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CHEMICAL TECHNOLOGY DIVISION
UNIT OPERATIONS SECTION
MONTHLY PROGRESS REPORT
JANUARY 1958

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Chemical Technology Division

UNIT OPERATIONS SECTION MONTHLY PROGRESS REPORT

January 1958

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Date Issued

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ABSTRACT

Absolute calibration of neutron yields from a polonium nitrate-fluorocarbon interface gave 8 neutrons/min, sq cm, mc/ml. In two Fluorox fluidized bed reactor runs UF_6 recoveries of 47 and 70% theoretical were attained. Washing and descaling operations for Loop P-1 have been completed. Preliminary studies of ThO_2 classification by hydroclones showed that particles as small as 0.5 micron could be classified. Continuous, self-sustaining operation of the Darex dissolver, stripper, and reflux condenser was maintained during a 48-hr period. Uranium losses to the sublimate were less than 0.1% in a 24 hr Zircex run. A 32 hr dissolution run was completed in which a fuel element fabricated of zircalloy-3 was dissolved in a $NaF-ZrF_4$ fused salt.

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SUMMARY

1.0 CHEMICAL ENGINEERING RESEARCH

Absolute calibrations using a graphite stack give neutron yields of 8 ± 2 neutrons/min $\text{cm}^2 \cdot \text{mc/ml}$ for the (α, n) reaction at a Po^{210} solution-fluorocarbon interface. Previously obtained results were higher by factors of 8-10, perhaps because of deposition of Po on equipment surfaces.

Installation and preliminary testing has been completed for a modified experimental apparatus to be used for studies of corrosion in a porous tube protected by transpirational flow.

2.0 FLUOROX

In two Fluorox fluidized bed reactor runs UF_6 recoveries of 47 and 70% of theoretical were attained. Analysis of material found in the off-gas filter substantiated previous observations that considerable corrosion of the reactor system was occurring. Two flame reactor tests were carried out with stable flame operation throughout the runs.

3.0 HF FUEL AND BLANKET PROCESSING

Washing and descaling operations for loop P-1 have been completed. The hydroclone circuit was plugged during the final run. About one-half of the 8 g of Pu (mostly preformed PuO_2) remaining in the loop after experimental studies were completed was removed by the first of the CrSO_4 descaling operations. Results for the final two tests with Pu show that fresh 1.4 M UO_2SO_4 does not dissolve deposited Pu and that the material precipitated by addition of soluble Pu deposited without any significant amount of circulation as a slurry.

Preliminary studies of ThO_2 classification by hydroclones showed that particles as small as 0.5 micron could be classified, but that additional development studies will be required to permit operation of an effective system. A Sharples air classifier removed material of over 8 microns, in one pass but apparently did not classify below 6 micron ThO_2 . About 220 g of ThO_2 has been flame calcined and recovered for product evaluation.

4.0 POWER REACTOR FUEL REPROCESSING

Darex Process

Continuous, self-sustaining operation of the Darex dissolver, stripper, and reflux condenser was maintained during a 48-hr period with periodic interruptions occasioned by temporary loss of dissolution resulting from momentary plugging of the dissolver outlet by platelets or flakes of undissolved stainless steel. Over-all material balances for HNO_3 , H_2O , and HCl during three separate periods of steady state operation were +4 to -5%,

+7 to -13%, and 0% respectively. Corrosion specimens of titanium and tantalum after approximately 200 hr. of operation showed slight weight gains and were coated with a thin film consisting of niobium, a nickel-iron complex, silicon dioxide, and silicon carbide. Vitallium was attacked at rates from 1 to 3-2/3 mils/mo. depending on the location in the system.

Decontamination Studies - Decontamination testing of various protective coatings and some selected materials of construction as control surfaces contaminated with concentrated Savannah River waste resulted in decontamination factors of 10^2 - 5.5×10^5 and 2.4×10^3 - 7.7×10^4 , respectively. None of the materials were completely decontaminated. The vinyl coatings as a group were superior to the other test coatings and Teflon and plate glass were superior materials in the control surfaces group. All materials, in general, were more easily decontaminated from the Savannah River waste than from Thorex waste containing protactinium-233.

Zircex - In a hydrochlorination run of 24 hr duration at 500°C, 98.4% of a 3.7 kg section of a fuel element was reacted at an average reaction rate of 1.25 mg/sq cm/min (based on 1/2 the original surface area). The uranium losses to the $ZrCl_4$ sublimate and as insolubles from the dissolution of the UCl_3 product in 10 M HNO_3 were 0.08% and 1.9% respectively. The utilization of anhydrous HCl gas was approximately 90%. Uranium disengaged by a glass wool filter in the line to the $ZrCl_4$ condenser was approximately 0.3% of the uranium reacted.

5.0 VOLATILITY

A 32 hr dissolution run was completed in which a dummy STR type fuel element fabricated of zircalloy-3 was dissolved in a NaF-ZrF₄ fused salt. The most important variable which affected the dissolution rate was the rate of addition of anhydrous HF.

A water-air system simulating the fused salt HF system to be used in the dissolution of zirconium fuel elements was studied to determine the effect of distributor design, submergence, and gas flow rate on the degree of agitated contact. The contact generally improved with increased submergence and increased gas rate. Arrangement of holes in the distributor plate and free area were important parameters.

