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HOT SEMIWORKS REDOX STUDIES

By

T. F. Evans and R. E. Tomlinson

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Chemical Development Unit
Separations Technology Sub-Section

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RICHLAND, WASHINGTON

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HOT SEMIWORKS REDOX STUDIES

I. INTRODUCTION

The separations Hot Semiworks at the Hanford Atomic Products Operation was built in order to: (1) develop optimum conditions for the economic operation of the Redox and TBP plants, (2) procure engineering design data which would allow the specification of process equipment required for new processes such as Purex, (3) provide facilities for the study of future process and engineering problems on a semiworks scale employing radioactive process solutions, and (4) provide facilities for immediate trouble shooting for urgent separations plant problems. The initial operation of this facility was designed to develop conditions for the economic operation of the Redox Plant. These studies, covering a period from November, 1952 to October, 1953, are described in this report.

The Redox process is used at Hanford for the separation of uranium and plutonium from fission products and from each other. The basis of the process is the preferential extraction of uranium and plutonium nitrates from an aqueous phase of high salting strength into an organic solvent (methyl isobutyl ketone) to effect the separation from fission products. This operation is conducted continuously in columns, packed with Raschig rings, through which the phases are passed counter-currently. Uranium and plutonium are separated by converting the plutonium to a lower valence state, in which form it is preferentially extracted back into an aqueous phase of high salting strength in a second column. Uranium is then returned to an aqueous phase of low salting strength in a third column. The products are further decontaminated in similar additional cycles. A detailed description of the process is given in the Redox Technical Manual.⁽¹⁾

Only summary results are quoted in this report. For more detailed information, reference is made to the individual run reports published separately (See references 3, 4, 5, 6, 7, 10, 11, 12, 13).

II. OBJECTIVES

This report describes a series of experiments conducted in the Hot Semiworks to evaluate the operability of several modifications to the Redox process which were attractive economically and promising on the basis of previous laboratory or theoretical studies. These studies were conducted in order that modifications might be made in the operating procedures of the Redox production plant in a manner combining maximum operating economy with a minimum of risk of disrupting production schedules through excessive rework and/or unnecessary equipment changes.

III. SUMMARY

The Hot Semiworks studies of the Redox process resulted in the demonstration of process modifications potentially capable of reducing the cost of operating the Redox process by about \$1000 per ton of uranium processed. In a production facility processing 200 tons of uranium per month, these savings would approximate \$2,400,000 per year. In addition, data were collected on other modifications which may be utilized to advantage in the future.

The downdraft dissolving procedure, in which nitrogen oxides are partially absorbed and reused as nitric acid, resulted in a decrease in acid consumption during slug dissolution from 5.0 moles of acid per mole of uranium dissolved to 3.0 moles per mole. The dissolution proceeded very smoothly to acid deficiency, and the total time required per cut was comparable with that required in an updraft dissolving. Subsequent decontamination by solvent extraction was at least as good as, and possibly better than, that obtained employing feeds from updraft dissolvings.

Several variations of a permanganate oxidation and manganese dioxide scavenging prior to solvent extraction resulted in gamma decontamination factors of 4 and ruthenium decontamination factors of up to 100, thus confirming laboratory studies of this head-end procedure. Although a single

[REDACTED]

addition of KMnO_4 was rapidly reduced in dissolver solution without effecting a ruthenium oxidation, a second increment added shortly after the first exhibited considerably greater stability. This "sacrificial kill" technique enabled the KMnO_4 to oxidize ruthenium to RuO_4 which could then be removed from the solution by distillation. The efficient scavenging action of manganese dioxide for zirconium-niobium was reconfirmed. Due to the effective removal of ruthenium by volatilization, the fission product limiting overall decontamination was shifted from ruthenium (with solvent extraction alone) to zirconium-niobium with head-end plus solvent extraction.

This KMnO_4 head-end procedure proved so promising in the Hot Semiworks that it was immediately adopted as a standard operating step in the Redox Plant. Employment of this head-end step in the Redox Plant has apparently increased overall plutonium recovery approximately 0.3 to 0.5 per cent, valued at \$300,000 to \$500,000 per year (net savings) when processing 200 tons of uranium per month. However other Redox Plant benefits attributed to this head-end development are considered even more important. The IA and IS Columns definitely exhibit less tendency toward emulsification, and the average production through each of these columns before a shutdown is required for flushing has been increased from a former value of 20 tons to 40 tons of uranium. Also, since adoption of the head-end step in the Plant, the resulting additional decontamination factor has been exploited to permit satisfactory operation of the Plant at approximately 50 per cent higher rates than would otherwise have been possible before installation of new larger columns (which are not yet installed). At lower Redox Plant processing rates this added decontamination factor potentially permits elimination of one uranium solvent-extraction cycle at a net operating savings of approximately \$400,000 per year, in the absence of waste backcycling.

A dual-scrub flowsheet was successfully piloted in the IA Column, with satisfactory product losses and decontamination being obtained, although the decontamination obtained appeared to be poorer than that obtained with the ORNL, June 1949 Flowsheet by a factor of about 2. This poorer decontamination is not considered conclusively proved, however, due to the limited number of comparative Semiworks runs and possible effects of uncontrolled variables. The dual-scrub flowsheet is potentially capable of permitting the

[REDACTED]

use of concentrated second cycle wastes as the source of salting agent for the first cycle, and the Hot Semiworks results are considered sufficiently promising to warrant trial operation in the Redox Plant.

Data were obtained on many other processing variations, some of which are noted here. Air sparging during the dissolution of irradiated uranium apparently has an adverse effect on the subsequent solvent extraction behavior of the fission products zirconium and niobium. Plutonium losses in the aqueous waste are much more sensitive than uranium losses to the aqueous/organic flow ratio in the extraction section of a Redox IA Column. Single-scrub flowsheets are apparently more stable operationally than dual-scrub flowsheets when emulsifying agents are present; also under certain conditions, an emulsifying system may be made more operable by increasing (20%) the extractant flow ratio. A silica gel bed effectively removed zirconium-niobium from the hexone-saturated 2EU stream, but its effective life between regenerations is limited and the regeneration technique used failed to restore its original efficiency. Encouraging data were collected on the reflux plutonium-cycle flowsheet, but emulsification and equipment failures prevented a complete demonstration of the flowsheet.

IV. INCENTIVES

The incentives for conducting this series of experiments lay in developing means for reducing the costs of operating the Redox production plant while maintaining or improving the yields and decontamination of products obtained. The data collected can be used to reduce operating costs, improve yields or decontamination factors, and/or increase operating rates as the immediate needs dictate.

The first major process modification studied was a revised head-end oxidation which was intended to rid the dissolver solution of most of its ruthenium, the major contaminant in the product streams. Although an early Redox flowsheet called for an oxidation with potassium permanganate in order to convert ruthenium to the volatile RuO_4 for removal by distillation, this step was abandoned when it was found in initial operation of the Redox Plant that the oxidant was rapidly destroyed in the dissolver solution without effecting the ruthenium oxidation. The incentive for a good ruthenium oxidation and distillation lay in the possibility that acceptable products could be obtained with two

~~solvent extraction cycles instead of the three cycles then in use in the production plant.~~ In contrast to a chemical and waste storage cost of \$50 to \$100 per ton of uranium for the head-end treatment in the absence of waste back-cycling, the chemical and waste storage costs per ton of uranium processed are approximately \$400 and \$125, respectively, for the third uranium and third plutonium cycles.

The second major modification studied in the present series of runs was the dual-scrub flowsheet for the original (IA Column) extraction of uranium and plutonium, in anticipation of the use of concentrated second cycle wastes as salting agent for the first cycle. Such back-cycling would result in a savings of about \$500 per ton of uranium processed. This saving would be realized through reduced chemical costs for salting agent and a reduction in underground waste storage requirements. In addition, the small amounts of uranium and plutonium in these waste streams would be recovered, having an additional value of about \$150 per ton of uranium processed on the basis of current waste losses and unit costs.

Several secondary process changes were also investigated. At present, the production plant uses approximately five moles of nitric acid per mole of uranium during the dissolution of the metal, although a lower limit of two moles is theoretically possible if the oxides of nitrogen evolved during the reaction are oxidized, absorbed, and returned to the dissolver as nitric acid. Previous investigations in the 321 Building Cold Semiworks at HAPO and at ORNL⁽¹⁵⁾ have demonstrated that downdraft dissolving is capable of saving two moles of nitric acid per mole of uranium dissolved, with an attendant cost reduction of about \$25 per ton of uranium dissolved. This investigation had only to show that subsequent solvent extraction is not adversely affected.

Aside from ruthenium the most important product contaminants are zirconium and niobium. These ions can be removed from solvent-free product streams by adsorption on silica gel.⁽⁸⁾ During the present

runs, the feasibility of using silica gel for decontaminating the product uranium stream without prior solvent stripping was tested.

