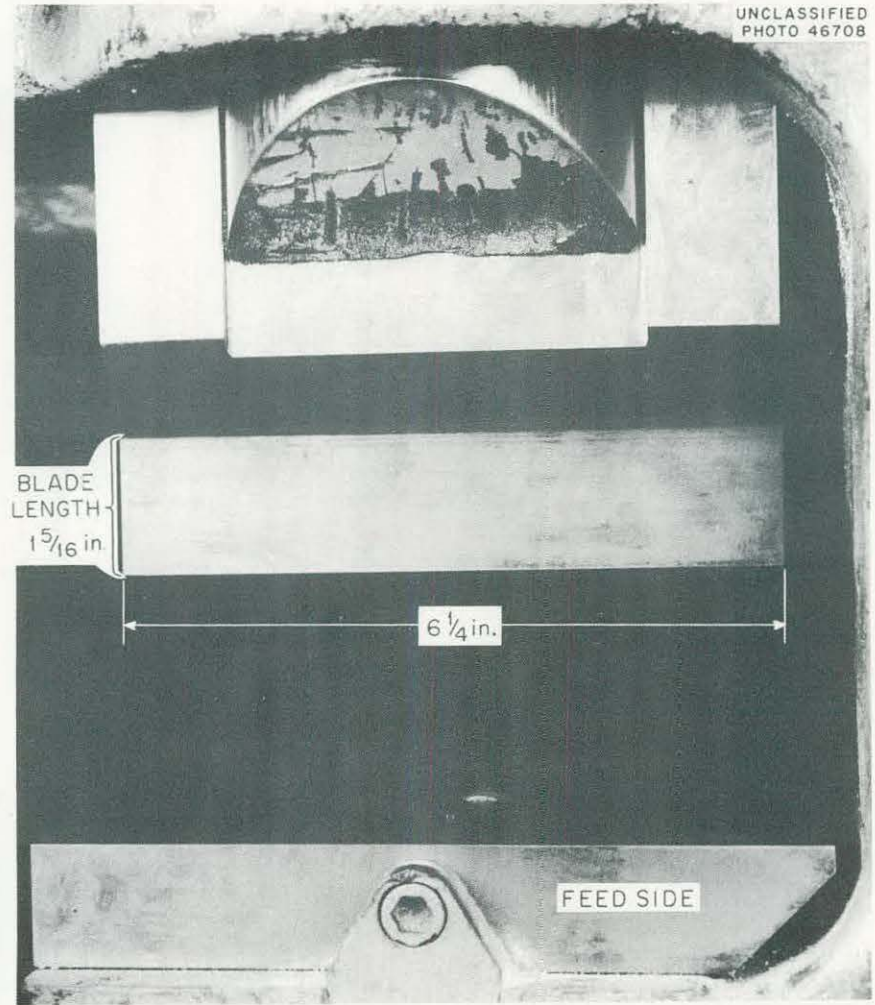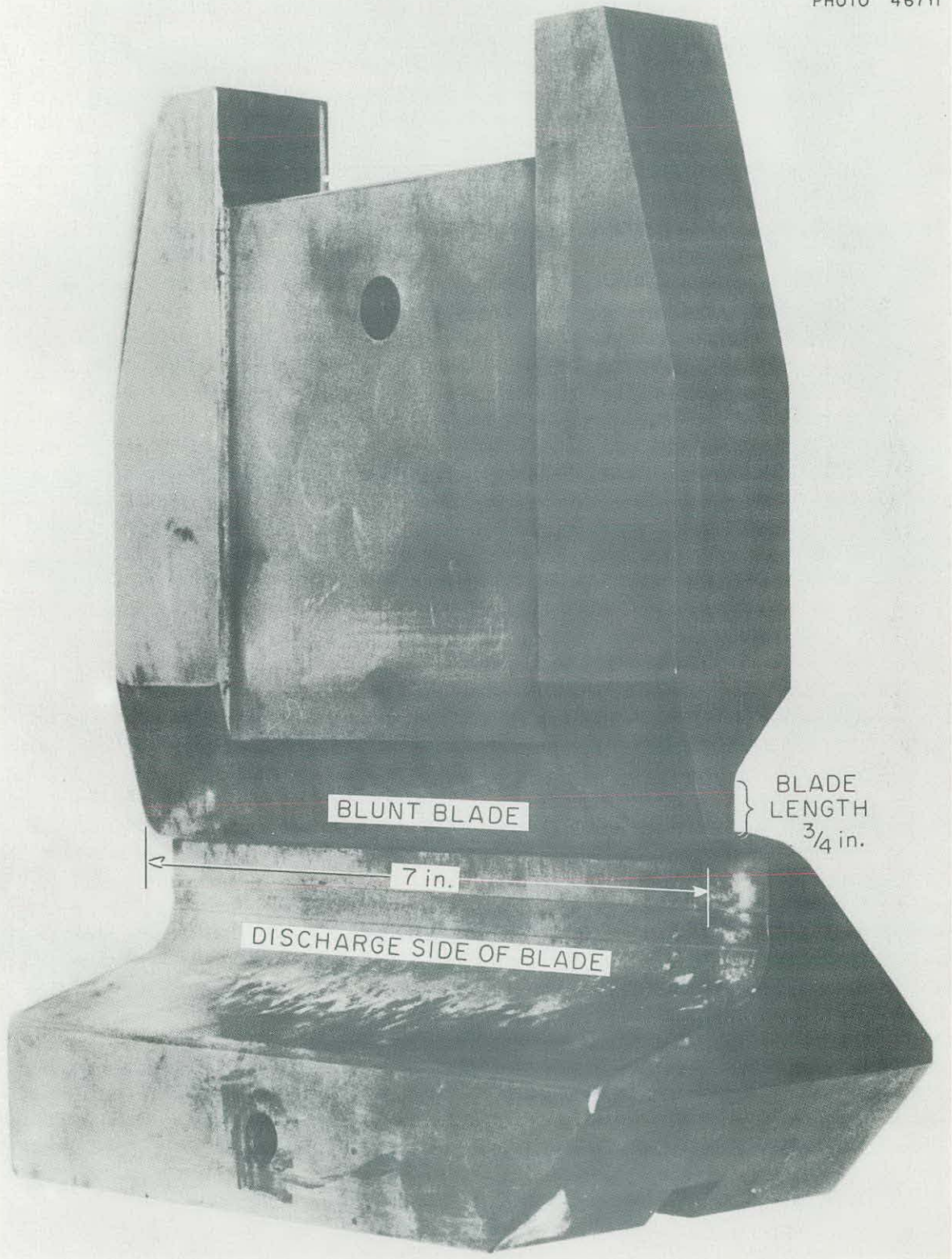
Fig. 5.6 Revised Plane of Contact Shear Blade.

Fig. 5.7 Original Plane of Contact Shear Blade.

