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UNIT OPERATIONS SECTION
MONTHLY PROGRESS REPORT
JANUARY 1959

NOTICE

OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

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ORNL-CF-No. 59-1-74

UNIT OPERATIONS SECTION MONTHLY PROGRESS REPORT

January 1959

CHEMICAL TECHNOLOGY DIVISION

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OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
Operated By
UNION CARBIDE CORPORATION
for the
U. S. Atomic Energy Commission

ABSTRACT

Two alternate systems, acetic acid-nickel and acetic acid-cobalt, were examined for possible replacement of the corrosion system: ferric chloride-nickel which is being used in the current transpiration corrosion protection studies. Two Fluorox fluidized bed runs were made, of 9 and 58 hr duration, in which dry air and oxygen were used as oxidizing and fluidizing gases. Tests of the hydroclone classification of thoria indicated that more than 95% of the +0.5 micron particles can be removed from a sample if 50% recovery of the -0.5 micron particles is acceptable. Fluidized bed denitration of ThNT did not produce large dense ThO_2 particles, but flame denitration of mixed thorium-uranium-aluminum nitrates produced spherical particles. Three alternate batch Darex flowsheets gave chloride removal to less than 350 ppm with 61% nitric acid feed, while dissolution studies of APPR fuel elements showed that complete dissolution of braze metal in aqua regia may be difficult. Leaching studies of unirradiated UO_2 pellets showed that the most important variable effecting dissolution rate was the total nitrate content of the dissolvent. Delivery of the SRE decanning equipment was scheduled for April 1, 1959. Temperature increases in cylinders of solid radioactive waste were calculated for APPR fuel processing using a Darex flowsheet and cooling times ranging from 1-8 yr.

CONTENTS

SUMMARY

1.0 CHEMICAL ENGINEERING RESEARCH

Previous measurements of the protection of a porous nickel tube by transpiration of distilled water have been made using a ferric ion oxidant. Because the corrosion system $FeCl_3$-Ni is diffusion controlled, kinetic rate data are difficult to obtain. The alternate systems, acetic acid-Ni and acetic acid-cobalt were examined and were predicted to be corrosion rate controlled. An activation analysis method would give accurate corrosion rate determination for the cobalt system at low rates.

2.0 FLUOROX

Two fluidized bed reactor runs were made. FBR-21, 9.25 hr in duration, used dry air as the oxidizing and fluidizing gas. In this test 92.6% of the theoretical UF_6 product was measured in the off-gas (product) stream. FBR-22, with dry oxygen as the oxidizing and fluidizing gas operated continuously for 58.4 hr.

3.0 HR FUEL AND BLANKET PREPARATION AND PROCESSING

Tests of hydroclone classification of ThO_2 indicated that over 95% of the above 0.5 micron material can be removed if 50% recovery of the below 0.5 micron material is acceptable. All conditions tested for fluidized bed denitration of $Th(NO_3)_4$ have produced porous agglomerations of small ThO_2 particles instead of growth of dense ThO_2. Addition of a Mo, Pd, and Al solution to the ThNT-UNH in CH_3OH feed for flame denitration gave three component oxides of about the same particle size (d_{50} = 2.5 microns) as Th or Th-U oxides. A product calculated to be 83% ThO_2, 7% UO_x, 10% Al_2O_3 (wt basis) flame fired at 1400°C contained a large fraction of 0.5-3 micron dia spherical particles. Five thousand ppm MoO_2 and 300 ppm Pd were added as recombination catalysts.

4.0 ION EXCHANGE SUMMARY

An apparatus for studying the rates of sorption of uranium on Dowex 21K using a differential resin bed has been designed and assembled. Resin is now being carefully sized and freed from all broken particles for use in the kinetic studies.

5.0 POWER REACTOR FUEL REPROCESSING

5.1 Darex (Flowsheet Development)-Batch Chloride Removal and Feed Adjustment

Laboratory scale (1 liter) and larger scale (10 liters) runs showed the following:

a. An updraft condenser used in conjunction with air sparging during the reflux step gave better chloride removal than a downdraft condenser using comparable sparge rates. Doubling the air sparge rate had no beneficial effect in the downdraft system.

b. An updraft or downdraft condenser was equally effective for the recovery of mixed acid ($HCl-HNO_3$). Air sparging was detrimental to chloride recovery with either type.

c. The Recycle flowsheet run at estimated steady state conditions showed adequate chloride removal to 220 ppm.

d. A new batchwise Double Recycle flowsheet gave chloride removal to 50 ppm.

e. The use of concentrated HNO_3 (92.5%-90%) eliminated the waste acid cut, and chloride removal to 35 ppm was possible in lab-scale tests.

Dissolution Studies. The dissolution of unirradiated APPR (SS-U) type fuel assemblies in a 6-in. dia Pyrex dissolver with aqua-regia (2 M HCl-5 M HNO_3) showed that:

a. The dissolution of unirradiated stainless steel and stainless steel-uranium simulated APPR fuel elements proceeded rapidly at 28 g/min at aqua-regia flow rates of 4.3 liters/min.

b. Foaming and/or surging of the solution within the dissolver reached a maximum of 9 ft when three elements stacked atop each other (total height ~ 6 ft) are dissolved.

c. A dissolution time of 1 hr for three elements appears possible if it is assumed that masking of surfaces by braze metal does not occur. Braze metal (Coast metals NP) appeared to be only slowly dissolved by hot aqua-regia.

d. The dissolver product may be airlifted without difficulty.

5.2 Feed Clarification

Laboratory filtration studies showed a feasible cycle time of < 1 hr for filtering the silica from a 325-liter batch of simulated Darex solvent extraction feed solution on a 1 sq ft sand bed filter. A split feed procedure - filtering the clear supernate from a sedimentation step followed by the thickened slurry - produced this result. The same volume of feed filtered as a well-mixed slurry took ~ 3 hr to filter under otherwise identical conditions.

5.3 Solvent Extraction Studies

In the Hanford assistance runs, the column capacity was greatly lowered by increased silicon content. Decontamination factors were lower for power reactor runs than for the standard Redox flowsheet, and were lower for Niflex type feed than for Darex type feed.

5.4 Mechanical Processing

Core Leaching. Instantaneous dissolution rates of from 3 $mg/cm^2/min$ to 278 $mg/cm^2/min$ were obtained for sintered unirradiated UO_2 pellets for 3, 5, 7, 10 and 13 M HNO_3 solutions in which the uranium concentration was increased from 0.5 to 2.0 M. For a given uranium concentration, the reaction rate increased rapidly with increasing acidity and/or total nitrate content. For a given acid concentration, the reaction rate was increased by an approximate factor of 1.5 to 2.5 as the uranyl nitrate was increased from 0.5 to 2.0 M. It was not possible to separate the effect of uranium and nitrate since the two were increased together; however, it appeared that the uranium concentration had little or no effect on the reaction rate.

Batch and continuous leacher concepts were selected for fabrication and experimental evaluation.

SRE Decanning. The SRE decanning device is being fabricated by Southern Machine Company of Chattanooga, the low bidder, for $9,125. Delivery of the unit will be made by April 1. A food canning unit is being adapted to remote operation for recanning the dejacketed SRE slugs.

Disassembly of Fuel Bundles. A "draw knife" device and a wedge separator for separating fuel bundles into "planks"of rods has been designed. A ferrule splitter to reduce fuel assemblies to individual rods has been designed and is being fabricated.

Prototype Fuels. Bids ranging from $21,000 to $75,000 were received for the fabrication of 75 prototype fuel assemblies, 6 ft long containing 36 stainless steel tubes in each assembly. Fifty of the assemblies are to be filled with ceramic and twenty-five units are empty.

Parts for twenty SRE prototype units are being fabricated in ORNL shops.

Segmenting Cell Layout. Initial design studies have been made to locate the shear, saw and decanning device for proper visibility, equipment operation, and utility of cell space.

Shearing. Contrary to last month's report, a line of blade contact shear may be satisfactory for shearing fuel bundles. Increased shearing speed, alteration of blade shape and flattening of the fuel assembly prior to shearing appeared to be necessary to produce sheared pieces of the desired properties.

6.0 WASTE PROCESSING

An 8 in. dia by 18 in. deep (3.9 gal) calciner heated with a 10 kw furnace has been installed and tested. A 3 in. dia by 10 ft distillation column packed with 1/4 in. Raschig rings has been installed for testing for decontamination of off-gases and liquids.

Temperature rise in cylinders of radioactive solid waste stored in an infinite salt medium was calculated as a function of time. Heat generation rates were calculated assuming APPR-1 fuel and Darex fuel reprocessing conditions. Maximum temperature rise in the waste ranged from about 700-1900°F for one-year cooled waste stored in a 9 in. radius cylinder, 400-1200°F for three-year cooled waste in a 14 in. radius cylinder, and 400-1400° for eight-year cooled waste in a 29 in. radius cylinder for thermal conductivities of the solid waste ranging from 1.0 to 0.1 Btu/(hr)(sq ft)(°F/ft).

1.0 CHEMICAL ENGINEERING RESEARCH

M. E. Whatley

Transpirational Protection - E. C. Moncrief

The transpirational protection program is directed toward the protection of porous surfaces from corrosion. The mechanism of protection consists of decreasing the fluid wall concentration by passing a noncorrosive fluid through the pores of the surface. Experimental studies to date have been made on the system: $FeCl_3$-nickel in which corrosion occurs by the reaction: $2\ Fe^{+3} + Ni = Ni^{+2} + 2\ Fe^{+2}$, and in which protection is provided by distilled water.

1.1 Selection of Alternate Corrosion Systems

Kinetics rate data for the system $FeCl_3$-nickel were difficult to obtain accurately since this system was diffusion controlled. The decision was made to consider alternate systems which would be reaction rate controlled. Calculations indicated that any system which corroded at a rate of less than .1 ipy at a 1 M concentration would probably be reaction rate controlled. A literature search of corrosion rates for nickel systems revealed that the acetic acid-nickel system would be best for experimental use.

Assuming the reaction of acetic acid with nickel is essentially:

$$2\ H^{+} + Ni = Ni^{+2} + H_2$$

it was felt that the evolution of hydrogen would not be vigorous enough to destroy the laminar sublayer at the wall. Consideration was also given to the effect on the reaction rate by passivation of the nickel by hydrogen. Uhlig (1) states that the condition which determines whether a substance capable of reaction will react or adsorb a reactant appears to be related to the work function, WF, (a measure of the heat of evaporation of electrons from the metal) of the metal and the heat of sublimation, ΔH_s, of the metal. Thus, since the state of adsorption corresponds to passivity, the condition for passivity is approximately given by $WF/\Delta H_s < 1$ and the condition for reaction, $WF/\Delta H_s > 1$.

For nickel, $\Delta H_s = 4.26$ electron volts and WF = 4.1-5.0 volts, giving $WF/\Delta H_s = 0.96-1.2$. However, since the value of WF is not precise, the

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(1) Uhlig, H. H., ed, Corrosion Handbook, p 25, John Wiley and Sons, Inc., New York, 1948.

question of passivation will have to be resolved experimentally. Nevertheless, it is possible that hydrogen passivation will not be a serious problem using acetic acid.

1.2 Construction of Reaction Rate Vessel

A vessel to be used for reaction rate studies on the acetic acid-nickel system has been designed and fabricated (see Figure 1.1).

The vessel was constructed from a 4-liter glass beaker. A plexiglass baffle assembly was provided to prevent vortexing during actual kinetic rate tests. The vessel has provisions for continuous purge as well as an external sampling line which will circulate a portion of the reactants continuously. This feature should eliminate inaccuracies in the data due to cross-contamination during sampling. The turbine blade impeller was assembled between two parallel circular plates to hold specimens during testing (see Figure 1.1, Unit Operations Section monthly report for December, ORNL-CF-58-12-35, for detail).

1.3 Development of Theoretical Equations

Two equations have been developed for predicting corrosion rates by applying theoretical considerations of diffusion and kinetics. These equations were developed for the $FeCl_3$-nickel system and apply for the case of corrosion of a porous tube with and without transpirational protection. Modification of the equations may be necessary where the ionic stoichiometry of the system used differs from that of $FeCl_3$-nickel or acetic acid-nickel (that is, where the concentration of the reactant is not twice that of the metallic product).

The following assumptions were made in developing the theoretical equations: (a) the kinetics reaction was first order $[n = 1]$, and (b) the mass transfer rate of the reactant to the wall was essentially constant along the length of the porous tube.

Case I: No transpirational protection

Where no transpirational protection is used, the basic diffusion equation consists of:

$$N_b = -D\frac{dC_b}{dR} \tag{1}$$

where

N_b = mass transfer rate of reactant, mol/cm^2-sec

D = diffusivity of reactant, cm^2/sec

C_b = fluid bulk concentration at some point along porous tube, mol/cm^3

R = porous tube radius, cm

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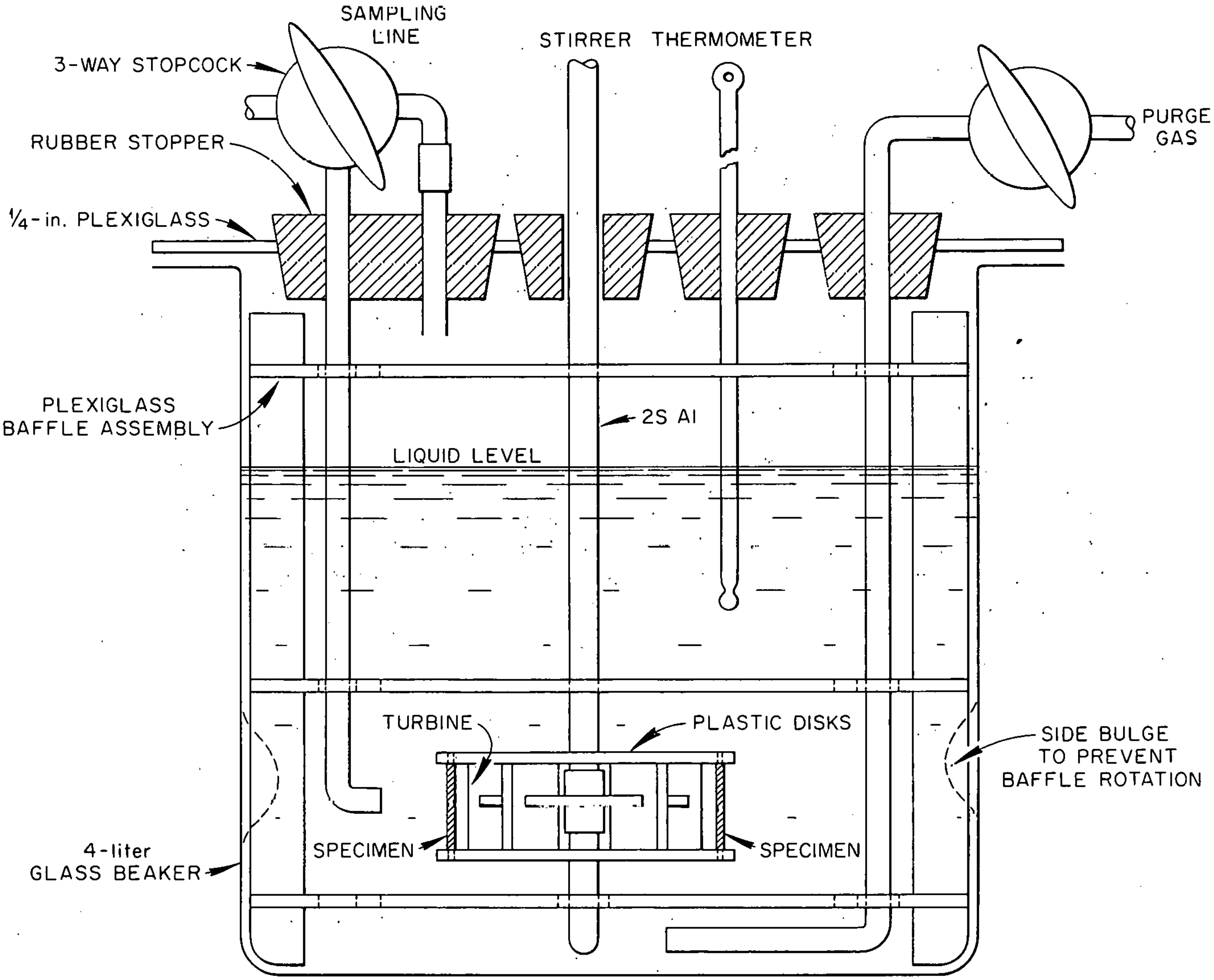

Fig. 1.1. Sketch of Reaction Rate Apparatus.

and the basic kinetics equation is:

$$\text{Rate} = kC_w \tag{2}$$

where

k = first order kinetics equation constant, cm/sec

C_w = concentration of reactant at wall, mol/cm^3

Applying material balance considerations and integrating over the length of the porous tube, the final nontranspirational equation becomes:

$$C_n' = \frac{N_b k Z}{Q_o R}\left[\frac{C_{bo}}{N_b} - \frac{Z}{Q_o R} - \frac{\delta}{D}\right] \tag{3}$$

where

C_n' = nickel ion concentration in effluent stream without transpirational protection, mol/cm^3

Z = porous tube length, cm

Q_o = original fluid bulk flow rate, cm/sec

C_{bo} = original bulk fluid concentration, mol/cm^3

δ = laminar sublayer thickness, cm

Case II: With transpirational protection

Where transpirational protection is used the basic diffusion equation (1) must be adjusted to include the effects of transpiration:

$$N_b = -D\frac{dC_b}{dR} - qC_b \tag{4}$$

where

q = transpirational flow rate, cm/sec

Again applying the basic kinetics equation (2) and material balance considerations, the final form of the transpirational equation becomes:

$$C_n = \frac{\dfrac{N_b\, e^{-\gamma}}{2q}\left[\left(\dfrac{C_{bo}Q_oR}{2N_b} + \dfrac{Q_oR}{2q}\right)\dfrac{\ln\left(1 + \dfrac{2qZ}{RQ_o}\right)}{Z} - 1\right]}{\left[\dfrac{q}{k} + \left(1 - e^{-\gamma}\right)\right]} \qquad (5)$$

where

C_n = nickel ion concentration in effluent stream with transpiration protection, mol/cm³
$\gamma = \delta q/D$

Application of Equation to Experimental Data

An attempt was made to evaluate the application of the equations to the experimental data of Jury and Simpkins (2). A value for diffusivity, D, was calculated from empirical data of Treybal (3). The laminar sublayer thickness, δ, was calculated from correlations of Chilton-Colburn (4) and from Kay (5).

The ratio C_n'/C_n from the experimental data of Jury and Simpkins was found to be 154. Using the calculated values of 2.57×10^{-5} cm²/sec for D and 5.66×10^{-3} cm for δ, the value of the ratio obtained by dividing equation 3 by equation 5 was 56. Using the same value for D and a value of 7.54×10^{-3} cm for δ, the ratio C_n'/C_n was calculated to be 682.

Thus, a slight change in the value used for δ changes the C_n'/C_n ratio greatly. Likewise, a slight change in D would produce a similar result. However, where accurate kinetics data are available, D/δ can be evaluated experimentally and used directly in the exp$[-\gamma]$ term of the transpirational equation (5). Therefore, it is felt that further evaluation of the equations must wait until such kinetics data are available.

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(2) Jury, S. H. and Simpkins, C. R., ORNL-CF-51-9-18.

(3) Treybal, R. E., Mass-Transfer Operations, p 25, McGraw-Hill Book Co., Inc., New York, 1955.

(4) Sherwood, T. K., Absorption and Extraction, p 40, McGraw-Hill Book Co., Inc., New York, 1937.

(5) Kay, J. M., An Introduction to Fluid Mechanics and Heat Transmission, p 144, Cambridge Univ. Press, 1957.

2.0 FLUOROX

R. W. Horton

The Fluorox program is the engineering development of processes which produce UF_6 without the use of elemental fluorine. The process under study is the oxidation of UF_4 with oxygen, $2UF_4 + O_2 = UO_2F_2 + UF_6$, with subsequent recycle of the UO_2F_2.

2.1 Fluidized Bed Development - C. D. Scott, D. H. Newman

The UF_4 oxidation process is being carried out in the 4-in. Fluorox fluidized bed reactor. Sized UF_4 is continuously fed into a UO_2F_2 bed which is fluidized in dry O_2 or air at 800-850°C. The UF_6 which is produced is removed in the gas stream and subsequently recovered in cold traps.

Two experimental runs were made in the 4-in. fluidized bed reactor. Run FBR-21 was a run of 9.25 hr duration in which dry air was the oxidizing and fluidizing gas and run FBR-22 was of 58.4 hr duration in which dry O_2 was used as the fluidizing and oxidizing gas.

Run FBR-21. Run FBR-21 was made to evaluate the use of dry air as the oxidizing and fluidizing gas in the Fluorox 4-in. fluidized bed reactor. The run was made at a bed temperature of 810°C ± 15°C and an average feed rate of 1.37 kg/hr. Total operating time was 9.25 hr and the run was terminated when it was felt that enough information was available for evaluation of the run. Total amount of UF_4 introduced to the reactor was 12.7 kg and 5.12 kg of UF_6 was collected in the cold traps.

The experimental apparatus was similar to that used in run FBR-20 (Unit Operations Section monthly progress report for September 1958, ORNL-CF-58-9-62) except that a condensation pressure analyzer (Unit Operations Section monthly progress report for December 1958, ORNL-CF-58-12-35) was installed in the off-gas system to measure the UF_6 concentration in the reactor off-gas stream.

The operating procedure used was the same as that used in previous runs, and operation throughout the run was essentially smooth with no operational difficulties in the reactor systems. It was impossible to maintain the bed temperature above 825°C which probably reflected the excessive scale buildup on the reactor wall. As in previous runs, the fluidizing gas (air) was dried in molecular sieve beds to a dew point of -100°C.

There was difficulty in maintaining a constant cold bath temperature in the CPA. This variation (0°C- -10°C) resulted in erratic values for the UF_6 concentration in the reactor off-gas; however, there was enough constant temperature operation for determination of the off-gas UF_6 concentrations since the reactor system was operated at conditions which approached steady state.

Complete experimental and analytical results have made it possible to evaluate the run in a manner similar to that used in previous run evaluations.

The amount of UF_6 measured in the reactor off-gas by the CPA was 434 g more than the amount collected in the cold traps and chemical traps (Figure 2.1). The measured value of the UF_6 is probably the most accurate value because there was an observed loss of UF_6 through the CPA system. The measured value also gives a much closer check in the material balances, in particular the UF_6 balance, than does the amount of UF_6 collected in traps. The material balances are prepared with both of the UF_6 values for purposes of comparison.

The plot of measured UF_6 concentration in the reactor off-gas versus run time (Figure 2.1) shows that the system approached a steady state condition after about 1 hr of operation. The difference in reaction rate of UF_4 in air and O_2 can be easily seen since the UF_6 concentration increased from 1.8% to 3.4% when the oxidizing gas was changed from air to O_2 at the end of the run.

The over-all material balance of all reactor streams entering and leaving was 100.4% (Table 2.1 and Figure 2.2) based on the measured UF_6 value, while the over-all uranium balance was 100.5%. These balances resulted in weight differences between entering and leaving streams of 69 g and 72 g, respectively, which are within experimental error.

The UF_6 balance was 98.4% complete based on the measured UF_6 value (Figure 2.3) and the 5610 g of UF_6 measured in the reactor off-gas was 92.6% of the the theoretical amount which should have been formed. UF_6 collected in cold traps and chemical traps was 85.4% of the theoretical amount.

Approximately 5.8% of the UF_6 formed was used up in side reactions with 0.2% reacting with the uranium oxides introduced with the feed, 1.4% reacting with reactor and thermowell walls to form corrosion products and 4.2% reacting with the water introduced with the feed. This amount of loss to side reactions probably represents a minimum figure in this apparatus.

The 92.6% of theoretical UF_6 measured in the gas stream was higher than any previous value of UF_6 recovery, and the 85.4% UF_6 collected in cold traps and chemical traps was 12% greater than UF_6 recovery in previous runs. These higher recovery figures are due mainly to reduced H_2O and uranium oxide content in the feed.