In the second plutonium cycle, the plutonium is transferred to the organic phase in one column to separate it from fission products and then transferred back to an aqueous phase in a second column. The resulting product stream is quite dilute in plutonium. Concentration of plutonium in the columns by refluxing the product stream to the first column was studied during four runs of the series. Improved decontamination of the plutonium was expected.⁽⁹⁾

V. FLWSHEETS

The distinguishing features of the Redox solvent extraction process are the use of methyl isobutyl ketone (hexone) as the solvent and aluminum nitrate (ANN) as the salting agent in the solvent extraction columns. With these basic components several flowsheets have been proposed which differ principally in the concentrations of salting agent and nitric acid in the various streams. The initial solvent extraction conditions used in the production plant and in the first eight semiworks runs were essentially those of the ORNL, June 1949, Flowsheet⁽¹⁾ as given in Table I. In this table, the second cycle conditions shown are those for a standard non-reflux plutonium cycle and a single-scrub uranium cycle. These conditions are based on experimental work done at ORNL.⁽¹⁴⁾ Figure 1 is a schematic flow sketch of the Hot Semiworks equipment for operation under these conditions.

In the ORNL flowsheet the scrub solution (IAS) furnishes the salting agent for the first extraction column and enters at the top of the column. When second cycle waste streams are used to prepare the IAS, laboratory studies⁽²⁾ have demonstrated that it is undesirable to introduce this stream at the top of the column because of a 2- to 5- fold loss in decontamination factor. Presumably this lowered decontamination results from extraction of some of the recycled fission products into the extract

(IAP). For this reason, the dual-scrub flowsheet, originally developed for the third uranium cycle in order to control iron, aluminum, and sodium concentrations in the final uranium product, was adapted to the IA Column.

In the dual-scrub flowsheet, the IAS is introduced near the middle of the IA Column (in some cases, mixed with IAF feed) and water (IAA) is added at the top of the column. This flowsheet was operated in both the first extraction cycle and the second uranium cycle during the last four runs. Figure 2 is a flow sketch which includes the modifications for dual-scrub operation of the IA and 2D Columns and the reflux flowsheet for the second plutonium cycle. The conditions for operation with these modifications are given in Table II. During the last four runs, combinations of the conditions given in Table I and II were employed, as described in Part VIII of this report.

The flow rates, averaged over the major portion of a run, were usually within ten per cent of the flow ratios given in Table I and II and were frequently within five per cent.

VI. EQUIPMENT

The Hot Semiworks contains equipment designed to process irradiated uranium slugs of full Hanford-level activity at an intermittent instantaneous rate of 0.1 ton/day. Extraction columns and associated equipment are provided for carrying out two uranium and two plutonium cycles and for reclaiming solvent. Equipment which may contain radioactive solutions is located in one of three concrete-shielded cells and is operated from a remote control panel. Wash tanks, decanters, solvent makeup tanks and head tanks, and a still for distilling recovered solvent are located in a second building, and aqueous makeup tanks and head tanks are located in a third. All tanks, columns, piping, and other equipment exposed to process solutions are fabricated of stainless steel. Figures 1 and 2 show schematically the principal equipment pieces located in the three "hot" cells and Figure 3 shows the general layout of the cells.

The seven extraction columns are packed columns operated with the interface at the top of the column in an enlarged disengaging section. Dimensions are given in Table III.

During the first two runs, tests were made to determine the flooding capacities of the columns using the ORNL flow conditions. They were as follows:

<u>Column</u>	<u>Flooding Volume Velocity, Sum of Both Phases</u>
IA	950 gal/hr/sq ft
IB	1200 gal/hr/sq ft
IC	1300 gal/hr/sq ft
2A	>500 gal/hr/sq ft, limited by the 2AS flow rate
2B	800 gal/hr/sq ft

"Cold" streams entering the columns flowed by gravity from head tanks located in the solvent and aqueous buildings. All the column feeds were controlled by air-operated Hammel-Dahl valves actuated through Fischer and Porter rotameters and Foxboro flow recorder-controllers. The aqueous head tanks were pressurized with 4 psig. air during the last four runs in order to improve the flow control. In general, the "cold" streams were well controlled except for occasional sticking of some of the rotameter bobs.

The control of the "hot" streams, however, was much less satisfactory, difficulty being encountered with the submerged Roth regenerative turbine pumps used to feed the radioactive solutions to the columns. The operation of this nominal 25 gpm pump at the extremely low flow rates required by Hot Semiworks operations developed a high radial thrust on the shaft bearing just above the impeller. The resultant bearing wear permitted an increased clearance between the impeller and volute dam, thereby resulting in a decreased pumping efficiency. This same type of pump has been

in operation in the Redox production plant since its start, and several of the original pumps are still in operation. Characteristically, the failing pumps would not prime properly, and several hours were consistently required to attain a reasonably steady flow rate. Through the series of runs, the capacity of the feed pumps decreased considerably until it ultimately became impossible to obtain the desired flow rates. The IAF pump failed completely after Run 8 and was replaced during an extended shut down at that time. The replacement pump failed during Run 11 and the 2DF-IAS pump was used for feeding IAF during the last two runs. As a consequence of surging flows associated with the failing IAF pumps, the IAF rotameter was damaged and became inoperative during Run 10.

The column interfaces were controlled by air-operated Hammel-Dahl valves in the aqueous effluent lines. The control valves were actuated by Foxboro interface recorder-controllers which received their signals from bubbler-type pressure detectors through Republic transmitters. The principal difficulties encountered were plugging of the dip tubes and control valves with precipitated salts. To prevent the evaporation of concentrated salt solutions in the dip tubes, a small steam purge was added to the inert gas flowing through the dip tubes on the IA, IB, 2A, and 2D Columns after Run 7. The purge was discontinued for Run 12 because of the possibility that it contributed to aqueous entrainment from the IA Column which was first observed during Run 8. The evidence is ambiguous, but it appears probable that the steam purge was not responsible for the entrainment.

Standard instrumentation included temperature, pressure, weight factor, and specific gravity indicators and recorders. Temperatures were measured at the points shown in figures 1 and 2 by Foxboro Dynatherm resistance elements and were recorded on Leeds and Northrup recorders or Foxboro recorder-controllers. Pressures in the head-end off-gas system were indicated by water manometers in the control room. While

liquid levels in "cold" tanks were observed in sight glasses at the tanks, the contents of tanks in the cells were indicated by weight factor and specific gravity measurements with bubbler-type pressure detecting instruments.

The dissolver was a 140-gallon tank provided with a basket for holding uranium slugs, an air sparger, a coil for heating or cooling, and a jacket for heating or cooling. Two alternative reflux condensers allowed updraft or downdraft operation. The updraft condenser, E-1-1, contained a Raschig-ring entrainment separator topped by a refluxing cooling coil. In the downdraft condenser more effective scrubbing of nitrogen oxides was obtained by providing intimate contact between the co-current vapors and refluxing liquid stream at a reduced temperature in a packed section containing longitudinal cooling tubes.

The centrifuge was a 26-inch diameter, solid bowl model manufactured by the Bird Machine Co., and normally operated at 1800 RPM. It was provided with a hydraulically-operated plow and skimmer and with bowl and case sprays.

Several tanks were provided with coils or jackets for heating and cooling. Tanks 6 (oxidizer), 12 (ICU and 2EU concentrator), 17 (2BP concentrator), and 55 (waste concentrator) were equipped with packed stripping or de-entrainment towers about eight feet high. (T-6 had only three feet of packing).

During the period of IAF pump replacement after Run 8, several modifications to the equipment were made. Auxiliary inlets were connected on the IA and 2D Columns 2 1/2 feet above the mid-column feed point to provide for the scrub entry during the dual-scrub operation of these two columns. At the same time, one foot of packing was removed from the top of these two columns in order to lessen the probability of flooding during dual-scrub operation. This flooding tendency was anticipated since the IAA (water) with density 1.00 is introduced at a point

where the density of the rising organic stream is as high as 0.97. An air lift of 1/4-inch stainless steel tubing was installed in the second plutonium system to allow refluxing of 2BP to the 2A Column. The third change made at that time was the addition of a silica gel bed in the 2EU line. The bed comprised a 5-ft section of 3-inch Schedule 40 stainless steel pipe packed with 12 to 28 mesh refrigeration-grade silica gel. For expedience, only upward flow through the bed was provided, with bed washing to be conducted in the same direction as the process flow. The experimental procedures for the Semiworks runs were patterned after those currently in use in the Redox production plant. The "standard" procedures are described here; experimental deviations are described in conjunction with the experimental results in Section VIII.

