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TO: J. C. Bresee

FROM: E. M. Shank

Acknowledgment

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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 the anion exchange resin Dowex 21K.

A series of equilibrium studies have been completed which show the effects of solution uranium concentration on resin loading. These data are shown in Figure 5.1. The loading solutions were all 0.02 M in sulfuric acid, and the uranium and total sulfate concentrations were as indicated. The high sulfate concentrations were obtained by adding sodium sulfate.

A run was made allowing from 4-8 liters of the loading solution to slowly flow through a small resin bed containing 1-2 g of resin during a period of 2-4 days. At this time the resin was assumed to have reached equilibrium with the loading solution. In several of the runs a sample of the solution leaving the resin bed was taken to see if it had the same composition as the loading solution. In no cases was there any indication that equilibrium was not very closely approached. The resin loading was determined by elution with a 1 N sodium chloride solution. Details of the apparatus and procedure have been presented in a previous report (1).

These data are for higher total sulfate concentrations than those reported in November (2). Under these conditions the effects of the sulfate concentration is evident. Three similar loading curves can be separated to represent the data for the three respective total sulfate concentrations. Except for some scatter at solution concentrations of ~ 0.002 moles of uranium per liter, the data appear to follow a smooth curve.

M. P. Aronchick and R. H. Wick of the Massachusetts Institute of Technology Engineering Practice School made a study of uranium loading at very low sulfate concentrations to see if a peak sorption occurred (3). They used solutions 0.0005 M in uranium and 0.015 M in sulfuric acid. The total sulfate concentration was varied between 0.0155 M and 0.025 M by adding the required amount of sodium sulfate. As mentioned in earlier reports (1, 4) the location of a point of maximum sorption at a given sulfate concentration may allow a re-evaluation of the UO_2^{++} - SO_4^- association constants. No maximum sorption was indicated by the data. However, there was a great deal of scatter, and no definite conclusions could be reached. The major source of the scatter was believed to have arisen from a failure to keep the uranium concentration exactly the same in all of the runs. At low uranium concentrations, the loading is so much more dependent on the uran-

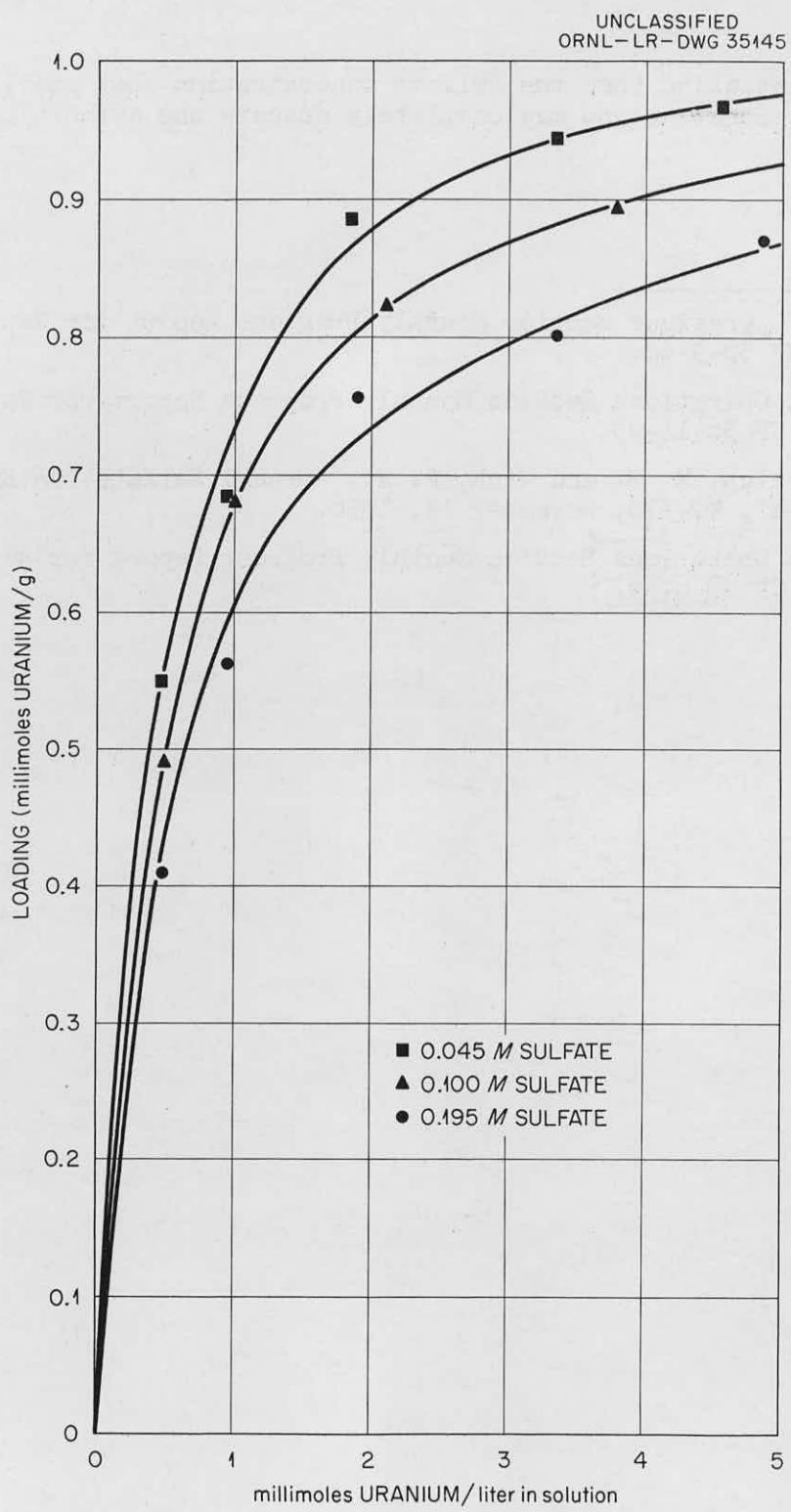


Fig. 5.1. Equilibrium Sorption of Uranium on Dowex 21K from Sulfate Solutions at 25°C.

ium concentration than the sulfate concentration that small errors in the uranium concentrations may completely obscure the effects of the sulfate.

- (1) "Unit Operations Section Monthly Progress Report for September 1958",
ORNL CF 58-9-62.
- (2) "Unit Operations Section Monthly Progress Report for November 1958",
ORNL CF 58-11-93.
- (3) Aronchick, M. P. and Wick, R. H., "Uranyl Sulfate-Ion Exchange Equilibria", KT-370, November 14, 1958.
- (4) "Unit Operations Section Monthly Progress Report for August 1958",
ORNL CF 58-8-59.

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6.0 POWER REACTOR FUEL REPROCESSING

C. D. Watson

6.1 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-UO₂ fuels into chloride free nitrate solutions suitable for processing in existing SS solvent extraction equipment. The chloride ion is necessary to effect dissolution of SS in HNO₃ but it must be removed to avoid corrosion of solvent extraction process equipment. Darex consists of three steps: dissolution, Cl⁻ removal, and concentration adjustment preparatory to solvent extraction. The process may be carried out continuously, semi-continuously or batchwise using nitric acid concentrations from 61 to 95 wt per cent in the Cl⁻ removal step.

6.1.1 Batchwise Cl⁻ Removal and Feed Adjustment

The present investigation seeks to develop a batch flowsheet using 61% HNO₃ in which Cl⁻ is reduced to < 350 ppm in the solvent extraction feed by treating the dissolution product with only that amount of HNO₃ which is consumed in dissolution and lost in the solvent extraction feed.

Five runs were made in a 4 in. ID feed adjustment tank using 10 liters of dissolver product in the flowsheet developed on a 1.4 liter scale (1). The first 4 runs, 30, 31, 32 and 33 (Table 6.1), were made to evaluate the effect of air sparging and to determine the effect of the path of vapor through the condenser on chloride removal. In run 35, a cut was taken just before reflux in an effort to reduce the initial Cl⁻ concentration. Neither the operation of the condenser, whether updraft or downdraft, nor the use of air sparging made a significant difference in the Cl⁻ concentration of the acidified concentrate, which should be an important factor in determining the final Cl⁻ concentration. In the reflux step air sparging had a beneficial effect while downdraft operation had a detrimental effect.