The apparent reaction rate constant determined for the operating temperature of 810°C with air as the oxidant was 1.29 hr^{-1} (Figure 2.4). This value compares favorably with the extrapolated value from laboratory data, 1.86 hr^{-1} (1).

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(1) L. M. Ferris, "A Study of the Reaction $2UF_4 + O_2 \rightarrow UF_6 + UO_2F_2$, II Kinetics Between 550 and 815°C, presented at the 133rd National ACS Meeting, San Francisco, California, April 13-18, 1958.

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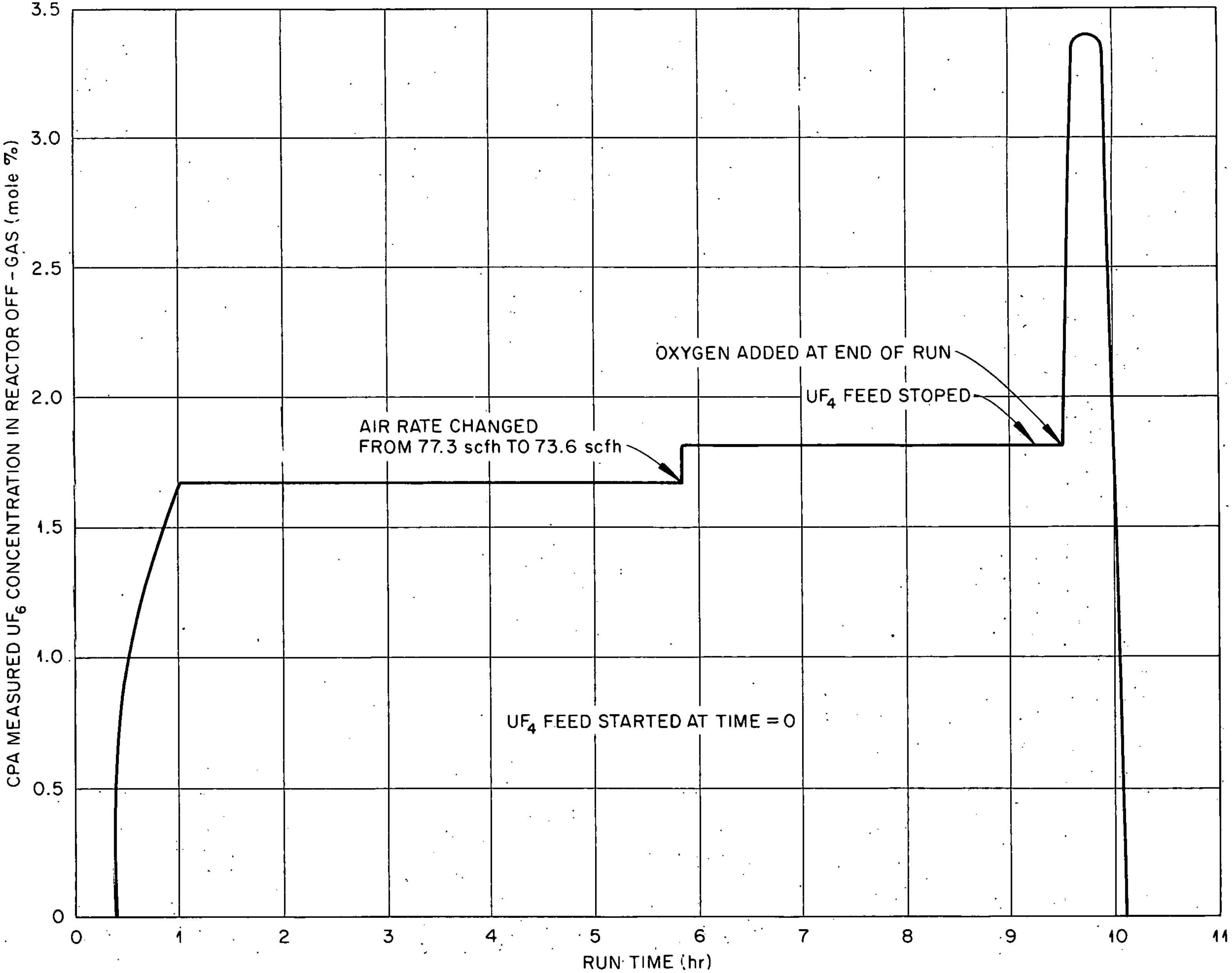

Fig. 2.1. UF_6 Concentration in Reactor Off-Gas as Measured by the Condensation Pressure Analyzer.

Table 2.1. Change in Amounts of Individual Compounds in Run FBR-21

	Entering Reactor, g		Leaving Reactor, g			
Compound	Total	Uranium	Total	Uranium	Total	Uranium
UF_4	12620	9580	1811	1373	-10809	-8207
UO_2F_2	5917	4580	11746	9080	+5829	+4500
UO_2	13	11	0	0	-13	-11
U_3O_8	6	5	0	0	-6	-5
Metal F	18	0	64	0	+46	0
H_2O	26	0	0	0	-26	0
O_2*	562	0	0	0	-562	0
UF_6-Collected**	0	0	5176	3490	+5176	+3490
(Measured)	(0)	(0)	(5610)	(3795)	(+5610)	(+3795)
Totals	19162	14176	18797	13943	-365	-233
			(19231)	(14248)	(+69)	(+72)

*The amount of O_2 entering the reactor was calculated to be the theoretical amount necessary for oxidation in the various reactions occurring.

**The amount of UF_6 reported as Collected is that amount collected in cold traps and chemical traps and the amount of UF_6 reported as Measured is that amount of UF_6 measured in the reactor off-gas by the Condensation Pressure Analyzer.

Material Balance (material leaving/material entering): 98.1% using UF_6 Collected
100.4% using UF_6 Measured

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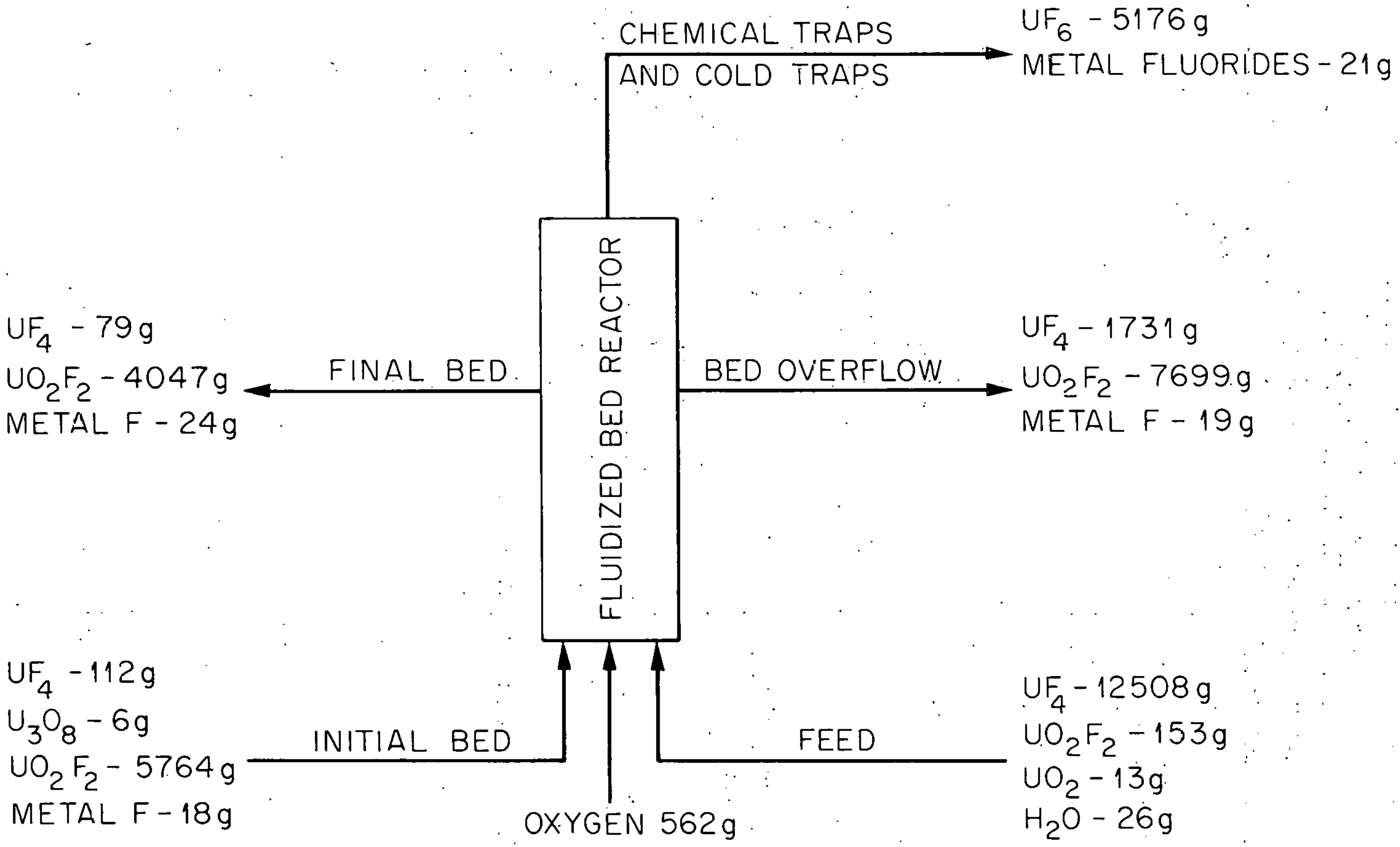

Fig. 2.2. Material Balance of the Constituents of Each Stream from Run FBR-21.

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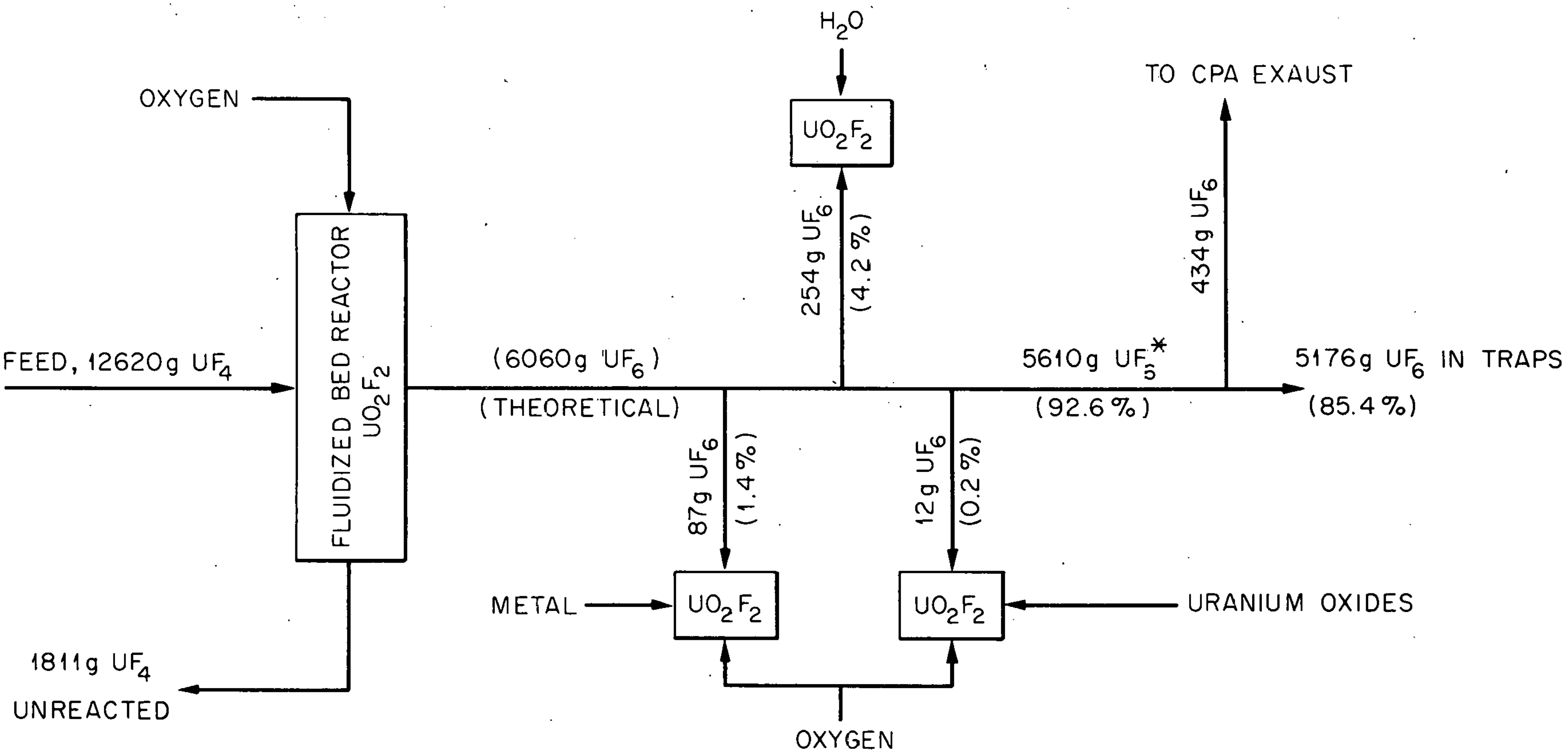

*UF_6 measured in reactor off-gas stream by CPA

Total UF_6 accounted for = 5529g or 91.2% of theoretical (based on UF_6 actually trapped from off-gas stream)
= 5963g or 98.4% of theoretical (based on UF_6 measured in reactor off-gas by CPA)

Fig. 2.3. Disposition of UF_6 Which was Formed in Run FBR-21.

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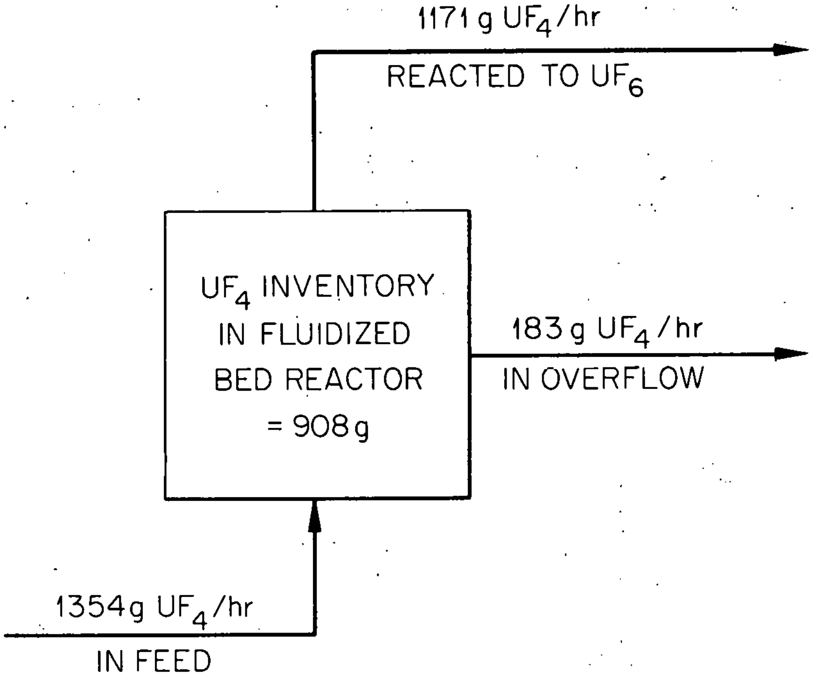

ALL FLOW RATES ARE AVERAGES BASED ON STEADY STATE OPERATION. REACTION RATE CONSTANT, k = (1171 g/hr/908 g) = 1.29 hr^{-1}

Fig. 2.4. UF_4 Material Balance Across the Fluidized Bed Reactor and Apparent Reaction Rate Constant for Run FBR-21.

As was expected the reaction rate in air was less than it was in pure O_2. Since the UF_4 feed rate in this run was maintained at somewhat higher values than the runs in which pure O_2 was used, the combination of higher feed rate and decreased reaction rate resulted in a higher UF_4 content in the bed. This concentration was 21.9% by wt at steady state while in most of the earlier runs with oxygen, UF_4 concentrations of less than 1% were maintained.

As a result of high UF_4 concentration in the bed there was appreciable build-up of material on the reactor walls which resulted in a reduction of heat transfer from the walls to the bed and in a decrease in the fluid bed volume. It is probably desirable to maintain the UF_4 concentration in the bed at less than 5%.

A UF_6 sample which was cold trapped out of the CPA off-gas stream and liquid transferred to a plastic sampling container, was analyzed for uranium content and impurities. Although the laboratory techniques for these analyses do not give accurate uranium analysis, they do give indication of impurities.

The following impurities were found by both wet chemistry and spectrographic methods:

Aluminum	0.2 ppm
Calcium	0.5 ppm
Chromium	120 ppm
Copper	0.3 ppm
Iron	500 ppm
Magnesium	0.4 ppm

The oxygen utilization of the oxygen in the total amount of air used during run FBR-21 was 10.4%. This is a higher utilization than was obtained with any of the runs in which pure oxygen was used.

Run FBR-21 demonstrated the feasibility of using dry air as the fluidizing and oxidizing gas for the Fluorox reaction in a fluidized bed reactor. The close agreement between the fluidized bed reaction rate constant with the rate constant found in the laboratory by thermogravimetric methods indicate that these values could be used in a scale-up of the operation.

Run FBR-22. Run FBR-22 was made to test the reliability of the experimental equipment over a long period of time and to provide enough operating time to reduce the effect of short term operating variables.

The run was made at bed temperatures of 800-825°C with one temperature excursion to 775°C and with an average UF_4 feed rate of 1.6 kg/hr. The total run time was 58.4 hr with 6.75 hr downtime for maintenance; however, during the first 49.8 hr there was only 0.9 hr downtime for routine maintenance.

The experimental apparatus and procedure was the same as that used in run FBR-21. During the last 8.6 hr of the run there was a total of 6.75 hr of downtime due to three major mechanical failures, (1) a broken fluidizing gas line, (2) a cracked overflow line, and (3) loss of several fins on the feeder impeller which resulted in introduction of a large amount of UF_4 to the bed in a short time.

The combination of these three failures produced a high-temperature, static bed with a high UF_4 concentration. These conditions resulted in sintering of some of the UF_4 in the bed, a build-up of solid material on the walls, and formation of large amounts of the intermediate U_4F_{17} which solidified in the relatively cool section above the heated bed and caused severe restriction to gas flow. After the mechanical failures had been corrected, it was impossible to refluidize the bed properly so the run was terminated.

A total of 83.8 kg of UF_4 feed was introduced to the reactor and 32.5 kg of UF_6 was collected in the cold traps.

The CPA was operated during part of the run; however, erratic operation of the analyzer due to inability to maintain a constant cold bath made it difficult to use the analyzer data effectively.

Complete analytical results from the run are not available.

2.2 Condensation Pressure Analyzer

The CPA (Unit Operations Section December monthly progress report, ORNL-CF-58-12-35) was calibrated by introducing a gas stream of known UF_6 concentration into the analyzer system and recording the analyzer readings which indicate the UF_6 concentration. The actual UF_6 concentrations were then compared to the indicated concentrations.

Calibration data (Table 2.2) show some differences between the actual and indicated values. In using the analyzer data to obtain indicated UF_6 concentrations, the data which has the most uncertainty is the temperature of the cold bath which surrounds the capillary sensing element. In the calibration tests and in subsequent operation it was found that this temperature could not be maintained constant and the actual temperature at the cold capillary was not always known.

The UF_6 concentration in the gas stream to the analyzer was known to an accuracy of about 5%, and some of the differences between actual and indicated UF_6 concentrations were greater than 5%. However, it is felt that the CPA will be useful in determining UF_6 concentration in a gas stream if the analyzer cold bath can be maintained at a constant, known temperature.

Table 2.2. Condensation Pressure Analyzer Calibration Data

Bath Temp., °C	Partial Pressure of UF_6, mm of Hg	Total Pressure, mm of Hg	UF_6 Conc., Indicated	Volume %, Actual	% Error $\left(\frac{\text{Indicated-Actual}}{\text{Actual}}\right) \times 100$
-9.2	8.0	157	5.1	4.8	+6.3
-9.2	8.0	231	3.5	3.3	+6.1
-15*	4.5	136	3.3	3.3	0
-15*	4.5	330	1.4	1.7	-17.6
-15*	4.5	91	4.9	4.8	+2.1

*The cold bath at these temperatures was an ice slush in a saturated aqueous solution of NH_4Cl. The theoretical temperature of such a bath is -16.2°C and for partial pressure considerations, this was the temperature used.

3.0 HR FUEL AND BLANKET PREPARATION AND PROCESSING

P. A. Haas

These programs include the process and equipment development studies required for preparation and reprocessing of aqueous homogeneous reactor fuel and blanket fluids. Direct denitration of thorium and/or uranium nitrate is being applied to production of 1-3 micron oxide particles by flame denitration and 50-500 micron particles by fluidized bed denitration. Active engineering studies include those required for special hydroclone classification of ThO_2 and for electrolytic removal of nickel from HRT fuel solution.

3.1 Hydroclone Classification of ThO_2 - E. L. Youngblood, D. A. McWhirter

An investigation has been made to determine if a 0.5 in. dia hydroclone could be used to remove large thorium oxide particles from feeds containing particles below 0.5 microns in dia in order to obtain a product enriched in below 0.5 micron material. The results showed that the percentage of thorium oxide particles below 0.5 micron would be considerably increased by hydroclone classification. Over-all yields of product from this test were low; however, yields should increase with feeds containing a larger fraction of feed below 0.5 micron. Complete removal of particles above 0.5 μ would be very difficult.

A single 0.5 in. dia hydroclone was used for the classification. The overflow stream containing the fine particles was given a second and third pass through the unit in an attempt to remove further the larger particles. All runs were made using a feed pressure of 59 psi to the hydroclone. The slurry was maintained at 80°C during operation to decrease the viscosity of the water, thus lowering the classification range of the hydroclone. Oxalic acid was added to disperse the feed slurry.

As shown by the size analysis given in Figures 3.1-3.3 the percentage of material less than 0.6 μ in dia was increased from about 5% in the original feed to 44% in the overflow from the third pass through the hydroclone. The over-all recovery of feed material in the overflow stream was low (Table 3.1); however, this recovery represents 15-81% of the material below 0.6 microns in the original feed.

The size analysis and per cent recovery of overflow product agree well with calculated values with the exception that the overflow material contained a higher percentage of particles larger than 1 micron than would be expected. This effect could be due to agglomeration of small particles during size analysis causing them to behave as larger particles.