VII. STANDARD EXPERIMENTAL PROCEDURES

Most of the Hot Semiworks Redox runs were made within the framework of a five-day work week with three operating shifts. Slug charging, jacket removal, and dissolving were carried out while the second extraction cycles of the proceeding run were being completed. The oxidation and feed adjustment were performed during the first part of the following week so the first extraction cycle could be completed by Friday of that week without interruption. During the second week, second cycle feeds were adjusted to the specifications given in Table I or Table II and the second plutonium and uranium cycles were carried out. At the same time, the slug charging, jacket removal, and dissolving steps for the next run were performed. The solvent extraction cycles operated about 60 hours each during an ideal run. Because of mechanical and emulsification problems encountered during Runs 9 and 10, the preceding schedule could not be maintained for those runs and it was necessary to interrupt the column operation for weekend shutdowns. In order to avoid these interruptions, four shifts were used during the last two runs. A high spot chronology of events is given in Table IV.

A. Dissolving and Head End

Irradiated slugs from the piles were charged to the dissolver with the aid of a special slug charger. The slugs used had, in general, an irradiation level of about 600 megawatt-days per ton (MWD/T) and were about 100 days from pile discharge when charged. A sufficient number of slugs were charged to provide a heel in the dissolver of 250 or 500 pounds of uranium after two 250-pound cuts had been dissolved.

The first step following charging was the removal of the aluminum alloy slug jackets. These were removed with a NaOH-NaNO₃ solution by a standard procedure which paralleled that used in the production plant. The chemistry of the process is discussed in the Redox Technical Manual (p. 303).⁽¹⁾ For a normal charging of 500 pounds of new slugs, 333 pounds of 26% NaNO₃ solution was added, the temperature was raised to about 95°C., and the air sparger was operated to give 2.5 SCFM. Eighty-seven pounds of 50% NaOH solution and 14 pounds of water were added and, after the reaction had subsided, the temperature was raised to 100 to 110°C. This amount of NaOH represents a NaOH/Al mol ratio of 1.8. The solution was maintained at the boiling point for three hours. It was then cooled, the sparger was turned off, and the solution was sent to the waste storage tank. The de-jacketed slugs were rinsed in hot water for an hour and were then ready for dissolution.

Two dissolution procedures were utilized. In the updraft procedure, which was followed in a majority of the runs, the E-1-1 reflux condenser was used. For a normal cut of 250 pounds of uranium, 600 pounds of 60% HNO₃ was added to the dissolver and the temperature was raised to the boiling point. The solution was maintained at the boiling point, generally without air sparging, until the specific gravity had reached about 1.79 at the temperature of the solution. The solution was jetted to the oxidizer and a second cut was made by the same procedure. The two cuts were combined in the oxidizer to provide the feed for a run.

For the downdraft procedure, the E-1-2 downdraft condenser was used in order to scrub nitrogen oxides from the exit gases. In order to oxidize the NO formed in the reaction to NO₂, approximately 5 SCFM air was introduced into the top of the dissolver during the downdraft dissolutions. Three hundred and ninety pounds of 46% HNO₃ was used per cut. The solution was maintained at a vigorous boil (in order to provide sufficient water for scrubbing in the condenser) until the specific gravity reached about 1.87 at which time the solution was cooled and jetted to the oxidizer, where it was air sparged for one hour. The second cut was made by the same procedure and the two cuts were combined for the run.

After the two cuts were combined in the oxidizer, Na₂Cr₂O₇ (or KMnO₄) was added as a holding oxidant and the volume and acidity were adjusted to the concentrations desired during the first extraction cycle or during further oxidation steps. In the last six runs, a ruthenium oxidation and distillation was included in the head-end operations. In most of these runs, two additions of KMnO₄ were made. After each addition, the solution was held near the boiling point from one to two hours and air sparged at about 10 SCFM. Excess permanganate was reduced and the MnO₂ formed during the oxidation was dissolved with Cr(NO₃)₃ or oxalic acid. In several of the runs, a fraction of the MnO₂ was left for zirconium-niobium scavenging.

Following the oxidation, the feed solution was centrifuged at 50°C. The effluent from the centrifuge was recycled to the oxidizer until the normal centrifugation rate of one liter per minute was established. Upon completion of the centrifugation, the cake, if present, was washed two or three times with 0.01 M HNO₃. The washings were routed back to the oxidizer for inclusion with the next run. Any MnO₂ cake was removed from the centrifuge to waste with several batches of ferrous sulfamate solution. Only minor adjustments of acidity and uranium concentrations were in general required after the centrifugation to bring the feed to the composition of Table I or II.

B. Solvent Extraction

The duration of a normal first-cycle solvent-extraction run was 50 to 70 hours, including time for start-up and shutdown. Tanks for the various streams were sized to hold enough feed for the complete run so, in general, sufficient volumes of the "cold" feeds for the entire run were prepared before starting the columns. Each solution was sampled and adjustments in composition were made until the feeds were within the limits given in Table I or II. Between the first and second cycles, the 2DF and 2AF were brought into specifications by concentration and acidity adjustment. Small increases in the specific gravity of the 2AF were made by butting the solution with stock ANN solution.

In starting up the columns, the first step was to establish the organic-aqueous interfaces. After filling the columns with the appropriate "cold" aqueous feeds, the organic streams were started with the interface control on automatic. As soon as the organic phase was cascading properly from the first column to succeeding columns, the other "cold" streams were started and rate checks were begun so as to have these feeds approximately on rate when the "hot" feed was started to the column.

Samples of the various streams were, in general, taken at eight- or sixteen-hour intervals while all the streams were near the desired flow rates. When the first sample in a series differed from succeeding samples, it was discounted somewhat, since the rates were frequently not well established and the columns may not have arrived at equilibrium at the time the sample was taken. Subsequent samples in the series were consistent unless there had been some disruption of the column operation.

After the "hot" feed was depleted, the columns were usually shut down in such a way as to transfer uranium and plutonium from the columns to the product tanks. Both aqueous and organic streams were

continued for approximately one hour. The organic phase was then displaced from the columns by adding "cold" aqueous streams, and the column contents were flushed to the receiver tanks. The columns were filled with "cold" aqueous feeds and allowed to stand full of liquid until the next run.

VIII. EXPERIMENTAL RESULTS

The first four runs were made with "cold" uranium. (Run 4 had trace amounts of plutonium and fission products.) They served mainly to establish the operability and to determine the operating characteristics of the equipment. In particular, possible causes of emulsions in the second plutonium system were investigated. The next four runs, with irradiated uranium, provided a test of the permanganate head-end for ruthenium decontamination. Runs 5 and 6 established comparability with the current Redox operation and had no permanganate oxidation. For the last four runs, the equipment was modified to allow a test of the dual-scrub flowsheet and the reflux-plutonium flowsheet. The first extraction cycles of two of the runs and half of a third were operated with dual-scrub flowsheet; in a portion of one of these runs, second cycle wastes were recycled. The metal for two of these runs was dissolved by the downdraft procedure.

The decontamination results given in this section are all expressed as logarithmic decontamination factors ($dF = \log_{10} DF$). Decontamination factors were, in general, calculated on the basis of the uranium or plutonium concentration in the stream considered, although in a few instances the volume of solution was used as a basis. That is, for the decontamination between solution No. 1 and solution No. 2,

$$DF = \frac{(\text{microcuries/gal.})_1}{(\text{lb U (or g Pu)/gal.})_1} \div \frac{(\text{microcuries/gal.})_2}{(\text{lb U (or g Pu)/gal.})_2}$$

A. Dissolution and Feed Preparation

Jackets were removed on eleven occasions with essentially the procedure given in Part VII. For runs in which more than 500 pounds of slugs were charged, the amounts of NaNO_3 and NaOH were increased proportionally. Representative conditions are given in Table V. Jackets were removed prior to all runs except 8 and 12 in which the dissolver heels were dissolved. During Run 6, the jackets were incompletely removed during the normal operation and the jacket removal step was repeated before the second dissolving cut was made. Conditions appeared normal during both jacket removal operations.

During the series of 12 runs, 24 dissolvings were made. There were three cuts each for Runs 1 and 2 and one each for Runs 3 and 8; the other runs had two cuts each. Of the 24 cuts, 18 were updraft dissolvings and six were downdraft. Representative conditions are given in Table VI and the principal data are summarized in Table VII. In several of the runs, samples of the individual cuts were not taken so only average HNO_3/U mole ratios for the blends of two or three cuts were obtained.

