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TRIP REPORT:

SEPARATION PROCESS RESEARCH AT ANL AND ORNL

By

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November 16, 1953

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SEPARATION PROCESS RESEARCH AT ANL AND ORNL

INTRODUCTION

The period September 14, 1953, through September 29, 1953, was spent in discussions of separation process research with personnel at the Argonne National Laboratory and at the Oak Ridge National Laboratory. Information obtained in these discussions is summarized in this report.

DISCUSSION

I. Fluoride Volatility Processes

A. Argonne Fluoride Volatility Process (Bromine Trifluoride Process)

The major effort in the Chemical Engineering Division at present is directed toward development of the Argonne Fluoride Volatility Process ("AFVP") through the pilot plant demonstration stage. An extensive laboratory investigation of process variables is currently in progress under the direction of Dick Vogel. The pilot plant, designed to employ a 10 Kg scale batch dissolver, is under construction and is due to be completed early in 1954.

The immediate goals of the development program are to eliminate the necessity for using elemental fluorine in the dissolution step and to devise a scheme for removal of PuF_3 and insoluble fission product fluorides from the dissolver in a manner which will not require alternate use of interhalogens and aqueous solutions in the dissolver. Use of elemental fluorine in the dissolution step may be necessary in order to prevent build up of bromine in the BrF_3 dissolving medium. Earlier work has shown that when irradiated uranium is dissolved in BrF_3 containing moderate amounts of Br_2, a small fraction of the plutonium is converted to volatile PuF_6. Separation of this small amount of PuF_6 from the UF_6 in the distillation operation would be difficult since the volatilities are nearly identical.

It is hoped that the use of elemental fluorine can be avoided by operating the dissolver in such a way as to distill off the UF_6 and Br_2 continuously as they are formed, thereby keeping the concentration of bromine in the pot liquid low. The pilot plant will be able to test this type of operation.

It is hoped to avoid the necessity for alternate use of interhalogens and aqueous solutions in the dissolver by carrying out the uranium dissolution in BrF_3 containing a suspension of finely divided aluminum fluoride. The hope is that the PuF_3 and insoluble fission product fluorides will deposit preferentially on the high surface area AlF_3 which can then be removed as a slurry in BrF_3. The cross-over to aqueous systems would then be effected in an auxiliary unit which might be either a filter or a small batch still.

The pilot plant will be able to test this mode of operation also.

1. Laboratory Studies

Problems currently under investigation in Vogel's section of the Chemical Engineering Division at ANL are summarized in sections a through k. Basic studies in progress in the Chemistry Division are discussed in sections l and m. Results of a cost study made by the Chemical Engineering Division at ANL are summarized in section n.

a. Kinetics of the reaction of uranium metal with bromine trifluoride.

The activation energy for this reaction has been determined to be ca. 6 Kcal/mole. Although this is in the region of activation energies normally found for diffusion-controlled processes, it is believed that the slow step in this reaction is not a diffusional process since the rate has been shown to be independent of agitation frequency.

The rate of this reaction has also been found to be profoundly influenced by minor impurities in the uranium. With highly purified uranium (carbon and nitrogen reduced to less than 10 ppm) rates of reaction reproducible to ± 10% have been obtained. With "normal" uranium metal the rates are much less reproducible but are on the order of three times greater than with highly purified uranium.

The effect of bromine on the rate of dissolution of uranium in BrF_3 is under study at the present time. Preliminary findings indicate that bromine has at most only a minor catalytic effect.

It is planned to study also the effect of other additives, notably SbF_5, which was found in earlier work to be a highly effective "catalyst" for this reaction.

b. Measurement of absorption spectra of gaseous mixtures of F_2, Br_2, BrF_3, and BrF_5.

A cell of 10 cm path length has been constructed for the purpose of studying the absorption spectra of mixtures of these gases. It is hoped that such techniques may prove useful for analysis of vapor samples. With such studies it may be possible also to ascertain whether BrF is formed in the reduction of BrF_3 by uranium metal.

c. Hydrolysis of BrF_3 solutions.

An improved procedure has been developed for hydrolyzing BrF_3 samples. This procedure employs a hydrolyzing solution which is 1 M in boric acid, 0.6 M in hydrazine, and 0.6 M in nitric acid. With this medium it is possible to accomplish the hydrolysis with a dilution factor of only ca. 50 as compared with the dilution factor of ca. 250 necessary when hydrolysis is carried out in aluminum nitrate solutions as in the earlier work.

