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CHEMICAL TECHNOLOGY DIVISION
UNIT OPERATIONS SECTION
MONTHLY PROGRESS REPORT
NOVEMBER 1956

OAK RIDGE NATIONAL LABORATORY
OPERATED BY

UNION CARBIDE NUCLEAR COMPANY

A Division of Union Carbide and Carbon Corporation

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CHEMICAL TECHNOLOGY DIVISION

UNIT OPERATIONS SECTION

MONTHLY PROGRESS REPORT

November 1956

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Note: The primary objective of this report is the monthly distribution of experimental data as acquired during that period in the course of engineering studies. Much of the data is of preliminary nature, and therefore, reasonable care should be exercised in its application. You are invited to contact the individual authors for substantiation of the data.

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SUMMARY

CHEMICAL ENGINEERING RESEARCH

Preliminary experiments with the three-stage pump hydroclone solvent extraction contactor have established that the approximate stage efficiency obtainable with a system acetic-acid-water hexane is nearly 100%. The experimental results agreed with values predicted from the theoretical effect of backmixing and the assumption of 100% contact efficiency for centrifugal pumps.

EXCAR

UF₆ with a tap density of 1.9 gm/cc can be briquetted to a reground tap density of 3.6 gm/cc with 9 tsf pressure. Sulfate-mercury Excar product was bomb reduced to metal and a maximum yield of 89.8% of theoretical was reported by Mallinckrodt Chemical Works.

FLUOROX

3.1 Fluidized Oxidation Studies

Results of three of a series of five UF₆ oxidation runs in the fluidized bed reactor are reported. Runs were from 1 1/2 hr to 6 hr in duration at temperatures of 575°C to 733°C. Qualitative corrosion data indicate inconel may be a satisfactory material of construction under carefully controlled conditions, where a resistant scale can be formed and maintained. Off-gas samples indicated the presence of UF₆.

The conversion reaction was assumed to follow pseudo first order kinetics and variation of the reaction velocity constant with temperature was estimated as $k = \exp(16 - \frac{17000}{T})$. An extrapolation of the experimental data by this method indicates the half time for the reaction to be about 1 hr at 700°C. Discussions of probable chemical reactions, feed preparation, reactor operation and control, dust losses and solid sampling techniques are also included.

3.2 Substrial Oxidation Studies

Three runs have been completed in a revised moving bed reactor using pellets as feed material. The non-availability of satisfactory feed material precluded good bed movement and acceptable levels of oxidation.

The oxidation obtained in the second run (using carbon dust) resulted in a decrease in the uranium IV content of 55.5% of the feed to 21.0%. The corresponding data for the third run (using carbon monoxide) were 32.5% to about 5%. The substitution of carbon monoxide for carbon in the form of finely divided particles results in improved temperature control and bed movement.

HR FUEL AND BLANKET PROCESSING

A-Loop - Quantitative plating out of ZrO_2 from $Zr(SO_4)_2$ UO_2SO_4 solutions was demonstrated in an extended test. Zirconium oxide when added as a solid did not plate out and removed, by erosion, plated oxide.

Flange Tests - The loop for testing flange assemblies with belleville springs was completed; load deflection curves were obtained for various configuration of belleville springs.

Solids Production - Seven, 200 g, batches of simulated fission and corrosion product solids were produced for development studies.

Hydroclone Development - Two, 0.16 in.-dia hydroclones for use on loops P-2 and P-3 were tested for flow rate, pressure drop and efficiency relationships.

Pressurizer Tests - No spontaneous reactions were observed for steam and $2H_2-O_2$ mixtures where the hydrogen-oxygen gas concentrations were less than 50% of the total mixture.

Blanket Processing Loops - P-1 loop construction will be completed by the end of November. Tests of the P-2 loop pressurizer indicated that good mixing could be obtained between gas and liquid if the inlet extended 2-in. into the vessel. Tests of the core vessels showed that proper placing of a baffle in the vessel would allow the gas accumulating in the vessel to escape to the outlet.

Electrolytic Production of H_2-O_2 - The stainless steel electrode used in testing electrolytic H_2-O_2 production in UO_2SO_4 showed a corrosion rate of greater than 4000 mpy. The method looks attractive if a suitable electrode material can be found.

ION EXCHANGE

The 36 in.-dia resin test loop was pulsed with a slip water ratio of 1.5, using 80 psi head from the hydraulic accumulator system. The resin moved 18 in. in a 24 in.-dia section in 6 sec. A 5 in.-dia. Higgins type contactor is being designed for the Y-12 scrap recovery program.

METALLEX

The large scale contactor for production of thorium metal at the rate of pound quantities/day is undergoing revision to correct certain equipment inadequacies revealed by preliminary tests.

POWER REACTOR FUEL REPROCESSING

Zircex⁴ Zircex rates have been obtained and emissivities calculated for Zircaloy-2 and U-2r alloys up to 60 wt % uranium. For all alloys studied, a plot of the logarithm of the reaction (hydrochlorination) rate versus reciprocal temperature is roughly linear. The reaction rate at a given

temperature increases with increasing uranium content. The effect of increasing uranium content on reaction rate becomes less as the temperature increases; for example, at 400°C, the spread in the reaction rates for the various alloys is an approximate factor of 4, whereas at ~700°C the spread is only an approximate factor of 1.5.

The emissivity of zircaloy-2 and 7.3% U-Zr alloy increases with increasing temperature. For 20, 40, and 60% U-Zr alloys the emissivity coefficient tends to increase with increasing uranium content and decreases with increasing temperature. Calculated natural convection coefficients for the various alloys varied from 2.3 Btu/hr ft² °F to 3.7 Btu/hr ft² °F.

Darex - A glassware continuous dissolver capable of producing up to 10 gallons of product/hr is being installed in Cell 1-A.

HCl Distillation - One stripping run was made in the 4-in. pyrex 12 bubble cap column. Results await the development of a successful analytical technique for determining Cl⁻ ion in the 30-100 ppm range in the presence of dissolved U, Cr, Ni, and Fe.

Mechanical Processing

Decladding Studies - The decladding of X-10 aluminum clad aluminum-silicon bonded natural uranium slugs was demonstrated successfully on a Mackintosh-Hemphill rotary straightening and derodding machine equipped with a unique guide developed at ORNL. Four to five passes through the machine using moderate pressure gave the best decladding.

Disassembly Studies - The disassembly of spent power reactor fuels by electrical discharge cutting technique continues to look promising. Successful cuts were made with disc and wire electrodes.

A conceptual design of a cut-off saw for removing end boxes and separating spent fuel assemblies into sub-assemblies has been made.

Materials Evaluation

Corrosion Studies - Titanium is unsuitable for a hydrochlorinator. Hastelloy-B and A-nickel are unsuitable as a vessel for the dissolution of UCl₃ in HNO₃. These two metals will resist a boiling solution of UCl₃ in water satisfactorily.

Pulse Column Interfacial Crud Removal - Satisfactory removal of synthetic cruds from an organic-aqueous interface was successfully demonstrated by pumping the interfacial cruds through a Fulflo fibre glass filter with CPD-2 Lapp pump.

Radiation Damage Studies - A 6-in. dia tube has been installed in the LITR for high flux gamma radiations. The tube has not been calibrated.

Waste Studies - The possibility of mixing dried (calcined) waste solids with asphalt to produce a non-leachable mass for storage in the ground is being explored.

1.0 CHEMICAL ENGINEERING RESEARCH

J. C. Bresee

Pump-Hydroclone Solvent Extraction Studies

1.1 Introduction

Peter C. Rekameyer, Donald Cameron, W. G. Sisson

A three stage pump-hydroclone solvent extraction contactor has been described in a previous report (CF-56-9-127, pages 6-9). The contactor was constructed to test the operation of a mixer-settler unit using centrifugal pumps as mixers and hydroclones as settlers and to study the control problems associated with the operations. Tests carried out with countercurrent flow of a solvent phase (hexone) and water in the absence of mass transfer have shown that the unit performs as would be predicted from earlier hydroclone separation studies. (CF-56-3-171, CF-56-6-177, pages 8-10).

Preliminary experiments have recently been conducted with the system acetic acid-water-hexone to establish the range of stage efficiencies to be expected during a detailed test program. It has been predicted mathematically that if the centrifugal pumps operate as approximately equilibrium mixers, the separation efficiency of the hydroclones should result in only slight reduction in the unit stage efficiency due to backmixing (CF-56-4-210, pages 7-13). The preliminary experiments were designed to test the assumption and the mathematical prediction.

1.2 Solvent Extraction Experiments

A total of twelve runs were made with the contactor. The first six runs were carried out with a single pump mixer and either one hydroclone or a dual-clone separator. In a single mixer-settler stage "backmixing" would have no effect on stage efficiency. The tests were conducted to detect differences between the two product stream concentrations and equilibrium values due to pump mixing efficiency.

It was found that, independent of flow rate over the range 1.2 to 2.4 liters/min, the product concentrations were at equilibrium. (Table 1.0 and the equilibrium curve in Figure 1.0).

The second set of six runs were made with three pump mixers and three dual-clone separators operated as a three-stage countercurrent solvent extraction system. For all six runs (as well as for the single stage runs) acetic acid was extracted by pure hexone from approximately 1 molar acetic acid in water.

TABLE 1.0
Summary of Results of Pump-Hydroclone Solvent Extraction Studies

Run	Aq. Feed Con.	Inlet Flow Rates		Contactor Operation		Product. Concs.		Product Clarification		Apparent Material Bal. Deviation	WTS *	Stage efficiency (%)	
	M	HAc	(liters/min.)		Mixer stages	Sep. stages	M	HAc	Vol. Per cent	100 (Δ HAc Rate)			
			H ₂ O	Hexane						H ₂ O			Hexane
1 a	0.82 ↓ 0.925 ↓		0.39	0.84	1	1	0.440	0.209	82	89	+ 15	1	100
1 b			0.58	1.30	1	1	0.424	0.211	83	93	+ 16	1	100
1 c			0.76	1.61	1	1	0.422	0.212	82	93	+ 11	1	100
2 a			0.44	1.02	1	2	0.436	0.226	100	96	+ 27	1	100
2 b			0.56	1.33	1	2	0.415	0.211	100	93	+ 19	1	100
2 c			0.76	1.62	1	2	0.431	0.217	83	96	+ 16	1	100
3 a			0.43	1.02	3	6	0.114	0.282	64	91	- 6	-	-
3 b			0.58	1.33	3	6	0.185	0.294	96	99	+ 6	(3.2)	(100 +)
3 c			0.74	1.65	3	6	0.146	0.288	79	89	- 5	-	-
3 d			0.43	1.02	3	6	0.190	0.310	100	100	0	3	100 (See Fig. 1.0)
3 e		0.58	1.35	3	6	0.200	0.325	100	95	+ 4	(3.2)	(100 +)	
3 f		0.84	1.79	3	6	0.140	0.300	76	95	+ 23	-	-	

* Number of theoretical stages.

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FIGURE 1.0
PUMP-HYDROCLONE SOLVENT EXTRACTION
GRAPHICAL CALCULATION OF NUMBER OF THEORETICAL STAGES
RUN NO. 3d

20. 10. 1964

Three of the six tests (Runs 3a, 3c, and 3f) were inconclusive due to poor phase separation in the product streams and probable unsteady state operation as indicated by material balance calculations. Due to the mutual solubility of hexone in water and vice versa, a material balance calculated by inlet flow rates and molarity changes results in a positive deviation, when the deviation is calculated as follows:

Apparent material balance deviation=

$$\left[\frac{O (C_{oo} - C_{oi}) - A (C_{ai} - C_{ao})}{O (C_{oo} - C_{oi})} \right] 100$$

where O = hexone feed rate, liters/min.

A = aqueous feed rate, liters/min.

C_{oo} = hexone product acetic acid conc., M.

C_{oi} = aqueous product acetic acid conc., M.

C_{ai} = aqueous feed acetic acid conc., M.

For a single stage contact with the concentrations and flow rates used here, the deviation is quite large (15-20%). For three stage countercurrent operation the deviation should be much smaller (0-5%) but still positive. The two negative AMBD's (Runs 3a and 3c) and the one large positive value (Run 3f) indicate unsteady state operation and the poor aqueous product clarifications (64-79%) verify that the contactor was probably operating unsteadily at the time samples were taken.

The results of the three remaining runs (Runs 3b, 3d, and 3e) indicate that the three stage contactor operated with a stage efficiency very nearly 100%. The calculational method was not sufficiently precise to obtain exact efficiency values, but the consistency of the three results suggests that similar results would be expected in any case.

The calculational method is illustrated in Figure 1.0. It was assumed that the operating line was straight and that the four entering and leaving stream concentrations determined the average flow ratios and therefore the operating line position. In the illustrated calculation, remarkable and probably fortuitous agreement was obtained between the experimental results and the results predicted from three theoretical stages of operation.

The tests will be extended to a wider range of variables, and the equipment will then be tested with uranium extraction into hexone and TBP.