Among the runs with irradiated uranium, there were eleven updraft cuts (one of which was preceded by a poor jacket removal step), three downdraft cuts, and one off-standard downdraft cut in which no air was introduced during the dissolution. Dissolving curves for the standard runs are given in Figure 4. While the peak rate of reaction occurred early in the updraft procedure and required the use of cooling water to prevent excessive pressure drop in the deentrainment tower, the maximum rate during downdraft dissolving occurred after about two hours at the boiling point and required no special operational control. Most of the updraft dissolutions were stopped with a small amount of acid still in the solution; the downdraft dissolutions, however, proceeded to acid deficiency before the anticipated final specific gravity of 1.87 (boiling) was obtained. The average acid consumption during the downdraft dissolvings was 3.0 moles of nitric acid per mole of uranium compared to a consumption of 5.0 moles per mole during the updraft dissolvings.

Following dissolution the blended dissolver solution was oxidized. The first four "cold" runs were intended principally for proving the operability of the equipment and the oxidation step was carried out for that purpose. In Runs 5 and 6, oxidation with sodium dichromate was used to duplicate the procedure then in use in the production plant. Variations of the permanganate oxidation for ruthenium decontamination were used in the remaining runs. During each oxidation, the solution was air sparged, usually at 10-15 SCFM during the digestion periods. The conditions are summarized below.

- Run 1. Added 0.15 M $\text{Na}_2\text{Cr}_2\text{O}_7$ and 0.04 M KMnO_4 and held at 100°C for six hours. $\text{Cr}(\text{NO}_3)_3$ added to reduce excess KMnO_4 to MnO_2 . Held for one hour at 95°C .
- Run 2. Same as Run 1.
- Run 3. No oxidation.
- Run 4. Added 0.15 M $\text{Na}_2\text{Cr}_2\text{O}_7$ and held at 100°C for four hours.
- Run 5. Added 0.10 M $\text{Na}_2\text{Cr}_2\text{O}_7$ and held at 100°C for two hours.
- Run 6. Added 0.08 M $\text{Na}_2\text{Cr}_2\text{O}_7$ and held at 100°C for four hours. The two cuts were oxidized separately.
- Run 7. Adjusted to 0.2 M HNO_3 and added 0.05 M $\text{Na}_2\text{Cr}_2\text{O}_7$. Added 0.07 M KMnO_4 and heated to 55°C for one hour. Heated to 75°C for one hour. No permanganate present. Added 0.07 M KMnO_4 and held at 75°C for one hour. Heated to 95°C for one hour. 0.01 M KMnO_4 present. Added 0.12 M $\text{Cr}(\text{NO}_3)_3$ to dissolve MnO_2 .
- Run 8. Adjusted HNO_3 to 0.2 M. Added 0.02 M KMnO_4 and heated to 95°C for one hour (sacrificial kill). Added 0.05 M KMnO_4 and heated to 55°C , 75°C , and 95°C successively for one hour each. 0.046 M KMnO_4 present. Added 0.11 M $\text{Cr}(\text{NO}_3)_3$ and heated to 95°C for one hour to dissolve

the MnO_2 . The $\text{Cr}(\text{NO}_3)_3$ used was marginal and some MnO_2 may have been left.

- Run 9. Adjusted HNO_3 to 0.05 M. Added 0.02 M $\text{Na}_2\text{Cr}_2\text{O}_7$ and 0.01 M KMnO_4 . Heated to 95°C for one hour. Added 0.03 M KMnO_4 and held at 95°C for two hours. Added 0.062 M $\text{Cr}(\text{NO}_3)_3$ to dissolve the MnO_2 and heated to 95°C for one hour.
- Run 10. Adjusted HNO_3 to 0.05 M and added 0.01 M KMnO_4 as a holding oxidant over the weekend. Added 0.01 M KMnO_4 (sacrificial kill) and heated to 95°C for two hours. Added 0.03 M KMnO_4 and held at 95°C for two hours. Added 0.015 M oxalic acid (catalytic kill) and heated to 95°C for one hour. Added 0.04 M oxalic acid and held at 95°C for one hour to dissolve 80% of the MnO_2 . Added 0.05 M $\text{Na}_2\text{Cr}_2\text{O}_7$. Brown precipitate present.
- Run 11. Adjusted HNO_3 to 0.05 M and added 0.01 M KMnO_4 as a holding oxidant. Added 0.01 M KMnO_4 and heated to 95°C for one hour. Added 0.04 M KMnO_4 and held at 95°C for four hours. No permanganate present. Added 0.01 M $\text{Cr}(\text{NO}_3)_3$ and held at 95°C for one hour. Added 0.027 M $\text{Cr}(\text{NO}_3)_3$ and held at 95°C for one hour to dissolved about 95% of the MnO_2 . Added 0.05 M $\text{Na}_2\text{Cr}_2\text{O}_7$ and centrifuged. The feed was reoxidized after it had stood for a week while attempts were made to start the IAF pump. For the second oxidation sufficient permanganate was added to oxidize all the chromic ion to dichromate and then a 0.02-0.03 M oxidation with total dissolution of MnO_2 was carried out.

Run 12. Added 0.05 M $\text{Na}_2\text{Cr}_2\text{O}_7$ and adjusted HNO_3 to 0.05 M.
Added 0.01 M KMnO_4 and heated to 95°C for one hour.
Added 0.04 M KMnO_4 and held at 95°C for two hours.
No permanganate present. Added 0.01 M and then 0.027 M $\text{Cr}(\text{NO}_3)_3$ with a one-hour digestion period after each addition.

The head-end decontamination results for the last six runs are summarized in Table VIII. Prior to Run 7 ruthenium was the limiting contaminant in the solvent extraction product streams, but the later runs were usually limited by zirconium-niobium (see Tables IX, X, and XIII). A ruthenium oxidation with permanganate, similar to that tested at the Hot Semiworks, was successfully operated in the production plant after Run 8, and is now a part of its standard operating procedure. While the absolute correlation of cause and effect in an operating production facility is impossible it appears probable that the use of the permanganate head-end has reduced plutonium losses to the IAW by about 0.3%.

In Run 7, observations of the stability of permanganate led to the development of the sacrificial kill head-end procedure. In this run, it was noted that the first addition of permanganate had been destroyed and no ruthenium decontamination had occurred by the end of the first hour at 75°C . A second increment of permanganate however, was destroyed much more slowly, its concentration being reduced from 0.07 M to 0.01 M after one hour at 75°C and one hour at 95°C . The rapid destruction of permanganate in fresh dissolver solution and the slower reduction in solutions to which permanganate had previously been added and destroyed had been encountered previously in laboratory experiments. These observations formed the basis for the sacrificial kill, which is a preliminary small addition and destruction of permanganate, used in all succeeding Hot Semiworks runs. The chemistry of the system is not fully understood.

Efforts to demonstrate a "catalytic kill," in which permanganate ion is reduced to MnO_2 with less than the stoichiometric amount of reducing agent, were unsuccessful. In the Run 10, the first small addition of oxalic acid was intended to reduce all excess KMnO_4 catalytically to MnO_2 and the second, to reduce 80% of the MnO_2 to Mn^{+2} . It is not known whether the first reduction was catalytic or stoichiometric, but manganese dioxide was present in the solution just prior to centrifugation. In Runs 11 and 12 further attempts were made to prove a catalytic reduction of excess permanganate, but they failed to do so since no permanganate was present at the end of the oxidation period.

B. Solvent Extraction

During the first eight runs, the extraction columns were operated with the ORNL, June 1949, conditions given in Table I. In addition, portions of the last four runs used the same conditions so that a direct comparison between the ORNL and dual-scrub flowsheets could be made. Although stream samples were taken during the first three "cold" runs and during the tracer-level run, the principal purpose of these was to prove the operability of the equipment and to discover sources of trouble. In Run 2, the second plutonium cycle operation was split into six short periods which differed in ANN source, ferrous sulfamate and sodium dichromate concentrations, presence or absence of hexone in the 2AF, and the 2A scrub section flow ratio in an attempt to discover the cause of 2A Column emulsification. No emulsification was experienced during any of the six periods of the run. Runs 5 and 6 were intended to duplicate the production plant operation and used no permanganate head end. In Runs 7 and 8, the solvent extraction behavior of a permanganate-oxidized feed was studied and all subsequent solvent-extraction studies were made with similar permanganate-oxidized IAF solutions.

During the last four runs, comparisons were made between the ORNL and dual-scrub flowsheets, fresh IAS and back-cycled second cycle

wastes, and updraft and downdraft dissolution. The interpretation of the results was complicated by various extraneous factors as discussed below. First cycle operational data are summarized in Table IX.

The losses of plutonium and uranium before Run 9 were relatively small and consistent. The relatively high losses of plutonium to the IAW during the last four runs were due to marginal IAX flow rates, as illustrated in Figure 5 in which the IAW plutonium losses are plotted against the aqueous to organic flow ratio in the extraction section of the IA Column. The aluminum nitrate molarity of the IAW was approximately 1.25 except for Run 9A in which it was about 10% higher. With the exception of Run 9B, the IAW uranium losses were less than 0.1%. The only other notable first cycle loss was that of plutonium to the ICU in the last run. Since the column operation appeared to be normal, the reason for the loss has not been explained.

