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TO: J. C. Bresee

FROM: E. M. Shank

Acknowledgment

The sections on Chemical Engineering Research, Ion Exchange, Power Reactor Fuel Reprocessing and Waste Processing have been reproduced from ORNL CF-58-11-93 to facilitate transmittal outside the United States Atomic Energy Commission.

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1.0 CHEMICAL ENGINEERING RESEARCH

M. E. Whatley

Measurement of Diffusion at an Interface - C. V. Chester

To better understand the solvent extraction process much effort has been and is being expended at ORNL and elsewhere to measure reaction kinetics of the extraction reactions. To date these efforts have been largely unsuccessful, due to the attempt to apply homogeneous reaction kinetics to two-phase systems.

An optical method has been devised for analyzing the concentration profile in the vicinity of a quiescent interface during steady-state diffusion at rather large molecular fluxes. The system under study is the extraction of uranyl ion from water by a TBP solution. Considerable effort has been directed to eliminating leaks in the diffusion cell and testing the optical system.

The possibility of measuring the concentration profile in a column of liquid containing an interface offers a means of observing the extraction reaction kinetics as well as the liquid diffusivities. Diffusivity may be measured in each phase directly from Fourier's equation for one dimensional diffusion at unsteady state:

$$\frac{\partial c}{\partial t} = -D \frac{\partial^2 c}{\partial x^2} \qquad (1)$$

where:

c = concentration of diffusing specie

t = time

x = distance

D = diffusivity

By measuring concentration profiles at several times during unsteady state, the partial derivatives may be evaluated, either graphically or numerically with interpolation polynomials, and the diffusivity calculated.

At steady state the molecular flux J up the column is a constant, and by Fick's Law:

$$J = -D_a \frac{\partial C_a}{\partial x} = -D_q \frac{\partial C_q}{\partial x} \qquad (2)$$

where the subscripts a and q, respectively, denote the aqueous and organic phases.

If the reaction at the interface is assumed to be simple first order and reversible, with a reaction rate constant K_1 in the extraction direction and K_2 in the stripping direction, then:

$$J = K_1C_{ai}-K_2C_{qi} \tag{3}$$

where the subscript i denotes measurement at the interface.

At equilibrium J = 0, and:

$$K_1C_a^* = K_2C_q^* \tag{4}$$

$$\text{or} \quad \frac{C_q^*}{C_a^*} = \frac{K_1}{K_2} = M$$

where M = distribution coefficient

Rearranging (3) and substituting (4)

$$J = K_2 \left(\frac{K_1}{K_2} C_{ai}-C_{qi}\right)$$

$$= K_2 (MC_{ai}-C_{qi})$$

$$= K_2 (C_{qi}^*-C_{qi})$$

Since J, M, C_{ai}, C_{qi} and C_{qi}^* can be measured (either directly or by extrapolation) in the diffusion cell, a means is available for measuring K_2 and K_1.

The question of the accuracy of measurement and sensitivity to the technique arises. The optical system will measure concentrations at positions known to about 0.02 mm. Thus if a concentration drop $(C_{qi}^*-C_q)$ is observed at the interface, it can be detected if it corresponds to a concentration change over 0.02 mm of the gradient in the organic phase, and it can be measured with considerable accuracy if it corresponds to 0.1 millimeter or more of the gradient. To phrase it another way, a resistance can be measured with some accuracy at the interface if it is equivalent to the resistance presented to diffusion by one-tenth millimeter layer of the organic.

From the previous equations:

$$J = -D_q \frac{\partial C_q}{\partial x} = K_2(C_q^*-C_q) = K_2(-\Delta C_q)$$

To find the equivalent resistance, let:

$$D_q\frac{\Delta C_q}{\Delta x} = K_2\Delta C_q$$

$$\text{or} \qquad \Delta x = \frac{D_q}{K_2} \geq 0.01 \text{ cm}$$

Typical values for uranyl ion diffusivities range from 10^{-5} to 10^{-6} cm^2/sec. Assuming 10^{-6} cm^2/sec, a measurable rate constant would be:

$$K_2 \leq \frac{10^{-6} \text{ cm}^2/\text{sec}}{10^{-2} \text{ cm}} = 10^{-4} \text{ cm/sec}$$

It will be noted that K_2 has the dimensions of velocity. This is due to the fact that the thickness of the reacting layer at the interface is not known, and throughput is measured rather than a homogeneous reaction rate.

If the reaction of a quiescent interface is assumed to take place within a molecular distance, say 10 Å, of the interface, K can be converted to a homogeneous reaction constant by dividing by the thickness of the reacting layer:

$$K_{\text{homogeneous}} = \frac{K_2}{10 \text{ Å}} = \frac{10^{-4}}{10^{-7}} = 10^3 \text{ sec}^{-1}$$

In terms of a first order half-time, this is:

$$t_{1/2} = \frac{\ln 2}{K} = 0.0007 \text{ sec}$$

Thus even a very fast reaction, down to a millisecond half-time, can be expected to produce an easily measurable departure from equilibrium at the interface.

5.0 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.

The analyses of solutions from equilibrium uranium sorption studies have been completed. These data are for series of runs made with varying uranium concentrations but constant sulfuric acid and total sulfate concentrations. Three series of such runs were made with uranium concentrations between 0.0005 M and 0.005 M. Each series was for a different total sulfate concentration.

The technique used in these studies has been described in a previous report[a]. A sample of approximately 1 g of resin was contacted with the specified solution for a period of 2 to 4 days by slowly flowing the solution through the resin bed. Some earlier work had been done using a batch method, but the present flow system was adopted to permit the final solution phase concentration to be specified.

The results for low sulfate concentrations are shown in Figure 5.1. As soon as more results are reported it may be possible to draw separate curves through the points for different total sulfate concentrations, but at present only one curve is shown. The agreement of these data with the previous batch work is not good. It appears that the earlier results were not at equilibrium, since the current data give higher loadings for approximately the same solutions. The differences in the two results are greatest at low uranium concentrations.

[a] UNOP September monthly report, ORNL CF No. 58-9-62.