The technique employed involves freezing out the BrF_3 sample, generally about 1 ml in volume, in a nickel or monel tube. This tube is then inserted, open end down, through a rubber stopper in the neck of a 1 liter polythene bottle to which has previously been added the hydrolyzing solution. Hydrolysis occurs as the sample melts and drips into the aqueous phase. The polythene bottle is housed in a tightly fitting plaster of Paris cast during the hydrolysis operation to prevent its bursting under the pressure built up by the gases released in the hydrolysis reaction. The sample weight is obtained by weighing the polythene bottle and contents before and after the hydrolysis reaction.

The standard analytical methods for plutonium, uranium, and bromide ion have been shown to be applicable to the hydrolysate prepared by this procedure.

The only difficulty experienced with this procedure to date has been with samples containing high concentrations of UF_6. With such samples incomplete recovery of uranium has been observed on occasion due to retention of solid UF_6 in the sample tube.

d. Refractive index of binary mixtures.

Data correlating refractive index with composition have been obtained for the three binaries: BrF_3-BrF_5, BrF_3-UF_6, and BrF_5-UF_6.

Measurement of refractive index has proven to be a useful analytical method in many of the investigations of BrF_3 systems conducted at ANL, notably in mapping certain of the phase diagrams.

e. Chemical stability of materials of construction.

Apparatus is being set up to enable ignition temperatures to be determined for various possible materials of construction in various fluorinating agents which might be encountered in a BrF_3 process.

f. Removal of PuF_3 from the dissolver by adsorption on suspended AlF_3.

There has been very little experimental work done on this procedure to date. Samples of a plutonium-uranium alloy containing plutonium at a 400 g/T level have been acquired for such studies. The efficiency of adsorption of PuF_3 by AlF_3 will be tested, and the handling characteristics of AlF_3 slurries in BrF_3 will be studied.

g. Phase diagrams.

Mapping of the phase diagrams for the binaries Br_2-BrF_3, BrF_3-UF_6, and BrF_5-UF_6 is largely complete. The liquid-vapor equilibria for the system BrF_3-BrF_5 is under study at the present time.

It is planned to map the phase diagram for one ternary system, either UF_6-BrF_3-BrF_5 or UF_6-BrF_3-Br_2. Study of the ternary system will be delayed until a decision can be reached as towhether it will be necessary to employ elemental fluorine to destroy the bromine formed in the uranium dissolution step. If it proves necessary to use fluorine in the dissolution step, the ternary involving BrF_5 will be studied, otherwise the ternary involving Br_2.

h. Kinetics of fluorination of BrF_3 and Br_2.

The kinetics of the reactions between $F_2(g)$ and $BrF_3(g)$, $F_2(g)$ and $BrF_3(l)$, $F_2(g)$ and $Br_2(g)$, $F_2(g)$ and $Br_2(l)$, and $F_2(g)$ and Br_2(soln in BrF_3) are under investigation at the present time.

i. Application of "AFVP" to submarine reactor fuels.

Previous work has shown that uranium can be recovered satisfactorily from STR fuel elements by fluorination with bromine trifluoride. Work in progress at the present time is designed to determine the feasibility of recovering uranium from SIR elements by similar techniques.

Two types of flowsheets are under consideration. One of these would be a batch operation in which the fuel element would be fragmented by dissolution in a suitable aqueous medium followed by evaporation to a dry solid residue suitable for fluorination with BrF_3. All operations would be carried out in the same vessel. With this

flowsheet there is a possibility of employing a disposable pipe section as a batch dissolver. After removal of the uranium and plutonium, the pipe section would be capped off and used as a container for storage of the fission products.

With the second flowsheet the fuel elements would be dissolved in an aqueous medium and evaporation to a dry solid residue would be accomplished in a spray drier. The hope is that a powder suitable for fluidization could be prepared in this way. The subsequent fluorination steps would then be carried out as gas-solid reactions in fluidized beds.

j. Lab-scale dissolving studies.

A lab-scale dissolver (2.3 l. pot capacity) has been constructed and was put into operation during the latter part of September. Various flowsheet modifications will be tested in this unit, particularly as to their effect on the plutonium behavior.

k. Corrosion studies.