1.0 CHEMICAL ENGINEERING RESEARCH

P. A. Haas

1.1 Interfacial Area Measurements - C. V. Chester, J. L. Whitten

The α, n reaction of fluorine at the interface between an aqueous Po^{210} solution and a liquid fluorocarbon is being used to measure interfacial area. The yield from the α, n reaction of the higher isotopes of oxygen in a polonium-210 nitrate solution was measured at 94 ± 1 neutrons/min, mc in the calibrated 5-ft graphite sphere at the ORNL High Voltage Laboratory. The yield from a polonium nitrate solution-fluorocarbon interface using teflon sheet for the interface was 8 ± 2 neutrons/min, cm^2 , mc/ml. This yield is an order of magnitude less than previous experiments had indicated. The reason for the discrepancy is not known; a possible cause is polonium plating on the equipment used in previous experiments. Tests are being conducted to investigate this and other possible causes.

To prevent recurring counter breakdowns, a new counter assembly has been constructed to include an all-welded aluminum housing and eight BF_3 tubes of a reliable ORNL design. Facilities for a dry nitrogen purge of the housing are included. The details are set forth in ORNL Instrumentation and Controls Division drawings Q-1923-1, Q-1923-2, and Q-1923-3; "Watertight Housing for BF_3 Counters-Model No. 2". This counter assembly has an approximate counting efficiency (for neutrons from a source in the center of the tube array immersed in a 12-in. x 18-in. dia. high jar of water) given by the expression:

$$E = 3.25 + 1.75 \sin \frac{\pi X}{7}, \quad 0 \leq X \leq 7 \text{ in.}$$

where E is the efficiency in percent and X is the distance of a source below the top of the BF_3 tubes in the housing in inches.

1.2 Transpiration Studies - P. A. Haas, H. Bixler*, S. Patrick*

A film theory has been developed and has been confirmed by electrical conductivity measurements (Chemical Technology Division Monthly Progress Report, September 1957, ORNL-2416) for corrosion protection by transpiration flow through a porous metal wall. The initial corrosion studies were limited by the apparatus, the $\text{HNO}_3 \cdot \text{H}_2\text{O}_2$ corrosion medium, and the analytical and sampling methods. Installation and preliminary testing of a modified system has been completed. The corrosive medium is $\text{HCl} \cdot \text{H}_2\text{O}_2$ with recycling through an allglass or plastic system except for the porous tube. Preliminary tests show that surface reaction rates may still affect the results with the $\text{HCl} \cdot \text{H}_2\text{O}_2$ system, but that gas formation and passivation problems have been eliminated. The revised apparatus eliminates flow pulsations and will permit Reynolds' numbers of up to 60,000 (previously 16,000) in the porous nickel tube.

* M.I.T. Practice School Students

2.0 FLUOROX

M. E. Whatley

2.1 Fluidized Bed Development

2.1.1 Fluidized Bed Reactor - J. B. Adams

In the Fluorox Fluidized Bed Reactor UF_4 -oxidation process, sized UF_4 and UO_2F_2 (inert product) are fluidized in dry oxygen at 750 to 850°C. The reaction under study is:

UF_6 product is removed in the gas stream and recovered. Solid UO_2F_2 by-product for recycle remains in the reactor. A FBR may be operated as a batch fed unit, with semicontinuous feed or with continuous UF_4 feed.

Measured UF_6 recoveries of 47 and 70% of theoretical were attained in two FBR- UF_4 oxidation runs. Complete material balances were not obtained since the runs were short in duration and limited amounts of UF_4 were fed. The reactor temperature was 800-820°C. Bottom feed--blowing powdered UF_4 into the base of the reactor with the fluidizing oxygen--was used successfully in both runs. A continuous screw feeder used for metering UF_4 in one run failed due to galling at the shaft seal forcing termination of the run. In the second run, a semicontinuous double-valve gas lock system for delivering weighed batches was operated successfully. The run was shut down, however, when the off-gas line plugged.

Evidence of corrosion products, particularly chromium fluorides, had been noted previously in the off-gas system and cold traps. The analysis of materials (Table 2-1) from the reactor and dust filter confirmed that considerable corrosion was occurring.

The elements analyzed for were those contained in the material of construction used--Inconel. The UF_4 used was essentially free of impurities. Dust taken from the filter was highly contaminated. The presence of titanium suggests that some part of the reactor system is made of Inconel-X, a titanium-bearing version of Inconel. Over several runs scale from the reactor walls built up in the reactor contents. A sample taken from the reactor was screened to separate samples of UO_2F_2 and scale for analysis. The scale contained relatively large amounts of impurities. The UO_2F_2 , however, was fairly free of impurities though not as pure as the original UF_4 feed used. The analysis for Ni is believed to be in error and most of the impurities in the UO_2F_2 probably are due to small amounts of scale that could not be removed from the sample.

Table 2-1 Analysis for Corrosion Products

Material	Spectrographic Analysis (%)						
	Cr	Ni	Fe	Ti	Cu	Mn	Si
UF ₄	0.0003	0.0001	0.005	--	0.00001	0.0004	--
Filter Dust	1.25	0.50	0.38	0.25	0.04	0.013	--
UO ₂ F ₂ from Reactor	0.005	0.1	0.03	--	0.005	0.002	0.01
Scale from Reactor	2.5	1.25	0.75	0.06	0.003	0.025	--

2.1.2 Reactor Solids Feeding Systems - C. D. Scott, W. G. Sisson

Two of the proposed solids feeding systems for the Fluidized Bed Reactor have been fabricated. These are the batch feeder and the rotary pump feeder (December Monthly). The batch feeder was used in run FR-15 and it introduced solids into the reactor satisfactorily after a vibrator was attached to the feed entrance line. The rotary pump feeder which can be used as a continuous feeder has been fabricated, is being calibrated, and will be used in future Fluidized Bed Reactor runs.