MAXIMUM TUBE CLOSURES
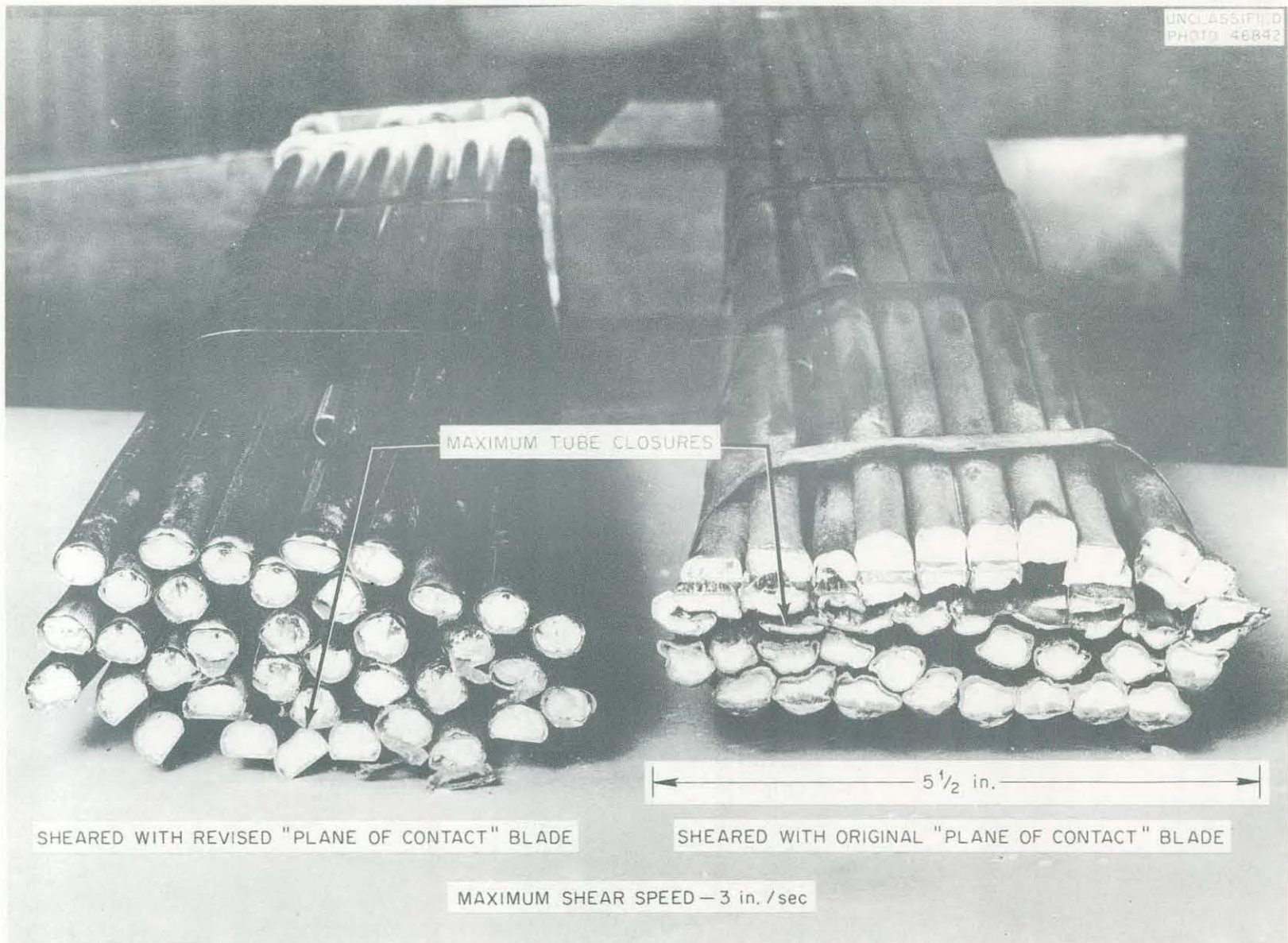
5 1/2 in.

SHEARED WITH REVISED "PLANE OF CONTACT" BLADE

SHEARED WITH ORIGINAL "PLANE OF CONTACT" BLADE

MAXIMUM SHEAR SPEED — 3 in. / sec

Fig. 5.8. Comparison of Results of Shearing Mark I Prototype Fuel Bundles with Different "Plane of Contact" Shear Blades.

The first blade which was used in this blade evaluation program was a
"line of contact" blade (Figure 5.9). This photograph exhibits the deficiency
of any straight blade edge in that the tubes spread out of the blade path as
the cutting progresses. A properly shaped blade would constrain the bundle
and prevent this spreading. The raised position of the prototype assembly
in the background indicates the need for a holding clamp which might also
function as a press to minimize void spaces between the tubes prior to
shearing.

A maximum of 0.7% by weight of the sheared material (see Table 5.3 in
the March UNOP monthly report) dislodged from shearing a Mark I into 3/4-in.
lengths was stainless steel fines, 50% of which was 840 micron size or smaller
(including an undetermined amount of steel from the retaining pieces to the
jig which kept the bundle from spreading horizontally). The side pieces
became noticeably abraded during the last 100 cuts of the 300 cut total
using the "plane of contact" blades.

Similarly, 88% of the porcelain fines (and 95% in the case of UO_2
fines - Figure 5.5) would be 840 micron size or smaller. A porous leach
basket of 1000 micron pore size would permit half the stainless fines to
pass through which would require removal in the feed clarification step.
The presence of jacket fines may prevent shearing and leaching of Zircaloy 2
clad oxides because of the potential explosion hazard of zirconium fines
in contact with HNO_3.

Liquid-Solid Separation. Filtration would be required if large volumes
of water were added to the enclosure around the shear head as the fuel shear-
ing progresses. For example, water might be sprayed on the cutting surfaces
and be drained together with wetted powder through a porous bottom collection
bucket. A preliminary test was carried out with a 10 sq. in. Poromesh
filter of nominal 150 micron pore size using water under a 15-in. head.
The flow rate decreased to less than 8 ml/min-sq-in. (Figure 5.10) for both
1/2-in. and 1-1/8-in. sheared lengths when the amount of chopped material
was increased to one-tenth of a Mark I prototype. This low rate probably
precludes the use of a filtration technique. Also, UO_2 would present a
greater filtration problem since the fines are generally smaller (Figure 5.5).

Collection and Transfer of Sheared Fuel. One of the most difficult
problems associated with shearing and leaching is a means of remotely trans-
ferring and collecting sheared solids. Clad rod fuel enters the process as
the complete fuel assembly and leaves as sheared disposable empty cylinders
and metal fines from which the fissile material has been leached.

The simplest experimental approach presently being considered to
solve most of the transfer problems is the use of a batch leacher containing a
porous basket liner (reported in the April monthly report). However, a
problem requiring solution in this approach is a method of transfer from
the leacher of stainless steel or zirconium fines in the 1000 micron size
range for separation in an external feed clarification step.