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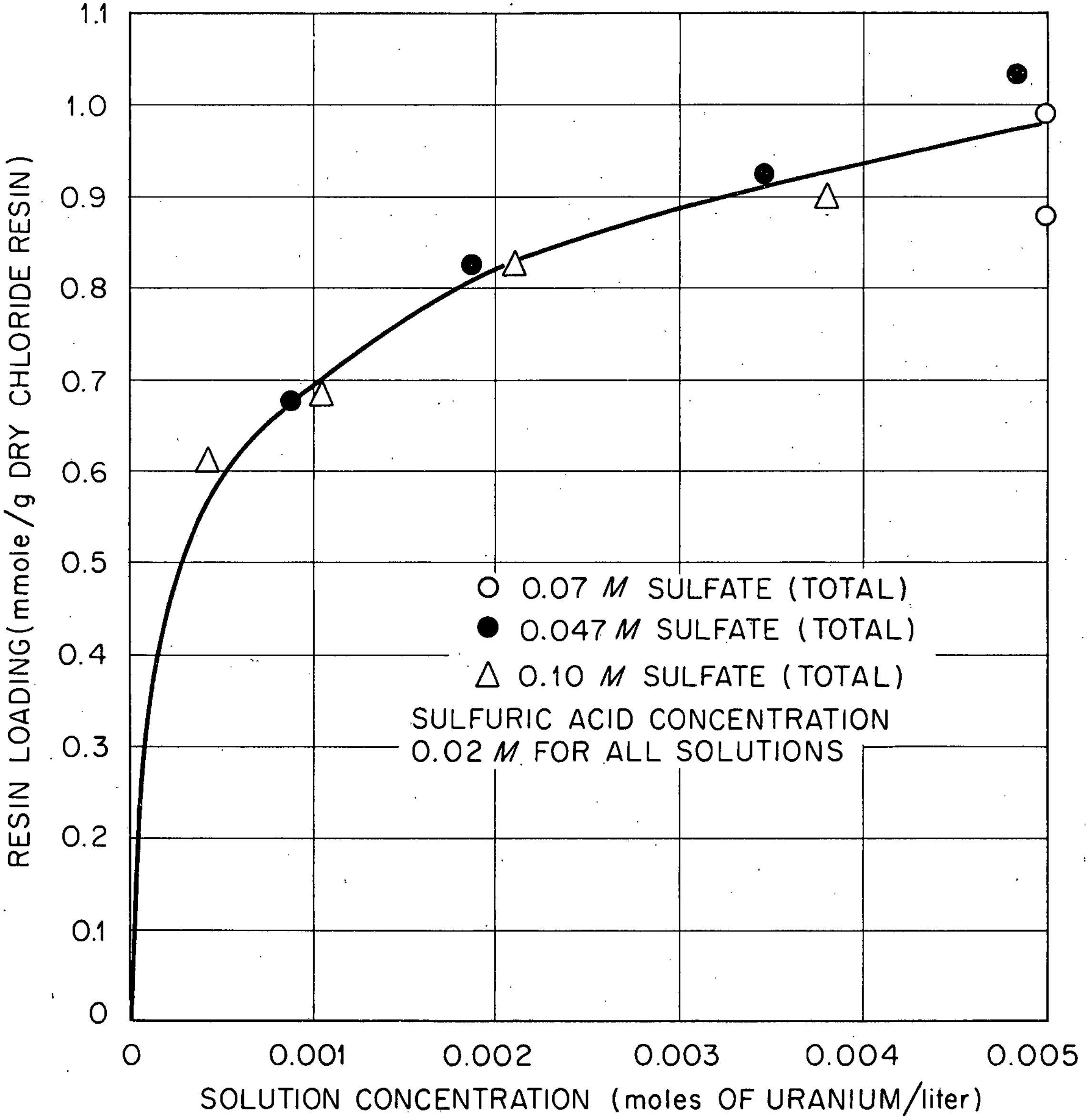

Fig. 5.1. Uranium Loading on Dowex 21 K.

6.0 POWER REACTOR FUEL REPROCESSING

C. D. Watson

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

6.1.1 Flowsheet Development and Modification

The purpose of the Darex process is to convert SS-U and SS-UO_2 fuels into chloride-free nitrate solutions suitable for processing in existing stainless steel solvent extraction equipment. Chloride is necessary to effect dissolution of SS in HNO_3 but it must be removed to avoid corrosion of feed adjustment, solvent extraction and waste handling equipment.

The Darex process consists of three basic steps:

1. Dissolution.
2. Cl^- removal.
3. Concentration adjustment prior to solvent extraction.

These steps may be accomplished continuously, semi-continuously or batchwise with nitric acid solutions (of 61 to 95 wt % HNO_3) to volatilize and/or decompose the chloride. Since the proposed Darex head-end in the PRFR pilot plant is to operate batchwise or semi-continuously, and since safety considerations may preclude the use of 95% HNO_3, flowsheets were developed to use the readily available 61% HNO_3 in both batchwise and continuous schemes.

Batchwise Flowsheet - The advantages of a batch flowsheet are simplicity and ease of operation. All steps are purely batchwise with no controlled continuous additions or withdrawals required. There is no recycle of radioactive, Cl^- containing HNO_3 except to the dissolution step where it is completely utilized in the next batch. The HNO_3 added to accomplish chloride removal is only that amount necessary to provide solvent extraction feed (3 M in HNO_3) and to regenerate mixed acid dissolvent for the following batch. The batch flowsheet assumes as a starting point the entire batch of dissolution product (DP) to be processed. Therefore, it does not matter whether the DP was generated in a batch or continuous dissolution.

A minimum equipment flowsheet for such a process is shown in Figure 6.1. Necessary equipment includes a dissolver, chloride removal and feed adjustment vessel, two condensers, a waste hold tank and two aqua regia tanks. Only one aqua regia tank is required if immediate H^+ and Cl^- analyses could be assumed. Operation is accomplished by first charging a batch of DP to the Cl^- removal vessel and then removing a waste cut (< 1.0 M

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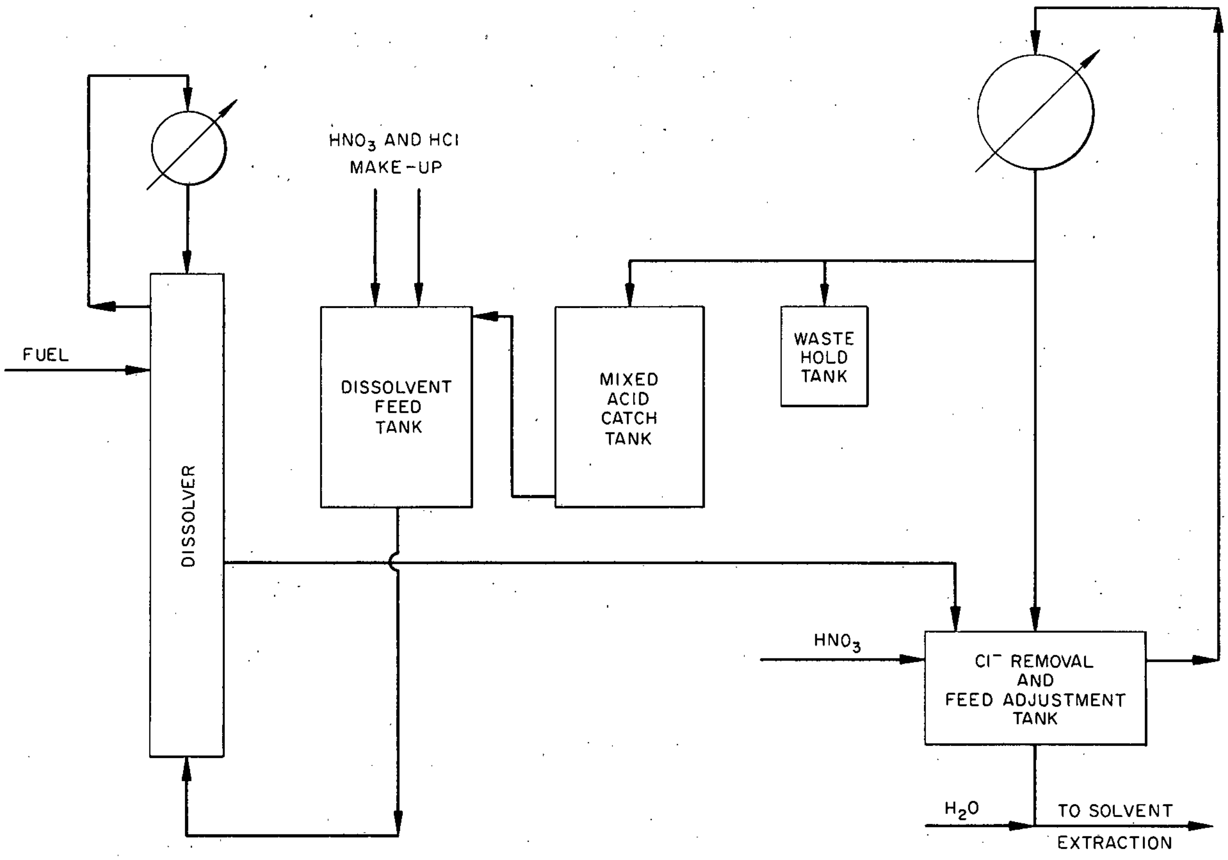