The slightly different flowsheet and the lack of important data make the interpretation of run 30 difficult. A flowsheet change lowered the total H⁺ of the acidified concentration in run 35, which contributed to poor chloride removal. In the runs where sparging was used, the Cl⁻ re-

(1) Unit Operations Monthly Progress Report for November 1958, ORNL CF 58-11-93.

Table 6.1. Data for Runs in 4 in. I.D. Cl^- Removal and Feed Adjustment Equipment

Run No.	Air Sparge 1 l/min	Condenser	Dissolution Product			Acid Waste			Add 13.3 M HNO_3 l	1st Mixed Acid			Add 13.3 M HNO_3 l	Acidified Concentrate			Reflux Time Hours	2nd Mixed Acid		Solvent Extraction Feed		
			Vol l	H^+ M	Cl^- M	Vol l	H^+ M	Cl^- M		Vol l	H^+ M	Cl^- M		Approx. Vol l	H^+ M	Cl^- M		Vol l	HNO_3 M	Vol l	HNO_3 M	Cl^- ppm
30	No	Updraft	10.0	3.05	1.75	1.8	0.80	0.32	1.8	7.5	5.8	1.5	4.3	6.5			1.5	1.8	10.4	11.5	3.43	1065
31	Yes	Updraft	10.0	3.34	1.66	2.0	1.14	0.50	1.8	7.5	5.65	1.1	4.0	6.0	9.66	0.67	2.0	1.6	11.0	11.5	2.77	135
32	Yes	Downdraft	10.0	3.17	1.67	2.0	1.20	0.45	1.8	7.5	5.4	1.2	4.0	6.0	9.49	0.58	2.0	1.7	11.3	11.5	2.81	330
33	No	Downdraft	10.0	3.19	1.73	2.0	0.85	0.32	1.8	7.5	6.0	1.57	4.0	6.0	9.66	0.58	2.0	1.7	11.2	11.5	2.92	565
35	During reflux only	Downdraft	10.0	2.98	1.74	2.0	0.70	0.22	1.8	7.5	5.55	1.37	4.0	5.0*	8.17	0.41	2.0	2.0	10.2	11.5	2.43	1200

* 1 l of 2nd mixed acid was taken off before reflux.

covery in the mixed acid was lower than in the unsparged runs. Since these five runs are the first runs that have been made in this equipment, nothing yet can be said about reproducibility, and batch-to-batch variations in results of one flowsheet could be of the order as the differences shown between different flowsheets.

The preferred method of operation is without sparging, since the dissolver product will be a highly radioactive solution, and a downdraft condenser should be used for better recovery of the oxides of nitrogen. From the data to date, the best compromise between these methods of operation and those which reduce the chloride content of the solvent extraction feed appears to be operation with a downdraft condenser and an air sparge, possibly at a higher rate than that studied, during the reflux step. This method should provide good Cl^- removal and recovery during the first mixed acid boil-off and give maximum Cl^- removal during reflux.

6.1.2 Continuous Dissolution

A check-out dissolution run was made in the 6 in. glass dissolver with a prototype APPR stainless steel fuel element weighing 4640 g. The element was dissolved in 15 min in 5 N HNO_3 -2 N HCl aqua regia fed at 4.5 liters/min. The average dissolution rate based on the total initial surface area of the element was 18.2 mg/sq cm·min and the F/S ratio (acid feed rate/initial surface area) was 0.265 cm/min. The dissolver product analyzed: 2.31 M H^+ , 2.25 M Cl^- , and 15.9 g Cr/liter (equivalent to 80 g SS/liter).

The simulated fuel element consisted of 18 plates 0.030" x 2-7/8" x 23" on 0.125" spacing, between two side plates 0.125" x 2-7/8" x 23".

6.2 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.

6.2.1 Estimated Filtration Rates for Darex Solutions

Based on test data taken on Darex solvent extraction feed solutions, the rates expected on a large scale are given in Table 6.2. These rates are for a temperature of 20°C; at 60°C the rates would be approximately doubled. Boiling the solution down to reduce its volume resulted in no improvement in solids accumulation rate since the increase in viscosity compensated for the reduced volume of solution to be filtered.

Table 6.2. Estimated Filtration Rates for Darex Solutions at 20°C

Liters of Filtrate/Sq Ft Filter Area, After Various Times			Other Conditions	
1 Hour	2 Hours	3 Hours	Pressure Drop	Filter Aid Addition
215	311	381	20" Hg vacuum	12 g/liter
168	242	296	20" Hg vacuum	8 g/liter
120	173	212	5" Hg vacuum	8 g/liter
48	69	85	6" gravity head	None

6.2.2 Effect of Pressure Drop and Filter Aid on Filtration Rate

A number of filtration runs were made on removal of silica from Darex solvent extraction feed solutions. The procedure and equipment have been described earlier (Unit Operations Monthly Progress Report for November 1958, ORNL CF 58-11-93). The effect of pressure drop and amount and type of filter aid addition to the feed solution were investigated. All data plotted as straight lines on a graph of total filtrate volume versus the square root of elapsed time (Figure 6.1).

Data from each run were fitted to the equation $V = B\theta^{1/2} + C$ (Legend on Figure 6.1). The slope B indicates the influence of liquid and cake properties and pressure drop on the rate of filtration. The intercept C reflects the initial resistance offered by filter aid precoat, the sand filter bed and the piping between the filter bed and the filtrate receiver. The influence of the intercept C on the over-all filtration rates becomes negligible when considering long filtration cycles. For purposes of comparing the effects of variables on filtration rate values of the slope B can be used with little error.

A change in pressure drop from 5 in. Hg vacuum to 20 in. Hg vacuum (a factor of four; runs 9-vs-4, 8, 10, 11, 12) result in an increase in over-all filtrate rate of only about 50%. This result indicates that the cake is compressible to some extent even when composed of ~ 1/2 filter aid by volume. Without filter aid in the cake a change in filtration pressure from 6 in. gravity to 5 in. Hg vacuum (a factor of about 10; run 1-vs-3) produced essentially no change in rate, indicating the high compressibility of the silica cake by itself. Addition of filter aid should be most valuable in the low pressure drop range where the compressibility of silica is highest.

The amount and type of filter aid used effected the filtration rates considerably. Two types of diatomaceous filter aid were used in tests: Celite 545*, a coarse grade, and Hyflo*, a medium grade. In general, the coarsest grade giving desired solution clarity should be used.

*Johns Manville.

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Test No.	Filter Support	Pressure Drop (in.)	Filter Aid Added to Solution	Filter Aid Precoat	Symbol	Series on Solution HS-1-A		All at $\sim 20^\circ\text{C}$		1½ in. dia pipe		Constants in Equation $V = B^{1/2} + C$
						B	C					
1	Std 8½ in. sand bed ^a	6 gravity	None	3 g Hyflo	○	10.0	-52					
2	7 in.-20 × 30 mesh sand	6 gravity	None	None	○	9.43	-35					
3	Std 8½ in. sand bed	5 vacuum	None	3 g Hyflo	○	9.38	-71					
4	Std 8½ in. sand bed	20 vacuum	8 g Hyflo/1	3 g Hyflo	○	26.1	-132					
5	Std 8½ in. sand bed	20 vacuum	16 g Hyflo/1	3 g Hyflo	○	27.2	-134					
6	Std 8½ in. sand bed	5 vacuum	2 g '545'/1	3 g Hyflo	△	13.7	-100					
7	Std 8½ in. sand bed	5 vacuum	2 g '545'/1	3 g Hyflo	△	14.9	-122					
8	Std 8½ in. sand bed	20 vacuum	8 g '545'/1	3 g Hyflo	△	33.9	-140					
9	Std 8½ in. sand bed	5 vacuum	8 g '545'/1	3 g Hyflo	△	23.0	-190					
10 ^b	Std 8½ in. sand bed	20 vacuum	8 g '545'/1	3 g Hyflo	△	35.8	-163					
11 ^c	Std 8½ in. sand bed	20 vacuum	8 g '545'/1	3 g Hyflo	□	35.4	-165					
12 ^d	Std 8½ in. sand bed	20 vacuum	8 g '545'/1	3 g Hyflo	□	36.5	-177					
13 ^e	Std 8½ in. sand bed	20 vacuum	20 g '545'/1	3 g Hyflo	□	38.2	-213					
Series on Solution HS-2-A												
14	Std 8½ in. sand bed	20 vacuum	4 g '545'/1	1 g '545'	●	29.0	-22					
15	Std 8½ in. sand bed	20 vacuum	8 g '545'/1	1 g '545'	■	31.4	-58					
16	Std 8½ in. sand bed	20 vacuum	12 g '545'/1	1 g '545'	▲	44.1	-49					
17	Std 8½ in. sand bed	20 vacuum	16 g '545'/1	1 g '545'	▼	44.8	-85					

^a~8 in. 20 × 30 mesh, ¼ in. 35 × 50 mesh, ¼ in. 65 × 100 mesh.

