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CHEMISTRY-SEPARATION PROCESSES FOR URANIUM PROGRESS REPORT

LABORATORY RECORDS 1954

TECHNICAL DIVISION

CHEMICAL TECHNOLOGY DEPARTMENT

PROGRESS REPORT FOR QUARTER

ENDING NOVEMBER 30, 1949

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TECHNICAL DIVISION

CHEMICAL TECHNOLOGY DEPARTMENT

F. L. Steahly, Department Head
F. R. Bruce, Laboratory Chief
J. O. Davis, Semi-Works Chief
D. G. Reid, Pilot Plant Chief

PROGRESS REPORT FOR QUARTER ENDING NOVEMBER 30, 1949

Edited by
W. K. Eister

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CLASSIFICATION CHANGED TO: _____
BY AUTHORITY OF: JID-1150
BY: R. Morrison 2/10/52
DATE ISSUED: JAN 13 1950

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ABSTRACT

Summaries of progress of chemical development and design on the following problems are reported: Metal Recovery—TBP Process, RaLa Process, 25 Process, Purex Process, Redox Dry Fluoride Process, Thorium Recovery, and Radiochemical Waste Processing.

INTRODUCTION

The philosophy of the Chemical Technology Quarterly Report is to be altered as of this issue. In the past an attempt has been made to report all the pertinent data obtained during the period by the department on all subjects under study in this report. In the future, topical reports will be issued as soon as sufficient data are available and therefore only brief summaries of the work in progress will be found. This will allow the quarterly report to be more timely, and should increase the ease of organization of the data files.

The major effort of the Laboratory, Semi-Works and Design Sections was the development of the TBP Process for the recovery of uranium from the Hanford metal waste. The semi-works equipment was started up, and the laboratory determined chemical requirements for various feed preparation procedures and the effect of solvent contaminants on the process.

The Pilot Plants major effort was the final stage of the development of the "25" process for the recovery of Uranium-235 from the materials testing reaction fuel units. The equipment necessary for the final concentration of the Uranium-235 has been turned over by the Laboratory to the Pilot Plant. This program should be completed before January 1950.

The process improvement work on the RaLa Process was continued by the Laboratory to develop an ion exchange procedure for the product purification, by the Semi-Works to develop the filtration procedure for the sulfate precipitation and metathesis, and by Design to design improved equipment for the present process operation.

The equipment for the "23" Process development on a pilot plant scale was completed and the preparations are undertaken for start up in the coming quarter at the completion of the "25" development.

The Thorium Recovery Process development for the recovery of thorium from the "23" Process waste has been demonstrated with both young and old waste,

and the effect of an acetone-nitrate feed pretreatment on the fission decontamination was studied.

The development of the Purex Process for the recovery of uranium and plutonium from the Hanford metal by tributyl phosphate solvent extraction was started in the laboratory with emphasis on the erection of a new set of packed columns to permit greater facility in developing solvent extraction data.

The Redox development has been completed with exception of the recovery of the plutonium from the 1BP solution by the Pilot Plant, and completion of the study on the nitrate-acetone feed pretreatment procedure in the laboratory.

A most interesting development during this quarter was the fluorination of irradiated uranium and batch distillation of the product.

A second study that was started in this quarter was the development of a uranium oxide slurry to be used as fuel in a homogeneous nuclear reactor. Only preliminary laboratory data have been obtained to date.

The zirconium-hafnium separation process proposed in the last quarterly report using tributyl-phosphate has since been undertaken by another laboratory and no further work is contemplated at present.

The development on radiochemical processing has been relatively inactive during this period, but during the next quarter, development of a "falling-film" type evaporator will be continued.

Major objectives will be to reduce foaming, improve decontamination, and minimize amount of solution hold-up in the evaporator.

SUMMARY

TBP Process. (1) The recovery and decontamination of uranium from Hanford waste was successfully demonstrated in a single solvent extraction cycle on a scale of five kilograms of uranium per day. The uranium loss was about 0.3% with the final product activity at equilibrium equivalent to natural uranium.

(2) The decision has been made to base future development work on the use of the caustic precipitation method for feed preparation.

(3) The contaminants in tributyl phosphate that affect the distribution coefficients were identified, and a procedure was developed for their removal. The recovery procedure for the solvent was also developed. A treatment procedure for the diluent was developed, but the contaminants were not identified.

RaLa Process Improvement. Filtration of the metal solution was necessary before the sulfate precipitation step, for satisfactory filtration of the sulfate and metathesis precipitate on sintered stainless steel was possible.

"25" Process. (1) Pilot Plant runs at 25% of MTP activity level demonstrated adequate uranium yield and exceeded the decontamination requirements.

(2) Ferrous sulfamate was eliminated from the first cycle to prevent the precipitation of mercury which is present as a catalyst. The fission product decontamination was not affected.

"23" Process. The preliminary testing of the equipment was nearing completion for the final process development on a scale of 50 kilograms of thorium metal per day.

Purex Process. (1) Laboratory studies indicate that the solvent extraction of uranium and plutonium with tributyl phosphate gave yield and decontamination in the first cycle equivalent to that of the Redox first cycle.

(2) The major advantage of the process is the employment of nitric acid as salting agent, greatly simplifying the waste problem.

Redox Process. (1) The procedure for the satisfactory recovery of plutonium from the pilot plant 1BP solution was developed by the laboratory.

(2) The ANL Redox Process gave 10^4 fission product decontamination in one cycle laboratory tests after special treatment of the metal solution and hexone feeds.

Dry Fluoride. (1) Irradiated uranium metal was fluorinated and the UF_6 product batch distilled. The fission product decontamination factor was 10^3.

(2) A one-slug fluorinator was developed at K-25.

TBP PROCESS FOR METAL RECOVERY

FEED PREPARATION--HANFORD

Laboratory studies were made to determine the chemical requirements and the operability of four alternate procedures for preparation of the Hanford metal waste for uranium recovery by solvent extraction with tributyl phosphate. The decision was made to use caustic precipitation method for future development. This precipitate is difficult to handle and a uranium loss of 0.2% is expected. However, with this process, the chemical requirement and ultimate waste volume are significantly reduced, and the initial precipitation may be carried out in the present storage tanks. Sodium diuranate was precipitated by the addition of sodium hydroxide, the precipitate separated from the liquor, and then dissolved in nitric acid.

The other methods studied were:

1. *Direct Acidification* - addition of nitric acid until complete solution at 3 to 5 *M* HNO_3 was obtained. This is similar to the procedure used for the UAP precipitation process, and has the advantage of no uranium loss.