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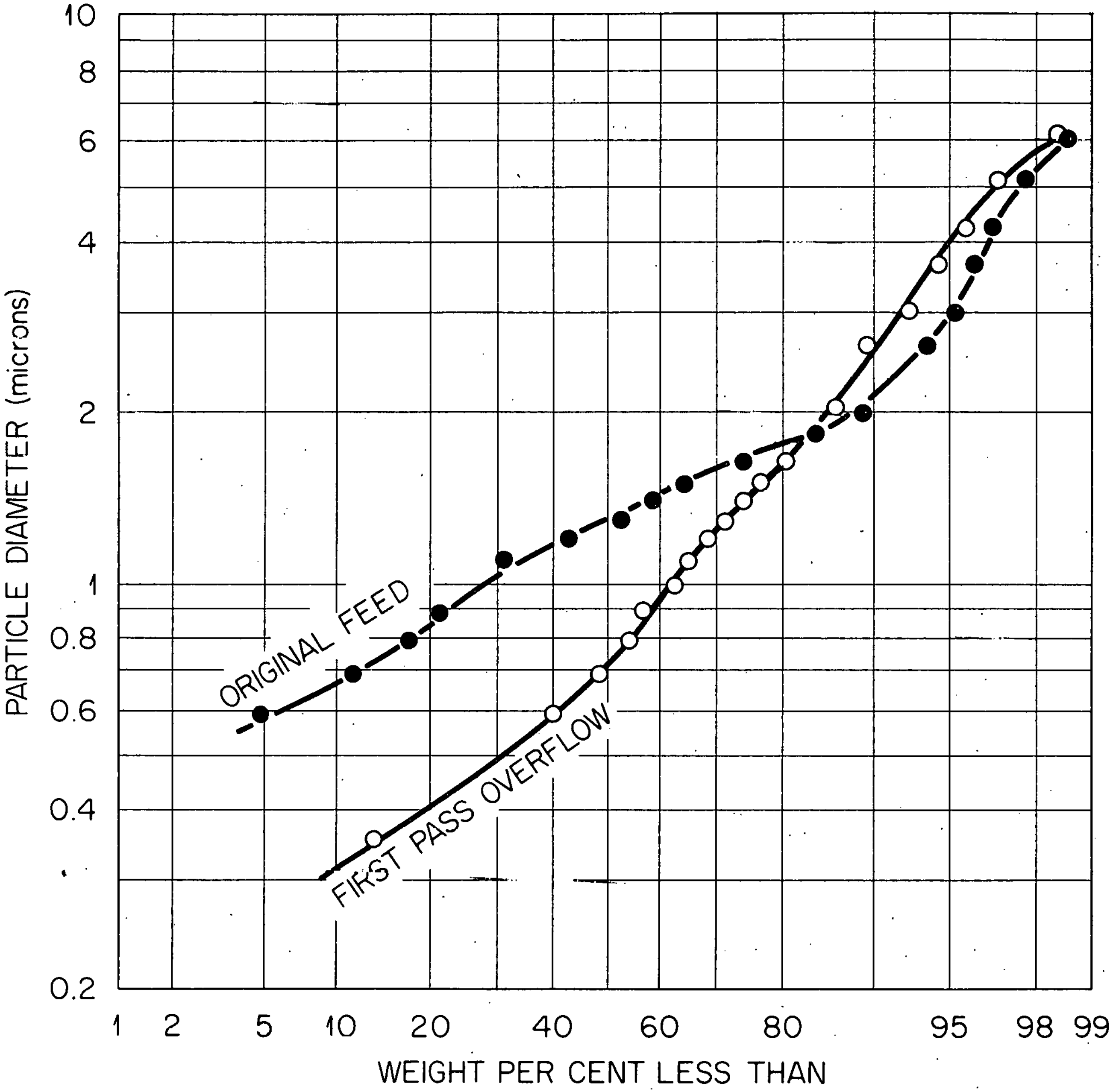

Fig. 3.1. Particle Size Distribution of Overflow Stream from First Pass Through a 0.5-in. Diameter Hydroclone.

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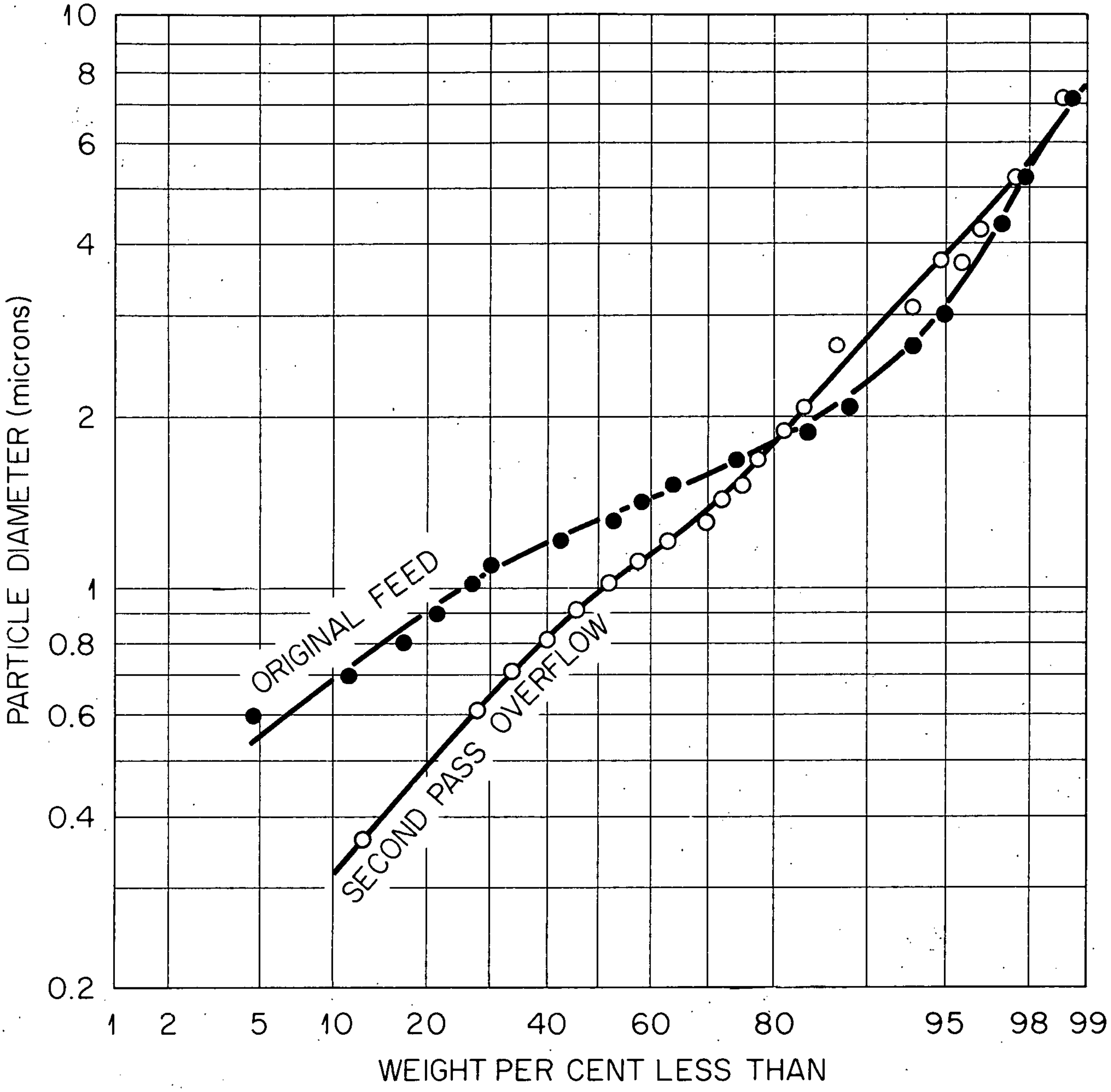

Fig. 3.2. Particle Size Distribution of Overflow Stream from Second Pass Through a 0.5-in. Diameter Hydroclone (Feed Used Was Overflow From First Pass).

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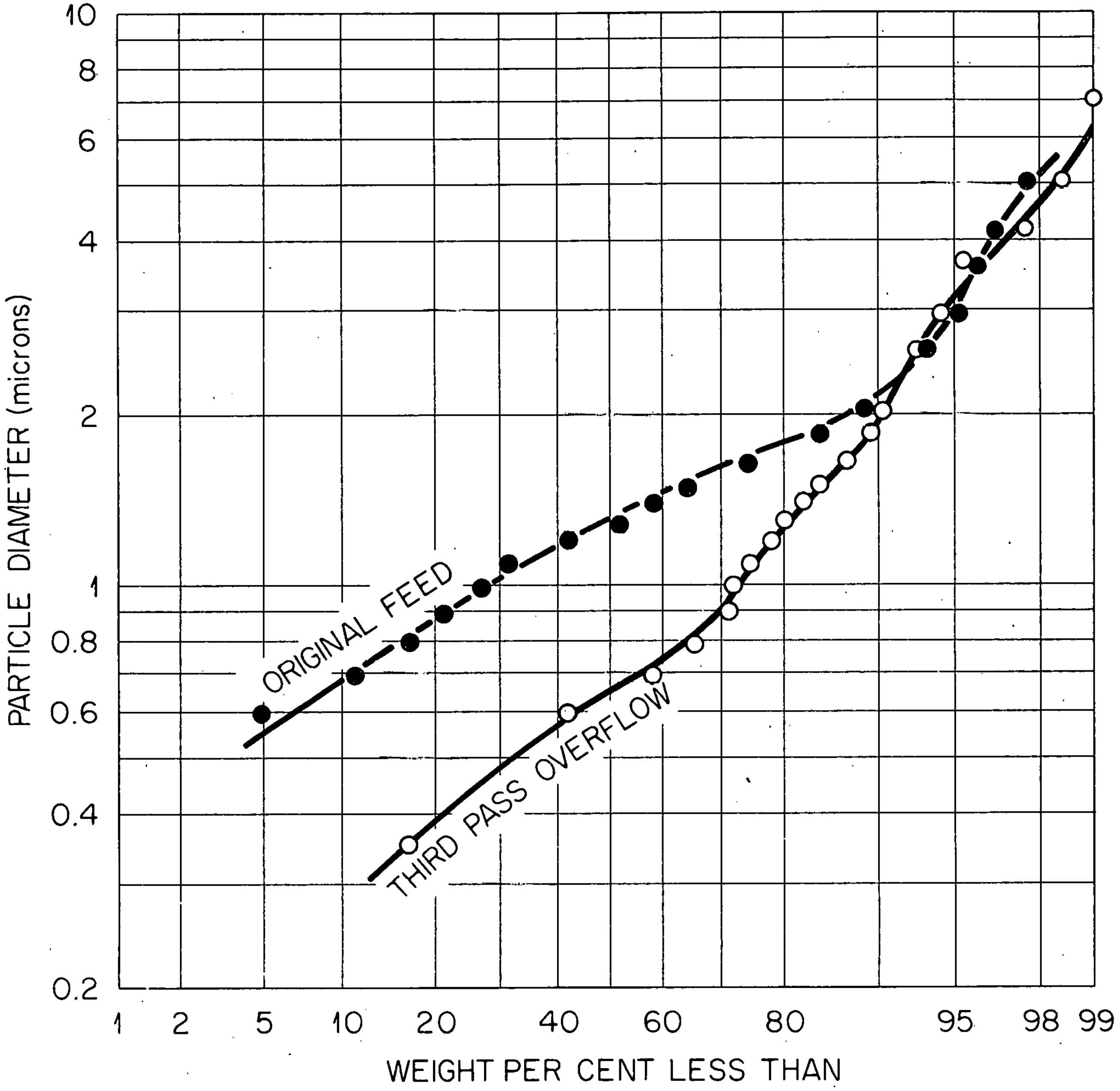


Fig. 3.3. Particle Size Distribution of Overflow Stream from Third Pass Through a 0.5-in. Diameter Hydroclone (Feed Used Was Overflow from Second Pass).

Table 3.1. Product Yield from Hydroclone Classification of ThO_2

Material	Volume, liters	Concentration, g/kg H_2O	Wt, g	% Smaller than 0.6 Microns	Wt of Below 0.6 Micron Material, g	Recovery of Original Feed in Overflow, %	Recovery of Original Below 0.6 Micron Material in Overflow, %
Initial feed	188	27.4	5140	5	257	-	-
1st Pass Overflow	140	3.72	521	40	208	10.1	81
2nd Pass Overflow	101	1.84	186	28	52	3.6	20
3rd Pass Overflow	72	1.17	84	44	37	1.6	15

3.2 Fluidized Bed Denitration - S. D. Clinton, R. D. Arthur

Two runs were made with the fluidized bed denitration equipment (described in Unit Operations Section monthly progress report for October, ORNL-CF-58-10-90) at bed temperatures of 500 and 400°C. In both runs a 2.5 M $Th(NO_3)_4$ aqueous solution was sprayed at an average rate of 14 ml/min into an initial fluidized bed of classified sand. A cake formed in the bed just below the spray nozzle during each run. There was no evidence of ThO_2 growth on the sand particles at either temperature. ThO_2 samples from each run showed the denitration reaction was greater than 99.0% complete.

During each of the two runs, 7.5 liters of the 2.5 M nitrate feed was sprayed into the fluidized bed reactor with none of the operating difficulties previously reported. The pressure setup atomizing nozzle from Spraying Systems Company used in preceding runs was replaced with a siphon set-up (fluid nozzle 2850 and air nozzle 64-5). Using the new feed nozzle there was no plugging, and the water coolant previously used to the nozzle was proved unnecessary. The Hills McCanna feed pump operated satisfactorily at flow rates between 10 and 15 ml/min. The nitrate feed line and storage tank were preheated to 40°C in order to prevent precipitation of $Th(NO_3)_4 \cdot 6H_2O$.

The fluidized bed developed a partial cake during both runs. During the 500°C run the superficial fluidizing gas velocity was 0.8 ft/sec. This gas velocity was increased to 1.3 ft/sec for the 400°C run with partial caking of the bed occurring after approximately 5 hr of operation.

The ThO_2 produced in both runs consisted of particles which could be screen classified to a size range less than 53 microns. The average particle size of this ThO_2 from both runs was between 13 and 15 microns. The ThO_2 produced at 500°C contained 0.34 wt per cent NO_3^-, and the oxide from the 400°C run contained 0.51 wt per cent NO_3^-. A material balance for the 400°C run on the ThO_2 produced from the nitrate feed gave a recovery of 94.5%.

The next run will be an attempt to duplicate the successful fluidized bed denitration of UNH reported by Argonne. This run should complete the fluidized bed denitration studies, and future ThO_2 preparation efforts in the size range of 50-500 microns will be with an agitated trough calciner. Installation of an experimental scale trough calciner borrowed from Y-12 is essentially complete.

3.3 Flame Calcination - C. C. Haws, V. L. Fowler, F. N. McLain

Test quantities of flame denitrated mixed oxides of Th-U were prepared. Studies were carried out to determine the effect of adding a third element to the feed. Aluminum nitrate was added with the objective of obtaining a lowered melting point, while molybdenum or palladium was added to test the possibility of producing a material containing a recombination catalyst.

Spheroidal particulates were obtained in one of the firings in which aluminum nitrate was added (see Figure 3.4). This is potentially a very significant development in that such spheres in the size range 1-2 μ might have a very low shear stress in a water slurry and might circulate easily in a slurry reactor.

Analytical results show the products of the Th-U-Mo and Th-U-Pd runs to be equivalent to previously prepared Th-U samples. About two-thirds of the molybdenum was volatilized during the firings in which this element was added (see Table 3.2). Ninety per cent of the palladium was volatilized at 1400°C, but only 10% in the 1200°C firing. These products will be tested for catalytic recombination activity.

Table 3.2. Flame Calcining Experiments

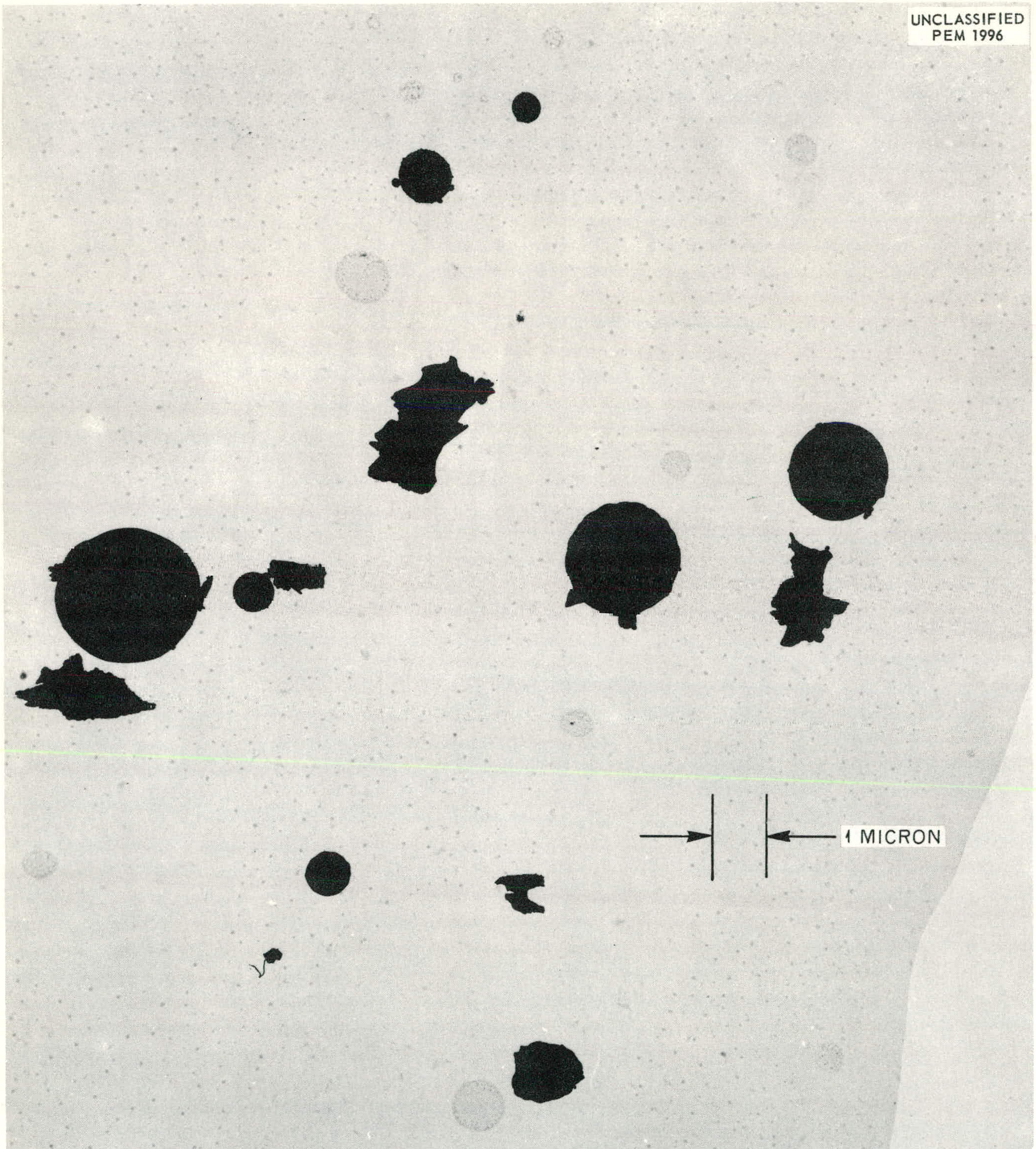
Preparation of Th-U Mixed Oxides

With a Third Element as an Additive

Run No.	Reflector Temp., °C	Quantity Produced, g	Additive: Calculated Feed Concentration, wt %	Additive: Product Concentration, wt %
46	1000	233	None	-
47	800	161	None	-
48	1440	161	0.53 MoO_3	0.165 MoO_3
49	1220	262	0.53 MoO_3	0.195 MoO_3
50	1425	143	0.017 PdO_2	0.0017 PdO_2
51	1205	244	0.017 PdO_2	0.0135 PdO_2

3.4 Electrolytic Removal of Nickel - E. L. Youngblood

Components have been selected for an engineering test of the electrolytic removal of nickel from HRT fuel solution as developed by Laboratory Section A. A glass-lined dissolver will be used for the electrolytic cell and an Excer rectifier (0-1500 amps, 0-15 volts) will probably be used for a power supply. The proposed schedule is complete installation of HRT-CPP scale apparatus in March.



SPHERICAL PARTICULATES OBTAINED BY FLAME DENITRATION OF A Th-U-Al SYSTEM
APPROX. COMPOSITION (wt %)

ThO_2	83
UO_2	7
Al_2O_3	10

Fig. 3.4. Flame Calcining Experiments (Run 53).

4.0 ION EXCHANGE

M. E. Whatley

Mechanism and Kinetic Studies - J. S. Watson

In order to make rational predictions of the operating characteristics of uranium anion exchange contactors, an understanding of the mechanism and kinetics of the exchange is necessary. Toward this objective an effort is being made to determine the equilibrium sorption isotherms and rates of sorption of uranium on Dowex 21K.

An apparatus for studying the kinetics of uranium sorption on Dowex 21K has been designed and assembled. The apparatus is shown schematically in Figure 4.1. Solution is pumped through a "differential" resin bed, and the rate of uranium sorption is determined by the concentration of uranium in the stream leaving the bed. The concentration is recorded continuously by a flow colorimeter and checked by batch samples. A rotameter measures the flow rate. A recirculation line allows the pump to be adjusted to the desired rate before the start of a run.

The container for the bed of resin is shown in Figure 4.2. The bed is one-half inch deep and three-fourths inch in diameter. A one-half inch deep section just above the bed is packed with fine glass beads for approximating a flat velocity profile. A similar section one-fourth inch deep is just below the bed to keep the bed full of solution during the run. The various sections of the resin container are separated by 80 mesh platinum screen.

For some of the loading solutions, a potentiometric ceric sulfate method will be used for uranium analyses (1). Since iron interferes with this method, it is desirable to keep as few iron or steel components as possible in contact with the solutions. At present, there are two possible sources of contamination: the pump and the colorimeter.

An "Eco Gearchem" pump was selected for the study. It gives a fairly smooth flow at the rates which are expected to be used in most of the runs (approximately 100 to 500 ml/min), and pulses which do occur in the flow rate are rapid and can be easily dampened by the air chamber. The pump is constructed with a Carpenter 20 stainless steel body and teflon gears.

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(1) "ORNL Master Analytical Manual", TID-7015 (Section 1), 1-219221.

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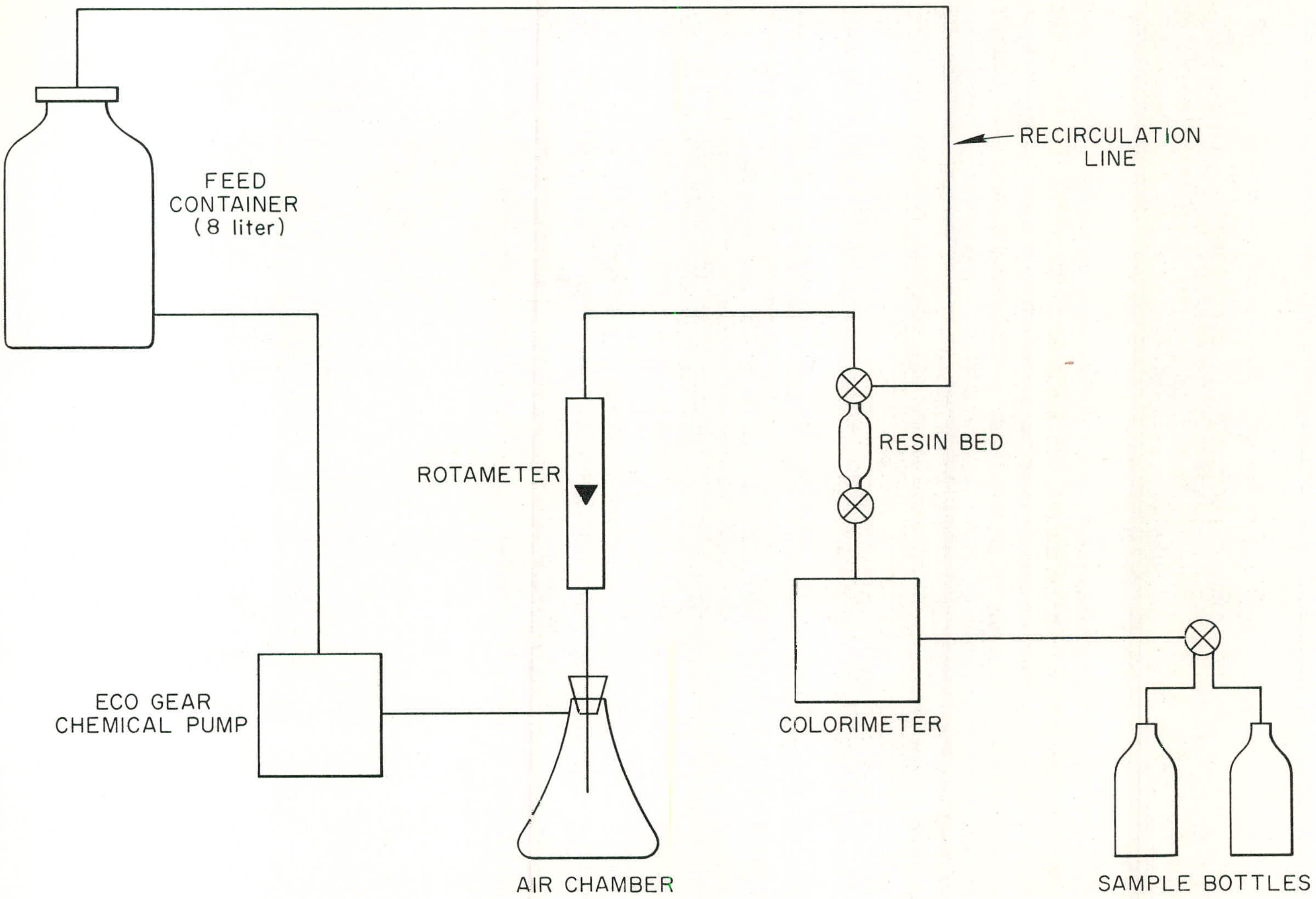

Fig. 4.1. Sketch of Ion Exchange Kinetics Studies Apparatus.

