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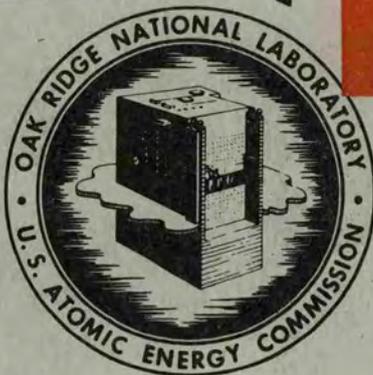
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CHEMICAL TECHNOLOGY DIVISION MONTHLY
PROGRESS REPORT, JANUARY, 1957

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All studies reported here are preliminary and conclusions are subject to change. The information is published as a formal report only to permit ready dissemination of data to interested persons.

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ABSTRACT*

I. Feed Materials Processing

Metallex Process. Separation of thorium mercuride from by-products of Metallex amalgam reduction by hot filtration was 60% effective. Scrubbing of Metallex product amalgams with fused $\text{AlCl}_3\text{-NaCl}$ or ZnCl_2 removed both by-products and thorium from the mercury. Metallex-produced thorium billets, 1 in. dia, were extruded to 0.25-in. rod. Rolling and drawing characteristics of the extruded metal appeared to be satisfactory.

Improvements in the large-scale equipment are essentially complete.

Fluorox Process. The rate of oxidation of carbon-free UF_4 is immeasurably low below $\sim 600^\circ\text{C}$. The UF_4 oxidation observed when UF_4 -carbon pellets are reacted with O_2 in the temperature range $200\text{-}600^\circ\text{C}$ is attributable to high local temperatures created by combustion of the carbon. The maximum local temperature produced by combustion at 400°C is predicted to be $800\text{-}1000^\circ\text{C}$.

The auxiliary equipment for the fluidized-bed installation is being improved.

Excer Process. Iron was shown to be effective for reducing uranyl ion to uranous. It may be effectively removed below specifications in the UF_4 product.

Uranium Recovery by Ion Exchange. Uranium was successfully recovered from fluoride-containing scrap in a 2-in.-dia Higgins continuous ion-exchange contactor.

In tests in the 12-in.-dia column at Grand Junction, the HETS increased slightly with increasing feed flow rate.

*Information on raw materials, Chemical Development Section C (K. B. Brown, Section Chief) reported in ORNL-2268 (unclassified).

II. Heterogeneous (Power) Reactor Fuel Processing

Fused Salt--Fluoride Volatility Process. In preliminary tests the volatility pilot plant operated without difficulty. The type 347 stainless steel charge melt vessel corroded excessively and a new nickel vessel is being fabricated. A few other changes were indicated and are being made.

In further tests on embrittlement of nickel by sulfur impurities, a foil test was developed sensitive enough to detect 1 ppm of sulfur in the fluoride melt.

Processing of stainless steel--containing fuel elements by the Fused Salt--Fluoride Volatility Process was indicated to be possible.

A nickel-packed column between the NaF bed and the UF₆ cold trap did not greatly increase the product UF₆ decontamination from ruthenium. Some PuF₆ formed in the fluorination step volatilized but did not reach the second NaF bed.

Darex Process. Type 304 stainless steel dissolved in 4 M HCl--6 M HNO₃ at rates varying from 25 to 130 mg/m²/cm² as the acid feed rate was increased from 20 to 200 ml/min.

Mechanical performance of the 4-in.-dia bubble-cap column and auxiliary equipment was satisfactory in preliminary tests on removing HCl from dissolver solutions.

By elimination tests tantalum was indicated to be the best material of construction for the dissolver and stripping column.

Zircex Process. The presence of carbonaceous impurities in the hydrogen chloride gas used in the Zircex process apparently increased the insoluble losses. The residue remaining after hydrochlorination with pure hydrogen chloride gas was readily slurried into water prior to leaching with nitric acid.

A high-cobalt alloy (S-816 or Vitallium) appears to be the most desirable material for construction of a combination hydrochlorinator-dissolver.

Hermex Process. In the initial Hermex uranium run in stainless steel apparatus gross γ and β decontamination factors over the dissolving-slagging step were 2.62 and 1.23, compared to factors of 7.7 and 6.7 for similar materials in runs in glass apparatus. Oxygen admitted to the dissolver during the run was only 0.45%, sufficient to oxidize quantitatively all fission products, and this is thought to be the reason for the lowered decontamination factor. For the run, the relative effectiveness of dissolution-slagging, cold filtration, and aqueous washing in removing fission products was 42:4:1 for gross γ and 22:1.4:1 for gross β .

Thorex Process. A third uranium cycle and additional protactinium and U-233 storage systems are being added to the pilot plant.

Aqueous Dissolution Studies. Zircaloy-2 was completely stripped from obsolete PWR reject elements by boiling 14 M sulfuric acid at rates as high as 73 mg/cm²/min and with uranium losses of about 0.02%.

Mechanical Processing. The successful removal of UO₂ from a zirconium tube (a PWR blanket element) was demonstrated with the MacKintosh-Hemphill decladding machine.

III. Homogeneous Reactor

HRT Chemical Processing Plant. Design and installation of the fuel processing plant were completed. Initial tests were made of the high-pressure system, and modifications are being made of the low-pressure system.

Preliminary design of the blanket processing plant is under way.

Experimental loop P-1 was installed and found satisfactory in initial tests. The titanium pump for loop P-2 performed satisfactorily in room-temperature tests.

IV. General Chemical and Engineering Studies

Waste Studies. Treatment with alkali followed by ion-exchange is proposed for aluminum nitrate-containing wastes. The bulk of the radioactive material, including high yields of the long-lived isotopes, is stored in small packages. Cheap storage is provided for material containing short-lived isotopes with low radiation energy. The bulk of chemicals and water is recycled instead of being discharged to the environment.

Ion-exchange Technology. Iron, as a stand-in for plutonium, was removed from a uranium stream by Dowex-50 ion-exchange resin.

A new liquid take-off was fabricated for the 36-in.-dia column.

The Jury continuous ion-exchange column operated satisfactorily in evaluation tests.

Metal Recovery Plant. To date 20 tons of uranium has been recovered from ORNL tank farm wastes.

Miscellaneous Studies. A sieve-plate column, which is less complicated than the bubble-cap columns now in use, removed TBP from a uranyl nitrate solution with a 25% efficiency.

Vacuum distillation, as a recovery method for TBP-diluent mixtures grossly degraded by radiation, appeared to be fairly efficient; about 90% of the TBP and diluent were recovered sufficiently pure for plant reuse.

Preliminary analysis of data from 1-in.-dia hydroclones indicated that good separation of Amsco diluents and water was achieved.

Construction of the High-activity-level Chemical Development Facility is 65% complete.

A report on transuranium element buildup in power reactor fuels was issued.

A report on fission product buildup in irradiated reactor fuels is nearly completed.

Part I. FEED MATERIALS PROCESSING

1.0 METALLEX PROCESS

In the Metallex process metal chlorides are reduced to finely divided metals or mercurides in the presence of mercury or active metal amalgams. By-products of the reaction are removed, and the metal is separated by filtering, pressing, and sintering.

1.1 Separation of Reduction By-products (O. C. Dean, C. P. Johnston)

By Hot Filtration. Residual water from aqueous washing of reduction product thorium amalgams is thought to be the source of over-specification oxide in sintered Metallex thorium. Efforts to separate unreduced thorium tetrachloride, sodium chloride, and feed salt impurities from the ThHg₃-bearing amalgam without the water wash step have been only partially successful. The solubility of thorium in mercury at 300°C has been reported as 5 wt % (Armour Research Foundation, subcontract 765 under W-7405-eng-26, Report No. 8, "The System, Th-Hg," Sept. 30, 1956). In two previous attempts to hot-filter the product amalgam in glass apparatus, the sintered glass filter had become plugged, with the result that only 20-30% of the thorium passed through the filter with the hot mercury. In experiments in stainless steel apparatus, with a sintered stainless steel filter near the outlet, 60% of the thorium metal in the mercury phase was recovered in the filtrate. The thorium amalgam for this experiment was prepared in the stainless steel apparatus by reduction (87%) of ThCl₄ at 300°C, and 80% of that reduced was recovered in the mercury phase.

The holdup in the reactor pot of 40% of the thorium in the mercury phase was thought to be due to the fact that the bottom of the reactor was flat, not dished, and to the probability that the filter did not remain at 300°C throughout the filtration. Improvements in reactor pot design are in progress. In the reactor used, the packing of the bottom outlet valve was water-cooled to prevent heat damage. The reaction mixture was withdrawn through the filter while still hot.

Fused Salt Scrubbing. In further efforts to eliminate the aqueous washing step, the reaction product of two reductions at 130°C, involving 18.6 g of thorium as thorium chloride, was scrubbed by agitation with a fused 50-50 mole % AlCl₃-NaCl mixture at 250°C. However, the fused salt removed both reduction by-products and thorium from the mercury, leaving in the mercury phase only about 20% of the thorium charged, plus aluminum resulting from reduction of the AlCl₃:

	<u>Expt. 1</u>	<u>Expt. 2</u>
Thorium charged, g	18.6	18.6
Thorium found in Hg phase, g	3.121	4.455
Na found in Hg phase, g	0.002	0.003
Al found in Hg phase, g	1.535	1.85
Cl ⁻ found in Hg phase, g	0.06	0.05

In one experiment the salt ingredients were added dry and the temperature was raised gradually to 250°C; in the other, the fused mixture was added in the molten state at 200°C.

In a third experiment, in which the thorium amalgam product was scrubbed with molten zinc chloride at 300°C, the thorium in the mercury phase was negligible. The zinc chloride was likewise reduced by the thorium amalgam.

1.2 Direct Extrusion of Metallex-Sintered Thorium Metal (Work done by Horizons, Inc. under a subcontract)

Six samples of sintered thorium metal produced by the Metallex process, five by the dry reduction route and one by the PDA route, were extruded from 1 in.-dia. billets to 0.25 in.-dia. rods (Fig. 1.1). One sample of extruded rod, with a VHN hardness of 62, was reduced by rolling to 3% of its original thickness without apparent cracking or loss in ductility. A second section of the same rod was reduced 77% in diameter by drawing, and exhibited no flaws during the operation. Rolling and drawing behavior were about the same as for Ames thorium.

In the apparatus used, the billets were heated in a Kentanium-lined die block under an inert atmosphere, then extruded upward through a die and ram which was forced down on the billet by a hydraulic press. The billet and die block were stationary during the extrusions. Some difficulty was encountered with thorium metal "leaking" past a poorly fitting bottom plug in the die block. The conditions for extrusion, densities, and some chemical properties of the extruded metal are presented in Table 1.1. Other information, such as hydrogen, oxygen, and nitrogen analyses and metallurgical properties are not yet available.

1.3 Equipment Modifications (G. K. Ellis)

Installation of a new transfer system in the large-scale Metallex equipment is essentially complete. The system will provide for rewashing and refiltering of quasi-amalgam product, transfer of filtrate to the filtrate tank, and transfer of sodium amalgam to the feed tank on the top floor. Provision has been made for helium sparging of water from quasi amalgam that is aging in the coagulation tank and vacuum removal of this contaminant. The deionizer, which is to provide pure water for the wash column, is not yet in working order.

A 7-hr run with amalgam only indicated that the earlier revisions in the piping for removal of gas and quasi-amalgam product from the contactor are successful.

2.0 FLUOROX PROCESS

In the Fluorox process, UF_4 is prepared by simultaneously reducing and hydrofluorinating uranium oxide. The UF_4 product of this reaction may be either reduced to metal or oxidized to UF_6 .

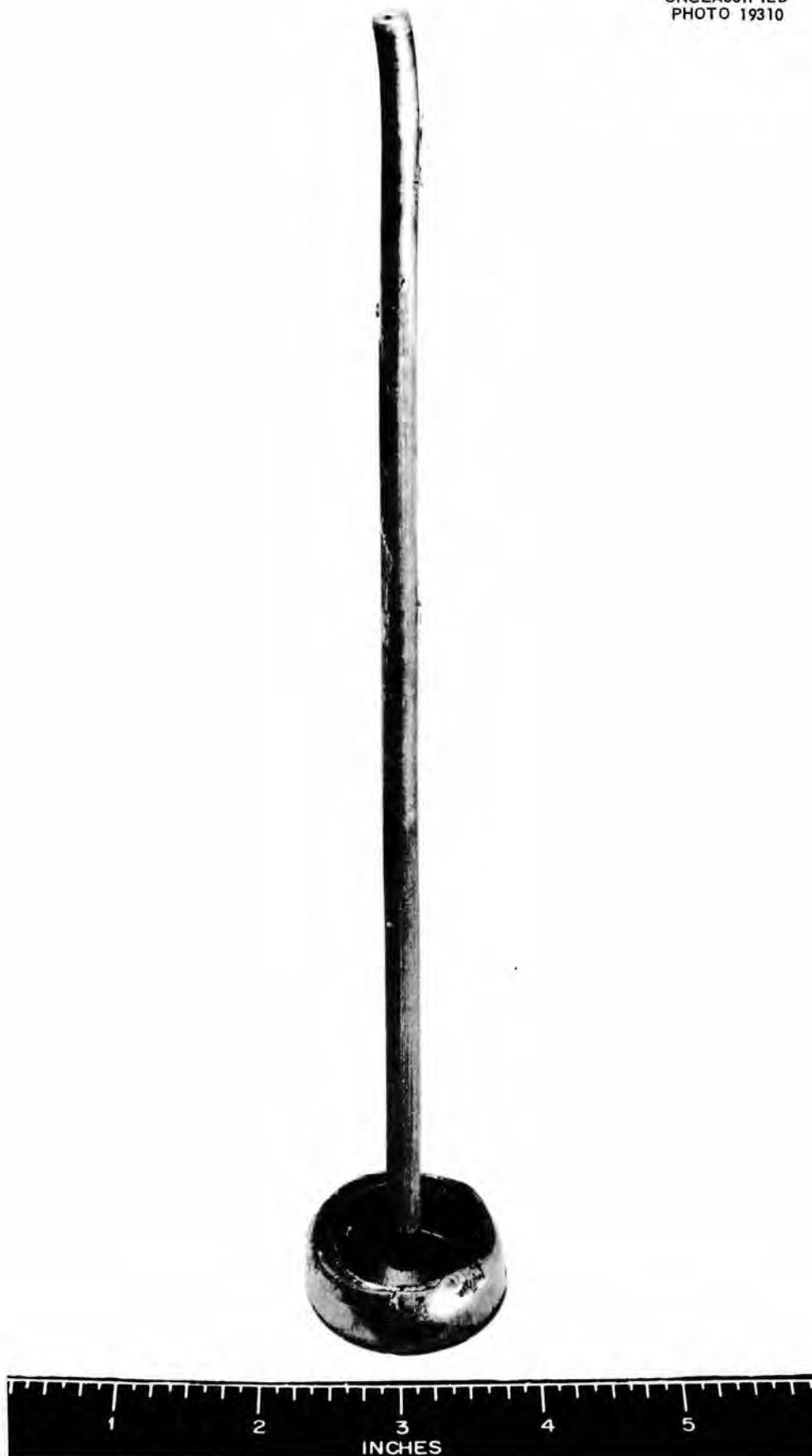


Fig. 1.1. Thorium Rod Extruded from Metallex Process Sintered Thorium.
The mushroomed metal at the bottom is caused by leakage.

Table 1.1

Conditions for Inert-atmosphere Extrusion of Metallex-Sintered Thorium

Horizons extrusion No.	1	2	3	4	5	6
ORNL Metallurgy No.	72B	66A	69A	76B-76A	62-66B	MX-52-2
Sintered compact density (g/cc)	6.95	7.74	9.1	8.1	8.2, 8.6	-
Extruded weight (g)	130.5	130.5	110	163	168.3	153
Extruded length (in.)	6.88	9.5	5.5	10.0	11.0	6.25
Extrusion press (psi)	28,000	25,500	30,600	30,000	26,800	29,400
Extrusion temp. (°F)	1,290	1,340	1,280	1,300	1,270	1,285
Density extruded metal (g/cc)	11.2	11.7	11.2	11.5	11.4	11.65
Hg (ppm)	10	170	10	28	10	11
Fe (ppm)	3020	30	332	53	368	198
Cr (ppm)	25	10	10	10	10	35
Ni (ppm)	100	62	65	70	95	55
Na (ppm)	100	75	62	50	105	64
ThO ₂ (%)	2.36	2.60	1.44	1.77	2.50	1.44
C (%)	0.36	0.10	0.16	0.09	0.03	0.04

2.1 Kinetics of UF_4 Oxidation (J. E. Savolainen, L. M. Ferris)

From data obtained in an extensive study performed to elucidate the nature of the reaction $2UF_4 + O_2 \longrightarrow UF_6 + UO_2F_2$ approximate reaction rate constants were calculated for the temperature range 600-900°C (ORNL-2180). The UF_4 used was >98% pure. Similar data for the temperature range 200-600°C were obtained in earlier work (CF-56-2-161) on removal of residual carbon from UF_4 -carbon pellets. A single Arrhenius plot of the two sets of data showed two linear regions, indicating a change in the activation energy at 600°C. The values were 30-40 kcal/mole in the temperature range 600-900°C and 8 kcal/mole from 200 to 600°C. No logical explanation could be offered for this behavior since no UF_4 phase change occurred at 600°C. In fact, the opposite effect would be expected if the UO_2F_2 formed by the reaction at the higher temperatures was semipermeable to either O_2 or UF_6 gas, in which case a diffusional process would govern the rate and the activation energy would be very low.

The low-temperature data were obtained with UF_4 pellets that contained ~0.4% carbon. It was speculated that the combustion of this carbon created very high local temperatures, resulting in abnormally high amounts of UF_4 being oxidized. Several samples of this UF_4 were therefore reacted with dry oxygen in a thermobalance at temperatures between 350 and 550°C. In each case the sample lost weight very rapidly immediately after oxygen was admitted to the system. The time required for this weight loss was very short, 1-2 min at temperatures in the range 400-550°C. After this initial period the rate of weight loss became negligibly small. A sharp rise in temperature accompanied the rapid weight loss. The loss of fluoride was shown by chemical analyses (Table 2.1). The 80% removal of carbon is in agreement with results of batch studies (CF-56-2-161). It must therefore be concluded that local heating due to combustion of residual carbon in UF_4 pellets produces the observed UF_4 oxidation. Further substantiation is obtained from the fact that no such behavior is observed when carbon-free UF_4 is used. In fact, weight losses of the magnitude found for the UF_4 -carbon pellets require ~10 hr even at 550°C when carbon-free material is used.

The maximum temperature attained by combustion of the carbon may be predicted by two means. From the curves of weight loss vs. time at a given temperature obtained on the thermobalance, it was found that the combustion process lasted only about 2 min in the temperature range 400-550°C, with the UF_4 being oxidized to the extent of about 5%. A half-time for the UF_4 oxidation reaction of ~30 min is obtained for these conditions if the reaction is assumed to be first order. Comparison of this figure with those obtained from batch rate data (ORNL-2180) shows that a temperature of 750-800°C is needed to produce the observed effect. In the second method the temperature rise is calculated from the equation $\Delta H = C_p \Delta t$ if the average heat capacity of the system is taken as that for pure oxygen (~7 cal/mole). Under the conditions of the experiments ~0.6 liter (stp) of O_2 is passed over the UF_4 sample during the 2-min reaction interval at 400°C, resulting in the combustion of ~15 mg of carbon. Using these figures, $\Delta t = \frac{94,000 \times 0.015 \times 22.4}{7 \times 12 \times 0.6} = 620^\circ C$, or a maximum temperature of ~1000°C.

Table 2.1 Reaction of UF_4 -Carbon Pellets with Dry O_2 at 350-550°C

Initial pellet composition (wt %): Total U, 74.92
 U(IV), 72.64
 F, 23.7
 C, 0.38

	Expt. A	Expt. B	Expt. C	Expt. D
Temperature (°C)	350	450	450	550
Initial Sample Weight (g)	5.106	2.036	5.106	5.069
Final Sample Weight (g)	5.074	2.024	5.088	5.041
Residue Composition (wt %)				
U	74.85	74.76	74.40	74.60
U (IV)	73.66	67.8	68.0	70.34
F	---	---	22.2	---
C	0.08	0.06	0.08	0.03
Time required for com- bustion of C (min)	140	2	2	1.5
Extent of UF_4 oxidation ^a (%)	0	7.2	4.7	3.9

a

Calculated from the sample weight loss assuming that all U (IV) in the residue exists as UF_4 .

2.2 Equipment Modifications (J. B. Adams, C. D. Scott)

Some of the auxiliary equipment in the fluidized bed set-up (Fig. 2.1) is being replaced to facilitate operation. The following equipment (Fig. 2.2) will be fabricated and installed:

1. A micrometallic filter system with arrangement for blowback cleaning and continuous solids collection. This will allow continuous operation without plugging.
2. Several copper cold traps which are to be used in a trichloroethylene-dry ice bath. These will be light enough for easy handling, and the trapping capacity will depend only on the number of traps in the system.
3. Two CaSO_4 chemical traps. These traps will be small enough for easy handling, yet will have sufficient capacity for stripping any escaping UF_6 from the stack gases.

This equipment has been designed to process more gas flow than the present system will generate, so that it will be possible to use the same equipment with a future system of larger capacities.

3.0 EXCER PROCESS

In the Excer process, uranium is converted by ion exchange to a form suitable for electrolysis and is then electrolytically reduced. When the process is applied to ore leach pulps, the unfiltered pulp may be fed directly to the ion-exchange column. In some cases the ion-exchange step may be omitted and the ore solution electrolyzed directly.

3.1 Reduction with Iron

Laboratory-scale Studies (I. R. Higgins, W. J. Neill). Further laboratory-scale experiments confirmed earlier results (ORNL-2227) indicating that reduction with iron might replace the electrolytic reduction step, and a preliminary flowsheet was prepared (Fig. 3.1). Since 3% of the sponge iron used in the experiments was insoluble in hydrochloric acid, an additional filtration step was included after the reduction step. The iron contamination of the products of these experiments was below that permitted by specifications:

Material	Ca	Si	Amount (ppm) ^{a, b}					
			Mo	Fe	B	P	S	Cl
UO_2Cl_2 solution	52.5	1.2	--	6.5	x	x	x	x
Ferrous solution ^c	23	x	2	x	x	<2	<10	x
UCl_4 solution	120	x	20	x	x	x	x	x
$\text{UF}_4 \cdot 3/4 \text{ H}_2\text{O}$ precipitate	340	--	--	20	--	x	60	300
UF_4 precipitate	540	--	--	17	1.1	x	33	<10

^aBased on parts of solution or parts UF_4 where applicable.