2. *Nitric Acid Precipitation* - addition of nitric acid to *p*H 5 to 6.5 to precipitate sodium uranyl phosphate which is then separated from the liquor dissolved by the further addition of nitric acid. The uranium loss was about 0.2%; the precipitate had much better settling characteristics than the caustic precipitate.

3. *Sulfuric Acid Precipitation* - sulfuric acid was added to *p*H 5 to 6.5 and then the procedure was similar to the nitric acid precipitation. The advantage of this procedure was the reduced cost of the acid, but had several drawbacks in that a thorough wash was required to remove the excess sulfate ion.

The nitric acid precipitation and direct acidification procedures are being used in the Semi-Works development program. Caustic precipitation has not been demonstrated on this scale because of lack of equipment.

These data, presented in ORNL 519, and 523, were submitted to the Design Group for cost analysis and equipment studies.

SOLVENT STUDIES

Chemical Stability of Tributyl Phosphate to Nitric Acid. The chemical stability of tributyl phosphate was evaluated by refluxing it five hours with increasing concentrations of nitric acid and then determining the effect on the extraction distribution coefficients for uranium, plutonium, fission products and nitric acid. At nitric acid concentrations exceeding seven molar, the plutonium and fission product distribution coefficient increased. Investigation of the possible contaminants indicated that mono- and di-butyl phosphate caused a marked increase in the plutonium and fission product distribution coefficient, while isobutraldehyde caused a significant decrease in the plutonium distribution coefficient.

In subsequent stripping studies it was shown that the back extraction of uranium, plutonium and fission products was not easily reversible from TBP containing mono- and di-butyl phosphate. Approximately 90% of the uranium and about 90% of the alpha and beta activity remained with the solvent after four equal volume strips with water. Uranium holdup in the stripped solvent was also observed for the decomposition products of butyl alcohol but only to the extent of about 0.1% of the amount originally present.

Tributyl Phosphate Specifications. The tentative specifications for tributyl phosphate are as follows:

(1) Reducing normality - less than 0.001 (measure of butyl alcohol)

(2) Acidity - zero (measure of mono- and di-butyl phosphate) ± ?

Tributyl Phosphate Analytical Procedure. The quantitative analysis of tributyl phosphate in presence of diluent solvent may be carried out by saturating the tributyl phosphate with uranium and then analyzing for the uranium. The accuracy of this method is ± 0.2% in the range of 1 to 30% tributyl phosphate, and the accuracy may be increased by taking into account the volume changes that take place.

Chemical Stability of the Diluent. The diluent is a petroleum fraction consisting of approximately 60% paraffins, 30% naphthenes, and 10% aromatics. Trade names for this petroleum fraction are Esso Varsol, and Gulf BT. Some component has been observed to react with nitric acid fairly easily, even at room temperatures. However, once this component is removed by reaction with strong acid, the remaining components are very stable and do not absorb fission products even after prolonged contact with TBP Process Solutions.

Solvent Treatment. The used mixed solvent can be recovered for reuse by washing at room temperature with one-tenth volumes of 3 *M* HNO_3, 1.5 *M* NaOH, 1.0 *M* NaOH, and finally water.

The new tributyl phosphate can be conditioned by two one-tenth volume dilute sodium hydroxide washes, followed by a water wash. The petroleum fraction can be conditioned by a nitric acid wash followed by a water wash.

EFFECT OF PHOSPHATE AND SULFATE ION CONCENTRATION

The uranium extraction by tributyl phosphate from metal waste has been found to be a function of the concentrations of nitric acid, uranium, sodium nitrate, sulfate ion, and phosphate ion. Sufficient data have now been obtained that indicate excess nitric acid is required to prevent the complexing of uranium by phosphate and sulfate in low concentrations of uranium. The complexed uranium is less extractable. The conditions for the TBP Process are such that adequate uranium recovery and decontamination are assured in the presence of the expected concentrations of sulfate and phosphate ion.

The data on these studies were presented in ORNL 258 and ORNL 260, and further work is in progress.

PLUTONIUM DECONTAMINATION AND RECOVERY

Adequate plutonium decontamination was obtained in batch counter-current runs by the addition of ferrous sulfamate, a reducing agent, to the scrub. The most recent results have indicated that the addition of the ferrous sulfamate directly to the metal solution feed, eliminating the scrub, may also be effective. This would reduce the acid requirement by about 25%. Under the present process conditions, the scrub adds only a decontamination factor of two, which is not required.

A study was started to determine the necessary conditions for the recovery of the plutonium.

SEMI-WORKS DEVELOPMENT

The TBP Process for recovery of uranium from the Bismuth Phosphate Process metal waste has demonstrated, on a scale of five kilograms of uranium per day, satisfactory uranium yield and satisfactory decontamination from fission pro-

ducts and plutonium. The total uranium loss was about 0.3%, with gross beta, gamma, and plutonium decontamination factors of 10^4, 10^3, and 10^2, respectively, using three year old Hanford waste. This exceeds the decontamination required—the fission product activity being 10% and 50%, respectively, of the beta and gamma activity of natural uranium, and meets the requirement for plutonium of about one part of plutonium per 10^8 parts of uranium.

A discussion of the procedure and results was reported in the Oak Ridge National Laboratory memo, Central Files Number 49-11-177.

Object and Program. The object of the semi-works study was to develop, in collaboration with the Chemical Technology laboratory group, operable conditions for the uranium recovery from feed of three representative uranium concentrations (20, 60 and 100 grams per liter). With these data, the optimum process conditions could be selected, depending upon the final feed preparation procedure. The future program will serve to:

1. Check use of feeds prepared by dissolving Hanford sludge.
2. Determine the cause and reduce the strip uranium loss.
3. Develop procedures for solvent pretreatment and recovery for re-use.
4. Obtain HETS information and determine the effect of varying feed conditions.

This program is scheduled to be completed by February 15, 1949.