While the decontamination achieved in Run 5 was appreciably lower than that obtained by the production plant under similar conditions, the decontamination during Run 6B was somewhat better and approached that obtained by the production plant. The principal difference in conditions was the discontinuance of air sparging during dissolution in Run 6B. The data indicate that the subsequent solvent extraction of zirconium-niobium was adversely affected by air sparging during dissolution. While no explanation or supporting evidence is offered, air sparging was eliminated for subsequent operation. With the introduction of the permanganate head end in Run 7, the decontamination of the products improved markedly with zirconium-niobium becoming limiting rather than ruthenium as in the preceding runs.

During Run 10, periods of severe emulsification in the IA Column were experienced with almost complete loss of IAX to the IAW. Following such periods, the column and the IAF pump were thoroughly flushed with solutions containing nitric acid, ferrous sulfamate, sodium fluoride,

and sodium hydroxide. No significant improvement was effected by the flushings, and the column would not pass the phases counter-currently even at greatly reduced flow rates.

Beginning with Run 9 and continuing through the remaining runs, the decontamination results became difficult to interpret. Whereas in Runs 4 through 8 the decontamination factor of the IAP was lower than those of the two product streams, in all subsequent runs the IAP had a higher decontamination factor than one or both of the product streams. In other words, more total activity appeared in the product streams than was observed in the IAP. In the ICU this condition was most evident in Run 9, but gradually disappeared with subsequent operation; the condition persisted in the IBP, however, throughout the final runs. It is most likely that the IAP contained a small volume of entrained aqueous phase containing a relatively high concentration of radioactivity, but that this phase was not detected by the sampling and analytical techniques. The same phenomenon has been observed in the production plant, but to a lesser degree. Several possible causes of the suspected second phase and emulsification are suggested below.

Fine silica particles which could have contributed to emulsion formation may have entered the first cycle in the IAS. Flushes of the newly installed silica gel bed were routed to the waste system through Tank 12 which was subsequently used as the IAS feed tank in Runs 9 and 10 and as the IAFS feed tank during Runs 11 and 12. The same tank was also used as the 2DF feed tank during the second uranium cycles of these same runs and was used to concentrate the 2EU from these runs. Since IA (and 2D Column) emulsification was always encountered when Tank 12 was used as a feed tank, and since the emulsification tendency gradually diminished, this condition is considered to be the most probable explanation for the observed emulsification and decontamination phenomena.

Either the aluminum nitrate or the ferrous sulfamate might have contained impurities which ultimately caused emulsification in the IA Column. The ferrous sulfamate used in Runs 9 and 10 was from the same batch as was used for the previous runs; that for 11 and 12 was prepared by dissolving iron in sulfamic acid at the Hot Semiworks. The source of aluminum nitrate was changed between Runs 8 and 9 as shown in Table IX. During Run 10, solid material, which was predominantly magnetic iron, was found in the IAS Tank and in smaller amounts in other tanks and solutions. It was found to be an effective emulsion stabilizer. A third source of aluminum nitrate, reagent grade crystals, was used for Run 11 and for the first half of Run 12. During the second half of Run 12, the material source was the same as that during Runs 9 and 10. None of these changes correlate well with the emulsification experience.

Another possible cause of the phenomena lies in the fact that the feed for Run 9 was not centrifuged and was routed through the waste system (to bypass the centrifuge feed pump which was temporarily inoperative) where it may have picked up foreign material. The feeds for Runs 11 and 12 were also routed through the waste handling tanks when the failure of the IAF feed pump required the use of alternate facilities.

The IA Column decontamination factors obtained provide a revealing comparison of the variables under investigation. Inasmuch as the high activity in the product streams relative to the IAP is not normal and appeared to be variable in itself, it is felt that the IAP results provide a better basis for comparison of Runs 9 through 12 than do the product decontamination factors. On the assumption that the source of salting agent was not a primary variable affecting decontamination, the IA Column results from those runs receiving a head-end treatment may be tabulated as follows:

IAP DECONTAMINATION FACTORS

<u>Flowsheet</u>	<u>Dissolution Procedure</u>	
	<u>Updraft</u>	<u>Downdraft</u>
Dual-Scrub	3.4 (9A) 3.4 (9B) 3.6 (12A) 3.8 (12B)	4.3 (11B)
ORNL - June, 1949	3.7 (7) 4.2 (8)	4.5* (10) 4.5 (11A)

* One sample only, but taken after 10 hours of stable column operation and considered valid.

NOTE: The decontamination factors quoted were obtained in the runs noted in parentheses.

Since the head-end efficiency of Run 7 was partially impaired by re-contamination from tank heels from Run 6 (See Table IX), it appears that the ORNL flowsheet affords a somewhat better decontamination factor than does the dual-scrub flowsheet. It also appears probable, though not certain, that the downdraft dissolving procedure permits slightly better decontamination by solvent extraction than does the updraft procedure. This difference, if real, could well be attributed to the difference in acidity of the uranium solution at the end of the dissolving procedure (see Table VII), since all updraft dissolvings were stopped with free acid present and all downdraft dissolvings proceeded to acid deficiency. The relatively poor performance in Run 9 could well be a reflection of the poor head end, but the lack of data prevents verification.

The above conclusions appear justified so long as the unsubstantiated result from Run 10 is assumed valid. If however, this result is excluded, then the two highest decontamination factors were obtained during the run which coincidentally employed downdraft dissolving and virgin crystalline aluminum nitrate as the salting agent. The reuse of crystalline salting agent from Run 11 second cycle wastes in the first cycle of Run 12A gave a poorer decontamination. The incremental decontamination loss experienced between Runs 11 and 12A was larger than can be explained by simple

re-extraction of the recycled fission products. While this increment might be attributed to the presence of hexone decomposition products arising from the concentration of the second cycle wastes, this mechanism appears improbable in view of the similarity of Run 12A results with those of Runs 9 and 12B. These considerations imply that the high decontamination factors of Run 11 resulted from the downdraft dissolving and not from the virgin crystalline salting agent, an implication which is strengthened by the Run 10 result. The conclusions originally reached from the tabulation above are therefore believed to be valid.

Two basic second uranium cycle flowsheets were operated during the eight "hot" runs. Conditions are given in Tables I and II. Initial attempts to operate the dual-scrub flowsheet, beginning with Run 9, were generally unsuccessful because of severe emulsification. In Run 10, the ORNL and HW #4 Flowsheets were operated, with difficulty, after numerous attempts to operate with various modifications of the dual-scrub flowsheet had failed. Flushes of the 2D Column with nitric acid-sodium fluoride solutions were ineffective in preventing emulsification. The dual-scrub flowsheet was operated successfully during Runs 11 and 12 with the 2DX flow ratio at 120% of the Table II rate.

On the basis of the emulsification experienced during Runs 9 to 12, the operational stabilities of various flowsheets are qualitatively ranked as follows, in order of decreasing stability:

1. HW #4 (single scrub, 2DX made 0.08 M HNO_3)
2. ORNL, June 1949 (Table I)
3. Dual Scrub (2DA = 0.7 M $\text{Al}(\text{NO}_3)_3$)
4. Dual Scrub (2DA = water, 2DX rate = 20% over Table II)
5. Dual Scrub (Table II)

Of these five flowsheets, Numbers 1 and 3 were operated for only a short time and are ranked with less confidence than the others.

Second uranium cycle data are summarized in Table X. In all the runs, the uranium losses were satisfactory when the columns were operating normally. The decontamination data from the later runs should be considered as non-representative since the feeds included ICU from periods of off-standard as well as normal first-cycle operation. In addition, the 2DF for the last two runs was recontaminated with IAF as the 2DF tank was also the IAFS tank for those runs. Within the experimental reproducibility, the dual-scrub runs gave at least as good decontamination as the ORNL runs. After the introduction of the permanganate head-end treatment zirconium and niobium were the limiting fission-product contaminants.

During the last four runs, data were collected on the operation of the silica gel bed in the 2EU line. The bed effectively removed Zr-Nb during Run 9 but appeared to have come to equilibrium with the incoming 2EU during Run 10. The data are given in Table XI.

Following Run 10, the bed was regenerated by flushing it with dilute HNO_3 , warm oxalic acid, and water in the same direction as the 2EU flow. The temperature of the oxalic acid was 85°C in the head tank but could not be determined at the bed. A total of 40 bed volumes of the oxalic acid flush removed about 2×10^5 microcuries of Zr-Nb radioactivity. It was removed at an initial rate of 20,000 microcuries per gallon of flush, but the rate dropped to 140 microcuries per gallon near the end of the flushing. Decreasing the rate of flushing from about 4 gal/hr to a considerably lower rate at the end of the regeneration period increased the radioactivity in the effluent to about 500 microcuries per gallon.