^b--- = analyzed for but not found; x = not analyzed for.

^cIncluded to show reagent contamination.

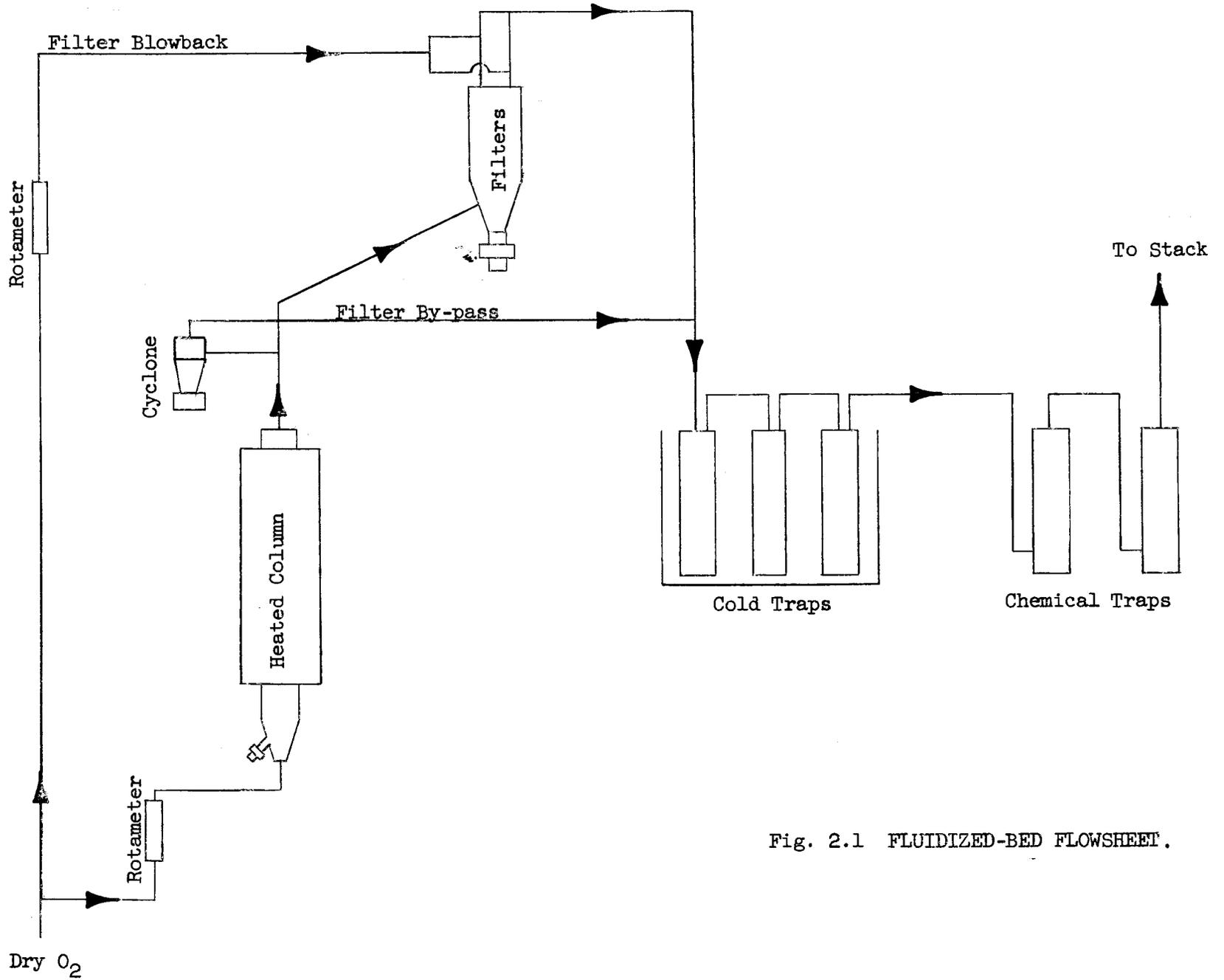
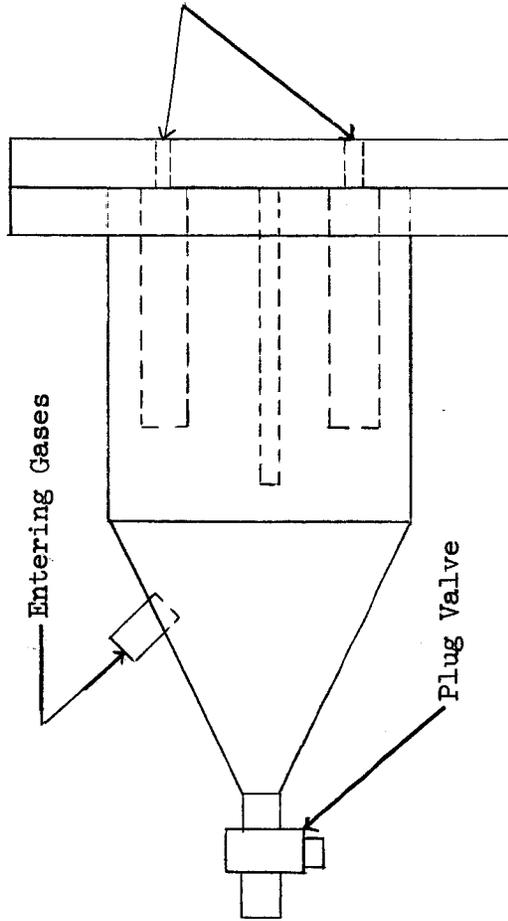


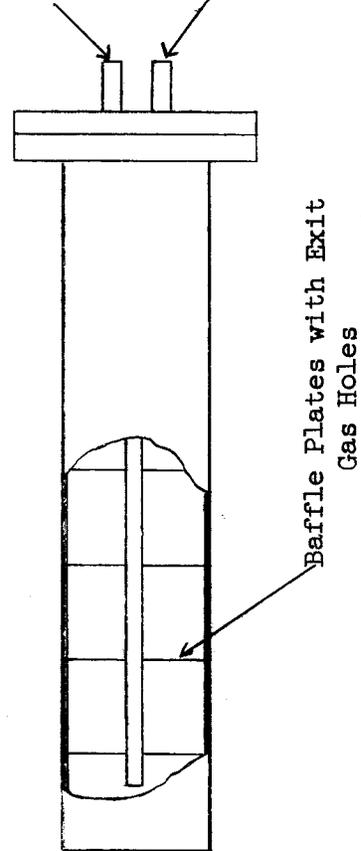
Fig. 2.1 FLUIDIZED-BED FLOWSHEET.

Exit Gases and Blowback



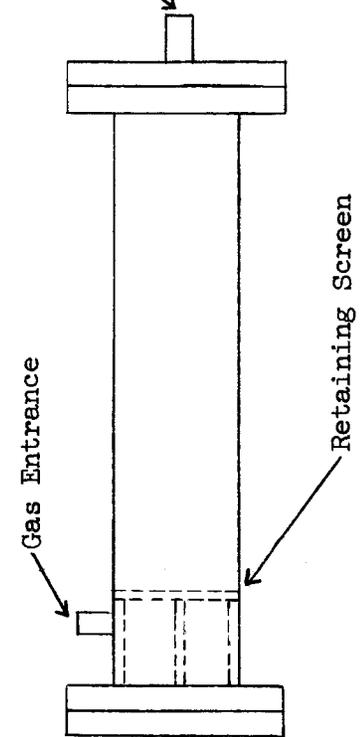
Monel Filter Housing with Two Nickel
Micro Metallic Filters

Entrance Gases Exit Gases



Copper Cold Trap to be Immersed
in Trichloroethylene-Dry Ice Bath

Gas Exit



CaSO₄ Chemical
Trap

Fig. 2.2 SOME AUXILIARY EQUIPMENT FOR FLUOROX PROCESS FLUIDIZED-BED SET-UP.

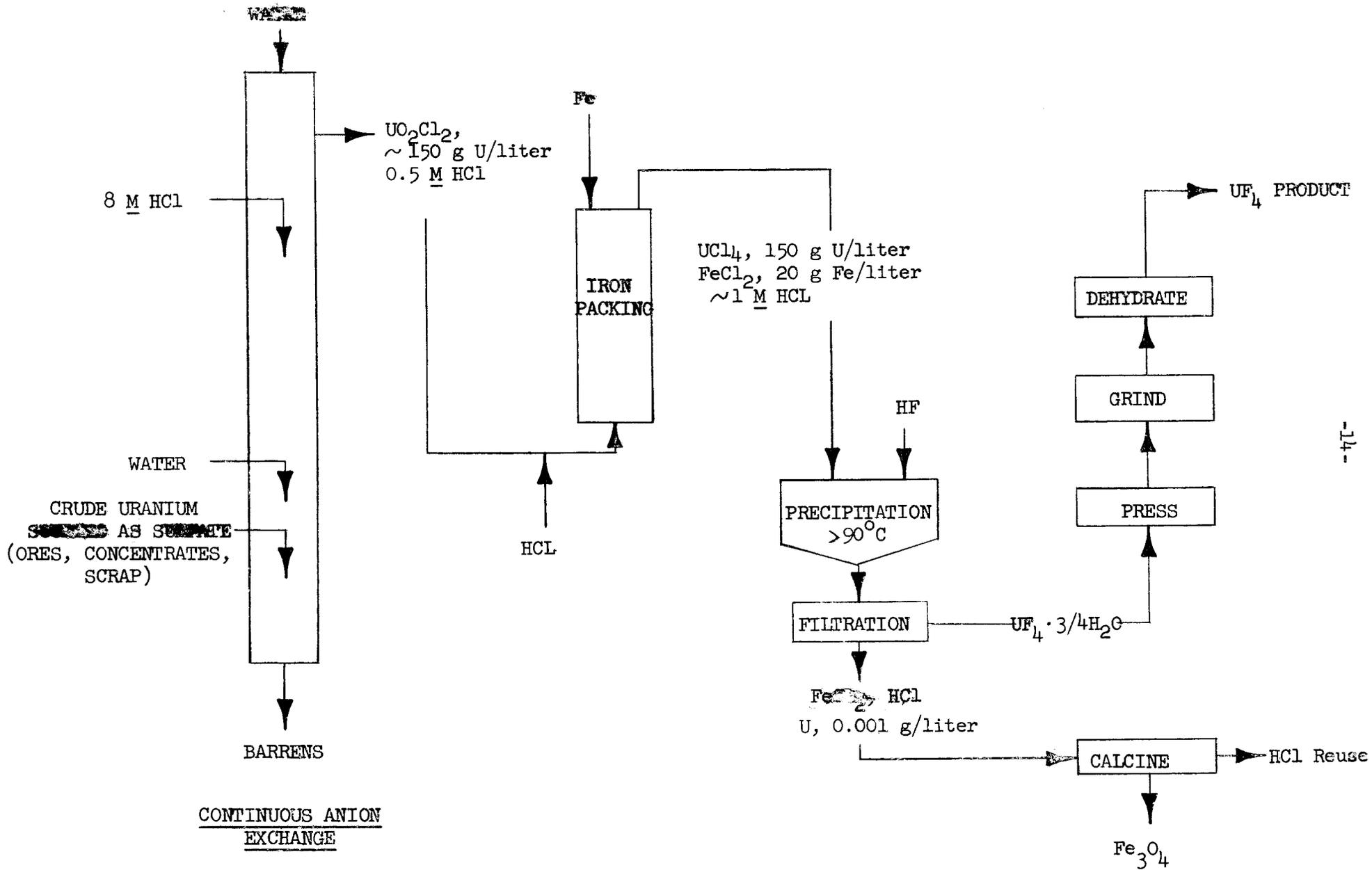


Fig. 3.1 EXCER PROCESS FLOWSHEET WITH IRON
REDUCTION STEP $Fe + UO_2Cl_2 \rightarrow FeCl_2 + UCl_4 + H_2O$

Calcium in the product was probably introduced with the UO_3 or HCl and sulfur with the iron or HF .

The UO_2Cl_2 feed for the reduction column was prepared by dissolving UO_3 in 2.5 N HCl . This solution, 150 g of uranium per liter, was reduced with 25% excess sponge iron. During the iron reduction some gas was evolved, and there was a distinct odor of H_2S . To the boiling UCl_4 solution product of the reduction was added 10% excess HF , and the $UF_4 \cdot 3/4H_2O$ precipitate was filtered off. Filtration was rapid, and the product had a surface area of 8.13 m^2/g of UF_4 . The filtrate contained 0.2 g of uranium per liter, in the form of finely divided UF_4 . The filter cake was washed with 1 N HCl and water and dehydrated by heating at 200-450°C for 2 hr.

Polyethylene containers were used throughout the experiments with the exception of the UF_4 precipitation step where a carbate beaker was used. The ferrous solution was made by dissolving a sample of sponge iron in 1 N HCl .

Pound-scale Studies (C. W. Hancher, P. N. Rigopoulos*). Reduction of UO_2Cl_2 with iron on a larger scale was also feasible and efficient:

	Input (moles)	Output (moles)
U(VI), 100 g/liter	0.42	0.42
HCl, 135 g/liter	3.70 (50% excess)	0.39

The UO_2Cl_2 solution was fed to a column packed with iron nails at a feed rate of 46 gal/hr per cubic foot of packing. Chemical analyses, by methods where accuracy is $\pm 5-10\%$, showed 104% reduction efficiency. The absence of unreduced uranium would eliminate the recycle required with electrolytic reduction methods.

Tests with African ore concentrate were likewise encouraging. The $UF_4 \cdot 3/4H_2O$ product from iron reduction and HF precipitation, followed by filtration in 1-lb batches and a single washing, was decontaminated from iron and silica by factors of > 10 :

	Amount (wt %)		Amount (wt %)	
	Ore Concentrate	$UF_4 \cdot 3/4H_2O$	Ore Concentrate	$UF_4 \cdot 3/4H_2O$
Total U	68.25	75.5	Fe	0.42
U(IV)	0.04	71.4	Mg	0.002
C	0.09		Mn	0.35
SO_4	6.17		Si	1.60
H_2O	4.74		Ti	0.01
P_2O_5	0.08		NH_3	1.7
Al	0.34		Ni	0.01
Ca	0.60		V	0.02
Cu	0.006		SO_4	0.07

The iron content could be reduced further by additional washing.

*On loan from Ionics, Inc.

The tap density of the $UF_4 \cdot 3/4H_2O$ was 1.5-2.0 g/cc. After pressing at 10 psi, the density was 3.7-4.0 g/cc. A Stokes tablet press with a total force of 4000 lb is being installed. It makes tablets 1/8-1/4 in. in diameter and 1/16-1/4 in. thick.

A fluidized bed dehydrator, with a permissible feed rate of 7 lb/hr, is being installed.

3.2 Simultaneous Reduction - Precipitation in Electrolytic Cell

Development of the electrolytic cell in which uranic salts are simultaneously reduced to uranous and precipitated as $UF_4 \cdot 3/4H_2O$ has been temporarily discontinued by both ORNL and Ionics, Inc. (working under a subcontract) in favor of the more promising method mentioned in Sec. 3.3. At both ORNL and Ionics, cell operation has been hampered by coating of the screen support for the falling-film mercury electrode with $UF_4 \cdot 3/4H_2O$, thickening of the mercury as it picks up impurities, and the difficulties of maintaining a flowing-mercury cathode.

3.3 Electrolytic Reduction with Precipitation Outside Cell

This work is being continued by Ionics, Inc. under a subcontract.

4.0 URANIUM RECOVERY BY ION EXCHANGE

4.1 Uranium Recovery from Fluoride-containing Scrap (I. R. Higgins, W. J. Neill)

Uranium was successfully recovered from solutions of uranium scrap containing fluoride in a 2-in.-dia Higgins continuous ion-exchange contactor (Fig. 4.1) containing Permutit-SK resin. The scrap was dissolved in dilute sulfuric acid, and the uranous ion was oxidized to the uranyl form by 30 min heating with MnO_2 . To reduce corrosion, excess fluoride in the feed was precipitated by magnesium sulfate, which was added before the oxidation. This method was not very efficient since 1-2 g of fluoride per liter remained in solution. The uranium was converted to the chloride form on the resin with 10 M HCl and eluted with water, with a consumption of about 5 lb of HCl per pound of uranium. This was apparently adequate to reduce the sulfate concentration from 1 M to 0.1 M. At the same time, the fluoride concentration was reduced below the level of detection. Concentrated brine could be substituted for HCl if a sodium removal step was inserted at a later point in the process (Fig. 4.2).

In one experiment sodium chlorate was used to oxidize the uranous ion, but excess chlorate was sorbed on the resin and decomposed to a gas.

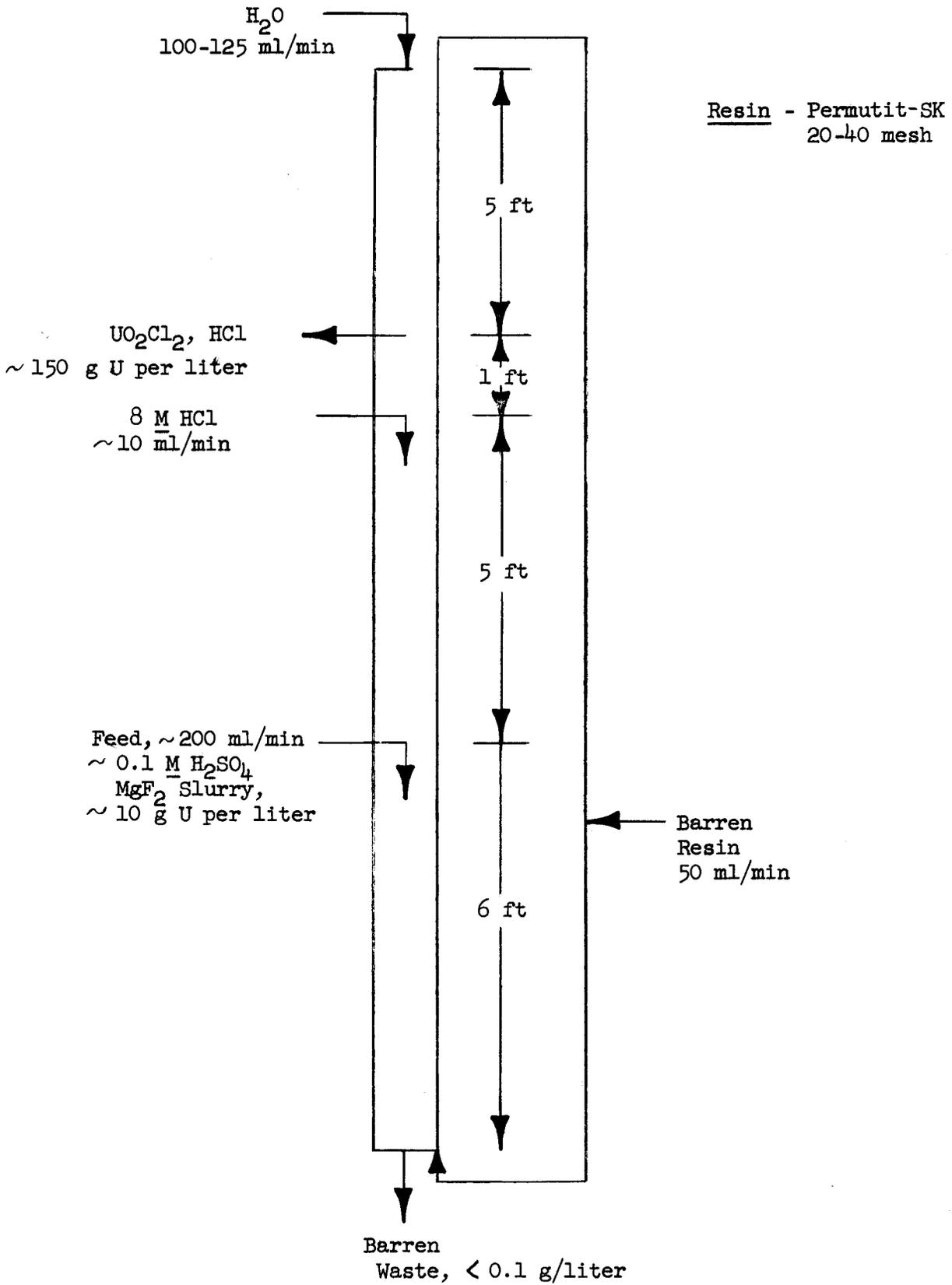
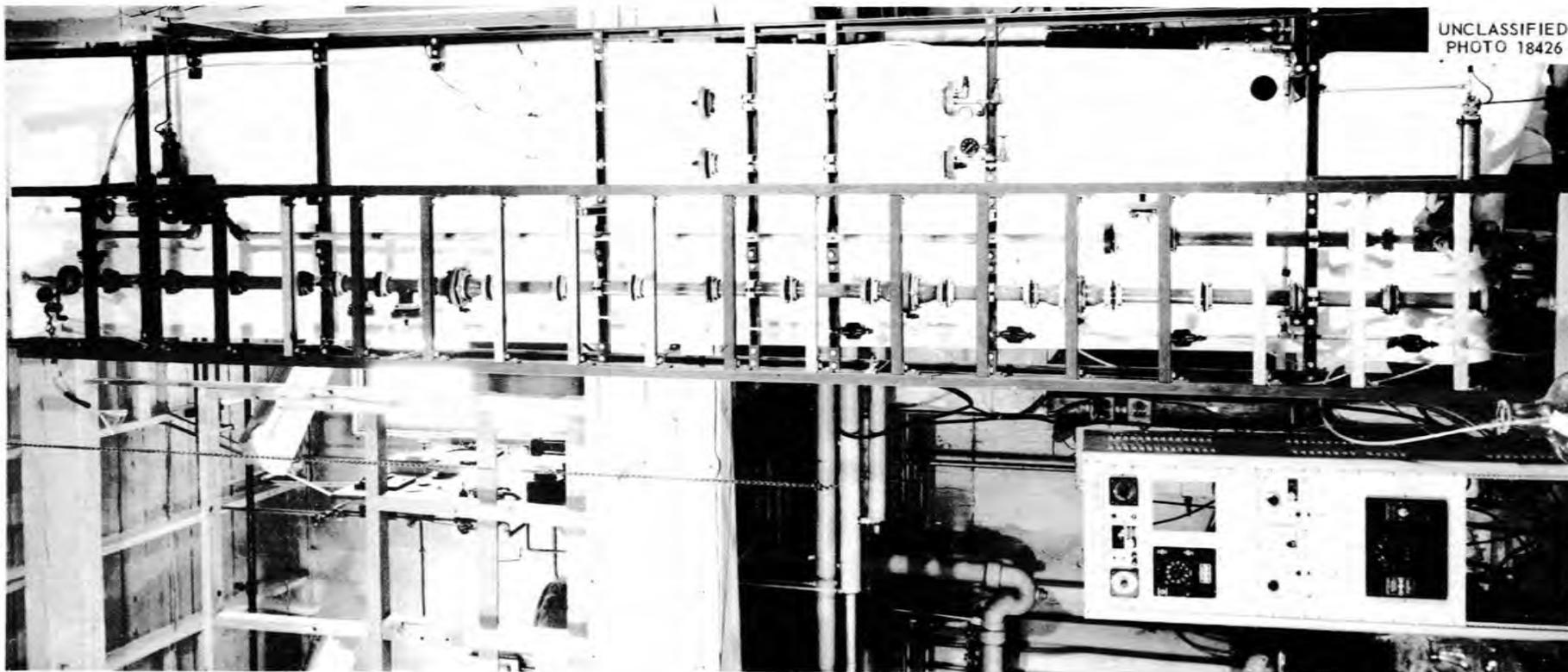


Fig. 4.1. SCHEMATIC CONTINUOUS ION-EXCHANGE CONTACTOR FOR TREATING BOMB LINER (IMPURE UF_4 , CONTAINING MgF_2) MATERIAL OR FLUOROX RECYCLED UO_2F_2 .