PILOT PLANT DESIGN

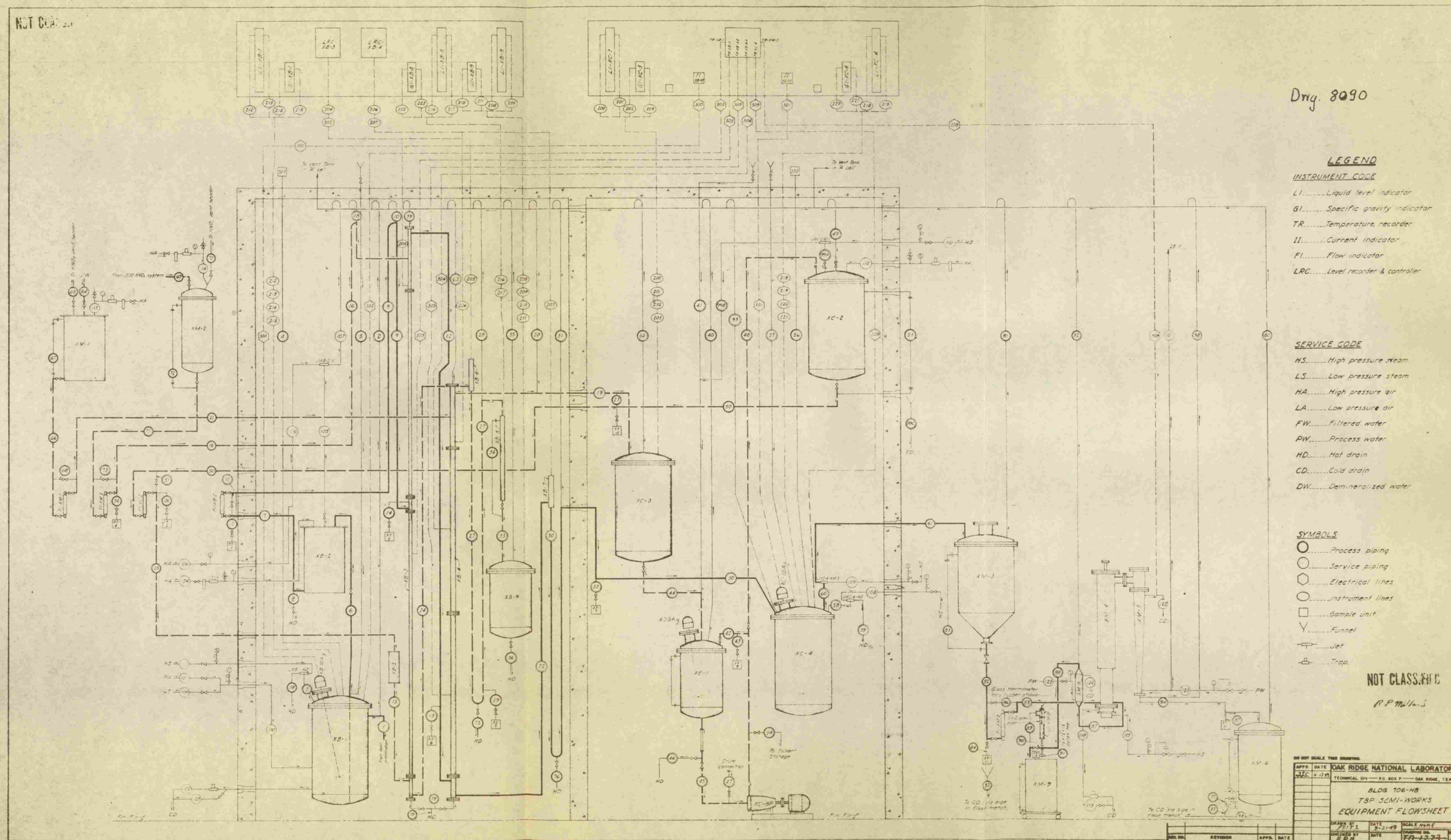
The design and construction of the TBP Pilot Plant in Building 706-HB has been reported in ORNL 543, TBP Process-Pilot Plant Design Report. A schematic equipment flowsheet for the TBP Process for the recovery of Hanford metal waste is shown in Fig. 1.

HANFORD SLUDGE SAMPLING EQUIPMENT

In order to obtain more active metal waste for experimental work in the TBP Metal Waste Recovery Pilot Plant in 706-HB, it will be necessary to secure several 400 pound batches of Hanford metal waste sludge. In order to accomplish this, sludge sampling equipment has been designed and built and will be used at Hanford in December, 1949.

The equipment includes the following items:

1. An 8 in. diameter by 23 ft sludge capsule containing a 4 ft air piston and an air hammer for obtaining the sludge.



Dwg. 8090
LEGEND
INSTRUMENT CODE
LI.....Liquid level indicator
GI.....Specific gravity indicator
TR.....Temperature recorder
II.....Current indicator
FI.....Flow indicator
LRC.....Level recorder & controller
SERVICE CODE
HS.....High pressure steam
LS.....Low pressure steam
HA.....High pressure air
LA.....Low pressure air
FW.....Filtered water
PW.....Process water
HD.....Hot drain
CD.....Cold drain
DW.....Demineralized water
SYMBOLS
.....Process piping
.....Service piping
.....Electrical lines
.....Instrument lines
.....Sample unit
.....Funnel
.....Jet
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XC-2
XC-3
XC-4
XC-8P
XB-1
XB-2
XB-9
XM-1
XM-2
XM-3
XM-6
XM-9
To Vent Tank in "A" cell
To Solvent Storage
Drum connection
Glass thermometer thru rubber stopper
To CD via pipe in floor trench

Figure 1

2. A rinse section for washing the outside of the capsule upon its ascent from the metal waste tank.
3. A transfer box for shielding the lower end of the capsule in transfer operations.
4. A carrier-dissolver for shipment of sludge to ORNL and for dissolving the sludge prior to chemical processing.
5. A base plate for aligning and supporting the aforementioned equipment at the Hanford site.

Tests indicated that the capsule is capable of handling any type sludge in the range of settled mud to wetted shale.

ORNL METAL WASTE RECOVERY PROGRAM

Plans are being made to construct a metal recovery plant for ORNL metal waste using tributyl phosphate extraction sometime after March, 1950. Economic studies to determine optimum plant size will be made during the month of December and January as additional data on feed preparation and pilot plant experimental runs become available.

RaLa PROCESS IMPROVEMENT

SULFATE PRECIPITATION AND METATHESIS

Successful vacuum filtration of the sulfate and metathesis precipitate on a sintered stainless steel filter plate was found to be dependent on the filtration of the metal solution preceding the sulfate precipitation. The metal solution was filtered through a diatomaceous earth filter aid which adsorbed a small amount of barium. A nitric acid wash, which was then added to the filtrate, was sufficient to elute the barium. The barium chemical loss through metathesis has been less than one percent.

The final reproducibility runs are in progress and the equipment revisions are now being designed for the production unit.