An effective removal system was developed. A 60° included angle cone
was installed on the bottom of the two leaching sections of the 100-kg leacher
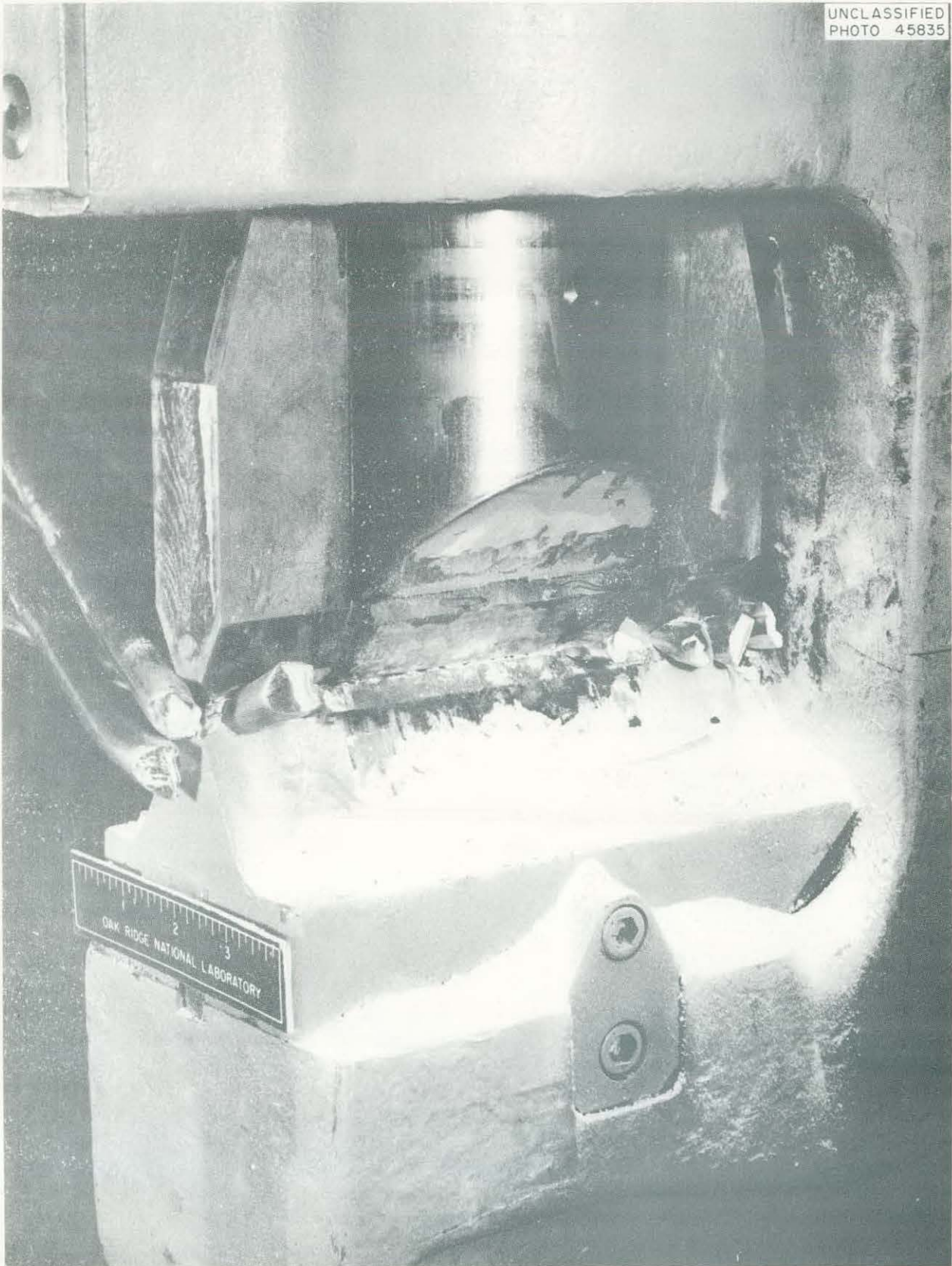
UNCLASSIFIED
PHOTO 45835

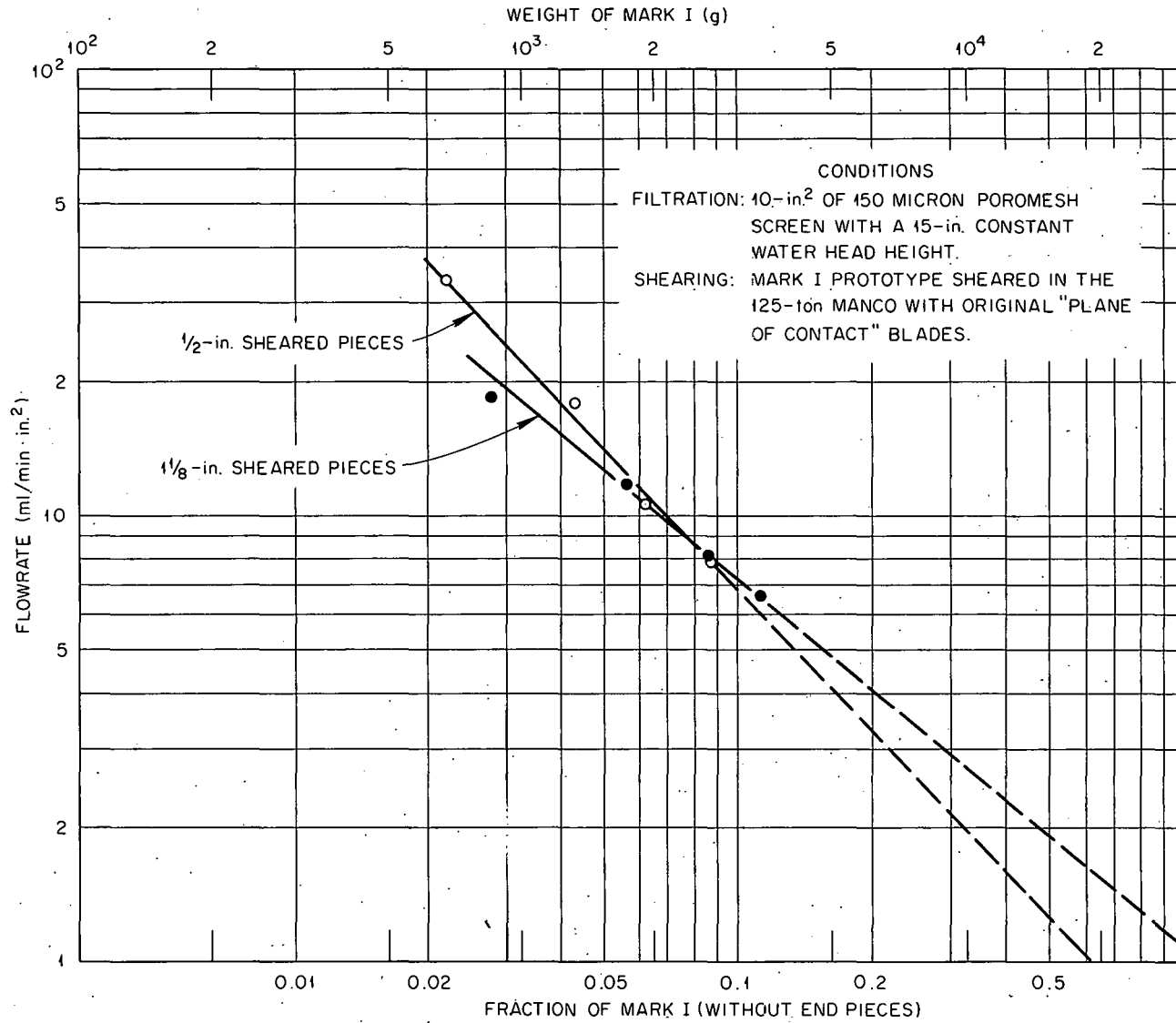Fig. 5.9. "Line of Contact" Blade Cutting Mark I Prototype.

WEIGHT OF MARK I (g)

CONDITIONS

FILTRATION: 10-in.^{2} OF 150 MICRON POROMESH
SCREEN WITH A 15-in. CONSTANT
WATER HEAD HEIGHT.

SHEARING: MARK I PROTOTYPE SHEARED IN THE
125-ton MANCO WITH ORIGINAL "PLANE
OF CONTACT" BLADES.

½-in. SHEARED PIECES

1⅛-in. SHEARED PIECES

FLOWRATE (ml/min·in.^{2})

FRACTION OF MARK I (WITHOUT END PIECES)

Fig. 5.10 Filtration Rates (ml/min·in.^{2}) for Various Weights of a Sheared Mark I Prototype Porcelain–
Filled Fuel Assembly on a Poromesh Filter at Two Lengths Sheared Piece.

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to concentrate the fines for removal in the 0.5-in. sch 40 uranyl nitrate product withdrawal line. Tests in a prototype cone showed that solids were easily removed by fluidization with a constant water stream from a 1/8-in. i.d. jet at rates from 0.3 to 0.5 gpm and removal through a 0.5-in. sch 40 withdrawal pipe operated with a 1/2-in. steam jet. A velocity of 3.5 ft/sec in the 0.5-in. line was sufficient to remove the fines.

The withdrawal line was successfully operated at distances up to 1.0-in. above the 7/8-in. flat disc bottom of the cone. The fluidizing stream outlet was 0.5-in. above the withdrawal outlet, directed downward, parallel, and rigidly attached to the withdrawal line. The distance between the bottom of the line and the disc bottom was maintained by 1/8-in. wide spacers which projected from the bottom of the vacuum line. This distance was optimized at 1/4-in. to permit a significant corrosion of the end of the withdrawal line without any significant effect on ability to remove fines.