2.2 Flame Reactor Development - C. D. Scott, W. G. Sisson, J. D. Phillips

The Fluorox Flame Reactor is used to continuously react finely divided UF_4 with oxygen in a $CO-O_2$ flame. The flame reactor runs were made, FR-9 and FR-10, in which UF_4 was introduced into a pure $CO-O_2$ flame for continuous periods without flame instability. These were the first successful flame- UF_4 runs that have been made with pure CO.

2.2.1 Equipment and Operating Procedures

Several changes in both equipment and operating procedure were made before it was possible to make the two runs. A finer UF_4 feed, 100% through 325 mesh, was used in a new solids feeding system. The feeding system (Fig. 2.1) is a fluidizing chamber into which a specific amount of UF_4 powder is charged. When fluidizing gas is introduced through the gas nozzle into the UF_4 powder, some of the fluidized UF_4 is carried out with the exit gas. Calibration is not complete; however, it appears that if the UF_4 powder level is maintained nearly constant, and not more than 25% of the UF_4 is removed from the chamber, the feed rate can be controlled within 10-15% by control of the gas flow to the chamber. This system reduces the quenching effect of high UF_4 feed rates and feed slugging because of its steady operation at low feed rates. Both FR-9 and FR-10 were made while using a ceramic burner with the same design as the previous lavite burner (June 1957 Monthly); however, the material of construction was "clay insulation material" which was furnished by the Ceramics Division. It was possible to maintain a more stable flame on the ceramic burner than on the all-metal burner (October 1957 Monthly Report), due to the excellent pre-mixing of the fuel gases in the ceramic burner and the concave construction of the burner itself. More corrosion was experienced with the ceramic burner than with the all-metal burner.

The pre-mixed fuel, pure CO and O_2 , was heated up to $500^\circ C$ before introduction to the burner assembly, which tended to reduce the quenching effect of the cold gases. The heated mixture made the flame much easier to ignite and maintain. The fuel gases could not be heated much above $600^\circ C$ because this temperature approaches the gas ignition temperature and would tend to cause fuel ignition in the inlet lines. Since the pre-heated gases resulted in a volume increase, the maximum gas flows due to flame stability were decreased.

Fig. 2.1. Fluorox Flame Reactor Fluidizing Chamber.

2.2.2 Experimental Results

The operating conditions (Table 2-2) showed that run FR-9 was made with a much lower total gas flow than run FR-10; however, there was also a correspondingly lower UF_4 fluidizing rate for FR-9. These two conditions gave estimated UF_4 hold-up times in the flame of about 0.4 to 0.5 sec. The hold-up times were determined from flame length and velocity of the entering fluidizing stream. Flame lengths were assumed to be the length of the reactor wall which was visibly red hot. Since the theoretical flame temperature for a 50% CO fuel is $2800^\circ C$, it was estimated that the actual flame temperature of the flame in FR-9 and FR-10 was $2000^\circ C$ to $2400^\circ C$. No attempt was made to collect any of the UF_6 ; however, a water scrubber was used in the off-gas system.

The solids material balances for the two runs (Table 2-3) did not account for all the material, but they were probably as good as can be expected considering the small amounts of UF_4 , the large amounts of gases, and the relatively large system employed. The material that was collected in the bottom of the reactor appeared to be similar to the feed material, except there was some sintering effect and particle agglomeration. Material removed from the reactor walls had the appearance of U_3O_8 or UO_2 , as would be expected since it was exposed to high temperature for a long period.

In run FR-10, a small amount of material was caked on the solids nozzle. This material appeared to contain a large amount of UO_2F_2 . No analytical results are available at this time.

Table 2-2. Operating Conditions for Runs FR-9 and FR-10

Run	Fuel Gas Rate (cfm)	% CO in Fuel Gas	Average Fluidizing Gas Rate (cfm)	Length of Run (min.)	Average UF_4 Feed Rate (g/hr)	Flame Length (inches)*	UF_4 Hold-up in Flame (sec.**)
FR-9	1.85	50%	0.08	29	12.4	12	0.58
FR-10	3.00	50%	0.15	32	28.4	16	0.42

* The flame length was approximated to be that length of the reactor wall which was visibly red hot.

** The estimated hold-up time of the UF_4 in the flame was based on the flame length and the velocity of the entering, fluidizing stream.

Table 2-3. Solids Material Balance from Runs FR-9 and FR-10

Run	UF ₄ Feed (grams)	Solid Material that was Recovered, (grams)				
		Bottom of Reactor	Reactor Walls	Burner Assembly	Offgas Chamber	Total
FR-9	6.0	5.0	0.5	--	--	5.5
FR-10	15.2	9.8	2.5	0.5	0.5	13.3

3.0 HR FUEL AND BLANKET PROCESSING

P. A. Haas

3.1 Loop P-1 Operation - J. W. Snider

Loop operation for this period consisted of two CrSO_4 descaling runs and four H_2O rinses. Loop preparation for the CrSO_4 descaling consisted of a N_2 purge followed by two nitrogen pressurization-evacuation cycles. The CrSO_4 was drawn into the loop by means of a vacuum with a mineral oil layer on the feed bottles to keep the CrSO_4 from being oxidized by the air during transportation.