Following the regeneration, the data in Table XII were obtained during Runs 11 and 12. The decontamination effected by the bed was quite low. This poor performance is believed to be a result of the inefficient regeneration procedure and not typical of silica gel performance.

The second plutonium cycle was operated under the ORNL - June, 1949 conditions of Table I during Runs 5 through 8. Operation was stable and without important incident. The data are given in Table XIII. Although the permanganate-oxidized feeds were better decontaminated after the first extraction cycle than the feeds for Runs 5 and 6, the difference appeared to be smaller after the second plutonium cycle. Even with the permanganate oxidation, ruthenium was an important contaminant in the 2BP.

During the last four runs, a reflux second plutonium cycle was operated under the conditions given in Table II. Steady-state operating conditions were never reached with respect to nitric acid and plutonium concentrations, as evidenced by the fluctuating analyses noted in Table XIV. Total reflux of the 2BP to the 2AS point was used, and column operation was followed through 2AW and 2AP line samples. In Runs 9 and 10, the plutonium concentration in the 2AP increased as expected, although in Run 10 it increased at a lower rate than during Run 9. During the last two runs, no valid data were collected because of mechanical sampling difficulties and emulsification.

The data for Runs 9 and 10 are summarized in Table XIV. Although the 2AF radioactivity was 90-95% Zr-Nb in both runs, ruthenium became limiting in the product during Run 9 (>95%); zirconium-niobium was limiting in Run 10 (80%). In view of the different results obtained during the two runs, the specific operating conditions are tabulated in Table XV. The main differences in conditions were the higher nitric acid and aluminum nitrate concentrations during Run 10 and the higher plutonium content of the feed in Run 9. The plutonium stripped from the columns after the runs had a gamma dF (relative to 2AF) of 3.6 for Run 9 and 2.6 for Run 10. From dissolver blend solution, the overall gamma dF's were 6.6 and 6.3, respectively; the first cycle in each case produced a poorly decontaminated plutonium stream.

IX. FUTURE WORK

The Redox investigations in the Hot Semiworks were terminated in October, 1953 in order that the facilities might be modified to study the Purex process prior to the operation of the new production scale Purex Plant at Hanford. The Semiworks was decontaminated to levels permitting major equipment alterations, and a separate report will be issued describing the decontamination procedures and results. Equipment additions and alterations are currently in progress which will enable a comprehensive study of the Purex process, including continuous recycle of solvent and acid recovery and reuse. A semiworks-scale study of the self-concentration of buried Purex aqueous wastes is also planned. These studies are scheduled to be initiated at full Hanford radioactivity levels about September, 1954.

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TABLE I

HOT SEMIWORKS ORNL (June 1949) FLOWSHEET CONDITIONS

Stream	Sp. Gr. at 25°C	U, <u>M</u>	HNO ₃ , <u>M</u>	Al(NO ₃) ₃ , <u>M</u>	Na ₂ Cr ₂ O ₇ , <u>M</u>	Fe(SO ₃ NH ₂) ₂ , <u>M</u>	Flow Ratio	Temp. °C
IAF	1.66	2.0±0.1	-0.2 ±0.1	.	Present*		100	65±5
IAS	1.32		-0.2 ±0.1	2.0 ±0.06	0.01±0.001		115	Ambient
IAX	0.80		Neutral Hexone				420	Ambient
IBX	1.20		0.05 ±0.005	1.3 ±0.08		0.05±0.005	32	Ambient
IBS	0.80		0.075±0.008				160	Ambient
ICX	1.00		0.03 ±0.01				180	Ambient
2DF	1.66	2.0±0.2	-0.2 ±0.1				100	50±5
2DS	1.32		-0.2 ±0.1	2.0 ±0.06			100	Ambient
2DX	0.80		Neutral Hexone				400	Ambient
2EX	1.00		0.03 ±0.01				130	Ambient
2AF	1.19		0.1 ±0.1	1.25±0.12	0.02±0.01		43.2	30±5
2AS	1.20		0.03 ±0.06	1.3 ±0.08	0.01±0.001		43.2	Ambient
2AX	0.82		0.5 ±0.05				57.6	Ambient
2BX	1.00		0.03 ±0.01				11.5	Ambient

* 0.2 M added initially; standard procedure merely calls for a positive qualitative test prior to feeding to solvent extraction columns.

TABLE II
HOT SEMIWORKS CONDITIONS FOR DUAL SCRUB
FIRST CYCLE AND URANIUM CYCLE; REFLUX PLUTONIUM CYCLE

Stream	Sp. Gr. at 25°C	U, M	HNO ₃ , M	Al(NO ₃) ₃ , M	Na ₂ Cr ₂ O ₇ , M	Fe(SO ₃ NH ₂) ₂ , M	Na ₂ SO ₄ , M	Flow Ratio	Temp. °C
IAF	1.66	2.0±0.2	-0.2 ±0.1		Present (1)			100	65±5
IAA	1.00				0.01±0.001			40	Ambient
IAS	1.40		-0.25±0.05	2.5 ±0.06	0.01±0.001			115	Ambient
IAX	0.80		Neutral Hexone					420(2)	Ambient
IBX	1.28		0.05±0.02	1.85±0.05		0.05±0.005		32	Ambient
IBS	0.81		0.15±0.03					100	Ambient
ICX	1.00		0.03±0.01					180	Ambient
2DF	1.66	2.0±0.2	-0.2 ±0.1					100	50±5
2DA	1.00		Sanitary Water					30	Ambient
2DS	1.40		-0.25±0.1	2.5 ±0.08				82	Ambient
2DX	0.80		Neutral Hexone					420(2)	Ambient
2EX	1.00		0.03±0.01					130	Ambient
2AF	1.28		0.1 ±0.1	1.8 ±0.2	0.04±0.01			43.2	30±5
2AS	1.31		0.0 ±0.1	2.0 ±0.06	0.02±0.002			36.7	Ambient
2AX	0.81		0.15±0.03					43.2	Ambient
2BX	1.01		0.05±0.02				0.1±0.02	17.7	Ambient

(1) (Same as footnote, Table I).

(2) In runs 11 and 12, the 2DX ratio was 521 and 546 respectively, and the IAX ratio was 500.

TABLE III
EXTRACTION COLUMN DIMENSIONS

<u>Column</u>	<u>Section</u>	<u>Packed Height, Ft</u>	<u>Packing Size, In. (1)</u>	<u>Column Diameter (2)</u>	<u>Organic Disengaging Section (5)</u>	
					<u>Length, Ft</u>	<u>Diameter (2)</u>
IA (3,4)	Extraction	18	3/8	2		
	Scrub	10	3/8	2	2	4
IB (3)	Extraction	10	3/8	2	2	4
	Scrub	17	3/8	1 1/2		
IC	Extraction	15	3/8	2 1/2	2	6
2D (3,4)	Extraction	18	3/8	2		
	Scrub	10	3/8	2	2	4
2E	Extraction	20	3/8	2	2	4
2A (3)	Extraction	15	3/8	1 1/2		
	Scrub	10	3/8	1 1/2	2	3
2B	Extraction	18	1/4	1	2	2

- (1) Stainless steel Raschig rings, diameter and length approximately equal.
- (2) Schedule 40 pipe size.
- (3) Dual purpose columns contained a 3/4-ft unpacked section for mid-column feed introduction.
- (4) Auxiliary mid-column inlet 2 1/2 ft above normal feed point for last four runs. One ft of packing removed from top of column for these runs.
- (5) In all cases, the bottom or aqueous disengaging section was one foot of unpacked pipe of the same diameter as the adjacent packed section.