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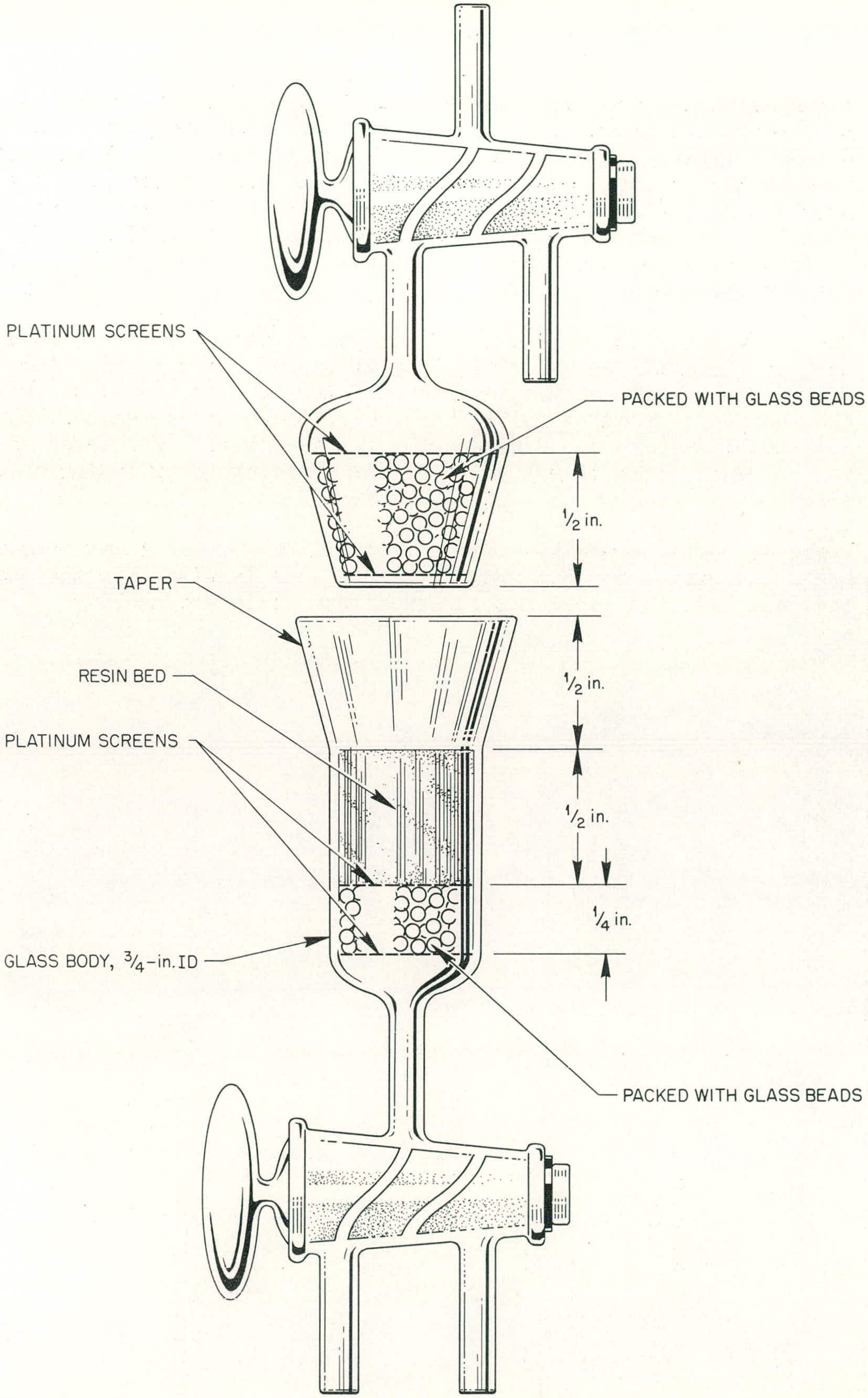

Fig. 4.2. Differential Resin Bed.

A qualitative corrosion test was made to determine if an excessive amount of corrosion products would be introduced from the pump into the system. Four liters of a solution 0.005 M in uranium, 0.020 M in sulfuric acid, and 0.05 M in total sulfate was circulated through the pump for approximately 6 hr. (All kinetic runs are expected to last less than 1 hr.) At the end of the test the total iron concentration in the solution was 2 ppm. This value was considered so low that no troubles in the uranium analyses are expected.

The colorimeter to be used was developed at Savannah River and has been used at the Metal Recovery facility at ORNL. Its principal shortcoming is a strong temperature dependence. During a period of several days the instrument reading on the same solution showed a regular variation with the room temperature. However, the instrument will be needed only for short periods (less than 1 hr), and the temperature variation should be minor.

Resin has been carefully screened and all broken particles removed for use in the runs. To obtain finer separations in size than the standard screen sizes, the resin was screened both while wet and dry.

5.0 POWER REACTOR FUEL REPROCESSING

C. D. Watson

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

The purpose of the Darex process is to convert SS-U and SS-UO_2 fuels into chloride-free nitrate solutions suitable for processing in existing SS solvent extraction equipment. Chloride is necessary to effect dissolution of SS in HNO_3 but it must be removed to avoid corrosion of process equipment. The present investigation seeks to develop a batch flowsheet, using 61% HNO_3, in which the chloride in the solvent extraction feed is reduced to < 350 ppm. This is to be accomplished by treating the dissolution product with only that amount of HNO_3 which is consumed in dissolution and lost in the solvent extraction feed.

5.1.1 Chloride Removal and Feed Adjustment

Three 10-liter runs (31, 37, 40) in the 4-in. ID feed adjustment equipment (Figure 5.1) are reported along with five laboratory runs (29, 34, 38, 39, 41) - Table 5.1. Run 31 was reported last month and is repeated here for comparison. This run compared to four others shows that the lowest final chloride concentration resulted from refluxing using an updraft condenser and an air sparge. The type of condenser made no difference in mixed acid recovery and air sparging had a detrimental effect on Cl^- recovery. It was thought that a higher sparge rate might allow the use of a downdraft condenser but run 37 shows that this is not the case. The higher sparge rate (2 liters/min) showed no improvement over another downdraft run (run 32 reported last month) with a sparge rate of 1 liter/min.

Run 40 (see Figure 5.2) is the Recycle flowsheet in which a large excess of HNO_3 is added in one continuous addition with mixed acid recycled for dissolution and regenerated 13 M HNO_3 recycled in the chloride removal procedure. The first portion (7.7 liters) of the acid is added while 7.7 liters of mixed acid is being removed (see columns 9 and 10, Table 5.1) thus maintaining a constant 6-liter volume (column 14). The composition of this first addition acid was chosen to approximate the steady-state recycle acid concentration (based on a series of recycle runs by Flanary and Goode).

The composition of the 10.3 liter second addition acid (column 13) represents a mixture of recycle acid and virgin 13.3 M HNO_3 used as makeup. The 10.3 liter second addition is made simultaneously with the takeoff of the first 10.3 liters of the second mixed acid, also at a constant 6-liter volume. The withdrawal of the last 3 liters of second mixed acid reduces the volume to somewhat less than 3 liters. This volume is then diluted with water to 9 liters.

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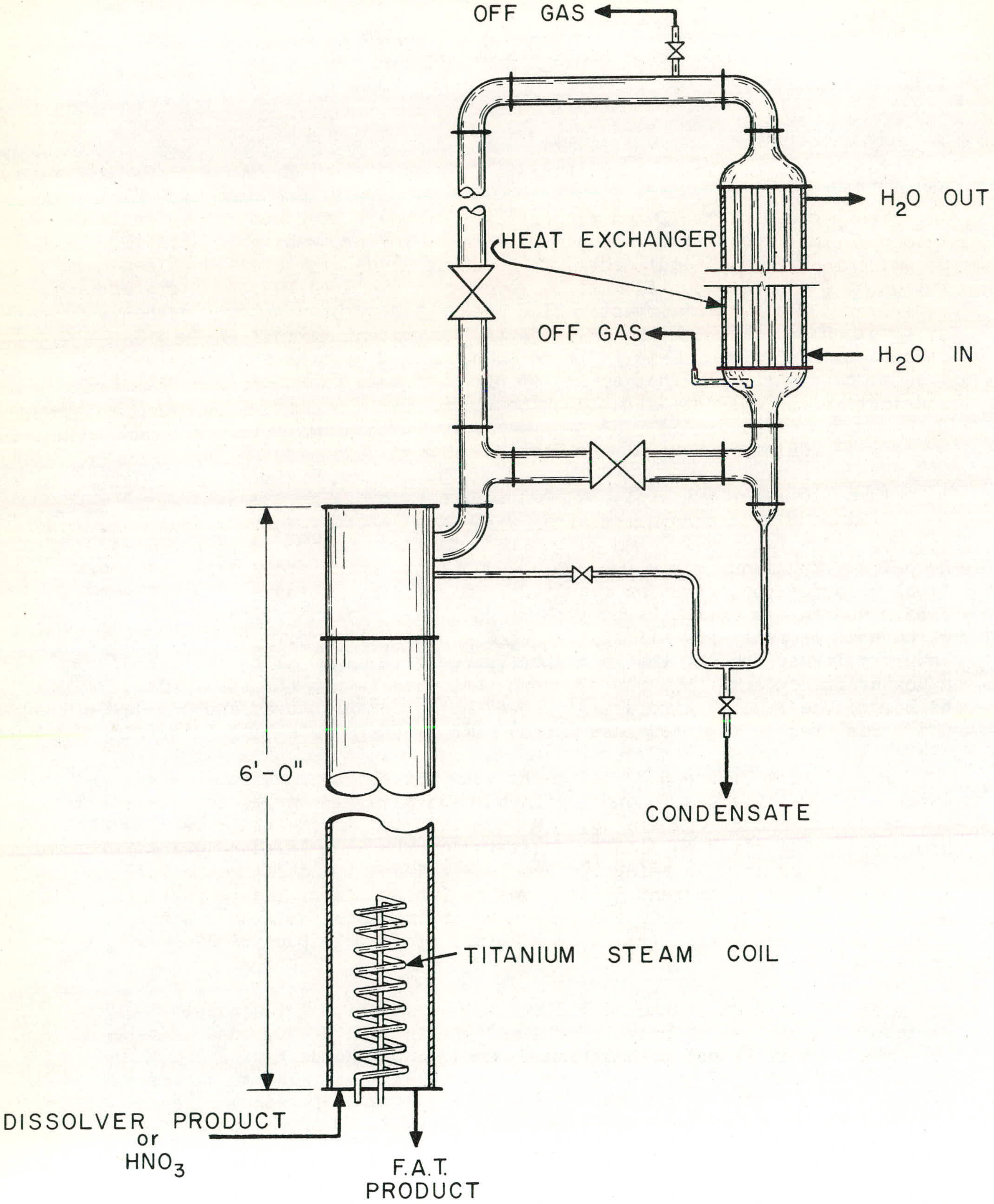

Fig. 5.1. 4in. I.D. Pyrex Chloride Removal and Solvent Extraction Feed Adjustment Tank

Table 5.1. Data from Batch Darex Runs

Col. No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
Run No.	Air Sparge	Condenser	Dissolution Product			Waste Acid			Add 13.3 *M* HNO_3 *l*	1st Mixed Acid			Add 13.3 *M* HNO_3 *l*	Acidified Concentrate			Reflux Time hr	2nd Mixed Acid		Solvent Extraction Feed		
			Vol *l*	H^+ *M*	Cl^- *M*	Vol *l*	H^+ *M*	Cl^- *M*		Vol *l*	H^+ *M*	Cl^- *M*		Vol *l*	H^+ *M*	Cl^- *M*		Vol *l*	HNO_3 *M*	Vol *l*	HNO_3 *M*	Cl^- ppm
31	1 *l*/min	Updraft	10.0	3.34	1.66	2.00	1.14	0.50	1.80	7.5	5.65	1.10	4.0	~6.0	9.66	0.67	2	1.60	11.0	11.5	2.77	135
37	2 *l*/min reflux	Downdraft	10.0	3.01	1.66	2.00	0.60	0.25	1.80	7.5	5.60	1.45	4.3	~6.3	9.91	0.76	2	1.90	10.4	11.5	3.18	480
40	1 *l*/min recycle	Downdraft	9.0	2.98	1.74	3.00	0.71	0.35	Contin. 7.7 12.85 *M* 0.1 *M* HCl	7.7	7.16	1.92	Contin. 10.3 13.05 *M* 0.05 *M* HCl	Const. ~6	Beginning 9.32	0.12		13.3	12.85 0.05 *M* HCl	9.0	1.65	220
29	¼ SCFH	Updraft	1.20	3.05	1.75	0.250	0.98	0.19	0.500	1.10	6.9	0.95	900	1.2	11.11	0.007	1	0.90	13.0	1.37	1.08	50
34	None	Updraft	1.40	3.19	1.73	0.40	0.5	0.15	Contin. 0.850	1.25	7.9	0.95	None	~0.56	8.28	0.75	2	None		1.60	2.34	0.14 *M*
38	¼ SCFH reflux	Updraft	0.98	3.01	1.66	0.175	0.50	0.20	0.595	0.80	6.1	1.1	None	~0.6	8.21	0.09	2	0.1	9.1	1.12	3.20	580
39	¼ SCFH reflux	Updraft	0.98	3.03	1.74	None			0.225 21.85 *M* (92.5%)	0.80	6.2	1.2	0.175	~0.57	11.08	1.07	2	0.075	14.1	1.12	3.47	35
41	¼ SCFH reflux	Updraft	0.98	2.98	1.74	None			0.225 21.3 *M* (90%)	0.80	6.1	1.13	0.165	~0.57	10.88	1.06	2	0.075	13.5	1.12	3.21	160

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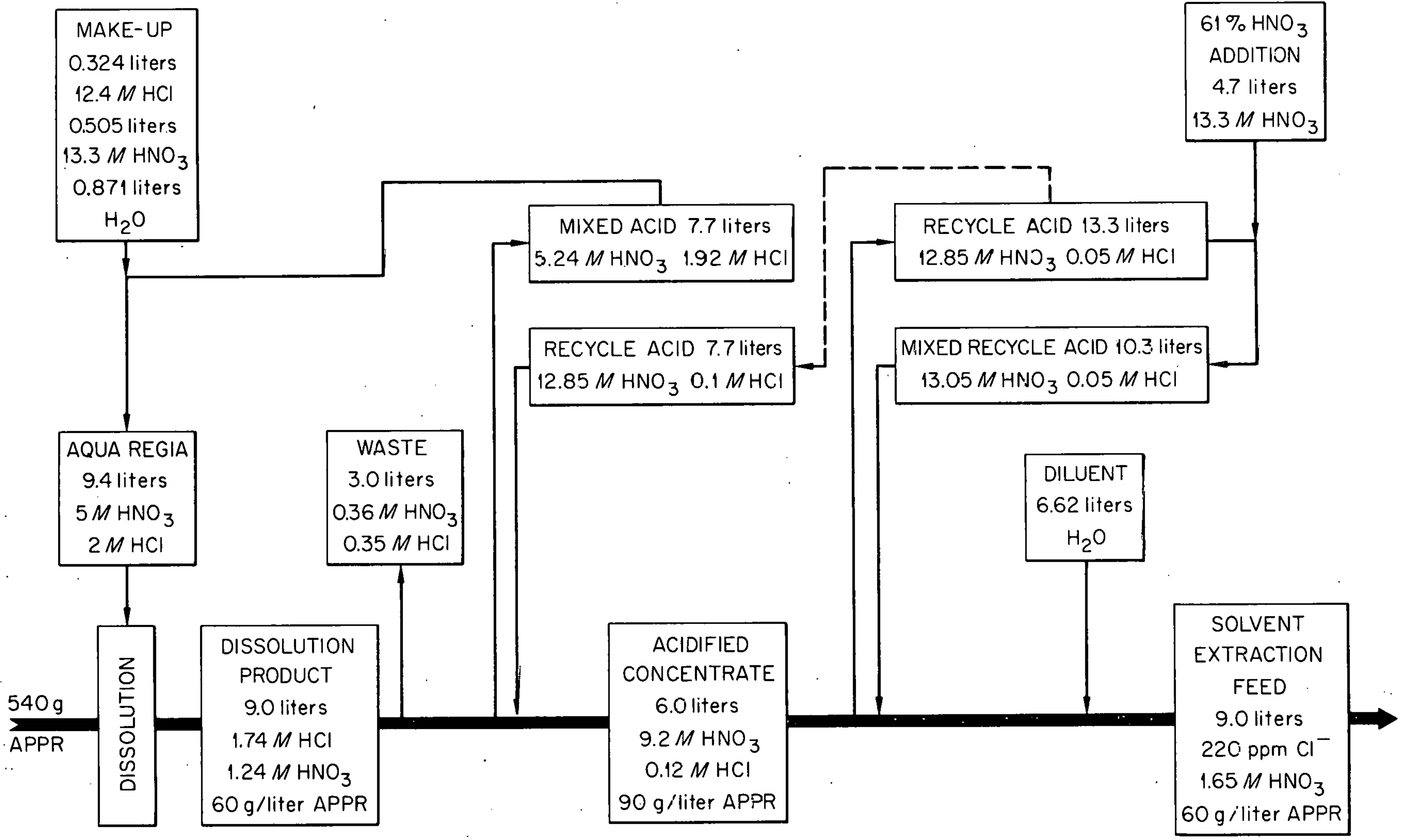

Fig. 5.2. The Darex Process:
Recycle Flowsheet for Batchwise Operation Using 61% HNO_3.
Run No. APPR-40

Run 29 is a Double Recycle flowsheet, similar to the "Mississippi" flowsheet in that an excess of HNO_3 acid is added, yet unlike it in that all acid additions are batchwise and refluxing is employed. The advantage of this flowsheet over the conventional Reflux flowsheets is that a larger HNO_3 addition is made just prior to refluxing, resulting in better Cl^- removal (to 50 ppm in run 29). Its advantage over the Recycle flowsheet, in addition to being batchwise, is that all the second addition is virgin HNO_3 containing no chloride. Run 29 is not a finished flowsheet but it proves the feasibility of double recycle. A flowsheet similar to Figure 5.3 should be easily developed using the data of run 29. This flowsheet, like the Recycle flowsheet, requires extra tankage above that necessary for the standard Reflux flowsheet to handle the additional HNO_3 recycle stream.

Runs 34 and 38 are conventional Reflux runs except that all the acid was added in one addition rather than being split into two additions as is done in the basic flowsheet. In run 34, the addition was continuous while run 38 used a batch addition. The runs were quite similar even though the method of HNO_3 addition varied. The high Cl^- value (column 16) in run 34 may be partially attributable to the lack of sparging.

The HNO_3 content (see column 15) of the acidified concentrate was low in both runs; this fact probably accounted for the high Cl^- content (column 22) of the feed. This HNO_3 concentration, which is probably the most important single determinant of final Cl^- concentration in a run of this type, is determined by the liquid-vapor equilibrium relationship and the concentration of salts in the liquid. It appears, therefore, that the logical way to obtain the desired higher HNO_3 concentration is to make an HNO_3 addition, just prior to reflux, to a reduced volume of concentrated solution as is done in the basic Reflux flowsheet (run 31).

Runs 39 and 41 again show the superiority of flowsheets using concentrated HNO_3 (92.5 and 90%, respectively). At these concentrations, an aqueous waste cut is not required and the Cl^- concentrations in the products are quite low (column 22) as could be predicted from the high HNO_3 content in the acidified concentrate (column 15).

5.1.2 Semi-Continuous Darex Dissolution

Six dissolution runs (CD-2 through 7) were made in the 6-in. glass dissolver (Figure 5.4) after making the necessary modifications to convert the overhead condenser to downdraft. The results of these runs are reported in Table 5.2. The information obtained from these runs indicates the following:

1. The proposed dissolution time of 1 hr for three APPR fuel elements at a 5-2 aqua regia flow rate of 4.5 liters/min is feasible.

2. The braze metal on the APPR is very resistant to dissolution in 5-2 aqua regia.

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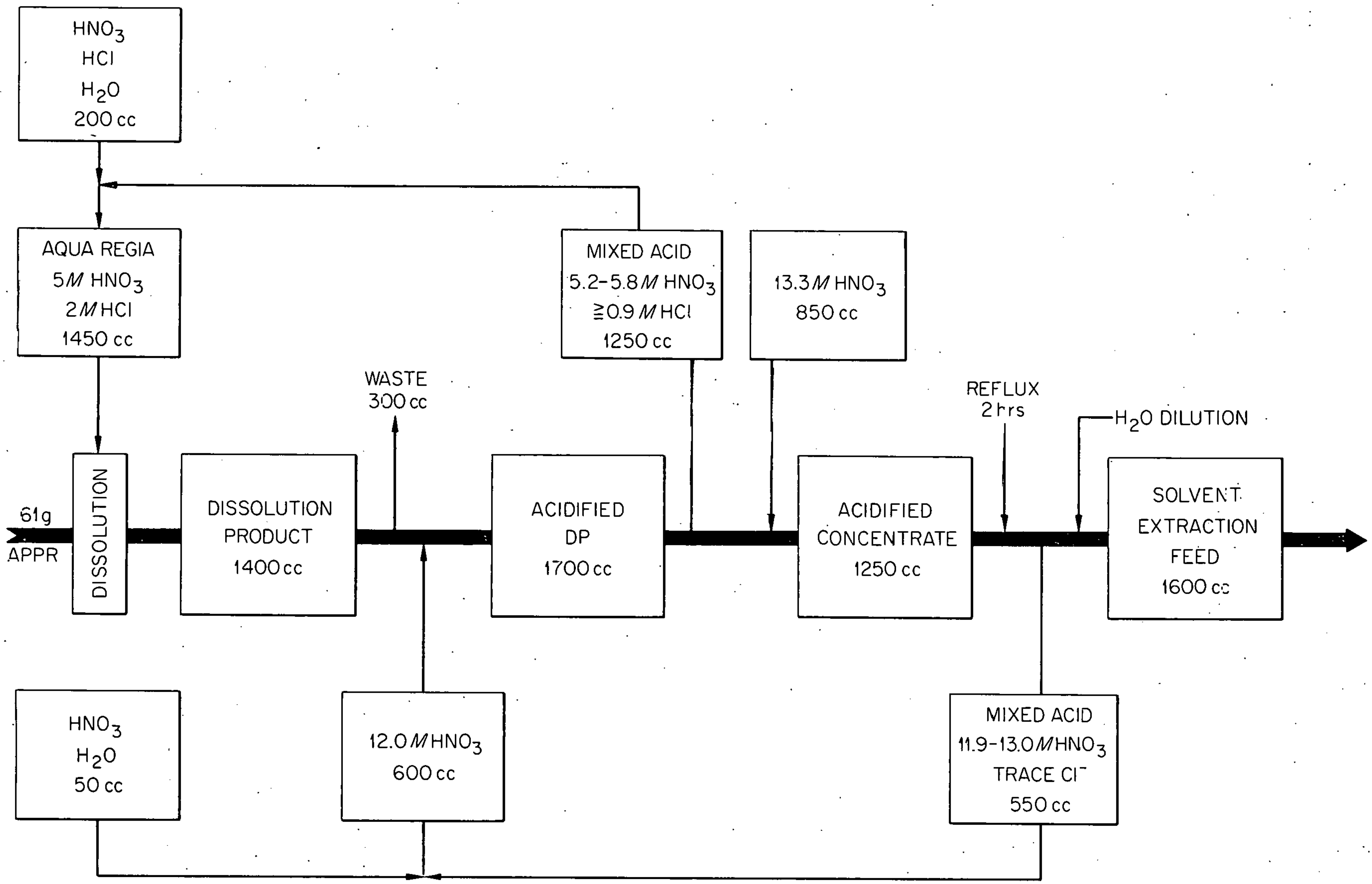

Fig. 5.3. Tentative "Double Recycle" Batch Flowsheet.