The hydroclone circuit has remained partially or completely plugged throughout these washing and descaling operations. Present plans are to remove the loop from the isolation laboratory and to disassemble components including the hydroclone and pump for inspection.

3.1.1 Loop P-1 Results - J. M. Chilton*, R. E. Leuze*, J. W. Snider

Results were completed for the final two experimental runs with Pu which were made starting with a fresh UO_2SO_4 solution for the first run. The plutonium-free feed solution did not dissolve previously deposited Pu. About 4% of 7.5 g Pu added during the second run remained in circulation and was removed as soluble Pu at the end of the run. Deposition on sample coupons was variable, but bracketed the value required to account for all the Pu assuming uniform deposition.

3.1.2 Run P-32 - The loop was drained after the previous run and 12.0 liters of new 1.4 M UO_2SO_4 was added to the approximate 1.0 liters hold-up. The first samples taken after the solution was circulated showed a plutonium concentration of 2.3 mg Pu/kg H_2O , corresponding to a value of 1/13 of the concentration of the drain from run P-31. The loop ran for 10 hr at temperature and samples were taken every 2 hr. None of the samples showed any dissolution of plutonium by the uranyl sulfate solution.

During this run, the hydroclone removed a total of 2.8 g of solids which were 93% uranium, 5% iron, 1% chromium, and 0.2% plutonium. Some solids, found in the circulating stream samples, were practically all uranium. The nickel concentration, over the 10 hr of operation, increased 25 mg/liter; this is equivalent to a corrosion rate of 15 mpy.

3.1.3 Run P-33 - The final run in this series was made by the addition of spikes of $\text{Pu}(\text{SO}_4)_2$ to the solution left from the previous run. The four injections made were equivalent to 335 mg Pu/kg H_2O . Samples taken during this period showed variable plutonium concentrations in solution; some values were impossibly high. The maximum solubility figure which was

* Responsible for Chemical Development Section A portion of P-1 Loop experimental program.

reasonable was 195 mg/kg H₂O, and this value steadily declined to a final solubility concentration of 25 mg/kg H₂O. After approximately 10 hr of operation, the hydroclone became inoperative and samples taken from the underflow pot showed no solids present. Various efforts made to remedy this situation, including a temperature cycle, were not successful. Nevertheless, this run was continued for a total of 90 hr, and three more injections of plutonium were made equivalent to a concentration of 645 mg Pu/kg H₂O, or a total of 7.5 grams. The final solution drained from the loop contained 26.1 mg/kg H₂O. As in the previous runs, the corrosion was followed by analysis of nickel in solution. On this basis, the corrosion rate was found to be 13 mpy.

Since the hydroclone line became plugged after a few hours of operation, only the first 5 samples taken contained any solids. These were found to be of approximately the same composition as in the previous runs. The total amount removed was 870 mg and the amount of plutonium was 7.5 mg. Uranium comprised 93% of these solids.

The sample coupons were removed from the loop at the end of this run and the individual coupons showed a wide variation in amount of plutonium adsorbed from 0.25 to 2.19 mg/cm². The lowest figure would correspond to a total adsorption of 2.43 g of plutonium and the highest to 21 g. Since 7.5 g was injected, and practically none remained in solution or was removed by the hydroclone, it can be assumed that the 7.5 g was practically all adsorbed. Combined with adsorption from previous runs, this would correspond to an average adsorption of approximately 1 mg Pu/cm² surface.

3.2 ThO₂ Slurry Development Studies

3.2.1 ThO₂ Classification - E. L. Youngblood

Preliminary tests have been made using a Borr-Oliver TM-3 hydroclone unit, consisting of three sections each containing 32 ten millimeter hydroclones, to determine its suitability as a continuous method of thorium oxide particle size classification. The unit has been modified to cascade the hydroclones in order to obtain a greater removal of fines from the underflow material. The results of the preliminary tests have not been conclusive and further tests are scheduled to determine the effect of feed concentration, feed rate, underflow rate and agglomeration on the operation of the system. For two hydroclone systems, the classification was better for CH₃OH slurries (Fig.3.1) than for aqueous slurries of ThO₂.

A Sharples air classifier has been used to classify about 165 lb of thorium oxide.* The first pass of the thorium oxide through the unit yielded 96 lb of fines of less than 8 microns in diameter (~94% less than 5 microns). A second and possibly third pass of the fines through the classifier was scheduled to determine the effect of multiple passes on removing the larger particles.

* This operation was performed by the ORGDP Technical Division.

Fig 31. Classification of ThO_2 by Hydroclones.

3.2.2 Sharples DV-2 Centrifuge - E. L. Youngblood

A surplus Sharples DV-2 centrifuge obtained from K-25 was tested to determine its suitability for removing thorium oxide from slurry produced by the Pilot Plant particle size classification system. The DV-2 centrifuge is equipped with solids discharge valves in the bowl which allows the solids to be discharged while the bowl is rotating. While the 6,200 g developed by the unit was adequate to give an excellent separation of thorium oxide and water at a feed rate of 2 gpm, the unit was not recommended for this application because of difficulties in discharging the solids from the centrifuge bowl and because of difficulties in cleaning the unit after shutdown.