Fig. 6.1. Equipment for Batchwise or Semi-Continuous Darex Using 61 wt % HNO_3.

in total acid) to the waste hold tank. A HNO_3 addition is made to increase Cl^- volatility and the first mixed acid cut is collected in the mixed acid catch tank; this cut contains about half the Cl^- present in the DP. It is at this point that the metals concentration is the highest and the volume the lowest (about 21.4% of DP). Another HNO_3 addition is made and refluxed to decompose the remaining Cl^-. The Cl^- free (< 350 ppm) product is boiled to remove excess HNO_3, and this cut is combined with the first mixed acid cut and adjusted to 5 M HNO_3-2 M HCl in a volume equal or less than the original dissolvent volume. Only H_2O dilution of the metals-containing solution is required to produce solvent extraction feed.

The waste cut (< 1.0 M H^+) mentioned earlier could be treated with excess caustic and used as the liquid in the off-gas scrubbing tower (not shown in the flowsheet). This procedure would minimize the volume of the Cl^--containing radioactive waste stream.

The laboratory work on which the flowsheet is based was performed using 1400 cc batches of dissolver product (DP) produced by dissolving prototype APPR elements (~ 10% depleted U) to 62 g metal/liter in 5 M HNO_3-2 M HCl. A material balance showing the volumes and compositions of the side streams and the metals-containing product at key points during the process is shown in Figure 6.2. The laboratory procedure was as follows:

1. Charge 1400 cc DP to 2 liter boiling flask.
2. Boil off 300 cc to waste.
3. Add 300 cc 61% HNO_3 - begin air sparge at ~ 1/4 SCFH.
4. Boil off mixed acid (~ 1050 cc) until volume of product $\cong$ 300 cc.
5. Add 600 cc 61% HNO_3 and reflux for 2 hr.
6. Boil off 220 cc mixed acid (HNO_3 with trace Cl^-).
7. Dilute to 1600 cc solvent extraction feed.

It is necessary to use a gas sparge in order to remove the required amount of HCl in the first mixed acid cut. Only O_2 and air were tried and they appeared equally effective. Data for both the batchwise and semi-continuous runs are presented in Table 6.1.

Semi-Continuous Flowsheet - The semi-continuous flowsheet has the advantages of a smaller chloride removal vessel and the time savings made possible by allowing the chloride removal step to begin after the dissolution has been only partially completed. This procedure assumes a dissolver which operates continuously with respect to the liquid phase; the aqua regia is fed and dissolution product is removed continuously with a small constant hold-up in the dissolver. The rest of the equipment is

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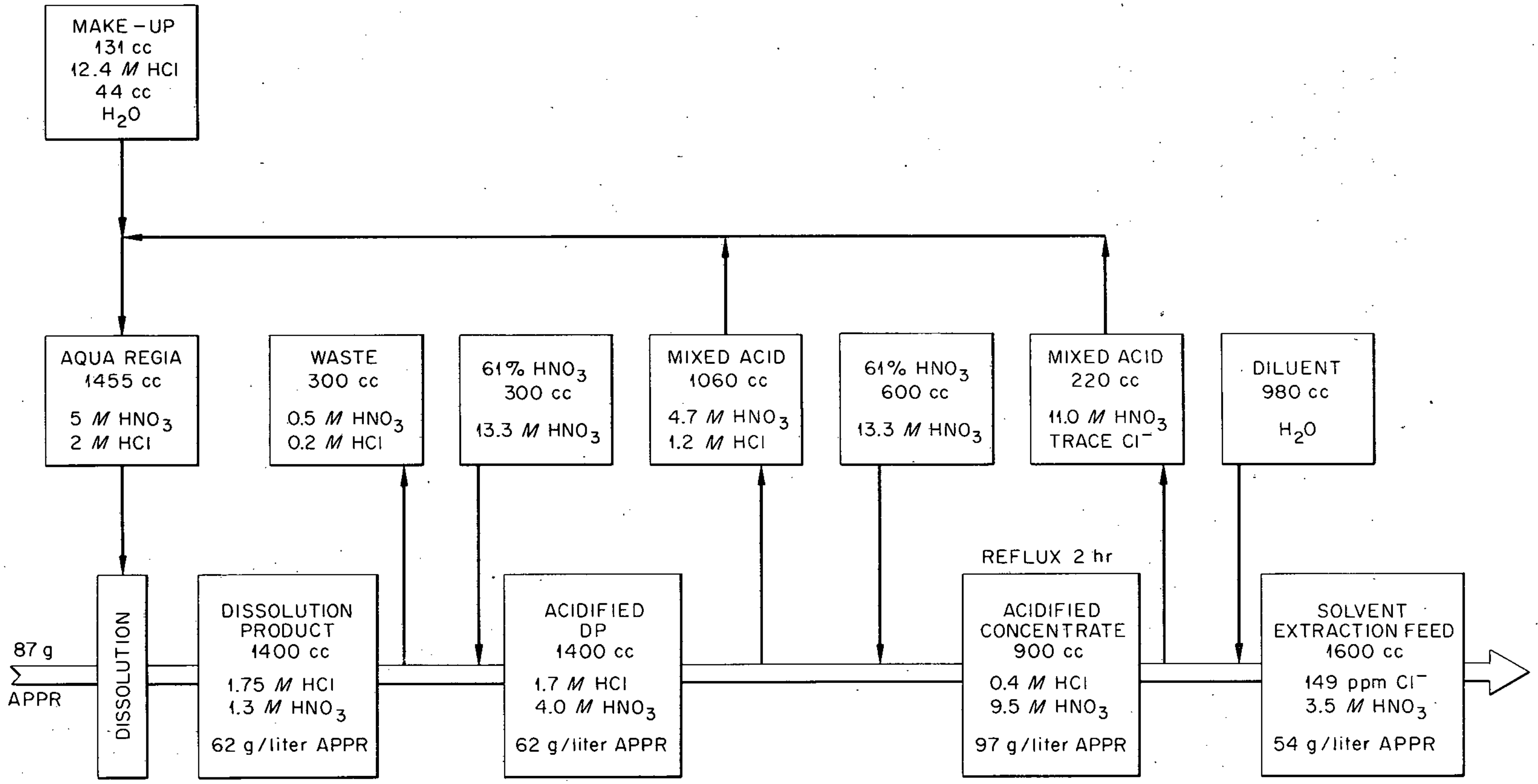

Fig. 6.2. Material Balance for Batchwise Operation Using 61 wt % HNO_3.