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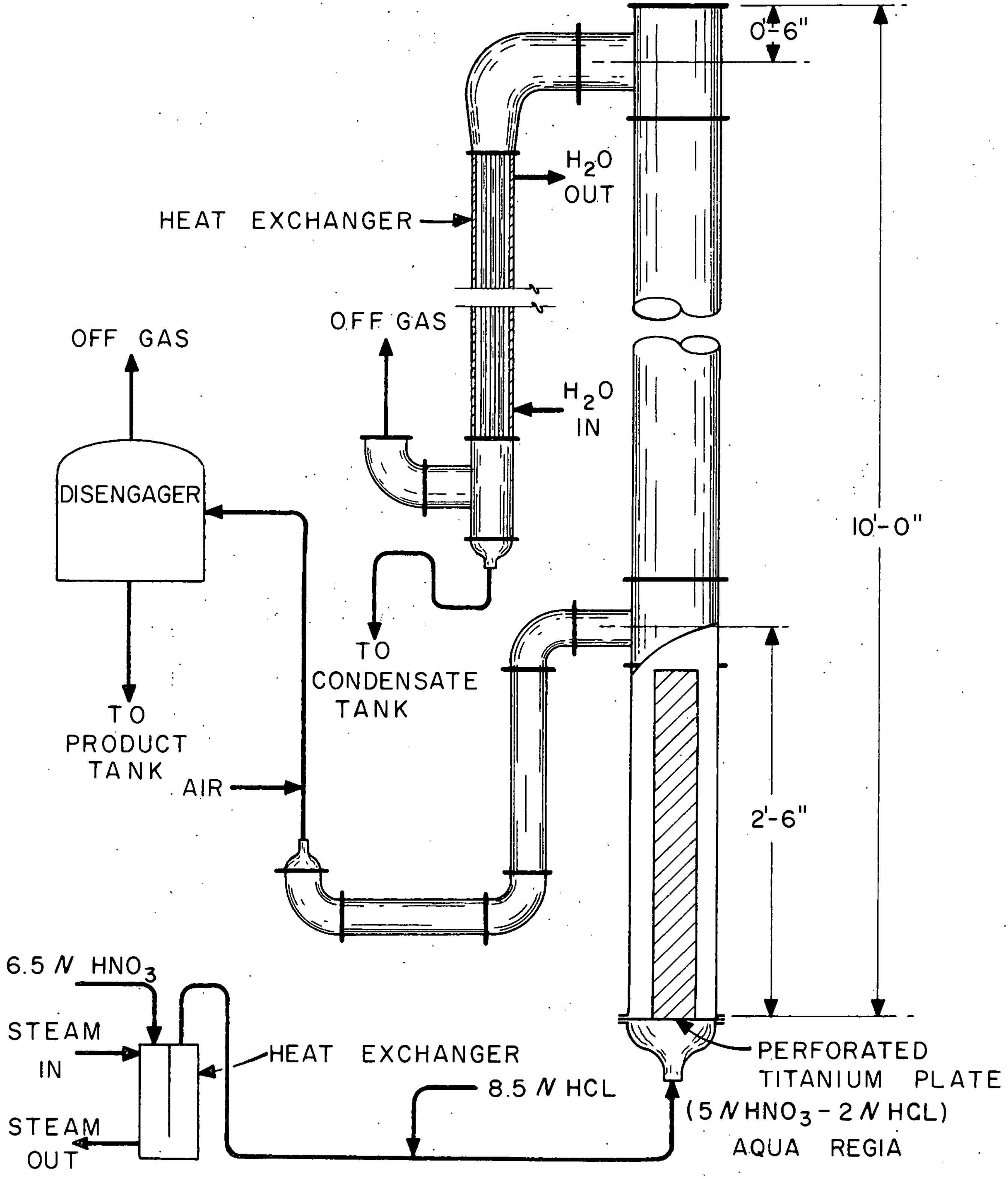

Fig. 5.4. 6 in. I.D. Semi-continuous Dissolver

Table 5.2. Dissolution of Unirradiated Prototype APPR Fuel Elements in Aqua Regia

Conditions:

Dissolver: 6 in. ID x 10 ft high pyrex

Aqua Regia Composition: 5 N HNO_3-2 N HCl

Aqua Regia Inlet Temperature: 80-90°C

Run No.	Number of Fuel Elements	Fuel Element Composition	Total Wt, g	Wt of U, g	Aqua Regia Flow Rate, liters/min	Dissolution Time, min	Dissolution Rate, g/min	Foam Height, ft
GD-2	1	SS	4,640	-	4.5	15	310	~ 6
GD-3	3	SS	16,344	-	4.1	52[a]	260	~ 9
GD-4	~ 1/2[b]	SS	~ Braze metal[c] (Coast Metals-NP) did not dissolve					
GD-5	1	SS+U	5,240	550	4.35	19	276	~ 6
GD-6	1	SS+U	5,450	447	4.20	19	283	~ 6
GD-7	1	SS+U	5,448	384	4.30	20	203[d]	~ 6

a. Shut down before complete dissolution because of inadequate off-gas facilities.

b. Portion of fuel element remaining from run GD-3.

c. Coast Metals NP composition: 50% Ni, 11.8% Si, 29.3% Fe, 3.5% P, 5.4% Mo.

d. For reasons unknown as yet, 1362 g of the fuel element was undissolved at shutdown, thus accounting for the low dissolution rate.

3. Airlifting the dissolver product at boiling or near boiling entails no real problem.

4. A 16 ft dissolver should be of sufficient height to prevent "burping" the dissolver solution into the condenser (based on one 3-element run).

5. A long cylindrical dissolver is operable.

Run GD-2 was made using a dummy stainless steel fuel element of the APPR type with the simulated plates tack welded to the side plates and stainless tubing was used to obtain a plate spacing of 0.125 in. The fuel element weighing 4640 g was completely dissolved in 15 min at a 5 N HNO_3-2 N HCl aqua regia flow rate of 4.5 liters/min with a resultant dissolution rate of 310 g/min. The dissolver operated satisfactorily with the exception of the condenser and it was found that the condensing capacity of the 2.1 sq ft single pass Pyrex heat exchanger is inadequate resulting in a loss of overhead acid (~ 2.2 M total H^+) to the off-gas.

The condensate was not returned to the dissolver but was collected separately from the dissolver product. Experience obtained in the operation of the 1-in. ID glass dissolver indicated that there was no advantage as fas as dissolution rate is concerned to return the relatively weak acid overhead to the dissolver so the loss of acid overhead to the off-gas was not detrimental to the operation of the dissolver.

Run GD-3 was made using three dummy stainless steel fuel elements weighing a total of 16,344 g. Two of the fuel elements were similar to the one used in run GD-2 but the third and last element charged to the dissolver had the plates brazed to the side plates. The dissolver was operated for 52 min. Shutdown of the run was necessitated because copious quantities of brown fumes (decomposition products of HNO_3 and HCl) were discharged on the roof of Building 4505. It is estimated that approximately one-half of the brazed fuel element was undissolved and based on this estimate the dissolution rate was 260g/min at a 5-2 aqua regia flow rate of 4.1 liters/min, slightly lower than the 310 g/min obtained at a 4.5 liters/min aqua regia flow rate. There was no visual difference in the operation of the dissolver during the three-element run as compared to a one-element run. The maximum height that the dissolver solution obtained was 9 ft and this height of solution occurred spasmodically.

Run GD-4 was made to dissolve the portion of fuel element remaining from run GD-3. Dissolution started immediately when the hot aqua regia contacted the element, indicating that there was no passivation as the result of the shutdown. However, it was observed that the braze metal did not dissolve and as dissolution was taking place, pieces of the braze metal fell through the perforated support plate into the acid feed line. Even though the braze metal was being contacted with hot, fresh aqua regia there was virtually no dissolution. The braze metal tends to be very brittle, and providing the pieces are small it may be possible to jet the metal from the dissolver or acid feed lines.

Runs GD-5, 6 and 7 were made to accumulate feed for chloride removal and solvent extraction feed adjustment reproducibility studies. Each run was made using a prototype APPR fuel element containing uranium. Run GD-5 was made using a fuel element weighing 5240 g and containing 552 g uranium. The dissolver was operated for 19 min with an 82.7 liter aqua regia consumption, resulting in complete dissolution of the fuel element with the exception of the braze metal.

The analysis of the dissolver product was: total H^+, 3.05 $\underline{M}$; Cl^-, 2.05 $\underline{M}$; 9.23 g U/liter; and 66.5 g SS/liter. A total of 65 liters of dissolver product and 4.5 liters condensate (total H^+, 2.4 $\underline{M}$; Cl^-, 0.81 $\underline{M}$) was collected. The results of run GD-6 were similar to those for run GD-5. However, some difficulty was encountered in run GD-7. A fuel element weighing 5448 g and containing 384 g uranium (received in Unit Operations in August 1956) was used for this run and after 20 min operation, 1362 g of the fuel element was not dissolved (dissolution rate 205 g/min). The side plates were completely dissolved. The remainder was portions of the "meat" plates, and it appeared that the cladding was gone from these.

All the runs made in the 6-in. dissolver have been at essentially the same aqua regia composition and flow rate (~ 4.5 liters/min of 5 N HNO_3-2 N HCl). The use of constant conditions was to determine the operability of a long cylindrical dissolver and to demonstrate the dissolution rate based on the design of the proposed Power Reactor Fuel Reprocessing pilot plant. The high fuel element consumption rate and limited availability prevents a detailed study of the various dissolution rate parameters.

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

Dissolver solutions of spent fuels require clarification because they may contain undesirable precipitates, undissolved fissile or fertile fuel and emulsion-forming agents (usually silica). Clarification of dissolver solutions by filtration through a sand bed is being investigated.

Laboratory filtration tests on Darex solvent extraction feed solution were continued using elevated temperature (50-60°C) and optimum level of addition of filter aid (12 g Celite "545"/liter or 1-1/2 volumes of Celite/volume of wet filter cake). Comparison showed that a split feed filtration procedure - filtering the clear supernate from a sedimentation step followed by the thickened slurry - resulted in a greatly reduced cycle time over direct filtration of the same feed as a well-mixed slurry.

Results (Figure 5.5) showed a cycle time of less than 1 hr for the split feed filtration using an approximate 4-liter batch on a 0.0123 sq ft laboratory sand filter (1) (equivalent to approximately 325 liters on a 1 sq ft filter) at 55°C under 5 in. Hg vacuum with 12 g Celite 545 added

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(1) Unit Operations monthly progress report for December 1958, ORNL-CF-58-12-35.

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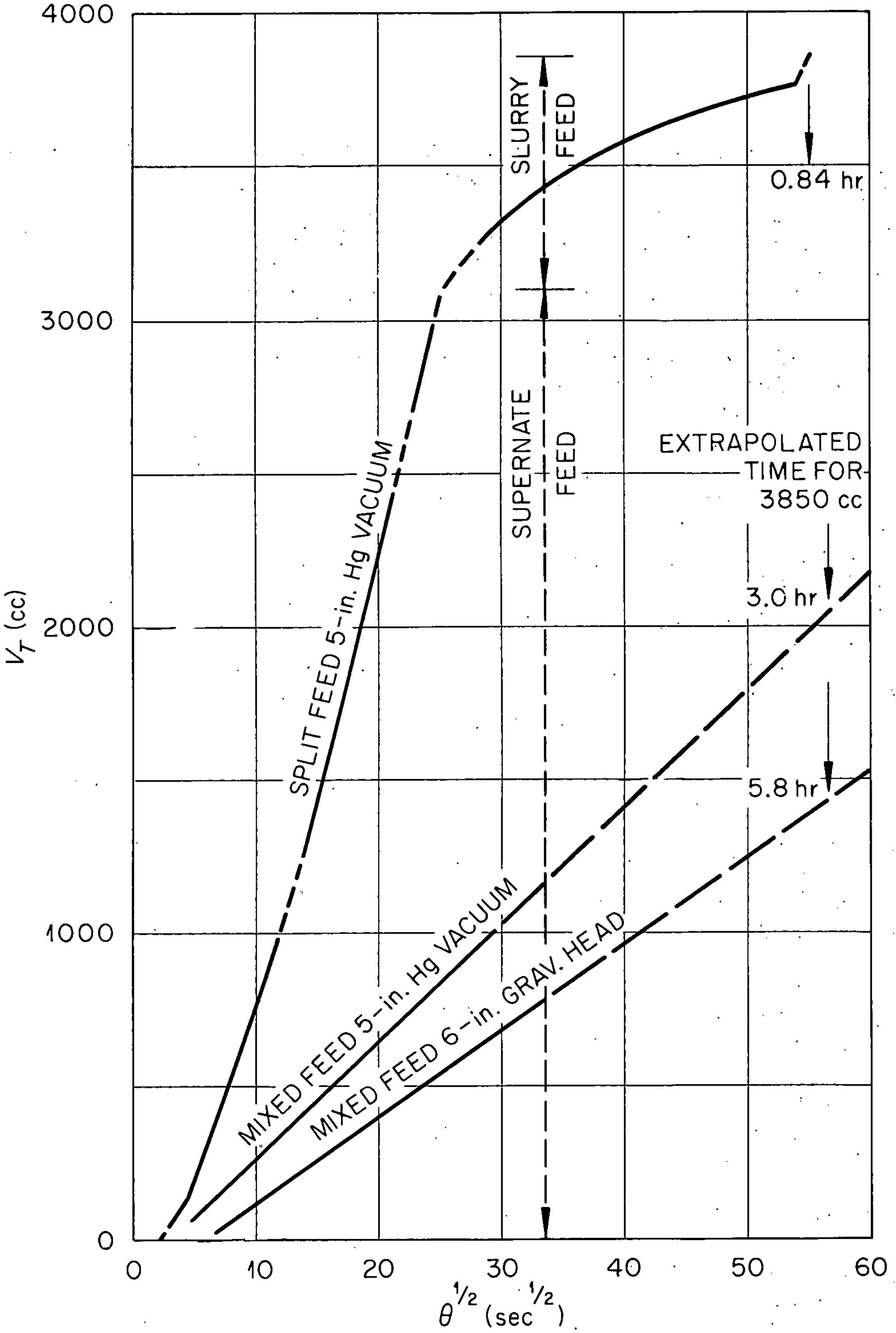

DAREX SOLUTION HS-2-4-A; 12 g CELITE 545/liter;
FILTERED ON STANDARD 1½-in.-DIA SAND BED AT 50-60 °C
SEE ORNL CF 58-12-35 FOR DESCRIPTION OF SOLUTION AND EQUIPMENT

Fig. 5.5. Filtration of Darex Solvent Extraction Feed Solutions.

per liter. Approximately 9 in. of cake was deposited, only ~ 1/8 in. of which was deposited from the first 3100 cc of supernate during the first 10 min, the remainder being deposited from the last 750 cc over an approximate 40-min period. The curvature in the V-vs-$\theta^{1/2}$ plot during the slurry filtration period was due to premature sedimentation of the cake on the filter.

For comparison, filtration tests with well-mixed samples of the same slurry are plotted on the same graph (Figure 5.5). Extrapolation of data from 800 cc batches of feed indicate a cycle time of ~ 3.0 hr under conditions identical with those used in the split feed procedure and of 5.8 hr if a 6 in. gravity head is substituted for a 5 in. Hg vacuum (equivalent to ~ 5 ft gravity head).

5.3 Solvent Extraction Studies - R. J. McNamee, F. L. Rogers

Solvent extraction studies are being made to assist the Hanford Atomic Products Operation in adapting the Redox process to the recovery of uranium from spent stainless steel type power reactor fuels.

The capacity of the 2-in. dia packed column being investigated was very dependent upon the silica content of the feed being processed. As little as .01 $\underline{M}$ silicon lowered the flooding rate from ~ 600 GSFH to ~ 300 GSFH.

Extraction efficiency was very high, and HETS values ranged from 1-2 ft. Uranium losses were on the order of several thousandths of a per cent using approximately 20 ft of extraction length.

Decontamination factors were increased by reducing the salting strength of the feed solution. However, the highest Darex decontamination factor obtained was approximately a factor of 4 lower than that obtained with the standard Redox flowsheet, due to the higher acidity necessary to prevent precipitation of the stainless steel. For the Redox process, the lower the acidity, the higher the decontamination factor. The highest decontamination factor obtained with the Niflex flowsheet was only about one-half of the maximum obtained with the Darex flowsheet, since a still higher acidity was necessary to maintain this feed at a stable condition. In general, the stability of the columns was very good provided that the acidity of the flowsheet was sufficiently high. However, the waste streams usually precipitated after leaving the column unless they were immediately acidified externally.

Details of the results of the experimental work to date are contained in a memorandum entitled "A Preliminary Report of Hanford Assistance Studies Performed at ORNL on the Reprocessing of Stainless Steel Power Reactor Fuels by the Redox Process", ORNL-CF-59-1-29.

5.4 Mechanical Processing - G. K. Ellis, G. A. West, D. E. Willis

5.4.1 Leaching Studies - G. A. West, K. Ladd, L. M. Ferris (Chemical Development Section A)

Instantaneous reaction rates of unirradiated sintered UO_2 pellets in boiling HNO_3 were measured at various U and H^+ concentration to aid in the design of experimental leachers for the Power Reactor Reprocessing program. In preliminary tests, the average instantaneous dissolution reaction rate of machined pellets in boiling 10 M HNO_3 was ~ 70 mg/sq cm/min as calculated from the initial area of smooth surfaced right cylinder pellets. The reaction rate did not decrease appreciably during a batch dissolution experiment as the acid was depleted to 5 M while the U concentration simultaneously increased to 400 g/liter (Figure 5.6). Dissolution rates measured by pellet weight changes were more accurate than those from solution changes due to inaccuracies introduced by sample volumes.

Further instantaneous dissolution tests of 2 min duration with rejected PWR type unirradiated pressed and sintered UO_2 pellets were made with prepared solution of nitric acid containing uranyl nitrate. Rates of from 3 mg/sq cm/min to 270 mg/sq cm/min were measured in 3, 5, 7, 10 and 13 M HNO_3 solutions over a uranium concentration of 0.05, 1.0, 1.5 and 2.0 M.

For a given uranium concentration the reaction rate increased rapidly with increasing acidity (Figure 5.7). For a given acid concentration the reaction rate increases by a factor of from 1.5 to 2.5 with increasing uranyl nitrate concentration of from 0.5 to 2.0 M. When the instantaneous dissolution rate was plotted against total nitrate concentration, it was possible to draw a single curve indicating the fundamental dependence of the dissolution process on nitrate concentration (Figure 5.8). Reaction rates obtained initially on glazed smooth surfaced pellets changed by as much as 20-40% when the same pellets were reimmersed in fresh solution. This difference in reaction rate is shown pictorially in Figure 5.9 for pellets immersed for two dissolution periods of 2 min.

Specifications for the pellets used in this study are as follows:

Westinghouse (WAPD) Specification to Mallincrodt for UO_2 Pellets

a. As sintered, 92% theoretical density, minimum (10.95 g/cm^3).

b. Sintered in dry hydrogen at 1725°C for 10 hr.

c. Furnace cooled in flowing hydrogen.

d. Total-U, 87.9 wt per cent minimum.

e. Hexavalent U, 1.9 wt per cent maximum.

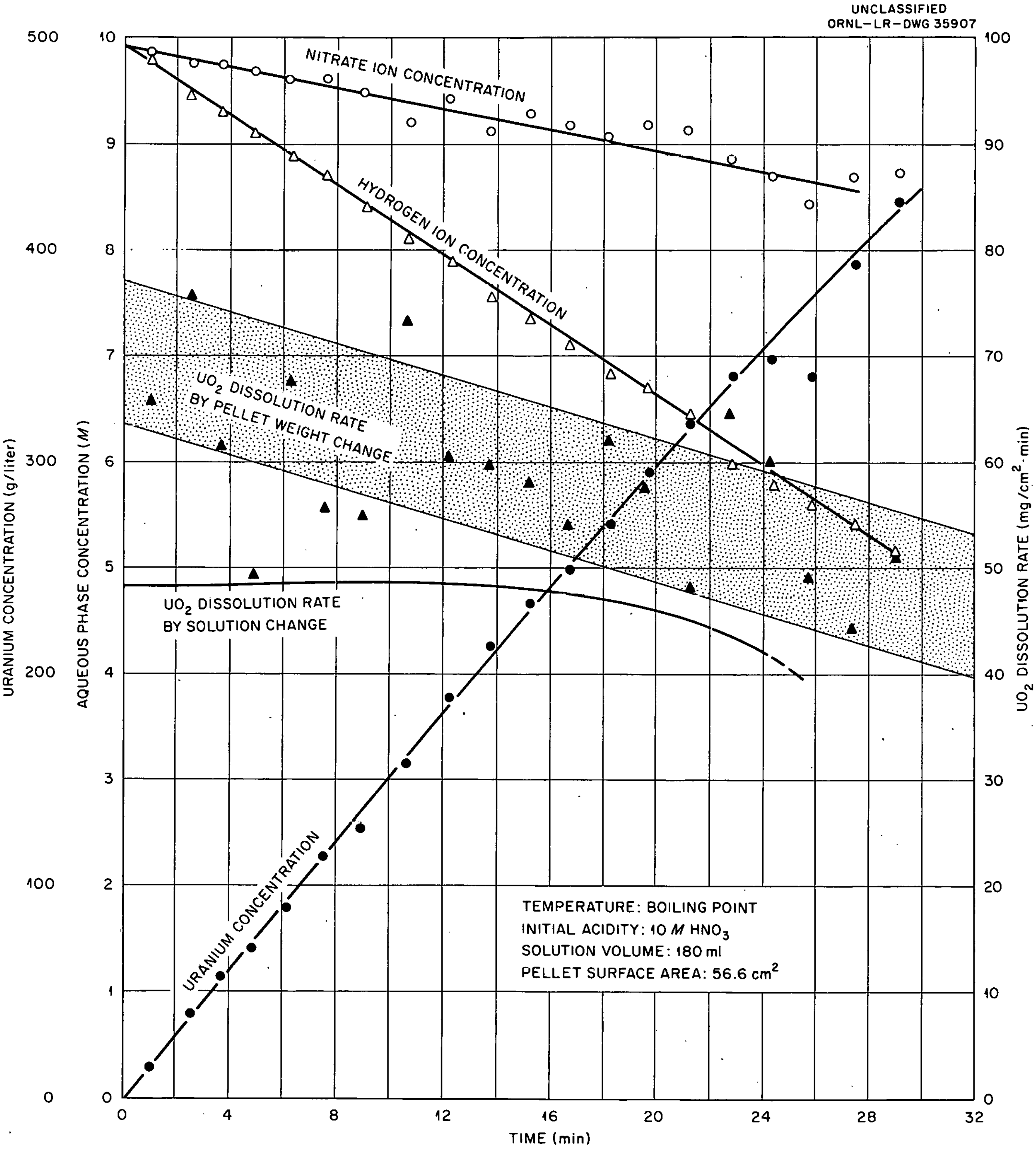

Fig. 5.6. UO_2 Batch Dissolution in HNO_3-$UO_2(NO_3)_2$ Solutions.