PURIFICATION OF BARIUM BY ION EXCHANGE

The Acetate-Citrate flowsheet (ORNL 467) for the purification of the barium in the metathesis product solution by ion exchange has demonstrated reproducible results in the laboratory on 1/30th scale and in Semi-Works on full chemical scale. The barium loss through the iron exchange step was approximately one percent. The approximate chemical composition of the final barium product was:

1.0 gram barium
0.04 to 1.2 grams sodium
0.0002 grams lead

Iron, nickel, and chromium were not detectable by colorimetric analysis.

The study of Alkali-Citrate ion exchange flowsheet was discontinued because it was dependent on centrifugation for the removal of iron, nickel, and chromium.

The study of the up-flow resin column and the IRC-50 resin was stopped because of insufficient time and manpower, and the feeling that the downflow column with Dowex 50 resin would be satisfactory at high activity levels.

The development of an ion exchange process using Versene was started, and the results are comparable with the Acetate-Citrate flowsheet. Versene is a water-soluble chelation agent and has the advantage over acetate in that lead,

iron, nickel, and chromium are not adsorbed in the Dowex 50 resin, and therefore two of the elution steps are eliminated and studies are now being made to eliminate the metathesis step. The major disadvantage is that *p*H control of the barium feed solution is required.

The equipment is being installed for demonstration of this process in the production unit at high activity levels.

25 PROCESS DEVELOPMENT

PILOT PLANT

The final phase of the 25 process development on approximately full chemcal scale and at 25% activity level is now in progress in Hanford irradiated uranium (235) aluminum alloy. In the two runs completed the uranium loss for two solvent extraction cycles was 0.36% with average gross beta and gamma decontamination factors of 3.0×10^6 and 1.2×10^6 respectively. The major uranium loss (0.3%) was in the feed filtration step with cycle wise decontamination factors of 1×10^4 and 3×10^2 for beta, and 6×10^3 and 2×10^2 for gamma.

The detail reports issued during this period covering the equipment revisions, preliminary pilot plant tests and accountability and security measures are ORNL 461, ORNL 490, and ORNL Central Files Number 49-9-215.

The scheduled completion date for this program is December 10, 1949.

METAL SOLUTION

A procedure for the complete dissolution of uranium-aluminum alloy slugs in nitric acid (mercuric ion catalyst) was developed by the Semi-Works for use in the Pilot Plant (ORNL 467 and memo ORNL Central Files Number 49-9-33). The final solution obtained was 1.7 to 1.8 molar aluminum nitrate and 0.2 to 1.0 molar nitric acid. Subsequent development on full scale in the Pilot Plant demonstrated that a two-shot adaptation of the semi-works procedure was more successful (ORNL 490).

CRUD REMOVAL

The solution of the uranium-aluminum alloy contained approximately five grams of insoluble siliceous material per liter. Approximately 230 liters of this solution were filtered by vacuum through the pilot plant filter (1 sq ft of "G" porosity Micro Metallic sintered stainless steel) in 20 hours.

Previous tests by the Semi-Works had indicated that the filter would be completely plugged after 10.40 liters had been filtered. Filtrations using Celite 545 filter aid indicated that the metal solution could be filtered in 7.5 hours on one square foot of filter area. Washing with aluminum nitrate

solution and concentrated nitric acid solution reduced the uranium in the filter cake from approximately two percent of the uranium processed to 0.02 percent (ORNL 490).

EFFECT OF MERCURY IN FIRST CYCLE FEED

Previous development of the 25 Process had not considered the effect of 0.002 molar mercuric nitrate in the feed that had been added as a catalyst during metal dissolution. A laboratory study showed that in the presence of sulfamate the mercuric sulfamate was precipitated. It was therefore necessary to eliminate the ferrous sulfamate from the first solvent extraction cycle and add it only in the second cycle. No detectable amount of mercury was extracted in the first cycle. Results of laboratory counter-current batch runs and pilot plant runs showed no significant loss in decontamination.

FINAL CONCENTRATION

A batch solvent extraction apparatus has been designed and constructed for the concentration of 25. Preliminary testing has been completed using normal uranium in the feed salted with 2.5 *M* $Al(NO_3)_3$, with diisopropyl ether as the solvent. Two runs were made with uranium concentrations in the feed of 12.5 and 76 g/*l*. Results of these runs indicate a uranium loss of 0.004% in extraction and a loss of 0.0006% in stripping with a total loss of 0.001%. On a weight basis, this represents a uranium loss of 0.66 mg in extraction and 1 mg in stripping for a combined loss of 1.66 mg uranium.

The operation of the apparatus was routine and was transferred to Building 706-HB for operation. This equipment will also be used for concentration of the uranium 233.

23 PROCESS

By early 1948, a solvent extraction process for the recovery of U^{233} from irradiated thorium had been developed in the laboratory by the chemistry and Technical Divisions at Oak Ridge National Laboratory. In order to obtain engineering data necessary for the design of a plant to recover the U^{233} produced in the Materials Testing Reactor, a 23 Pilot Plant was designed and constructed at ORNL during 1948 and 1949. A description of the 23 Pilot Plant equipment, and a summary of 23 process chemistry are given in ORNL Central Files Number 49-11-328, "Orientation Manual for the 23 Pilot Plant", to be issued in the coming period.

The scale of the equipment used for this development is more than adequate for processing the material coming from the thorium blanket of the MTR.

Equipment. The general features of the 23 Pilot Plant equipment are similar to the solvent extraction pilot plant used for 25 and Redox process investigations, except that equipment capacity is less. Twenty-one major equipment units, including tanks, condensers and filters, and two 1½ inch packed columns are used for the hot feed preparation and the one cycle of solvent extraction. The average volume of hot process tanks is 40 gallons, and the maximum capacity of the plant is 50 kilograms of irradiated thorium per day. Shielding consists of two feet of concrete, and direct maintenance procedures are used. Eleven 55 gallon tanks with accessories for mixing, pumping, weighing and filtering are used for the preparation of process reagents, and five major equipment pieces are used for solvent recovery.

Procedure. The present 23 process consists of the following steps: dissolution of irradiated thorium metal in nitric acid, continuous counter-current solvent extraction of the 23 in a packed column, scrubbing the product with aluminum nitrate, and stripping the product with dilute nitric acid in a second column. Hexone appears to be the most attractive solvent tested, and this solvent will be used in the early pilot plant runs. Work on laboratory and semi-works scales has shown that the process described above will recover 99.9% of the 23 and that the product is separated from thorium, protactinium, and fission products by a factor of 10^4. A detailed chemical flowsheet for the 23 process is given in Fig. 2.