TABLE 6.1. DATA FOR BATCHWISE AND CONTINUOUS DAREX RUNS USING 61 wt % HNO_3

Run No.	Type	Sparge $\frac{1}{4}$ scfh	DP Vol. (l)	Waste			Addition of 13.3 *M* HNO_3 (cc)	Mixed Acid			Addition of 13.3 *M* HNO_3 (cc)	Acidified Product			Reflux Time (hr)	Product after Reflux			Mixed Acid (Trace Cl^-)		Solvent Extraction Feed		
				Vol. (cc)	H^+ (*M*)	Cl^- (*M*)		Vol. (cc)	H^+ (*M*)	Cl^- (*M*)		Vol. (cc)	H^+ (*M*)	Cl^- (*M*)		Vol. (cc)	H^+ (*M*)	Cl^- (*M*)	Vol. (cc)	HNO_3 (*M*)	Vol. (cc)	H^+ (*M*)	Cl^- (ppm)
20	Semi-cont.	None	2	450	0.5	0.1	300	1450	5.8	0.95	800	~1200	8.72	1.65	4	1100	7.57	0.21	300	10.25			
21	Semi-cont.	None	1.96	450	0.85	0.25	475	1500	6.5	1.05	800	~1250	9.45	0.87	2		8.69	0.22	200	10.3			
23	Semi-cont.	O_2	1.4	200	1.15	0.47	280	1100	5.0	1.1	600	~900	9.03	0.37	2	900	8.67	485 ppm	200	10.65	1600	3.5	175
24	Semi-cont.	Air	1.4	300	0.9	0.26	350	1070	5.7	1.0	600	~900	9.58	0.30	2	910	9.41	393 ppm	200	10.87	1600	3.8	150
25	Batch	Air	1.4	300	0.67	0.15	350	1090	6.05	1.2	600	~900	9.7	0.3	1.5		9.27	570 ppm					
26	Batch	Air	1.4	300	0.7	0.2	300	1060	5.95	1.2	600	~900		0.4	2	900		<0.025	220	11.0	1600	3.49	149
27	Batch	Air	1.4	250	0.7	0.35	250	1000	5.05	1.3	600	~900	9.54	0.38	2	~870	9.2	<0.025	300	10.5	1600	2.8	218
28*	Batch	Air	1.4	250	0.6	0.20	250	1060	5.5	1.25	600	~900			2			<0.025	250	11.0			<360

*Laboratory results incomplete.

the same as that shown in Figure 6.1. Fuel is charged batchwise to the dissolver; dissolvent is fed continuously; dissolution product flows into the chloride-removal and feed adjustment vessel. When the desired level is reached in this vessel, heat is applied and a waste cut is boiled off (at the same rate as the DP addition) to the waste hold tank. When the desired waste volume has been collected, a batchwise HNO_3 addition is made and the overhead condensate is redirected into the mixed acid catch tank. The chloride is volatilized during this step and the mixed acid collection is continued until the desired low volume remains in the feed adjustment vessel. (The dissolution would be completed less than half-way through the mixed acid boil-off). From this low volume point, the flowsheet is identical to the batchwise flowsheet.

The laboratory work was performed with 1400 cc batches of DP metered to the Cl^- removal vessel to simulate the discharge of a continuous dissolver. The procedure was as follows:

1. Charge 700 cc DP to 2 liter boiling flask.
2. Continuously add 300 cc DP while removing 300 cc to waste.
3. Add 300 cc 61% HNO_3 batchwise and begin air sparge.
4. Continuously add the remaining 400 cc DP while removing 400 cc mixed acid and continue to remove mixed acid until volume of concentrate is reduced to ~ 300 cc.
5. Add 600 cc 61% HNO_3 and reflux 2 hr.
6. Boil off 250 cc mixed acid (HNO_3 with a trace of Cl^-).
7. Dilute to 1600 cc solvent extraction feed.

Since the amount of DP and 61% HNO_3 additions are the same in both cases, the material balance for semi-continuous operation is very similar to that for batch operation (Figure 6.3). The waste cut here is slightly more concentrated (~ 1.0 $\underline{M}$ H^+) and the first mixed acid cut is slightly weaker in HNO_3. Apparently there is a little more loss due to decomposition in the semi-continuous system. From the second HNO_3 addition through the preparation of solvent extraction feed, the steps are the same with slight variations in volumes and compositions.

These flowsheets are not presented as carefully worked out optimizations and indeed require further adjustments and polishing, but they do show that Darex is a flexible process. They also serve to illustrate the principle that chloride can be removed to the specified < 350 ppm by the judicious application of only that amount of HNO_3 required for solvent extraction feed adjustment and for the regeneration of dissolvent for the next batch.

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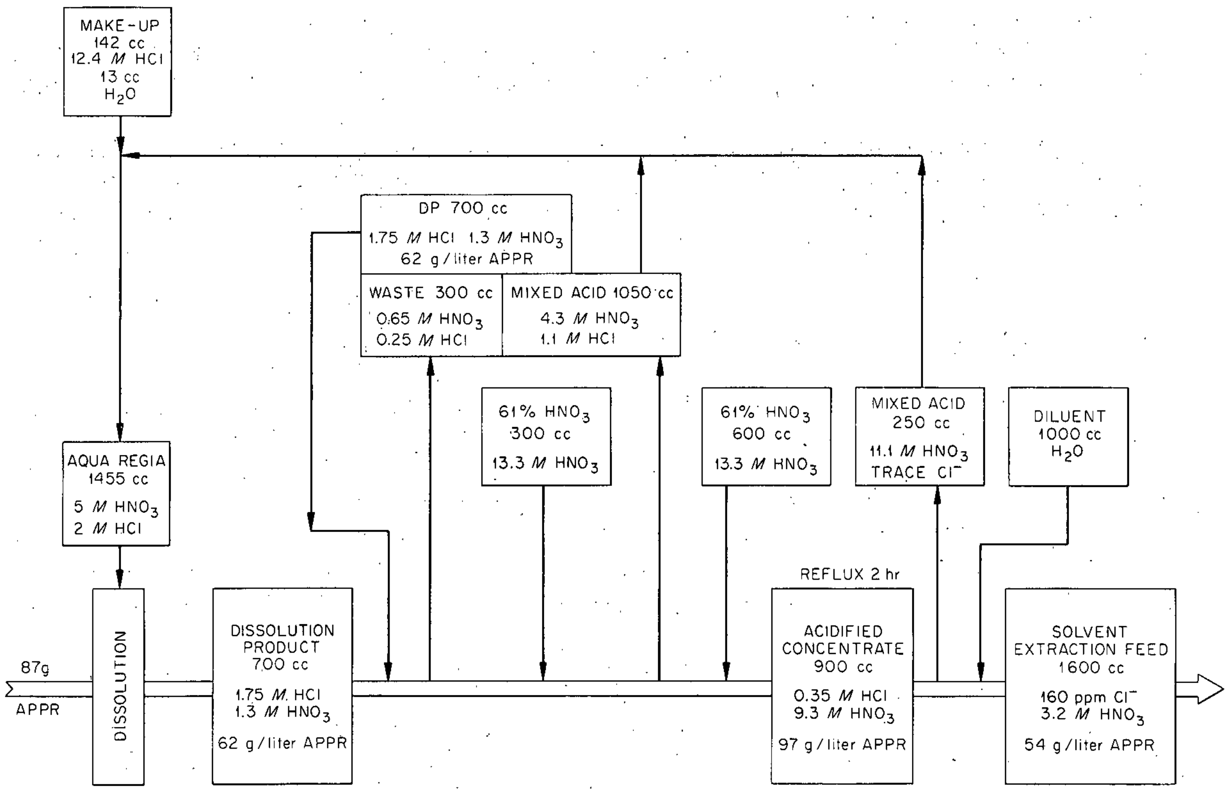

Fig. 6.3. Material Balance for Semi-Continuous Operation Using 61 wt % HNO_3.