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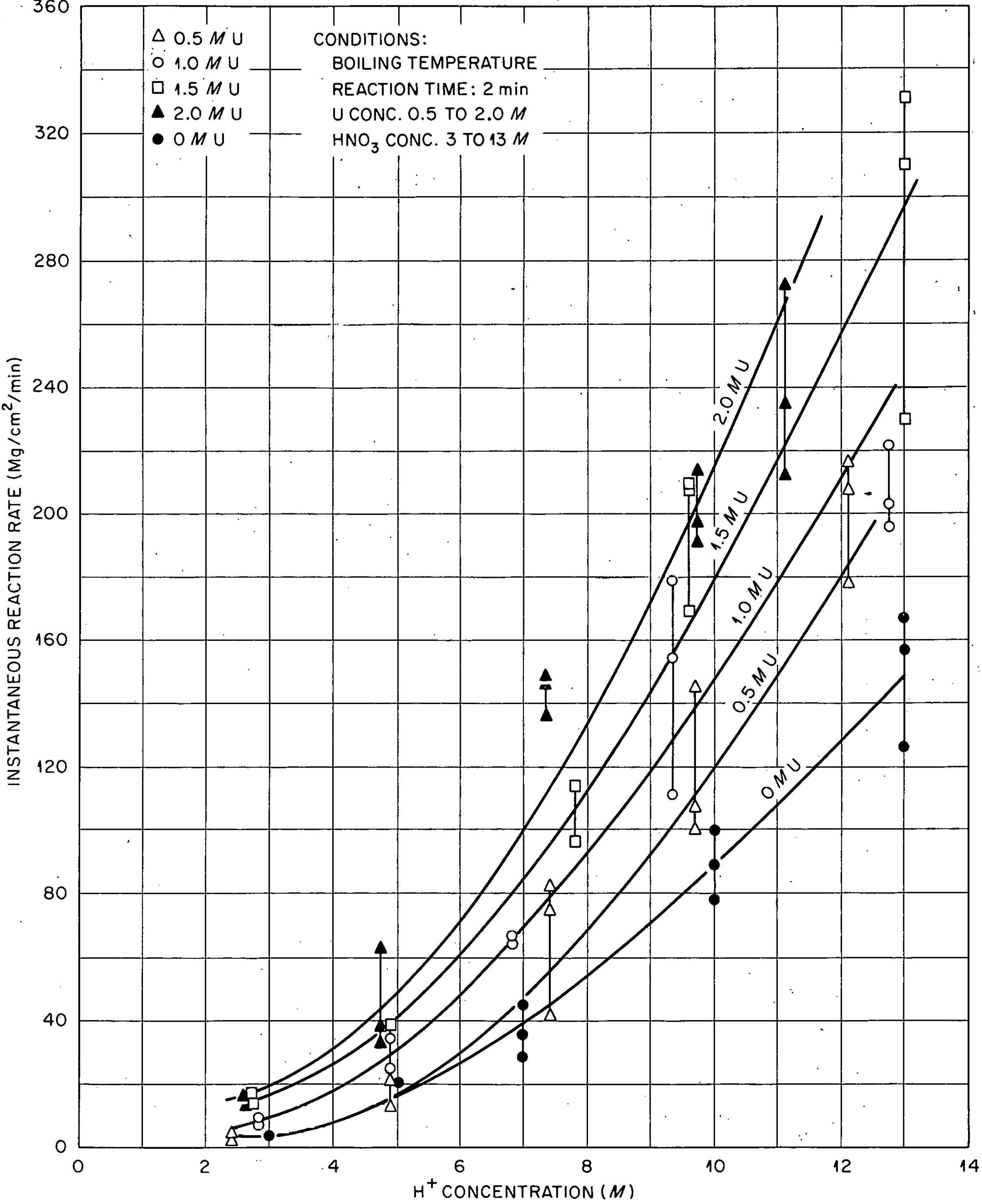

Fig. 5.7. The Effect of Nitric Acid Concentration on UO_2 Dissolution Rates at Various Uranium Solution Concentrations.

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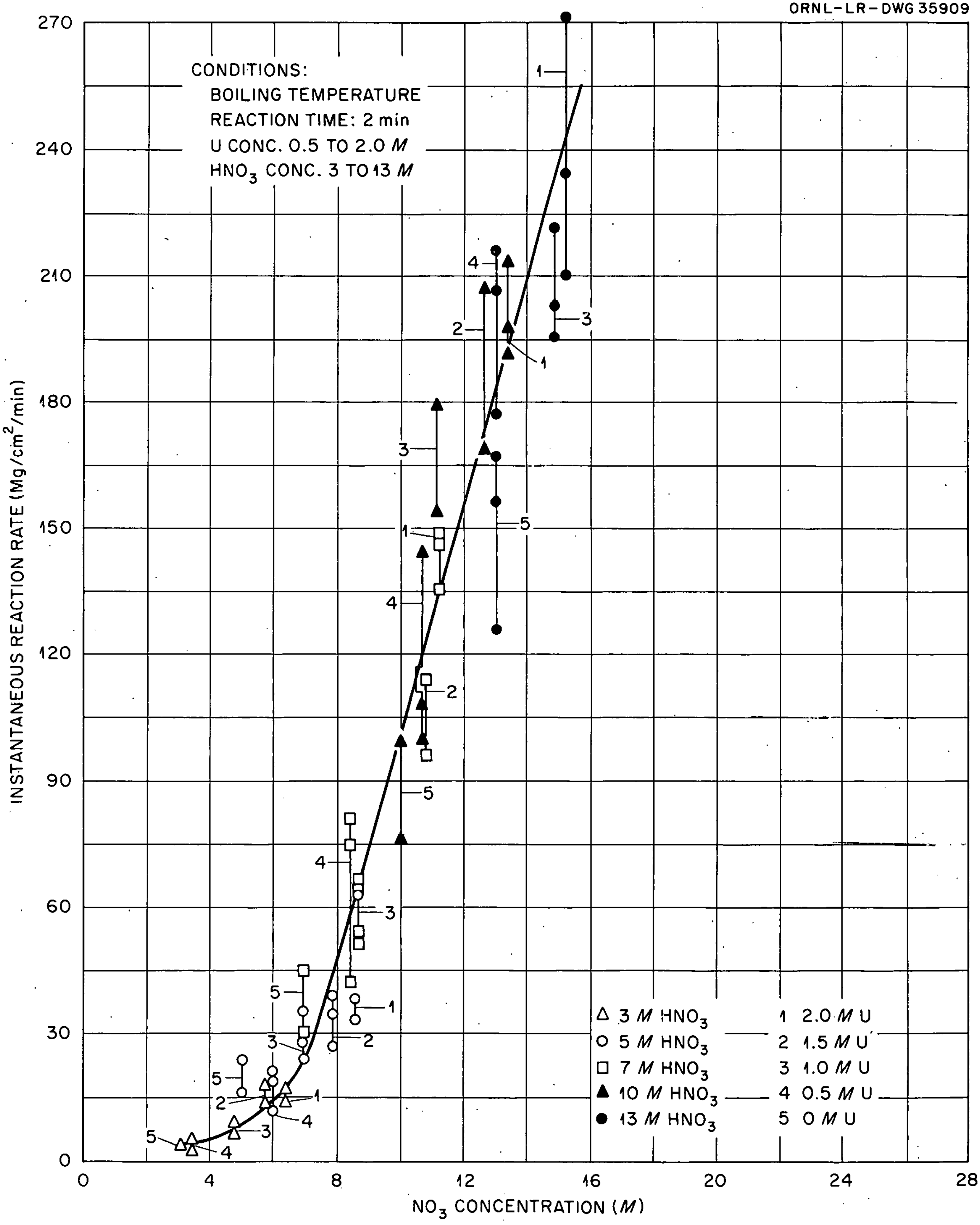
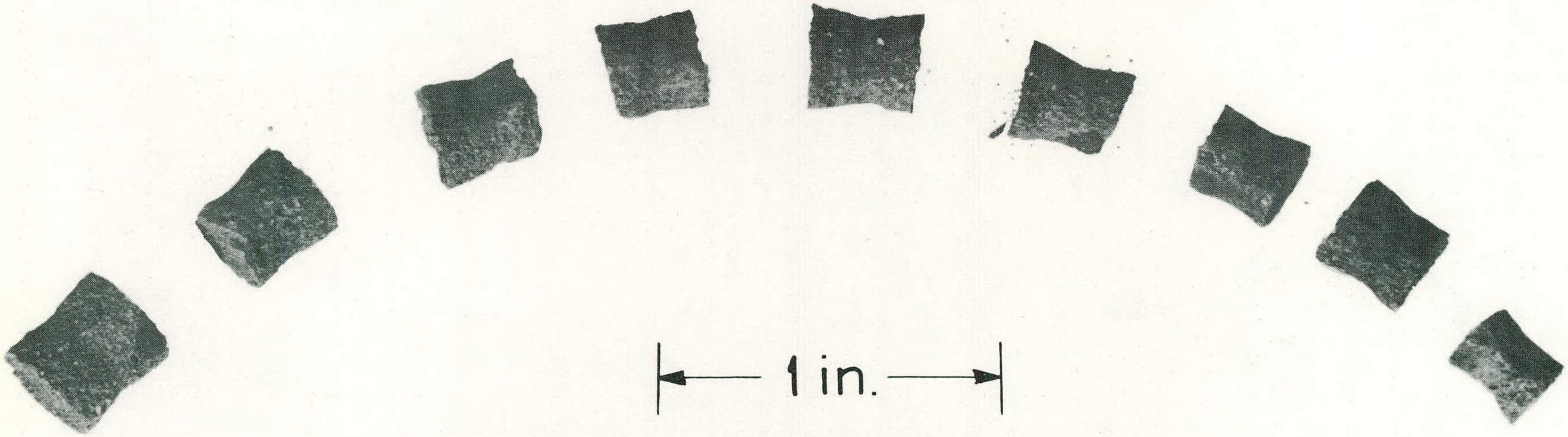


Fig. 5.8. The Effect of Nitrate Ion Concentration on the Dissolution of UO_2.



4 MINUTE REACTION

UO_2 IN 13 M HNO_3 - 1.5 M U SOLUTION

Fig. 5.9.

f. Compacted, cold pressed at a specific pressure of 138 tons/sq in.

g. Centerless ground to correct dimensions.

Pellet Measurements:

Size: 0.327" OD x 0.390" long = 0.531 cm^3 =~7 g/pellet.

Density: 13.3 g/cm^3.

Additional tests are to be made by leaching sheared pieces of PWR fuel, Zr-2 clad UO_2 pellets, and Consolidated Edison fuels, stainless steel clad ThO_2-UO_2 pellets.

Design and Testing of Continuous and Batch Leachers. Continuous leachers of promising design will be fabricated and evaluated for leaching chopped fuel. Several design concepts are already available from previous studies, some of which will be evaluated on a small scale before a final type is selected. The most difficult mechanical problem appears to be the transferring of the cladding out of the leacher after the UO_2-ThO_2 core leaching step. Concepts are of two general types, "screw" or a "drum" depending upon the method used for transferring solids through the leacher.

One interesting continuous leacher concept involves the alteration of a Syntron spiral conveyor (see Figure 5.10). The spiral track is about 18 in. wide and spirals upward at an angle of 30° with horizontal. In operation, material is progressively thrown up the track by vibrating upward at an amplitude of 1/16 in. and damping the return vibration. This unit has been installed and a timing device has been connected for varying the period of its operation. Qualitative studies to determine its potentiality as a leacher have begun to aid the design of alteration and to determine the extent of the material transfer problem. Sheared portions of porcelain containing prototype fuel elements are being used to investigate the problems of material transfer. Sucrose contained in sections of 0.5 in. dia tubing have been prepared for preliminary countercurrent leaching studies with water dissolvent.

Design modifications of this conveyor for leaching of UO_2-ThO_2 from the fuel element sections by countercurrent contact with a boiling nitric acid solution are being made. The most difficult problem is to isolate the vibrating section for containment of boiling nitric acid, allowing for observation and the connection of instrumentation, feed and off-gas lines, without introducing a load, including chopped material to be leached, in excess of 200 lb. This value is the estimated maximum load at which the conveyor will function.

Another continuous leacher concept of which a small plexiglass prototype is available is the rotating drum device reported in ORNL 2265. A third recent continuous leacher concept is the horizontal drum (Figure 5.11). In this concept, all connections to the drum are made through the top lid to make disposal and replacement of the unit easy. The drum revolves on rollers attached to the bottom of the leacher cubicle. Material transfer

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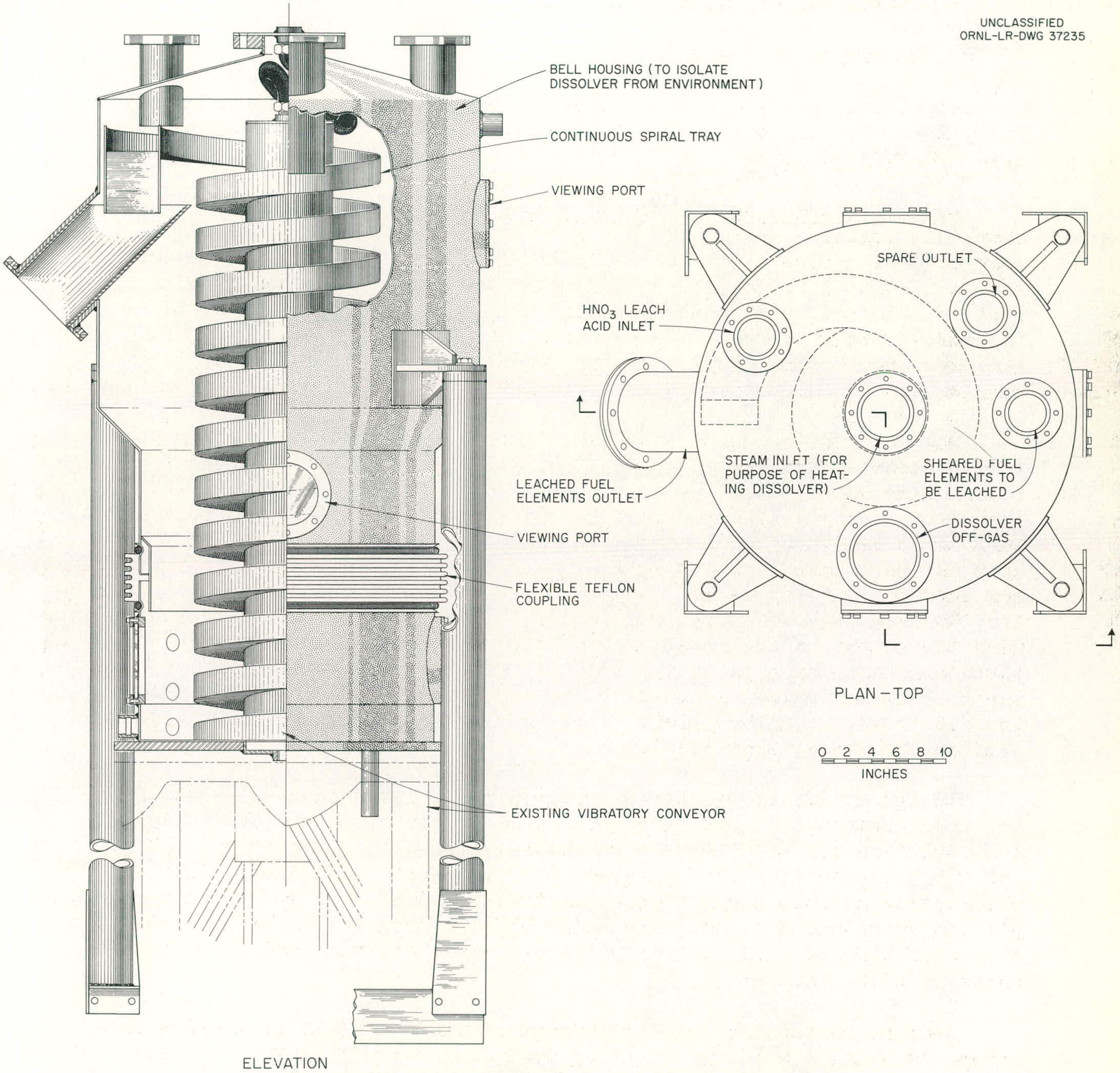

Fig. 5.10. Continuous Vibrating Tray Dissolver - Modified Syntron Spiral Conveyor.

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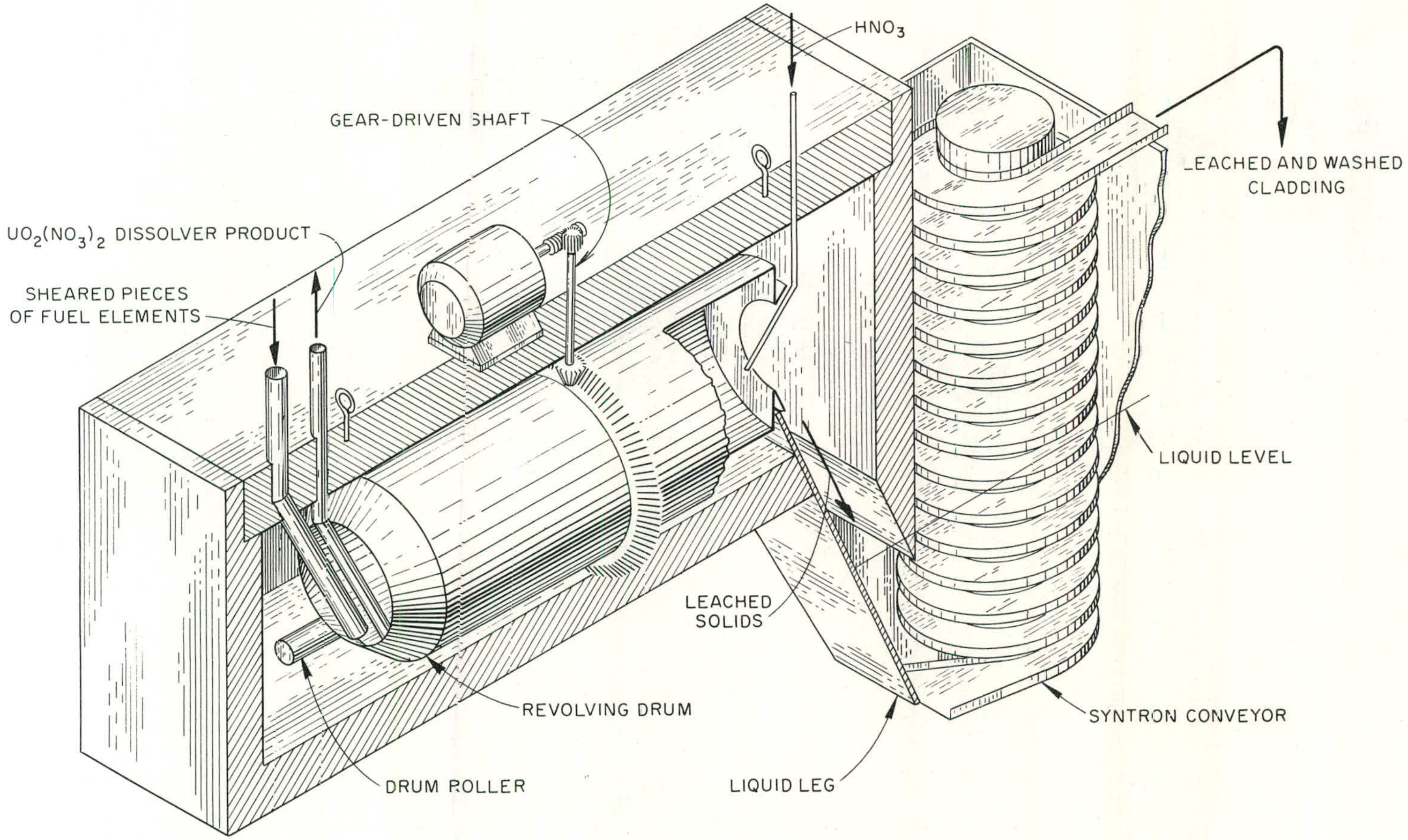

NOTES:

1 DISSOLVER AND INSTRUMENTS ARE ATTACHED TO SLAB LID FOR REMOVAL AND DISPOSAL OF ENTIRE UNIT.

2 WASHING AND MATERIAL TRANSFER OF LEACHED MATERIAL OCCUR IN SYNTRON CONVEYOR.

3 AGITATION OF CONTENTS SHOULD DISLODGE UO_2 FROM THE SHEARED PIECES AND IMPROVE CONTACT OF UO_2 WITH DISSOLVENT.

4 COUNTER-CURRENT CONTACT OF UO_2 WITH ACID OCCURS IN DRUM.

5 REVOLVING DRUM CONTAINS SPIRAL FLITES WHICH TRANSFER SOLIDS FROM INLET TO OUTLET.

Fig. 5.11. Horizontal Drum Continuous Dissolver Concept.

of pellets through the leacher is obtained by periodically revolving the drum containing perforated flights at a low speed.

If no flights are desired the axis of the drum could be sloped toward the exit so that the motion of the solids would be in a spiral direction through the drum. Residence time would be obtained by varying the speed or period of rotation, or the angle of slope. The leached solids could be dumped into a conveyor through a liquid leg in the bottom of the conveyor and washed free of fissile or fertile material in the conveyor before being emptied into a package for disposal. The agitation would help to separate mechanically UO_2 from metal cladding and furnish a greater surface area for dissolution.

5.4.2 SRE Decanning

The Southern Machine Company of Chattanooga made a low bid of $9,125 which was approved for fabrication of equipment to declad the SRE fuel (stainless steel clad, NaK bonded uranium rods). Fabrication is to be completed by April 1, 1959.

Recanning of the slugs is necessary for their transfer, storage and subsequent charging into the Interim pilot plant dissolver. The recanning method proposed seals twelve 3/4 in. OD x 6 in. long slugs from one fuel rod in a single 3-3/16 in. dia aluminum container with a lid fastened in place by a canning machine. The machine, cans, and lids are commercially available and the only shop fabrication required is for minor changes necessary to adapt the machine for remote operation. Fabrication of an aluminum disc for the odd can size might possibly be required.

Another recanning method considered and now abandoned was to can individual slugs in aluminum tubes with one end welded. The final end seal would be made by swaging the extended portion to reduce the diameter and increase the wall thickness followed by a flattening operation to effect a seal. Tests on this type of seal showed that it would be leak-tight against 15 psig pressure.

5.4.3 Disassembly of Fuel Bundles Prior to Shearing

Separation of the fuel bundle into either tubular elements or slabs of tubular elements and then shearing them into short lengths is being considered as an alternate to shearing of the entire bundle. Separation of the bundle in each case is to be made experimentally by hydraulically pushing the bundle through a stationary die which cuts through the cylindrical ferrules spacers holding the tubes together. A device for separating individual elements has been designed (Figure 5.12). A "draw knife" to produce planks or slabs of elements is shown in Figure 5.13.

An additional method, a wedge separator, for separating slabs is being designed. In this procedure advantage would be taken of the inherent brit-

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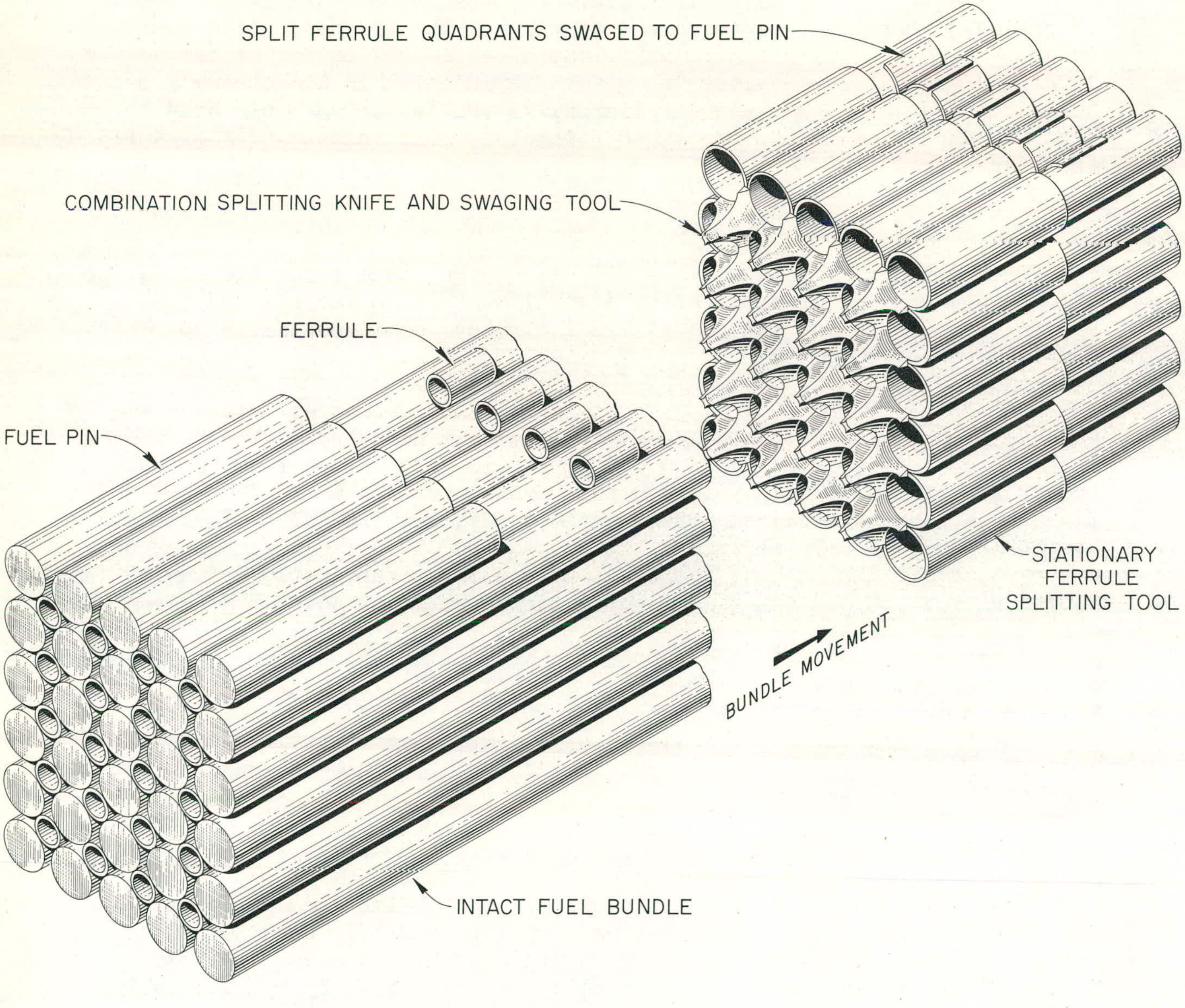

Fig. 5.12. Ferrule Splitting Tool for Separating Individual Tubular Elements from a Fuel Assembly.