Pilot Plant Program. The testing and calibration of 23 Pilot Plant equipment will start on November 1, 1949, and will continue on a low priority until the completion of the 25 Pilot Plant Program, at which time the full compliment of 8 technical men and 12 operators will be assigned to the 23 group.

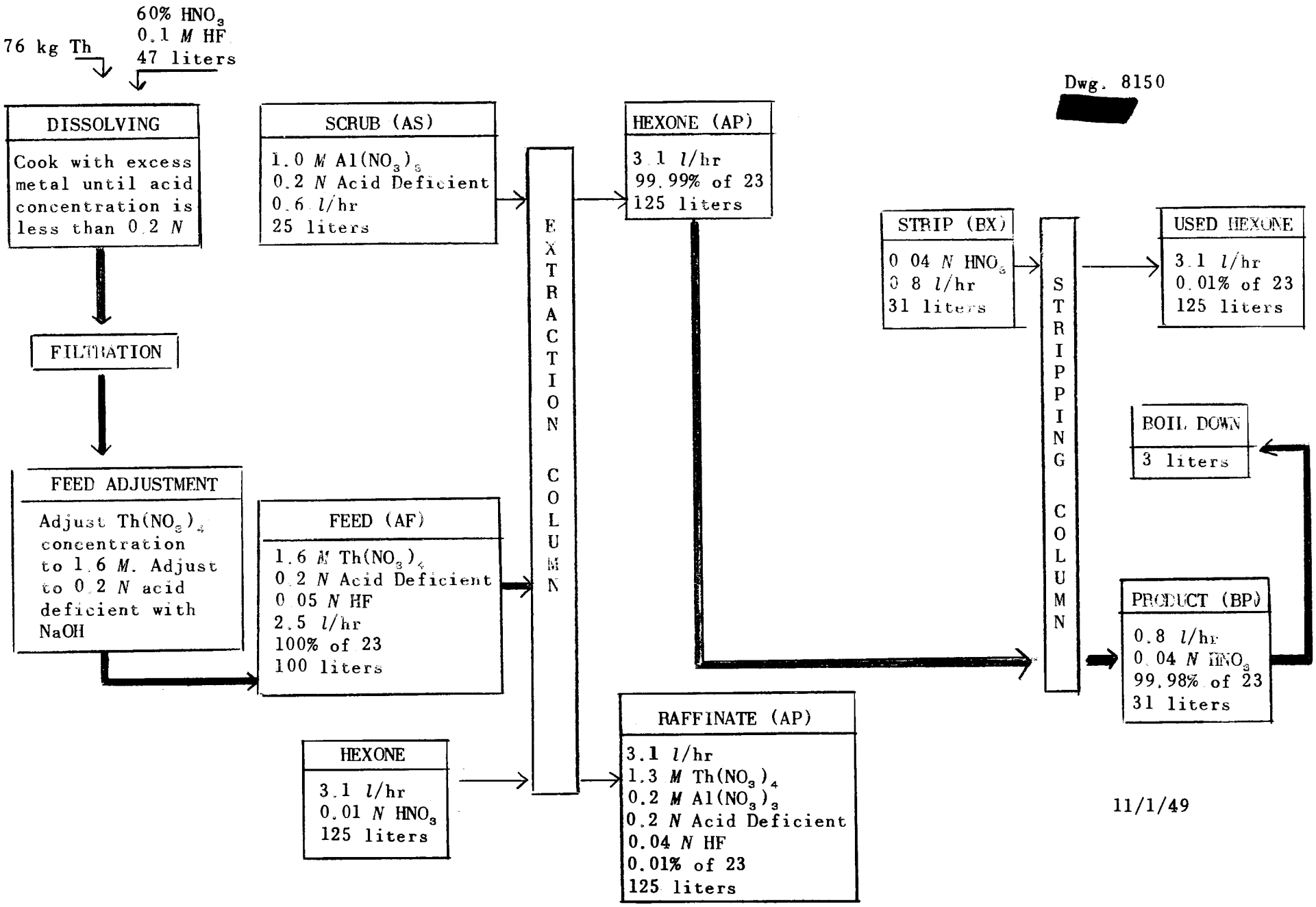


FIG. 2 **23 PROCESS PILOT PLANT CHEMICAL FLOWSHEET**

Hot runs will begin about December 15, 1949. There is available for the 23 program 740 kg of thorium metal which has been irradiated for four months at Hanford, and cooled from six to twenty months. Twenty-five hot runs will be made over a three to four month period, during which approximately 280 grams of U^{233} will be separated.

PUREX PROCESS

Laboratory scale work is in progress on a continuous solvent extraction process for the recovery and decontamination from fission products of plutonium and uranium for Hanford production material. The solvent used is tributyl phosphate (TBP) diluted with "varsol", and the salting agent is nitric acid. Since a solid salting agent is not used, the waste solutions can be greatly reduced in volume by distilling off the nitric acid, and, thereby, simplifying the problem of waste disposal. The acid would be recovered for reuse. The fission products would be recovered in a small volume, comparatively undiluted with solid process reagents, and would be an excellent starting material for the isolation of specific fission products.

Process Procedure. Briefly, the process is as follows: Fuel rods are dissolved in nitric acid, the plutonium stabilized in the tetravalent state, and the uranium concentration adjusted to the proper value by dilution with nitric acid. This feed solution is contacted in an extraction column (1A) with the solvent. The plutonium and uranium transfer to the solvent phase leaving the bulk of the fission products in the nitric acid waste stream. This solvent product is contacted in a second column (1B) with dilute nitric acid containing a reducing agent. The plutonium is reduced to the trivalent state which is highly aqueous soluble and leaves the column in the acid product stream. The uranium remains in the solvent and is stripped out with water in a third column, (1C). These three columns constitute the first cycle. The uranium and plutonium products from this cycle are put through additional extraction and stripping cycles to obtain additional separation from fission products.

Preliminary Results. Preliminary laboratory scale work substantiating the feasibility of the process has been reported in ORNL 479. Data on plutonium distribution coefficients for the tri, tetra, and hexavalent states are given as functions of nitric acid and uranium concentrations.