6.1.2 Semi-Continuous Dissolver

A check-out run was made in a 6 in. I. D. glass dissolver. A prototype stainless steel APPR fuel element weighing 4000 g was dissolved in approximately 15 min using 5-2 aqua regia as the dissolvent. The aqua regia flow rate was approximately 4.5 liters/min resulting in a dissolver product containing 60 g/liter stainless steel. It was observed that a number of undissolved platelets were carried out of the dissolver with the dissolver product. This indicates that some type of a screen should be incorporated into the design of a dissolver to prevent the carry-over of undissolved metal into the chloride removal and feed adjustment tank.

The construction of a 4-in. I. D. x 6 ft long chloride removal and feed adjustment tank with the necessary auxiliary equipment is nearing completion. This equipment will be used to demonstrate the laboratory developed flowsheets mentioned earlier in the report at a 7 to 10 fold scale-up.

6.2 Zircex - J. B. Adams, G. B. Dinsmore

It has been shown* that the hydrochlorination of zirconium-uranium alloy fuels with hydrogen chloride gas containing CO_2, H_2O and O_2 impurities increases the quantity of nitric acid insoluble uranium losses in the uranium chloride product. A single hydrochlorination test of a 115.9 g sample of an STR plate was made with highly purified HCl gas (0.02% O_2, 0.01% CO_2) and gave losses of 1.9%. This test indicates that highly purified gas alone will not reduce the nitric acid insoluble uranium losses to a tolerable 0.1% or less.

Part of a cylinder of hydrogen chloride was purified by alternately venting the gas phase and equilibrating the liquid and gas to differentially remove impurities and leave the liquid contents of the cylinder highly purified. Spectrographic analyses (Table 6.2) of the cylinder contents show that most of the impurities had been removed during a previous hydrochlorination of a large piece of an STR sub-assembly (run HC-84). By a further simple purging-equilibration cycle impurities were reduced to an extremely low level. Water was not analyzed for but any remaining was removed by passing the HCl through an activated carbon bed just before use.

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*KT-319, M.I.T. Practice School, T. J. Carter and R. A. Stone, Zircex Kinetics and Uranium Loss Study, M.I.T. File No. EPS-X-328.

Table 6.2. Analysis of HCl Cylinder Mol %

Impurity	Cylinder As Received[a]	After 1/2 Used[b]	Purified[c]
O_2	0.49	0.16	0.02
CO_2	0.06	0.06	0.01
N_2	3.63	0.7	0.17
A	0.04	0.01	0.01
H_2O	0.20	-	-[d]

a. From Frontier Chemical Company.
b. About 1/2 of the cylinder used in Zircex run HC-83.
c. Purified by periodic venting to waste.
d. In the run with purified HCl, moisture has removed to a very low level by passing the HCl through an activated carbon bed.

A small piece (115.9 g; 1-1/2" x 2-1/2" x 1/2" long) of a single plate from a STR sub-assembly was hydrochlorinated with the purified hydrogen chloride. The metal sample was suspended over a fused silica dish used to catch the UCl_3 residue in the hydrochlorinator vessel. The reactor was purged with helium overnight and dried by heating. Hydrogen chloride was introduced at a slow rate through an activated carbon trap while heating the reactor walls to about 400°C.

As the metal-gas reaction started, as noted by evolution of hydrogen gas in the off-gas caustic scrubber, the HCl rate was adjusted to deliver 5-7 cu ft/hr. $ZrCl_4$ was condensed in a 4-in. air-cooled glass pipe and collected in the caustic scrubbing liquor. The walls of the reactor were maintained at 400°C. The reaction stopped after 2 hr.

After cooling, the reaction products were collected, weighed and analyzed. The distribution of the uranium (Table 6.3) showed 1.92% remained as nitric acid insoluble material in the reactor residue.

6.3 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.

Filtration tests for removal of precipitated silica from dissolver solution on a sand filter were started. Small scale filtration equipment (Figure 6.4) was set up. Initial tests with a Darex solvent extraction

Table 6.3. Distribution of Uranium in Run HC-84

			Analysis		Wt of Uranium	
Sample	Wt, g	Volume, liters	% U Total	% U Insoluble	Total (g)	Insoluble
Residue in dish	0.8053	-	46.38	0.98	.3735	.0079
Residue in sieve plate	2.04	-	3.34	0.22	.0682	.0045
NaOH scrub liquor	-	10.77	0.0013[a]	-	.0140	-
Precipitate from scrub liquor	90.35	-	0.21	-	.1897	-
					.6454	.0124

[a] Analysis in g/liter.

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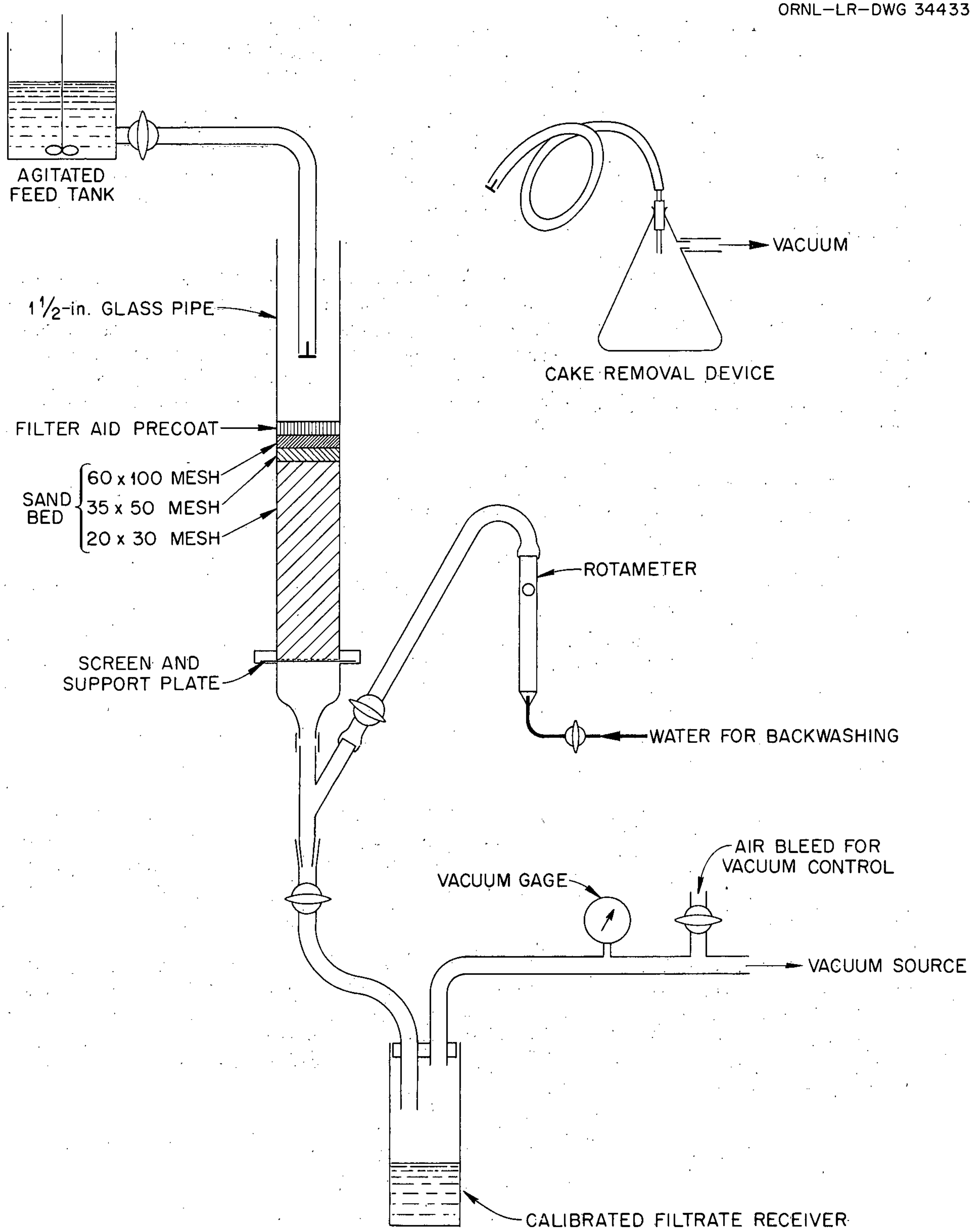