2.0 EXCER

C. W. Hancher, R. O. Payne

The purpose of the Excer program is to produce reactor and gaseous diffusion grade (C.A.P. Specification) green-salt (UF_4) by a low temperature, aqueous method. The process consists of the following major process steps: (1) feed material preparation (2) uranium reduction and conversion (3) physical modification of product and (4) dehydration (Fig. 2.1).

2.1 Electrolytic Reduction and Conversion

It was noted in a previous report that UO_2Cl_2 could be electrolytically reduced to UCl_4 in an aqueous solution and then converted to the precipitate, $UF_4 \cdot 3/4 H_2O$ by reaction with aqueous HF at 90°C or above. This modification of the reduction and conversion steps of the Excer process has this advantage of the elimination of mercury and slurry handling from the electrolytic cell, but the possible disadvantage of lower tap density of the product.

A standard water treatment cell, designed by Ionics, Incorporated (Figs. 2.2 and 2.3) has been adapted for use as a chloride conversion cell. When a conversion cell is used for reduction UCl_4 or $U(SO_4)_2$ can be produced. Each has a set of advantages and disadvantages. Chloride ion is easier to remove after precipitation but materials of construction for it are more difficult, whereas when sulfate is used stainless steel is acceptable for a material of construction, but the SO_4^{2-} ion is difficult to remove from the $UF_4 \cdot 3/4 H_2O$ slurry system.

2.2 Brigetting

$UF_4 \cdot 3/4 H_2O$ produced by chloride reduction and external precipitation or the simultaneous mercury-precipitation method often does not have the tap density required by specification (3.0 g/cc or greater). If this low tap density material (1.5 - 2.8 g/cc) is pressed the density may be increased to greater than 3 g/cc (Table 2.1). A hydraulic press of 10 ton capacity is now available with a die of 1/2 sq. in. area.

2.3 Dehydration

UF_4 analyzing about 0.4% water was re-run at a terminal temperature of 450°C. The water content was not reduced. A discussion of the procedure for analysis of water in UF_4 was held. The procedure appears to inadequate for analyzing in the range of 0.5% water content or lower. A new procedure suggested by Mallinckrodt personnel is being set up.

The practical dehydration limit appears to be the water content of UF_4 in equilibrium with the atmosphere. Mallinckrodt reports that their UF_4

PROPOSED FLOWSHEET FOR MODIFIED EXCER PROCESS
USING A CHLORIDE NON-PRECIPTATING TYPE CELL

Figure 2.1

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One Cell Pair (May Be Repeated)

Fig. 2.2 Ionics Designed Excer Electrolytic Cell

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Fig. 2.3 Two Cell Pair Ionic Designed Excer Cell

TABLE 2.1

Results of Briquetting Studies for Densification
of Excer UF₆ Product

Before Briquetting Tap Density (1.9 gm/cc) Water (0.45%)		
Pressure (psi)	Billet Density (gm/cc)	Reground Tap Density (gm/cc)
2000	3.7	2.3
4000	3.9	2.6
6000	4.0	2.9
8000	4.2	3.0
10000	4.4	2.8
12000	4.6	2.6
14000	4.7	3.0
16000	4.9	3.4
18000	5.0	3.6

with a surface area of 0.2 to 0.3 square meters per gram has a water equilibrium value of 0.02% water. Excer mercury product has surface area of 1-2 square meter per gram. Therefore, its equilibrium value may be greater than 0.02% water.

The equilibrium water value will be determined experimentally as soon as possible.

Preliminary tests have been made using a fluidized bed for dehydration (Fig. 2.4). No chemical results have been obtained.

2.4 Bomb Reduction

The final test of UF_4 produced by any method is how well it will reduce to metal. A 22 lb lot of sulfate-mercury Excer product was sent to the Uranium Division, Mallinckrodt Chemical Works. They fired 10, 2-lb bomb reductions. The results were so scattered that few conclusions could be reached except that more tests are needed (Table 2.2). The highest per cent reduction was 89.8% of theoretical reduction.

Figure 24
EXPERIMENTAL FLUIDIZED BED
OXIDATION REACTOR

NOTE: 7 THERMOCOUPLES SPACED AT 4 INCH INTERVALS WELDED TO OUTER REACTOR SURFACE OVER HEATED LENGTH.

28-9/19/56

TABLE 2.2

Results of Preliminary Bomb Reduction of Mercury-Sulfate

Excer Product

Bomb No.	UF ₄ to be Reduced	% Theoretical Metal Yield*
1	U ⁺⁶ 73.10%	46.9
2	U ⁺⁴ 68.9%	88.8
3		0.0 (metal shot)
4	AOI 0.18%	43.5
5	H ₂ O 0.60%	86.0
6		78.4
7	Hg 500-50 ppm	0.0 (metal shot)
8		74.2
9	SO ₄ ⁻² 0.10%	89.8
10	F 22.9%	61.3

3.0 FLUOROX

3.1 Fluidized Oxidation Studies - J. B. Adams, D. H. Newman, S. D'Urso, R. Wolff, P. Rekenmeyer

Results of 3 of a series of 5 UF_6 oxidation runs in the fluidized bed reactor* are now complete. Runs were of 1/2 hr to 6 hr duration at temperatures of 575°C to 733°C.

3.1.1 General Operational Procedure

A suitably sized feed (35 x 100 mesh) was prepared by 3 stage size reduction in crushing rolls of 3 x 8 mesh UF_6 pellets accompanied by interstage screening and recycle of oversize to the rolls. The pellets were prepared at ORNL in the experimental moving bed reactor by starch-reduction HF-hydrofluorination of pelleted UO_3 . From a 70 lb pellet sample 32 lb were recovered as 35 x 100 mesh material.

Runs were initiated by charging the reactor with 3000 g batches through a 1/2-in. nipple in the top flange of the reactor and bringing the reactor to the desired operating temperature in a nitrogen atmosphere thus assuring a dry feed. The reactor temperature was allowed to stabilize under nitrogen fluidization at the operating flowrate, about 35 cfm metered at 70°F and 1 atm. At this time, a feed sample was withdrawn from the reactor. Over a period of 1 to 5 min. nitrogen was gradually replaced with oxygen, maintaining a constant rate of flow, until the fluidizing gas was oxygen only. Samples of the reactor contents were then taken from time to time until the run was terminated.

Control of fluidization was achieved by observation of pressure drop and pressure drop fluctuation across the unit, by the temperature differential between the thermocouple (#8) in the center of the bed and the thermocouple (#7) at the top of the cone, and by visual observation of the bed surface through a sight glass.

The quality of fluidization obtained was poor, being characterized by slugging. The slugging action and the resultant pressure drop fluctuations provided a convenient indication of the onset and maintenance of fluidization. Mixing and heat transfer were apparently good; however, since the temperature differential between thermocouples #7 and #8 read within from 5 to 20°C of each other if the bed was fluidized, and from 50 to 200°C apart if the bed was not fluidized. This phenomenon was utilized as the major method of control. The sight glass allowed direct observation of movements of the bed surface as well as allowing a visual estimate of how much dusting was occurring at any time.

3.1.2 Solids Sampling

Samples were removed from the fluidized bed reactor during operation through a plug valve into a capped nipple.

* UNOP Monthly Report for July 1956. (CFR-56-7-170).

The stagnant solids contained in the takeoff nipple were blown back several times with dry nitrogen to ensure complete removal and mixing with reactor contents. This was also done periodically during normal operation to reduce errors in conversion measurements due to material being kept out of the reaction zone. A fresh sample was then drawn and allowed to cool in the takeoff nipple. After sufficient cooling the sample was transferred through the valve to the lower capped nipple and finally withdrawn directly into a sample bottle after closing the valve.

3.1.3 Dust Entrainment

Some trouble with excessive dusting was encountered during certain periods and the off-gas lines were vacuumed clean after each run to prevent lines from clogging. However, only 3.5 lb of solids were removed from the vacuum cleaner after over 100 hr of operation. Part of this resulted from experimental runs on drying $UF_4 \cdot 3/4 H_2O$. The majority of the remaining dust was blown from the bed during several attempts to operate at high gas flow rates (50-60 ft³/hr at 70°F and 1 atmosphere), during a valve failure in which a full cylinder of oxygen discharged through the bed in a few seconds and at times during solid sampling when excessive nitrogen flow was used in blowing back the sampling line. Actual dust entrainment rates during normal operation was not known but were probably low. However, installation of dust removal equipment capable of returning all dust in the reaction zone - cyclones or porous metal filters - is under consideration to provide for more accurate material balances and less troublesome operation.

3.1.4 Corrosion

Test specimens of inconel were placed in the reactor during recent runs in an attempt to measure corrosion rates. In addition, the reactor itself served as a specimen.

Results from the tests were inconclusive because of widely varying operating conditions.

The most reliable qualitative evidence was provided by the internal thermowell. Except at the bed interface a dense, adherent, scale had formed with little or no attack evident beneath it. At the bed interface level, however, the thermowell was badly attacked. Inspection of the reactor indicated scale formation on all interior surfaces with some attack evident at the bed interface and below. Further tests under more carefully controlled conditions will be run during the next period of operation.

Corrosion rates in the reactor are a most important consideration in the development of the UF_4 oxidation process. If inconel is not resistant, resort to a refractory liner, as was done in the previous moving bed reactor work at ORNL, and other methods of heating may be required. However, extreme temperature peaks that occur at times in moving bed reactors are not encountered in correctly operated fluid beds.

of the off-gas stream.

3.1.5 Gas Sampling

In recent runs, results of which are not complete at this time, samples of the reactor off-gas stream from the downstream of the dust filter were metered through a miniature cold trap. The trap consisted of a glass U-tube packed with glass-wool and placed in a dry ice, trichloroethylene bath. The inert gas discharge from the trap was metered through a small rotameter. Each trap was taken to the analytical laboratory while still frozen where the sample was hydrolyzed, washed from the tube, and the liquid analyzed for uranium. Of six samples analyzed each contained uranium all of which was present in the hexavalent form. The largest amount found was about 1 g. Observation of one of the traps indicated the presence of a white solid which gave the appearance of subliming from one part of the tube to another on application of body heat. One tube which was not purged of moisture-bearing air before being put into the dry ice, trichloroethylene bath contained bright orange-yellow patches of solid matter after sampling was completed. Application of body heat to the tube immediately on removal from the bath resulted in a violent reaction at the surface of the glass, producing a small area too hot to touch while the body of the tube remained at the bath temperature. The present samples combined with previous observations at various times of uranium compounds volatile at 25°C, and analysis of solid residues supply sufficient indirect evidence of formation of UF₆ during oxidation of UF₄.

From data taken during sampling periods a rough estimate of UF₆ concentration in the main off-gas stream was made. At the present time it is estimated that only 10 to 20% of the expected yield of UF₆ appeared in the off-gas stream. However, presentation of the results will be made in a future report after more accurate analysis of the data has been completed. Parasitic reactions of UF₆, discussed later, indicate why less than 100% yield is to be expected in the present equipment.

3.1.6 Experimental Data - Interpretation of Chemistry and Kinetics

A summary of analytical data taken during Runs 1, 2, and 3 are given in Table 3.1.

The study of the chemistry and kinetics of UF₄ oxidation requires consideration of the following reaction

assumed to represent the stoichiometry of the conversion.

Additionally, when using an impure feed material as in the present runs, the equations

are assumed to represent pertinent side reactions.

TABLE 3.1
Analysis of Samples

	No.	Condition	Elapsed Time (Hrs.)	U Total (%)	U ⁴⁴ (%)	AOI (%)	F (%)
Run I 575°C	1	N ₂ Flow (several hours)	-	76.70	65.49	8.34	20.9
	2	O ₂ Flow (low rate)	1/12	75.68	64.41	9.99	21.1
	3	O ₂ Flow	1/3	75.86	61.01	7.38	20.9
	4	O ₂ Flow	5/6	75.83	59.59	2.92	20.8
	5	O ₂ Flow	3	75.40	57.32	2.14	20.9
	6	O ₂ Flow	5	75.84	56.29	0.26	20.8
	7	O ₂ Flow	6	76.00	55.37	0.76	20.8
Run II 690°C	1	N ₂ Flow (3 hr)	-	75.80	65.05	4.06	21.5
	2	O ₂ Flow	1/2	75.20	56.60	0.99	21.2
	3	O ₂ Flow	1	75.37	55.00	0.86	20.9
	4	O ₂ Flow	1 5/6	75.17	53.22	0.41	20.3
Run III 733°C	1	N ₂ Flow (3 hr)	-	75.38	65.77	5.52	21.0
	2	O ₂ Flow	1/2	75.34	49.28	0.94	20.3

Further, such parasitic reactions as

may occur at various times and parts of the equipment.

The original reactor charge in each run contained moisture picked up during feed preparation. Hydrolysis of UF_4 could have occurred during the heatup period. On the other hand water removed during dehydration may hydrate UF_4 and UO_2F_2 dust in the external piping and on the dust filter.