Using laboratory countercurrent batch extraction equipment to simulate a complete first cycle, overall uranium and plutonium losses of about 0.1 percent have been demonstrated with gross beta decontamination factors of 3×10^3 for uranium, and 7×10^3 for plutonium. The flowsheet for this run was as follows:

1A Pu-U extraction

*1AF: 0.65 *M* UNH, 6 *M* HNO_3, $\beta = 2.2 \times 10^8$ c/m/ml
Pu $\alpha = 10^6$ c/m/ml

* This feed was made from 'X' Slug dissolver solution cooled 150 days and spiked with Pu tracer.

1AX: 15% TBP, 85% "Varsol", 0.15 *M* HNO_3

1AS: 3.5 *M* HNO_3

Flow ratio: AF/AX/AS = 3/10/2

1B Pu-U partition

1BF: solvent product from 1A extractor

1BX: 0.03 *M* ferrous sulfamate, 1 *M* HNO_3

1BS: solvent of composition used in 1AX

Flow ratio : BF/BX/BS = 10/3.3/3.3

1C U strip

1CF: solvent product from 1B extractor

1CX: water

Flow ratio: CF/CS = 13.3/13.3

The major portion of the work on this process, at present, is being devoted to improving the decontamination obtainable in the first extraction (Column 1A). Results indicate that a beta decontamination factor of 9×10^3 can be obtained by reducing the acid concentration of the feed and scrub solutions to approximately 3 *M*.

Solvent Study. The treatment of tributyl phosphate with concentrated nitric acid and sodium dichromate produces a substance which is capable of essentially quantitative extraction of Pu^{+4} from HNO_3 solutions. Parallel investigations for the TBP Process for metal recovery has led to the conclusion that this substance was probably a mixture of mono-butyl phosphate and dibutyl phosphate. Unfortunately, these agents were also found to cause a high extractibility of uranium and fission products with poor scrubbing and stripping qualities.

Stability of the diluent, Varsol, in nitric acid has been found to be a function of aromatic content. Varsol with aromatics and unsaturates removed by sulfonation with 98% H_2SO_4 has been found to be very stable even in the presence of 16 *N* HNO_3.

Decontamination studies have indicated that high decontamination factors are dependent on high purity of the tributyl phosphate with respect to butanol, mono-butyl phosphate, and dibutyl phosphate. Traces of the latter two substances can be removed by washing the TBP-Varsol mixtures with basic solutions.

REDOX PROCESS

PILOT PLANT DEVELOPMENT

The final report (ORNL 463) has been issued on the pilot plant development of the Redox process for the recovery and decontamination of plutonium and uranium from Hanford production material.

PLUTONIUM RECOVERY FROM THE PILOT PLANT IBP SOLUTION

The conditions for the recovery of the plutonium from the pilot plant IBP solutions were determined by a laboratory study. Sufficient decontamination with satisfactory yields will be obtained by processing back through the first cycle for the required uranium-plutonium separation and then through a second plutonium cycle.

The pilot plant processing will start about December 10, 1949.

DECOMPOSITION OF DISPLACEMENT FLUID

Near the end of the Redox pilot plant development program a study resulting from increasing plutonium losses lead to the discovery that the methylcyclohexane, used as the displacement fluid because of its inert characteristics, contained a significant amount of crud. A considerable amount of uranium was in this crud. The result of the laboratory study did not indicate the cause for crud formation, nor did it indicate that the crud had any relation with the plutonium loss. The presence of this crud does indicate that further study would be required if this method of pumping the hot solution was used in the production plant.

FEED PRETREATMENT FOR ACID FLOWSHEET

Since the acid (ANL) Redox flowsheet affords an insurance against significant plutonium losses and an economy in the aluminum nitrate salting agent, additional investigations of the use of the nitrite-acetone feed pretreatment and solvent purification techniques were carried out to evaluate the feasibility of high decontamination in the ANL process. Utilizing the nitrite-acetone feed pretreatment for increasing ruthenium decontamination and exhaustive nitric

acid-dichromate hexone pretreatment for zirconium decontamination, factors of 10^4 to 10^5 have been obtained through extraction and scrubbing stages in the first cycle in contrast to 10^2 as experienced heretofore with untreated feeds. Due to the simplicity of the above procedure it would seem to have considerable advantage over the presently proposed ozonization technique for ruthenium decontamination.

The feed pretreatment as conceived at present is as follows: Adjust 2 *M* uranium dissolver solution to 0.2 *N* HNO_3 deficiency, add 0.05 *M* $NaNO_2$ at room temperature, readjust to 0.3 *N* HNO_3, add 1% volume acetone, heat at 85-90° C for 2-3 hours, cool, then readjust to 2 *M* uranium, 0.3 *N* HNO_3, 0.1 *M* $Na_2Cr_2O_7$.

The solvent purification consists of 3-4 consecutive treatments as follows: hexone washed with equal volume of 1.5 *M* HNO_3, 0.1 *M* $Na_2Cr_2O_7$, followed by an equal volume H_2O wash, and finally an equal volume of 0.5 *M* NaOH wash.

DRY FLUORIDE DEVELOPMENT

FLUORINATION OF IRRADIATED URANIUM

Uranium metal irradiated 335 days in the ORNL pile and cooled 27 months has been converted to uranium hexafluoride and batch distilled. The resulting gross beta decontamination factor for uranium was 10^3. The plutonium remained with the fission products.

The principal equipment consisted of a nickel fluorinator and two cold traps connected in series by means of copper tubing. Throughout fluorination the uranium metal was in contact with the thermocouple well. This temperature was 400-500° C when 20 grams of uranium were fluorinated per hour. During the first part of the reaction virtually all the fluorine admitted to the fluorinator reacted with the uranium. An excess of fluorine and external heat was used to remove the last traces of uranium metal and lower uranium fluorides from the reactor. The uranium hexafluoride was condensed in the cold traps which were immersed in trichloroethylene-dry ice slush. After fluorination the uranium hexafluoride was distilled into another trap.

Uranium metal samples of 44.1 and 64.1 grams were used in these runs. Uranium remaining in the fluorinator was 0.3% in the first run and 0.08% in the second while 0.9% and 1.6% remained in the trap after distillation. About half of the plutonium remained in the fluorinator, and the rest of it stayed in the cold trap after distillation of the uranium hexafluoride. Gross β decontamination was 15 over the fluorination step and 25 for distillation resulting in an overall decontamination factor of 10^3. Gross γ activity in the uranium was reduced to background. The ruthenium decontamination factor was about 100, zirconium and columbium activities were down to background, and total rare earths, cesium, and strontium decontamination factors were 10^3 for the first run and about 400 for the second.