Studies of the corrosion of possible materials of construction by various process systems are continuing.

It has been found that the corrosion of monel by aqueous aluminum nitrate solutions is considerably inhibited by sulfamic acid. The effect is greater if the metal has been previously exposed to a fluorinating medium and hence is coated with a fluoride film.

l. Basic chemistry of BrF_3 systems.

The Chemistry Division at ANL is continuing work in the chemistry of interhalogen systems. Irving Sheft is studying the reaction of PuF_4 with BrF_3. It has been found that treatment of PuF_4 with BrF_3 converts a small fraction of the plutonium (never more than ca. 15%) to a volatile species presumed to be PuF_6. The yield of volatile plutonium decreases with each successive treatment, however. In a typical experiment the yield of volatile plutonium might be ca. 10% in the first fluorination, something less than 1% in the second fluorination, and only trace amounts in the third fluorination. Since similar behavior is obtained with PuF_4 prepared in a variety of ways and since the yield of volatile plutonium apparently cannot be increased by prolonging the time of contact with BrF_3, it is believed that the decreasing yield of volatile plutonium is not due to a decreasing rate of solution of PuF_4 or any such effect. In order to test this, it is planned to study the conversion of PuF_4 to PuF_6 using a homogeneous (and necessarily very dilute) solution of PuF_4 in BrF_3 as the starting material.

H. H. Hyman is studying the Br_2-BrF_3 system. The electrical conductance of the Br_2-BrF_3 system has been measured over the region of low bromine concentration. It is found that the conductance passes through a minimum with increasing concentration of bromine. From this behavior it is inferred that the transference numbers of the various current carrying species in this system must be considerably different. Hence, it is planned to extend the investigation to include measurements of the transference numbers of the ionic species present in BrF_3 and in Br_2-BrF_3 solutions. It is planned also to study the absorption spectra of these systems in parallel with the conductance studies.

m. Preparation of PuF_6.

B. Weinstock and J. G. Malm are setting up to prepare PuF_6 in quantity by direct high temperature fluorination of PuF_4. The techniques which will be used are very similar to those employed successfully by Florin at Los Alamos. In addition to studying the physical properties of PuF_6, it is planned to study the behavior of PuF_6 in BrF_3, i.e., having sizable quantities of PuF_6 available will permit the PuF_4-PuF_6 equilibrium in BrF_3 to be approached from the other side. This work should thus provide an answer as to the feasibility of preparing PuF_6 in good yield in BrF_3 systems.

n. Cost comparison: AFVP vs. Purex

Preliminary cost analysis of the Argonne Fluoride Volatility Process has been made by Walt Rodger's section in the Chemical Engineering Division. A comparison was made with Purex on the basis of a 200-ton per month plant. The saving in annual operating cost estimated for the fluoride volatility process ranges from around $700,000 for a conservative fluoride process to some $6,300,000 for an "optimum" fluoride volatility process. In the latter process external dejacketing of slugs would be employed, slugs would be dissolved with a mol ratio of BrF_3 to U of 4/1, and Br_2 and UF_6 would be removed as rapidly as they are formed in the dissolution. The plutonium would be recovered by solvent extraction on a scale such that the feed volume to the plutonium extraction cycles would be only 50 gal. per ton of uranium processed. The breakdown for this case is shown in the accompanying table.

COST COMPARISON OF AFVP WITH PUREX

(Basis: 200 tons U/mo.)

Annual Operating Cost

	Purex	AFVP
Recovery and decontamination of U and Pu	$7,457,000	$7,552,000
Conversion of UNH to UF_6	6,385,000	--
TOTAL	13,842,000	7,552,000

For the purpose of these computations a fluorine cost of $1.00/lb. was assumed. Waste storage costs were taken as $1.00/gal. for both Purex and the AFVP.

No attempt has been made to arrive at a concrete estimate of the capital cost of a 200-ton per month fluoride volatility plant, but this is presumed by the Argonne people to be in the neighborhood of $50,000,000.

It should be emphasized that these cost comparisons must be regarded as serving only to define a range of reduction in operating cost which might be attainable with a fluoride volatility process. No accurate cost figures can be expected until more experience is gained in large-scale handling of interhalogens.

B. Chlorine Trifluoride Process

The original exploratory work on this process was done by personnel at K-25. This program was terminated at K-25 more than a year ago, however, and any further work on this process will be done at ORNL.