Possibilities for elimination of product UF_6 by parasitic reactions are abundant, mainly by corrosion and hydrolysis reactions and under certain conditions by reaction with uranium oxides and uranium tetrafluoride.

Based on an ion balance and the assumption that % AOI represents UO_2 , only, the feed compositions are estimated as shown in Table 3.2.

The quality of green salt available was obviously poor.

An examination of the analytical data suggested the following method of studying the kinetics of the oxidation reaction:

Oxidation of UO_2 to U_2O_8 occurs rapidly as does fluorination of oxides by UF_6 formed simultaneously in the conversion reaction. The net effect is to convert all UO_2 in the feed to UO_2F_2 within a short time after startup by the overall reaction $\text{UO}_2 + \text{UF}_4 + \text{O}_2 \longrightarrow 2\text{UO}_2\text{F}_2$.

TABLE 3.2
Calculated Composition of Feed Samples

Component	Run 1	Run 2	Run 3
% UF_4	76.7	80.4	80.3
% UO_2F_2	14.5	13.9	12.4
% UO_2	8.3	4.1	5.5
% HF	0.6	0.4	0.1
% Unaccounted	- 0.1	1.2	1.7

The immediate drop in %U⁺⁴ and %AOI (Table 3.1 and Fig. 3.1) on admitting oxygen to the reactor supports this hypothesis. Therefore, it is assumed that the bed will consist of UF₄ and UO₂F₂ only after a relatively short period of operation.

Laboratory studies* have indicated that experimental results may be represented as a pseudo first order reaction. Constant surface area per unit weight of UF₄ was assumed and rates of vaporization of UF₄ and UO₂F₂ and effect of oxygen partial pressure were neglected.

Therefore - $\frac{d(w)}{dt} = k(w)$ is assumed to apply, where

w is the weight of UF₄ in the reactor at any time.

Since the total weight of the bed varies with time and was not known, a function not involving bed weight directly was developed** to represent w UF₄.

Given:

W_{t0} = total weight of bed at t₀

W_t = total weight of bed at t, t > t₀

w₀ = weight of UF₄ in bed at t₀

y = % of UF₄/100 = 1.32% U⁺⁴/100

$$W_t = W_{t0} - 1/2 \frac{352}{314} (w_0 - w) + 1/2 \frac{32}{314} (w_0 - w)$$

$$\text{but } y = \frac{w}{W_t} = \frac{w}{W_{t0} - 0.51 (w_0 - w)}$$

$$\text{and } w = \left(\frac{y}{1 - .51 y} \right) (W_{t0} - .51 w_0)$$

* ORNL-2216 by L. M. Ferris

** Derived by George Jensen, MIT Practice School

Fig. 3.1 $\% U^{+4}$ vs. Reaction Time

Since $(w_{t_0} - .51 w_0)$ is a constant and drops out during integration between limits, the function $\frac{y}{1 - .51 y}$ may be used to represent w .

$$\int_{w_1}^{w_2} \frac{dw}{w} = k \int_{t_1}^{t_2} dt$$

$$\ln \frac{w_1}{w_2} = k (t_2 - t_1)$$

Therefore a plot of $\frac{y}{1 - .51 y}$ vs. t allows an estimate of k .

Figure 3.2 illustrates the application of this technique. Extrapolations of data plotted in Fig. 3.1 were used as an aid in determining the slopes.

An Arrhenius plot, k vs. $\frac{1}{T}$, given in Fig. 3.3, represents the variation of k with temperature as $k = A \exp.(\frac{-E}{RT})$.

An estimate of the constants based on the best visual straight line fit to the present limited data gives

$$\ln k \approx (16 - \frac{17000}{T})$$

$$\text{or } k = \exp. (16 - \frac{17000}{T})$$

Fig. 3.2 Graph for Determination of Reaction Velocity Constant

Fig. 3.3 Correlation of Reaction Velocity Constant with Temperature

3.2 Industrial Oxidation Studies - H. W. Franz^{*}, R. H. Toye^{**}, D. H. Newman,
W. G. Sisson

Experiments using a 4-in. dia moving bed reactor have been carried out to study the controlled oxidation of uranium tetrafluoride to produce the hexafluoride and uranyl fluoride. The object of these experiments was to augment the insufficient data previously obtained and to correlate process variables with maximum yields.

The moving bed reactor (Fig. 3-3, Drawing #13982 of Report No. CF-56-4-210) has been modified to make the vertical axis of the preheat section coincide with that of the reactor proper, to obtain a straight vertical downward bed movement. Oxygen in controlled amounts was introduced within the preheated bed in the presence of carbonaceous material.

Moving Bed Studies - During November, the revised moving bed reactor was used initially as a drying device to eliminate residual moisture and volatile ammonium and fluorine compounds from selected composited batches of pellets. Batches varied in weight from about 25 lbs to about 150 lbs. These dried pellets were then used as feed material for the oxidation experiments. Three oxidation runs were undertaken, the first two of which had decolorizing carbon dusted on the pellet surfaces, while during the last run a slight flow of carbon monoxide was introduced within the reactor as a substitute for the decolorizing carbon.

In general, feed composition was not satisfactory in that the amounts of uranium compounds other than the tetrafluorides were somewhat excessive. The decolorizing carbon used in the first two runs tended to segregate which caused erratic internal bed temperatures. The first two runs were terminated when the feed material within the reactor proper fused and bed movement ceased. Excessive fluctuating reactor pressures were also experienced during the first run. These excessive pressures were corrected during the last two runs by applying vacuum to the last unit of the off-gas system.

The third run was an extended arc of about 22 hr duration in which the carbon content of the feed was controlled by a known amount of carbon monoxide flowing into the reactor preheat section. Reactor pressures were also somewhat controlled by the use of vacuum applied to the exit of the off-gas system. The first half of the third run proceeded satisfactorily. During the last half of the third run, however, bed movement became erratic and finally ceased when the second batch of feed material reached the reaction zone.

Table 3.3 shows the chemical composition of the several feeds which were used in these three runs. In all runs the pellet feed was screened so that pellets of about 6 to 3 mesh were used.

* Kennecott Copper Corporation

** Koppers Company, Incorporated

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TABLE 3.3

Reactor Feed Material

Run No.	Feed No.	Lbs. Used	Total U	U ¹⁴	F	AOI	C	
							Original	Added
108-1	F 1	104.5	75.66	73.2	23.4	19.19	.12	none
	F 2	28.5	78.58	29.31	12.0			
	F 3	132.5	76.11	55.0	18.5		.05	0.4
108-2	F 1	133.0	(1)77.16	20.24	14.8	5.87		
	F 2	21.0	(2)75.50	34.11	16.8	5.33		
	F 3	12.5	(3)75.78	41.39	17.9	7.66		
	F 4	84.0	(4)76.11	55.0	18.5		.05	0.4
108-3	F 1	115.5		32.48	14.7	13.1		
	F 2	48.5						
	F 4	117.0	(5)	68.87	21.9	2.6		

(1) Was PR 1 through PR 10 of run 108-1. See Table 3.4.

(2) Was P 1 of 108-1. See Table 3.4.

(3) Was P 2 of 108-1. See Table 3.4.

(4) Was remainder of F 3 of run 108-1.

(5) Remainder of F 1 of 108-1.

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Table 3.4 shows the chemical composition of the several products resulting from the pre-run and from the run proper of the controlled oxidation of the feed material.

Table 3.5 contains the more important data under which the three oxidation experiments were performed.

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TABLE 3.4

Reactor Products

Run No.	Product No.	Lbs.	Total U	U ²³⁵	F	AOT
108-1	PR1 through PR5	98.0				
	PR 6	12.0			16.0	
	7	6.5			13.9	
	8	6.5			14.3	
	9	3.0			13.6	
	10	8.0			16.1	
	P 1 (1)	23.5			16.8	
	P 2 (2)	15.0			17.9	
108-2	PR 5	17.0	76.03	44.71	20.1	4.96
	6	7.5	75.39	30.20	17.0	5.51
	7	7.5	76.86	23.44	16.5	6.49
	8	8.0	77.00	21.28	14.5	3.46
	P 1	8.5	76.64	27.81	16.4	4.50
	2	7.0	76.56	20.98	16.5	3.26
	3	6.5	76.24	28.31	17.7	1.85
	4	9.0	75.98	30.64	16.7	2.06
	5	10.0	76.60	29.46	16.6	2.29
	6	8.5	74.46	29.45	16.4	2.24
	7	1.0	76.24	33.59	16.7	2.44
(1) P 1 and P 2 was product made from 108-F-3. Remainder of 108-F-3 was removed from reactor often. Bed stopped moving and was reserved for 108-2-F-4						
108-2	R 1	37.5				
	2	28.0				
108-3	P 1 through P 12	88.5		4.98		3.02
	P 14 through P 24	69.0		53.0		0.79

TABLE 3.5

Test Conditions for First Three Oxidation Experiment

Run No.	Preheat Temp. (°C)	Bed Temp. (°C)		Reactor Pressure (in. of Hg)	Feed Rate (lbs/hr)	Product Discharge Rate (lbs/hr)
		Above O ₂	Below O ₂			
108-1	550 - 700	625-850	600-750	4.1 - 9.6	20.0	-
108-2	600 - 700	Approx. 615	550-775	0.2 - 1.8	20.0	-
108-3	700 - 750	815 - 850	Approx. 700	0.1 - 1.3	20.0	12 - 15

4.0 HR FUEL AND BLANKET PROCESSING

E. O. Nurmi

Equipment development and engineering evaluation studies of components for the HRT Fuel and Blanket Reprocessing Plant were continued. Results of high pressure loop tests flange test hydroclone design evaluation preparation of simulated corrosion product solids, and hydrogen-oxygen explosion limit explorations are reported.

4.1 HRT - Core Fuel Processing Studies: Behavior of Zirconium Salts in Core Fuel Solution in A-Loop

R. W. Horton, R. D. Arthur, G. E. Woodall, D. A. McWhirter

An extended test (500 hr) demonstrated that zirconium will plate out almost quantitatively on metal surfaces as the oxide when introduced into .04 M UO_2SO_4 solution at 300°C as zirconium sulfate solution. A suspension of zirconium oxide which had been externally precipitated was used as a feed solution under the same conditions and essentially no zirconium oxide "plating out" resulted.

The 500 hr test period during which zirconium sulfate was used as feed was intended to determine the "equilibrium" point at which zirconium oxide scale would remain at a constant thickness due to erosion, thermal stress, or flaking off for other reasons. If this point were reached it was expected that zirconium recovery from the system would equal input from that time on. During this part of the test 34 g of zirconium (as the sulfate) were introduced into the system and 6 g were recovered from sampling and by collection in the hydroclone underflow pot. The "equilibrium" point was not reached. In the remainder of the test 15.4 g of zirconium were added to the system as zirconium oxide suspension and 13.7 g were recovered from sampling and the underflow pot.

Tables 4.1 and 4.2 show analyses of feed, loop, and drain samples for the zirconium sulfate and zirconium oxide portions of the test. A zirconium material balance is shown in Table 4.3 and analyses of scale samples make up Table 4.4. Photographs of the circulating pump are included as Figs. 4.1 and 4.2.

The test was carried out in "A" Loop at 300°C and 1600 psi. The loop proper is constructed of 347 S. S. Schedule 80 0.5 in. pipe, with a by-pass circuit including a hydroclone, heater, and surge tank. Circulation is provided by a Westinghouse canned rotor pump rated at 100 ft, head at 1 gpm. The pump was operated on 80 cycle current during the test resulting in a flow of 3.6 gpm in the main system and 0.35 gpm in the branch circuit. The resulting velocities were 5 fps in the main loop and 3 fps in the branch.

TABLE 4.2

Analytical Data for ZrO_2 Portion of LR-50

Conditions of test:

Loop temperature 300°C
 Preheater " 310°C
 Loop pressure 1600 psi
 Loop flow 3.8 gpm (5 fps) (80 cycle power supply)
 Preheater flow 0.35 gpm (3 fps) (This circuit includes hydroclone)

Feed and sampling rate 100 ml/30 min.