^b100 ppm gelatin added.

^cDuplicate of run 8.

^d250 ppm S_1O_2 + 100 ppm gelatin added.

^eWater instead of Dorex solution.

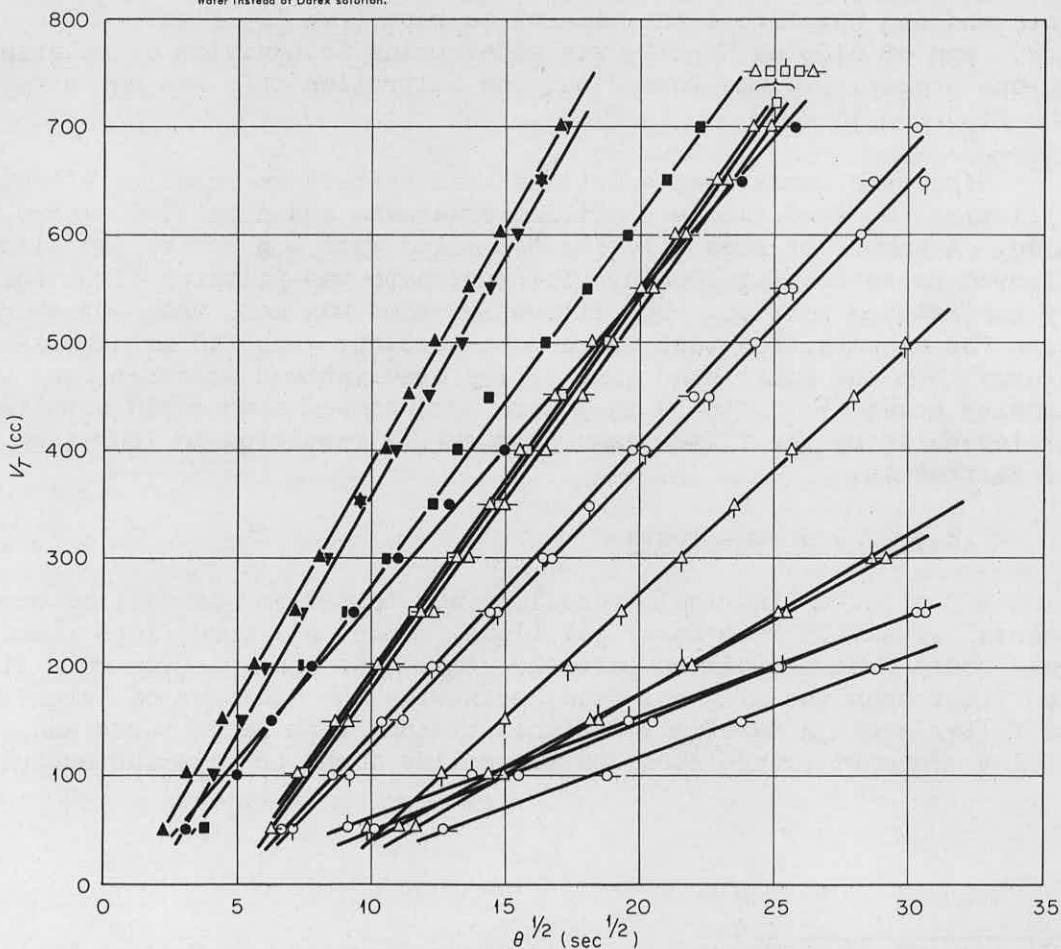


Fig. 6.1. Filtration Data on Dorex Solvent Extraction Feed Solutions.

Comparison of various runs (Figure 6.1; runs 4 and 5; runs 6 and 7; runs 4, 9, 10, 11 and 12; runs 14, 15, 16, and 17) shows that (a) the type of filter aid used makes little difference at low levels of addition (≤ 0.25 vol FA/vol silica); (b) at high levels of filter aid addition (≥ 1.5 vol FA/vol silica) filtration rates level off and probably start to decrease, i. e., filtration resistance increased faster than the cake porosity as total cake volume and depth increase; and (c) Celite 545 gives higher filtration rates than Hyflo at addition levels above ~ 0.25 vol FA/vol silica. A plot of the slope, B, (from the equation: $V = B\theta^{1/2} + C$) versus vol FA/vol silica (Figure 6.2) illustrates these relationships. No runs were made at filter aid addition levels greater than 2 vol FA/vol silica so that the shape of the curves at the maximum filtration rate is not clearly defined as being sharp or flat.

Treatment of siliceous solutions with gelatin (2) to form a silica-gelatin polymer was attempted. However, the feed solutions available were essentially devoid of soluble or colloidal silica. Direct treatment with gelatin (100 ppm) followed by heating for 1 hr at 80°C produced no precipitate and did not effect the filtration rate (run 10, Figure 6.1). When ~ 250 ppm of SiO_2 as Na_2SiO_3 was added prior to addition of gelatin, a flocculent precipitate was formed but the filtration rate was not affected (run 12, Figure 6.1).

Since the Darex feed solutions used settled so readily, a test on splitting the feed into a clarified supernate and a settled slurry was made. A sample of feed solution was mixed with 8 g Celite 545/liter and allowed to settle for 10 min. The supernate was filtered first followed by the settled portion. The filtration time was more than 40% shorter than for a comparable test where both portions were fed as a well-mixed slurry. On the other hand qualitative observations on other runs where gravity heads (5 in. to 10 in.) were used showed that rapid settling particles built up the filter cake prematurely resulting in increased time of filtration.

6.2.3 Hydroclone Tests

A 0.4 in. cylindrical hydroclone was tested for partial or complete removal of silica from Darex solutions. Under all conditions tested a gel formed from the silica particles that made the solution more difficult to filter than the original feed, even with the addition of larger amounts of filter aid. A carefully designed cyclone with large ports and operated at low heads to reduce shear on the solids might be more successful.

(2) Groh, H. J., "Removal of Silica from Solutions of Nuclear Fuels", DP-293, Savannah River, June 1958.