UNCLASSIFIED
PHOTO 18426

Fig. 4.1. Higgins Continuous Ion-Exchange Contactor, 2 in. dia.

4.2 Uranium Recovery from Ore (C. W. Hancher)

Results of tests in the 12-in.-dia Higgins column installed at the National Lead mill at Grand Junction, Colorado, were used to calculate the HETS (height equivalent to a theoretical stage) and NETS (number of equivalent stages) for the loading and stripping sections (Fig. 4.3):

Section	Length (ft)	NETS	HETS	
			Actual (ft)	Design (ft)
Loading	5	3.9	1.2	1.8
Stripping	7	1.5	4.7	2.7

The feed flow rate was 7 ppm and the L/V flow ratio was 87. When the feed flow rate was increased to 10 gpm, with a L/V ratio of 83, the HETS in the loading section (6 ft) increased to 1.5 ft but the NETS remained 3.9. The HETS for the stripping section could not be calculated at the higher feed rate because of lack of data. The agreement between actual and design values in the loading section was good even though the feed uranium concentration was 0.9 g/liter and the design value was 0.6 g/liter. At the end of the run the equivalent fractions of uranium were:

	In Solution	In Resin
	Loading Section	
Top	0.0551	0.8460
Bottom	0.0002	0.0308
	Stripping Section	
Top	0.0	0.0308
Bottom	0.200	0.8640

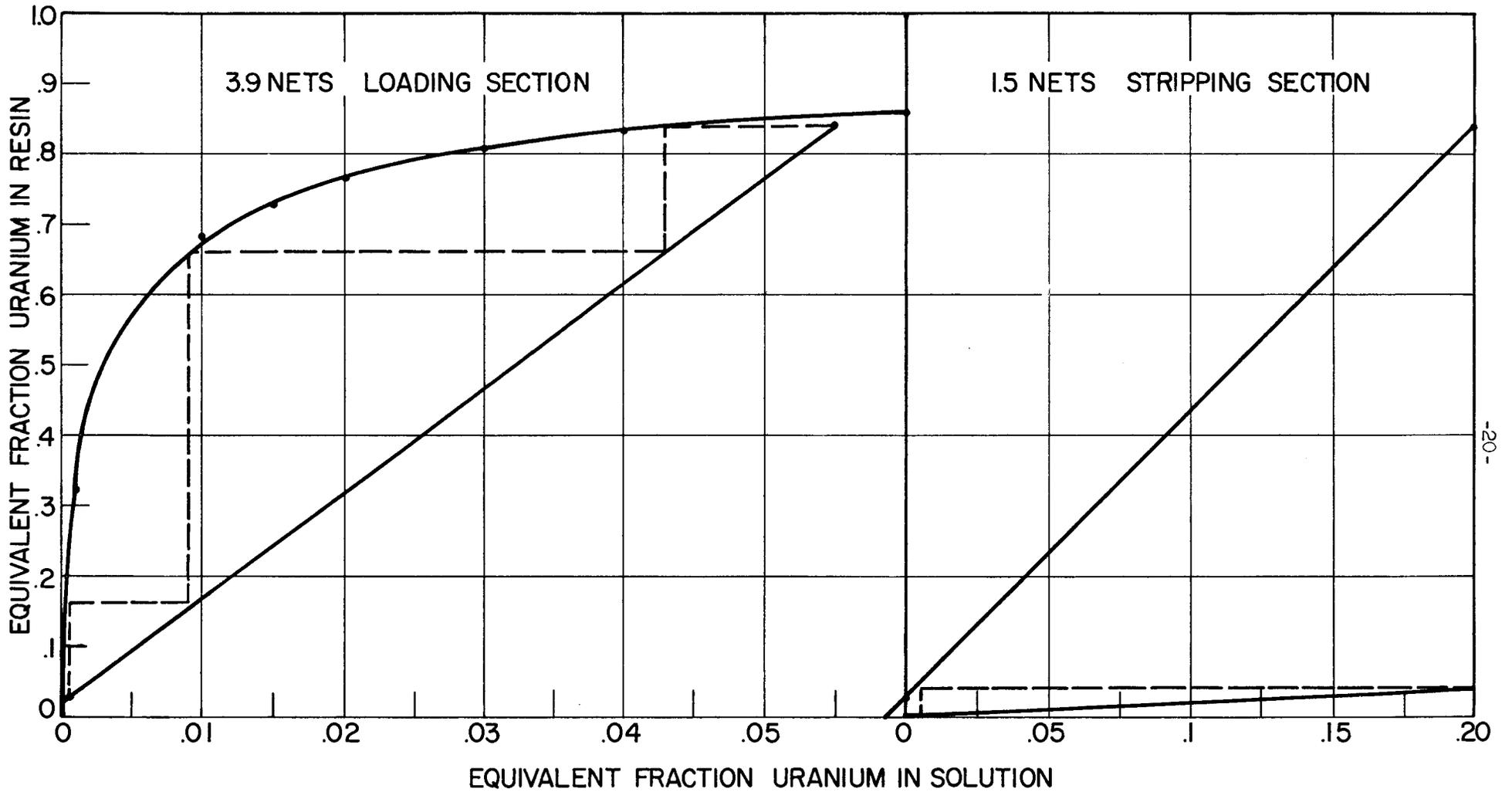


FIG. 4.3 McCABE-THIELE DIAGRAM FOR GRAND JUNCTION TEST II

PART II. HETEROGENEOUS (POWER) REACTOR FUEL PROCESSING

5.0 FUSED SALT--FLUORIDE VOLATILITY PROCESS

In the fused salt--fluoride volatility process, clad and/or alloyed uranium fuel elements are hydrofluorinated, in fused fluoride, to form UF_4 . The UF_4 is fluorinated to UF_6 , which volatilizes, is collected in NaF traps, and is eventually desorbed.

5.1 Volatility Pilot Plant Operation (W. H. Lewis, F. N. Browder, W. H. Carr, J. E. Bigelow, F. W. Miles, R. B. Keely)

Results of initial pilot plant runs were generally satisfactory. All molten salt heating equipment was operable although in some cases controls had to be set much higher (up to $300^\circ C$) than the desired vessel temperature to reach operating conditions. Autoresistance heating, though not uniform, was acceptable. Because of unexpected corrosion of the type 304 stainless steel charge melt vessel, a new nickel vessel is being fabricated. The lid of the old vessel did not seal sufficiently tight to ensure exclusion of moist air, even with a high purge rate, and the closure is being redesigned. The autoresistance heating circuit will be altered to eliminate the need for an auxiliary heater around the outlet pipe.

Piping was installed to enable purging of the charge melt vessel at a rate about 60 times higher than before.

Charge Melt Vessel Tests. Two runs were made with nonradioactive molten salt to study salt-handling equipment and techniques. Salt was not fluorinated in either run.

In Run C-1, salt was introduced in two batches of 27.8 and 81.6 kg, respectively. The first batch was melted in the charge melt vessel and transferred to the fluorinator without incident, where it was allowed to freeze but was remelted without trouble. Because of a higher melting point than anticipated ($550^\circ C$ rather than $520^\circ C$), salt in the freeze valve had not melted when the charge melt furnace was turned on for the second batch, and this batch melted but remained in the vessel. Additional heating of the transfer line melted the plug, and the salt then drained to the fluorinator in about 2 min.

Transfer to the waste container started smoothly and at the expected rate, but the salt began running full-line rather than trickling when it passed through the freeze valve. Transfer could have been accomplished very quickly, but was interrupted once to determine the difficulty of stopping the flow by releasing the pressure in the fluorinator. Flow stopped almost immediately, so transfer was resumed. A 15-kg heel was left in the fluorinator.

In Run C-2, the charge melt vessel was purged with at least 10 volume changes of N_2 , which entered at the bottom and exited through the vent header at the top prior to the heating. While the vessel was being heated, the N_2 entered the top of the vessel. This purge was initially set at 1.0 scfm, but transfer was not successful until the rate was dropped to 0.5 scfm. After the salt had been transferred to the fluorinator, it was sparged for 7.5 hr with 2 cfm N_2 ; this resulted in a pale green, 5-mil-thick deposit on the walls of the snow trap upstream from the nickel mesh.

The salt was transferred from the fluorinator in four batches into charge cans at the waste station. Except for a delay in the first transfer caused by a plug in the freeze valve, the first three transfers were accomplished without incident. On the fourth transfer, the controls did not operate properly, and about 4 kg of salt overflowed from the charge can. Since the normal waste can has sufficient capacity for an entire fluorinator batch, this situation could arise only when salt is being recovered for reuse.

After each run, heavy corrosion in the stainless steel charge melt vessel was evidenced by a deposit of black shiny material containing 80% UO_2 and a magnetic rust-colored scale. After Run C-2, the bottom outlet of the charge melt vessel was plugged and could not be opened by heating.

Corrosion products from the charge melt vessel were probably responsible for the plug in the waste line freeze valve; pressures of the order of 10 psi in normal flow direction did not break the plug, but the line was opened by a lower-pressure blow-back.

In additional tests on corrosion in the charge melt vessel in the absence of salt, flaking of the metal continued. Corrosion samples included in one test in which the N_2 purge rates were ~ 10 times greater than in C-1 showed weight losses of

304 stainless steel	0.32%	Black iron	0.22%
316 stainless steel	0.31%	Inconel	0.15%
347 stainless steel	0.51%	Nickel	0.0%
Copper	0.68%		

Tests of Absorbers. Absorber bed heating was studied in miscellaneous run M-4. Starting with beds at $100^\circ C$ and furnaces set for $400^\circ C$, about 8 hr of heating was required to bring the center of the beds to $400^\circ C$ and about 6 hr with furnaces set for $600^\circ C$. With furnaces closed, about 48 hr was required for cooling.

Process equipment and lines were conditioned by a flow of fluorine (run M-5). Within about 6 hr after startup, water-soluble fluoride deposited in the fluorine inlet pipe to the scrubber, causing sufficient pressure build-up to require shutdown. The deposit was broken by beating on the pipe, and the run was continued for a total of 15 hr.

In a later reconditioning of part of the system that had been exposed to air, pressure cycling in the scrubber caused caustic solution carryover into the vent header. The caustic drained from the header through vent lines to other parts of the system.

Tests of Cold Traps. Cold trap performance was checked in runs M-6 and M-7. The run conditions were similar except that in M-6 the gas flow rate was varied from 0 to 2 cfm and in M-7 there was no gas flow. Cold trap FV-220 reached operating temperature (-40°C) in the chilled section in about 1.5 hr. The chilled section of cold trap FV-222 never reached design temperature (-62.2°C) but ranged from -40°C to -55°C , depending on gas flow and on whether inlet and outlet heaters were on; brine temperatures ranged from -43°C to 59°C , depending on the heat load. Inlet heaters did not maintain temperatures above the triple point of UF_6 ; this may be critical unless the gas has sufficient heat capacity to carry the necessary additional heat from the duct.

5.2 Design Studies (R. P. Milford, J. B. Ruch, J. S. Watson)

Fluorine Purification Trap. A NaF trap for removing HF from the fluorine stream is being designed. The up to 5% HF in the fluorine as purchased could contaminate the product or interfere with UF_6 absorption on the product NaF traps. The HF trap will probably be a 4-ft section of sch. 40 monel pipe or its equivalent packed with 1/8-in. NaF pellets. The first 2 ft will normally be heated to 100°C to prevent formation of $\text{NaF}\cdot x\text{HF}$ complexes, which might plug the trap. The upper 2 ft will be cooled to room temperature with water coils, at which temperature the vapor pressure of HF over NaF is only ~ 0.01 mm Hg. Electrical heaters will be provided to heat the bed to 300°C for regeneration of the NaF, and flanged openings will be installed to allow easy dumping and recharging of the bed.

Design of High-activity-level Volatility Studies Laboratory Facility. Design has started on a high-activity-level volatility laboratory facility to be located in Cell 2 of the new high activity level chemical development facility, Building 4507. The equipment will be designed to handle an initial salt charge of 880 g and to dissolve a 100 g uranium wafer. The highest activity level anticipated will be obtained with enriched material with 10% burnup and decayed for 10 days. The facility will employ the hydrofluorination, fluorination, absorption, and cold trap equipment formerly used in non- and low-activity development work plus features and changes considered necessary for such an installation.

5.3 Laboratory Studies

Fluoride Corrosion of Metals (G. I. Cathers, M. R. Bennett). Because of the corrosion of the stainless steel charge melt vessel in the pilot plant, laboratory corrosion tests were made with metal rods. Types 316 and 347 stainless steel and inconel were severely attacked by molten $\text{NaF-ZrF}_4\text{-UF}_4$ at 1200°F (650°C). Nickel was corroded somewhat less.

The tests were made by partially immersing the corrosion specimens in molten NaF-ZrF₄-UF₄ while gas was bubbled through. With air passed through drierite as the gas, the three iron-containing alloys had scale above the salt line after 2 hr (Fig. 5.1), with much less on the inconel than on the stainless steels. Results were similar after 18 hr with drierite-dried nitrogen, but there was some back-diffusion of air into the reactor. When this was eliminated there was no scaling after 26 hr when the sparging gas was nitrogen dried with anhydrone and then passed through copper foil at 750°C. In all cases where there was scaling there was an accumulation of solids below the salt surface. The solids contained ZrO₂ (identified by T. N. McVay of the University of Alabama consulting with the Metallurgy Division). The corrosion is believed to be due to destruction of the protective chromium oxide film on the stainless steel.

Processing of Stainless Steel—containing Fuel Elements (L. M. Ferris, J. E. Savolainen). Initial dissolution rates for type 347 stainless steel in various molten fluoride salts saturated with anhydrous HF were determined as a function of salt composition and temperature:

Salt (mole %)		Temp (°C)	Dissolution Rate (mg/m/cm ²)	Salt (mole %)			Temp (°C)	Dissolution Rate (mg/m/cm ²)
NaF	ZrF ₄			NaF	ZrF ₄	LiF		
50	50	800	1.82	27	38	35	700	2.00
		700	1.36				600	1.00
		600	0.10				700	2.02
43	57	700	3.36				600	0.25

Specimens of stainless steel weighing about 3.7 g were supported in an air-lift pump immersed in 100 ml of the molten salt mixture, into which solvent anhydrous HF gas was passed. After 1 hr the specimens were removed and weighed, and the dissolution rate was calculated.

Sulfur Embrittlement of Nickel (G. I. Cathers, M. R. Bennett, J. E. Savolainen, L. M. Ferris). Embrittlement of nickel by as little as 1 ppm of sulfur contaminant in 50-50 mole % NaF-ZrF₄ was demonstrated in a test based on the high scavenging efficiency of nickel for sulfur. The test consists in immersing a 5-mil-thick nickel foil, 1 by 2 in. (1.5 g), in 150 g of salt in a graphite reactor, above which a nitrogen atmosphere is maintained. Previous tests, made with 60-mil nickel wire in a nickel reactor, had indicated that, with sulfur concentrations below 100 ppm, embrittlement was not particularly severe since the effect was limited to the outer surface of the wire and some of the sulfur was lost to the reactor wall. With the foil test the salt/nickel ratio is about 100/1, and at a sulfur diffusion rate of 0.4 mil/hr (value stated by a representative of the International Nickel Co.), the 5-mil foil is penetrated in a few hours.

In 2 hr at 600°C in a fluoride melt containing 100 ppm of sulfur there was essentially complete loss of mechanical strength of the nickel, with

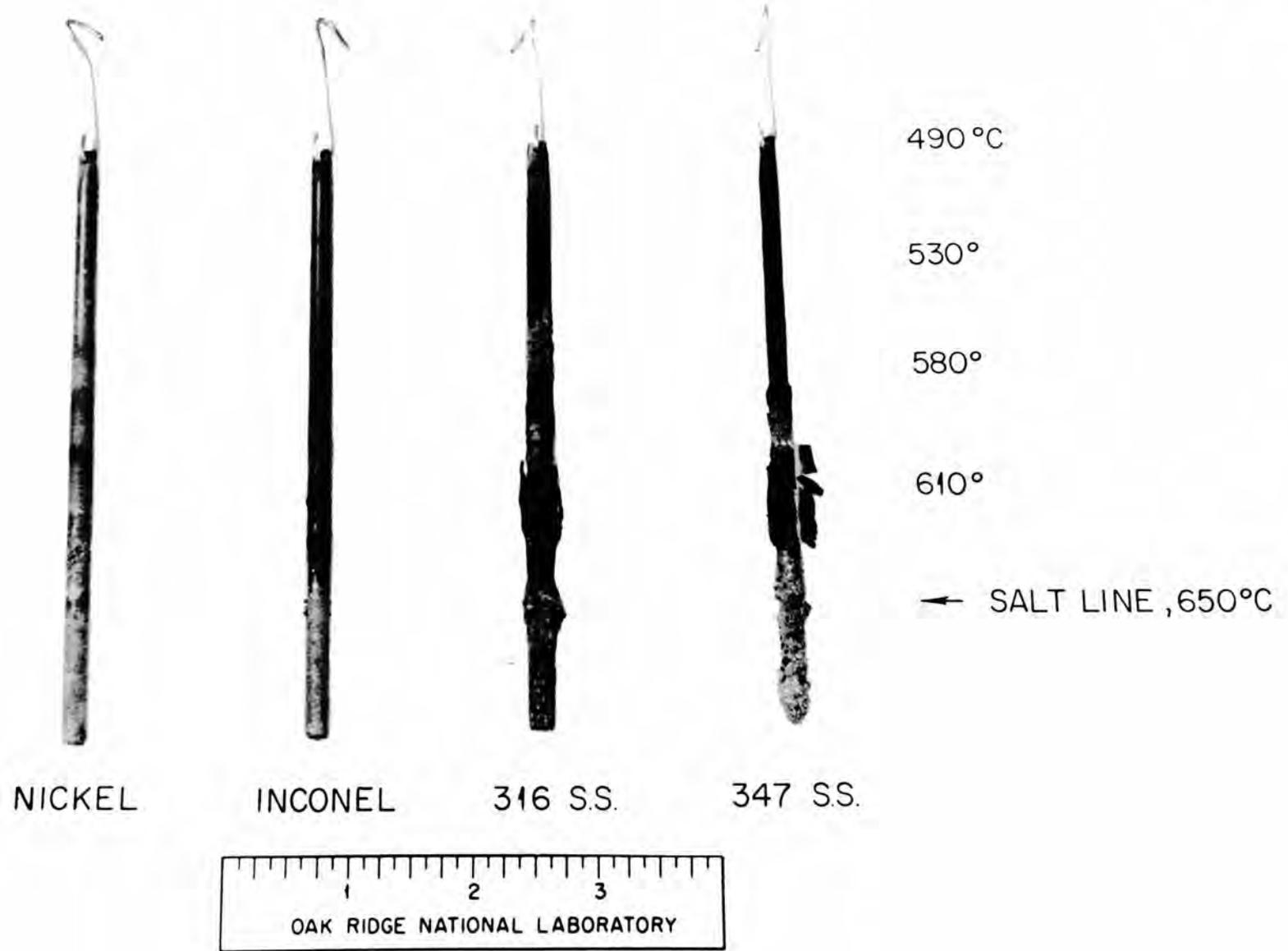


Fig. 5.1. Corrosion Test Specimens - Air for 2 hr.

Ruthenium Behavior (G. I. Cathers, R. L. Jolley). A Column filled with nickel packing held at 120°C was not particularly effective in removing ruthenium activity from the UF₆ product collected in one volatility run. The ruthenium decontamination factor was only 1.6. This experiment was designed to test whether ruthenium plating out on metal surfaces could be used to achieve additional decontamination in the volatility process. The column was a 12-in. length of 1-in. nickel tubing filled with 192 g of 2 3/32-in.-o.d., 30-gage nickel Fenske packing with a total area of 0.36 m². It was placed between the second NaF bed and the UF₆ cold trap, and used for about 130 min in a normal volatility process desorption run. The decontamination factor was calculated from the activities found in the nickel column and in the final product. The activity in the nickel packing was removed with an alkaline-tartrate-peroxide solution, although the effectiveness of this method has not been fully evaluated. About 0.025% of the processed uranium was found in the nickel trap.

The low ruthenium decontamination in the nickel trap is perhaps not too surprising in view of the small amount of activity involved and the small surface area used. The product contained only 28 ruthenium γ c/m/mg U. The activity removed by the nickel was calculated to be 200 c/m per square centimeter of nickel surface. The removal of ruthenium with a nickel column would probably be more effective with a greater surface area or by operation at a higher temperature.