Feed: .04 M UO_2SO_4 , .02 M H_2SO_4 plus 2.0 g Zr on ZrO_2

Date	Time	U, g/kg	H^+ , Mol.	Ni, g/kg	Zr, mg/kg	Remarks:
11-12	1700	8.51	0.016	0.028	102	Loop Samples
11-12	2100	8.56	0.019	0.020	68	
11-12	Avg. of 10				106	
11-13	0100	8.86	0.023	0.017	70	
11-13	0500	9.44	0.025	0.017	30	
11-13	0900	9.40	0.023	0.019	260	
11-13	1230	9.04	0.027	0.015	52	
11-13	1400	9.04	0.028	0.014	50	
11-13	1500	9.04	0.026	0.014	58	
11-13	2300	9.30	0.029	0.010	132	
11-14	0500	9.30	0.029	0.011	140	Plain feed (No ZrO_2 used in this series)
11-14	0700	9.30	0.029	0.013	152	
11-13	0430 to	Avg. of 12			119	
11-14	0700				225	
11-14	1650				198	
	1655				200	
	1700				130	
	05				223	
	10				88	
	15				165	
	25				120	
	35				113	
	45				135	
	55				113	
	1825				78	
	1855				95	
	1925				123	
	1955					

TABLE 4.2 (Continued)

Sample	Total Solids (g)	% Zr (solids)	Zr (g)	% U (solids)	% Fe (solids)
1st UF Pot Drain Note # 1	14.17	57.93	8.21	2.15	1.29
2nd UF Pot Drain	2.80	66.16	1.85	1.32	1.36
3rd UF Pot Drain	1.63	61.59	1.00	1.12	1.31
4th UF Pot Drain	0.97	67.32	0.65	1.00	1.38
1st UF Pot Rinse Note #2	1.68	63.37	1.06	1.57	1.95
2nd UF Pot Rinse	0.52	67.54	0.35	1.72	2.15
3rd UF Pot Rinse	0.33	61.00	0.20	1.38	1.68
Loop Drain	2.40	61.33	1.47	1.56	2.0
<p>Note # 1 Four underflow pot volumes were drained in one hour, with the volume being replaced in the system with plain feed at the end of each drain.</p> <p>Note # 2 Three drains were made as above, 24 hours later, no intervening additions to the system.</p>					

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TABLE 4.3

Zirconium Material Balance, LR-50Total Input1st half (as $Zr(SO_4)_2$)

48.7 liters feed at 0.69 g Zr/liter 33.66 g Zr

2nd half (as ZrO_2)

7.7 liters feed

2.0 at 1.71 g Zr/liter

2.0 at 2.26 g Zr/liter

2.0 at 2.02 g Zr/liter

1.7 at 2.02 g Zr/liter

15.42 g Zr

Total 49.08

Total Recovered1st half ($Zr(SO_4)_2$ feed)

Samples 48.2 liters 0.666 g Zr

UF Pot Drains 5.240 g Zr

Loop Drains 4.855 g Zr

Scale from pump 5.089 g Zr

15.850 g Zr 15.85 g Zr

2nd half (ZrO_2 feed)

Samples 7.7 liters at 0.7 g Zr/liter 0.540 g Zr

UF Pot Drain 11.710 g Zr

UF Pot Rinse 1.610 g Zr

Loop Drain 1.470 g Zr

15.330 g Zr

Total 31.18

1st half recovery 15.85 ÷ 33.66 = 0.47

2nd half recovery 15.33 ÷ 15.42 = 0.99

Overall recovery 31.18 ÷ 49.88 = 0.635

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TABLE 4.4

Results of Electrolytic H_2 - O_2 Production TestMaterials: H_2SO_4 Solution of 2 ml of conc. H_2SO_4 per 100 ml of H_2O UO_2SO_4 Solution with 270 g U/l and 25 mol% excess SO_4^{2-}

Temperature: 20 to 60°C

Solution	Frequency (Cycles/min)	Voltage (volts)	Current (Amps)	Time to Collect 283 cc (sec)	Current Efficiency (cc/min-amp)	Gas Analyses (Volume %)	
						O_2	H_2
H_2SO_4	0	6	13.0	110	11.9	23.1	75.0
		6	11.75	155	9.4	- -	- -
		6	10.0	230	7.4	- -	- -
		6	14.0	172	7.0	- -	- -
		6	12.0	240	5.9	- -	- -
	216-218	6	14.0	225	5.4	14.0	88.5
		6	13.0	233	5.6	- -	- -
		6	12.0	275	5.2	- -	- -
		12	18.0	156	6.0	14.4	85.6*
UO_2SO_4	0	6	3.5	665	7.3	- -	- -
	-	12	9.0	194	9.2	23.5	76.5*
	60	6	4.0	1096	3.9	23.7	76.3*
	63	6	4.0	1030	4.1	22.4	76.4
	120	6	4.0	1083	3.9	20.7	79.3*
	216	12	8.0	985	3.1	18.6	81.4*

BLANK OF AIR TO CHECK O_2 ANALYSES

20.3 - -

* These values are 100-% O_2 since previous analyses showed no residue after H_2 and O_2 were removed.

TABLE 4.4

Analysis of Scale from Pump, LR-50

Sample	% Zr	% Fe	% Cr	% Ni	% U	% SO ₄
I	61.3	6.45	0.29	0.17	5.5	2.47
II	52.0	7.27	0.32	0.09	4.8	2.87
III	67.5	5.88	0.34	0.06	4.5	1.87

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Photo-18995
UNCLASSIFIED

Pump Impeller
Scale hard and
dense .002 in.
thick

Thermal Barrier
Scale same as on
impeller

Scale soft
and light
colored

-45-

Fig. 4.1 Pump Impeller and Thermal Barrier

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-46-

Fig. 4.2 Pump Volute

The feed solutions were made up from a stock of 0.04 M UO_2SO_4 ~0.02 M in H_2SO_4 to which zirconium sulfate (or oxide) was added. The oxide suspension was maintained with an air sparge in the feed tank. Both types of feed were injected into the high pressure system with a Lapp diaphragm pump. During the zirconium sulfate portion of the test a zirconium concentration of 0.7 g/kg was the highest that could be maintained without excessive hydrolysis in the feed tank. The oxide suspensions averaged 2 g Zr/kg.

Sulfate feed was injected at a rate of 100 ml/hr and samples were drawn at the same rate. No samples contained visible amounts of dissolved solids. The oxide feed was pumped in at the rate of 200 ml/hr, in two portions, and samples drawn at the same rate. All samples taken contained suspended solids, but no difference was noted whether samples were taken with the feed pump running or not running.

The zirconium sulfate portion of the test continued for 492 hr (actual operation) in a 5-week period. At the end of each 5-day work week the equipment was shut down and the hydroclone underflow pot was emptied and the loop drained. All solids from these drainings were recovered. At the end of this portion of the test, the Westinghouse pump was removed from the loop and opened for examination (results of examination described in another paragraph).

After reassembly of the pump, the oxide portion of the test continued 40 hr, during which time 18.4 g of zirconium oxide were pumped into the system and ~0.8 g were removed in samples. The remaining 17.6 g would result in a solids concentration of 105,000 mg/kg in the hydroclone underflow pot if all the solids were accumulated there. During this time the concentration of solids in loop samples had increased gradually from 100 mg/kg to 200 mg/kg (Table 4.2). It was felt that the capacity of the underflow pot had been reached at this time, and solids feed was stopped. A series of samples at short intervals, during which the sample volume was replaced with solids-free feed, followed immediately. The decrease in solids concentration in these samples was greater than would be expected from the dilution effect, indicating a possibility that the hydroclone was removing solids from the system even though the underflow pot concentration was very high. The loop was shut down for 8 hr at this time, then re-started.

After 1 hr of circulation (cold), the hydroclone underflow pot was drained in the following manner: (1) 200 ml (slightly more than 160 ml volume of pot) was withdrawn and volume in loop replaced with plain feed (no solids); (2) 10 minutes later the above procedure was repeated; (3) a third drain was made after a 10 minute interval; (4) the final 200 ml drain was made after a 30 minute interval. The analytical results of these drains are included in Table 4.2. The most significant figure is the 85,000 mg/kg solids concentration of the underflow pot shown in the initial drain. Some portion of the solids removed in subsequent drains was undoubtedly separated

from the circulating system during the 10 min intervals (which were equivalent to 6 loop volumes past the hydroclone), but the decreasing amounts in consecutive samples indicate that the underflow pot concentration was more than 85,000 mg/kg at the end of the test run. If the loop concentration at the end of the solids feed period is taken as 200 mg/kg of solids, then a concentration factor of 425 was reached.

The 98% zirconium material balance for the oxide portion of the test is a positive demonstration of the possibility of circulating preferred solids in a high temperature UO_2SO_4 solution without "plating out", and of the ability of the hydroclone to remove these solids.

At the end of the zirconium sulfate test period, a leak through rear bearing closure of the Westinghouse pump developed during a loop-cooling period. As the pump at this time had operated 2000 hr (over 1500 80 cycle power) at 300°C without inspection, it was decided to dis-assemble the pump and make an inspection.

The pump head and impeller were found to be completely covered with a thin layer of hard, dense scale, ranging in color from brown to a light tan (Fig. 4.1 and 4.2). An area of 3 square in. was laid off on the impeller and the scale was scraped off and weighed. The 0.229 g recovered indicated 0.10 g/in.² of scale, and assuming a density of 3, it was calculated that the thickness was 0.002 in., which agreed with visual estimates. A total of 8.25 g of scale were scraped from various areas in the pump and analyzed. The various portions were divided in three groups based on appearance, Group I being the hard, dense material, and II and III softer and lighter colored. The analyses (Table 4.4) indicate roughly the same chemical composition in all samples.

Inspection of pump parts revealed very little evidence of corrosion or wear. Bearing clearances averaged ~ 0.002 in., which is the same as when new. The thermal barrier labyrinth showed very little wear. The thermal barrier was not removed from the pump head, and the thermal barrier seal ring was not inspected. This seal was tight both before and after the pump inspection.

In reassembling, a gold gasket was used in place of gold-plated stainless for the rear bearing flange. The flange bolts were tightened to 90 ft lbs of torque and the joint was pressure tight. The main flange gasket - stainless steel, gold-plated, made at ORNL shop - was re-used. The initial closure at 400 ft lbs torque was not tight. The bolts were retightened to 420 ft lbs and the seal was satisfactory.

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4.2 High Pressure Flange Tests

C. C. Haws, J. Beams, R. C. Early, F. N. McLain

A test loop has been assembled for testing belleville springs for possible use in the Chemical Pilot Plant. Emergency B loop repairs needed to carry out this test have been completed. Adequate data for evaluation of a promising spring system will be collected during the coming month.

Preparatory to assembling test flanges for the belleville springs, load deflection curves were obtained for a single spring and for a system of three springs operating in parallel. The data obtained are plotted in Fig. 4.3. Each data point shown represents an average obtained from the three loading cycles conducted on each spring system. Note that a single spring gave a straight line up to a 4000 lb load, indicating that operation was below the yield point. Design of the spring specified a 3300-3800 lb operating range. The departure of the parallel spring system from a straight line is probably due to sliding inter-spring friction. The system of 3 springs in parallel was empirically selected for the present test on the basis of this chart and the knowledge that bolt loadings within the 10,000-15,000 lb range would be encountered. Other systems will be tested and evaluated for the proposed service.

Photographs of interest to the work are included. Figure 4.4 shows the test fixture upon which the springs were tested. A Baldwin test machine in the Metallurgy Division was used to apply the loadings and to measure the deflections. A typical flange assembly, using three springs in parallel, is shown in Fig. 4.5. The test loop consisting of three flange pairs with spring assemblies loaded (nominally) to 7000, 9000, and 11,000 lb is shown in Fig. 4.6. The fourth flange assembly in the upper center of the picture is a standard CP joint which was included for comparative purposes.

4.3 Production of Simulated HRT Fission and Corrosion Products

N. A. Brown, R. D. Arthur, J. Beams, R. C. Early, V. L. Fowler,
F. N. McLain, D. A. McWhirter, G. E. Woodall

During this month Unit Operations has produced seven batches of simulated HRT fission and corrosion products. In addition, two batches of solids produced by Chemical Development Section A were processed in the autoclave at Chemical Development's request.

Of the seven batches of solids produced, one batch was blanket solids and was produced by the procedure outlined in UNOP October Monthly Report (CF #56-10-83). The other six batches were core solids. Four of these batches were produced according to the procedure first given in UNOP August Monthly Report (CF #56-8-215). The remaining two batches were made using a modified procedure, which, it was hoped, would result in a halide-free product.

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Fig. 4.3 High Pressure Flange Test
Test Fixture
Test: Single Belleville
Springs arranged
in series.
UNOP 11/15/56

Photo-18833
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Fig. 4.4 High Pressure Flange Tests
Typical flange assembly showing
use and location of Belleville
Springs.

UNOP

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Fig. 4.5

High Pressure Flange Tests

Belleville Spring Test Loop

FIG. 4.6

HIGH PRESSURE FLANGE STUDIES

Load-Deflection Characteristics for Two Arrangements of Belleville Springs

Room Temperature

No Lubricant

Unop.

11/15/56

The procedure for the production of the halide-free solids was as follows. All glassware used in the process was cleaned using a chromic acid cleaning solution followed by two H_2O rinses, a concentrated NH_4 rinse and two more H_2O rinses. All other equipment (stainless steel) was washed with concentrated NH_4OH and rinsed two times with H_2O . 257.5 g of ferric sulfate, 240 g of zirconium sulfate, and 156 g of chrome potassium sulfate were mixed in 25 liters of demineralized H_2O and were heated to $60^\circ C$. The slurry was held at $60^\circ C$. The slurry was held at $60^\circ C$ while ~ 4 NH_4OH was added to a pH of 7 to precipitate the hydroxides, after which the slurry was agitated ~ 15 min. The slurry was allowed to settle and the liquor was decanted off. The solids were then treated two times by adding 4 liters of concentrated NH_4OH , agitating the mixture for $1/2$ hr, allowing the solids to settle and decanting the liquor off. This was followed by 4 H_2O washes of 10 liters each, agitating for 15 min. and allowing $3/4$ hr² for settling.