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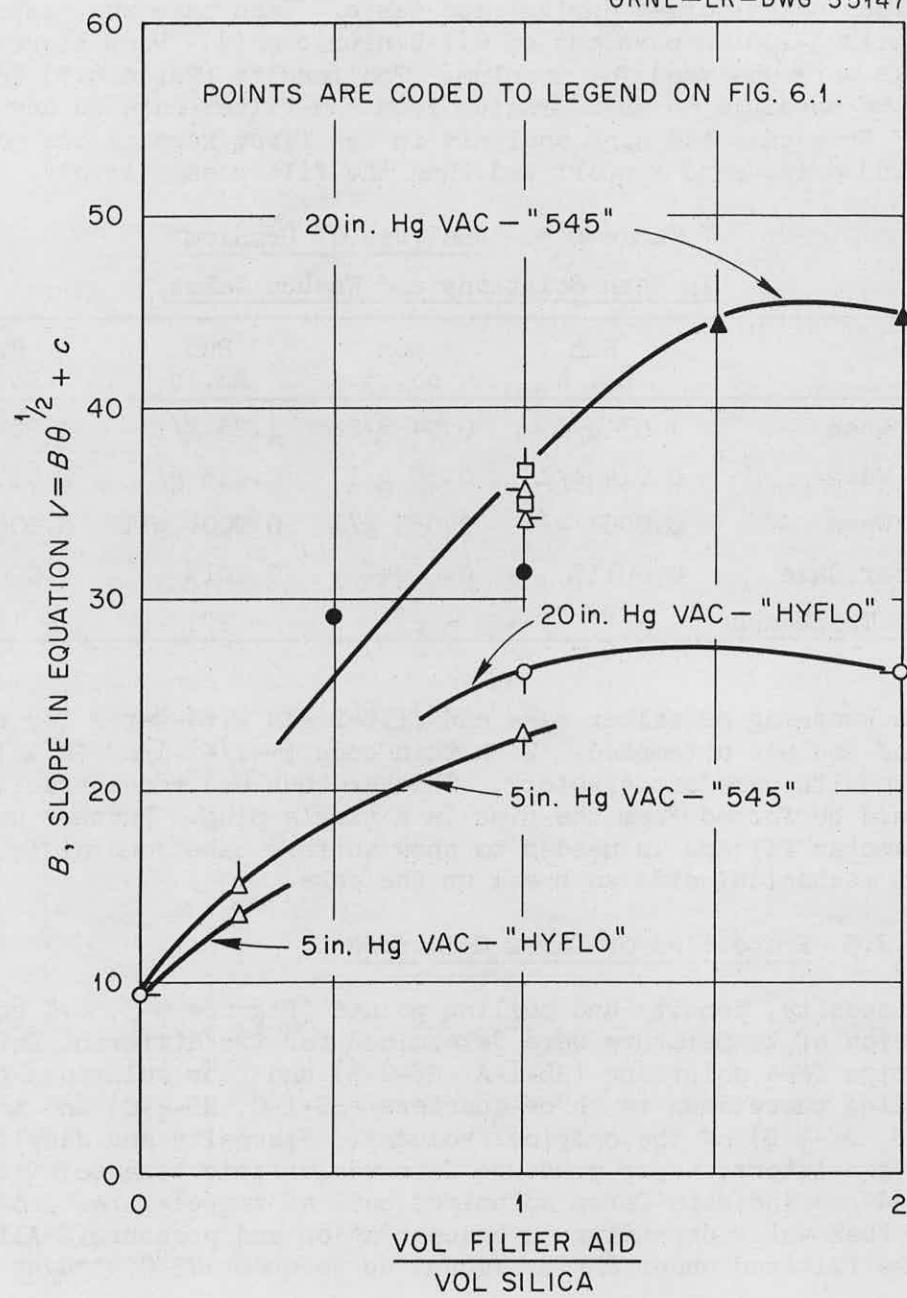


Fig. 6.2. Effect of Filter Aid Addition on Filtration Rate.

6.2.4 Cake Washing and Removal.

Tests on washing uranium from filter cakes were made on several of the filter cakes formed during rate tests. Each cake was washed successively with 3-100 cc portions of 0.1 N nitric acid. Wash liquors and filter cake were analyzed for uranium. The results (Table 6.3) indicate it should be possible to wash uranium from the filter cake to any desired level. Note that the high analysis in the first wash is due more to hold-up in the 8 in. sand support bed than the filter cake itself.

Table 6.3. Analysis of Uranium in Wash Solutions and Washed Cakes

	Run No. 4	Run No. 5	Run No. 8	Run No. 9
1st Wash	1.03 g/l	0.94 g/l	1.23 g/l	1.06 g/l
2nd Wash	0.014 g/l	0.39 g/l	0.013 g/l	0.038 g/l
3rd Wash	0.0001 g/l	0.035 g/l	0.0004 g/l	0.0009 g/l
Filter Cake	0.0011%	0.0004%	0.001%	0.0005%
Cake Thickness	~ 1"	~ 2"	~ 1"	~ 1"

Backwashing of filter cake and filter aid with water for removal from the sand bed was attempted. With thin beds (~ 1/4"-1/2" in a 1-1/2" dia pipe) results were satisfactory. Thicker beds had considerable strength and could be forced from the pipe in a single plug. Further work in larger diameter filters is needed to show whether cake removal is feasible without mechanical aids to break up the cake.

6.2.5 Properties of Darex Solutions

Viscosity, density and boiling points (Figures 6.3, 6.4 and 6.5) as a function of temperature were determined for two different Darex solvent extraction feed solutions (HS-1-A, HS-2-A) and four solutions prepared by boiling these down to three-quarters (HS-1-C, HS-2-C) and to one-half (HS-1-B, HS-2-B) of the original volumes. Viscosity and density data appear fairly consistent; vapor pressure data was erratic because of crude apparatus used but indicate Darex solutions boil at temperatures from 4° to 12°C higher than water depending on concentration and pressure. All solutions could be filtered under 20 in. vacuum up to about 75°C without flashing.

Chemical analysis of the two original solutions are given in Table 6.4. Both solutions contained ~ 25 cc of dehydrated silica filter cake per liter of solution. The silica appeared granular and settled rapidly giving a clear solution in 5-10 min. The cake formed by centrifugation was compressed to half the volume of that obtained on gravity settling.

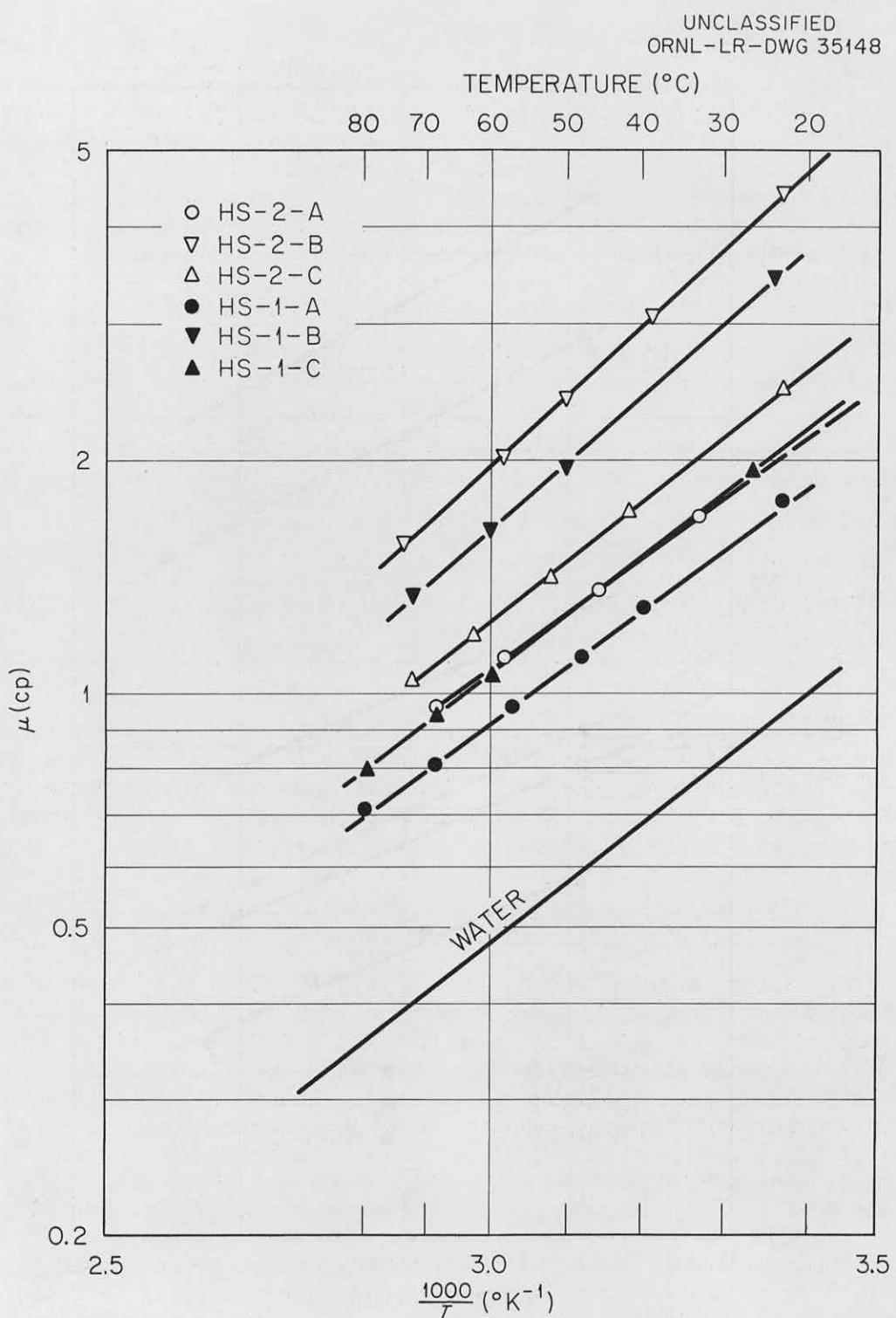


Fig. 6.3. Viscosity-Temperature Relations for Darez Solutions.