Plutonium Behavior (G. I. Cathers, R. L. Jolley). Irradiated uranium was decontaminated from plutonium by factors of 7×10^3 and 1.1×10^4 in two series of volatility runs. The product UF₆ in all eight runs completed contained less than 6 plutonium α c/m/mg U. Definite evidence was obtained of some PuF₆ volatilization from the fused salt fluorination step over to the first NaF bed. The plutonium in the second NaF bed was below the analytical detection limit. The plutonium collected in the NaF absorption step was calculated as equivalent to an absorption decontamination factor of 70 in the first series, 49 in the second series. Decontamination factors of 83 and 112 were obtained for the fused salt-fluorination step.

6.0 ZIRCEX PROCESS

In the Zircex process a fuel element is hydrochlorinated to form a volatile compound of the diluent and/or cladding zirconium. The uranium or thorium is recovered from the nonvolatile residue by aqueous dissolution and solvent extraction. Fuels that may be so processed are those of the Consolidated Edison, Commonwealth Edison, Rural Cooperative, and Submarine Thermal reactors.

6.1 Hydrochlorination (J. E. Savolainen)

Previous laboratory experiments on hydrochlorination of zirconium alloys were made with commercially available HCl gas compressed in cylinders,

which contains about 0.5% carbonaceous impurities. In some experiments larger amounts of additives— CCl_4 , water, methane—interfered with the reaction. In the presence of CCl_4 or methane, a nonreactive material deposited on the surface of the zirconium alloy. The deleterious effect of these additives suggested that the impurities in the original gas may also be deleterious. This was confirmed in hydrochlorinations at 500°C with pure HCl gas, in which uranium losses in the insoluble residue were 1.7-2.7%:

Reaction Time (hr)	Uranium Distribution (%)			g U/g ZrO_2 in Insoluble Solids	g Solids/kg Fuel
	Insoluble in 8 M HNO_3	Soluble in 8 M HNO_3	Volatile		
1.5	2.74	97.0	0.23	0.034	7.20
2.25	2.15	97.8	0.04	0.055	5.47
3	1.68	98.2	0.04	0.044	5.40

When commercial HCl was used, losses at 450 and 600°C were 4.2-7.7%. The residue after hydrochlorination with pure HCl was a replica of the initial fuel element section. It had practically no mechanical strength and disintegrated on addition of water to form a slurry which could be easily transferred. Residues from hydrochlorination with commercial HCl gas were not readily slurried with water.

The pure HCl gas was generated from analytical grade hydrochloric acid by dropping it into CaCl_2 at 100°C . The evolved gas was passed over anhydrous CaCl_2 to remove water vapor and was then used to hydrochlorinate STR fuel element sections at 500°C . After the hydrochlorination, the furnace was cooled and the nonvolatile residue was slurried with water and then leached with 8 M HNO_3 .

6.2 Corrosion Tests* (W. E. Clark, A. H. Kibbey)

A survey is being made of possible materials of construction for Zircex process equipment. As a result of a series of tests carried out under process conditions, some of these materials have been eliminated from further consideration.

Experiments with titanium and tantalum in HCl-H_2 mixtures at 400 - 600°C indicate that neither material can be used for the hydrochlorinator. At 400°C tantalum was embrittled badly after 24 hr, while a titanium sample had almost completely disintegrated after 17 hr. At higher temperatures the same effects were noted, but in correspondingly shorter times.

The only material that has qualified for dissolver construction over all ranges of nitric acid concentration is tantalum (Table 6.1). The failure of titanium in the vapor of 15 M HNO_3 plus HCl is being investigated further.

* Conducted by Battelle Memorial Institute under a subcontract.

Table 6.1 Zircex Dissolver Corrosion Tests

Times are ± 10 hr

Metal	Specimen Position	Cumulative Corrosion Rate (mils/month)															
		0.5 M HNO ₃ 0.4 M UO ₂ ⁺⁺ 1.2 M Cl ₂ ⁻				3 M HNO ₃ 0.4 M UO ₂ ⁺⁺ 1.2 M Cl ₂ ⁻				5 M HNO ₃ 0.4 M UO ₂ ⁺⁺ 1.2 M Cl ₂ ⁻				15 M HNO ₃ 0.4 M UO ₂ ⁺⁺ HCl bubbled through			
		160 hr	330 hr	500 hr	665 hr	160 hr	325 hr	500 hr	670 hr	160 hr	323 hr	500 hr	665 hr	160 hr	325 hr	490 hr	660 hr
Tantalum	Vapor	g*	g*	g*	g*	g*	g*	g*	g*	g*	---	g*	g*	g*	g*	g*	g*
	Interface	g*	g*	0.007	g*	g*	g*	g*	g*	g*	---	g*	g*	g*	g*	g*	g*
	Liquid	g*	g*	g*	g*	g*	g*	g*	g*	g*	---	g*	g*	g*	0.001	g*	g*
Titanium	Vapor	0	g*	g*	g*	g*	0.009	0.010	g*	0.163	---	0.165	0.158	g*	0.009	0.072	27.0
	Interface	g*	g*	g*	0.002	0.029	0.023	0.016	g*	0.039	---	0.020	0.011	0.015	0.026	0.16	0.016***
	Liquid	0	g*	g*	g*	0.013	0.004	0.008	g*	0.034	---	0.008	0.003	0.034	0.076	0.48	0.33
S-816	Vapor	0.381	0.192	0.137	0.102	0.301	0.185	0.156	0.134	1.40	---	0.822	0.847	1.64	1.76	1.68	17.7
	Interface	0.431	0.228	0.167	0.129	0.515	0.346	0.295	0.276	1.76	---	1.36	1.537	2.01	2.37	2.51	15.4
	Liquid	0.299	0.177	0.122	0.100	0.564	0.388	0.350	0.344	2.15	---	1.77	1.817	1.83	2.73	3.13	4.07
S-590	Vapor					0.207	0.12			1.05	0.93		Tests	3.97			
	Interface	Not yet tested				0.510	0.36	Tests		2.12	2.46		cont.	3.45			
	Liquid	Not yet tested				0.596	0.43	continuing		2.25	2.22			3.73			
Vitallium	Vapor									0.045	0.06		Tests	1.29			
	Interface	Not yet tested				Not yet tested				0.57	0.48		cont.	1.73	Tests continuing		
	Liquid	Not yet tested				Not yet tested				0.67	0.52			1.41			
Haynes 25	Vapor					0.283	0.23			0.97				5.46			
	Interface	Not yet tested				0.569	0.46	Tests		8.42	Tests discontinued			3.92			
	Liquid	Not yet tested				0.670	0.54	continuing		1.60				4.18			
Carpenter-20	Vapor					0.162	0.12			27.9				1.28			
	Interface	Not yet tested				0.393	0.42	Tests		6.32	Tests discontinued			1.20	Tests continuing		
	Liquid	Not yet tested				0.467	0.33	continuing		2.08				1.25			
Carpenter-20S	Vapor					0.056	0.06			77.1				7.68			
	Interface	Not yet tested				0.536	0.47	Tests		2.09	Tests discontinued			2.19			
	Liquid	Not yet tested				1.174	0.98	continuing		2.62				2.95			
Hastelloy-C					1.8 - 14.5; tests discontinued				2.5 - 7.8; tests discontinued				7.8 - 9.0; tests discontinued				

*g = Small weight gain corresponding to negligible corrosion rate.

** Results after 543 hr of exposure.

*** Based on weight gained.

Hastelloy-B, "A" Nickel, Monel, Ilium R, Inconel, and 304 ELC were also tested and with one or two exceptions failed under all conditions listed.

The high-cobalt alloy S-816 was suitable with acid concentrations below 5 M (Fig. 6.1), and embrittlement in the hydrochlorinator would not be expected. It therefore shows promise for construction of a combined hydrochlorinator-dissolver. It would not be desirable for use with more concentrated acid because of the increase of corrosion rate with time. Alternate dissolver-hydrochlorinator tests are planned for further evaluation of this material. Tests with the promising high-cobalt alloys S-590 and Vitallium (Haynes-21) are continuing.

The dissolver tests involve exposure of metal specimens to solutions containing 0.4 M uranium ion (added as UCl_3 but subsequently oxidized to UO_2^{++}), 1.2 M chloride ion, and nitric acid concentrations of 0.5, 3, 5, and 15 M.* The solutions, kept at reflux temperatures ($\sim 110-122^\circ C$), are continuously agitated. Each material tested is exposed in the solution phase, the vapor phase, and at the solution-vapor interface. The test is continued for approximately four weeks (672 hr) and a material is considered to justify further testing if its maximum corrosion rate is 3 mils per month or less.

7.0 DAREX PROCESS

In the Darex process, fuel elements containing stainless steel are dissolved in dilute aqua regia, the chloride is stripped off with nitric acid, and the uranium is recovered by solvent extraction. Fuels that may be processed by this method are those of the Consumers Public Power and Yankee Atomic Power reactors.

7.1 Dissolution

Batch Studies (W. E. Clark, A. H. Kibbey). The weights of type 304L stainless steel required to react to completion with (i.e., "saturate") 100 ml of 2 M HCl containing 2 to 6 M nitric acid at $90-100^\circ C$ were determined. In confirmation of prior results (not yet reported) obtained both by this group and by M. L. Hyman, the maximum solubility of this stainless steel in aqua regia was obtained with 2 M HCl-5 M HNO_3 :

<u>Initial HNO_3 Conc. (N)</u>	<u>Solubility (g/liter)</u>	<u>Final Acid Conc. (N)</u>
3	51.8	0.73
4	56.1	0.73
5	66.3	1.13
6	61.4	2.43

All solutions were initially 2 M in HCl. The temperature was $90-100^\circ C$. The concentration of iron in the solution was used to calculate the weight of metal dissolved.

*Since Cl^- is decomposed in this solution, a stream of HCl gas is passed through the solution continuously.

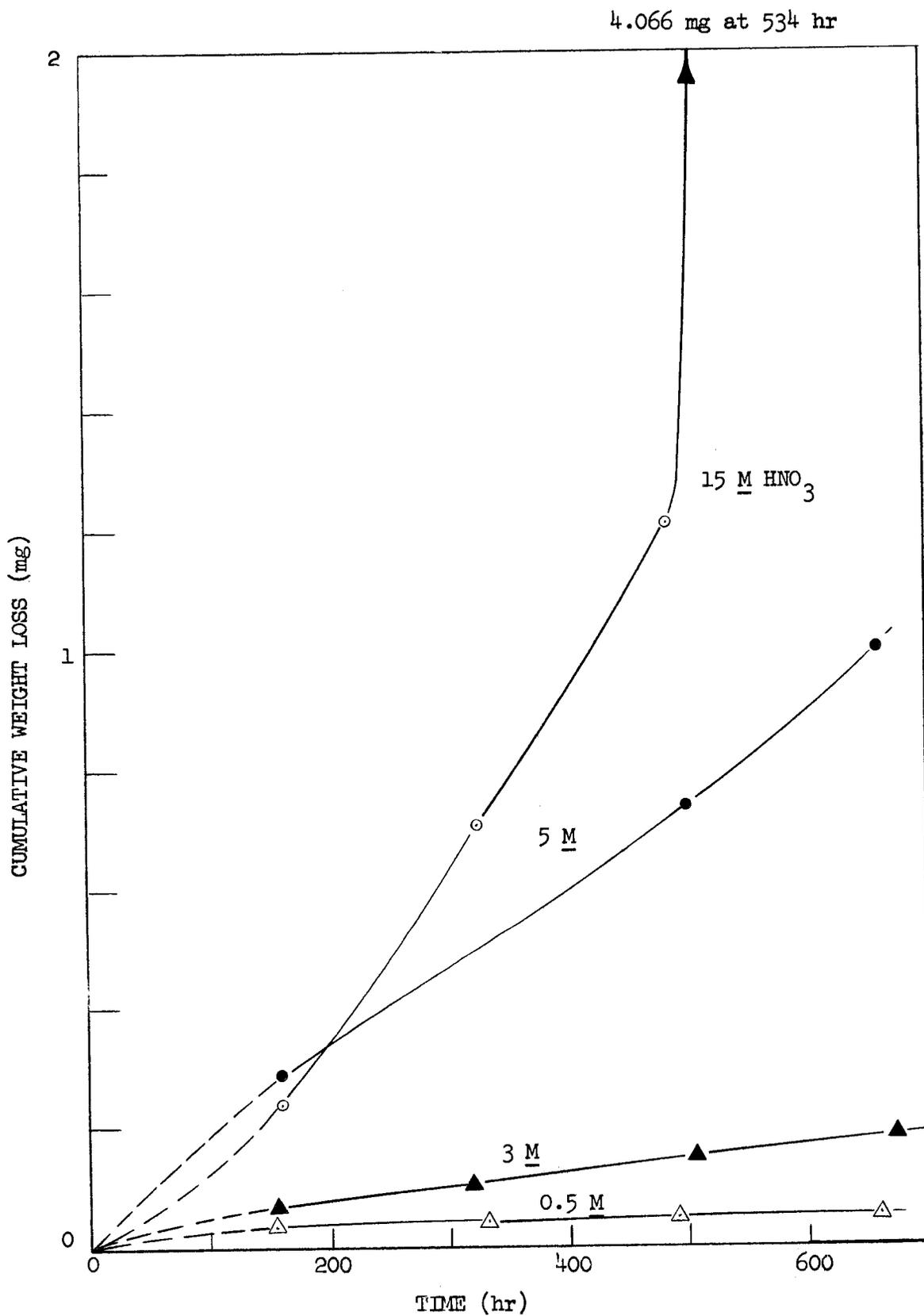


Fig. 6.1. Corrosion of High-cobalt Alloy in Zircex Dissolver Solutions (Liquid Phase).

Continuous Dissolution Studies (R. J. McNamee, J. J. Perona). Type 304 stainless steel dissolved in 4 M HCl—6 M HNO₃ at rates of 25 to 130 mg/m/cm² as the acid feed rate was increased from 20 to 200 ml/min. In 6 M HNO₃—2 M HCl the rate varied from 25 to 63 mg/c/cm². Reaction rates were plotted against the acid feed rate/surface area ratio (Fig. 7.1) to make the data independent of the liquid level in the dissolver and therefore valid for scale-up purposes.

Product-stream stainless steel concentrations were calculated to vary from 325 to 40 g/liter (Fig. 7.2). When centrifuged, samples of the product stream yielded a gelatinous precipitate which was water soluble. The indication was that saturated solutions were produced.

7.2 HCl Distillation (C. D. Watson, F. G. Kitts)

Leaks in the auxiliary equipment of the 4-in.-dia pyrex 12-plate bubble-cap column were eliminated, and the equipment was tested with aqua regia solutions of stainless steel and uranium. Mechanical performance was satisfactory, and in runs 2 and 3 the chloride was reduced to less than 30 ppm at the tenth plate (Fig. 7.3). The feed and the stripping vapor used were:

Run No.	Feed Composition			Total Metal (g/liter)	HNO ₃ in Stripping Vapor (mole %)	V/L Flow Ratio
	Cl ⁻ (N)	NO ₃ ⁻ (N)	H ⁺ (N)			
1	1.75	4.5	3.9	65	32.0	8/1
2	1.75	4.5	3.9	65	38.3	1.5/1
3	2.15	6.8	5.2	55	38.3	1.5/1

With azeotropic (38.3 mole %) nitric acid as the stripping vapor, dense red-brown vapor flowed overhead in the condenser and the strip condensate contained less than 0.1 of the chloride in the feed while the product stream was essentially chloride-free. Analysis of the vapors indicated their chlorine content, reported as Cl₂, to be approximately 50%. The principal method of chloride removal therefore seemed to be by decomposition rather than by stripping as HCl. With 32 mole % HNO₃ there was no NO₂ in the overhead condenser, and all the chloride entering in the feed was accounted for in the strip condensate; chloride in the product stream was negligible.

7.3 Solvent Extraction (J. R. Flanary, J. H. Goode)

Dissolution of the APDA Radial Blanket (depleted uranium and stainless steel) by the Darex process is expected to yield a feed solution containing ~1 M uranium, 1 M stainless steel, and 1 M HNO₃. Such feed could be processed in a Purex plant for plutonium and uranium recovery. A more concentrated feed would be unstable with regard to salt precipitation at normal operating temperatures. Batch countercurrent experiments simulating the extraction-scrub contactor in the first solvent-extraction cycle were conducted as follows:

Aqueous feed (40 vol): 215 mg U/ml, 50 mg SS/ml, 1 M HNO₃, 0.01 M NaNO₂, Pu(IV) tracer
Aqueous scrub (20 vol): 3 M HNO₃
Solvent (100 vol): 30% TBP³ in Amsco 125-82

Results indicated that the uranium loss was reduced to 0.01% with about 2 extraction stages, whereas about 4.5 extraction stages were needed to reduce the plutonium loss to 0.01%.

7.4 Corrosion Studies* (W. E. Clark).

Survey tests for Darex materials of construction are in progress. The only material thus far tested that stands up under the dissolver conditions used is tantalum (Table 7.1). The presence of any marked effect due to ruthenium (simulating fission products) in the solution cannot be considered to be either proved or disproved.

8.0 HERMEX PROCESS (O. C. Dean)

In the Hermex process uranium metal and alloys are purified and decontaminated from fission products by dissolution in mercury and subsequent recovery from solution. The results of previous Hermex work (reported in Power Reactor Fuel Processing reports, listed on p.iii) showed decontamination factors for irradiated uranium, results of Hermex purification of scrap uranium, and material balances for glass dissolver equipment. More recently, stainless steel equipment was built (Fig. 8.1) and operated to evaluate the various steps in the Hermex process for metal decontamination and metal losses. Fifty grams of uranium can be dissolved in 400 ml of mercury in each batch equilibration in this equipment.

8.1 Experimental Work

Stainless steel was substituted for glass as a material of construction because glass, particularly in the sintered glass filters, was suspected as an oxygen source, contributing to high uranium losses. One of the objectives of the experiments was to rigidly control the oxygen supply, since it was thought that the presence of oxygen during dissolution contributed both to decontamination and to metal loss. The oxygen supply was controlled by alternately evacuating and back-flushing the apparatus with argon purified by passage over drierite, magnesium perchlorate, and hot uranium turnings. Oxygen in the system was therefore only that residual in the argon plus that entering by in-leakage. Leakage during the runs was probably negligible because the apparatus leak rate was low and a 5-psi positive pressure of argon was maintained. The apparatus was constructed so that a stream of argon could be passed through the dissolver or crystallizer-filter, or a static head maintained. An argon flow of 0.2 cc/min was maintained through the dissolver and a static head over the filter. The oxygen concentration, as measured by a mass spectrograph, was 400 ppm for raw argon, 130 ppm for purified argon, and 64 ppm for the effluent from the dissolver.

*Carried out by Battelle Memorial Institute under a subcontract.

Table 7.1. Darex Corrosion Tests

"Midpoint" dissolver solution composition:

4 M H⁺ 0.15 M Cr³⁺
 1.9 M Cl⁻ 0.06 M Ni⁺⁺
 4.7 M NO₃⁻ 0.20 M UO₂⁺⁺
 0.55 M Fe³⁺ Sp. gr. = 1.27 at 25°C

Metal	Specimen Position	Corrosion rates (mils/month)									
		162 hr		165 hr		329 hr		353 hr		519 hr	
		Without Ru	50 ppm Ru	Without Ru	50 ppm Ru	Without Ru	50 ppm Ru	Without Ru	50 ppm Ru	Without Ru	50 ppm Ru
Tantalum	Vapor			g*	g*			g*	g*	g*	g*
	Vapor			g*	g*			g*	g*	g*	g*
	Interface			g*	g*			g*	g*	g*	g*
	Interface			g*	g*			g*	g*	g*	g*
	Liquid			g*	g*			g*	g*	g*	g*
	Liquid			g*	g*			g*	g*	g*	g*
Titanium	Vapor			0.021	0.018			0.047	0.039	0.06	0.05
	Vapor			g*	0.069			0.037	0.028	0.04	0.05
	Interface			g*	g*			0.006	g*	0	0
	Interface			g*	g*			0.006	g*	0	0
	Liquid			g*	g*			0.008	0.005	0	0.01
	Liquid			g*	0.003			0.006	0.007	0	0.01
S-816	Vapor	0.83	1.80			0.56	1.10				
	Vapor	1.28	1.06			0.82	0.74				
	Interface	1.94	2.17			1.29	1.46				
	Interface	2.14	1.79			1.44	1.29				
	Liquid	2.13	2.06			1.51	1.47				
	Liquid	1.77	1.33			1.33	1.08				
										Tests continuing	

* g = small weight gain corresponding to negligible corrosion rate.