After these washes, 10 liters of H_2O was added, the solids slurried, and the pH of the slurry adjusted to 6.5 to 7.0 by the addition of 4 M H_2SO_4 . The solids were again allowed to settle and the supernate removed. Four additional H_2O washes of 10 liters each were made as described above. The solids were then removed from the mixer and filtered, using filter paper prewashed with concentrated NH_4OH .

The solids were then slurried in 1 liter of 10 g/liter UO_2SO_4 and the pH of the slurry adjusted to ~ 2 using concentrated H_2SO_4 . The slurry was then placed in the autoclave and heated at $300^\circ C$ for 10^4 hr. An over-pressure of 500 psi of O_2 was used. This treatment converted the hydroxides to the oxide form.

4.4 Production of Zirconium Oxide for A-Loop Tests

N. A. Brown, R. C. Early, F. N. McLain, D. A. McWhirter, G. E. Woodall

Two hundred g of zirconium oxide was prepared for use in A-Loop tests. This material was prepared from zirconium sulfate, 575 g of which was required. The procedure used for the treatment was the same as that for processing core solids and is described in UNOP August Monthly Report (CF #56-8-215).

4.5 Dissolution of Simulated HRT Fission and Corrosion Products in Sulfuric Acid

N. A. Brown, S. D. Clinton, R. D. Arthur, J. Beams, R. C. Early, F. N. McLain, D. A. McWhirter

During the past month four batches of simulated HRT fission and corrosion products were used in two tests of the efficiency of H_2SO_4 for dissolving the solids. The equipment used was the same as that described for the second H_2SO_4 dissolution test in the September UNOP Monthly Report (CF#56-9-127).

In both of these tests two batches of solids were placed in the glass column and 80 g of U as UO_2SO_4 was added. This mixture was then evaporated to dryness. 10.8 M H_2SO_4 was added, in the first test at a ratio of 5 ml of acid/g of solids, and in the second at a ratio of 10 ml of acid/g of solids.

In the first test, the slurry was boiled at total reflux for 8 hr, after which it was diluted to ~4 M H_2SO_4 . This was followed by 6 hr of refluxing, after which H_2O was taken off to regain an acid concentration of ~10.8 M. Shortly after beginning a second concentrated acid reflux, the column broke and the contents were lost. Observation of the test led to the belief that the acid ratio (5 ml/g solids) was too low and the second test was made at a ratio of 10 ml/g solids as soon as the column could be replaced.

In the second test, the 10.8 M acid-solids slurry was refluxed for 8 hr, diluted to ~4 M H_2SO_4 , and refluxed for 8 hr, concentrated to ~10 M H_2SO_4 , and refluxed 8 hr, and finally again diluted to ~4 M H_2SO_4 and refluxed 6 hr. The dissolution was estimated to be better than 99% complete; however, analytical results confirming this are not yet available.

No additional tests in the glass column are planned at the present time. The tantalum-lined HRP-CP dissolver has arrived and work orders for its installation have been issued. When this installation is complete several dissolution tests will be performed using this equipment.

4.6 HRP-CP-Hydroclone Development Studies

P. A. Haas, V. L. Fowler

Two (2) 0.16 in. dia. hydroclones with dimensions proposed for loops P-2 and P-3 have been given flow rate and efficiency tests. This size was proposed to give a smaller capacity unit to go with the small P-2 and P-3 volumes. The observed capacities were 0.12 gpm for 100 ft of liquid pressure drop (Fig. 4.7). The efficiency of one unit was 48% for the TM-Y ThO_2 for which 0.40 and 0.25 in. dia. units have efficiencies of about 35 and 42%.

Both 0.16 in. dia. units have 0.035 in. dia. overflow ports, 0.050 in. dia. underflow ports, and about 0.032 by 0.050 in. dia. feed ports. The first unit for which tests were completed is a "low pressure" design as shown on drawing D-21435. The other test model includes design features proposed for use with loop P-2 (See drawings D-27009 and D-27010). Two primary features requiring checking are a gold sealing ring and an inverted underflow pot. If these features are acceptable, they will permit draining and removal of the hydroclone and complete disassembly to permit inspection and removal of plutonium.

FIGURE 4.7 FLOW VERSUS ΔP FOR 16 IN. D HYDROCLONES

4.7 HRP-EP-Test Pressurizer Studies with H_2 and O_2

P. A. Haas, V. L. Fowler, F. R. McLain, R. C. Early, J. Beams

The schedule of experiments to study the behavior of H_2 and O_2 in the test pressurizer convection loop has been completed. The results indicate that loop P-2 can be safely operated with the presently proposed conditions. Detailed results for runs TP-10 through TP-15 will be reported in the December Monthly report.

Spontaneous reactions did not occur for $2H_2-O_2$ concentrations below 50%. By electrically heating small nickel or platinum wire coils, explosion type reactions were usually obtained for calculated concentrations of over 30%. Calculated concentrations of 20 to 30% occasionally resulted in rapid reactions. Since about 44 or 48% is reported as a lower explosive limit, the reactions for concentrations calculated to be below this limit probably were due to segregation since the mixing spray nozzle was not used. Also heat losses resulted in cold spots and segregation due to steam condensation.

None of the observed reactions resulted in equipment damage. The final, most severe tests of shock damage to the pressurizer were made by exploding 300 psi of H_2 and 150 psi of O_2 mixed in the pressurizer at below $100^\circ C$ to give essentially 100% concentration. These tests gave sharp reports heard outside the cell wall as compared to the rumbles heard for explosions with steam diluent at $260^\circ C$. Tests with a fast recorder indicated pressure peaks of 800 to 1500 psi at the pressure element. This element is connected by the same size (3/16 in. i.d.) tubing as the main loop lines to the pressurizer in loop P-1. This indicates that the shock waves should not result in excessive pressures in the loop P-1 pump can.

4.8 HRP-Blanket Processing Development Loops

P. A. Haas, S. D. Clinton

4.8.1 P-1 Loop - All of the craft work on the P-1 loop and accessory systems should be completed by November 26. Most of the remaining work centers around the loop instrument panel board and must be completed by the electricians and instrument mechanics. All pipefitting and welding should be essentially completed by November 20. Initial tests using water in the loop should be started during the last week of November.

Three modifications have been proposed for the P-1 loop and are now in the process of being designed. These proposals consist of a facility for exposing metal coupons to the plutonium loop solution, a means for the addition of slurries to the loop, and a by-pass bomb sampling device. Installation of these additions will not begin before the latter part of December.

4.8.2 P-2 Loop Pressurizer - Tests have been completed on a plastic model of the proposed P-2 loop pressurizer to determine the position of the inlet and exit streams which give sufficient mixing without removing any gas. The inlet and outlet ports on the spherical pressurizer are in line with each other and are tangential to the inner spherical surface (Fig. 4.8). A 1/4 in. S.S. pipe was set at various distances into the inlet port, and flow rates through the pressurizer were varied up to 8 gpm. Flow patterns in the pressurizer were observed by using crystals of potassium permanganate.

It was recommended that the end of the S. S. pipe be positioned 2 in. from the top of the inlet port (see dimension on Fig. 4.8). Using this position the inlet stream exhibited good mixing with the liquid in the pressurizer at all flow rates tested (0 to 8 gpm), and at the maximum flow rate the mixing was not turbulent enough to cause any deformation of the liquid surface.

4.8.3 P-2 Loop Core - Tests to determine flow patterns with water and air mixtures in a plastic model of the proposed P-2 loop core have been completed. Initial tests with the spherical core model (Fig. 4.9) showed an accumulation of air at the top of the sphere near the exit stream. A baffle was inserted into the core model to break up this air pocket.

Two of the four different baffles inserted in the core model were successful in allowing the air to escape through the exit stream (Fig. 4.9). Of the two, the baffle with the smaller surface area was recommended for use in the proposed P-2 loop core (see detail of baffle, Fig. 4.9). The insertion of this baffle into the core model increased the pressure drop across the inlet and outlet streams from approximately 3 to 5 cm of Hg at a flow rate of 5 gpm. These baffles were machined from a 1/16 in. thick sheet of lucite.

4.9 Electrolysis as a Method of H_2 - O_2 Addition for Loops P-1 and P-2

P. A. Haas, V. L. Fowler

Electrolysis of a side stream in a high pressure cell has been proposed as one method of adding H_2 and O_2 to loops P-1 and P-2. If the electrolysis of the UO_2SO_4 solution would produce a 2 to 1 hydrogen-oxygen ratio, the gas produced would be an exact continuous replacement of the gas lost by recombination to H_2O . Another possible advantage is the possibility of selecting the electrolysis conditions to maintain the H_2 - O_2 concentrations within a selected range even with variations in recombination rates. Low temperature, low pressure studies were made to check the efficiency of gas production, the effect on the uranium behavior, and the amount of heating and corrosion for proposed electrolysis conditions.

Figure 4.8

Mock-Up of P-2 Loop Pressurizer

----- Position of Successful Baffles
----- Position of Unsuccessful Baffles

Figure 4.9
Mock-Up of P-2 Loop Core

A high pressure electrolytic cell specifically designed for Pu loops (D g. D-26387) was set up to use essentially a square wave of 0 to 4 cycles/sec (Fig. 4.10). The gas produced was collected by displacement of H_2O or UO_2SO_4 solution from gas sample bottles. Gas analyses were obtained and were used along with voltage, amperage, and gas collection rates to calculate current efficiencies. Nickel and U^{+4} concentrations were also maintained.

At frequencies above 1 cycle/sec., current efficiencies based on the volume of gas produced were about 30% for the UO_2SO_4 solution. (Fig. 4.11). The calculated rate of recombination in loop P-1⁽¹⁾ is 0.0381 ft³ STP of H_2 per hr. At the low pressure conditions studied, this rate of H_2 production would require about 9 amperes. The heat introduced into the solution would be about 100 watts.

The amount of U^{+4} buildup during the low pressure electrolysis was negligible. Analyses showed about 1/2% of the uranium present at U^{+4} ; this amount would probably also be reported for pure, unelectrolyzed UO_2SO_4 solution.

Nickel concentrations and the composition of the gas produced both indicate rapid corrosion of the stainless steel. The product gases were 14 to 24% O_2 (Table 4.4 and Fig. 4.12). The difference between these values and the stoichiometric 33% can be considered the oxygen used to oxidize the stainless steel to corrosion products. This would be equivalent to between 1/2 and 1 g of stainless steel corrosion products per hr from the electrolysis cell if it were used to supply H_2 to loop P-1.

The dimension changes of electrodes and the nickel buildup in solutions confirmed the corrosion rates estimated from the concentration of product gas. Electrolysis of UO_2SO_4 solution in a beaker in the laboratory (2) resulted in an average 0.0027 in. decrease in electrode thickness. This loss of 2.8 g of stainless steel agrees with the waste UO_2SO_4 solution concentration of 455 ppm Ni. From measurement of a duplicate electrode, the electrolysis cell electrode lost 0.0046 in. diameter or 1.3 g of stainless steel. This compares well with about 0.2 g of Ni in the H_2SO_4 and UO_2SO_4 solutions. About 7000 cc of gas averaging about 21% O_2 was produced in the electrolytic cell. The 1300 cc of O_2 which was not released as gas $[7000 \cdot .79 - 0.21]$ would be 0.12 g equivalents and would oxidize about 2.5 stainless steel. This agrees very well with 1.3 g removed from one electrode. The electrolytic cell corrosion rates for the conditions studied were 4.320 mpy for the center electrode and 1200 mpy for the cell walls at the H_2 production rate required by loop P-1.

The rapid corrosion of stainless steel 347 electrodes makes their use unattractive for loop P-1 because of the low (~20%) oxygen concentration of the gas produced and the large amounts of corrosion products formed.

(1) CF-56-8-187 P. G. Lafyatis 8/28/56.

(2) Letter from W. J. Clossey to W. E. Unger, dated October 3, 1956.

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- a. SOLUTION RESERVOIR
- b. ELECTROLYTIC CELL (DWG. D-26387)
- c. SPARK PLUG TYPE LEAD
- d. CENTER ELECTRORE
- e. GAS SAMPLE BOTTLE
- f. STORAGE BATTERIES
- g. CAM OPERATED SWITCH-VARIABLE SPEED DRIVE MOTOR
- h. AMMETER
- i. CAM AND SPRING

VOLUMES:

CELL: 130 cc

SAMPLE BOTTLE: 283 ML.