TABLE IV
CHRONOLOGY

Run 1	11-17-52 to 12-23-52
Run 2	12-4-52 to 1-14-52
Run 3	2-2-53 to 2-19-53
Run 4	2-4-53 to 3-4-53
Run 5	3-9-53 to 3-20-53
Run 6	3-19-53 to 4-2-53
Run 7	3-26-53 to 4-15-53
Run 8	4-16-53 to 4-29-53
Equipment decontaminated; IAF pump replaced and equipment modified	4-25-53 to 7-16-53
Run 9	7-17-53 to 8-11-53
Run 10	8-1-53 to 9-11-53
IA Column flushes. HNO_3 - $\text{Fe}(\text{SO}_3\text{NH}_2)_2$, NaOH, HNO_3 -NaF, H_2O	8-14-53, 8-17-53, 8-18-53
2D Column flushes. HNO_3 -NaF, HNO_3 , H_2O	9-2-53, 9-9-53
Run 11	9-2-53 to 9-26-53
IAF pump failure	9-12-53
Run 12	9-23-53 to 10-9-53

TABLE V
JACKET REMOVAL CONDITIONS

Temperature, °C	
Dissolver pot	102-105
Scrubber pot	80-90
Cooled off-gas	10-15
Filtered off-gas	25-30
Vacuum, inches of water	
Dissolver pot	6-11
Filter outlet	13-20
Pressure Drop, inches of water	
Condenser	1-5
Off-gas filter	0.3
Air Sparge Rate, SCFM	2.5
Time at boiling, hours	3
Total time, hours	4

TABLE VI
METAL DISSOLUTION CONDITIONS

Temperature, °C	
Dissolver pot	103-107
Condenser	25-35
Scrubber pot	80-95 ⁽¹⁾
Cooled off-gas	15-20
Filtered off-gas	25-35
Vacuum, inches of water	
Dissolver pot	5-15
Filter outlet	20-30
Pressure Drop, inches of water	
Condenser	0-10
Off-gas filter	0-2
Air Introduction Rate	(2)

- (1) Scrubber pot temperature was about 25-50°C before Run 5.
- (2) In Runs 1 through 5A, air was sparged through the solution at 5 SCFM. In all other runs using the updraft condenser, no air was introduced during dissolution.

In all runs using the downdraft condenser, 5 SCFM of air was introduced at the top of the dissolver pot during dissolution, except during Run 10 when no air was introduced.

TABLE VII
METAL DISSOLUTION DATA

						<u>Molecular Ratios</u>	
<u>Run No.</u>	<u>Cut</u>	<u>Time at Boiling Hours</u>	<u>Final Sp. Gr. (hot)</u>	<u>Pounds U Dissolved</u>	<u>Heel after Dissolving Pounds</u>	<u>HNO₃ Consumed</u>	<u>HNO₃ in solution</u>
						<u>U Dissolved</u>	<u>U in solution</u>
Updraft Condenser							
1	1	7	1.82	515	214	ca.5.3	(3)
	2	10	1.82				
	3	6	1.82				
2	1	4	1.82	483	213	ca.5.6	(3)
	2	8	1.82				
	3	15	1.82				
4	2	12	1.80	227	264	6.0	-0.03
5	1	8	1.80	265	485	5.1	-0.03
	2	11	1.80	285	200	4.6	0.19
6	1 ⁽¹⁾	18	1.61	200	486	6.0	0.81
	2	8	1.79	281	205	4.7	0.16
7	1	5	1.79	523	412	5.0	0.17
	2	5	1.79				
8	1	13	1.76	357	54	5.3	0.18
9	1	8	1.79	519	216	5.1	0.17
	2	8	1.79				
12	1	6	1.80	215	241	5.0	0.07
	2	13	1.82	213	28	4.8	0.34
Downdraft Condenser							
3	1	24	1.90	230	446	ca.2.7	(3)
4	1	29	1.89	224	222	3.0	-0.25
10	1 ⁽²⁾	8	1.68	158	787	4.5	-0.21
	2	16	1.87	339	448	2.9	-0.24
11	1	8	1.85	242	692	3.0	-0.22
	2	5	1.87	236	456	3.0	-0.15

(1) Poor jacket removal; procedure repeated before next cut.

(2) No air introduction during dissolution.

(3) No acid analysis of dissolver solution.

TABLE VIII
HEAD END DECONTAMINATION

Run	Reactants, Molarity ⁽¹⁾						Decontamina- tion factor (log)	
	HNO ₃ at Start	Holding ⁽²⁾	Sacrificial ⁽³⁾	KMnO ₄ Oxidant ⁽⁴⁾	Residue ⁽⁵⁾	MnO ₂ — Centrifuged ⁽⁶⁾	Gamma	Ru
7	0.1	--	0.07	0.07	0.01	0		1.2
8	0.05	--	0.02	0.05	0.05	0 ⁽⁷⁾	0.6	2.1
9	-0.1	--	0.01	0.03	(8)	0	0.13	(8)
10	-0.1	0.01	0.01	0.03	(8)	0.01	0.44	1.5
11	0.1	0.01	0.01	0.04	0	ca. 0.005		0.9
	-0.2	--	0.02	0.03	(8)	0	0.58	
12	0.1	--	0.01	0.04	0	ca. 0.0	0.47	0.9

(1) See text, Part VI-A, for a description of the operating procedures.

(2) KMnO₄ added as a holding oxidant over a weekend.

(3) KMnO₄ added in first increment (sacrificial kill).

(4) KMnO₄ added to effect ruthenium oxidation.

(5) KMnO₄ present at end of ruthenium oxidation period.

(6) Calculated MnO₂ concentration prior to centrifugation.

(7) The reductant added was marginal, and some MnO₂ may have remained.

(8) No analysis obtained.

TABLE IX
FIRST CYCLE OPERATIONAL DATA

Run No.	Dissolving	Head End		Valid Running Time, Hrs.	IA Flow-sheet	IAS Source ⁽²⁾	IA Scrub Height, Ft	Extraction L/V	Losses ⁽¹⁾				Decontamination						
									IAW		IBP U	ICU Pu	ICW U	IAP		IBP		ICU	
		Pu	U						γ dF (3)	% Ru (4)				γ dF (3)	% Ru (4)	γ dF (3)	% Ru (4)		
5	Up	None		61	ORNL	N	10	0.49	0.4	0.04	5x10 ⁻⁵	0.4	0.007	2.8	70	3.1	50	2.8	65
6A	Up ⁽⁵⁾	None		27	ORNL	N	10	0.49	0.4	0.02	2x10 ⁻⁵	0.4	0.002	2.5	65	3.5	65	2.8	--
6B	Up	None		36	ORNL	N	10	0.46	0.3	0.01	10 ⁻⁵	0.1	0.002	2.8	95	3.9	--	3.2	95
7 ⁽⁶⁾	Up	1.2	(7)	56	ORNL	N	10	0.49	0.12	0.06	2x10 ⁻⁵	0.07	0.002	3.7	50	3.9	10	3.6	35
8	Up	2.1	0.60	40	ORNL	N	10	0.49	0.4	0.02	3x10 ⁻⁴	0.02	0.03	4.2	5	4.4	5	4.6	10
9A	Up	(7)	0.13	24	Dual Scrub	D	9	0.62	0.20	0.02	10 ⁻⁵	0.1	0.04	3.4	5	3.2	5	2.7	5
9B	Up			40	Dual Scrub	D	9	0.56	1.5	1.5	10 ⁻⁴	0.05	0.01	3.4	5	3.0	5	2.7	5
10	Dn	1.5	0.44	20	ORNL	D	9	0.38	(9)	(9)	10 ⁻⁴	100 ⁽¹⁰⁾	0.07	4.5 ⁽⁸⁾	10	--	<5	3.7	10
11A	Dn	0.8 ⁽¹¹⁾	0.58 ⁽¹¹⁾	18	ORNL	C	6.5	0.56	1.9	0.03	10 ⁻⁴	0.03	0.001	4.5	35	4.0	15	4.0	35
11B	Dn			12	Dual Scrub	C	6.5	0.52	1.0	0.07	5x10 ⁻⁵	0.3	0.000	4.3	10	3.9	<5	4.1	10
12A	Up	0.9	0.47	38	Dual Scrub	B	6.5	0.41	0.05	0.04	7x10 ⁻⁵	3.0	0.03	3.6	10	3.2	5	4.1	25
12B	Up			21	Dual Scrub	D	6.5	0.44	0.20	0.02	6x10 ⁻⁵	3.5	0.002	3.8	5	3.4	<5	4.2	35 ⁽⁴⁾

NOTES:

- (1) Losses are per cent of IAF fed to columns.
- (2) (N) General Chemical Co., 72% solution neutral as received, made acid deficient.
 (D) General Chemical Co., 68% solution 0.2 M acid deficient as received.
 (C) Allied Chem. and Dye Corp., reagent grade crystals dissolved and made acid deficient.
 (B) Concentrated second cycle wastes from Run 11B.
- (3) Log decontamination factor, relative to dissolver solution (Relative to IAF for Run 7.)
- (4) Remainder is Zr-Nb.
- (5) The jacket removal preceding this cut was ineffective. The jacket removal procedure was repeated before dissolving the metal for Run 6B.
- (6) The IAF was apparently recontaminated with a heel from 6B, the Ru dF of the IAF being 0.6.
- (7) No valid analysis.
- (8) One sample.
- (9) The IAW analyses were too variable to be meaningful.
- (10) The ferrous sulfamate was inadvertently not added to the IBX.
- (11) The feed was reoxidized and recentrifuged after it had stood for one week during efforts to get the IAF pump running.