With this geometry and throughout the range of these variable conditions, including the distance of the withdrawal line above the 7/8-in. disc, all tests removed at least 98% of a 308 g sample of 1000 micron size steel fines with a maximum of 6 liters of water in 30 sec or less. The remainder of the fines could be removed (except some very fine material adhering on the cone walls) in two additional vacuum jettings. Without the use of the 1/8-in. fluidizing stream as much as 50 g of fines remained in the cone after the first vacuum jetting. Most of these fines were held in the stagnant region behind the 1/8-in. wide spacers.

Leachers. A shearing and leaching process has been designed, equipment has been built, and installation is essentially completed for shearing and leaching non-irradiated 3-7/8-in. square prototype (36 0.5-in. dia tubes) assemblies of stainless steel clad UO_2. This process includes two leacher types, a 100 kg of UO_2 batch leacher and a spiral vibrating leacher (see Figure 5.10 in January monthly report) in which leaching of UO_2 is by a countercurrent downward flow of nitric acid. This facility will be operated cold in advance of installation in the High Level Segmenting Facility for shearing and leaching irradiated fuel assemblies. Fabrication of the batch leacher is 95% complete. The vibrating spiral leacher was completed and is ready for initial operation. Detailed construction drawings are finished and construction has commenced on an inclined drum leacher. An inclined tray leacher is in the conceptional design stage.

The vibrating spiral leacher is an alteration of a Syntron spiral conveyor and is described in the January 1959 Unit Operations monthly report. From preliminary material transfer studies of the unit, the solids holdup on the spiral was 53 lbs for a single layer of 0.5-in. dia 1-in. long empty stainless steel tubing and estimated to be 217 lbs for UO_2 filled tubing. There appeared to be adequate liquid coverage of the single layer with a minimum water flow rate of 1 gpm. There was no interference with bulk solids transfer at flow rates up to 3 gpm, except that stainless steel fines and porcelain could not be transferred up the conveyor against any reasonable liquid flow rate. UO_2 fines washed out of the trays will present no problem for they will be dissolved in the holdup liquid at the bottom of the leacher. However, the stainless fines must be jetted out periodically to prevent interference with material transfer of stainless clad UO_2 entering the spiral.

In the inclined drum leacher (Figure 5.11) metal clad UO_2 is transferred through the spiral countercurrent to nitric acid leach by rotating the inner cylinder housing the spiral. The rate will be regulated to provide UO_2-free nitric acid washed metal cladding for disposal at the end of the spiral.

Leaching Studies. Three batch leaching runs were made in 13 $\underline{M}$ HNO_3 (reported in the April monthly report), two with 565 g UO_2 and the third with 1210 g UO_2 with lengths of 0.5-in., 1.0-in. and 2.75-in. sheared pieces of 0.4-in. dia stainless steel tubing filled with UO_2 pellets (Figure 5.12). The two runs using 1-in. and 2-3/4-in. lengths of stainless clad UO_2 were conducted at boiling temperature. The run with 1/2-in. lengths was started at room temperature, slowly raised to boiling in a period of 45-min and maintained at the boiling point for 2-hr to observe the extent of the reaction. No foaming was observed at any time, but the reaction of acid with UO_2 fines started immediately at room temperature.

The 13 $\underline{M}$ HNO_3 was reduced to ~11 $\underline{M}$ after complete reaction of each batch of the 1/2-in., 1-in. and 2-3/4-in. sheared lengths in 20, 25 and 85-min, respectively. The average leaching rates were 0.09, 0.17 and 0.02 g/min/g of original U, respectively.

Fuel Disassembly. The primary approach to mechanical fuel processing includes shearing the entire fuel assembly with end caps removed except for the Nuclear Ship Savannah fuel assembly which will be quartered. However, disassembly into slabs and individual elements is being considered as a possible alternate approach to the preparation of shear feed.

It was not possible to disassemble a Consolidated Edison prototype fuel assembled with Coast Metals 50 brazing metal, using the same impact wedge which successfully disassembled the Consolidated Edison assembled with Nicrobraz 50 (see March monthly report, Unit Operations Section) because of the greater ductility of this different braze material. The composition of the two brazing metals are:

Nicrobraz 50		Coast Metals 50	
Nickel	- 74%	Nickel	93.2%
Phosphorus	- 10% ± 1%	Silicon	3.5%
Chromium	- 13% ± 2%	Boron	1.9%
		Iron	1.4%

It is the embrittling quality of the 10% phosphorus in Nicrobraz which makes disassembly easy. The Coast Metals braze will probably not be considered for use in fuel elements because of the high neutron absorption cross-section of the boron constituent.

5.4.2 SRE Mechanical Reprocessing - G. A. West, J. C. Rose

Decladding. The mechanical equipment for decladding the SRE fuel element (0.79 in. o.d. x ~8 ft long, 0.010 in. NaK bond, stainless steel clad with 0.010 in. wall) has been fabricated by the Southern Machine Co., Chattanooga, Tennessee. The equipment was installed in Bldg. 4505 for shakedown tests before final installation in the segmenting hot cell.
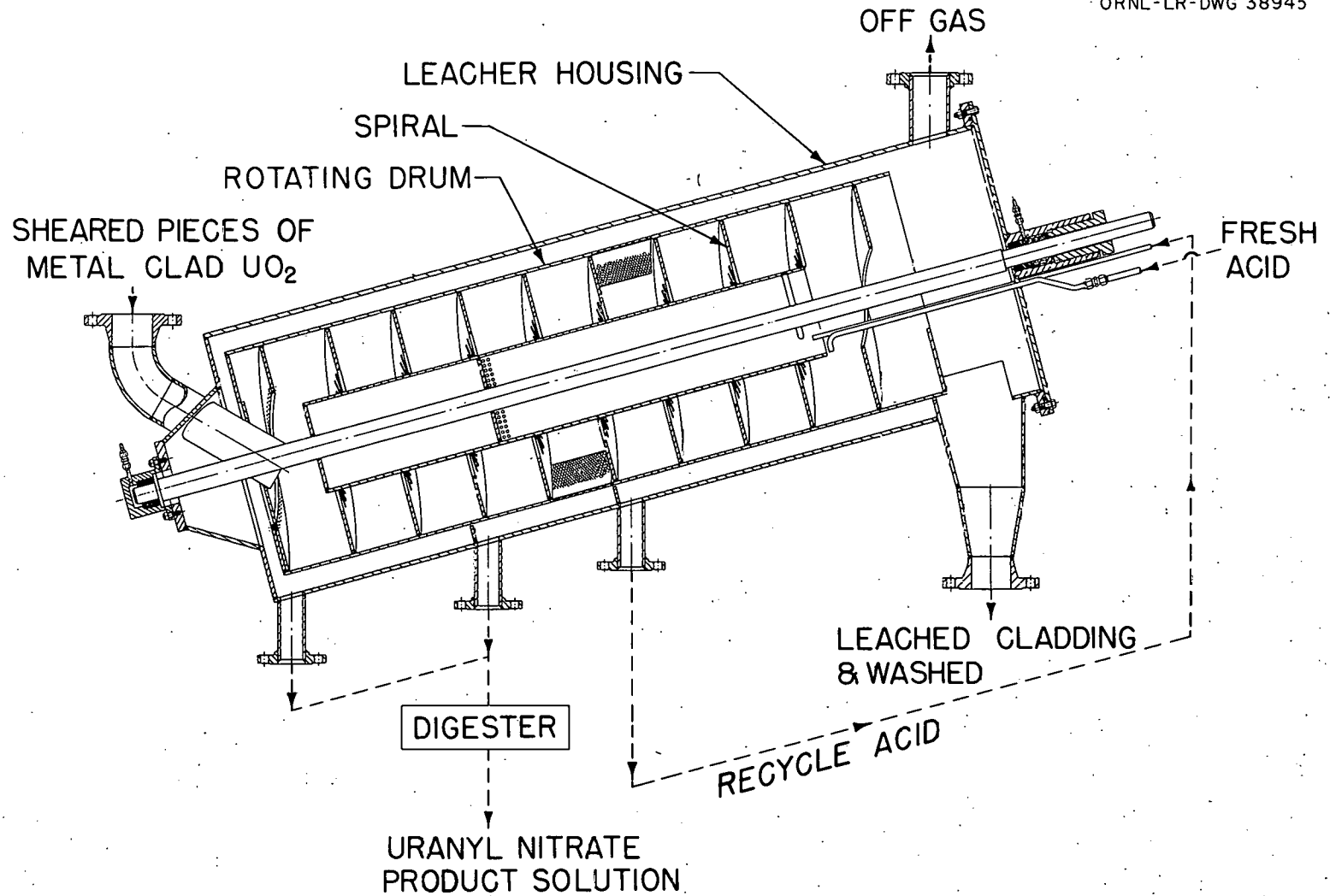
OFF GAS