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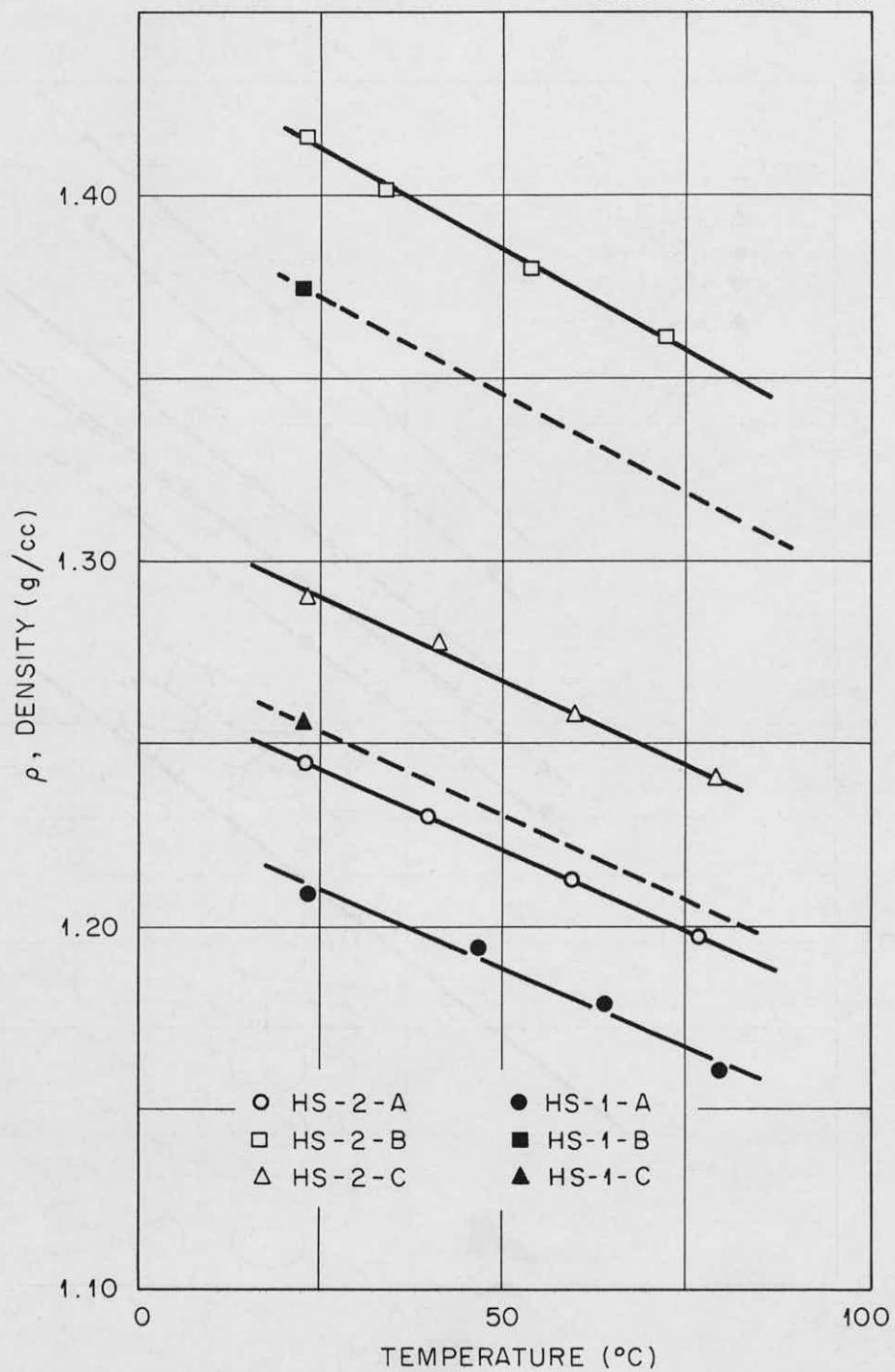


Fig. 6.4. Density - Temperature Relations
for Darez Solutions.

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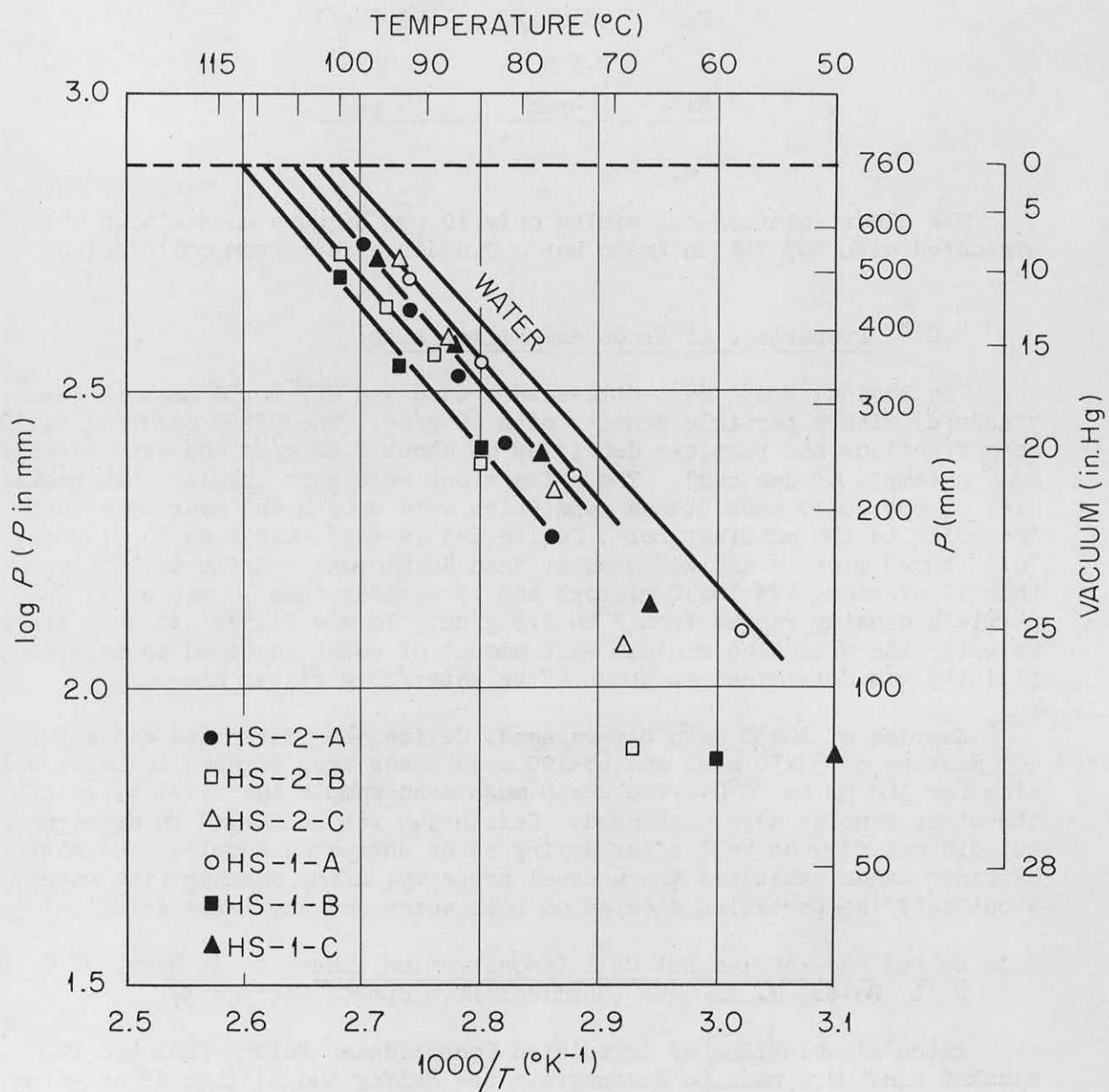


Fig. 6.5. Boiling Points of Darex Solutions

Table 6.4. Analyses of Darex Solutions Used

	HS-1-A	HS-2-A
U	2.69 g/l	4.56 g/l
Fe	33.0 g/l	29.3 g/l
H ⁺	2.5 N	2.65 N
Si	10 ppm	10 ppm

The clear solution containing only 10 ppm Si gave no emulsion when contacted with 30% TBP in Amsco nor a Tyndall effect from colloidal silica.