TABLE X
SECOND URANIUM CYCLE OPERATIONAL DATA⁽¹⁾

Run No.	Running Time, Hrs.	Flowsheet	U Losses ⁽²⁾		2DF		2DU	2EU	
			2DW	2EW	γ dF ⁽³⁾	% Ru ⁽⁴⁾	γ dF ⁽³⁾	γ dF ⁽³⁾	% Ru ⁽⁴⁾
5	50	ORNL	3×10^{-4}	0.2	2.7	55	4.7	5.0	--
6	50	ORNL	0.02	0.1	3.3	95	5.0	5.2	25
7	52	ORNL	4×10^{-5}	0.04	3.5	30	5.4	5.5	55
8	39	ORNL	5×10^{-4}	10^{-4}	4.0	10	6.2	5.7	25
9	18	Dual Scrub	0.002	10^{-4}	2.8	<5	5.0	4.8	5
10A	10	ORNL	10^{-4}	(5)	2.9	<5	(5)	5.9	5
10B	14	HW #4	10^{-4}	(5)	2.9	<5	(5)	5.7	5
11	16	Dual Scrub	6×10^{-3}	10^{-3}	3.1 ⁽⁶⁾	<5	6.0	5.7	10
12	54	Dual Scrub	0.01	0.01	2.6 ⁽⁶⁾	5	5.0	5.0	5

NOTES:

- (1) 2DF was a composite of the ICU from the complete first cycle.
- (2) Losses are % of 2DF fed to columns.
- (3) Log decontamination factor, relative to dissolver solution. (Relative to IAF for Run 7.)
- (4) Remainder is Zr-Nb.
- (5) No sample.
- (6) The ICU was contaminated with IAF when the same vessel was used to feed the IAFS and 2DF.

TABLE XI
DECONTAMINATION OF 2EU BY SILICA GEL

	Throughput, Gel Bed Volumes	2EU Gamma Activity Log (microcuries/gal)		dF	% Zr-Nb	
		Influent	Effluent		Influent	Effluent
Run 9	21	3.0	1.5	1.5	>95	55
	35	3.8	1.9	1.9	---	45
	49	2.3	2.2	0.1	90	70
	76	3.2	2.3	0.9	95	90
	96	---	2.4	---	---	75
Run 10	174	1.9	2.4	-0.5	95	--
	216	1.8	1.8	0.0	95	--
	219	2.5	2.2	0.3	---	--

NOTE:

The current specification for gamma contamination in Redox uranium product is that equivalent to 100% of natural uranium activity and is approximately equivalent to 40 microcuries per gallon at one molar uranium.

TABLE XII
DECONTAMINATION OF 2EU BY REGENERATED
SILICA GEL

	<u>Throughput, Gel Bed Volumes</u>	<u>2EU Gamma Activity Log (microcuries/gal)</u>		<u>dF</u>	<u>% Zr-Nb</u>	
		<u>Influent</u>	<u>Effluent</u>		<u>Influent</u>	<u>Effluent</u>
Run 11	40	---	1.5	---	---	--
	58	2.1	1.8	0.3	---	--
	64	2.1	1.9	0.2	90	90
	73	2.2	1.9	0.3	90	85
Run 12	106	3.3	2.6	0.7	90	75
	130	3.1	2.7	0.4	90	90
	139	2.8	2.7	0.1	95	--
	149	3.0	2.8	0.2	95	90
	156	3.1	2.3	0.8	95	90
	165	3.0	2.8	0.2	95	90
	178	3.1	2.9	0.2	95	95
	192	3.1	2.9	0.2	90	90

TABLE XIII
SECOND PLUTONIUM CYCLE OPERATIONAL DATA
ORNL FLOWSHEET

Run No.	Running Time, Hours	Pu Losses ⁽¹⁾		Decontamination ⁽²⁾				
				2AF		2AP	2BP	
		2AW	2BW	γ	% Ru ⁽³⁾	γ	γ	% Ru ⁽³⁾
5	97	0.3	0.02	3.1	65	4.8	4.9	--
6	85	0.3	--	2.8	65	5.5	5.6	85
7	49	0.3	0.002	3.5	10	5.6	5.8	65
8	50	0.4	0.006	4.1	5	5.2	6.0	40

(1) Losses are % of 2AF fed to columns.

(2) Log decontamination factor from dissolver solution. (Relative to IAF for Run 7.)

(3) Remainder is Zr-Nb.

TABLE XIV
SECOND PLUTONIUM CYCLE OPERATIONAL DATA
REFLUX FLOWSHEET

<u>Time, Hrs.</u>	<u>2AP Conc., Pu g/gal</u>	<u>2AW Loss % of 2AF</u>	<u>HNO₃ Conc., lb/gal</u>		<u>2AP Gamma dF (log) (based on 2AF)</u>
			<u>2AP</u>	<u>2AW</u>	
<u>RUN 9</u>					
3	2.8	0.1	0.02	0.05	2.2
10	---	14	---	0.07	---
18	8.2	11	0.004	0.06	3.5
27	17.8	0.6	0.000	0.03	3.7
35	21.3	0.9	---	0.14	2.6
39	---	0.8	0.32	0.09	1.6
46	31.0	0.1	0.30	0.05	3.1
51	63.3	0.5	0.31	0.26	3.9
60	---	5	---	0.11	---

2AF rate = 1.86 Pu g/hr. dF of 2AF = 2.9 from dissolver solution.

<u>RUN 10</u>					
7	1.5	0.1	0.21	0.06	2.3
13	9.7	0.1	0.73	0.06	1.6
20	4.7	0.2	0.23	0.05	1.4
28	3.6	18	0.48	0.01	1.4
39	8.0	0.07	---	0.05	1.2
48	10.9	0.01	0.46	0.06	1.4
62	38.2	32	0.40	0.13	1.3
70	57.1	0.2	0.48	0.10	2.0

The 2AX flow fluctuated widely for the first 15 hours during Run 10.

2AF rate = 0.66 Pu g/hr (dF = 3.4) for the first 32 hours and 1.06 Pu g/hr (dF = 3.9) after that time.

TABLE XV

SECOND PLUTONIUM CYCLE OPERATING CONDITIONS

Stream	Run	Sp. Gr.	Pu g/gal	HNO ₃ , M	ANN, M	Cr ⁺⁶ , M	Na ₂ SO ₄ , M	Flow Ratios
2AF	9	1.26	1.78	0.13	1.62	0.027		100
	10	1.28	0.80 ⁽¹⁾	0.17	1.77	0.01		100
2AS	9	1.31		-0.20 ⁽²⁾	1.96	0.021		87
	10	1.33		-0.03	2.13	0.020		85
2AX	9	0.81		0.16				125
	10	0.81		0.14				126
2BX	9	1.01		0.042			0.11	43
	10	1.00		0.046			0.09	44

(1) 2AF = 1.29 Pu g/gal for last half of run.

(2) Neutralized to zero acidity after 34 hours of operation.

TABLE XVI

CHEMICALS USED

1. Water - filtered and chlorinated (plant sanitary water).
2. Hexone - shell, water-washed, distilled from a water heel.
3. ANN - see Table IX.
4. HNO_3 - duPont, technical grade, 60% solution.
5. NaOH - Hooker Chemical Co. or Penn. Salt Co., technical grade, 50% solution.
6. Ferrous sulfamate - Runs 3 - 9: Allied Chemical and Dye Corp., Baker and Adamson quality, 55% solution. Runs 1, 2, 10-12: Sulfamic acid and iron powder.
7. $\text{Na}_2\text{Cr}_2\text{O}_7$ - Mutual Chemical Co., technical grade.
8. KMnO_4 - Allied Chemical and Dye Corp., USP crystal.
9. $\text{Cr}(\text{NO}_3)_3$ - Allied Chemical and Dye Corp., purified crystal.
10. NaNO_3 - Chilean Nitrate Sales Corp., technical grade.
11. Na_2SO_4 - Stauffer Chemical Co., technical grade.

FIGURE 1
EQUIPMENT FLOW SKETCH HOT SE

FIGURE 1
EQUIPMENT FLOW SKETCH HOT SEMIWORKS

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HW-31767

Chemical Development Unit
 Hanford Atomic Products Operation
 General Electric Company 1-27-54.

ACC686RICHLAND, WASH

TK
 CONC
 DEC.

FIGURE 2

EQUIPMENT FLOW SKETCH HO1

FIGURE 2

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HW-31767

EQUIPMENT FLOW SKETCH HOT SEMIWORKS

"A" CELL

"B" CELL

"C" CELL

Note: See Figures 1 and 2 for functional use of equipment pieces.

FIGURE 3
"HOT" EQUIPMENT PLAN

Chemical Development Unit
Hanford Atomic Products Operation
General Electric Company
1-27-54

SPECIFIC GRAVITY AT B.P.

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HW-31767

Aqueous/Organic Flow Ratio in IA Extraction Section
 Chemical Development Unit
 Hanford Atomic Products Operation
 General Electric Co. 1-27-54