LEACHER HOUSING

SPIRAL

ROTATING DRUM

SHEARED PIECES OF
METAL CLAD UO_2

FRESH
ACID

LEACHED CLADDING
& WASHED

DIGESTER

RECYCLE ACID

URANYL NITRATE
PRODUCT SOLUTION

Fig.5.11. Inclined Drum Leacher for Countercurrent Nitric Acid
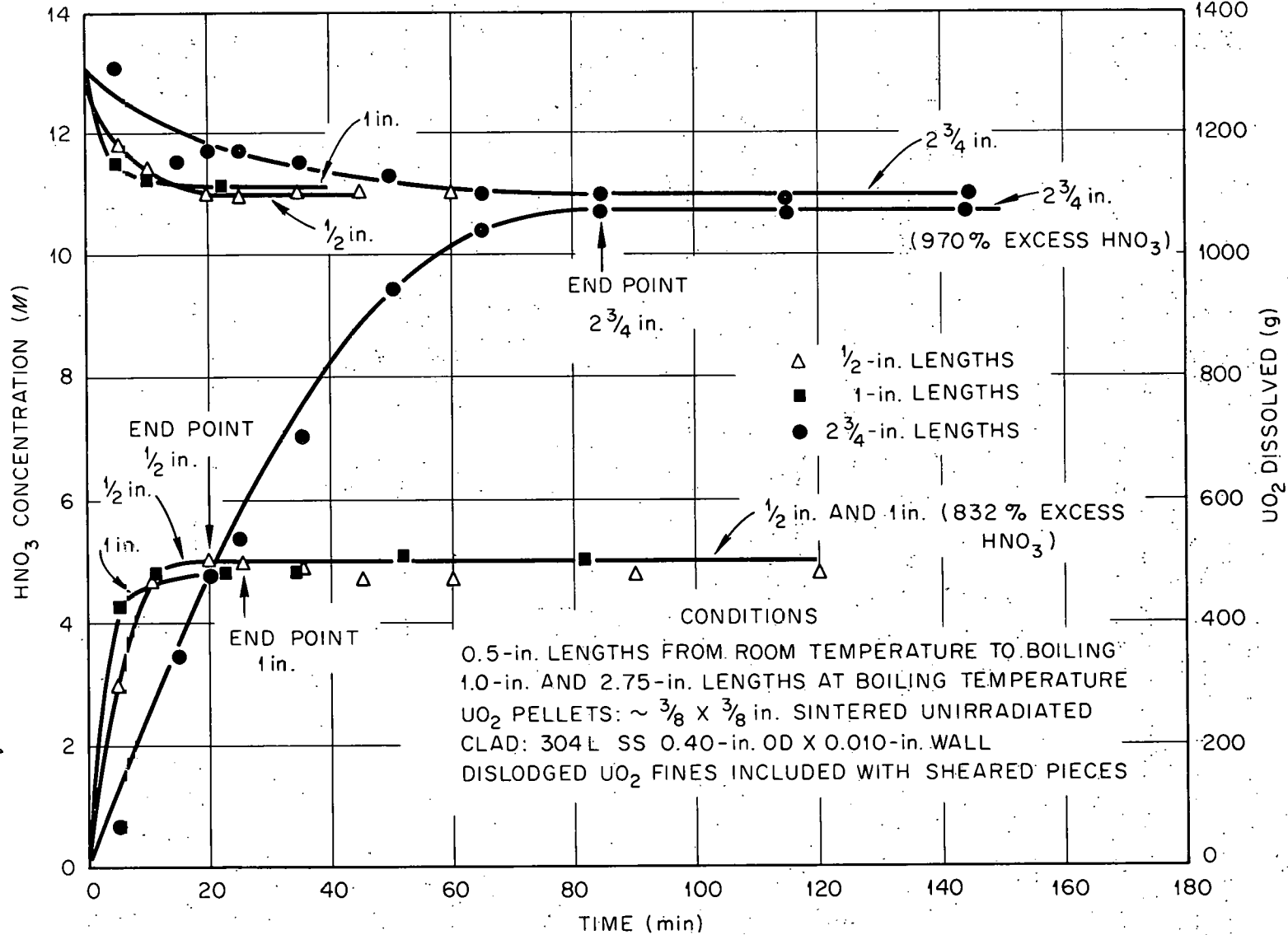Leaching of UO_2 from Sheared Pieces of Metal Clad UO_2.

Fig.5.12. HNO₃ Leaching of Sheared SS Clad UO₂ vs Time.

The principle operation of the decladder is to expand hydraulically the 10 mil stainless steel jacket and to push the 12 slugs, 0.75-in. o.d. x 6-in. long, out of the cladding with the same hydraulic fluid after the end plugs have been removed by roll cutters in a separate operation of the equipment. A threaded tubular "jack-screw" pushes the slugs from the jacket if the hydraulic technique fails. This mechanical technique will be tested as a method of mechanically preparing the fissionable material for direct re-processing using the present nitric acid processing techniques in stainless steel equipment.

Other operations with the SRE fuel are (1) the collection of the NaK bonding material removed from the cladding and the reaction with steam in a special reaction vessel, (2) the steam cleaning of uranium slugs from oil and entrained NaK, and (3) the recanning of the 12 slugs in an aluminum can for storage and handling. The hydroxide produced in the NaK-steam reaction is to be diluted and discharged to the hot waste system, nitrogen will be mixed with the hydrogen evolved in an amount to give < 4% H_2 which is discharged to the cell exhaust through a water aspirator.

NaK Reactor. A special vessel has been designed to receive the 98.4 ml of NaK discharged from a single SRE fuel element for reaction with steam and discharging to waste. Laboratory tests of the NaK (22% Na-78% K) reaction with steam shows that the reaction proceeds uneventfully with a controlled steam rate of 0.2 to 0.4 lb/hr. This steam rate produced hydrogen at a rate of ~1 liter/min. The theoretical volume of hydrogen produced from 98.4 ml of NaK is 32.3 liters. Due to oxide coating on the NaK and to oil surrounding water droplets only about 50% of the water actually reacted with the NaK. It is possible that a faster hydrogen evolution rate, up to 1.6 liter/min, can be safely accommodated in a total reaction time of 20 minutes. The maximum safe reaction rate is to be determined in future tests.

The laboratory reaction vessel was a 2 liter boiling flask connected to a reflux condenser, a nitrogen purge system, and a wet test meter. The reaction temperature ranged from 120 to 243°C during the test. The minimum temperature of 120°C was maintained when the reaction was not in progress by submerging the bottom portion of the flask in an oil bath at 120°C. Particles of NaK were observed to flash in the vapor phase and react violently at a steam rate of 0.46 lb/hr. The reaction temperature reached 220°C and water was condensed and refluxed back to the flask which contributed to the violent reaction.