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FIGURE 4.10 BP LOOP ELECTROLYTIC CELL-LOW PRESSURE TEST APPARATUS

FIGURE 4.1 CURRENT EFFICIENCY OF ELECTROLYSIS

FIGURE 4.12 COMPOSITION OF ELECTROLYSIS GAS

At the loop temperature of 260°C , corrosion rates would probably increase and the current efficiency would decrease. Titanium electrodes require a large overvoltage with 24 volts passing less than 1 ampere during 1 room temperature test. Electrolysis with higher voltages resulted in a dense gray precipitate (probably titanium oxide) throughout the UO_2SO_4 solution.

5.0 ION EXCHANGE

C. W. Hancher, J. S. Taylor

The Ion Exchange Program was started to develop necessary equipment and chemical processes to improve existing processes. Ion exchange, fixed bed or continuous, is a unit operation of great flexibility. Often performing difficult separating or concentrating steps with ease and savings of equipment costs, chemicals and manpower.

The problems now under active consideration are:

(1) the 36-in. dia. resin test loop for hydraulic studies of larger contactor, (2) ore processing feasibility study for low-grade western ores (0.1-0.5% U_3O_8), (3) the 3-in. dia. contactor for uranium-plutonium separation in the Purex plant, (4) the Y-12 scrap recovery for processing normal and enriched scrap of the 3-5% uranium range.

5.1 36-Inch Resin Test Contactor

The 36-in. resin test contactor problem has suffered because of fabrication errors. After the contactor was filled with 125 cu. ft. of resin the outlet screens broke. When all of the resin was taken out of the contactor, so that the screens could be removed it was found that the 6 mesh back-up screen had been left off during fabrication and only the fine 60 mesh screen was holding the resin.

The outlet screens were repaired and the contactor was put back into operation. During the first attempt to pulse the bed, it moved smoothly, 18-in. in the 24-in. dia. section in 6 sec. with 80 psig in the hydraulic accumulator system. (Plan A, Fig. 5.1). The slip water ratio was approximately 1.2-1.5 to 1.0. However, one of the accumulator tanks immediately filled with resin. The 24-in. dia. surge section screen had ruptured. The screen was fabricated correctly. The replacement screen will have added reinforcing, to withstand the pressure drop across the screen sections.

5.2 Ore Processing

The Grand Junction Report of Tests II, and III, September 7-19, 1956, will soon be completed.

Drawings are being completed for the 200 ton/day contactor. This contactor may be rubber lined with metal screen inserts.

Samples of UO_3 yellow-cake were taken during the Grand Junction Test, (Table 5.1).

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HYDRAULIC ACCUMULATOR SYSTEM FOR 36" RESIN TEST LOOP

PLAN - A

Figure 5.1

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C - Check Valve

HYDRAULIC ACCUMULATOR SYSTEM FOR 36" RESIN TEST LOOP

PLAN - B

Figure 5.1

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TABLE 5.1

Yellow-Cake Sample from the Grand Junction Test II and III

Material	PPT. # 1 %	PPT. # 2 %	PPT. # 3 %	PPT. # 4 %	PPT. # 5 %	PPT. # 6 %	PPT. # 7 %
U ₃ O ₈	77.1	76.1	80.1	77.7	79.8	79.8	77.1
V ₂ O ₅	0.05	0.03	0.02	0.006	0.02	0.02	0.02
PO ₄	0.79	0.88	1.02	1.29	1.03	1.11	1.11
Mo	0.39	0.14	0.11	0.11	0.16	0.17	0.14
B	0.00047	0.00036	0.00017	N11	N11	N11	N11
Cl	0.0004	0.0005	0.0005	0.0003	0.0004	0.0003	0.0004
F	0.22	0.12	0.14	0.10	0.13	0.14	0.15
Cu	0.06	0.04	0.05	0.15	0.01	0.14	0.11
As	0.064	0.021	0.014	0.012	0.025	0.014	0.029
SO ₄	15.4	15.2	12.2	14.7	11.3	13.2	14.4
NH ₃	1.83	2.00	1.98	1.99	1.58	1.53	2.12
Fe	0.10	0.14	0.14	0.29	0.15	0.18	0.22

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5.3 Product Purification

The modification of 3-in. dia Higgins ion exchange contactor for plutonium-uranium isolation has been completed.

The contactor is being prepared for testing by the MIT Practice School. They will test uranium removal by using a solution of iron-uranium instead of plutonium-uranium.

5.4 Y-12 Scrap Recovery

The assistance program for the Y-12 Scrap Recovery problem has been continued. Jointly, at their expense, we are designing a 5-in. dia Higgins type ion exchange contactor (Fig. 5.2). This contactor will be used on normal and slightly enriched scrap material. It has been proposed that the scrap material be ground to -100 mesh, leached in concentrated H_2SO_4 , CaO added to complex the fluorides, and ion exchanged similar to ore slurries. Two molar HNO_3 will be used as a stripping agent so that this solution would be compatible for solvent extraction second cycle (Fig. 5.3).

ION EXCHANGE SYSTEM

Figure 5.2

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PROPOSED Y-12 GENERAL SCRAP RECOVERY
FLOW SHEET

Figure 5.3

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6.0 METALLEX

G. K. Ellis

J. C. Rose and R. O. Payne

The Metallex process for the economical production of specification grade thorium is currently being revised to eliminate several problems which caused a shutdown of the process during preliminary runs earlier this year (Fig. 6.1). A failure of the product removal and feed lines was the most serious process deficiency. Limited revision to remedy this inadequacy, followed by a test run to determine the success of the alteration is the immediate objective. Upon satisfactory completion of this phase, other revisions and additions are contemplated, primarily to insure product purity, promote safety, and facilitate operation of equipment during future runs. Also presented are data comparing metallex and conventional thorium purities.

6.1 Process Revisions

Specifically, there were three failures as indicated above.

(1) The quasi product did not flow properly through the jackleg as it came out of the contactor. (2) The feed materials reacted and plugged the line at a point of mixing before entry into the reactor. (3) A Uscalite jackleg in the wash column top was seriously distorted by the excessive temperatures of the product.

The first defect should be remedied by eliminating the jackleg and substituting an overflow method for maintaining the cell holdup at its optimum 3.5 liter volume with continuous product removal. In addition, a header is presently being fabricated for attachment to the contactor which will allow several advantages (Fig. 6.2). The product is discharged through an angle of 45° into the vertical 3-in. header, this angle allowing maximum opportunity for product removal from the reactor. The previous product removal line will be used as a drain. This drain line will be valved, as shown in the accompanying sketch, for removal of reactor contents at the end of a run. A 1-in. line at the top of the contactor-reactor functions as an emergency overflow in the event of product overflow line becoming plugged. Blind flanges are conveniently located for cleanout access. Flanged connections are used as shown to facilitate maintenance.

The sodium amalgam and thorium tetrachloride feed materials will enter the contactor at separate locations, the mixing action taking place inside the vessel instead of outside.

The jackleg in the wash column top will be removed to minimize damage to Uscalite piping. HCl gas and water vapor will be kept from the stainless steel lines and contactor vessel by insuring a negative pressure at the wash

FIG. 6.1

FIG. 6.2. METALLEX WITHDRAWAL HEADER

column top with relation to any point in the lines or contactor above, through the use of a gas eductor. An oil flow through the contactor cooling jacket, the oil being cooled by water circulating in coils placed in the oil reservoir, should provide sufficient cooling for the highly exothermic reaction in the contactor. An optimum reaction temperature (and product temperature) of 130°C is desirable.

Better product purity will be obtained by performing all operations with dry salt in a dry helium atmosphere. For example, a dry box will be installed over the screw-feeder unit. It will also be necessary to adapt an existing hood for use in parcelling the dry salt into smaller, more conveniently handled, units.

Operation of equipment during the coming production run will be facilitated by using a recirculation Moyno pump (Fig. 6.1) to facilitate materials handling in the following operations.

- (1) Rewashing of product.
- (2) Refiltering of product.
- (3) Charging of feed amalgam to feed tanks on the top floor of the building in which the process is located.
- (4) Filtrate waste transfer to transfer tanks.

6.2 Contactor Study

An experiment was conducted to locate the product removal line in the contactor side for a 3.5 liter holdup during agitation of liquid contents. Mercury approximated the usual contactor contents. Agitation increased the liquid level height by about 1/2-in. for all volumes used greater than about 1 liter. The probable liquid operating level is from 4.6 to 5.2 in., corresponding to 3500 to 4000 ml holdup volume. Experimental data for the level measurements are shown in Table 6.1, and a plot of this information in Fig. 6.3.

6.3 Thorium Metal Product Purity

The presentation of product analysis of thorium metal purporting to show representative analysis of impurities of either, production metal or the Metallux thorium may be misleading because of the limited information available from either source. However, there may be some advantages to a presentation showing qualitatively the success or lack of success in meeting the tentative working specifications for thorium metal by two production routes. Note that insufficient operation experience ~~has~~ been accumulated with the Metallux process to define adequately "typical impurities". (Table 6.2).

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TABLE 6.1

Mercury Level Height Studies in a 1.5-gal. Dispersall Top-Drive ContactorWith and Without Agitation

Agitation - Cup Rotary type, 1410 RPM

Temperature - 25°C

Cumulative Mercury Volume (ml)	Height of Mercury Without Agitation (in.)	Height of Mercury With Agitation (in.)	Increase in Level With Agitation (in.)
875	1.19	1.63	0.44
1375	1.81	2.25	0.44
1875	2.31	2.75	0.44
2375	2.75	3.38	0.37
2875	3.50	3.75	0.25
3375	3.94	4.19	0.75
3875	4.50	5.00	0.50
4375	5.12	5.50	0.38
4675	5.32	6.00	0.68

FIG. 6.3. INCREASE OF MERCURY HEIGHT WITH
AGITATION IN 1.5 GAL. DISPERSALL CONTACTOR
FOR 500 ML INCREMENTS OF MERCURY ADDED.

TABLE 6.2

Thorium Quality Specifications

Impurity	Working Specifications		"Typical" Metallurgical Metal (ppm)
	Temporary (ppm)	Target (ppm)	
(1) C	800	400	430
N	300	150	225
(2) O	1500	800	450
(6) Zr	3500	200	*
(3) Al	400	25	*
Ca	100	70	*
Cr	100	50	20
Cu	100	50	*
(5) Fe	250	100	1200
Mg	100	20	*
Mn	25	25	*
Ni	100	50	140
(4) Si	100	50	20
(8) U	25	10	*
Zn	20	20	*
B	4	1.0	*
Cd	0.5	0.5	*
(7) Dy	2	0.5	*
(7) Eu	2	0.5	*
(7) Gd	4.5	0.2	*
(7) Sm	0.5	0.1	*
H	*	10	10

(9) Metal density 11.55 to 11.65 or 11.60 to 11.70. Target specification is greater than 11.55.

(9) Total thorium 99.5% minimum (as determined by difference). Minimum hardness should be greater than 50 Brinell.

* This information is not available.

The concentration of impurities in both production and Metallex metal refer to the preparation of a billet using a consumable-type arc-melting electrode. This method results in lower thorium oxide, nitrogen, carbon, aluminum, and silica, while zirconium oxide was eliminated from the melt. The average hardness values (B.H.N.) decreased from 73 for induction-melting to 42 for arc-melting in one group of runs.

7.0 POWER REACTOR FUEL REPROCESSING

C. D. Watson

Problems active during this period were:

- (1) Zircex (Hydrochlorination of Zr-U alloy fuels).
- (2) Darex (Aqua-regia dissolution of S.S.-U fuels).
- (3) HCl Distillation.
- (4) Mechanical Processing.
- (5) Materials Evaluation.
- (6) Pulse Column Interfacial Crud Removal.
- (7) Radiation Damage Studies.
- (8) Waste Studies.

Problems inactive during this period were:

- (1) Continuous Product Purification.
- (2) Head End Clarification Studies (magnetic filter).
- (3) Recovery of Spent Solvent with a Hydroclone.
- (4) Universal Slug Loader (discontinued).

7.1 Zircex, etc.

J. J. Perona, R. J. McNamee, and F. L. Rogers

The objectives of the problem are to obtain data for the design of full-scale hydrochlorinators, and to demonstrate the hydrochlorination of zirconium-uranium fuel elements. Examples of power reactor fuels which may be processed eventually by the hydrochlorination reaction are those of the Consolidated Edison, Commonwealth Edison, Rural Cooperative, and Submarine Thermal Reactors.

Studies to obtain design data include (a) reaction rates from 400 to 700°C, (b) the heat transfer aspects of the hydrochlorination process, (c) UCl_3 entrainment in the hydrochlorinator, (d) dissolution of UCl_3 residue in HNO_3 , and (e) corrosion of materials of construction. The influence of metallurgical properties such as "cold working" on reaction rate is being

investigated.