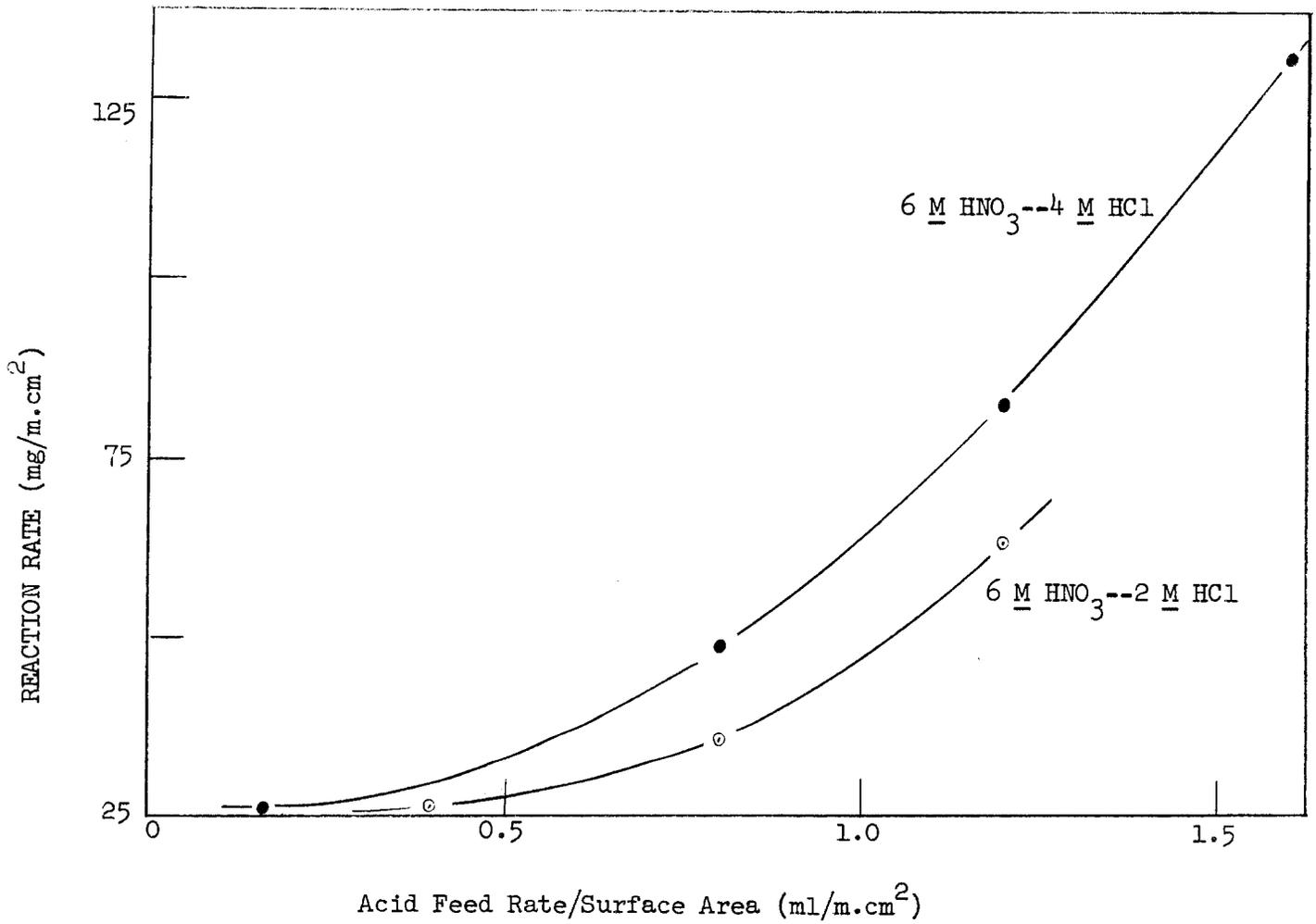


Fig. 7.1. Rate of Dissolution of Type 30⁴ Stainless Steel in Aqua Regia as a Function of Acid Feed Rate/Surface Area Ratio.

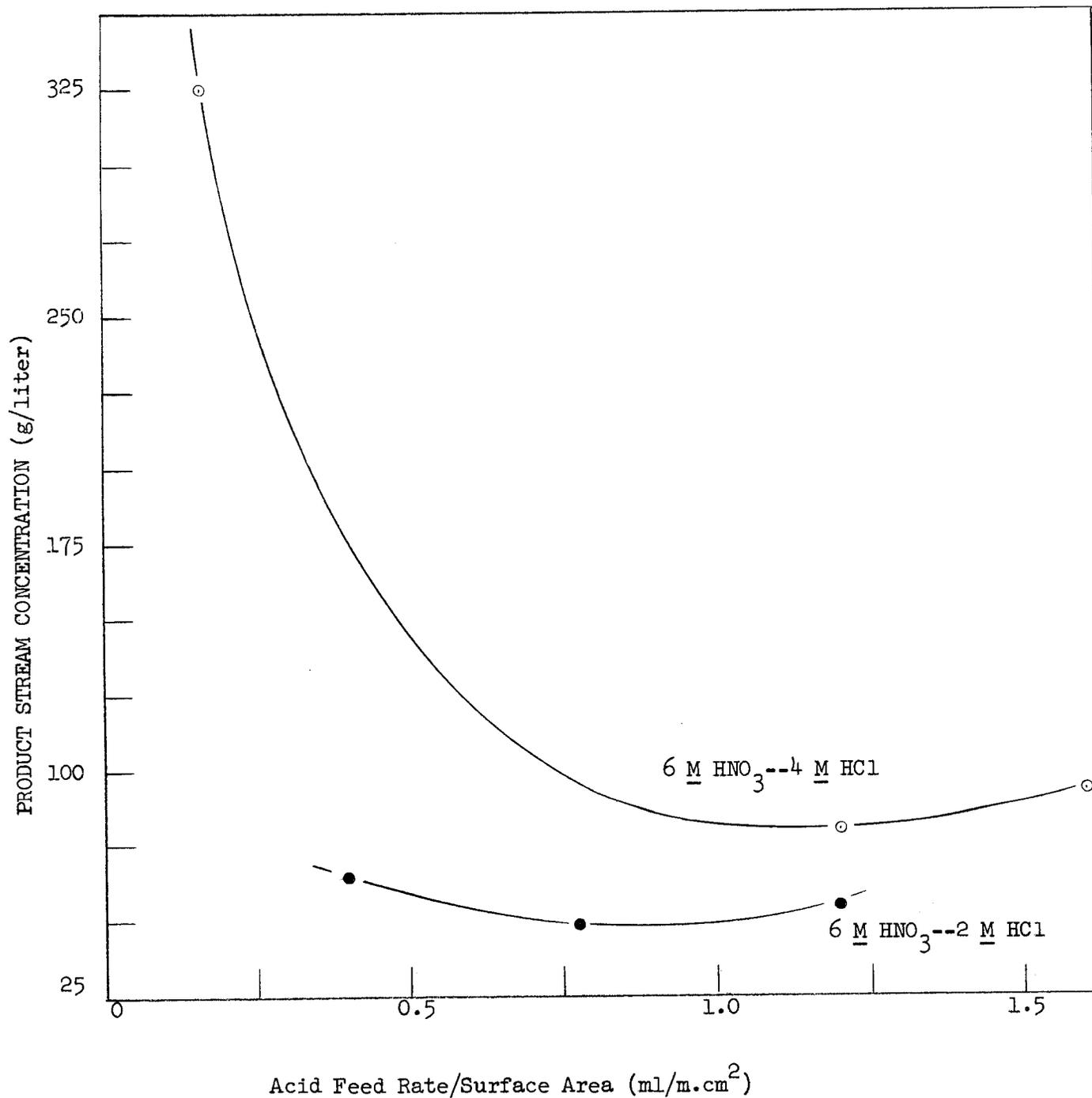


Fig. 7.2. Calculated Product Stream Concentrations as a Function of Acid Feed Rate/Surface Area Ratio.

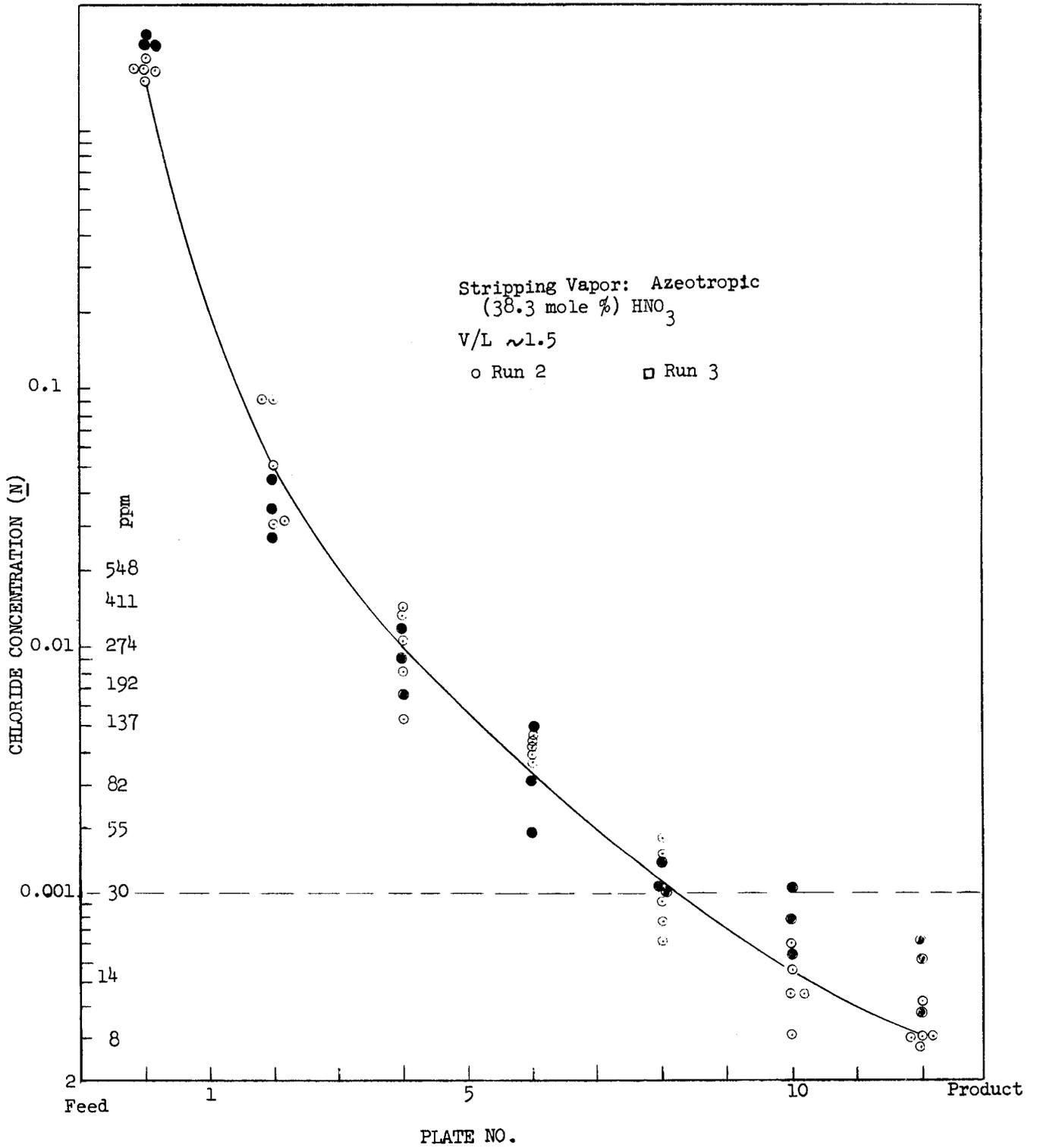


Fig. 7.3 Chloride Concentration Profile in Stripping Column.

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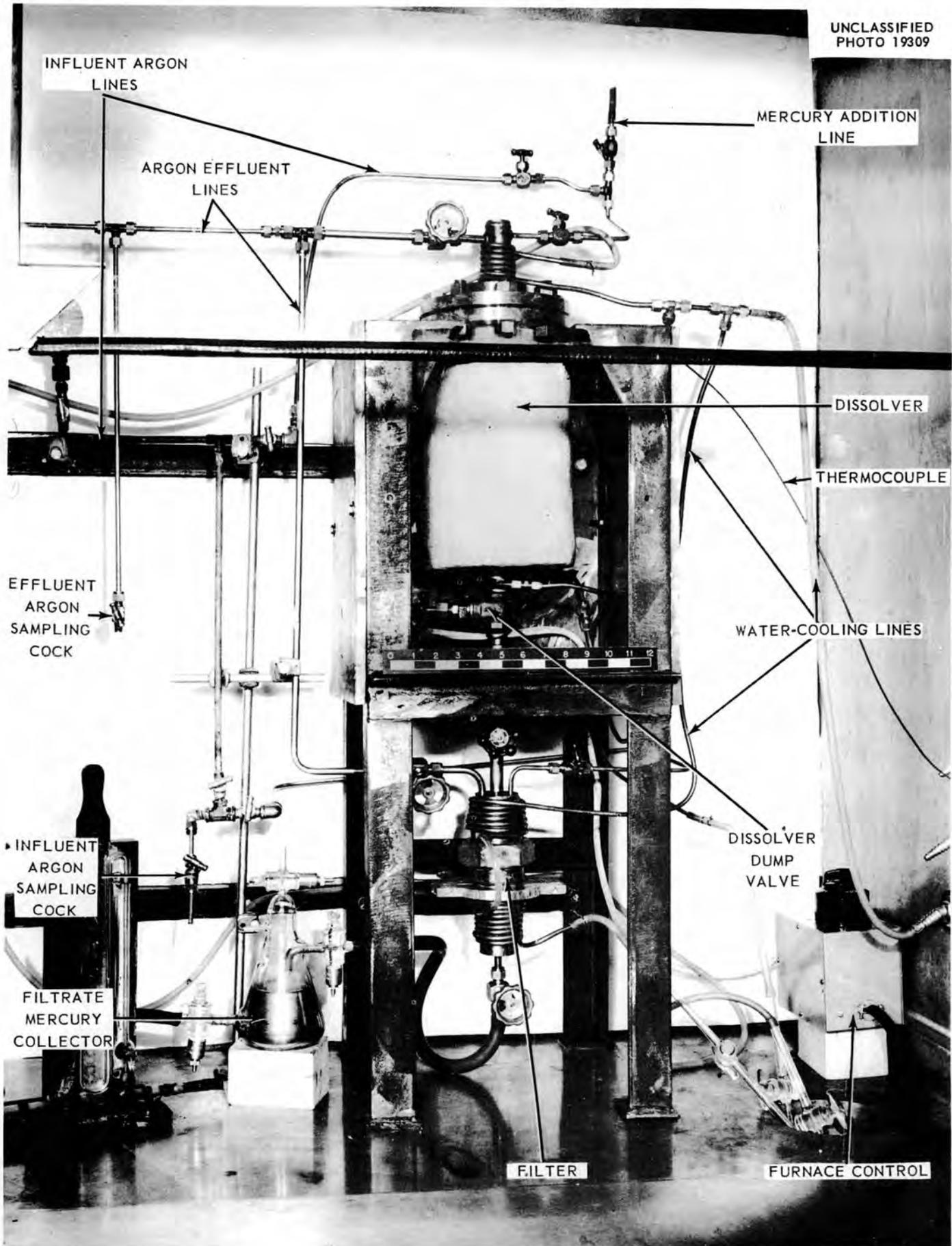


Fig. 8.1. Small Stainless Steel Hermex Dissolver.

In run 1, 35 g of unirradiated uranium was dissolved in 400 ml of boiling (360°C) mercury, and in runs 2 and 3, 35-g wafers of irradiated uranium were dissolved in 400 ml of boiling mercury. The dissolver tap and off-gas lines were water-cooled to decrease the mercury loss, the valve packings were water-cooled to prevent heat damage and consequent leakage, and the crystallizer-filter was water-cooled to promote crystallization of UHg_4 prior to filtration. In the first run, the stainless steel filter in the dissolver discharge line was not used, but in runs 2 and 3 it was used to hold up slag particles in the dissolver. In the first two runs UHg_4 crystallized in the water-cooled valves of the dissolver discharge lines, clogging them. In run 3 the valve bodies were maintained at 350°C while the shafts and packings were water-cooled. Some damage to packing occurred, allowing a small amount of leakage during transfer.

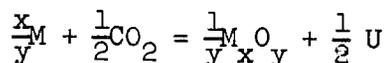
After transfer of the hot amalgam to the crystallizer-filter and cooling, the UHg_4 was separated from the free mercury by filtration, leaving a quasi amalgam $\sim 4\%$ in uranium. The crystallizer-filter was detached from the dissolver, with care to prevent contact of amalgam with air, and the UHg_4 quasi-amalgam phase was removed in a vacuum dry box under argon. The quasi amalgam was washed with 1 N HCl. Samples were taken of the original uranium fed to the dissolver, the washed and unwashed quasi amalgam, the nitric acid solution used to wash out the dissolver after the dissolution, and the dilute HCl in which the quasi amalgam was washed. The various phase samples were analyzed for uranium and fission products.

Results. No analytical data were taken for runs 1 and 2 because of clogging of the water-cooled discharge valves with crystallized UHg_4 . The following recommendations for apparatus changes were made as a result of behavior difficulties encountered:

1. The inlet inert-gas line to the dissolver should be brought down to the surface of the mercury for better contact of gas with boiling mercury.
2. There should be a more efficient condenser and trap system on the dissolver off-gas line to prevent mercury loss.
3. There should be an external means of indicating the liquid level on the dissolver pot and on the crystallizer-filter.
4. The diameter of the dissolver discharge line should be increased and means provided to maintain 350°C temperature without injuring valve packings.
5. The stainless steel filter at the bottom of the dissolver should be press-fitted to prevent by-passing of slag particles from the dissolver. There should be a means of easy removal of this filter without dismantling the entire apparatus.
6. The space above the filter in the crystallizer-filter should be increased to accept the entire dissolver batch, and the filter should be close to the bottom and be a press fit.

Run 3 was successful in that no clogging occurred and analytical data could be taken (Tables 8.1-8.5) for the run. Since the only steps in the Hermex process studied were dissolving, hot filtration, crystallization, filtration, and washing, and not the amalgam retorting and uranium melting, the decontamination factors are reported by individual steps (Table 8.4). The low values for the dissolving step for decontamination factors (column 1, Table 8.4) and for fission product removal (column 1, Table 8.5) are believed to be due to a low supply of oxygen. The oxygen requirement for the fission products is estimated at 5.82×10^{-4} ml. The oxygen supplied in the argon was calculated as 2.6×10^{-6} ml, a factor of 224 too low.

From Table 8.5 it can be seen that, of the steps studied, the dissolving-slugging step is the most effective in removing fission products. The mechanism of the reaction is:



The free energies of reaction at 633°K are:

Negative		Positive	
M	ΔF	M	ΔF
La	-15	Pu	+4
Nd	-12	Nb	+32
Ce	-14	Ru	+102
Sr	-9	Cs	+65
Zr	-1		

Table 8.1 Summary of Data for Run 3

Feed: uranium slug section, irradiated in ORNL graphite reactor,
 $nvt = 3.6 \times 10^{20}$ n/cm², decayed 3.5 yr
 Temperature: 360°C
 Dissolving rate: 10 mg/min/cm²
 Atmosphere: 5 psi purified argon at 0.2 cc/min
 Solvent: triple-distilled mercury (5500 g)

Stream	Total Wt (g)	Sample Wt (g)	Vol of Dissolved Sample (ml)	Uranium Conc. (mg/ml)
Dissolved feed U	18.51 ^a	1.26	20.2	62.60
Unwashed quasi amalgam	532	12.8	74.0	6.65
Washed quasi amalgam	474	20.8	80.0	11.50
Mercury filtrate	3221	49.5	204.0	0.008
Dissolver wash (aq)	--	--	1100.0	1.04
Quasi-amalgam wash (aq)	--	--	10.0	9.32

^aWeight obtained by difference, beginning and end of dissolution; in doubt because of mercury drag-out.

Table 8.2 Fission Products in Streams for Run 3

Contaminant	Feed	Activity (dis/m/mg U x 10 ⁻⁵)				
		Unwashed Quasi	Washed Quasi	Filtrate	Dissolver Aqueous Wash	Quasi-Amalgam Aqueous Wash
Gross γ	0.655	0.25	0.228	0.94	7.15	2.07
Gross β	1.36	1.11	1.018	5.47	7.72	5.31
Cs β	0.289	0.0813	0.0723	0.218	3.18	0.829
Sr β	0.214	0.150	0.1365	0.395	1.373	1.35
TRE β	0.762	0.700	0.626	---	2.38	3.24
Ru β	0.0624	0.0468	0.0422	0.246	0.303	0.0414
Zr, Nb γ	0.1246	0.0101	0.0419	0.162	1.45	0.231
Pu α	0.00404	0.00253	0.00153	---	0.0033	0.0133

Table 8.4 Decontamination Factors for Run 3
(Based on ratios of disintegrations/min/mg U)

Contaminant	Feed/ Unwashed Quasi	Feed/ Washed Quasi	Unwashed Quasi/ Washed Quasi
Gross γ	2.62	2.87	1.1
Gross β	1.23	1.34	1.09
Cs β	---	3.55	---
Sr β	1.43	1.57	1.1
TRE β	1.09	1.22	1.12
Ru β	1.33	1.48	1.11
Zr, Nb γ	---	2.98	---
Pu α	1.60	2.64	1.65

Table 8.5 Removal and Loss Data for Run 3

Component	Removal (%)			
	Dissolving ^a and Slagging	Filtration ^b	Aqueous Washing ^c	Overall ^d
Uranium (losses)	512	0.474	0.417	6.47
Mercury (losses)	32.0	--	--	16.0 ^e
Gross γ	55.7	6.8	1.32	67.2
Gross β	29.0	1.9	1.62	31.5
Cs β	56.5	3.57	1.21	73.5
Sr β	32.8	0.88	2.63	40.2
TRE β	16.0	--	1.77	23.0
Ru β	25.0	1.87	0.28	36.6
Zr, Nb γ	59.8	0.62	0.77	68.3
Pu α	4.2	--	1.1	64.5

^aIncluding hot filtration.

^bCold filtration after crystallization.

^cAgitation of quasi amalgam with cold 1 N HCl.

^dIncluding experimental handling.

^eInadequate condenser on dissolver.

Table 8.3. Material Balances on Run 3

Stream	Activity (dis/min x 10 ⁻⁸)								Uranium	Mercury
	Gross γ	Gross β	Cs β	Sr β	TRE β	Ru β	Zr, Nb γ	Pu α	(g)	(g)
Feed	14.65	30.5	6.45	4.79	17.0	1.392	2.78	0.0904	18.51 ^a	5499.5
Unwashed quasi	5.25	23.3	1.52 ^b	3.15	14.7	0.985	0.212 ^b	0.053	21.00	532
Washed quasi	4.8	21.25	1.70	2.86	13.1	0.882	0.875	0.032	20.89	474
Filtrate	0.995	0.58	0.23	0.0419	--	0.0261	0.0172	--	0.106	---
Dissolver aq. wash	8.15	8.84	3.64	1.57	2.73	0.347	1.66	0.0038	1.144	---
Quasi aq. wash	0.1935	0.495	0.0772	0.126	0.301	0.00386	0.0215	0.00124	0.093	---
Material balance, % recovery of feed	93.3	108	88	99.5	102.5	97.3	92.5	63	120	84
Samples									1.26	865

^aWeight doubtful due to drag-out of mercury with slug at end of run. This value is summation of product stream analytical values.

^bResults doubtful. Best material balances obtained by adding washed quasi amalgam and aqueous quasi wash.

9.0 THOREX PROCESS

In the Thorex process irradiated aluminum-clad thorium fuel elements are dissolved in nitric acid and the thorium and U²³³ are recovered by solvent extraction.