Scouting tests show that the NaK-water reaction could not be carried out satisfactorily with moist nitrogen or water droplets. The moist nitrogen reaction (N_2 bubbled through water at 90°C) was extremely slow (~0.3 ml NaK reacted per minute). The water droplet addition caused spasmodic reactions in which large quantities of hydrogen was evolved. A safe N_2-H_2 ratio would be difficult to maintain with such a reaction system.

6.0 VOLATILITY

R. W. Horton

Dry Hydrofluorination - L. E. McNeese

The Oak Ridge National Laboratory Volatility Process for recovery of irradiated uranium from heterogenerous matrix-type zirconium base fuel elements consists of hydrofluorination of the fuel element to the corresponding metal fluorides, fluorination of the resultant UF_4 to volatile UF_6, and UF_6 purification by a NaF sorption-desorption.

A gas-metal reaction between a metallic fuel element and anhydrous HF in the temperature range of 550-1050°C appears promising as a means of fuel element hydrofluorination. Experimental data on gas-metal hydrofluorination have been reported in ORNL-CF-59-1-17, ORNL-CF-59-2-45, ORNL-CF-59-4-47, and ORNL-CF-59-5-47.

Since the major reaction product, ZrF_4, is volatile at temperatures above 902°C, a study was initiated for development of a collection-condensation system of ZrF_4 and other volatile metal fluorides produced by the gas-metal reaction.

A ZrF_4 condensation-collection system has been designed and installed. Three runs were made in which ZrF_4 was sublimed from the reactor vessel, condensed, and collected. Condensation rates varied from 150 to 501 g ZrF_4 per hour with noncondensable rates of 0.23-2.1 liters N_2/g ZrF_4.

The ZrF_4 condenser, shown schematically in Figure 6.1, consisted of a 54-in. vertical section of 4-in. dia sch 40 Monel pipe having an autoresistance heated ZrF_4 inlet 3-in. from the bottom. A 12-in. Dynel star-shaped blowback filter was provided at the top for final solids removal. A condensate collection vessel was provided at the bottom of the condenser. The condenser was air cooled by natural convection.

The Inconel autoresistance heated inlet is shown in Figure 6.2. A double tube design was used in order to provide a high temperature at the inlet tip. Since the cross section of the 1-in. dia tubing was 30% greater than that of the 3/8-in. pipe, the heat generation rate in the tubing was reduced to 75% of that in the pipe. The condenser wall in the vicinity of the inlet operated at approximately 250°C when the tip was operated at 950°C.

The 3/8-in. pipe served as an off-gas line for the dry hydrofluorination reactor. The 3/8-in. pipe was attached to the reactor at a point heated by nichrome wire furnaces so that a resistance heated tip was not required. The heat generation rate in the section of Inconel pipe inside the furnaces was lowered by increasing the cross section with nickel metal. (The electrical resistivity of nickel and Inconel are 57 and 590 ohms/cir mil ft at 0°C, respectively.)
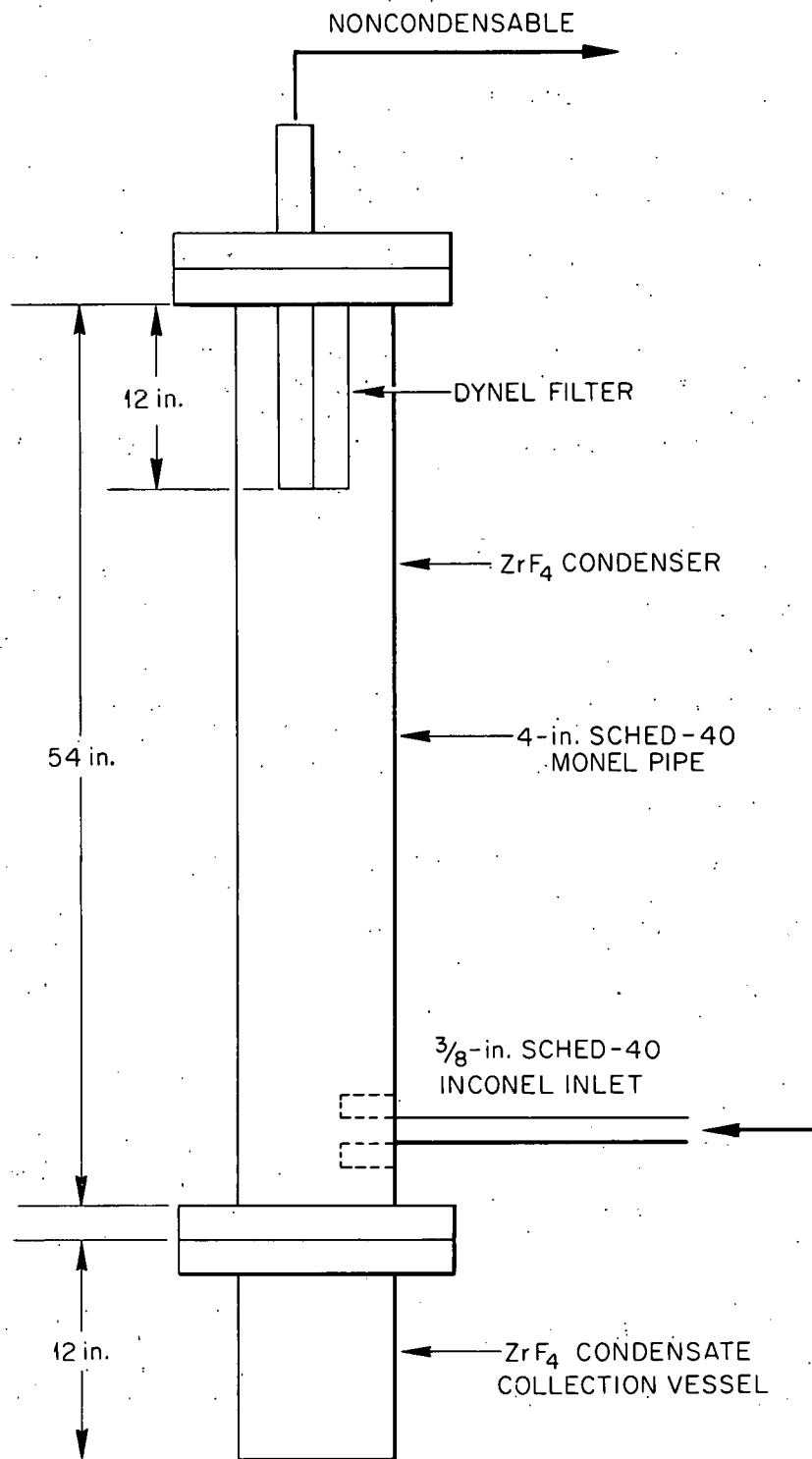
-58-

NONCONDENSABLE

12 in.

DYNEL FILTER

ZrF_4 CONDENSER

54 in.

4-in. SCHED-40
MONEL PIPE

$\frac{3}{8}$-in. SCHED-40
INCONEL INLET

12 in.

ZrF_4 CONDENSATE
COLLECTION VESSEL

Fig. 6.1. Air-Cooled ZrF_4 Condensation-Collection System.