Work is now in progress to improve the plutonium separation from the fission products which is probably dependent on the temperature of the reactor walls.

ONE-SLUG FLUORINATOR DEVELOPMENT

A cooperative program between K-25 and ORNL has been completed for the development of equipment and techniques for the fluorination of uranium metal.

The successful fluorination of normal uranium metal (single X and W slugs) was demonstrated and the rate of fluorination and effect of temperature was studied.

The minimum time requirement estimated for the complete fluorination of an X slug (1000 grams of uranium) was eight hours; 14 hours was required for a W slug (3500 grams of uranium).

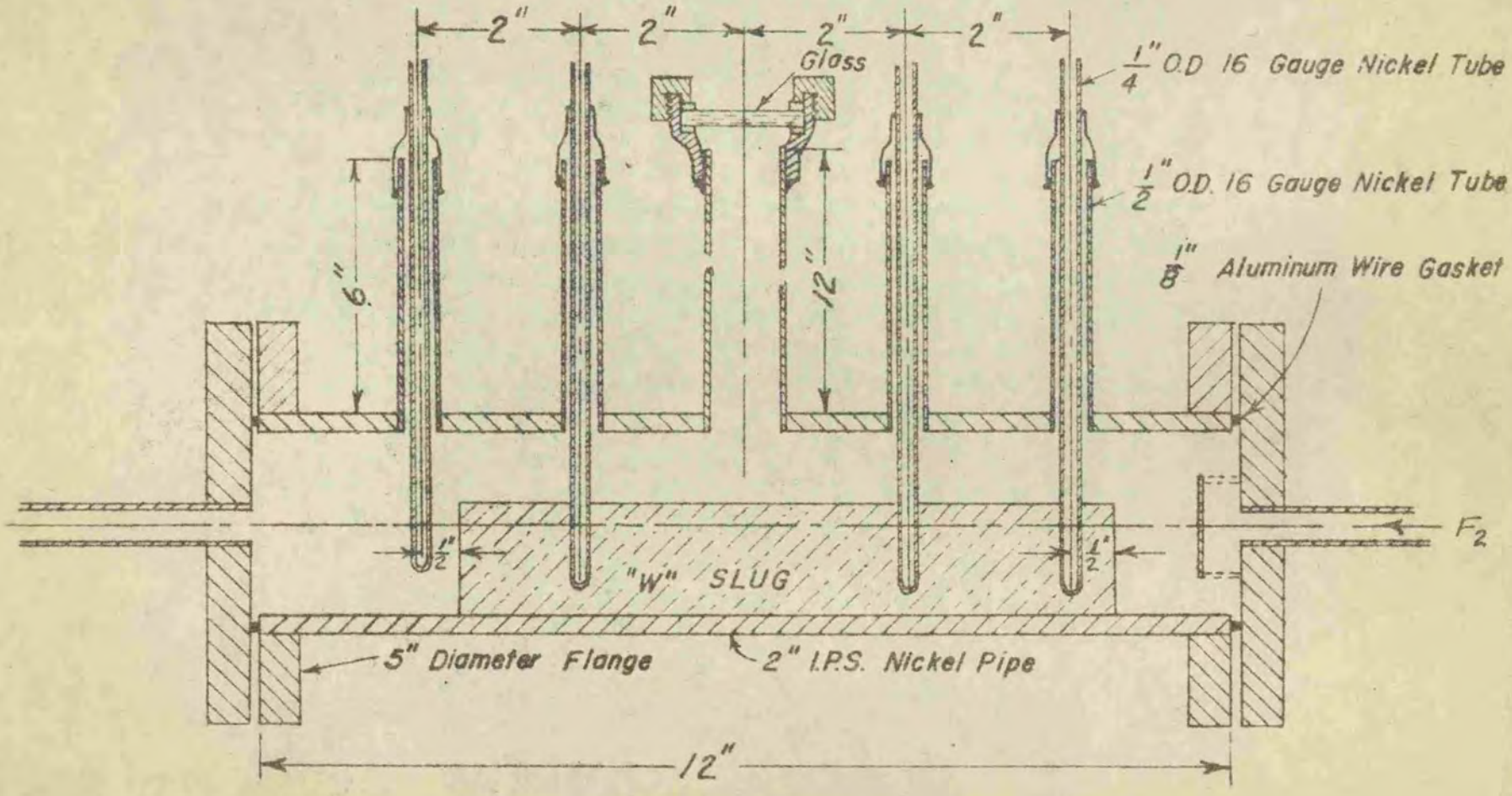
The limiting factor in these experiments was the conversion rate of UF_4 to UF_6; uranium metal to UF_4 being a very rapid reaction. The reaction proceeded at a uniform rate in the temperature range of 570° to 1500° F. Difficulty in control was experienced at the end of each run when little metal remained.

The equipment consisted of a nickel reactor (Fig. 3), copper tubing, and copper traps. No particular equipment problems were encountered.

The report on this phase of the development will be issued by the K-25 Engineering Development Division.

It is planned to construct a fluorinator at ORNL for single irradiated X and W slugs.

DWG. 8158 [redacted]



VERTICAL SECTION OF REACTOR

FOR FLUORINATING URANIUM SLUGS

[redacted]

FIGURE 3

THORIUM RECOVERY

Laboratory scale work is in progress on a continuous solvent extraction process for the recovery and decontamination of thorium from fission products. The solvent used was tributyl phosphate (TBP) diluted with "Varsol", and the salting agent was nitric acid. Since a solid salting agent was not used, the waste solutions can be greatly reduced in volume by distilling off the nitric acid simplifying the problem of waste disposal. The acid would be recovered for reuse. The fission products would be recovered in a small volume, comparatively undiluted with solid process reagents, and would be an excellent starting material for the isolation of specific fission products. A memo describing this process in detail has been issued (ORNL Central Files Number 49-11-211).

The application of this process to waste cooled only three to six months gave a fission product decontamination of only two. Studies are being continued to improve this.

NEW FACILITIES - ARCHITECTURAL DEVELOPMENT

The Semi-Works facilities, attached structurally to the Radio-Isotope Research quarters are now well into the working drawing stage. These drawings should be ready to go out for bid, with specifications, about the end of February, 1950.

Premanentization of the 205 Building will soon get under way; the working drawings and specifications have had their final check for comment by the using parties. There will be no delay caused by bidding on this work; it is fixed fee and will start rather quickly.