Reaction rates have been obtained and emissivities calculated for zirconium-uranium alloys containing up to 60 wt % uranium over the temperature range of 400 to 680°C. For all alloys studied, a plot of the logarithm of the reaction rate versus reciprocal temperature is roughly linear (Fig. 7.1). The reaction rate at a given temperature increases with increasing uranium content (Table 7.1 and Fig. 7.1). The effect of the alloy composition on reaction rate becomes less as the temperature increases; for example, at 415°C the spread in reaction rates for the various alloys is an approximate factor of 4, while at 635°C the factor is only about 1.5 (Fig. 7.1). The partial pressure of HCl in the hydrochlorinator was roughly constant at 0.6 atm over this series of runs.

Emissivity constants have been calculated for all runs by energy balances, since a significant portion of the heat of reaction is dissipated to the walls of the hydrochlorinator by radiation. [These calculated emissivities tend to increase as the uranium content increases, while the effect of temperature is different for the various alloys (Fig. 7.2)].

The reacting specimen dissipates the heat of reaction by three modes: (a) as sensible heat to the gases entering and leaving the system, (b) by convection from the reacting specimen to the surrounding gases to the walls of the hydrochlorinator, and (c) by radiation from the specimen to the walls.

Convection coefficients were calculated from the Lorenz equation for natural convection, which follows:

$$\frac{h_c L}{k_s} = 0.54 g \left[\frac{Z_g \cdot C_p \mu_g}{k_g} \right]$$

$$\text{where } Z_g = \text{the Grashof number} = \left[\frac{L^3 \rho^2 \beta g (\Delta t)}{\mu^2} \right]_g$$

L = height of specimen

k_g = thermal conductivity of the ambient fluid at the temperature of the specimen.

ρ = density of fluid

β = coefficient of volumetric expansion of the fluid

g = gravitational constant

(continued on page 86)

TABLE 7.1

Hydrochlorination Rates, Convection Coefficients, and Emissivities of
Zirconium-Uranium Alloys

Temperature	Rate (mg/cm ² min)	Convection Coefficient (Btu/hr-°F ft ²)	Emissivity	Composition
680°	22.7	3.6	0.34	7.3% U-92.7 Zr
621	17.5	3.7	0.31	↓
586	18.2	3.4	0.58	
528	6.4	3.1	0.22	
600	16.6	3.7	0.36	Zircaloy-2
524	9.0	3.3	0.40	↓
492	6.7	3.3	0.32	
450	2.5	2.7	0.29	
427	3.5	3.0	0.34	
591	20.1	3.5	0.41	20% U-80% Zr
415	2.5	2.3	0.50	↓
610	26.5	3.6	0.36	40% U-60% Zr
445	5.3	2.9	0.28	↓
400	3.8	2.6	0.50	
600	26.0	3.5	0.39	60% U-40% Zr
478	13.3	2.9	0.89	↓
445	11.6	3.0	0.73	

+ Zircaloy-2
 ○ 7.3% U-92.7% Zr
 △ 20% U-80% Zr
 ● 40% U-60% Zr
 □ 60% U-40% Zr
 $P_{HCl} \sim 0.6 \text{ atm}$

Figure 7.1. REACTION RATE VERSUS RECIPROCAL TEMPERATURE FOR THE HYDROCHLORINATION OF URANIUM-ZIRCONIUM ALLOYS

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Figure 7.2. EMISSIVITY VERSUS TEMPERATURE FOR URANIUM-ZIRCONIUM ALLOYS UNDERGOING HYDROCHLORINATION

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Δt = temperature difference between specimen and fluid

μ = viscosity of fluid

C_p = heat capacity of fluid

The thermal conductivity and viscosity of $ZrCl_4$ vapor could not be found in the literature, nor the critical properties with which to estimate them; therefore, for this series of runs in which the gas is composed of about 60% HCl , 27% H_2 and 13% $ZrCl_4$, natural convection coefficients were calculated assuming a gas composition of 70% HCl and 30% H_2 . These coefficients ranged from 2.3 to 3.7 Btu/hr $^{\circ}F$ ft².

Coefficients calculated from the Dittus-Boelter equation for forced convection were on the order of 10^{-2} Btu/hr $^{\circ}F$ ft², indicating that the velocity of the gases through the hydrochlorinator due to the HCl feed stream, being below the velocity range in which the forced convection equation is applicable, is insignificant compared to natural convection. Convection between the specimen and the gases was found to be controlling, due to the relatively large area of the hydrochlorinator walls.

7.2 Darex - J. J. Perona, R. J. McNamee, K. J. Fritz

The objectives of this problem are to develop the dissolution process for stainless steel-uranium reactor fuels in dilute aqua regia and to ultimately demonstrate the continuous dissolution of full-scale power reactor fuel elements. Examples of power reactor fuels which may be processed eventually by Darex are those of the Consumers Public Power, Yankee Atomic Power, and Army Package Power Reactors.

Continuous dissolution rates will be measured as a function of acid feed composition and acid feed rate. Other aspects of the dissolution process which will be investigated are (a) effect of metallurgical properties on dissolution rate, (b) effect of liquid level in the dissolver on condenser duty, (c) off-gas composition and rate, (d) product stream digestion and clarification, and (e) corrosion of materials of construction.

A continuous bench-scale dissolver system has been constructed with a maximum capacity of about 10 gal/hr of solution. A successful shakedown run was made with 5 N HNO_3 - 2 N HCl fresh feed at a rate of 4 gal/hr, yielding a reaction rate of about 50 mg/(cm²)(min). Although the same stainless steel was used as in batch dissolution tests, an immeasurably small amount of insoluble fines was produced in the product solution.

The continuous bench scale dissolver system is now being moved into Cell 1 where it will serve to feed the stripping column for HCl removal experiments, as well as to produce dissolution data.

The construction of the full scale dissolver system has been postponed pending the results of the bench-scale tests.

7.3 HCl Distillation

The purpose of HCl distillation is to demonstrate the removal of the chloride ion from the stream leaving the Darax dissolver. The chloride concentration must be reduced to less than 30 ppm to prevent interference with solvent extraction processing and to prevent corrosion of the stainless steel processing equipment. The investigation will include studies of the effects of composition of stripping vapor, V/L ratio, total metallic ion concentration and SS/V ratio.

A stripping run with a 304 L S. S. solution (~60 g/L, U-15 g/L) as feed was made using the 4-in. pyrex 12 bubble cap column and auxiliary components as indicated in Fig. 7.3. Analytical data for the run is not yet available because of difficulties which have arisen in the Cl^- determination, but from the standpoint of equipment performance the run was operationally successful.

Operational Procedure

To begin the run, the jacketed pot was changed to a pre-determined level with a $\text{HNO}_3\text{-H}_2\text{O}$ solution 32 mole % in HNO_3 , the acid make-up tank was filled with 20 mole % HNO_3 and the container of previously prepared feed solution (60 g/liter 304 S.S. and 15 g/liter natural U dissolved in 5 N HNO_3 -2 N HCl) was connected to the system. Steam was admitted to the jacket of the pot at a pressure of 40 psi; it was soon found necessary to increase this to 60 psi in order to produce an appreciable boil-up of 20 mole% HNO_3 stripping vapor. As boiling progressed, 20 mole % HNO_3 acid make-up was admitted to maintain a constant level and composition in the pot. After approximately 1 hr of boiling, feed was admitted at the same time the strip condensate receiver was changed. (Note: up to this time this stream should have contained only $\text{HNO}_3\text{-H}_2\text{O}$). In about 12 min, the color of the feed solution had reached the product cooler so the product receiver was changed at this time (see rate above). The first set of samples was taken at 1/2 to 3/4 of an hr after feed was first admitted. Steady state probably had not been attained at this time. The streams sampled throughout the runs were plates Nos. 1, 2, 4, 6, 8, 10, and 12, strip condensate and product. Readings taken throughout the run were feed, strip, and acid make-up rotameters, steam pressure, and pot level, relative to initial level. Three subsequent samplings were made at about 55 min intervals with readings being taken about every 15 min. During the course of the run the steam pressure was gradually increased to 80 psi with accompanying increases in the acid make, strip condensate and feed streams. (As mentioned in earlier reports a V/L ratio of 1.5 was maintained throughout the run.) After start-up had been accomplished, the operation of the column was rather uneventful; its operation was very stable even through start-up and at the higher steam pressures.

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Fig. 7.3 Apparatus for HCl Distillation

Since the run, the column has been disassembled and is presently being installed in Cell I B, Building 4505. Further runs are contemplated as soon as the column can be reassembled and thoroughly tested in its new location.

7.4 Decladding Studies - F. G. Kitts

Twenty-five X-10 (4-in. x 1.1-in. natural U) slugs have been successfully dejacketed using the Mackintosh-Hemphill rotary straightener. Upon rolling the aluminum-silicon braze bond between clad and core is broken, and the aluminum tubular clad increases ~0.10-in. in diameter, while decreasing ~0.10-in. in length and ~0.005-in. wall thickness. (Table 7.2) The end caps break off in the process, apparently caused by a combination of fatigue, work hardening and the tensile pull resulting from the shortening of the tubular portion. The rolled expanded cladding has rough edges and non-uniformity of shape making exact measurements very difficult. Data included in Table 7.2 are rough, average values and should be interpreted more as a guide to the order of magnitude of the changes affected than as absolute, reproducible measurements.

Figure 7.4 shows the uranium slug itself and its clad appearance before and after rolling.

The dejacketing of these slugs was made possible by equipping the Mackintosh-Hemphill rotary straightener with a unique continuous feed and guide tube developed at ORNL which directs and contains the slugs in passing through the three sets of rollers of the machine. (Fig. 7.5) The tube consists of a rigid pipe with six openings cut to the proper size and angled to allow the rollers to operate through the pipe and grip the smaller diameter slug within the pipe. The inside diameter of the pipe is chosen about 1/8-in. longer than the expected outside diameter of the expanded clad. It was found that making several passes (3-6) with a smaller amount of deformation per pass was more effective in completely breaking the Al-Si bond than attempting complete clad removal in one or two passes with a greater amount of work per pass.

TABLE 7.2
Slug Dimensions

	X-10 Slug		
	Dimension Original	After Rolling	Dimension Change
Length of tubular clad, inches	3.86	3.76	-0.10
O.D. of clad, inches	1.18	1.32	+0.14
Wall thickness of clad, inches	0.042	.038	-0.004

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Fig. 7.4 "Aluminum Jacketed Slugs After Rolling in the Derodder"

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Fig. 7.5 "Continuous Feed and Guide Tube Installed in Derodder"

7.5 Disassembly Studies - G. A. West

7.5.1 Electrical Discharge Cutting

A model M-500 Elox electrical discharge machine, manufactured by the Cincinnati Milling Machine Company, Inc., for the Elox Corporation by Michigan, is currently being operated to determine its adaptability and cutting characteristics in disassembling spent fuel elements. Electrodes of both rotating discs and continuously reeled wire are being evaluated. The coolant tank has been redesigned so that elements up to 6 ft can be accommodated. A second possible adaptation is a conceptional design of a 13 ft lathe bed that will accommodate the Elox head so that the longest fuel assemblies may be disassembled.

(a) Disc Electrodes:

The optimum electrode material according to the manufacturer is leaded brass which is machined into a template to obtain the desired configuration of weight. The electrodes are "sacrificial" and for optimum cutting, must be redressed after a few hours of use. Rotating disc electrodes, ~ 8 in. dia., with 2, 6, and 17 cutting fins have been fabricated of leaded brass and demonstration cuts made. These discs, with 0.040 in. thick fins, exhibited a maximum longitudinal cutting rate of about 1-in./min cutting through a stainless steel side plate (0.065 in. thick) of a simulated APPR fuel element. This rate could not be maintained for periods longer than 2 or 3 min due to the uneven consumption of the electrode which resulted in grounding the electrode to the work and cessation of cutting. It was concluded that a disc type of electrode could be adapted for disassembling but it is not the optimum method for production use.

(b) Wire Electrode:

The Elox machine was adapted for wire electrode cutting by mounting reels and pulleys for continuous reeling of the wire. (Figs. 7.6 and 7.7). Leaded brass wire, 0.0201 in. dia., was used to make a transverse cut of the simulated APPR fuel element. About 5 min were required to cut through the side plate (~0.065 in. x 2.84 in.). A horizontal cut, cutting through side plate and cutting the side of the 18 fuel plates, was attempted. Difficulty was encountered by the wire binding after about a 1-in. cut, but it is felt that this can be overcome by installing a follow-up wedge. More evaluation tests are to be made by adapting the wire electrode to cut horizontally, and if this is successful, to follow with multiple wires so that all the fuel plates can be disassembled with one cutting.

7.5.2 Sawing

A conceptional design has been completed by the Engineering and Mechanical Division incorporating a cut-off saw (abrasion disc) and auxiliary equipment

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Fig. 7.6 "Elox Electrical Discharge Cutting with Wire Electrode"

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Fig. 7.7 "Elox Electrical Discharge Cutting with Wire Electrode"

to demonstrate a technique of disassembling and handling all spent power reactor fuel handles (Fig. 7.8).