9.1 Pilot Plant (E. M. Shank, W. R. Winsbro)

The Thorex pilot plant will be modified to include a third uranium cycle to improve the uranium decontamination and an additional 5000-gal decay system (APC) for collection of the protactinium-containing extraction column waste stream. Eventually an additional 5000-gal product storage system (BTC) will also be added.

Third Uranium Cycle Design. This facility, which will have a capacity of 3 kg of uranium per day, will be installed in cell 3 of Bldg. 3019, and will cost \$150,000. Construction has started and is scheduled for completion by May 1. Detailed design and construction schedules have been prepared for meeting this construction deadline. Engineering design required preparatory to drafting is essentially complete for the engineering flowsheet and equipment design, and is now entering the equipment layout and structural design stages. The philosophy of design and layout for all process equipment has been reviewed and approved by the Criticality Committee. Instrumentation is being designed by the ORNL Instrument Department. The spare dissolver (S-1-S) and feed adjustment tank (S-2-S) for the Thorex pilot plant being fabricated by the Nooter Corporation of St. Louis, Missouri, have been returned to Nooter for the repair of process welds which did not meet the "tighter than code" specifications set up for fabrication. One vessel is now scheduled for delivery on February 1, 1957, and the other on March 1, 1957.

APC and BTC Vessel Design. Each vessel will have a capacity of 5000 gal. Since corrosion will be more severe for APC storage than for BTC, the APC vessel will be fabricated to specifications considerably tighter than the ASME Code whereas the BTC vessel will be fabricated to code alone.

Both vessels will be fabricated by the Alloy Fabricators Division of Continental Copper and Steel Industries, Inc., Perth Amboy, New Jersey. Certified drawings for both vessels have been approved, and fabrication of the BTC vessel is underway.

Pilot Plant Run HD-21 Summary. One 10-day run, HD-21, was made with irradiated thorium.

A total of 610 kg of irradiated thorium and 150 kg of recycled thorium was processed, using the co-decontamination flowsheet, to recover 750 kg of thorium product. A total of 1390 g of U²³³ was sorbed on ion-exchange resin. One U²³³ elution was made to isolate 1280 g of product. Sustained solvent-extraction operation could not be maintained owing to the poor operation of the IC-column, the cause of which has not yet been determined. Solvent

extraction losses were abnormally high, 1-12% for thorium and 3-8% for uranium. The high thorium loss occurred in the IAW and was due to the failure of the IAX pump and to the frequent interruptions in column operation resulting from poor operation of the IC-column. The high uranium loss was in the IICW and is due to insufficient stripping length in the IIC-column. (While this loss is considered a solvent extraction loss, it is not a plant loss since the IICW is recycled as IAX and IIBS.)

The final gross γ decontamination factors observed for the run were 2.2×10^4 for thorium and 3.3×10^4 for uranium:

Activity	First Cycle		Second Cycle		Over-all	
	Thorium IAF/ICP	Uranium IAF/ICP	Thorium IIAF/IIBT	Uranium IIAF/IICU	Thorium IAF/IIBT	Uranium IAF/IICU
Gross γ	2400 ₄	2200 ₄	9	15	2.2×10^4	3.3×10^4
Pa γ	3.8×10^4	3.7×10^4	1.5	1	3.7×10^4	3.7×10^5
Ru γ	630	580	8	210	5000 ₄	1.2×10^5
Zr-Nb γ	1700	1600	10	15	2.7×10^6	2.4×10^6
TRE β	7500	6900	> 340	1400	2.5×10^6	9.7×10^6

Criticality Studies. A study to determine existing criticality limitations and to establish operating parameters or needed equipment modifications was undertaken. The uranium isolation product receiver sampler drain, which is connected to the process rework system, was eliminated as a possible danger. No other serious limitations exist and normal plant control procedures are adequate safeguards to permit processing thorium irradiated up to 10,000 g of U^{233} per ton.

Thorium Oxide Production. About 1240 lb of standard thorium oxide was prepared and 290 lb of special-fired thorium oxide was shipped.

Radiation Exposure. The average radiation exposure to 21 operating personnel was 39 mr/man-week for the month.

9.2 Pulsed Column Interfacial Solids Removal (C. D. Watson, R. J. McNamee)

Equipment (ORNL-2228, Figs. 13 and 14) for continuously removing liquid from the interface of a pulsed solvent-extraction column, filtering it, and returning the filtrate to the column was installed on a 2-in.-dia 26-ft-high glass column. In extraction of nonirradiated Thorex process feed, the system operated satisfactorily for several runs. However, in later runs, severe emulsions which could not be broken by the filter system formed; e.g., the emulsion at the interface built up from 4 in. to 7.5 in. in 30 min. Installation of two condensers cooled with ice water so that the emulsion was cooled from 70°F to 50°F at the pump discharge reduced the emulsion somewhat in a 45-min run. A longer run would be necessary to determine the real value of this modification. With the cooling unit in place, the emulsion layer built up to 8 in. in 10 min more, dropped to 5.75 during the next 15 min, and stayed at this level for the remaining 20 min of the test.

9.3 Process Improvement Experiments (R. H. Rainey, A. B. Meservey)

Calculations indicate that about 0.1 mole of nitrite per liter per day* may be formed by the self-irradiation of Thorex feed made from irradiated thorium decayed only 30 days before processing. The nitrite produced in the solution prior to the feed adjustment step will be destroyed, but nitrite produced after this step will affect the solvent extraction process. Laboratory countercurrent batch extractions demonstrated that 0.1 M NaNO_2 in the feed decreases the decontamination factor from about 600 to about 2:

	Decontamination Factors			
	Gross γ	Ru γ	Zr-Nb γ	TRE β
Feed containing 0.1 M NaNO_2	2.1	2.5	2.6	800
Control without nitrite	490	590	130	2000
Feed containing 0.1 M NaNO_2	5.3	1.6	--	--
Control without nitrite	1400	650	--	--

Concentrations as low as 0.01 M NaNO_2 were sufficient to reduce the ruthenium decontamination by a factor of 10 and 0.001 M NaNO_2 by a factor of 2.

In previous work on Purex and other acid type solvent extraction flowsheets nitrite improved the ruthenium decontamination. An evaluation of the KAPL Thorex flowsheet, which uses 1.0 N acid feed and scrub, was made with both first- and second-cycle feeds. With a feed made from irradiated metal and the digestion-evaporation treatment in the pilot plant, decontamination factors were: gross γ , 50; Ru γ , 10; Zr-Nb γ , 250; and TRE β , 1.6×10^2 . The KAPL flowsheet gives higher decontamination from the rare earths because of high TBP saturation. The ruthenium decontamination is about the same with the two flowsheets, but protactinium and zirconium-niobium decontamination is a factor of 10 better with the ORNL flowsheet.

Previous work has demonstrated the improvement in ruthenium decontamination with increasing acid deficiency of the feed solution. One undesirable effect, however, has been the increase in thorium loss with acid deficiency. Partial neutralization of the acid deficiency in the last extraction stages decreases the thorium loss while maintaining some of the improved ruthenium decontamination. Reduction of the acid deficiency in the fourth extraction stage of a countercurrent batch extraction, having five extraction stages, from 0.30 to 0.15 with nitric acid reduced the thorium loss from 1.91% to 0.26%. Partial neutralization at the fifth stage, which can be effected with acidified solvent, was less effective than the fourth stage neutralization.

The present feed adjustment treatment requires the feed to be heated to 155°C and digested at this temperature for 1 hr. Modifications in this procedure have lowered the ruthenium decontamination. When feed was heated

*Mahlman, H. A., "Radiation Induced Nitrite Formation from Concentrated Nitrate Solutions," Thesis, University of Tennessee, December, 1956.

to 155°C and then sparged several times with water, the ruthenium decontamination factor was about 50 as compared with about 500 for the present treatment. Acid solutions which were made acid deficient and not heated showed even lower ruthenium decontamination.

The quantitative effect of the acid deficiency of the extraction column has been established at two conditions of acid deficiency in the feed, using laboratory countercurrent runs. At a feed acid deficiency of 0.45 N the Ru decontamination factor was 470 for neutral scrub vs 610 for 0.13 N acid deficient scrub. This difference was probably not statistically significant. At a feed acid deficiency of about 0.03 N, however, the decontamination factor was 130 with neutral scrub and 360 with the 0.13 N acid deficient scrub. The organic phase in all stages contained less ruthenium with the acid deficient scrub than with the neutral scrub. The improved decontamination factor resulting from the higher acid deficiency at the feed point is also evident from the above data.

10.0 AQUEOUS DISSOLUTION STUDIES

10.1 Dissolution and Dejacketing of Zirconium Fuel Elements with 14 M H₂SO₄ (W. E. Clark, A. H. Kibbey)

The Zircaloy-2 jackets of obsolete PWR fuel element rejects (10% molybdenum—90% uranium core) were removed rapidly and in most cases completely by treatment with 14 M sulfuric acid at 230°C. The nominal dissolution rate obtained over about 6 min was 73 mg/m/cm². The attack was apparently intergranular in nature since the solution became dark, presumably as a result of suspended particles of finely divided zirconium. The end of rapid attack was marked by a clearing up of the solution, leaving only a few of the larger particles undissolved. A sample of zircaloy-2 taken from the end piece of an STR fuel element gave a nominal rate of 37.1 mg/m/cm². In this case there was only slight darkening of the solution.

In the dissolution of the PWR cladding, removal of the clad was incomplete at an acid/zirconium ratio of 42/1 and it was necessary to use fresh acid to complete the removal. At a ratio of 84/1 the cladding was completely removed. In each case the uranium dissolved from the core was approximately 7 µg/ml, which amounted to about 0.02% of the uranium in the samples used. The maximum rate of attack was obtained with 14 M acid, which confirms results of preliminary experiments. At concentrations of 12 and 16 M the nominal rates were 9 and 37 mg/cm²/min, respectively, and the cladding was incompletely removed even by subsequent treatment with excess fresh acid.

The attack on the metal is of an oxidizing nature, as is evidenced by odors of reduced forms of sulfur (SO₂, H₂S) which are given off during the reaction.

11.0 MECHANICAL PROCESSING

11.1 Decladding (C. D. Watson, G. A. West)

In further tests on the Mackintosh-Hemphill rotary straightener (CF-56-7-101, Fig. 2) the zirconium tube was successfully removed from a PWR blanket element. This tube, which is 0.413 in. o.d. and 10.25 in. long, contains UO_2 wafers. Two passes through the rollers were required. The end cap was snapped off after only 3 mils expansion of the zirconium tube. The UO_2 wafers were reduced to powder, which could be poured from the tube. Visual observation indicated that no UO_2 remained on the walls of the tube.

Two rods containing carbon steel cores bonded with lead (to simulate Na-K) to a stainless steel cladding were prepared for additional tests.

11.2 Cut-off Saw

Designs were completed of two types of abrasion disk saws (Figs. 11.1 and 11.2) for disassembling spent reactor fuel bundles. The components consist of the facility for receiving the fuel assemblies, the abrasion disks to remove end boxes and separate the core and blanket material, and means for discharging the separated assemblies from the table. Cost estimates of the two concepts and lifetests of abrasion saw blades have been started.

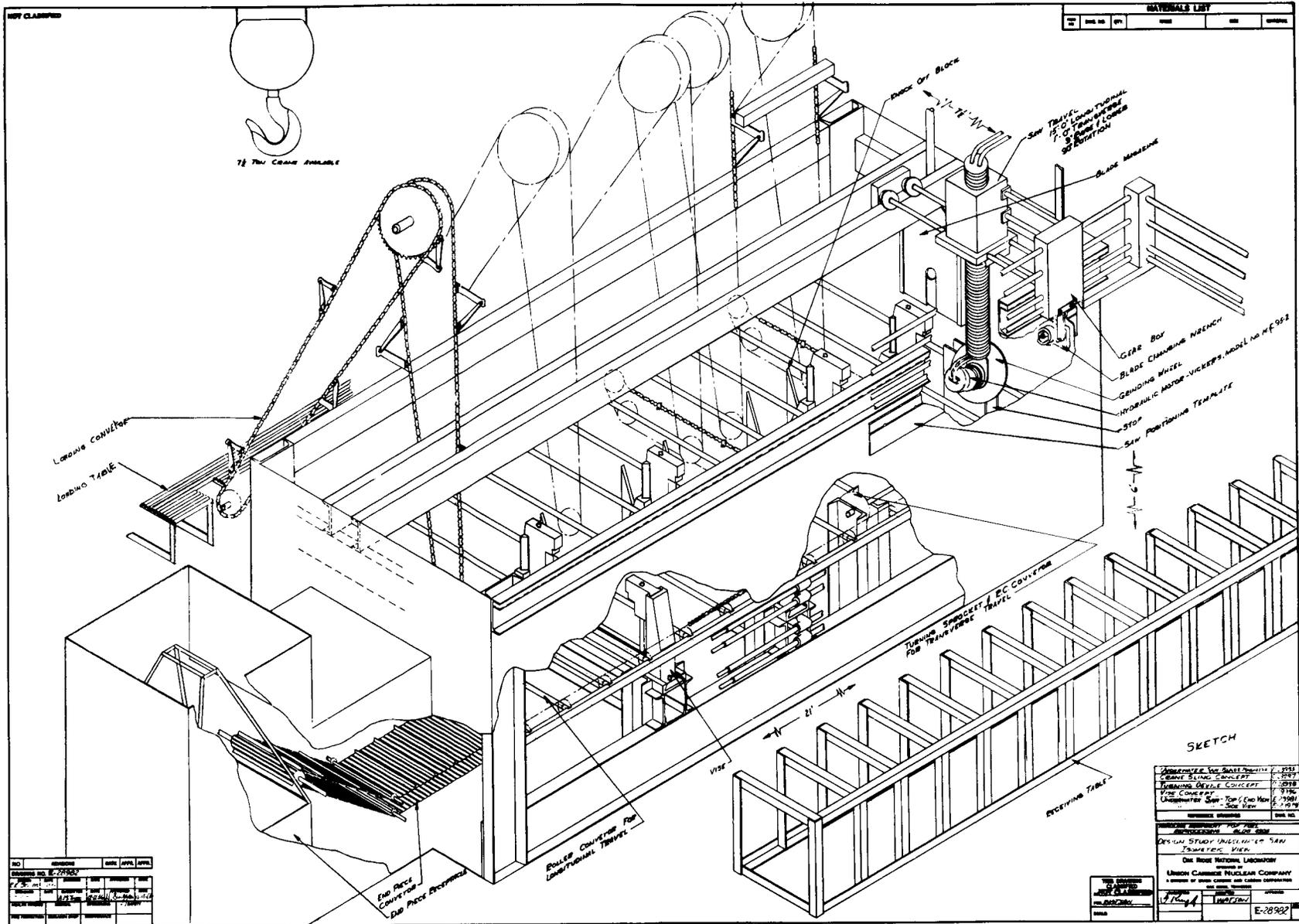


Fig. 11.1. Underwater Cut-Off Saw, First Design.

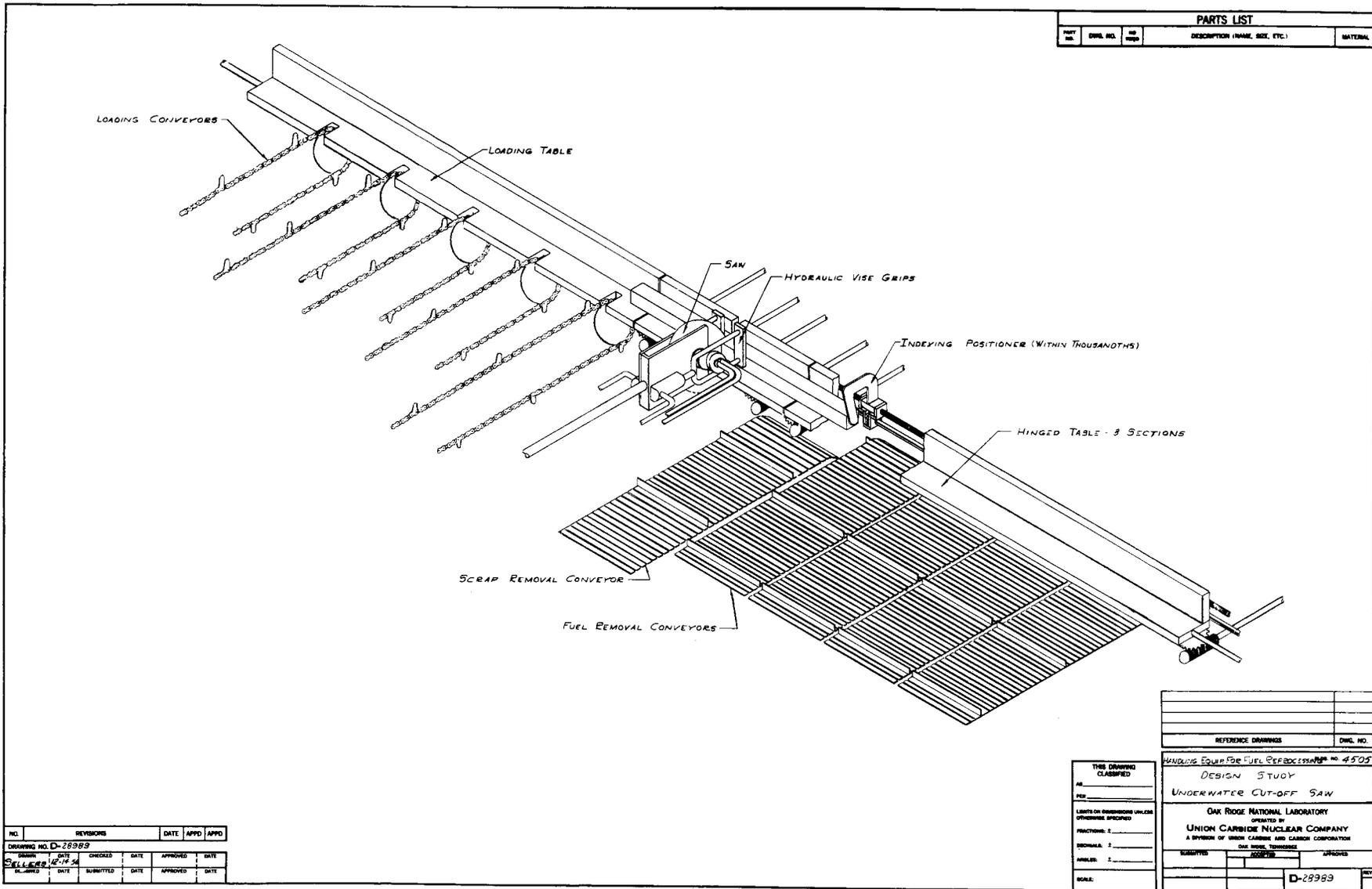


Fig. 11.2. Underwater Cut-Off Saw, Second Design.

Part III. HOMOGENEOUS REACTOR FUEL AND BLANKET
DEVELOPMENT AND PROCESSING

Previous homogeneous reactor work is reported in the HRP quarterly progress reports.

12.0 HRT CHEMICAL PROCESSING PLANT

(W. E. Unger, W. D. Burch, E. O. Nurmi, A. M. Rom, B. F. Bottenfield, H. O. Weeren, G. B. Berry, W. J. Clossey, F. C. McCullough, W. F. Schaffer, R. E. Brooksbank, N. A. Brown, J. R. Engle, B. H. Hamling, R. H. Winget, P. A. Haas, R. W. Horton, S. D. Clinton, C.C. Haws)

12.1 Fuel Processing Plant

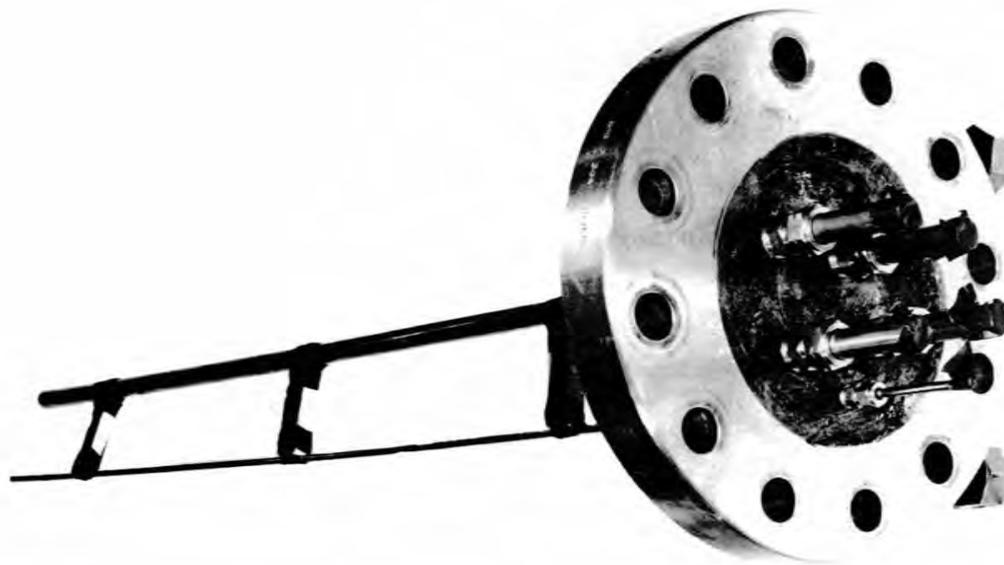
Design. Design of the fuel processing plant is essentially complete. A 500-gal storage tank for accumulation of wastes, pending processing for uranium recovery in the Thorex plant, is being designed. It will be 24 in. by 20 ft long, the geometry being dictated by the criticality limit on uranium concentration of 0.45 kg/ft. The solutions stored in the tank will have decayed to an activity such that the evolution of volatile and gaseous fission products will not be significant and the tank can be vented directly to the stack. It will be made of Carpenter-20 stainless steel. Cooling coils will be provided to minimize corrosion. Ultimately the solution accumulated in the storage tank will be transferred in a 40-gal carrier to the Thorex plant for processing. The carrier will be critically safe if all uranium in the storage tank remains in solution. This will be verified by sampling before transfer to the carrier is begun.

Construction and Operation. Following a two-month period of shakedown operation in which all testing of the HRT fuel processing plant high-pressure system was completed, operations were halted for extensive modifications to the low-pressure system. These modifications include a dissolver system with two 100-gal decay storage tanks to permit obtaining a solution sample of the fission and corrosion products removed from the reactor by hydroclone operation. The modifications are 50% complete and include steam, water, and refrigerant service lines in service Cell A and 80% of the process equipment in Cell C.