Fig. 6.4. Experimental Sand Filter Equipment.

feed solution (Figure 6.5) show that the addition of filter aid to the feed solution and use of 20" Hg vacuum gave greatly increased filtration rates over tests using only gravity head.

At 20°C, filtrate production rates of 41 gal/sq ft in 1 hr, 60 gal/sq ft in 2 hr and 73 gal/sq ft in 3 hr were obtained. These rates could be increased by a factor of 2 or 3 by increasing the solution temperature to reduce its viscosity. The solution produced about 25 cc wet drained filter cake per liter of feed.

Most of the solids were quite granular and settled rapidly indicating that most of the silica was dehydrated. The clear filtered solution was free of solids on centrifugation, but analyzed 10 ppm Si. No emulsion formed on contact with a 30% TBP-Amsco solution. Neither could a Tyndall effect for colloidal particles be noted. The gelatin treatment for precipitation of colloidal silica produced no precipitate until silica was added to the solution.

6.4 Entrainment of Undissolved Enriched Fuel Fines to A Non-Critically Safe Area - J. B. Adams, G. B. Dinsmore

During the dissolution of spent enriched oxide fuel cores in a dissolver geometrically safe only in the bottom dissolution area, the dissolution off-gas may entrain critical amounts of fine undissolved fuel particles to the enlarged non-critically safe upper portion of the dissolver. Preliminary tests were made to determine the likelihood of fuel fines being entrained in this manner during the dissolution of Consolidated Edison fuel (stainless steel clad UO_2-ThO_2). It has been estimated that a concentration of 1600 g/liter of UO_2-ThO_2 in water would create a nuclear criticality hazard.

A stream of air (to simulate gas produced during dissolution) was passed through a bed of ferrosilicon (specific gravity ~ 6, average particle size 120 μ) in a 2-in. dia tube filled with water simulating the suspension of fine UO_2-ThO_2 (specific gravity $\cong$ 9-10, average particle size 100 μ).

The maximum suspension concentration found was approximately 90 g of ferrosilicon/liter of solution at 1 in. above the settled bed of ferrosilicon at a superficial air velocity of about 0.5 ft/sec. In general, it appears it would be very difficult to obtain a concentration of $\sim$ 1600 g ThO_2-UO_2/liter of water suspension with air velocities up to 0.5 ft/sec. Additional tests will be made.

6.5 Solvent Extraction Studies - R. J. McNamee, B. C. Finney, F. L. Rogers, K. Ladd

Solvent extraction studies are being made to assist the Hanford Atomic Products Operation to adapt the Redox process for the recovery of uranium

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FILTRATION CONDITIONS

Solution: Darex solvent extraction feed solution (from APPR fuel) Sp Gr = 1.20 at 20°C, $\mu \cong 1.8$ cp. at 23°C analyzing 2.69 g U/liter, 33.0 g Fe/liter, 10 mg Si/liter and 2.52 N H^+. Solution contains about 25 cc of filter cake per liter.

Sand bed in a $1\frac{1}{2}$ ID glass pipe with screen and perforated plate support (see Fig. 6.4)

Symbol	Test No.	Sand Size and Amount (g)			Hyflo Filter Aid Precoat (g)	Filter Aid Addition	Pressure Drop
		20 × 30 Mesh Sand	35 × 50 Mesh Sand	60 × 100 Mesh Sand			
●	8	375	13	13	3	8 g Celite 545/liter feed	20 in. Hg vacuum
○	2	375					6 in. gravity head
△	1	375	13	13	3		6 in. gravity head

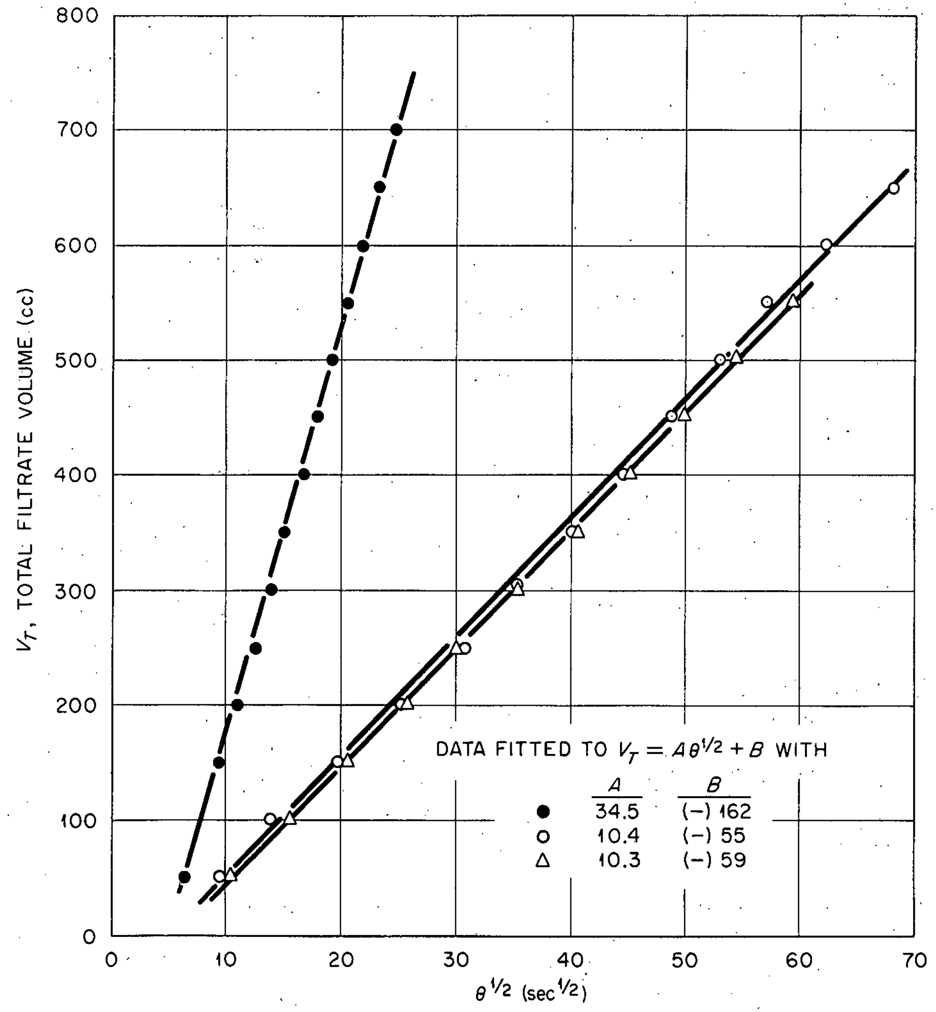

Fig. 6.5. Filtration of Darex Solvent Extraction Feed Solutions.

from spent stainless steel-type power reactor fuels. Column capacity, efficiency, and stability of various proposed flowsheets are being investigated.