3.2.3 Flame Calcination - C. C. Haws, K. O. Johnsson

An extended run was made to test the operability of the methanol-thoria feeding system, the efficiency of the product collection system, and to obtain a quantity of flame calcined material for laboratory evaluation. The operability of the equipment was demonstrated by six smooth start-ups and essentially trouble-free operation for 40 hr. During the test period, 220 g of thoria was fed to the flame and recovery was estimated to be over 75%. Recovery of dry solids in the vacuum filter was much lower (~5%) than expected from a previous short run for which this unit yielded 25%. Most of the material from the current run was found in the spray cooling system.

Both the ultrasonic dispersor for slurries and the critical orifice "whistle" supplied by Aeroprojects, Incorporated, and tested at ORNL proved superior to equipment in prior use in Unit Operations Section. A quantitative comparison of either device with existing methods is impossible since no adequate measures of performance exist. The ultrasonic dispersion of thoria in alcohol was observed to offer a considerable improvement over simple centrifugal pump dispersion. The high equipment cost for a given capacity may limit application of this method. The dispersal of the thoria dust in a gas stream effected by the Aeroprojects "whistle" offers a combination of the solids dispersal and feeding steps. Slides taken of the dust produced show qualitatively a more effective dispersal as compared to slides prepared by other methods.

Tests were made to evaluate the effects of the injection of liquid methanol on $O_2-C_2H_2$ flame temperatures. The temperature of a reducing oxygen-acetylene flame as indicated by a thermocouple 4-in. from the gas orifice was $1600^\circ C$. At 5-in. from the orifice indicated temperatures were 1100 to $1350^\circ C$ at several radii. Alcohol injection divided the flame into two regions. The inner (and cooler) cone had its apex at the gas orifice and gave indicated temperatures ranging from $1300^\circ C$ at 1-in. from the orifice to $1250^\circ C$ 6-in. from the orifice. The flame in this inner cone was supported principally by the burning of the alcohol. An outer cone whose combustion was principally that of acetylene sheathed the inner cone. The indicated temperature of this outer cone was generally above $1500^\circ C$.

Temperatures with methanol injection should be increased by increasing the ratio of fuel gases to liquid injected and from better atomization-mixing-preheating of the gases with the alcohol feed. Spraying Systems nozzles offering these improvements have been purchased.

4.0 POWER REACTOR FUEL REPROCESSING

C. D. Watson

4.1 Darex - F. G. Kitts, B. C. Finney, J. Beams, F. L. Rogers

The purpose of the Darex process is to convert SS-U and SS-UO₂ fuels into chloride-free nitrate solutions suitable for processing in existing solvent extraction equipment. Chloride must be added to effect dissolution of SS in HNO₃ and then removed to avoid corrosion in both solvent extraction and waste-handling equipment. In the present concept of Darex, dissolution and chloride stripping are accomplished in a loop system; HNO₃ is recovered from the highly acidic stripped product in a feed adjustment step prior to solvent extraction. Continuing investigations will study the effect of loop operating conditions on dissolution rates, chloride removal and recovery, and off-gas evolution when dissolving fuels with various SS/U ratios.

Following the apparent success of Darex Loop Run No. 45 described in last month's report (Chemical Technology Monthly Report for December 1957), around-the-clock operation was attempted in Run No. 47 which resulted in 50 hr of continuous operation. The first half of the run went quite smoothly, although dissolution was lost momentarily at two separate times approximately 8 hr apart. After 25 hr, operation became rather erratic and after 50 hr the run was stopped. As predicted, the trouble was found to be an intermittent partial plugging of the dissolver outlet by platelets or flakes of what appeared to be undissolved stainless steel. Three material balances representing three 7-1/2 hr periods (approximately) of steady state operation during the first half of the run are presented in Figs. 4.1, 4.2, and 4.3. These are similar to the balance for Run 45 presented last month and were calculated in a similar manner.

Since the chloride level throughout the system remained essentially constant the chloride lost in the off-gas was assumed equal to the total amount added. The loss of nitrogen containing species to the off-gas was assumed the same as that in the previous long run. Work is proceeding on the refinement of analytical techniques for the off-gas components.

The dissolver has been replaced with another titanium vessel with about 4 times the hold-up volume (1.9 liters) and equipped with an external overflow level control rather than with an internal standpipe used in the previous model. The depth of liquid in the new dissolver is 6-1/2-in. vs. 3-in. in the old one. The heating capacity was raised to 2 kw and the preheater eliminated. Two more stripping plates were added for a total of 13. A 6-in. long titanium section was added just above the top plate of the 4-in. stripping column to facilitate entry of the line from the dissolver, carrying the dissolver product and off-gas into the column.

During these modifications the corrosion specimens were removed from the dissolver and the top plate of the stripper after having been exposed

Fig. 4.1. Material Balance for Run 47 Part I. Basis: 1 mole (55.4g) SS dissolved in 12.4 min.

%Material Balances (out/in)

	HNO ₃	H ₂ O	HCl
Overall	104	87	100
Dissolver	101	106	97
Stripper	103	91	103

14% of total HNO₃
make-up added directly
to dissolver

Fig. 4.3. Material Balances for Run 47 Part III. Basis: 1 mole (55.4 g) SS dissolved in 13.5 min.

to 200 hr of operating conditions. All the titanium specimens, both dry box and inert gas welded and unwelded, showed a slight weight gain. The tantalum specimens also gained in weight. The Vitallium alloy showed attack of 1 mil/mo. in the liquid on the stripper top plate, 3.7 mil/mo. in the dissolver liquid and 1.5 mil/mo. in the vapor in both locations. All specimens and interior equipment surfaces were coated with a tightly adherent film. Niobium was the primary constituent of the film followed in order by a iron-nickel complex, chromium, silicon carbide, and silicon dioxide.