Components added to the system include the 5-gal tantalum-lined dissolver vessel (Fig. 12.1), two 100-gal decay storage tanks, nine new valves, 10 additional freeze plugs, a sampling facility, two transfer tanks, and nine double-pipe heat exchangers. The decay tanks, transfer tank, all the valves, and seven heat exchangers are fabricated of Carpenter-20 stainless steel for added corrosion resistance to the sulfuric acid used in the dissolution.

Fig. 12.2 is a photograph taken January 21 of the south half of Cell C, in which the new equipment is located. The decay tanks are just visible in the lowest portion of the cell. The dissolver will be installed in the "open" space just to the right of the three valves visible in the lower center portion of the picture.

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Fig. 12.1. 5-gal Tantalum-Lined Dissolver and Top Flange.



Fig. 12.2. Dissolver System Installed in South Half of Cell C.

In service Cell A, a new valve rack (Fig. 12.3) was installed on the south wall of the 813-ft level to handle new steam, water, and refrigerant valves and flowmeters. Solenoid valves in lines to the new freeze plugs are visible on the manifold at the bottom of the rack. A new instrument rack, which will contain transmitters for level and specific gravity measurements on the decay storage tanks, will be located just to the left of the valve rack.

These modifications to the low-pressure system necessitated changes to the main graphic control panel. The two panels depicting the original low-pressure system were replaced with three new panels. Installation of new instruments and wiring for them is under way.

Component Testing. Belleville springs have shown no significant advantage in reducing bolt loadings on the HR chemical plant flanged joint. In tests with series arrangements of these and other springs, the expected increase in deflection, and resultant decrease in bolt loading, was not obtained.

Assembly	Flange Assembly No.	Bolt No.	Initial Bolt Loading (lb)	Hot Bolt Loading (lb)
3 springs in parallel with one assembly at each end of bolt	3 3	57 58	7300 7200	20,300 16,500
2 springs in parallel with 2 assemblies in series	1 1	1 2	7800 7300	17,500 16,200
2 springs in parallel with one assembly at each end of bolt	4 4	X1 X4	6800 7300	14,100 15,100

No explanation for the results is offered. In earlier tests a single assembly of three springs in parallel gave hot bolt loadings of 14,300 and 15,400 lb, and with such an assembly at each end of the bolt (flange assembly 3) loadings of 10,000-12,000 lb were expected. They were actually higher than in earlier tests. Also, creep was not appreciable in the earlier tests, and the differential thermal expansion was such that a system with two springs in parallel would not be stressed beyond the yield point. Hot bolt loadings for flange assemblies 1 and 4 were expected to be 10,000 lb but, instead, were 14,000-17,000.

12.2 Blanket Processing Plant

Design. Preliminary design is in progress and flowsheets are in the drafting stage for the blanket processing plant. This will be similar to the core plant, in that the continuous centrifugal removal of plutonium from UO_2SO_4 blanket solution exploits the hydrolysis and precipitation of plutonium at the operating temperature of the reactor. The plant will be designed to operate continuously for 90 days, with provision for processing the entire blanket for

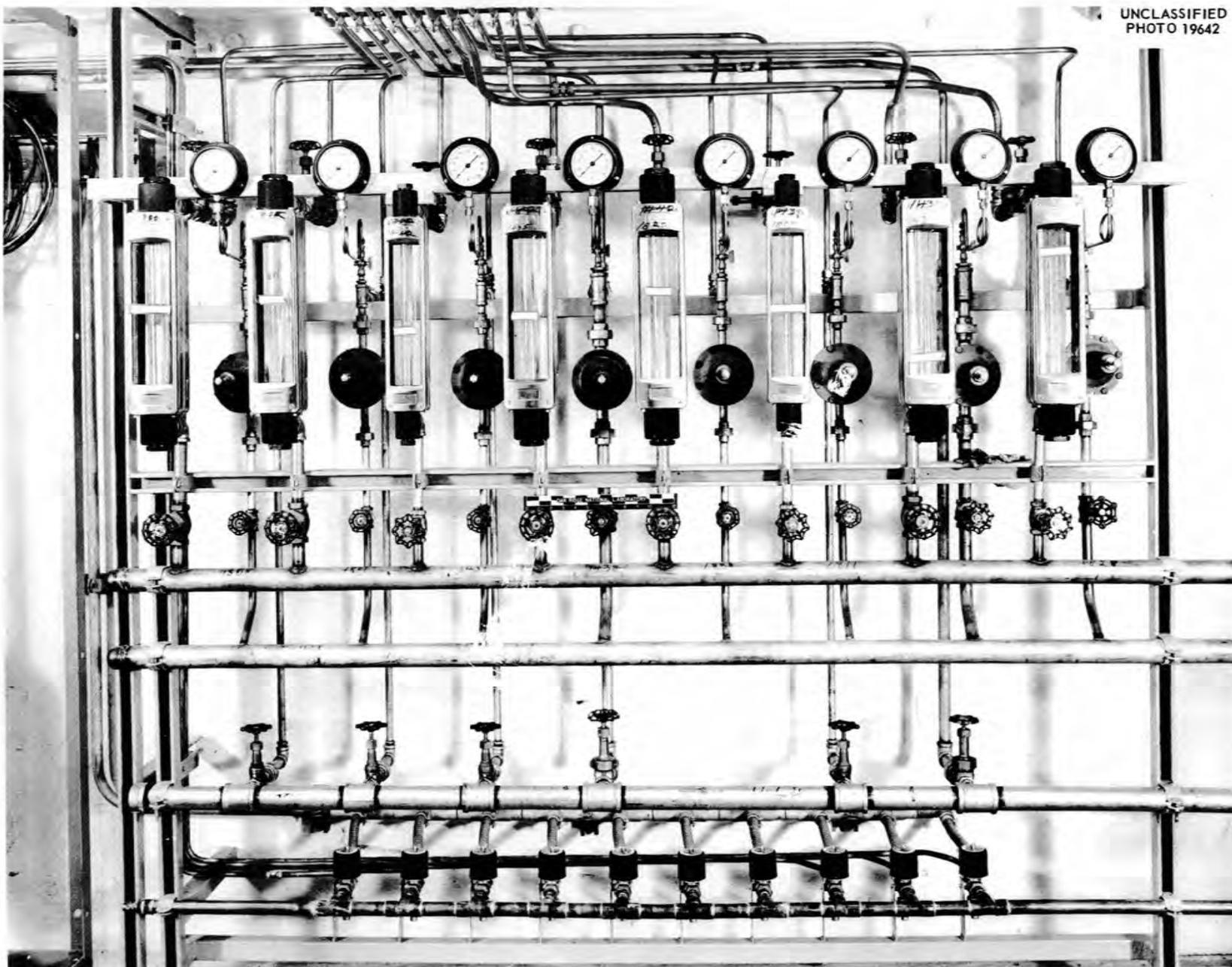


Fig. 12.3. Valve Service Rack and Auxiliary Instrument Panel for Dissolver System.

recovery of D_2O . Relatively little is known of the chemistry of the high-concentration UO_2SO_4 system (1.4 m) that would make it necessary to depart radically from basic design philosophies adopted for the design and construction of the core processing system. Materials of construction, types of equipment, material and welding specifications, maintenance philosophies, etc. will be largely the same as those previously specified for the core plant.

Construction Operation. The completion of construction for the blanket plant, originally scheduled for June 1, 1957, has been deferred until April 1, 1958, thus permitting three months of operational shakedown prior to operation with the UO_2SO_4 blanket, beginning July 1, 1958. Procurement of long-delivery items has been initiated.

12.3 Experimental Loops

P-1. Installation of loop P-1 was completed and initial operating tests were started. The first two test runs were made with H_2O and O_2 overpressure, during which loop temperatures of 150 and 200°C were attained. The third run was made for cleaning purposes with a 3 wt % Na_3PO_4 solution and an O_2 overpressure in the loop. A temperature of 240°C was reached. The Westinghouse 150-A pump has run for three different time periods of approximately 4 hr each.

Before the pump was started, the loop was pressure-tested with nitrogen. The continuously operated part of the loop was made leak-tight to a pressure of 1500 psi. The only difficulty was leakage around a gold wire gasket between the scroll case and the loop pump at pressures greater than 1500 psi at the end of the second run. After two thermal cycles the torque on the scroll case bolts had dropped from 300 to 40 ft-lb, indicating that the gold wire had been considerably flattened. The bolts were re-torqued to 200 ft-lb, and, upon cooling at the completion of the third run, the torque required to loosen the bolts was approximately 80 ft-lb. A gold-plated stainless steel gasket is being fabricated to replace the gold wire.

Since there are no loop heaters, all heat to the loop solution must be supplied by the work input of the 150-A Westinghouse pump. After the first two runs with the loop exposed to the atmosphere, two layers of aluminum foil insulation were placed around the pressurizer and main loop. The loop temperature was 240°C and was still increasing when the third run was ended. No trouble is expected in reaching the operating temperature when the loop container is sealed and placed under a vacuum, minimizing the convection heat losses.

Supplementary equipment, by-pass bombs and removable coupon holders, have been designed, and are being fabricated for installation on P-1 loop. The slurry-addition bomb and the in-line removable samplers have been combined as one item. This equipment together with the removable coupon holder will be housed in an auxiliary dry box on the right-hand side of the loop container.

Investigation of an electronic sealing device for the polyvinyl sleeves to receive and contain contaminated parts and samples was completed and the selected equipment placed on order. Delivery is expected early in February.

P-2. The loop P-2 components have been designed to meet the extreme requirements of in-pile operation. In tests at room temperature a modified ORNL canned rotor pump performed satisfactorily. All parts of this pump exposed to the fluid pumped are titanium except the high-density aluminum oxide bearings and journals. The impeller is a 4-in. dia, and three-phase stator windings give shut-off heads of 53 ft at 60 cycles per second and 113 ft at 95 cycles per second electrical input. The aluminum oxide bearings and journals showed no wear for 30 hr of operation with H₂O. The measured differences between the journal o.d.'s and the bearing i.d.'s were 0.0020 to 0.0028 in. at the shop when built and 0.0018 to 0.0022 in. at the end of the test. The suction head necessary to prevent cavitation was about 10 ft at 1 gpm and 20 ft at 5 gpm.

A heat exchanger designed to permit removal of 10 kw of heat from loop solution at 260°C was tested with several variations of air and H₂O coolant combinations. Either water sprayed into the air or a coolant water stream of about 4 gpm entering at 30°C or less removed the required amount of heat from the loop solution at 260°C. Either 100 psia air or water sprayed into air removed 0 to 3 kw. There does not seem to be any arrangement which would give continuous, smooth control with the present heat exchanger for heat removal rates of 3 to 7 kw.

The heat exchanger has three parallel 1/4-in. IPS Sch. 80 titanium pipes for the uranyl sulfate solution side, cast in aluminum with three parallel 1/4-in. IPS Sch. 40 stainless steel water tubes (Fig. 12.4). This geometry puts a double wall between the loop solution and coolant and thus minimizes the possibility of coolant contaminations; gives an increased area per unit of length and thus minimizes the heat flux; minimizes the thermal stresses in the titanium as a result of the increased area and thinner pipe walls as compared to a single larger pipe.

The values of $UA = q/\Delta T$ were determined for log mean temperature differences (Fig. 12.5). The peak in the value for water was probably due to nucleant boiling, which gave a high coefficient for a narrow velocity range. These values are rough approximations only since the steam film would be replaced by a uranyl sulfate solution film in the loop. The amounts of heat that could be removed by the various cooling methods can be easily calculated from the UA values. These values for inlet temperatures of 30°C and loop solution temperatures of 260°C were determined.

For water:

Let the outlet temperature be 40°C

$$\Delta T = \frac{\Delta T_{\text{inlet}} - \Delta T_{\text{outlet}}}{\ln \frac{\Delta T_{\text{inlet}}}{\Delta T_{\text{outlet}}}} = \frac{230 - 220}{\ln \frac{230}{220}} = 225^\circ\text{C}$$

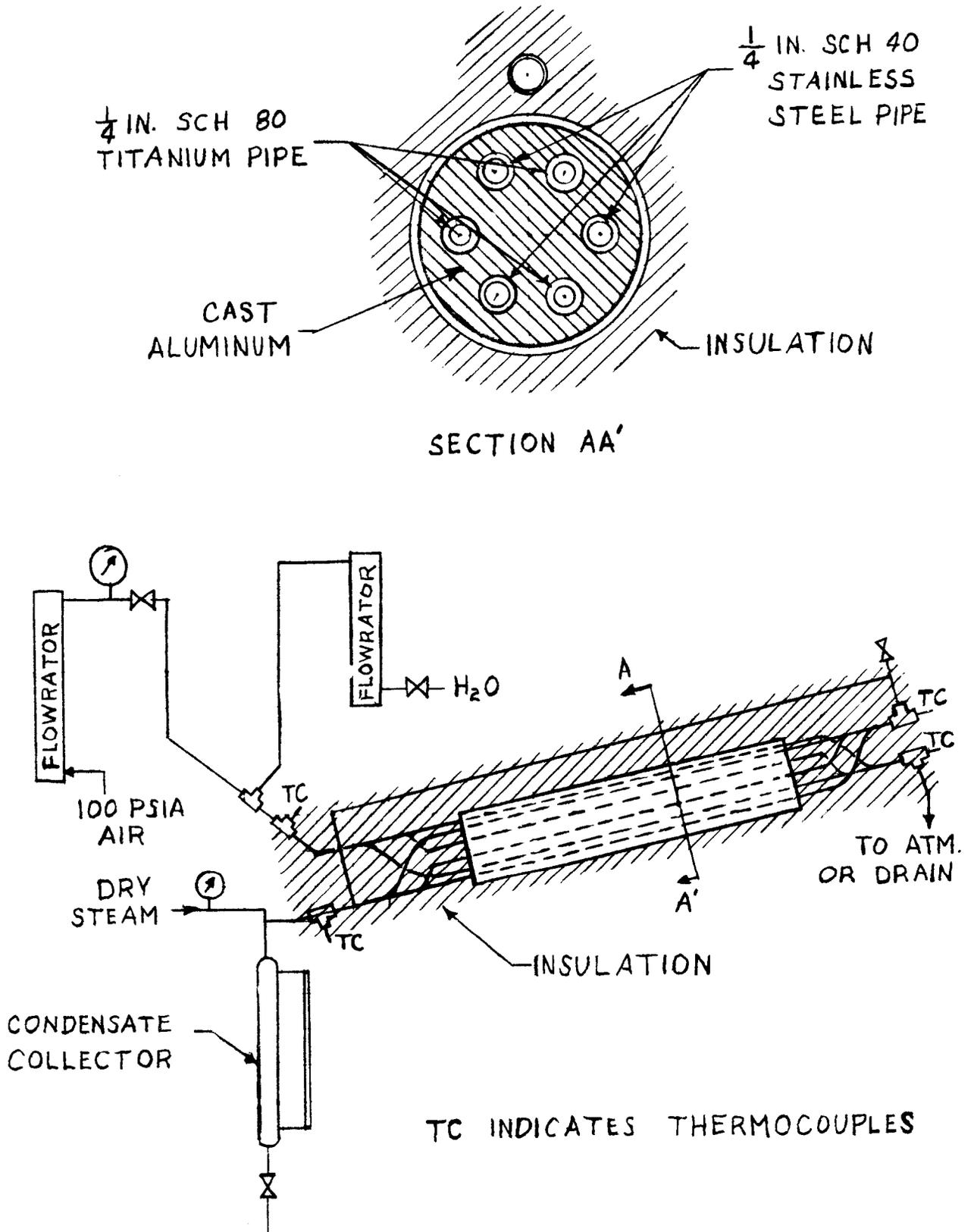


FIG. 12.4 TEST APPARATUS FOR LOOP P-2 COOLER

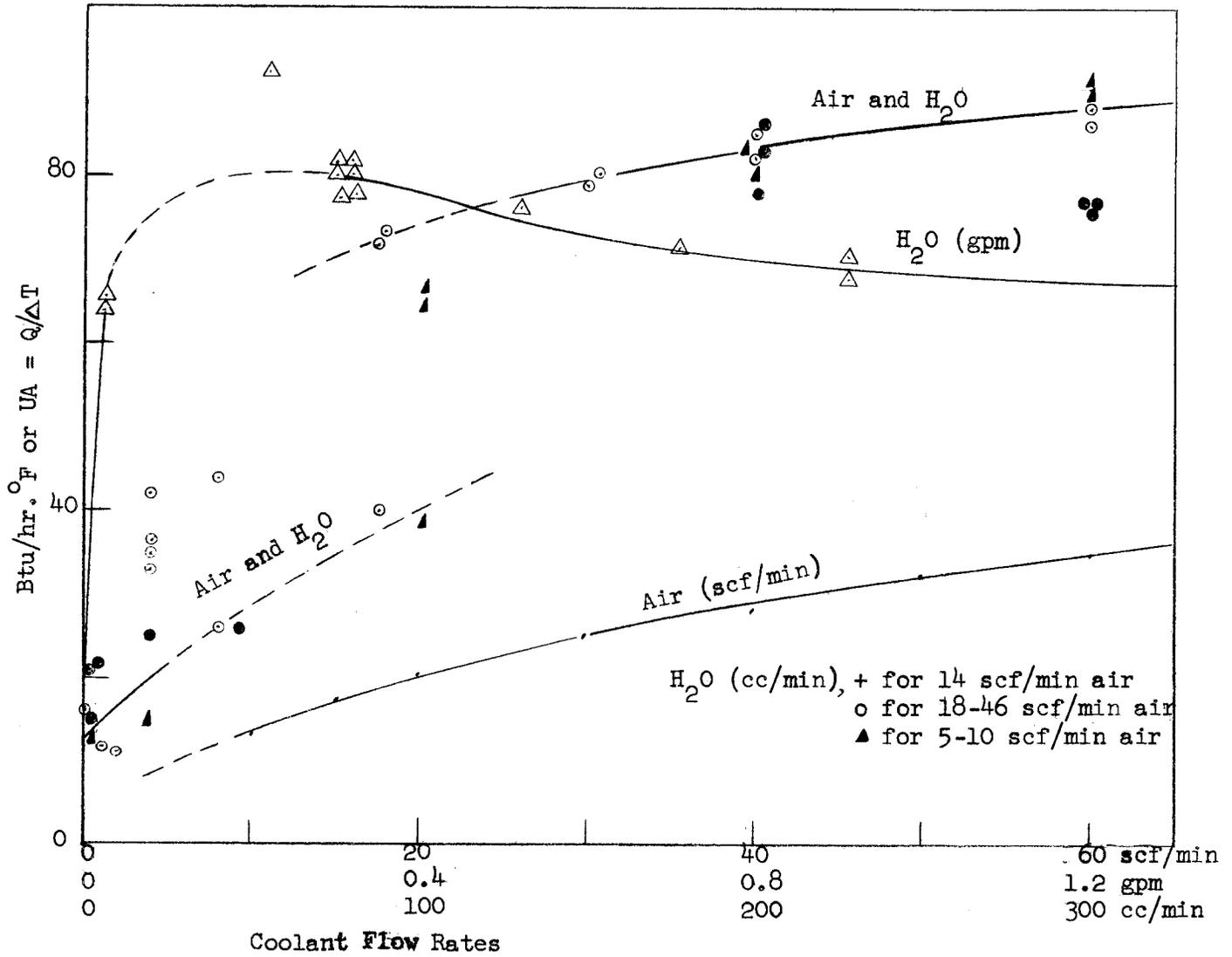


Fig. 12.5. Heat Transfer for Loop P-2 Heat Exchanger.

Steam: 16-83 psig for water (121-163°C), 79-83 psig for other tests.

UA is a characteristic rate of heat transfer for this heat exchanger in Btu/hr.^{°F}

q is the rate of heat transfer in Btu/hr

ΔT is a log mean temperature difference between the cooled and heated streams.

T₂ and T₁ are exit and inlet temperatures, respectively.

$$q = (UA)(\Delta T) = (70)(410) \text{ Btu/hr} = 8.1 \text{ kw}$$

The water flow required to remove this heat for a 10^{°C} temperature rise is given by:

$$\text{Flow in gpm} = \frac{q}{C_p(T_2 - T_1)} = \frac{480 \text{ Btu}}{\text{min}} \frac{1}{(1.8)(10)} \frac{\text{gal.}^\circ\text{F}}{8.3 \text{ Btu}} = 3.2 \text{ gpm}$$

For air the maximum flow possible is about 70 scf/min. Then

$$\text{Heat capacity} = \frac{70}{359} (7)(60) = 82 \frac{\text{Btu}}{\text{hr.}^\circ\text{F}}$$

Assume that the exit temperature is about 110^{°C}. Then

$$q = C_p(T_2 - T_1) = (82)(110 - 30)(1.8) = 11,800 \text{ Btu/hr} = 3.3 \text{ kw}$$
$$q = (UA)(\Delta T) = (35)(340) = 11,900 \text{ Btu/hr} = 3.4 \text{ kw}$$

For an air-H₂O mixture:

The exit temperature will be about 90^{°C}

ΔT will be about 320^{°F}

$$q = (UA) \Delta T = (90)(320) = 28,800 \text{ Btu/hr} = 8.2 \text{ kw}$$

The air with water sprayed into it does not give completely reproducible heat removal rates for water inputs of 20 to 120 cc/min. When this range is approached from the high-water-rate side, the heat transfer remains high, probably because the walls remain wetted down. When the water rate is gradually increased starting with initially dry tubes, the high rate is not obtained until the water rate exceeds 100 cc/min. There are liquid water droplets in the exit air stream throughout all the tests with water rates of over 20 cc/min.

Part IV. GENERAL CHEMICAL AND ENGINEERING STUDIES

13.0 WASTE STUDIES

(I. R. Higgins, W. J. Neill)

A new flowsheet (Fig. 13.1) for treating aluminum nitrate waste is being tested, which is a combination of previously investigated steps. The proposed treatment consists in removing the bulk of the fission products by scavenging and thereby reducing the radiation degradation of ion-exchange media in a subsequent step; using an efficient cleanup step for plutonium, rare earths, strontium, and cesium; depositing the aluminum in cheap storage; and reusing as much of the chemicals and water as possible in the complete reprocessing cycle to minimize their release to the environment. The bulk of its radioactive material, including the long-lived isotopes, would be sealed in portable tanks as concentrates containing only carrier quantities of nonradioactive chemicals. Separation of radioactive material will be included as commercial possibilities.