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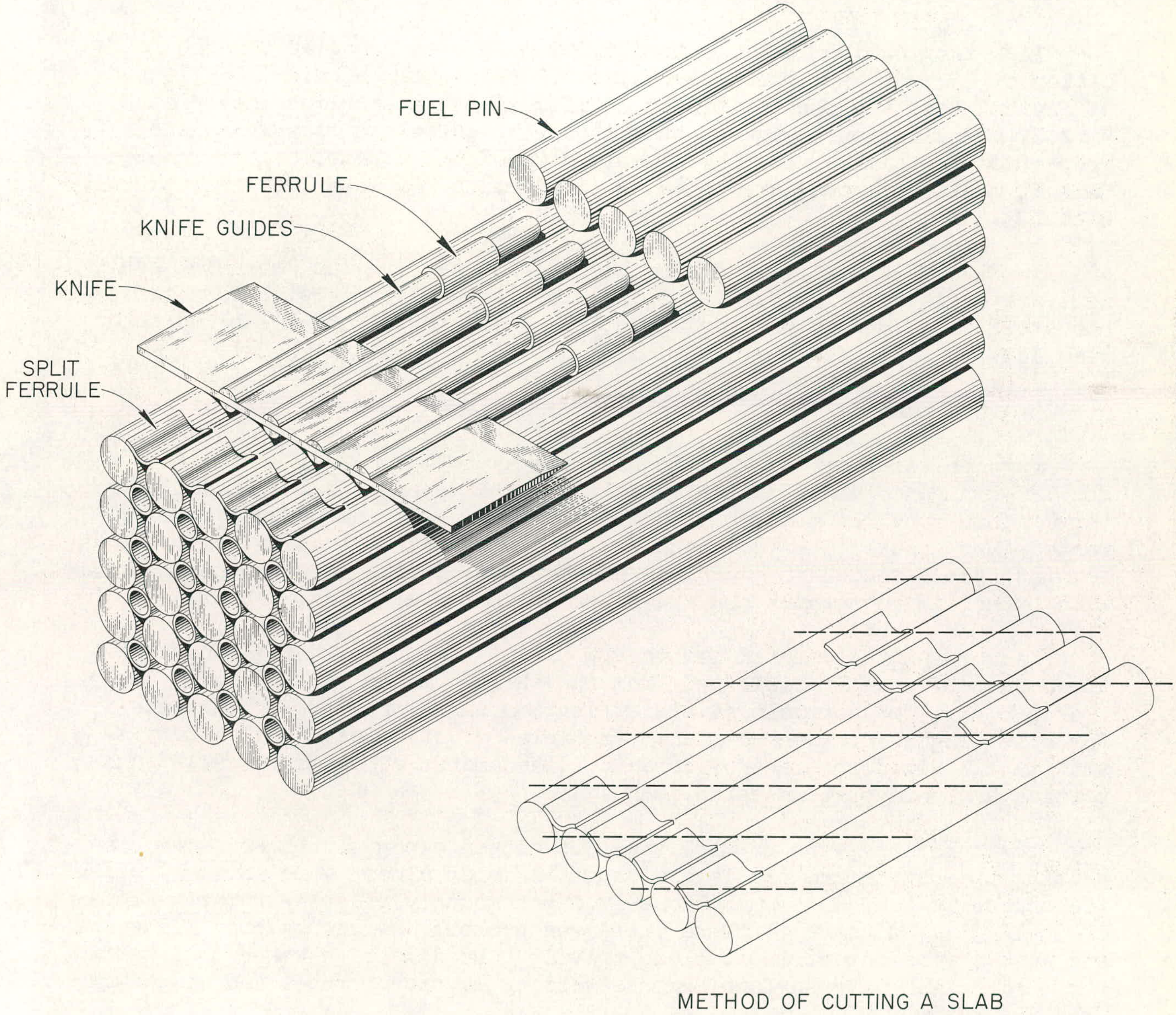

Fig. 5.13. Ferrule Splitting Tool for Separating Slabs of Tubular Elements from a Fuel Assembly.

tle quality of the nicrobraze which bonds the ferrules to tubes, or the braze would be deliberately further weakened by exposing it to an embrittling or oxidizing atmosphere. A wedge is then forced between the layers of tubes separating them into slabs.

5.4.4 Prototype Fuels

Bids ranging from $26,000 to $75,000 have been received for the fabrication of 75 prototype fuel assemblies. Continental Technical Services of Dayton, Ohio was the low bidder. Fifty of the assemblies (designated Mark I, modification 1) are to be filled with porcelain rods whose shear properties are similar to UO_2. Twenty-five of the assemblies (designated Mark I, modification 2) are to be supplied empty for later loading at ORNL with UO_2.

Twenty SRE prototype fuels to be used for testing the decanning equipment are being made in the ORNL shops. Twelve prototypes will contain carbon steel slugs and no bonding agent, the remaining eight will be bonded with NaK.

5.4.5 Shearing

Further experimental work in shearing a prototype fuel bundle with the 125-ton Manco shear indicated a line of blade contact may be satisfactory. This conclusion is contradictory to the preliminary observation reported last month. The fuel bundle, which was sheared in 1 in. and 0.75 in. lengths, consisted of 36 stainless steel tubes (35 mil wall thickness) filled with porcelain rods which had the material characteristics of UO_2.

Decreasing the sheared length 25% (from 1 in. to 0.75 in.) increased the amount of ceramic dislodged from the sheared faces by a factor of 2.25 (Table 5.3). The particle size distribution was approximately the same for both lengths of sheared fuel. Particles of stainless steel were present in all sized portions of ceramic. The amount of stainless with each portion has not yet been established.

The tube ends were no more than 50% closed except in those tubes comprising the bottom and top layers, some of which almost were entirely closed (see Figure 6.8 of Unit Operations December monthly progress report, ORNL-CF-58-12-35). Closure of these tubes was probably caused by poor blade shape and also by the direction of blade travel. The direction was not always vertical to the tube surface because various layers of tubes can move away from the blade.

During the shearing operation, after the outside layers had been cut but before the middle layers were cut, the outside layers were mashed and closed against the 45° slope of the blade. The same tendency for mashing occurs when the blade entered the outside layers at an angle caused by compression of these layers toward the center before sufficient bearing was

Table 5.3. Porcelain Size Distribution from Shearing a 36-Tube 0.5-in. Dia Stainless Steel, Porcelain Filled Prototype Fuel Bundle

Conditions: (a) Shear type, 125-ton Guillotine Manco

(b) Six cuts at a blade velocity of 0.33 in./sec with a line of edge contact blade

(c) Physical properties of porcelain simulating UO_2

Tensile strength	5-10,000 psi
Compressive strength	90,000 psi
Flexural strength	10-20,000 psi
Hardness	7-9 mol scale
< 10% Porosity modulus of elasticity	20-30x10^{6} psi

	Porcelain Size Distribution (wt %)	
Porcelain Particle Size	Length of Sheared Piece Inches	
(microns)	1.0	0.75
> 1680	3.2	2.0
> 840	10.2	9.1
> 297	29.2	31.5
> 149	18.5	20.4
< 149	38.9	37.0
	100.0	100.0
Per cent of porcelain dislodged from sheared faces	12 wt %	27 wt %

obtained for shearing. A new blade type has been designed which presents no sloping edges on the bundle side of the shear to mash the tube edges (Figure 5.14). Also, for the purpose of eliminating the wrong angle of cut, a die has been designed and will be fabricated for testing the effects of a preliminary pressing of the fuel bundle before shearing.

The bundle spread in a horizontal direction during shearing so that after several cuts a portion of it was out of the blade throat. This problem was solved by building a jig which held the bundle between the knife edges. Vertical expansion was observed in one cut of an inert end to the extent that the bundle could not be pushed through the shear throat to make the next cut. Because of this effect, it may be necessary to saw off inert ends of the bundle rather than shear them. An alternative would be to build a jig which would contain the bundle vertically as well as horizontally.

A significant separation of ceramic from metal clad in the form of ceramic fines (presenting a large surface for dissolution) was observed in shearing at 0.5 in. increments.

A search is now being made for a suitable hydraulic press which can be used with a commercially available die set to accommodate various blade shapes. This design is desirable because of the limitations of shears immediately available for use in the program for evaluating blade life, blade type and blade velocity while shearing the 3-7/8 in. square prototype fuel bundle. An existing oil-gear hydraulic pump unit is being tested for use with the 125-ton Manco to increase the blade velocity. The present velocity is about 11 ft/min. It may be possible to increase this to ~ 1 ft/sec with the use of the oil-gear unit. The Manco is of limited use, however, because of its short 4.5 in. blade travel.

A dry box for housing a 1-1/2 in. Manco hydraulic shear has been fabricated for use in furnishing UO_2-ThO_2 cylindrical metal clad feed for dissolution studies.

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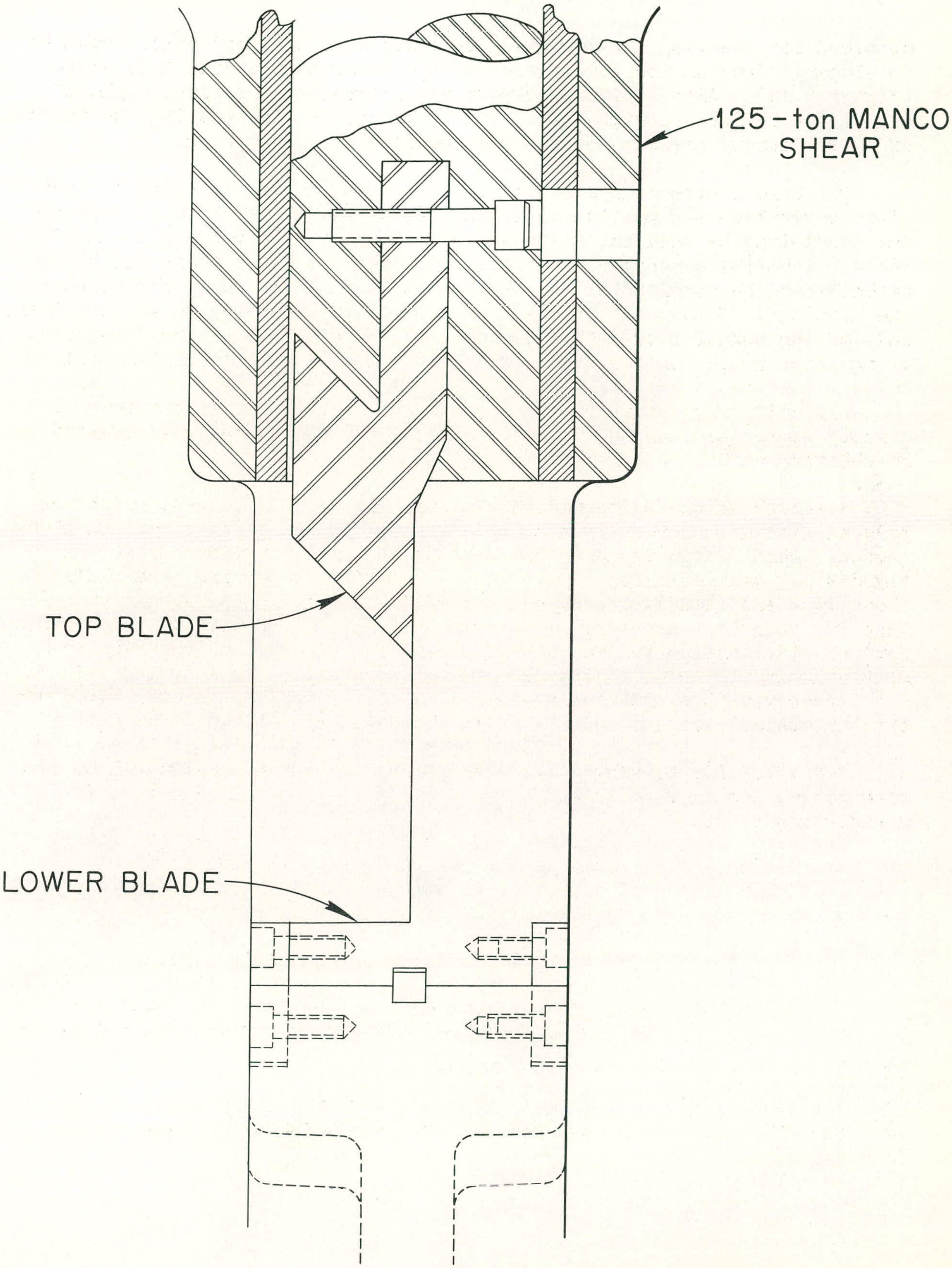

Fig. 5.14. Revised Blade for Shearing $3\frac{7}{8}$-in. Square Prototype Fuel Bundle.

6.0 WASTE PROCESSING

M. E. Whatley

6.1 Reduction to Solids - C. W. Hancher, J. S. Taylor

The purpose of the reduction to solids problem of the waste processing program is to provide engineering data for reduction of radioactive waste for ultimate disposal. This report contains a description of two experimental set-ups which have been installed:

1. Calcination equipment (8" dia x 18" deep pot).
2. Distillation equipment (3" dia x 10 ft packed bed).

Calcination Equipment. The calcination equipment consists of the following (see Figures 6.1, 6.2 and 6.3):

1. Feed tank (steam coil and mixer).
2. 10 kw furnace 9-1/2" dia x 24" deep.
3. 15 sq ft heat exchanger for condenser.
4. Calcination pot (8" dia x 18").

The evaporated waste solution would be gravity fed from the feed tank to the calciner pot. The calciner is equipped with liquid level system (electrical probe type) which operates a solenoid valve in the feed line. This procedure keeps the calcination pot full of liquid as the liquid is evaporated.

The vapor from the calciner pot flows to the heat exchanger where it is condensed. The liquid leaves the condenser via a water trap. The noncondensable gases, if any, flow through a caustic bubbler trap and then through a stainless steel wet test meter to the cell exhaust.

Distillation Equipment. The distillation equipment consists of a 3-in. dia column packed with 1/4 in. Raschig rings 10 ft high (see Figure 6.4). A steam heat exchanger services as the reboiler. The condenser is water cooled. There are two feed points between the packing and the reboiler.

The distillation column will be used to clean up and separate the fission products in the calciner off-gas from the water and noncondensable gases.

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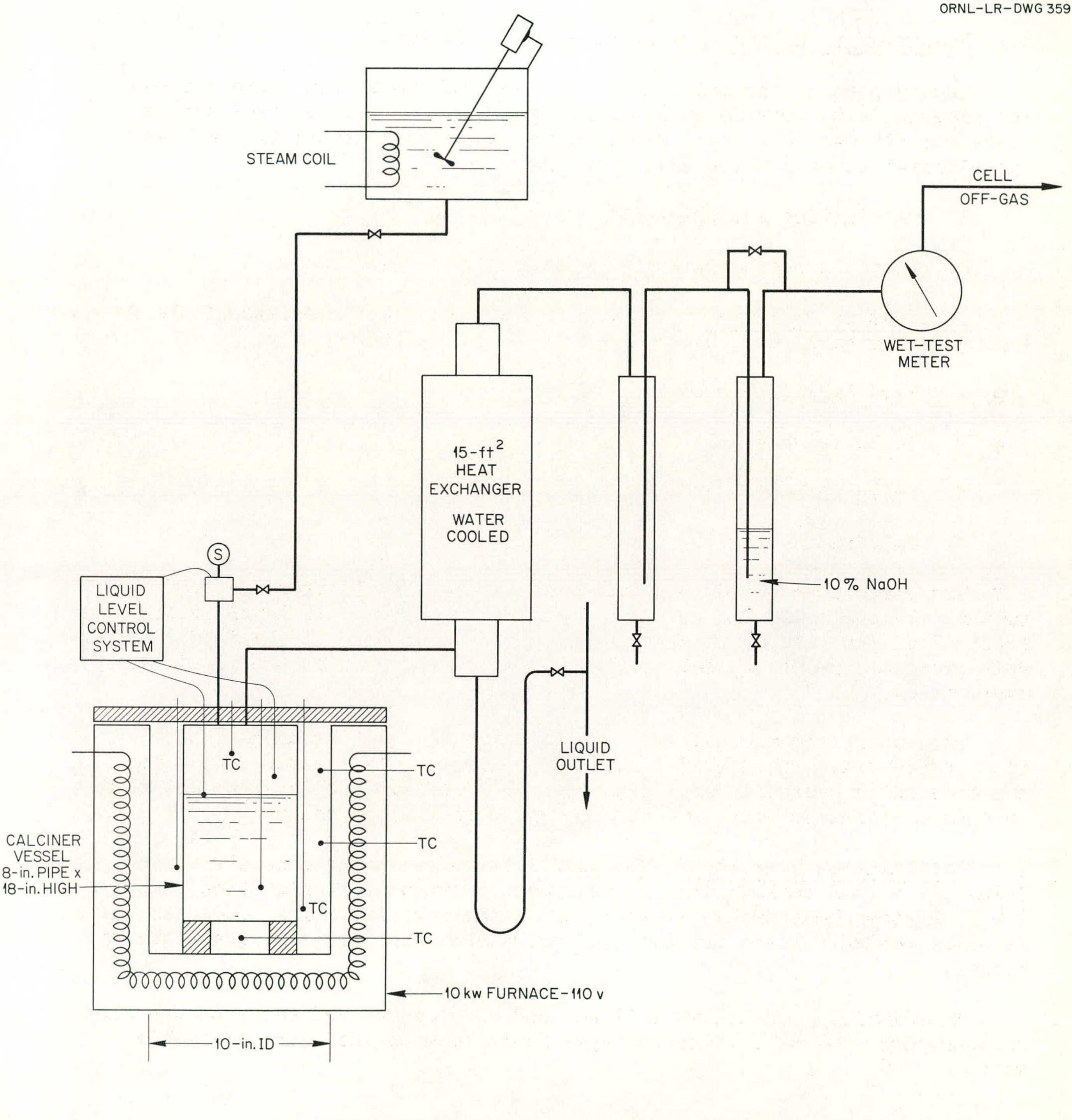

Fig. 6.1. Experimental Calcination Equipment Setup.

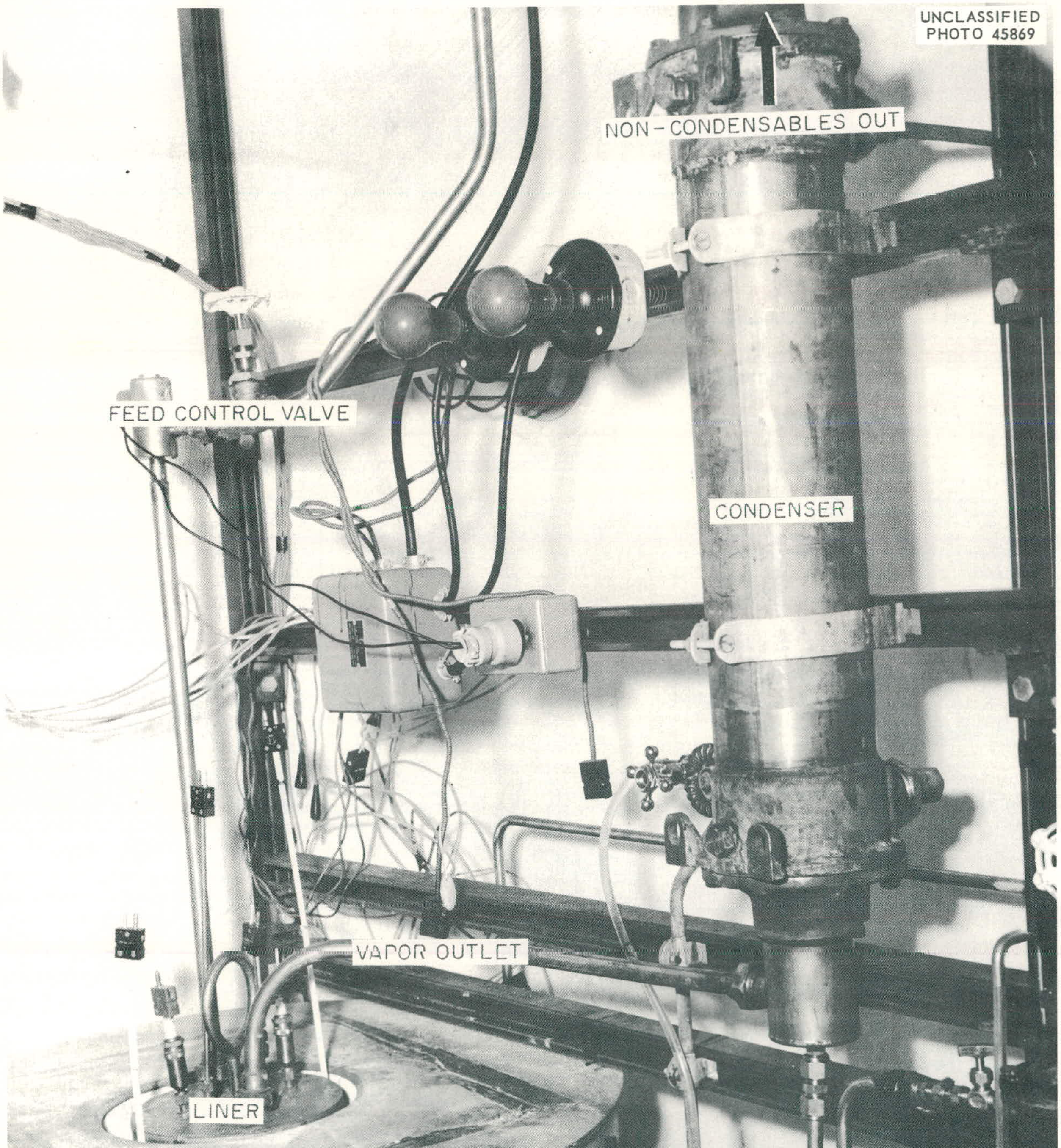

Fig. 6.2. Waste Calciner Equipment.