Although uranium extraction efficiency has been high, decontamination factors have been low (as indicated by companion "hot" runs made by the pilot plant) and solution instabilities have been encountered.

The cold runs are being carried out in a 2-in. dia glass column, 22 ft extraction section, 4 ft scrub section, packed with 1/4"x3/8" stainless steel Raschig rings.

Redox runs were made using standard, Darex, and Niflex ($HF-HNO_3$ dissolution of stainless steel fuels) flowsheets. Preliminary results, subject to revision after a more thorough analysis of the data, are given in Table 6.4. Although the uranium losses were extremely low due to the length of the column, interesting results were obtained by analyzing data from samples of aqueous taken from the column at intervals from the feed point down to a point 12 ft below. From these data, by trial and error calculations, the HETS for the standard run and the Darex run were estimated to be 6 ft and 12 ft, respectively.

These estimates were made by assuming a HETS, which then established a single point on the equilibrium line. A graphical calculation of HETS was made using the resulting assumed line and compared to the assumed HETS. When the assumed and calculated HETS matched, this value was assumed to be a reasonable approximation of the system (in the absence of equilibrium data).

It appears the equilibrium is more favorable for the Darex flowsheet. It may be noted that a HETS previously obtained with the pulse column at 60 cpm, using a Yankee Atomic Darex flowsheet (30% TBP-Amsco solvent, 3 M H^+ scrub, 30 g/liter SS, 2 M H^+ feed, flow ratio 1:0.2:1.5) was about 4 ft. However, the equilibrium for this flowsheet was less favorable.

An efficiency run for the Niflex flowsheet was not made, due to the inability to maintain a stable feed solution. The stable feed prepared for the flooding determination could not be duplicated. An investigation of this problem is currently in progress.

6.6 PWR Decladding and Core Dissolution - G. A. West, J. C. Rose, J. Beams (with T. A. Gens, G. E. Woodall, J. F. Land - Chemical Development Section B)

Preliminary hot cell tests of the Zirflex flowsheet and Sulfex flowsheets were completed. Batch dejacketing and core dissolution of each of sixteen PWR blanket fuels (UO_2 pellets clad with Zr-2) with burnups from 250 to 2,500 Mwd/ton were made. Decladding dissolvents, 6 M NH_4F-1 M NH_4NO_3 and 9 M HF were used in sixteen and two runs, respectively. Core dissolutions were made with 10 M HNO_3.

Table 6.4. Hanford Assistance Runs

	Standard	Darex		Niflex
Run No.	1	3b	3a	8
Feed composition (M)				
U^{+6}	1.24	0.6		0.5
ANN	1.11	-		0.84
H^+	0.2 AD*	0.2 AD		0.4
$Na_2Cr_2O_7$	0.14	0.2		0.2
$NaNO_3$	0.33	1.5		0.25
S.S.	-	1.2		0.25
NH_4NO_3	-	-		1.25
AlF_3	-	-		0.42
Si	-	-		0.001
Scrub composition (M)				
ANN	1.3	1.3		1.3
H^+	0.2	0.2		0.15 AD
$Na_2Cr_2O_7$	0.01	0.01		0.01
Feed:scrub:solvent flow ratio	1:0.15:2.3	1:0.5:2.5	1:0.25:2.0	1:0.2:1.85
Throughput, GSFH	472	445	-	-
% U loss	0.0017	0.0017	-	-
Flooding rate, GSFH	589	557	> 640	664

*Acid deficient.

Four hot runs were also completed on Consolidated Edison type fuels (4% UO_2-96% ThO_2 pellets clad with stainless steel) with burnups from 100 to 4,300 Mwd/ton. These runs were made to obtain data for possible revisions of the Sulflex flowsheet which will be used in future hot cell test runs.

The twenty-two hot runs were successfully completed in about 350 hr of operation without equipment failure. A replacement dissolver was used in the hot runs because of (1) a weld failure after 12 cold runs in the first Carpenter-20 dissolver and (2) uneven heating which contributed to precipitates forming and the resultant plugging of the teflon filter. The new steam jacketed dissolver constructed of Carpenter-20 material was annealed for 30 min at 2000°F and air-blast cooled to prevent weld failure.

The filter was eliminated and transfer of solutions was accomplished by vacuuming through dip tubes. Both the solids and precipitates were carried over with the supernate and collected in a conical bottom lucite vessel which allowed visual observation of supernate volume. The precipitates and solids which settled in the conical bottom were collected for analysis.

Results of these hot runs will be presented in a joint report with the Chemical Development Section. The results of the cold runs performed earlier are presented in the Chemical Development October 1958 monthly report.

6.7 Mechanical Processing of Power Reactor Fuels--Tentative Program Proposal - C. D. Watson, W. A. Schaffer, G. K. Ellis, G. A. West

6.7.1 Introduction and Purpose

The purpose of the program outlined herein is to aid the Interim Chemical Reprocessing Program of spent power reactor fuels to which the Laboratory is committed and to provide sufficient information on mechanical processing to allow a decision to be made as to its probable future usefulness in a central facility. Experimental work both in the cold with simulated or prototype fuel and with spent fuel, wherever possible, is proposed as follows:

A. Dejacket

SRE-SS clad, NaK bonded, U

PRDC-SS clad, Na bonded, U-Mo

B. Shear and Leach

Yankee, GCR and Nuclear Ship Savannah-SS clad UO_2

Commonwealth Edison and PWR--Zircaloy-2 clad UO_2

Consolidated Edison and Rural Coop-SS clad UO_2-ThO_2

C. Disassembly

All the above fuels are to be disassembled to sub-assemblies, if required. Provisions are also to be made to chop the entire assembly wherever possible,

The cold work of this program will be performed in the Unit Operations Section, at the plant of a sub-contractor or in the PAR facility. All hot work will be performed in the PAR facility.

It is assumed that all mechanical equipment necessary to carry out all of the above operations must be purchased and received by July 1, 1959. All sub-contracts must of necessity be let no later than December 15, 1958 or January 1, 1959.

6.7.2 Program

In general, the program that follows is to be accomplished by the following groups of people:

Unit Operations and Design Sections

These two sections will be responsible for the over-all design criteria, program coordination, procurement, testing and evaluation and operation of the hot facility.

There are two primary and closely related objectives in the program of mechanical processing. First, an equipment flowsheet is to be developed by which irradiated reactor fuel elements may be mechanically treated to expose the core material at a rate which will permit dissolution of 300 kg per day of exposed core material. Secondly, an engineering test facility will be operated to evaluate mechanical techniques and to furnish design criteria and information useful to sub-contractors for detailed design and fabrication.