The new Research Building is now well developed and has just been subjected to the first progress check of working drawings with little change needed. The drawings and specifications will be finished about a month later than at first anticipated; they will now be done about the first of March, 1950.

The office-shop building for 706-HB use has not progressed much further, but it is possible that this may be available soon after the first of the year. The drawings are at present being studied by the contractor.

RADIOCHEMICAL WASTE PROCESSING

WASTE COLLECTION AND MONITORING SYSTEM

The detailed plans for the alterations for the ORNL liquid waste system proposed in ORNL 268 have been completed and the equipment alterations are scheduled to be started in January, 1950.

LIQUID WASTE EVAPORATOR OPERATION

During the past three months, the chemical waste evaporator has operated on a 24 hour per day, 7 day per week schedule with three brief shutdowns for minor maintenance. The maintenance work was accomplished with a minimum exposure to radiation after several rinses of the evaporator and its associated equipment with nitric acid.

No scaling has been noticed since the evaporator first started into operation in June, 1949. Both types of liquid waste solutions have been evaporated, normal chemical waste (*p*H 11, specific gravity 1.02), and metal waste supernatant solution (*p*H 11, specific gravity 1.15, containing appreciable slurry). Concentration factors have ranged from 35:1 or better for dilute wastes to 6:1 for the metal waste supernates. Decontamination factors have ranged from 1×10^2 to 3×10^3 based on the ratio of total curies discharged to total curies processed. Evaporation rates as high as 500 gallons per hour have been employed (Design capacity: 300 gph).

The principle cause of low decontamination factors in most runs has partially been frequent foamover. Although Dow Corning Silicone "A" antifoam agent was effective, foaming was still a major cause of low decontamination. A cone water spray nozzle of ½ gpm capacity was installed to act as a foam breaker. Foaming has become less serious as a result of these measures and of more careful operation. Two runs were made (about one week's operation) without a foam over in the evaporator.

ION EXCHANGE COLUMNS FOR DECONTAMINATION OF EVAPORATOR CONDENSATE

To further reduce the activity of the condensate from the evaporator, ion exchange columns will be installed during the next period. Both cation and anion exchangers will be used. A duplicate set of columns will be provided to allow continuous evaporation during exchanger regeneration. The resin columns

will have a capacity of 600 gallons per hour. Laboratory and semi-works data have indicated that an additional decontamination factor of 20 to 100 can be obtained by the use of resin exchangers. The resin column is expected to reduce all condensate to less than 10 beta counts per minute per ml during normal operation for an overall decontamination factor over an average evaporator feed of 10^5.

SOURCE AND FISSION MATERIAL ACCOUNTABILITY SURVEY

The first phase of source and fissionable material survey has been completed and reported in ORNL 506. The proposition of an overall analytical material balance SF control of enriched uranium, natural uranium, uranium-233, thorium, and plutonium is discussed and the difficulties involved in sampling, analysis, volume measurement, breeding product production, operation, and waste disposal are discussed. All ORNL processes which use any of the source and fissionable materials have been reviewed in the light of material accountability in the report.

PERSONNEL

F. L. Steahly, Department Head - Chemical Technology

June Parrott, Secretary
Agnes Hair, Secretary
A. Johnson, Janitress (Hrly.)

W. K. Eister, Special Assignment

C. W. Schersten, Assistant to Department Head

F. R. Bruce, Chief - Laboratory Section

	Technicians	
T. C. Runion, Group Leader - Metal Recovery		
C. V. Ellison	J. L. Bamberg	R. C. Lovelace
W. E. Tomlin	V. L. Fowler	H. F. Soard
W. B. Lanham, Group Leader - Purex	L. A. Byrd	E. R. Johns
	W. B. Howerton	C. F. Keck
A. T. Gresky		
R. E. Leuze, Group Leader - Dry Fluoride	H. B. Graham	A. B. Green
C. P. Johnston		
R. E. Blanco, Group Leader - RaLa	G. C. Blalock	
Arlene Kibbey		
Special Assignment Group		
L. E. Morse - Homogeneous Reactor	J. W. Clark	
D. C. Overholt - Thorium Recovery	J. M. DeLozier	R. B. Quincy

J. O. Davis, Chief - Semi-Works Section

Ruth Pennington, Secretary

A. C. Jealous, Assistant Chief - Metal Recovery	G. B. Dinsmore	W. H. Luster
	G. R. Guinn	T. D. Napier
T. A. Arehart	G. Jones	F. L. Rogers
F. Mills		J. C. Rose
E. O. Nurmi		
I. R. Higgins, Group Leader - RaLa	J. B. Goodman	D. B. Masters
		W. E. Shockley
W. A. Horne		
R. H. Vaughan		
J. B. Ruch, Group Leader - "25"	J. E. Farmer	R. O. Payne
C. D. Watson, Group Leader - Testing & Design	C. J. Shipman	
G. A. West		

J. W. Gost, On Loan to Health Physics Division.

D. G. Reid, Section Chief - Pilot Plants

Phyllis Davis, Secretary
R. B. Waters, Draftsman

A. M. Rom - Process Data Coordinator

K. K. Kennedy - Assistant

N. J. Rigstad, "25" Pilot Plant - Chief Supervisor

Operators
R. E. Purkey (807 Bldg.)

E. M. Shank - Senior Supervisor (A)

T. R. McLellan, Chief
R. F. Benson
H. R. Thomas
F. M. Grizzell
H. C. Thompson

J. W. Landry - Shift Supervisor

F. E. Harrington, Senior Supervisor (B)

W. E. Ledbetter, Chief
H. S. Caldwell
W. Jennings
D. E. Spangler
J. Groover

E. C. Stewart, Senior Supervisor (C)

E. E. Shields, Chief
G. D. Davis
B. J. Strader
R. C. Shipwash
J. T. Wiggins

G. S. Sadowski, Senior Supervisor (D)

H. L. Sexton, Chief
N. L. Beeler
R. Burnett
J. Lockmiller
J. F. Land

C. D. Hylton - Shift Supervisor

H. K. Jackson - "23" Problem Leader

D. E. Ferguson
R. J. Klotzbach
W. H. Lewis
E. L. Nicholson
C. A. Gifford
C. H. Jones
D. H. Summers

J. A. Lane, Department Head - Design

Eunice Greenway*, Secretary

F. L. Culler, Group Leader - Chemical Process Design

Lucille Kuykendall, Typist

F. N. Browder
H. E. Goeller
F. C. McCullough
R. P. Milford
W. G. Stockdale
W. E. Unger

* Dual Capacity.