6.2.6 Properties of Sands and Filter Aids

The nominal 20x30 mesh Ottawa sand used was 98% 20x30 mesh (U. S. standard) with a particle density of 2.60 g/cc. The 35x50 mesh and 65x100 mesh fractions had particle densities of about 2.62 g/cc and were screened from a sample of sea sand. These fractions were more angular than particles of the 20x30 mesh Ottawa sand which were smooth and near spherical. According to the manufacturer*, Celite 545 is 5.5% less than 10 microns, 70.5% 10x40 microns and 24% greater than 40 microns. Hyflo is 45% less than 10 microns, 49% 10x40 microns and 6% greater than 40 microns. The particle density ranges from 2 to 2.3 g/cc. To use filter aid as a slurry in water the estimated minimum safe amount of water required to maintain fluidity was determined as about 47 cc water/10 g filter aid.

Samples of 20x30 mesh Ottawa sand, Celite 545 filter aid and a 50%-50% mixture of 35x50 mesh and 65x100 mesh sands were exposed to Darex solution for 168 hr at 80°C. The 20x30 mesh sand sample lost 1.7% by weight; the other samples were unchanged. Celite 545 was unchanged in appearance but did not flow as well after drying as an untreated sample. The mixture of finer sands exhibited the unusual property; after washing with water, about half the particles floated on both water and the Darex solution.

6.3 Sulfex and Zirflex Hot Cell Demonstration Runs - G. A. West, J. C. Rose, R. L. Boles, T. A. Gens (Chemical Development Section B)

Batch dissolutions of irradiated Consolidated Edison fuel and PWR blanket pins were made to demonstrate the Sulfex and Zirflex dejacketing flowsheets, respectively. The results from four runs with irradiated (100-430 Mwd/ton) Consolidated Edison type reactor fuels (SS clad, 96%

*Johns Manville.

ThO_2 -4% UO_2) indicated that the procedure and/or equipment for the Sulfex flowsheet might have to be changed to prevent core losses from fluoride contamination. An alternate procedure might be the inclusion of uranium recovery facilities for treatment of the dejacketing solution.

Core losses of uranium, thorium and plutonium to the 6 M H_2SO_4 de-cladding solution were often excessive. However, the extent of losses due directly to burnup or to the 6 M H_2SO_4 alone cannot be well defined. For details see Hot Flowsheet Demonstrations, Monthly Progress Report, Chemical Development Section B, December 1958.

The data from 18 batch runs with irradiated PWR blanket fuels, demonstrating the Zirflex flowsheet, is being compiled.

Many of the radioactive solutions resulting from Zirflex and Sulfex dejacketing solutions were decanted and leached stepwise with boiling water and 6 M HNO_3 to obtain analytical samples for uranium analyses.

The dissolution equipment was removed from the hot cell and the cell decontaminated to less than 1 mr/hr without an overexposure to personnel. The radiation level before decontamination on equipment and the cell surfaces ranged from 2 to ~ 100 r/hr.

6.4 Mechanical Processing of Fuels

6.4.1 SRE Decanner

The design of the SRE decanning device (shown in Figure 6.6) was completed and submitted to several vendors for bids. The lowest bid received was \$9,000 from the Southern Machine Company of Chattanooga, Tennessee. Several design concepts of a method of recanning the bare SRE fuel has been made. Recanning into an extruded aluminum tube with the open end closed by some pressing or swaging operation is the most promising.

6.4.2 Prototype Fuel - (C. W. Collins, REED Division)

A prototype fuel bundle has been designed (Figure 6.7) to serve as an inexpensive substitute for the seven fuels considered for chopping and leaching studies. The bundle is 3-7/8" x 3-7/8" x 6' long consisting of thirty-six stainless steel tubes 1/2" OD x 35 mils thick filled with porcelain rods to simulate ceramic fuels. A purchase requisition for one hundred bundles has been issued, seventy-five units filled with porcelain and twenty-five empty units for later filling with UO_2 . The purchase cost is estimated to be \$10,000-\$20,000 excluding the UO_2 .

6.4.3 Core Leaching Studies - G. A. West, L. M. Ferris (Chemical Development Section B)

Dissolution studies to obtain rate and penetration data for UO_2 in nitric acid solutions were begun. These data are needed for the design

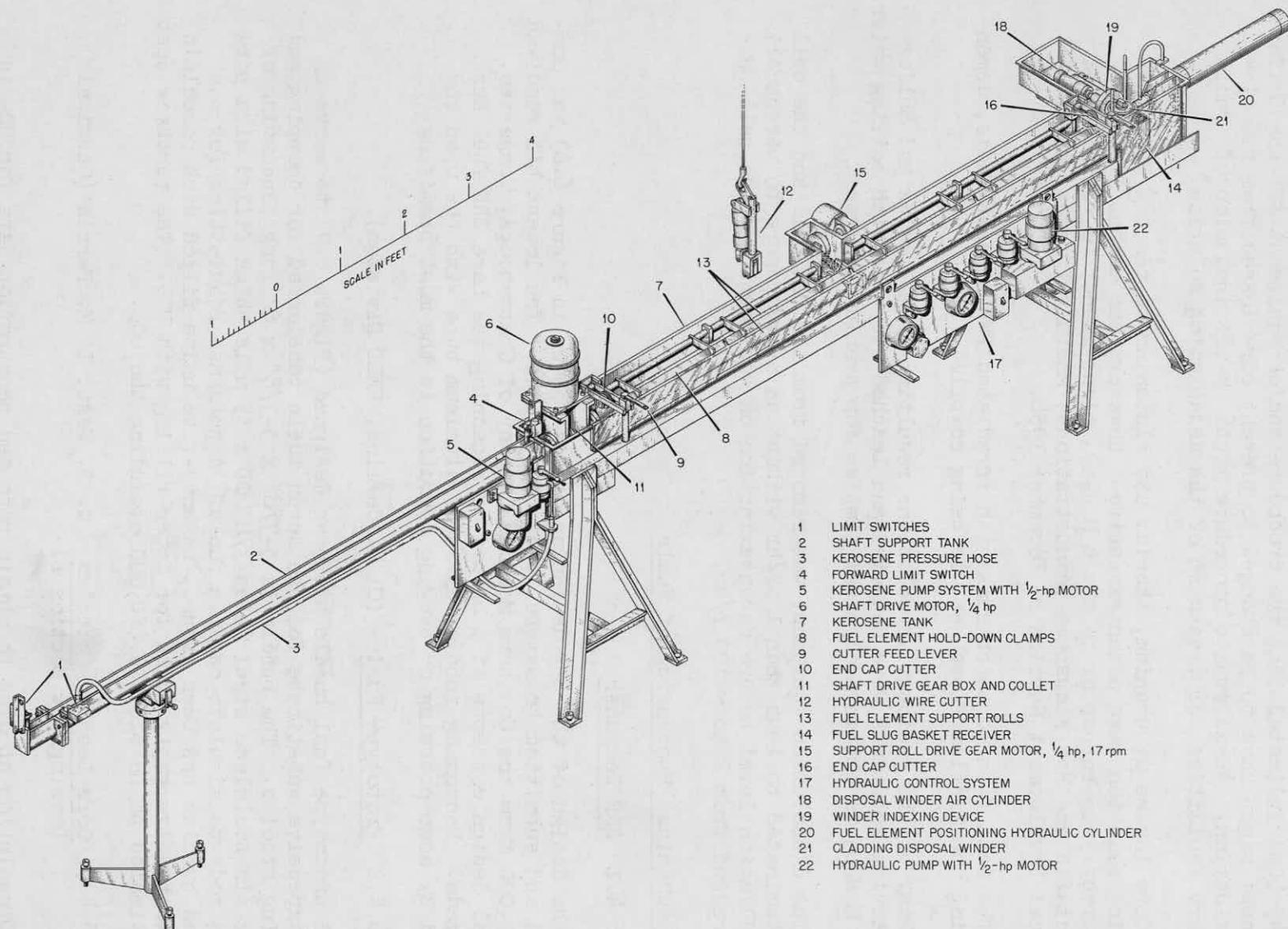


Fig. 6.6. Mechanical Decladding Equipment for SRE (NaK Bonded) Fuel Elements.