A cost estimate of the concept is being made.

7.6 Material Evaluation (Corrosion Tests) - G. A. West, G. B. Dinsmore

Material evaluation tests are in progress to determine the corrosion resistance of various materials of construction that may be used in the reprocessing spent power reactor fuels. Evaluation of materials for the Zircex (hydrochlorination) process were continued during this period. The tests for the Darex (aqua-regia) process were completed per the preceding report period. (CF-#56-10-83).

Titanium-70 has undergone tests against various media of the Zircex process; i.e., HCl gas and $\text{HNO}_3\text{-UCl}_3$ solutions at various acid concentrations. It had excellent resistance (<0.2 mm corrosion) in individual media tests but failed in the cycling test of alternate HCl gas at 500°C and boiling $2\text{ N HNO}_3\text{-UCl}_3$ (11g U/liter) solution. The corrosion rate after two periods in $\text{HNO}_3\text{-UCl}_3$ and three periods in the HCl gas was 86 mils per month. (Table 7.3).

Tests were continued to evaluate materials that will withstand corrosion where UCl_3 , produced by the hydrochlorination, is dissolved by either nitric acid or water. Titanium, A-nickel and Hastelloy-B were tested in room temperature and boiling solutions of 2N , 8N , and $15.7\text{ N HNO}_3\text{-UCl}_3$ (11g/liter) and in $\text{H}_2\text{O-UCl}_3$ (11g U/liter). Titanium with a corrosion rate of <0.05 mm, exhibited excellent resistance to all the above solutions. A-nickel and Hastelloy-B were severely attacked by all solutions except the room temperature ($\sim 27^\circ\text{C}$) $\text{H}_2\text{O-UCl}_3$ solution. (Table 7.4)

Radiation Damage Studies - C. D. Watson, G. A. West

A 6-in. dia. aluminum tube encapsulated on one end with cadmium to capture thermal neutrons and produce a gamma shown inside the tube has been installed in the LITR. The expected gamma flux is of the order of $10^7/\text{hr}$. The source has not yet been calibrated. It is anticipated that the Vanderbilt ferric ferrous method and the ceric ammonium sulfate method will be used for the gammas and foils for the neutrons.

Table 7.3

Effect of Cycling Titanium-70 in Anhydrous HCl Gas and HNO_3 -HCl Solution

- Conditions: 1. Anhydrous HCl gas at 500°C
 2. 2 N HNO_3 -HCl (11 g U/liter at boiling temperature)
 3. Specimens (4 ea.) rinsed with water, dried and weighed after each test period.

Media	HCl Gas	HNO_3 - UCl_3	HCl Gas	HNO_3 - UCl_3	HCl Gas
Test Period (hrs)	500	96	96	48	96
Corrosion/Period (mpm*)	0.15	0.11	0.10	0.46	86.2
Corrosion, Total (mpm)	0.15	0.11	0.12	0.15	10.0

* mls per month

Table 7.4

Corrosion Resistance of Titanium, A-Nickel and Hastelloy-B Against
 $\text{HNO}_3\text{-UCl}_3$ and $\text{H}_2\text{O-UCl}_3$ (11 g/liter) Solutions

- Conditions: 1. Specimens exposed for 528 hrs unless otherwise noted.
 2. Corrosion rate, in mils per month, is, (1) the average of two specimens in vapor phase and two in liquid, and (2) for the total hrs exposed.
 3. Specimen surface area: Titanium 2.6-in.²; A-nickel 5.7-in.²; Hastelloy-B 2.2-in.².

Media	Temp. (°C)	Titanium		A-Nickel		Hastelloy-B	
		Vapor	Liquid	Vapor	Liquid	Vapor	Liquid
		(mpm)	(mpm)	(mpm)	(mpm)	(mpm)	(mpm)
$2\text{N HNO}_3\text{-UCl}_3$	27	N11	N11	0.075	21.0	Failed**	Failed**
	105	0.001	0.030	7.0	56.0		
$8\text{N HNO}_3\text{-UCl}_3$	27	0.002	0.003	1.24	101.5	-	-
	117	0.020	0.010	56.0	649.0	-	-
$15.7\text{ N HNO}_3\text{-UCl}_3$	27	0.001	0.003	Failed*	Failed*	-	-
	122	0.010	0.010			-	-
$\text{H}_2\text{O} - \text{UCl}_3$	27	N11	N11	0.01	0.04	-	-
	100	0.001	0.001	1.00	6.65	-	-

* Violent attack (25 min test)

** Violent attack (1.5 hr test)

Waste Studies - C. D. Watson, G. A. West

A preliminary look is being taken of the possibility of intimately mixing calcined waste solids with asphalts for storage in the ground. Mixing the solids with asphalt, it is hoped, would result in the production of an unleachable mass that would resist the leaching of ground water for many years.

Answers to the following questions will be necessary for an evaluation of the proposed method.

- (1) Amount of solids that can be added without total loss of pliability.
- (2) The extent of leaching from the asphalt mix.
- (3) The effect of radiation (cracking) on the mix.
- (4) Conceptual flowsheet and cost analysis.

7.7 Pulse Column Interfacial Crud Removal - R. J. McNamee, C. V. Chester,
J. R. Eblen

To avoid the extraction and/or entrainment of activity from interfacial crud into the organic product, it would be desirable to remove this crud from the interface in the settling section at the top of an extraction column. A method to effect this by continuously removing liquid from the column interface, filtering it, and returning the filtrate to the interface has been evaluated. Satisfactory crud removal was effected with Fulflo filters and a Lapp CPD-2 pulsafeeder on synthetic cruds. Pressure drops through the Fulflo filters were found to be insignificant at recirculation flow rates expected, even after considerable solids loading. A bed of granular alumina might also be used in addition to a Fulflo. Although having a higher pressure drop, it has the advantage of adsorbing fission product activity. A Lapp pump is necessary, as a centrifugal produced an emulsion.

In crud removal demonstration tests the interface of a 6-in. non-pulsed glass column was treated by continuously circulating liquid from it through a pump, a filter, and back to the interface. The components of the system were evaluated, and those found satisfactory are being installed on the 2-in. extraction pulse column in Building 3503.

7.7.1 Interfacial Recirculation System

Figures 7.9 and 7.10 are photographs of the recirculation system of the crud removal experiment from the front and side, respectively. In this system, liquid was syphoned off at the interface, and led to the suction of

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Fig. 7.9

Fig. 7.10

either a small centrifugal or a Lapp CPD-2 pump through 3/8-In. stainless tubing. The discharges of the pumps were connected through a common manifold to a Fulflo filter and a sand filter in parallel. Valves were provided so that either or both or 2 rotameters. The effluent from the rotameters was returned to the column through 1/4-in. stainless tubing in the plane of the interface and tangentially to the axis of the column. (See UNOP September Monthly CF#-56-9-127). Figure 7.12 shows the syphon interfacial takeoff and the return line. The takeoff is to the left.

Figure 7.11 is a picture of the interface with about 1/8 in. of crud on it. Fig. 7.12 is a picture of the same interface after the circulation system had been operating about 15 min. Figure 7.13 shows an interface which has been cleaned.

7.7.2 Filtration

Filtration of the stream from the interface is desirable to (1) break the emulsion, and (2) remove any solids which may be stabilizing the emulsion of which the crud consists. The filters investigated were a Fulflo model SSXWC-10-3/4 and a sand filter. The sand filter consisted of a 1-ft section of 3-in. pyrex pipe, flanged into heads to take the necessary lines. The support for the sand bed was a piece of 200-mesh stainless steel screen gasketed across the bottom of the pipe. Flow was down through the bed.

A. The Fulflo Filter

To obtain design data, an extensive series of pressure drop measurements was made on Fulflo filters. Three different grades of glass fiber cartridges were investigated, the K15R10S, K10R10S, and K6R10S. The first is the finest mesh cartridge made in glasswool, and the last the coarsest. To permit correlation with other filtration media, the data are expressed as the constant in the equation

$$\Delta P = \frac{K G \mu L}{A}$$

where ΔP = pressure drop, volumetric

G = flow rate

μ = viscosity of fluid

L = thickness of medium parallel to flow

A = area of medium normal to flow

K = characteristic constant of medium

K will have the dimensions of reciprocal length squared. (In beds of particulate solids, K is inversely proportional to the square of particle diameter.)

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Fig. 7.11

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Fig. 7.12

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Fig. 7.13

The constants for the different filter cartridges are listed in Table 7.5. The most striking aspect of the data is that the variation in K from cartridge to cartridge of the same grade is much greater than the variation, if any, between the different grades of cartridges.

To determine the capacity of the Fulflo, successive 100-g portions of freshly precipitated barium sulfate were filtered from a slurry in the filter. Pressure drop readings were taken after each addition. The average resistance constants, K , were calculated, and are tabulated for two series in Table 7.6.

The spectacular difference between the resistances of the two filters when clean should be noted. The increase in the resistance constant from each addition of BaSO_4 is tabulated under ΔK .

The filter cartridge in Series 1 was improperly seated, allowing some slurry to go around the end of the cartridge. This by-passing became more pronounced as the resistance of the cake on the filter built up, and probably accounts for the lower values of ΔK in this series. (The G through the cartridge would actually be lower than what was measured). The low value of ΔK in the last run of Series 2 is the result of part of the cake falling off the cartridge.

Although the specific resistance of the Fulflo medium is high, the large area (50 in.²) and relative thinness (0.75-in.) of the medium allow quite a modest pressure drop. For example, a flow rate of 300 c.c./min. expected in operation, through a cooled Fulflo of resistance 50×10^6 in.⁻² will require a pressure drop of 0.3 psi.

The only disadvantages of the Fulflo are (1) the tendency of the threads on the assembly nut to gall, and (2) the possibility of seating the cartridge eccentrically, allowing the slurry to short-circuit the filtration medium. The latter disadvantage may be overcome by increasing the size of the guide vanes on the assembly stud.

B. Sand Filter

Design correlations exist for pressure drop through beds of granular solids. (*) A series of runs were made using 80-200 mesh chromatographic alumina to determine the effect of a range of particle size on pressure drop. Chromatographic alumina was chosen as it is potentially advantageous for removing ruthenium by adsorption from the filtrate.

The data are given in Table 7.7. The variation is the result of blinding the bed by fine solids in the system during the first two series of runs. Thus the high resistance of 2-in. bed is averaged out over a

(*) Parry, Chemical Engineers Handbook, 3rd Edition, pg. 393. McGraw Hill, New York, 1950.

TABLE 7.5
Summary of Pressure Drop Data for Fulflo Filters

Filter Medium	Condition	$K = \frac{A \Delta P}{L \mu G} \text{ in.}^{-2}$
K15R10S ⁽¹⁾	New	8.03×10^6
"	New	7.81
"	Loaded	17.2
"	New	77.6
"	New	14.9
K10R10S ⁽²⁾	New	15.0
"	New	62.3
K6R10S ⁽³⁾	New	65.4

- (1) Fine grade
 (2) Medium grade
 (3) Coarse grade

TABLE 7.6
Effect of BaSO_4 Loading on K15R108 Faltlo Filters

BaSO_4 Filters (Grams)	$K = \frac{A \Delta P}{L \mu G}$, in.^{-2}	ΔK
Series 1 (1)		
0	77.6×10^6	-
100	101.1	23.5×10^6
200	113.2	12.1
300	113.4	0.2
400	122.7	9.3
Series 2		
0	14.9×10^6	-
100	31.8	16.9×10^6
200	44.3	12.5
300	57.2	12.9
400	60.6	3.4 (2)

(1) Results invalid, due to improper seating of cartridge.

(2) Part of cake had fallen off cartridge.

TABLE 7.7

Resistance of 80-200 mesh Chromatographic Alumina

Bed depth, in.	$\frac{A \Delta P}{G \mu L} = K, (\text{in.}^{-2})$
1.0	27.1×10^6
2.0	35.8
3.0	27.9

deeper bed in the third series, giving a more representative resistance for that series (similar to the first run before blinding occurred).

The specific resistance of the 80-200 mesh alumina is the same order of magnitude as that of the Fulflo cartridges. However, the smaller filtration area a deep bed of the filter will require greater pressure drop than the Fulflo cartridge for a given flow. Although it is possible to use chemically active materials in the bed of a sand filter, the danger of getting fine abrasive solids from it into the system makes this filter of doubtful worth for this application. It would have to be followed by a Fulflo to provide protection against this.

7.7.3 Pumps

A Lapp CPD-2 Pulsafeeder and a small centrifugal pump were used in the recirculation system. The centrifugal pump was very satisfactory, producing a stable emulsion of the aqueous and organic phases. The Lapp proved satisfactory in every respect. It did not produce emulsions, and is easier to make leak-tight than a centrifugal.

Previous reports in this series:

January 1956	56-1-175
February "	56-2-154
March "	56-3-177
April "	56-4-210
May "	56-5-197
June "	56-6-177
July "	56-7-150
August "	56-8-215
September "	56-9-127
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