The scavenging step is performed by adding concentrated aluminum nitrate waste to about 0.5 M sodium hydroxide. From 1 M aluminum solution containing tracer fission products and 1 g/liter of iron, lanthanum, strontium, and cesium ions, 99.9% of the rare earths, 99% of the strontium, 98%-99.5% of the zirconium and niobium, and 80% of the ruthenium were carried. When dried to a powder, the precipitate from 1 liter occupied 4 cc and was pressed to 2.5 cc.

The sodium aluminate--sodium nitrate solution containing all the cesium and residual rare earths, strontium, and other fission products is passed through phenolic resin cation exchanger, which has an unusual affinity for cesium. The total decontamination through the ion-exchange treatment step is $>10^4$ for rare earths and $>10^3$ for strontium and cesium. The cesium may be eluted from the resin with the solution best suited to a cesium gamma source preparation.

The aluminum is removed from the sodium aluminate solution by adding carbon dioxide to precipitate aluminum hydroxide. The aluminum hydroxide is granular and settles to a slurry containing 1-3 M aluminum on a bulk basis. The precipitate carries 75% of the ruthenium and nearly 100% of the remaining zirconium and niobium.

Rather than discharge the final NaNO_3 - Na_2CO_3 solution, whose bulk radiation is from ruthenium, to the environment it is proposed that an electrolytic cell be used to produce sodium hydroxide and nitric acid. This is not the most economical source of these chemicals, but eliminates the necessity for high decontamination of this stream. Waste water may also be recycled.

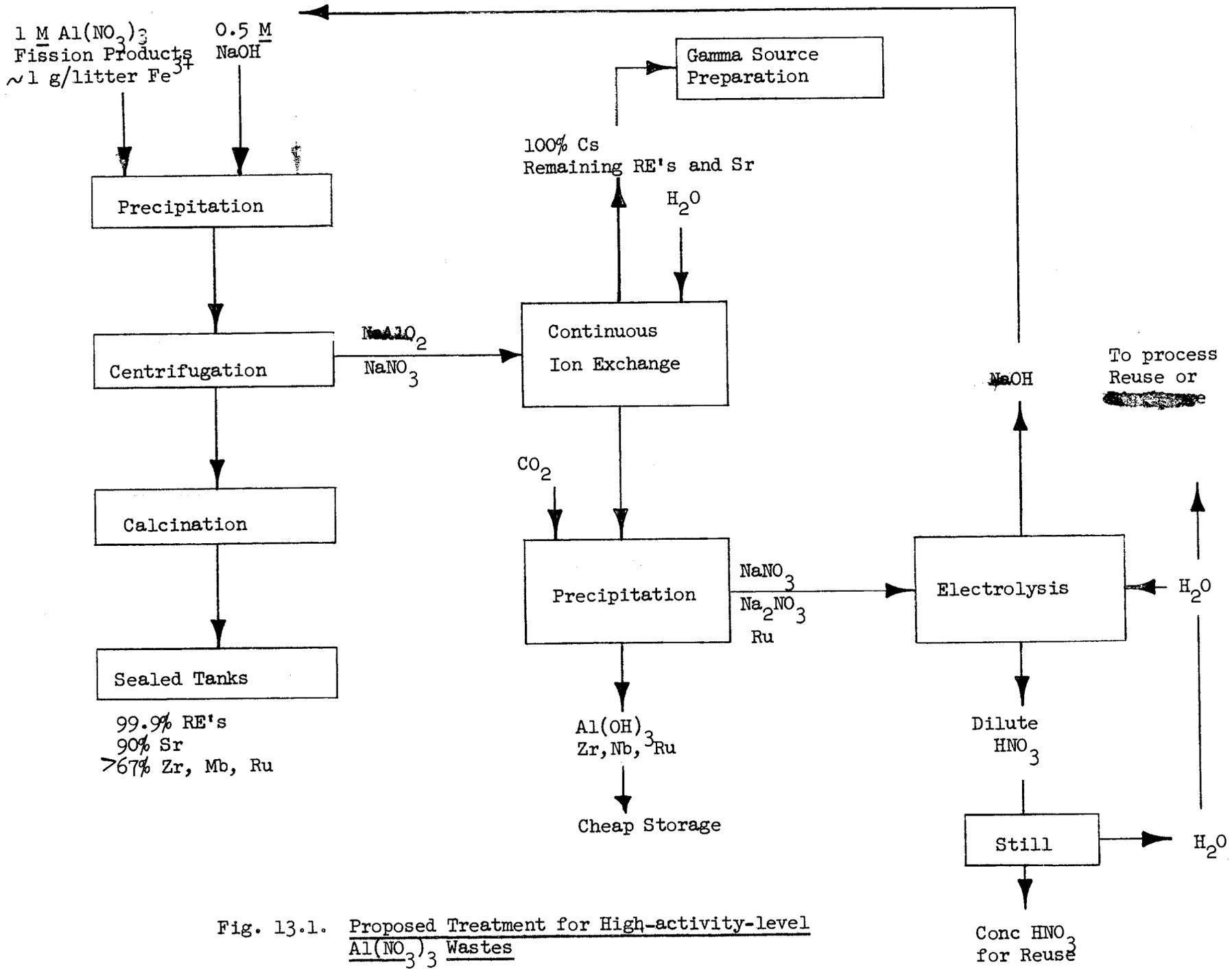


Fig. 13.1. Proposed Treatment for High-activity-level $\text{Al}(\text{NO}_3)_3$ Wastes

14.0 ION-EXCHANGE TECHNOLOGY

(C. W. Hancher)

14.1 Separation of Uranium from Plutonium

An M.I.T. Practice School group made a study of separation of uranium from plutonium in a 3-in.-dia Higgins ion-exchange contactor, iron being used as a substitute for plutonium. Removal of iron from the uranium stream was good, but scrubbing of uranium from the iron stream was poor:

	Uranium (g/liter)	Iron (g/liter)
Feed	8.30	1.00
Product	0.40	4.00
Waste	3.00	0.008

The complete compilation of data and calculations will be published in a topical report. The resin used was Dowex 50.

14.2 36-in. Resin Test Loop

The M.I.T. Practice School completed an investigation of some of the hydraulic conditions resulting from pulsing the resin in the 36-in.-dia column. The resin was pulsed with a 20-psi pressure drop and with a slip water ratio of 1.2 to 1.7. The slip water ratio appeared to be a function of column diameter, since it was 4.0 in the 12-in.-dia contactor. The major resistance to resin flow is the wall area. Therefore, as the wall area/volume ratio decreases, the slip water ratio should also decrease.

The liquid take-off did not function correctly with a punched stainless steel plate on the resin side. When the punched plate was removed from in front of the screen the liquid through-put was normal for a 60-mesh screen. A new type of liquid take-off has been fabricated (Fig. 14.1).

14.3 Evaluation of Jury Column*

Experiments with the Jury continuous countercurrent ion-exchange column, using the system Ca^{++} —Dowex 50W— Na^+ have been carried out as part of a program on development and evaluation of continuous ion-exchange equipment. Column operation was stable and conventional control instruments were used to maintain the hydraulic balances required to isolate the loading and regenerating sections of the column. Only 1 wt % of a Cl regenerant is required in contrast to the usual saturated brine solution for regeneration purposes. In the vicinity of fluidizing flow rates the HETS lay in the 6-in. range. Water was softened continuously from hundreds to several parts per million. It was possible to operate at liquid flow rates up to 100 gal/hr.ft².

*Work done under a subcontract, F. N. Peebles, Associate Prof. and R. M. Boarts, Prof. and Head of Dept. of Chem. Eng., University of Tennessee.

**S. H. Jury, "A Continuous Countercurrent Ion-exchange Column with High Production Capacity Due to Freedom Fluidization," ORNL memo CF-53-1-213; Nucl. Sci. Abs., 8, 9 obs. No. 173 (1954).

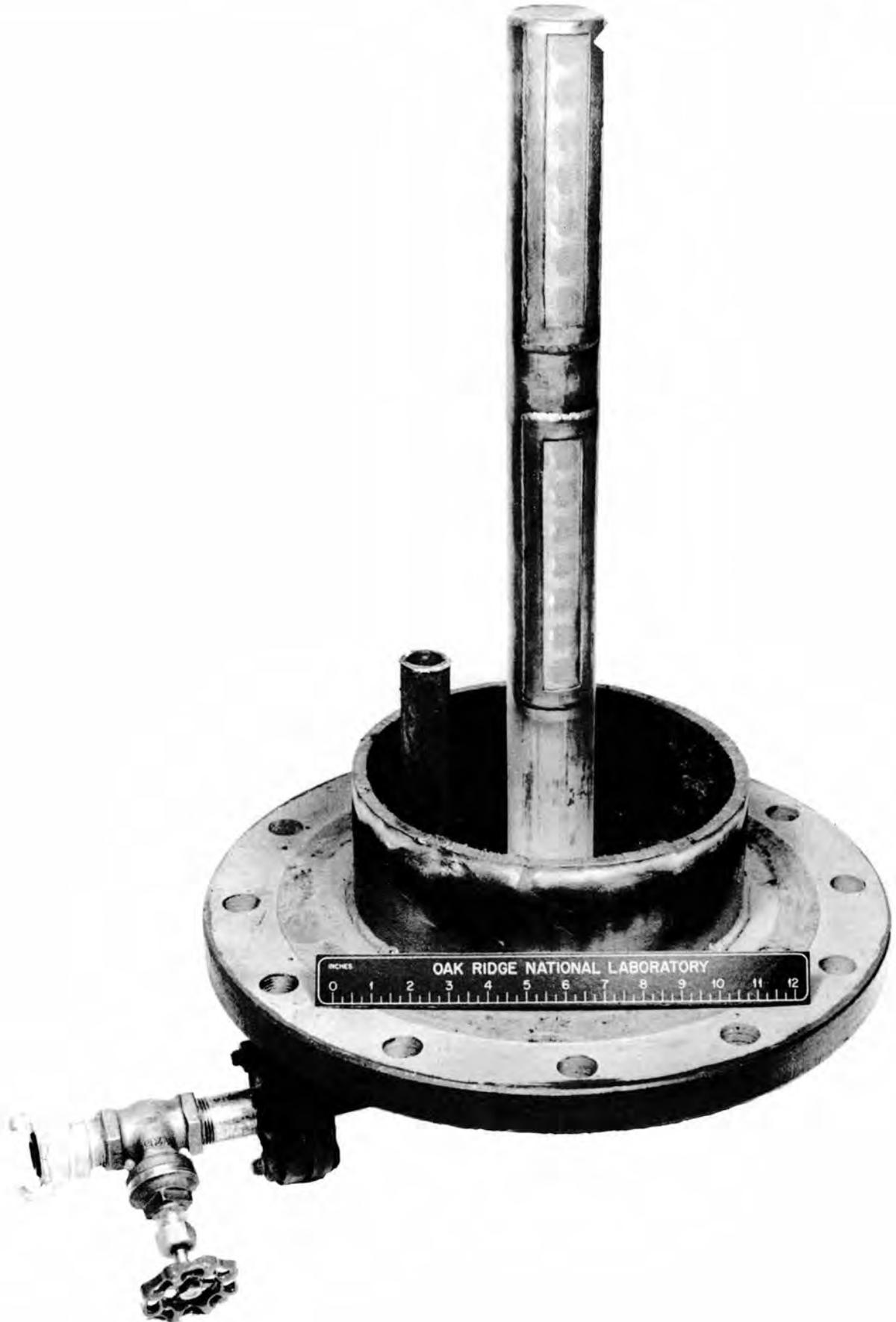


Fig. 14.1. Liquid Take-Off for 36-in.-dia Resin Test Loop.

With higher liquid flow rates the resin bed became fluidized even though pressure drops up to 50 psi were applied to the hydraulic ram section.

Typical equilibrium stage heights were 0.3-1.0 ft. These values are significantly higher than the corresponding values predicted by use of the rate equation developed for this system. The discrepancy is attributed to nonuniform flow in the moving bed. The low values (~ 0.05 ft) of the stage heights predicted theoretically continue to serve as an impetus for the development of continuous ion-exchange methods.

Preliminary resin attrition rate measurements indicated approximately 0.02% fines (diameter $< 840 \mu$) accumulation per pass through the ion-exchange column. This value was obtained with a plug valve used to regulate the resin flow rate. When a motor-driven rotating feeder was used to regulate the resin flow rate, the accumulation of fines was approximately 2% per pass through the column.

The local rate of ion exchange for the system Ca^{++} —Dowex 50W— Na^+ can be described in terms of diffusion phenomena, taking into account the diffusional resistance offered by the liquid and solid phases. Experimental data from the sorption and regeneration reactions were used to confirm the rate equation developed from the diffusion theory. This equation relates the ion-exchange rate to the local liquid composition, average solid (dense bed) composition, and physical properties of the system. Two mass-transfer coefficients which appear in the rate equation were determined from the same data. These coefficients are liquid flow rate dependent, and empirical equations which describe the relations were developed.

15.0 METAL RECOVERY PLANT

(W. H. Lewis, R. E. Brooksbank, C. D. Hylton, J. L. Matherne, W. R. Whitson)

15.1 Plant Operations

To date, 20 tons of uranium has been recovered from ORNL tank farm wastes, tanks W-7 and W-10. The average uranium throughput was 441 lb/day during the 12 days the solvent-extraction equipment was operated. Essentially, all pulse column downtime was caused by the lack of feed.

Visual inspection of tank W-10 showed a 5-in.-thick circular layer of sludge at the outer edge of the tank. Further attempts to slurry this small amount of sludge with water were considered impractical, and uranium carbonate solution from tank W-7 was pumped to W-10. The carbonate solution is being recirculated through the W-10 sluicing mechanism prior to delivery to the plant.

Excessive foaming and gassing resulted during acidification and volume reduction of the carbonate-laden waste. Sodium nitrate precipitated in the feed evaporator (A-6) during the cooling period, causing instrument probes, jet lines, and a 2-in. drain line to become plugged.

One shipment of specification-grade 2 M uranyl nitrate solution containing 3.4 tons of uranium was shipped to Y-12 for subsequent processing.

15.2 Equipment Performance

Frequent plugging of the feed pump was eliminated by installing two 20-mesh wire screens in the suction line to the pump. The screens were arranged so that one unit could be cleaned while the other was in service. The cone type check valves in the feed pump were replaced with ball check valves in an effort to keep the smaller solids that pass through the screen from lodging in the check valve housing.

The W-10 sluicing nozzle failed when the locking pins that fasten the head to the rotating shaft worked out of their grooves, which permitted the rotating head to oscillate without turning the nozzle. The rotating head was welded to the shaft, thus eliminating the need for pins.

During the volume reduction of the first batch of carbonate waste, the evaporator became pressurized, causing a transfer of solution through an instrument line into the control room. Two electrical circuits were shorted by solution that drained into the control center. Normal operation was resumed after decontamination.

The operation of 40-hp W-10 slurry pump was interrupted after 2.5 months of continuous service because of an overloaded electrical circuit. The top two thrust bearings were damaged badly, causing the pump impeller to drop down against the housing plate. The damaged pump was replaced with a similar type 10-hp unit.

15.3 Construction and Modification

Work on the concrete block walls for additional shielding in M-Room is 90% complete. This wall will reduce the radiation dosage received by personnel in an operating area.

Work on the dissolver pit has progressed slowly because of the in-leakage of surface water into the pit. All service lines were welded into position, and a 2-ft curb liner was installed.

16.0 MISCELLANEOUS STUDIES

16.1 Steam Stripping of Tributyl Phosphate (C. D. Watson, C. V. Chester)

Tributyl phosphate must be removed from evaporator feed streams to prevent formation of its hydrolysis products. Bubble-cap columns have been used, but they are expensive, hard to decontaminate, and subject to corrosion. Sieve-plate columns, which are less complex and would overcome these objections, are being evaluated for efficiency. In preliminary runs in a 6-in.-dia sieve-plate column, four actual plates consistently reduced the TBP content of a uranyl nitrate solution from more than 200 ppm to less than 5 ppm, corresponding

to an average plate efficiency of 25% (Table 16.1). Since the analyses for TBP are probably precise to ± 2 ppm, the variations in product concentrations in series 2 and 3 are probably not significant. However, preheating the feed (run 3) decreased the slope of the operating line and decreased the number of theoretical plates required for a given stripping operation.

16.2 Solvent Recovery by Vacuum Distillation (J. R. Flanary)

Although the DBP and MBP are easily removed from the irradiated TBP-diluent mixture by alkaline washing, other radiation-induced impurities remain. Vacuum distillation of such solvent appeared to be a fairly efficient method of recovery. About 90% of the TBP and diluent were recovered by this method.

Samples of irradiated TBP-Amsco mixtures were fractionally distilled at ~ 2 mm Hg pressure, and the distillates were tested for uranium retention and emulsification tendencies. In an experiment with 50% TBP (dry) irradiated at 477 watt-hr/liter, which had a uranium retention of 38 mg/ml, recovery was 86%, and maximum uranium retention in the distillate was ~ 1 mg/ml in the last fractions distilled at temperatures above 155°C . (This retention may be due to degradation of the organic material during the distillation.) The uranium retention of the still residue was 94 mg/ml, and this material caused emulsification when contacted with Purex-type feed and dilute nitric acid stripping solutions. In another experiment with alkaline-washed, but colored, Thorex pilot plant solvent, the combined water-white distillate (88% recovery) had a uranium retention of only 0.002 mg/ml.

16.3 Study of Hydroclones*

Superficial analysis of data from liquid-liquid separations with a 1-in.-dia hydroclone indicates that separation of the liquids was fairly good at low flow rates with correspondingly low pressure drops. This may indicate that larger clones at moderate flow rates may give fairly good separations and not require the higher pressures associated with the operation of small hydroclones at comparable flow rates. This in turn may mean that ordinary jets could be used to pump through a cascade of several larger clones to give satisfactory through-puts. The design of the 1-in. hydroclone used was a scale-up from the best of the 1/4-in. hydroclones previously tested. The liquids were 10 to 1 ratios of Amsco 125-82 and water, which were also used with a 0.2 and 0.4-in.-dia hydroclone tests. The phases for the feed stream were mixed by a jet, which has become the standard procedure. A report covering work to date is scheduled for completion about Feb. 15, 1957.

16.4 High-Activity-Level Chemical Development Facility (E. J. Frederick)

Construction of the high-activity-level chemical development facility by the Helrich Construction Company is estimated to be approximately 65% complete. Completion by the scheduled date, March 15, 1957, is expected.

*Work done by B. L. Baker at University of South Carolina under a subcontract.

Manufacture of the glass viewing windows by Corning Glass Company is also on schedule. Delivery of the windows is expected to begin Feb. 15, 1957.

16.5 Transuranium Build-up in Power Reactor Fuels (J. O. Blomeke)

Report ORNL-2126, "The Buildup of Heavy Isotopes During Thermal Neutron Irradiation of Uranium Reactor Fuels," was issued.

16.6 Fission Product Build-up in Irradiated Reactor Fuels (J. O. Blomeke)

Report ORNL-2127, " U^{235} Fission Product Production as a Function of Thermal Neutron Flux, Irradiation Time, and Shutdown Time," is to be issued in two parts. Part I is in press. Calculations for Part II have been completed.

Table 16.1. Data Obtained in Removal of Tributyl Phosphate from Uranyl Nitrate Solution

Feed uranium content: 70 g/liter
 Plate free area: 2.7%
 Data obtained at fourth feed plate.

Run No.	Feed			Stripped Product		Condensate		Mass Bal. ^a (Defect as % of feed)	Calc. Reflux Cold Feed (ml/min)	Calc. Vapor Rate Condensed (ml/min)	L/V Flow Rate	f-factor	No. of Theoret- ical Plates	Avg. Plate Effi- ciency
	Rate (ml/min)	Temp. (°C)	TBP Conc. (mg/liter)	Rate (ml/min)	TBP Conc. (mg/liter)	Rate (ml/min)	TBP Conc. (mg/liter)							
1a	586	20	420	(661) ^b	31	308	430	-46.5	74	382	1.73	0.36	0.7	0.18
2a	546	20	210	655	6	426	260	<-0.1	70	496	1.32	0.468	0.95	0.24
2b	542	20	220	617	3	426	260	-5.6	60	495	1.25	0.467	1.08	0.27
2c	550	20	(215) ^b	635	4	424	270	+3.3	70	494	1.29	0.466	1.0	0.25
3a	(567) ^b	100	260	560	2	454	320	-3.1	0	454	1.23	0.429	1.2	0.30
3b	567	100	(260) ^b	630	4	460	260	-11.2	0	454	1.37	0.435	1.2	0.30

^aNegative sign indicates more total TBP in feed than in combined product and condensate.

^bEstimated or calculated indirectly.

APPENDIX

17.0. BIBLIOGRAPHY OF DOCUMENTS ISSUED BY THE CHEMICAL TECHNOLOGY DIVISION
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- CF No. 56-12-2, W. H. Carr, et al., "ORNL Volatility Program: Objectives and Budget Proposal" (Secret)
- CF No. 56-12-48, R. H. Winget, "Summary of Run HRT-CP-7"
- CF No. 56-12-49, R. H. Winget, "Summary of Run HRT-CP-6"
- CF No. 56-12-51, R. E. Blanco, D. E. Ferguson, "Status Report for Chemical Development Sections A and B: Week Ending November 30, 1956"*
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- CF No. 56-12-110, R. H. Winget, "Summary of Run HRT-CP-10"

*Included in Feed Materials and Power Reactor Fuel Processing and Homogeneous Reactor Progress reports (listed on p. iii of this report).

- CF No. 56-12-115, J. R. Engel, "Preliminary Solids-Injection Experiments on the HRT Mockup at Y-12"
- CF No. 56-12-122, R. E. Blanco, D. E. Ferguson, "Status Report for Chemical Development Sections A and B: Week Ending December 21, 1956" *
- CF No. 57-1-13, K. J. Fritz, "High Pressure Flange Studies"
- CF No. 57-1-19, S. H. Stanker, "Cold Trap Problem Statement"
- CF No. 57-1-29, R. E. Blanco, D. E. Ferguson, "Status Report for Chemical Development Sections A and B: Week Ending December 29, 1956" *
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* See footnote p. 69.

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