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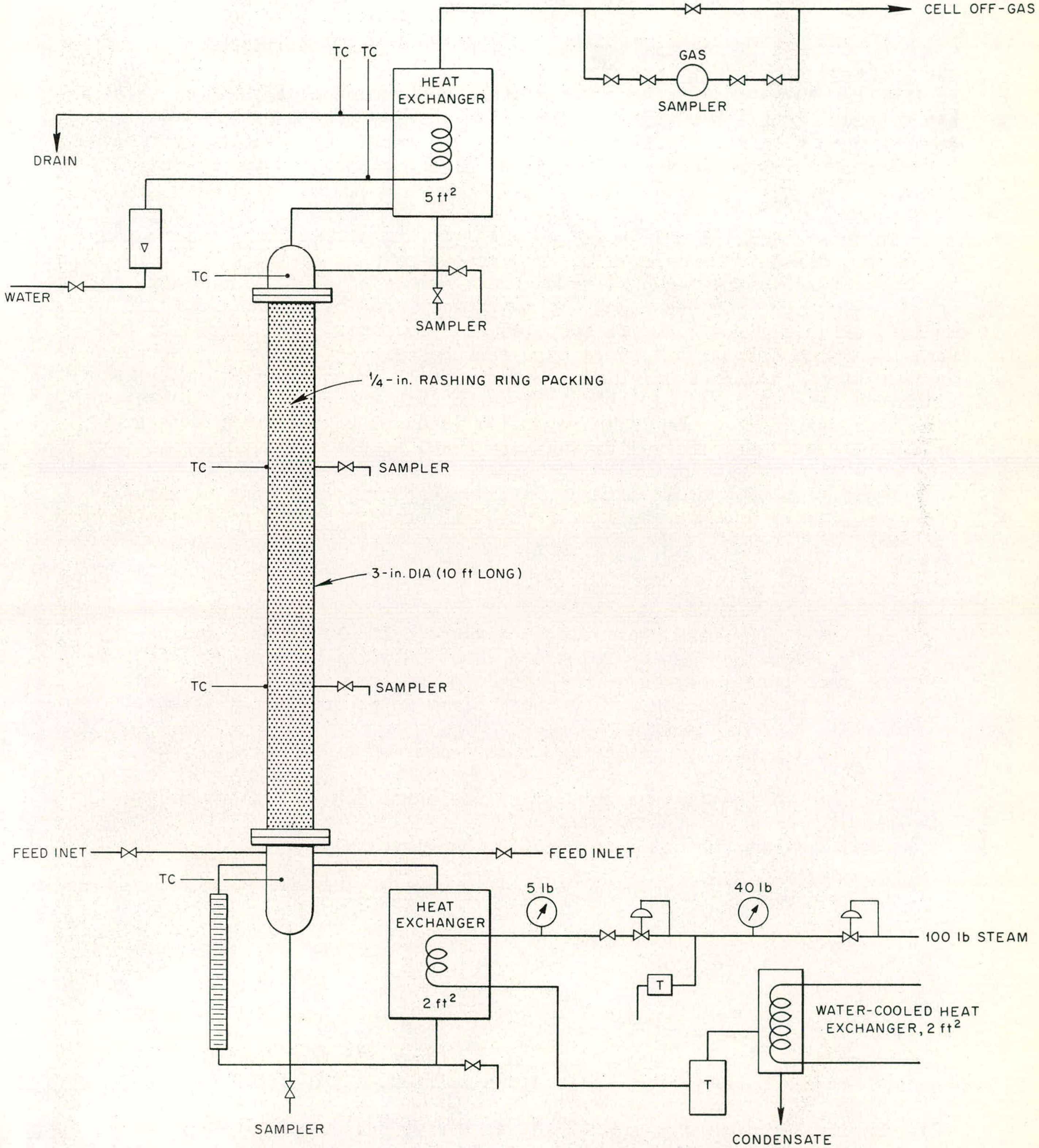

Fig. 6.4. The 3-in. Diameter Packed Bed Distillation Column.

6.2 Temperatures in Stored Radioactive Solids - J. J. Perona

The storage of radioactive wastes must be arranged so that the decay energy is dissipated without the buildup of temperatures which might threaten the structural integrity of the storage system or cause chemical reactions which might evolve gases. The first storage system being studied depends upon ultimate dissipation of the heat into a solid medium by conduction. Such a system does not require supplying and monitoring a cooling fluid.

In this system, a hole would be drilled into a salt dome or into the earth to a depth to be determined by a cost study and by the compressive strength of the waste cans (perhaps several thousand feet). The waste cans would be lowered into the hole, forming a very long cylinder in a solid medium, infinite in extent for computational purposes. The necessity for some clearance between the waste cans and the cylindrical cavity imposes an insulating air space which must be considered in the heat transfer calculations (Figure 6.5). In calculations to date the properties of salt have been assumed for the infinite medium (thermal conductivity 2.80 Btu/hr(sq ft)($^{\circ}$F/ft) and thermal diffusivity 0.101 sq ft/hr) (1, 2).

Storage in salt domes offers the advantages of relatively high thermal conductivity and assurance of dryness to prevent corrosion of the storage cans.

The following assumptions were made:

1. The temperature profile of the waste cylinder at the time of storage is given by Poisson's equation with heat loss at the surface by convection into a fluid at the temperature of the salt with the same convection coefficient as occurs during storage.
2. The thermal properties are independent of temperature.
3. Loss of heat by the surface of the earth can be neglected.
4. The decay heat is generated in the waste only.
5. The sensible heat of the waste is negligible.

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(1) "Lange's Handbook of Chemistry", N. A. Lange, Editor, Handbook Publishers, Inc., Sandusky, Ohio, Ninth Edition, 1956, pp 1542 and 307.

(2) "Chemical Engineers Handbook", J. H. Perry, Editor, McGraw-Hill Book Co., Inc., Third Edition, 1950, p 223.

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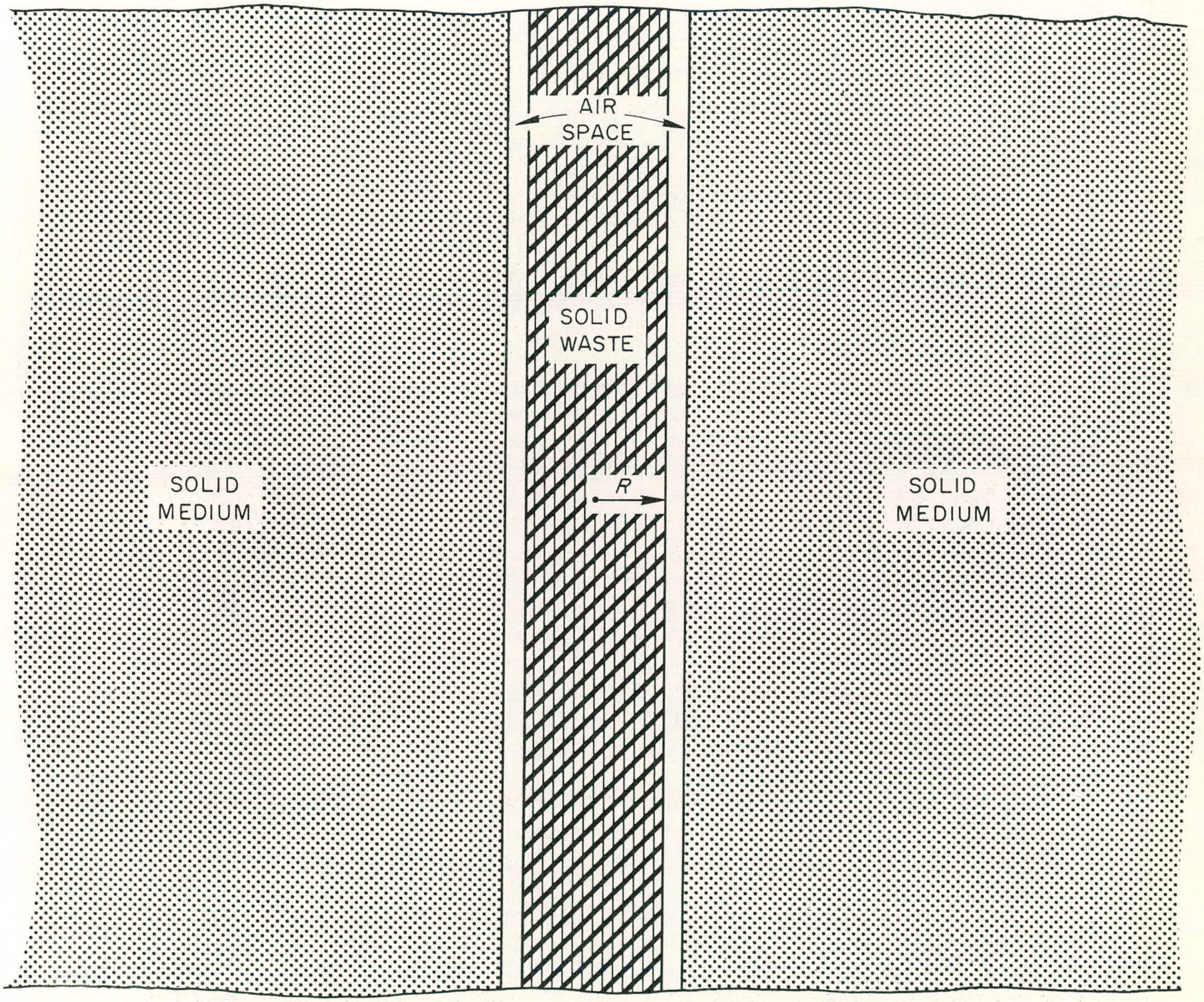

Fig. 6.5. Radioactive Solid Storage System.

Calculations were carried out in two parts:

1. Temperature was calculated as a function of time and radius in the infinite solid medium. The equation of heat conduction:

$$\Delta^2 T = \frac{1}{\alpha}\frac{\partial T}{\partial t}$$

was reduced to finite difference equations and numerically evaluated using the Oracle digital computer.

2. Temperature gradients in the solid waste were obtained from a solution of Poisson's equation:

$$\Delta^2 T + \frac{Q}{k} = 0$$

because the time required for the solid waste to approach thermal equilibrium with the surface of the cavity was insignificant compared with the time required for the rate of heat generation to decay appreciably or for the cavity surface temperature to change appreciably. The temperature change across the air space was calculated assuming natural convection under steady-state conditions.

The temperature at the cavity surface reached its maximum temperature after 2.5 to 3 months' storage time for one-year cooled waste, 5 to 6.5 months' storage time for three-year cooled waste, and 5 to 6 years' storage time for eight-year cooled waste for cavity radii ranging from 5 to 30 in. The temperature gradients in the waste and across the air space decreased continuously with time as the waste decayed. Adding the temperature gradients in the waste and across the air space to the cavity surface temperature, it was found that the maximum temperature at the center of the waste cylinder occurred after 1 to 2 weeks of storage for one-year cooled waste, one month of storage for three-year cooled waste, and 0.5 to 1.5 years of storage for eight-year cooled waste. The time required for maximum temperature to occur increased as the radius increased and as the thermal conductivity of the waste increased.

Heat generation rates were calculated using the irradiation conditions for the Army Package Power Reactor (3) and assuming a Darex fuel reprocessing flowsheet (4) (Table 6.1). For the conversion of liquid waste to the solid state a concentration factor of 10 was assumed. The initial heat

---

(3) "Specifications for Army Package Power Reactor (APPR-1) Fuel and Control Rod Components", R. J. Beaver, R. C. Waugh and C. F. Leitten, ORNL-2225, July 24, 1957.

(4) "Recovery of Enriched Uranium from Uranium Dioxide-Stainless Steel Fuel Elements by Solvent Extraction", J. R. Flanary and J. H. Goode, ORNL-CF-58-4-2, April 13, 1958.

generation rates were 100, 30 and 10 Btu/(hr)(gal solid waste) corresponding to one-year, three-year and eight-year cooled waste.

Table 6.1. Assumed Irradiation and Fuel Reprocessing Conditions

Average thermal flux	2.7×10^{13}
Burnup	29% U-235
Life (80% load factor)	1.9 yr
Uranium enrichment	93%
Specific liquid waste volume	29 gal/lb U-235

Maximum temperature rise is plotted as a function of waste thermal conductivity with parameters of convection coefficient for one-year cooled waste in a 9 in. radius waste cylinder, three-year cooled waste in a 14 in. radius cylinder, and eight-year cooled waste in a 29 in. radius cylinder in Figures 6.6, 6.7 and 6.8. Thermal conductivities were varied from 0.1 to 1.0 Btu/(hr)(sq ft)(°F/ft) and convection coefficients from 0.7 to 1.3 Btu/hr(sq ft)(°F).

Conclusions as to permissible storage conditions cannot be drawn until thermal conductivity measurements of the wastes have been made.

Nomenclature

T - temperature, °F

α - thermal diffusivity, sq ft/hr

t - time, hr

Q - uniform heat generation rate, Btu/hr(cu ft)

k - thermal conductivity, Btu/hr(sq ft)(°F/ft)

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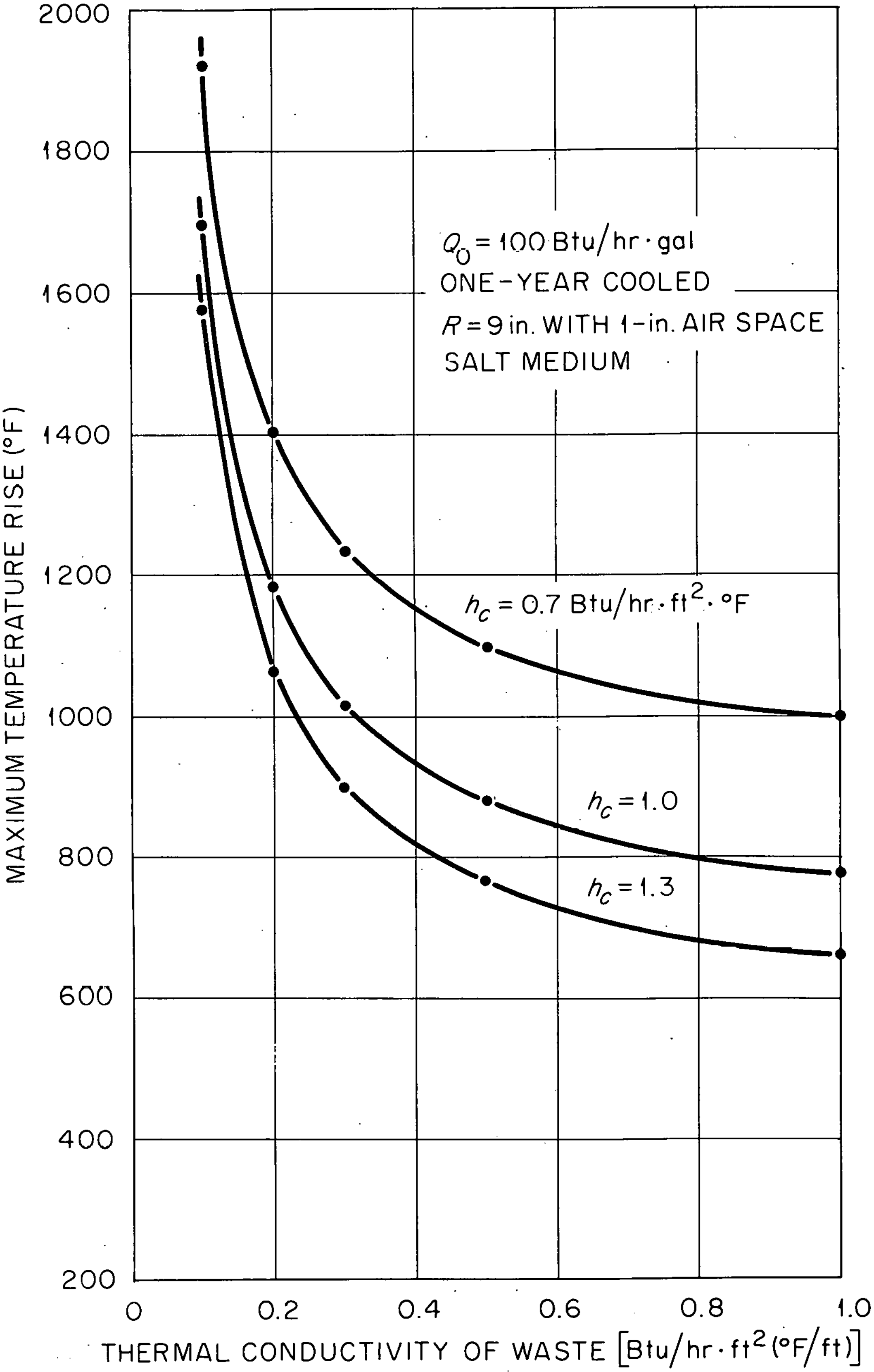

Fig. 6.6. Maximum Temperature Rise as a Function of Thermal Conductivity and Convection Coefficient for One-Year Cooled Waste in a Cylinder with a 9-in. Radius.

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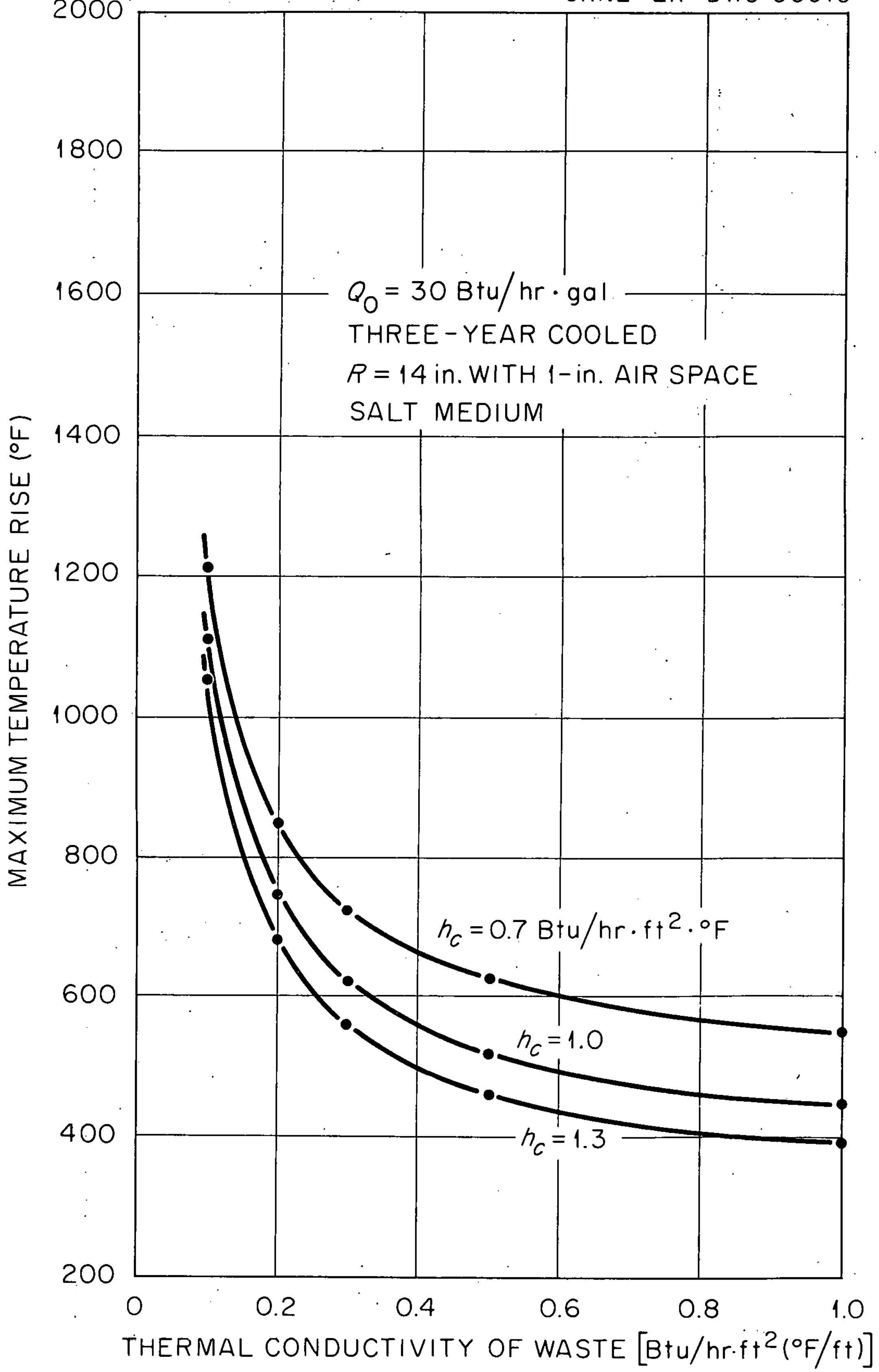

Fig. 6.7. Maximum Temperature Rise as a Function of Thermal Conductivity and Convection Coefficient for Three-Year Cooled Waste in a Cylinder with a 14-in. Radius.

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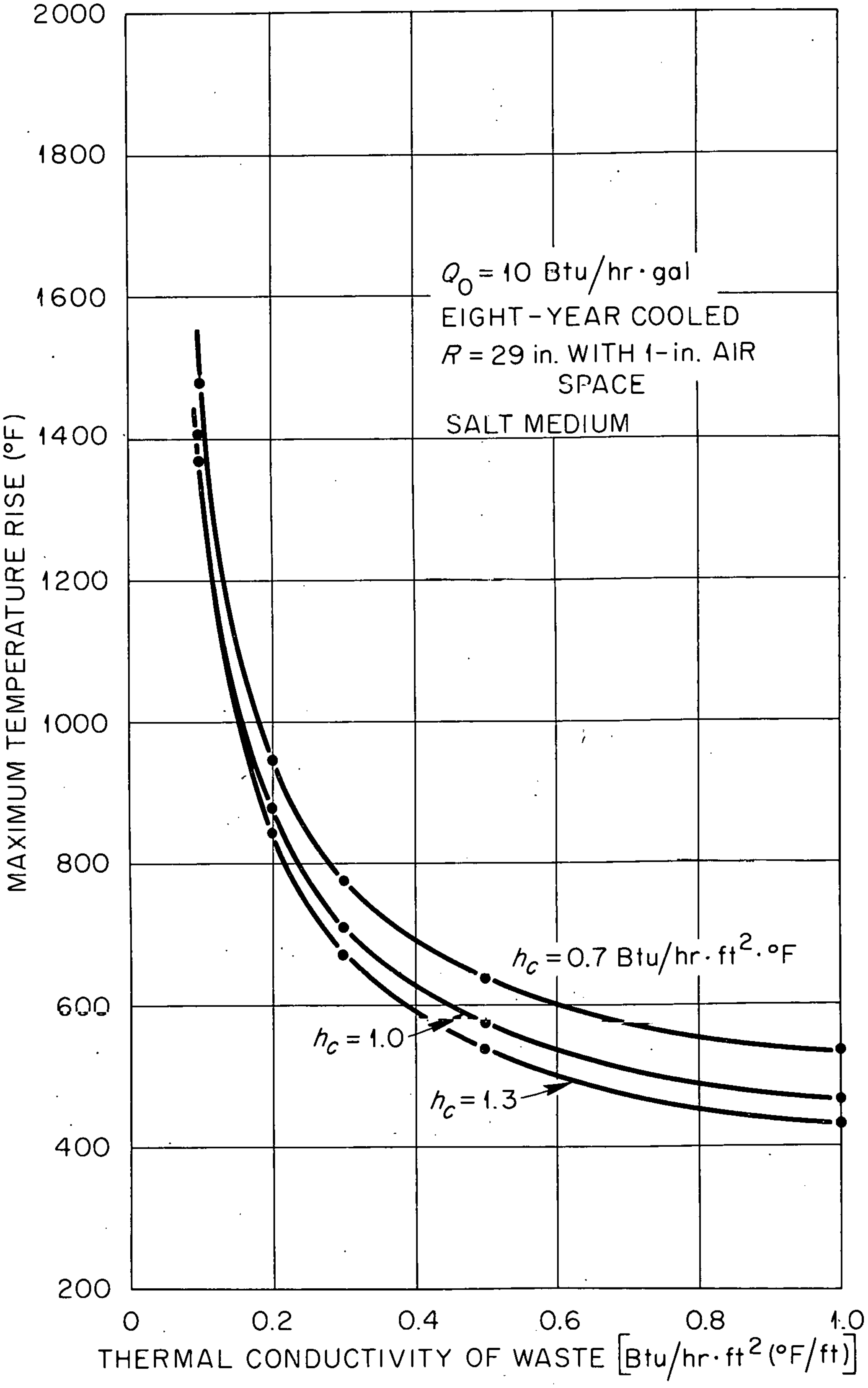

Fig. 6.8. Maximum Temperature Rise as a Function of Thermal Conductivity and Convection Coefficient for Eight-Year Cooled Waste in a Cylinder with a 29-in. Radius.

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