SCHED-40
MONEL
PIPE

4-in. DIA

1-in. DIA x 0.0625-in.
WALL INCONEL TUBE

0.085-in. THICK
INCONEL PLATE
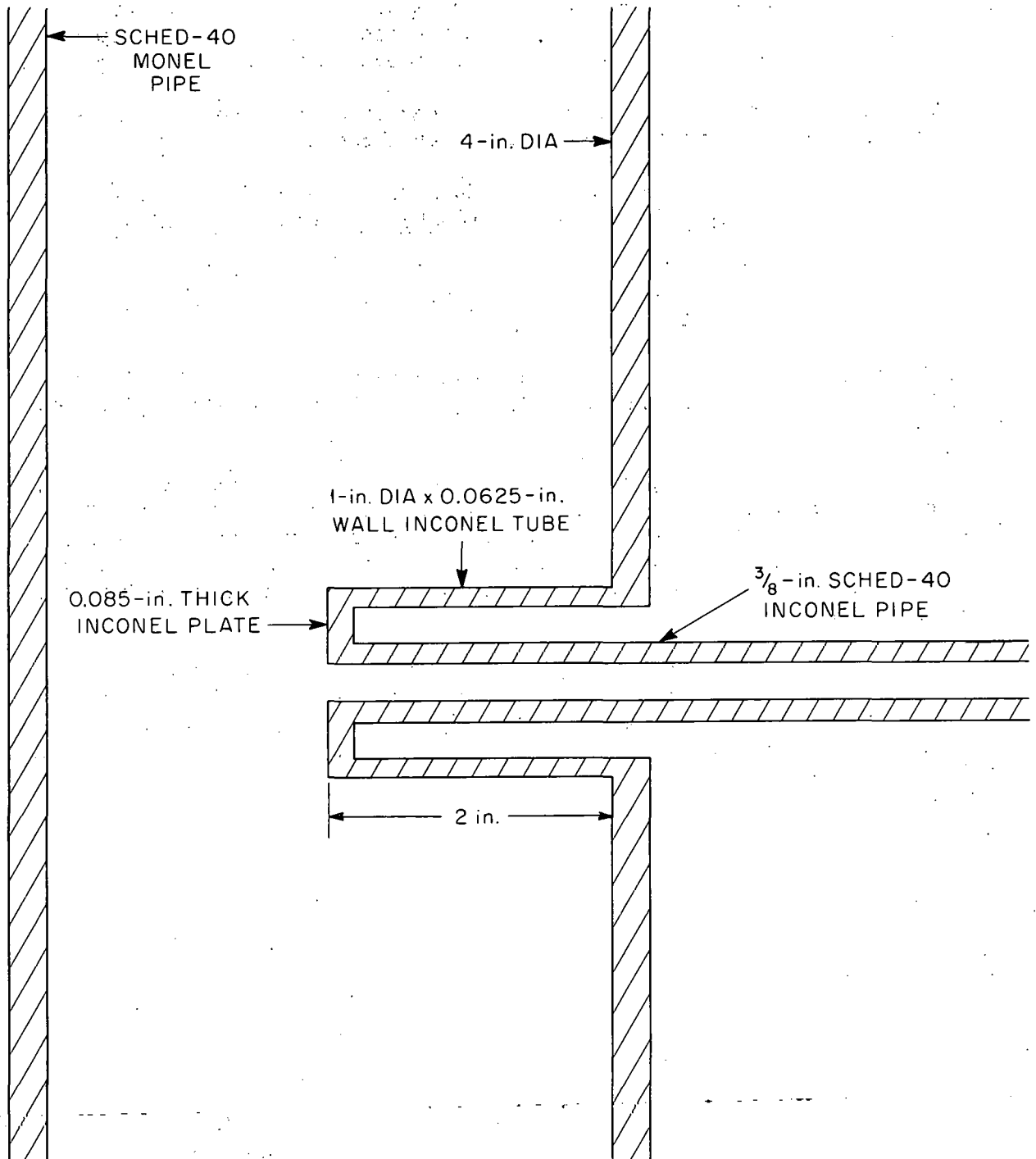
3/8-in. SCHED-40
INCONEL PIPE

2 in.

Fig. 6.2. Autoresistance Heated Condenser Inlet.

A series of three runs was made in which 450-1500 g ZrF_4 was sublimed from the reactor and collected in the condenser system in the presence of a N_2 flow to simulate H_2 produced by the gas metal reaction between Zr and HF. No HF was present, so a glass collection vessel and a Lucite upper flange could be used for observation of the condensation-collection process.

Condensation rates and noncondensable gas rates for the three runs are given below. Operating time for all runs was three hours.

Run	Condensation Rate (g ZrF_4/hr)	N_2 Rate (SCFH)	ZrF_4 Concentration (g ZrF_4/liter N_2)
1	150	2.0	2.7
2	501	4.0	4.4
3	410	30	0.48

The ZrF_4 vapor phase concentration obtainable as a result of 100% HF utilization in the gas-metal reaction and 100% ZrF_4 volatilization is 3.73 g ZrF_4/liter H_2.

In each test, the ZrF_4 was successfully collected in the catch vessel. The material was finely divided and had a tap density of 2.6 g/cc. The Dynel filter satisfactorily removed ZrF_4 entrained by the noncondensable stream. More than 95% of the solids caught on the filter was returned to the catch vessel by a blow back. No pressure buildup occurred during three hours of operation.

Methods of further processing the condensate are being evaluated. These methods include dissolution of the residue in a low melting fluoride eutectic with subsequent uranium recovery by conventional volatility processing, and recovery of uranium from the residue by direct fluorination of the sublimate.

7.0 WASTE PROCESSING

M. E. Whatley

Reduction to Solids

The purpose of the waste processing program is to provide engineering data for the design of a pilot plant for reduction of radioactive waste to solids for ultimate disposal. During this report period, thermal conductivity values of calcined solids were measured and preliminary flooding data with water for the 3-in. dia off-gas distillation column were collected.

7.1 Thermal Conductivities Measurements - C. W. Hancher, J. J. Perona, J. S. Taylor

The thermal conductivities of granular Darex, Purex and TBP-25 calcined solids were measured at room temperature by the transient method described in the April UNOP monthly report (ORNL CF 59-4-47). The results are shown in Table 7.1. These results are consistent with results reported by other sites using different methods. For these determinations, the calcined solids were dumped out of the pots and screened with a 1 mesh screen before being introduced into the thermal conductivity measuring equipment. This breaking of the cake is a reasonable representation of the condition of the solids after handling in a waste processing plant. Since the granular solids have lower thermal conductivities than cellular solids, the procedure should have yielded conservative numbers.

The thermal conductivity of calcined solids from simulated TBP-25 waste was determined over the temperature range 80 to 1500°F by using the same equipment mounted in a furnace (see Figure 7.1). The data can be represented by the linear expression

$$k = 3.1 \times 10^{-5} \ T(°F) + 0.07.$$

At about 1000°F the thermal conductivity was greater than 0.1 Btu/hr ft °F, which was the value assumed for many of the heat transfer calculations previously reported.

7.2 Distillation Treatment of Off-Gas - J. J. Perona, C. W. Hancher

During preliminary testing it was impossible to control the steam pressure to the reboiler within small enough limits to obtain accurate steady-state measurements in the distillation column. Therefore the steam system was replaced with a 12 KW (220 volt) electrical heater. The heater is clad with 347 ss for nitric acid service. The water flooding point for the 3-in. dia x 10 ft column filled with 1/4-in. Raschig rings was 550 lb H2O/hr sq ft (see Figure 7.2). This distillation column will be used for treatment of the off-gas from the waste calcination pot.