4.2 Anhydrous HCl Zircex Engineering Studies - J. J. Perona

In a 24-hr gas-phase Zircex run at 500°C, 98.4% of a 3.7 kg section of an unirradiated fuel element was reacted. The average reaction rate, based on one-half the initial surface area, was 1.2 mg/sq cm min.

The uranium loss to the sublimate was 0.08% and the loss as insolubles in 10 M HNO₃ was 1.9%. A glass wool filter in the line from the hydrochlorinator to the ZrCl₄ condenser prevented excessive uranium loss to the sublimate. If the uranium found in the filter had reached the ZrCl₄ condenser, the loss to the sublimate would have been approximately 0.4%. The filter was packed to a density of 0.34 g/cc and maintained at 400°C throughout the run. The superficial gas velocity through the filter was 0.52 ft/sec.

The utilization of HCl gas as determined by a chloride analysis of a sodium hydroxide off-gas trap was 90%.

This run was the first on an engineering scale in which the uranium loss to the sublimate was held below 0.1%. Assuming that the "insoluble" loss could be recovered in a fused salt system, it appears that uranium recoveries of 99.9% can be achieved by the Zircex process with HCl utilization of about 90%.

4.3 Decontamination Studies

Decontamination testing of protective coatings for the duPont-operated Savannah River plant (as an aid in the selection of plant maintenance coatings) was completed. The contaminant for the second and last phase of the tests was concentrated Savannah River waste solution resulting from reprocessing uranium slugs. The first phase of the test was performed with LAW Thorex waste solution from reprocessing short-cooled thorium slugs. (Reference, Chemical Technology Division Monthly Report December 1957, ORNL-2468).

The coatings evaluated were air-dried paint systems applied on 16 gauge mild steel panels, 2-1/2-in. square. The Savannah River plant's maintenance department prepared one set of panels and the various plant manufacturers department prepared one set of panels and the various paint manufacturers supplied factory-applied panels for control comparison. The test was, in

* Technique in removal and handling of the filter was crude, and some uranium was undoubtedly lost prior to analysis.

principle, a comparison of vinyl and epoxy systems; however, other systems were included. The Savannah River waste solution used was made 2.2 N in acid. The activity level varied, due to decay, from 3.02×10^3 to 2.3×10^3 Rep/hr/0.2 ml. The 0.2 ml is the amount of contaminant applied on the center portion of each panel. The decontamination solutions used were: (1) water and (2) 3 N HNO_3 .

The vinyl base group of paints exhibited higher decontamination factors (up to 10^5) than the other groups tested and decontaminated equally well or better than Teflon, plate glass, 304 stainless steel, titanium, rigid polyvinyl chloride, and polyethylene (Table 4-1). It was also noted that the uranium waste solution decontaminated easier than the thorium waste solution.

A vinyl base coating, "Peel-Filmite", supplied by the DuBois Company, Incorporated, decontaminated to a value of 5.05×10^3 , which was three times greater than the next best coating, Nukemite-33, and 21 times greater than 304 stainless steel. Arrangement of paint types in decreasing order of decontaminability is:

1. Vinyl
2. Lacquer
3. Hypalon (polyethylene)
4. Epoxy
5. Polyester
6. Phenolic
7. Saran
8. Alkyd

Tests were conducted on a group of control and miscellaneous materials for comparison purposes. These are also presented in Table 4-1. The materials used for controls were: (1) Teflon, (2) plate glass, (3) polyethylene, (4) type 304 stainless steel, (5) titanium, (6) rigid polyvinyl chloride, and (7) Haynes 25 alloy.

The step-wise decontamination test procedure which was used was as follows:

1. Panels contaminated with 0.2 ml of solution.
2. Solution air-dried at room temperature.
3. First decontamination using a water flush for two minutes.
A jet stream of water was not employed in removing the activity.
4. Panel dried and activity read in mr/hr.
5. Final decontamination. Scrub bed panels in a 3 N HNO_3 solution for 5 minutes using a Gardner Wear Testing machine with Chinese hog bristle brushes. The brushes, ~ 4-in.² surface area, were weighted for a 1-lb total pressure on the panel and were operated 370 strokes during the 5-min. period.

6. Panels rinsed in water and dried in air at room temperature and activity read in mr/hr.
7. The decontamination factors calculated taking into account the decay of the contaminant.

Table 4.1. Decontamination Tests on Protective Coatings

1. Contaminant: Savannah River Waste Solution (SROW) 2.2 N acid, from reprocessing uranium slugs.
2. Activity Applied: 200 λ volume, read from 3.025 to 2.284 Rep/hr.
3. Specimens: Coated steel panels, 2 $\frac{1}{2}$ in. $\times$ 2 $\frac{1}{2}$ in. $\times$ 16 gauge.

Notes: (1) { Column "A" refers to Savannah River Plant prepared panels.
 { Column "B" refers to manufacturer prepared panels.

(2) Table listing is in decreasing order of D. F.'s.