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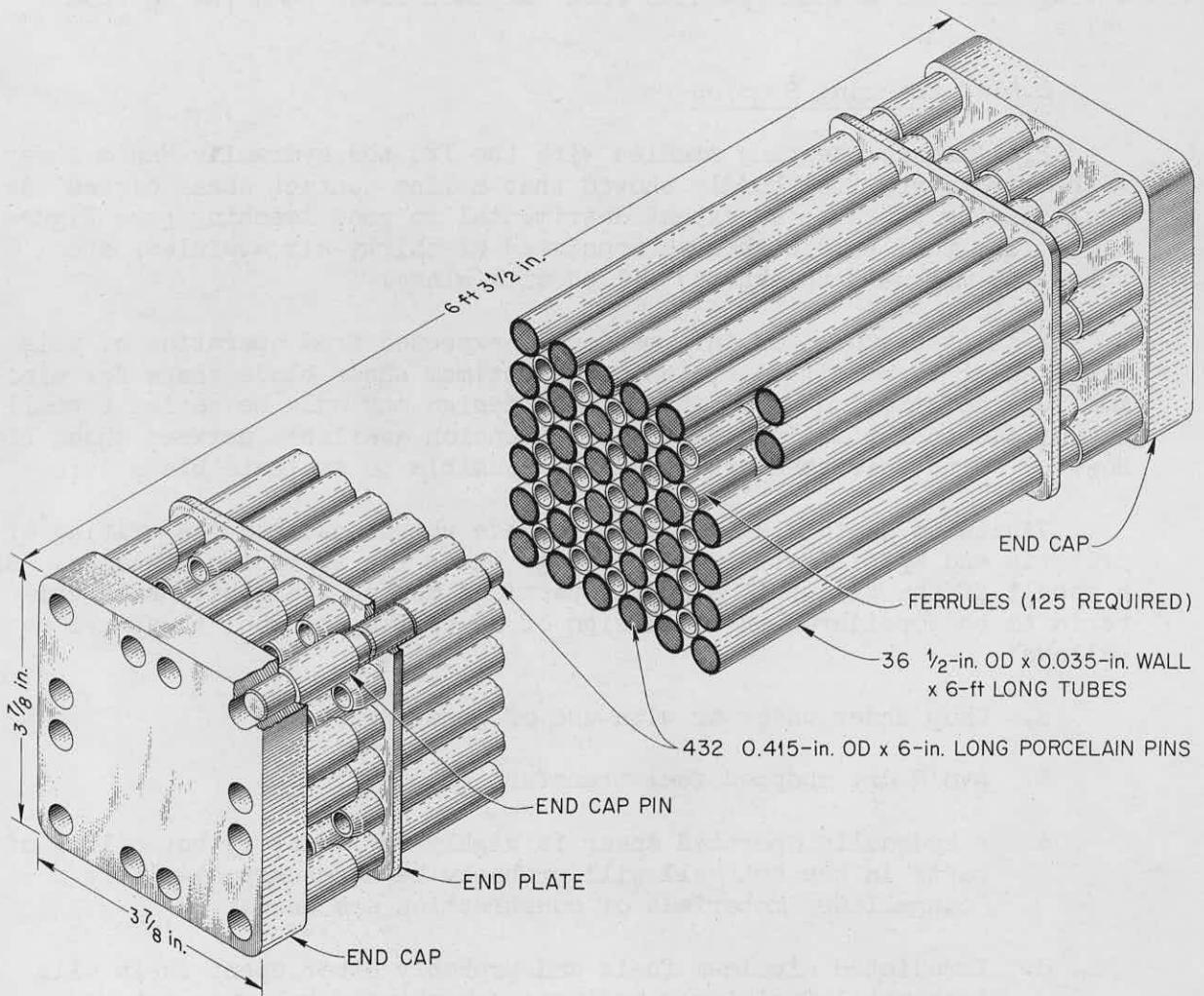


Fig. 6.7 Prototype Fuel Element Mark I

batch or continuous leachers.

Short time (~ 2 min) dissolutions of UO_2 in 10 M HNO_3 gave a solution containing ~ 24.4 g of U per liter. Based on the initial surface area of smooth surfaced right cylinder pellets, an average dissolution rate of 60 $mg/cm^2/min$ was obtained. The partially dissolved pellets were extremely porous with considerably more surface area than the original pellets indicating that the actual reaction rate was much lower than the calculated value.

6.4.4 Shearing Studies

Preliminary shearing studies with the 120 ton hydraulic Manco shear with a prototype fuel bundle showed that a line contact shear closes the fuel bearing tubes to an extent detrimental to good leaching (see Figure 6.8). The fuel bundle sheared consisted of thirty-six stainless steel tubes (35 mil wall thickness) filled with glass.

A limited amount of information is expected from operation of this Manco shear to permit selection of an optimum shear blade shape for minimum tube deformation. The shear blade design may only be varied a small amount due to the limited 4-1/2 in. dimension available between shear blades. However, with this shear it should be possible to evaluate blade life.

Visits to Hanford and Idaho were made which assisted the writing of criteria and specifications for a large shear for spent fuel bundles. As a result of the discussions and inspections during the visit, some criteria to be considered in the design of an ORNL spent fuel shear are as follows:

- a. Chop under water or with use of spray jets.
- b. Avoid dry chopped fuel transfer, if possible.
- c. A hydraulic operated shear is highly satisfactory but oiling of parts in the hot cell will probably be necessary even though "nongalling" materials of construction are used.
- d. Irradiated aluminum fuels and probably other spent fuels will lack metal resiliency and this property probably cannot be counted on to aid mechanical transfer.
- e. A cyclone appears adequate for removing particulate matter picked up from the chopping operation and, in addition, may be used as a discharge cleaner for vacuuming the facility.
- f. General Mills manipulators probably cannot be relied on as a production device. A method of removing them to a separate cell for decontamination and repair is highly desirable.

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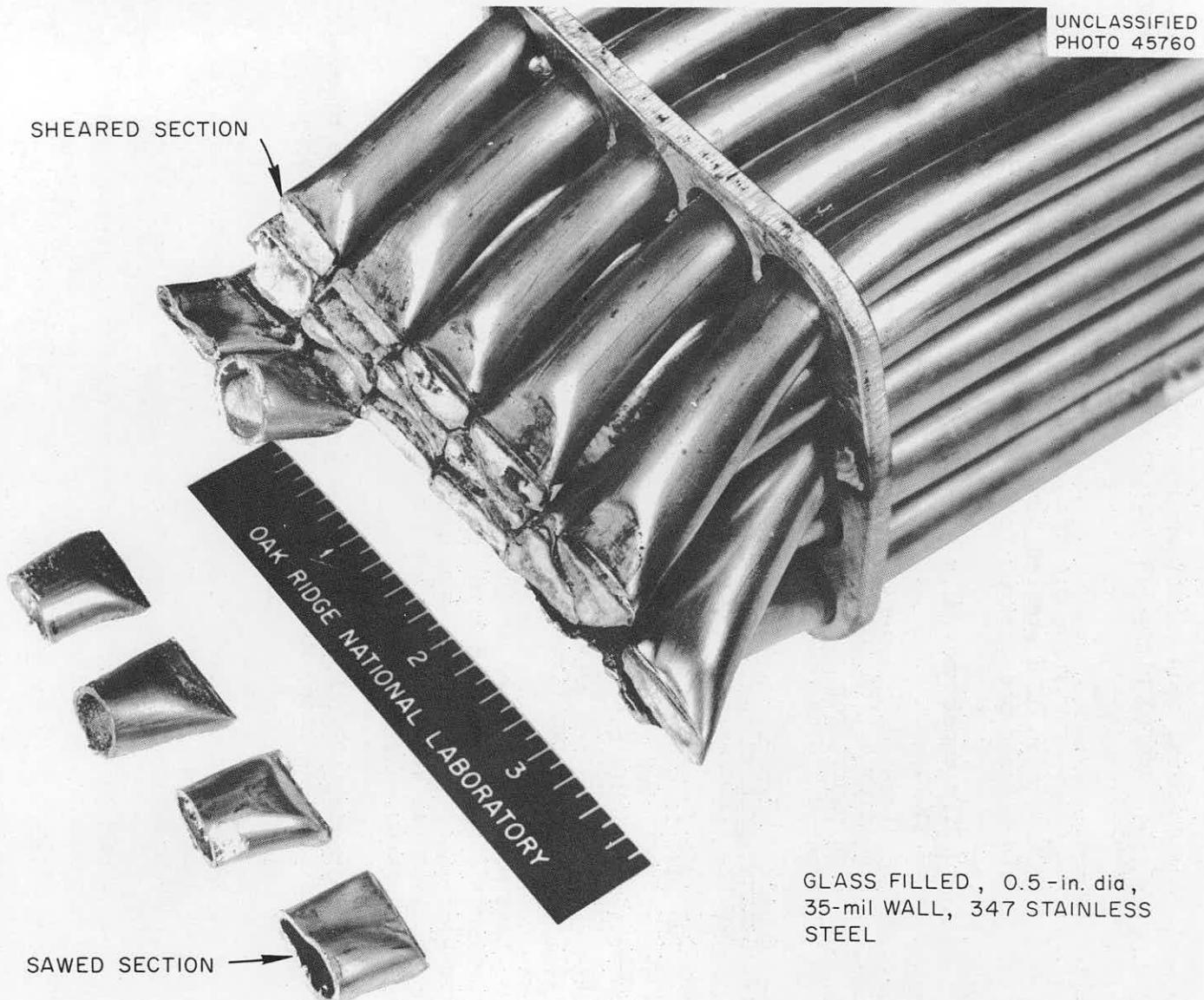