Table 7.1. Thermal Conductivities of Granular
Solids from Calcination of Waste

Run No.	Type of Waste	Bulk Density g/cc	K Btu/hr-ft-°F	Temp °F	Granular Density g/cc
R-11	TBP-25	0.45	0.054	77	0.44
R-12	"	0.45	0.045	86	0.44
R-13	"	0.45	0.043	80	0.47
R-14	"	0.40-0.43	0.063-0.075	80	0.43
	Purex	0.77	0.063	80	0.83
R-1,2,3	Darex	0.9	0.053	77	0.68
R-4,5,7	"	0.6-0.8	0.097	77	1.10

BULK DENSITY 0.43 g/cc

$k = 3.1 \times 10^{-5} \; T(°F) + 0.07$

k, THERMAL CONDUCTIVITY (Btu/hr · ft · °F)
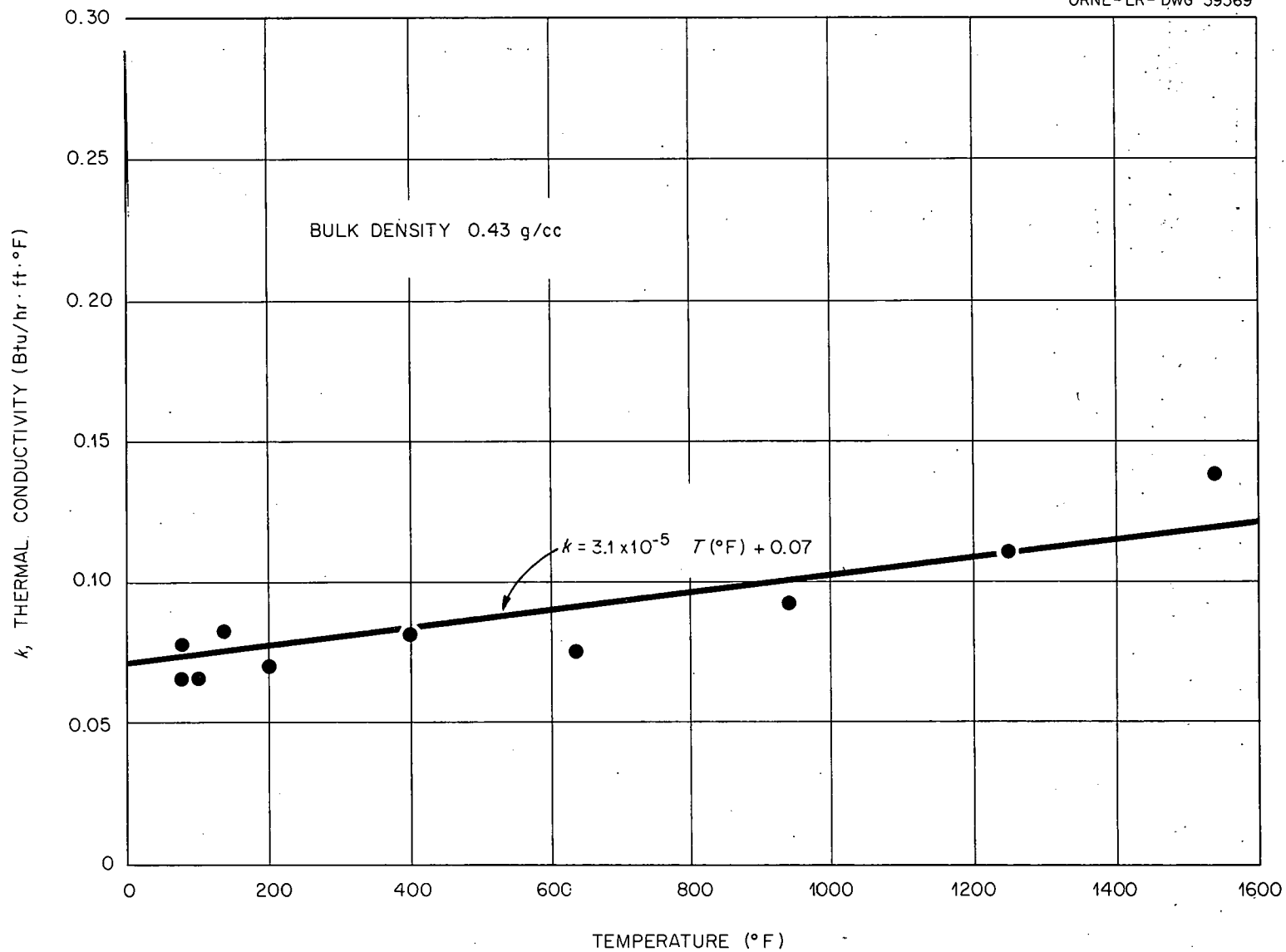
TEMPERATURE (°F)

Fig. 7.1. Thermal Conductivity of Granular Solids from Calcination of TBP-25 Waste.

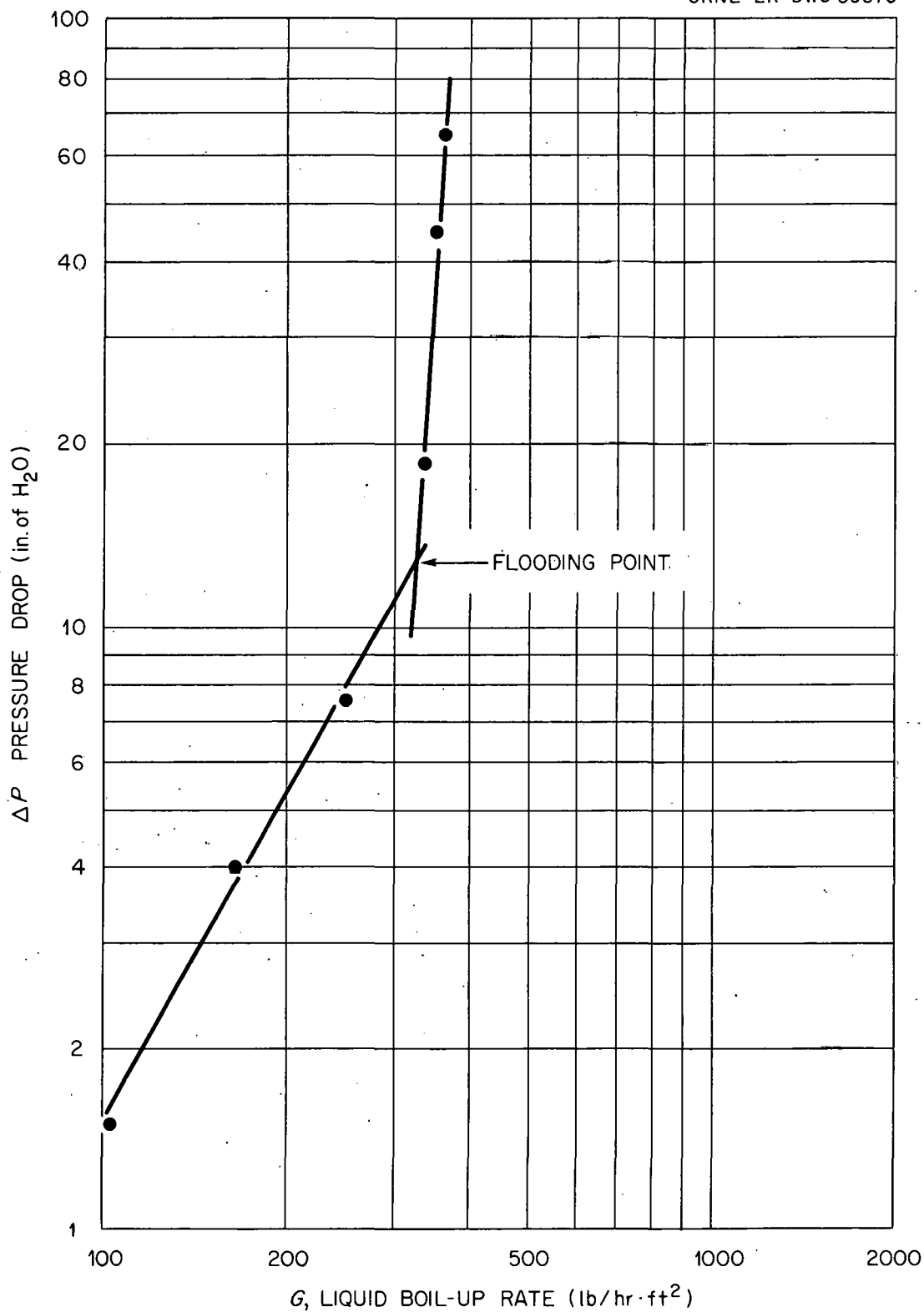Fig. 7.2. Flooding Point for 3-in. Distillation Column Packed with ¼ -in. Raschig Rings Using H_2O.

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