Manufacturer and Trade Name	Decontamination Factor						Average
	Water Flush		Acid Scrub		Over-all		
	A	B	A	B	A	B	
Vinyl Base							
DuBois (Peel-Filmite)	973	4,200	174	201	168,000	842,000	505,100
Nukem Prod. (Nukemite-33)	17,800	11,000	14	7	252,290	79,000	165,645
Nukem Prod. (Nukemite-40)	12,850	21,300	10	2	128,500	38,900	83,700
Amercoat Corp. (Amercoat-31)		20,490		2		45,100	45,100
Amercoat Corp. (Amercoat-33HB)	10,850		4		40,300		40,300
Amercoat Corp. (Amercoat-23)	9,695	11,300	2	5	17,796	56,400	37,098
Amercoat Corp. (Amercoat-55)	1,144	18,350	4	4	5,200	66,200	35,700
Amercoat Corp. (Amercoat-33)		11,600		3		32,200	32,200
Amercoat Corp. (Amercoat-35)	3,270	9,970	3	3	10,250	33,100	21,675
Carboline Co. (Polyclad 120-1-DG)	6,060	7,750	2	4	11,650	31,300	21,475
Metal & Thermit (Ucilon-K)	1,042		17		18,000		18,000
David E. Long Corp. (Series-A)	3,910		4		16,940		16,940
duPont (Eng. 6200, system-1)	3,930	5,080	2	2	11,850	11,850	11,850
duPont (Eng. 6200, system-2)	3,150	5,080	2	3	6,020	16,700	11,360
Carboline Co. (Polyclad 933-1-DG)	4,520	4,040	3	2	12,500	8,620	10,560
Metal & Thermit (Ucilon-T)		2,260		4		8,100	8,100
L. E. Carpenter (Viretox)*	1,550		3		4,210		4,210
Prufcoat Lab. (Series-A)	835		4		2,970		2,970
duPont (Eng. 1200)	35	30	94	28	3,260	843	2,052
Amercoat Corp. (Amercoat-88)	28	34	2	2	73	60	67
Epoxy Base							
Amercoat Corp. (Amercoat-74)	2,070	3,930	1	1	2,740	4,220	3,480
Devos & Reynolds (Devran-600)	992	1,042	1	1	1,440	1,485	1,462
Prufcoat Lab. (Series-EP)	672		1		935		935
Carboline Co. (No. 180-57)	91	327	2	4	177	1,420	798

*Wallpaper.

Table 4.1 (continued)

Manufacturer and Trade Name	Decontamination Factor						Average
	Water Flush		Acid Scrub		Over-all		
	A	B	A	B	A	B	
Epoxy Base							
D. E. Long Corp. (Series-E)	433		1		553		553
duPont (Eng. 6426)	352	378	1	1	361	440	400
Metal & Thermit (Unichrome XL-2535)		137		2		215	275
Amercoat Corp. (Amercoat-66)		119		1		154	154
Lacquer							
Dittbrenner Associates (Polychem-1500)	6,050		14		84,250		84,250
Polyester							
Evershield Corp. (Liquid-Tile)		560		3		1,565	
		3,920		1		5,400	3,483
Amercoat Corp. (Amercoat-1679)		93		2		145	
		97		2		145	145
Polyethylene (Hypalon)							
duPont (100-E-47394, Hypalon)	6,500	7,625	2	2	14,100	12,900	13,500
Saran							
Peninsular Chem. (Penkote-500)	379		3		1,295		1,295
Phenolic							
duPont (Eng. 6102)	1,780	1,950	2	1	2,680	2,380	2,530
Carbolina Corp. (Phenoline-305)	100	336	1	5	122	1,440	781
Alkyd							
duPont (Eng. 5102)	183	110	1	1	225	157	191
Controls							
Teflon sheet, 1/8 in. thick		12,650		6			
		14,450		5		77,200	77,200
Plateglass, grade-B		6,900		8		57,800	
		19,550		3		51,400	54,600
Polyethylene sheet, 1/8 in. thick		36,100		5		28,200	
		14,650		3		38,500	33,350
347 Stainless Steel (2-B Finish)		522		27		14,000	
		2,930		11		33,100	23,550

Fig.5.1. Hydraulic Studies Apparatus.

Fig. 5.2 Gas Distributor Plates

Fig 53 Gas Distribution Plates

700 890

Fig. 5.4 Distributor Plate Data

Fig. 5.5 Distributor Plate Data

be employed is the measurement of the temperature in a packed bed at several points along the radius and the height, and to analyze the temperature transients with the differential equations for heat generation and transfer. The relatively high heat of absorption of UF_6 on NaF , the low thermal conductivity of the NaF bed, and the low specific heat of the gas combine to make this an attractive method of study.

The equipment has been designed and installation is virtually complete. The shakedown runs will substitute HF for UF_6 because it is more easily handled and behaves with regard to absorption similar to UF_6 .

5.3 HF -Fused Salt Dissolution of Zirconium - R. W. Horton, M. E. Whatley
G. Jones, Jr., C. C. Nance, D. H. Newman

Zircalloy-3 was dissolved at rates ranging from 0.15 to 0.26 lb/hr in a dissolution test of 32 hr duration. The dissolution was carried out at three temperatures - $600^\circ C$, $650^\circ C$, and $700^\circ C$ - and with hydrofluoric acid rates ranging from 4.7 to 12.5 fps superficial gas velocity (or 0.84 to 2.25 lb/hr). Zirconium dissolution rates varied with temperature and inversely with addition rate, the range being 10.3 to 16.2%.