The mechanical flowsheet may consist of disassembly of the fuel element, shearing to L/D ratios of about unity, and leaching of the sheared portions in either a continuous or a batch leacher. The most difficult problems expected are material transfer of solids, particularly in and out of the dissolver, and development of a shear capable of shearing heterogeneous metal and abrasive ceramic materials on a production basis with a satisfactory shear blade life.

Until mechanical processing equipment is received from sub-contractors, the experimental program will consist generally of the testing and evaluation of the Ty-Sa-Man saw. A Syntron spiral vibratory conveyor will probably be used as a basis for the continuous leacher if it can be shown that chopped material can be passed through this device without difficulty. The saw and associated fuel element holding devices will receive initial attention because of the more immediate need for them in the SRE program.

A device for decanning SRE NaK bonded fuel has already been designed and bids for fabrication solicited. An enlarged model of this device, if it is successful, would be used to reprocess PRDC NaK bonded fuel.

ORNL Engineering and Mechanical Division

The Engineering and Mechanical Division will design the SRE dejacketing device and associated equipment required for its operation in the PAR facility. In addition, they will furnish the design for altering existing experimental equipment, disassembly saws, shears and leachers in the Unit Operations Section and the experimental facility required for cold testing of this equipment. Likewise, they will design the materials handling equipment for the flow of spent fuel into and out of the PAR facility. Total estimated cost for the initial design, 321 man-days, is $18,000.

REED Division

The Reactor Experimental Engineering Division group will complete the prototype fuel design and fabrication, shear design, and possible disassembly saw design (4 man-years, $60,000).

Machine Fabricators

All devices will be fabricated and procured through outside contractors by purchase requisitions.

Dejacketing (Decanning)

a. SRE Decanner

  1. Engineering and Mechanical Division will finish drawings by November 21, 1958.

  2. Proposal to vendors.

  3. Visit to vendors during December 1-December 15 followed by letting of contract.

b. Design will be continued for recanning, cooling, removal of NaK, off-gas removal and burial of jackets, carrier transfer and fire protection.

c. Decanner will be received by June 1, 1959 and cold tested.

  1. Fifty short prototypes already available (along with one actual fuel rod.

  2. Hot test - August 1959 in PAR.

d. Redesign and alter decanner where necessary to accommodate PRDC and acquire new machine between June 1960 and January 1961.

PAR Layout

The over-all mechanical program of disassembly, decanning, shearing and leaching must be compatible with the physical layout of the PAR and not interfere with normal PAR operation. Size limitations and location of equipment imposed by the PAR facility must be ascertained as soon as possible so that design criteria for the shear, transporters (solids and liquids) and leachers can be completed before December 31, 1958.

Unit Operations Section Layout

A layout of existing equipment shear, disassembly saw and leacher for the Unit Operations third floor area and cell 4a must be accomplished before the end of January 1959 along with the detail design for alterations of the existing 100 ton shear, Ty-Sa-Man saws and conversion of the vibratory conveyor to a vibratory leacher. This equipment will be used to obtain data useful in designing the PAR equipment and some of this equipment may actually be used in the PAR facility.

Prototype Fuels

It is proposed that the REED Division design a simplified stainless steel jacketed ceramic fuel and a Zircaloy-2 jacketed ceramic fuel which would adequately represent all the problems associated with the actual fuels to be mechanically processed. Fabrication of the simplified version would be let to an outside vendor - estimated cost $20,000-$30,000. Design work should be completed by January 15, 1959.

Disassembly and Bundling

At this time, it is planned that the Ty-Sa-Man saws normally used in the PAR facility will be used to remove inert end adapters and tube sheets and reduce fuel assemblies to sub-assemblies if required. Jigs or hydraulically operated vises or both will have to be added to the present saws for them to be adequate for the PRFR program. It is proposed that the REED Division design the holding devices and a sub-contract be let to provide the equipment as required or new saws be purchased or both. Ty-Sa-Man is interested in building the necessary clamping devices. Strapping fuel bundles with a standard commercial strapping device will probably be required as an aid in shearing. This feature may become a part of the disassembly saw.

A shear capable of shearing or chopping fuel bundles up to 9 in. dia into 1 in. lengths may simplify the disassembly problem. The REED Division will assist in the design of the shear to handle fuels up to and including that of the NS Savannah, assuming that the tonnage required is not beyond the space limitations in the PAR facility. Manco and other companies will be asked to assist the design effort and bid on the shear - estimated cost $50,000-$75,000.

Design problems associated with shearing are:

a. Shape of shear die and ease of changing dies.

b. Power requirements and maintenance.

c. Off-gas, dusting and transfer of dusts.

d. Holding and feeding device.

Leaching

Batch and continuous leaching of chopped fuels is a major problem which should be assigned immediately to an outside firm. A batch dissolver with provisions for solids removal should be designed and fabricated followed by a continuous version. Estimated cost:

Batch	$20,000-$50,000
Continuous	$50,000-$75,000

Leaching studies on a laboratory bench scale are needed prior to fixing the leacher design.

8.0 WASTE PROCESSING

M. E. Whatley

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 design of reduction of radioactive waste to solids process for ultimate disposal. This report covers all of the completed tests using high level waste in the hot cell, Building 4507.

The purpose of this series of experiments was to determine the amount of fission products evolved when different types of wastes were calcined to dryness. The amount of fission products reporting to the condensate and the amount removed by the caustic scrubber downstream of condensate receiver are reported.

A thin walled stainless steel cup of 600 ml capacity was placed within a stainless bomb which was heated in a programmed manner to boil the 200 ml of waste solution to dryness and subsequently calcine it at 700°C. The bomb was vented to an off-gas train which collected the activity. A condenser removed the condensibles which were collected, the noncondensibles were passed to a packed bed caustic scrubber and then through three caustic bubblers in series. Finally the off-gas was passed to the plant hot off-gas which operated at 3 to 10 in. of water vacuum. (This system was used to evaluate the behavior of the evolved gases and is not necessarily recommended as a scheme for plant use.)

Darex waste was simulated by dissolving the appropriate metal powders in the high level acid waste (6.0 $\underline{M}$ HNO_3, 0.5 $\underline{M}$ H_2SO_4). Sulfex decladding waste was simulated by spiking synthetic solutions with the high level waste.

The amount of fission products evolved during the reduction to solids ranged from $2x10^{-3}\%$ to $3x10^{-1}\%$ of the starting total (Table 8.1).

Table 8.1. The Percentages of Fission Products Evolved From Different Waste

Type[a] of Feed	Gross β, c/min/ml in Feed	Gross γ, c/min/ml in Feed	% of Total β in Condensate	% of Total γ in Condensate	% of Total β in Off-Gas	% of Total γ in Off-Gas	% of Total β Evolved	% of Total γ Evolved
Darex	$9x10^{+9}$	$1x10^{+10}$	$2x10^{-2}$	$3x10^{-2}$	$6x10^{-3}$	$3x10^{-2}$	$3x10^{-2}$	$6x10^{-2}$
Darex	$9x10^{+9}$	$9x10^{+9}$	$2x10^{-3}$	$5x10^{-3}$	$4x10^{-5}$	$4x10^{-4}$	$2x10^{-3}$	$5x10^{-3}$
Sulfex	$6x10^{9}$	$6x10^{9}$	$2x10^{-2}$	$3x10^{-1}$	$1x10^{-4}$	$8x10^{-5}$	$2x10^{-2}$	$3x10^{-1}$

[a] Waste neutralized with NaOH to pH 7.0 or greater.

[b] Possibility of contamination.