Fig. 6.8. Sheared Section of $3\frac{7}{8}$ -in. Square Prototype Fuel Assembly.

- g. Absolute filters made of only glass fibres should be used on the cell ventilation system.
- h. A mechanical stop cannot be depended upon to determine the length of the sheared piece. A lead screw properly timed gives the best results.
- i. The shape of cutting die has not yet been well defined although some version of a stepped blade looks best. Shearing at a fast rate deforms the sheared face the least.
- j. The life expectancy of a shear blade for shearing bundles is not yet known.
- k. A holding device for clamping spent fuel during the shearing operation cannot yet be specified, although a clamp as close to the shear blade as possible seems desirable.

6.5 Hanford Assistance Solvent Extraction Studies - R. J. McNamee, F. L. Rogers, K. Ladd, R. L. Boles

Two additional Darex-type solvent extraction flowsheets using Hexone as the solvent were investigated during the past month. The results are summarized in Table 6.5. Losses continue to be extremely low. The principal effect noted was that the flooding rate was decreased by approximately a factor of two (from ~ 600 GSFH) by the presence of silicon.

Last month, estimates of the HETS for runs 1 and 3b were presented, approximated by a trial and error calculation. Since equilibrium studies have been made, these values have been recalculated. It was found that the previous values (6-12 ft) were too high. The corrected values are 1.9 ft for both runs 1 and 3b.

A memorandum (ORNL CF 59-1-29) was written summarizing the results of the Hanford Assistance Program as of the end of December, 1958.

Table 6.5. Hanford Assistance Runs

Run No.	Feed Composition (M)					Scrub Composition (M)					Feed:Scrub Solvent	Through-put	% U Loss	HETS (ft)	Flooding Rate (GSFH)
	UNH	H ⁺	Na ₂ Cr ₂ O ₇	NaNO ₃	SS	Si	ANN	H ⁺	Na ₂ Cr ₂ O ₇	Flow Ratio	(GSFH)				
3e	0.45	0.3*	0.2	0.9	0.9	0.011	1.3	0.15*	0.01	1:0.3:2.06	268	0.0027	1.2	333	
3h	0.4	0.2*	0.2	1.1	0.8	0.016	1.0	0.12*	0.008	1:0.24:2.48	-	-	-	295	

*Acid deficient.

8.0 WASTE PROCESSING

M. E. Whatley

8.1 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 to solids for ultimate disposal. This report contains the results of the current runs as well as all runs reported previously using high level waste in the hot cell, Building 4507.

8.1.1 Reduction of High Level Waste to Solids

The purpose of this series of experiments was to determine the amount of fission products evolved when different types of wastes were dried and calcined. 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 first to boil 200 ml of waste solution to dryness and subsequently to calcine the dried solids at 700°C. The bomb was vented to an off-gas train which collected the activity. A condenser removed the condensibles, 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 because it allowed evaluation of the behavior of the evolved gases and radioactivity and is not necessarily recommended as a scheme for plant use.

Purex high level waste was used for the calcination evaluation tests. Three types of feeds were prepared:

- a. Purex waste neutralized with NaOH.
- b. Purex waste neutralized with NaOH, with clay added to minimize leaching of fission products.
- c. Acid Purex waste.

Purex waste was neutralized with 500 g of NaOH per liter. The resulting mixture was calcined at 750°C. The fission product evolution was about the same amount as the neutralized Darex waste reported earlier (Table 8.1).

To neutralized Purex waste clay was added the following materials to reduce possible leaching of fission products with water. The formula (supplied by the Waste Group of the ORNL Health Physics Division) for the waste mix was:

194 g of Ga. Kaolinite
15 g of H_3BO_3
28 g of NaOH
200 ml of H_2O
100 ml of waste solution

The formula was difficult to mix. The resulting solid volume after heating to 770°C was 3 to 5 times greater than the neutralized waste solid volume.

After the waste solid was cooled it was leached with 200 ml of cold water. The leachate after 24 hr contained 1×10^8 cts/min/ml β activity and 1×10^7 cts/min/ml γ activity (Table 8.2). The activity level in the leachate did not increase significantly in 8 days of leaching.

Acid Purex waste was reduced to a solid with no material added. The amount of fission product evolved was about the same as from the reduction of the neutralized waste (see Table 8.1).

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

Type of Feed	Gross β in Feed, cts/min/ml	Gross γ in Feed, cts/min/ml	% of Total β in Condensate	% of Total γ in Condensate	% of Total β in Caustic Scrubbers	% of Total γ in Caustic Scrubbers	% of Total β Evolved	% of Total γ Evolved
Darex ^a	9×10^9	1×10^{10}	2×10^{-2}	3×10^{-2}	6×10^{-3}	3×10^{-2}	3×10^{-2}	6×10^{-2}
Darex ^a	9×10^9	9×10^9	2×10^{-3}	5×10^{-3}	4×10^{-5}	4×10^{-4}	2×10^{-3}	5×10^{-3}
Sulfex ^a	6×10^9	6×10^9	2×10^{-2}	3×10^{-1}	1×10^{-4}	8×10^{-5}	2×10^{-2}	3×10^{-1}
Purex ^a	8×10^9	8×10^9	3×10^{-3}	1×10^{-3}	3×10^{-5}	5×10^{-5}	3×10^{-3}	1×10^{-3}
Purex ^{a-c}	2×10^{11}	2×10^{11}	5×10^{-3}	1×10^{-2}	7×10^{-6}	1×10^{-7}	5×10^{-3}	1×10^{-2}
Purex ^d	8×10^9	8×10^9	5×10^{-1}	7×10^{-1}	1×10^{-3}	3×10^{-3}	5×10^{-1}	7×10^{-1}
Purex ^d	2×10^{11}	2×10^{11}	2×10^{-3}	3×10^{-3}	8×10^{-6}	6×10^{-6}	2×10^{-3}	3×10^{-3}

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

b. Possibility of contamination.

c. Clay added to waste.

d. Acid waste.

Table 8.2. Composition of Leachate from Reduction
to Solids Test with Clay Added to Minimize
Leaching of Fission Products

	Volume, ml	Gross β	Gross γ	Sr	Ce	Cs	Ru	Zr-Nb	TVRE
		cts/min/ml							
Feed	100	4×10^{11}	4×10^{11}	1×10^{10}	4×10^{10}	4×10^9	2×10^{10}	1×10^{11}	5×10^{10}
Condensate	240	3×10^7	6×10^7	1×10^5	9×10^4	3×10^6	5×10^7	5×10^6	8×10^4
Leach									
24 hr	200	1×10^8	1×10^7	9×10^7	2×10^6	6×10^6	1×10^6	4×10^6	2×10^7
48 hr		1×10^8	9×10^6						
72 hr		2×10^8	5×10^7						
96 hr		7×10^7	7×10^7						