The 32 hr test period covered eight different phases in which either temperature or HF addition rate was varied. The total non-condensable off-gas stream is passed through a wet-test meter which allows both volumetric rate and cumulative volume measurement. The nitrogen entering the system is metered and this volume subtracted from the total leaves the volume of hydrogen evolved. Gas samples taken periodically are analyzed to check this value. The rate of hydrogen evolution is used as a basis for calculating the reaction rate for hydrogen fluoride and zirconium.

Table 5-1 presents the average values during each test period for hydrogen fluoride feed rate and hydrogen evolution rate. The acid utilization and metal dissolution rates calculated from these values are also shown. A summary of the entire test, Table 5-2, shows the weight of zirconium dissolved as determined by hydrogen evolution and by loss of weight of the dummy fuel element. The weight values are of doubtful value because of the heavy layer of fused salt and corrosion product film (tentatively identified as $7NaF \cdot 6ZrF_4$), which was found on the element when it was removed from the dissolver (Fig. 5.6). As indicated in the photograph, the welds which held the element together dissolved and allowed the plates to separate. The effect of this collapse on dissolution rate is not known.

Table 5-1. HF-Fused Dissolution of Zirconium

Summary of Dissolution Rate Study

Run No. - D-2

Date - December 12 and 13, 1957

Salt - 32 Mol % ZrF_4 , 68 Mol % NaF

Temp (°C)	HF Feed Rate (lb/hr)	Hydrogen Evolved (lb/hr)	HF Utilization (%)	Zr Dissolution Rate (lb/hr)	Duration (hr)	Total Zr Dissolved (lb)
600	1.16	0.00690	11.8	0.1559	6.0	0.935
600	1.49	0.00817	10.9	0.1846	4.0	0.738
650	0.84	0.00674	15.9	0.1523	4.0	0.609
650	1.06	0.00864	16.2	0.1952	4.0	0.781
650	1.52	0.00987	12.9	0.2230	4.0	0.892
700	1.15	0.00884	15.2	0.1998	4.0	0.799
700	1.42	0.00999	14.0	0.2258	2.16	0.488
650	2.25	0.01169	10.3	0.2642	3.0	0.793

Table 5-2. Summary of Zirconium Dissolution

(Eight Phases of Run D-2)

Wt Zr Dissolved Calculated from Avg. Rate x Time for Each Phase	Wt Zr Dissolved Calculated from Cumulative Off-gas Meter Readings	Wt Zr Dissolved from Change in Weight of Element
6.04	6.0	5.39

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2 3 4 5 6 7 8 9 10 11 12

Fig. 5.6. Dummy Fuel Element After Dissolution Test.

The relative effects of temperature and acid addition rate on the rate of zirconium dissolution are shown in Figs. 5.7, 5.8. It appears that dissolution rate can be improved most readily by increasing the acid addition rate. As acid addition rate is increased the percent of acid utilized is decreased as shown in Fig. 5.9, resulting in greatly increased recycle requirements. The optimum acid addition rate is not yet determined.

The total exposed surface of the element at the start of the test was 700 sq in. or 4500 sq cm. Using this area, the specific dissolution rate varies from 0.025 to 0.043 mg/sq cm/min. These rates are lower than the experimental rates published in ORNL-2183 by Wymer, which range from 0.5 to 8.0 mg/sq cm/min. The heavy corrosion film formed in the test reported here had apparently blocked many of the passages in the element and caused a reduction in the effective contact area.

The dissolution was done in a copper-lined stainless steel vessel closed with inconel flanges. All connecting lines were copper, except the molten salt transfer line which was inconel. The vessel was heated by a conventional muffle type of furnace using resistance heaters. A general view is shown in Fig. 5.10.

A substitute fuel element patterned on the MTR type was fabricated from scrap zircalloy-3. The element was 11-in. long, 2.5-in. wide, and had 17 plates, making a depth of 3.25-in. The total weight was 10.8 lb and the total surface 703 sq in.

The salt used was 38 mol% zirconium fluoride and 62 mol% sodium fluoride at the start of the dissolution test. Approximately 40 lb of salt were required to bring the liquid level in the dissolver to 14-in., a depth which submerged the dummy fuel element about 1-in.

Anhydrous hydrofluoric acid was vaporized from a weighted cylinder by heating, and the flow of gas was controlled by a manually set pneumatic control valve with monel trim. A Teflon tube rotameter was used to indicate gas flow. The metering was quite accurate when the HF vapor was maintained at +40°C, which is necessary because of polymerization which occurs at low temperature. The unreacted HF passed through the dissolver off-gas line to a water-cooled coil and thence to a dry ice-trichlorethylene cooled condenser. The condensed HF was recovered in a steel cylinder and weighed. The non-condensable gases-hydrogen and nitrogen-passed through a wet test meter and thence to the building off-gas system.

Fig. 5.7. HF-Fused Salt Dissolution of Zirconium. Test D-2 12-12 and 12-13 1957 Zr dissolution rate vs temperature of molten salt.

-39-

Fig. 5.8. HF-Fused Salt Dissolution of Zirconium. Test D-2 12-12 and 12-13 1957 Zr dissolution rate vs HF addition rate.

-40-

Fig. 5.9. HF-Fused Salt Dissolution of Zirconium. Test D-2 12-12 and 12-13 1957 % HF utilization vs HF addition rate of three temperatures.

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Fig. 5.10. Dissolver and Related Equipment.

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