The current program at ORNL calls for completion of an economic evaluation of the chlorine trifluoride process by the end of 1953. At present, two engineers and two chemists are engaged in this study.

This cost study will be made on the basis of a 3 ton/day plant. The type of plant envisioned will employ dejacketing of slugs by the usual techniques, drying of slugs under a vacuum or an inert gas, and intermittent charging of dejacketed, dried slugs to a continuous dissolver. This unit will consist of a vertical tower of always-safe diameter. Slugs will be charged near the top of the tower and will be allowed to stack randomly on a perforated supporting plate located about halfway down the column. The dissolving medium (0.3 ClF_3-1 HF) will be introduced near the top of the tower. Metal will be dissolved according to the reaction

$$U(s) + 3ClF_3(\text{soln with HF}) \longrightarrow UF_6(\text{soln in } ClF_3\text{-HF}) + 3ClF\ (g)$$

in the upper section of the tower. The resultant solution, containing UF_6 in ClF_3-HF, will drain downward through the perforated support plate and thence through a packing which fills the bottom half of the dissolver. A temperature gradient will be maintained across this packed section sufficient to insure that the liquid arriving at the bottom of the tower will be "pure" UF_6 free of ClF_3 and HF. The lower half of the dissolver thus serves as a fractionating tower for separation of UF_6 from ClF_3 and HF.

The vapor leaving the top of the tower will contain ClF_3, HF, ClF, and some UF_6. This will pass through a reflux condenser which will return liquid ClF_3-HF-UF_6 to the top of the tower. The gas emerging from this condenser will consist mainly of ClF. This will be passed through a converter unit where elemental fluorine will be introduced and ClF_3 regenerated by the reaction

$$ClF\ (g) + F_2(g) \rightleftarrows ClF_3\ (g).$$

The ClF_3 thus formed will be condensed and returned to the dissolver as liquid, along with the small quantity of make-up ClF_3 which will be required. Off-gas from this condenser will consist of unreacted ClF and F_2, certain of the more volatile fission products and possibly some "inert" gases. Treatment of the off-gas, e.g., by caustic scrubbing (possibly employing as the scrub solution the caustic waste solution resulting from the jacket removal step), will be necessary before these gases can be vented to the atmosphere.

It is presumed that the insoluble PuF_3 and the insoluble fission product fluorides will slurry with the liquid UF_6 and will emerge from the bottom of the dissolver as a suspension in liquid UF_6. This mixture will be fed continuously to a fractionating column where the bulk of the UF_6 will be taken off as vapor. The UF_6 taken off as overhead from this column will be sufficiently pure that it can be fed directly into a diffusion plant. The insolubles, PuF_3 and fission product fluorides, will be taken off as a slurry in a fraction (perhaps 10%) of the UF_6 from the bottom of this distillation column. This slurry will be fed continuously to a battery of critically-

safe batch processing units, either batch stills or filters, where the UF_6 will be separated from the insolubles. The recovered UF_6 will be recycled to the feed point to the distillation tower.

The solid residue, containing the PuF_3 and most of the fission product fluorides, will be dissolved in an appropriate aqueous medium, e.g., $Al(NO_3)_3$, and the plutonium recovered by solvent extraction.

In such a plant the dissolver will be operated at 125 p.s.i., the distillation tower at ca. 40 p.s.i.

The economic evaluation currently in preparation will provide a basis for a decision as to whether to continue work on the chlorine trifluoride process. If it is decided to continue work on this process, it is planned to embark upon a program of component testing. Pilot scale units (1/25 plant scale or 3/25 ton per day) will be constructed and the various plant operations tested over a range of conditions with "cold" materials. These units will then be assembled into a pilot plant which will test the overall operation with hot feeds.

Some of the more obvious problems which will have to be solved in such a pilot plant program are:

1. Compressing and handling elemental fluorine at 125 p.s.i. (Current K-25 practice avoids handling fluorine at pressures greater than 40-50 p.s.i.)
2. Design of a slug charging mechanism.
3. Devising techniques for transporting PuF_3 and insoluble fission product fluorides as a slurry in UF_6.
4. Improving the yield in the ClF_3 regeneration reaction. (The conditions under which it is currently planned to carry out this reaction, 300°C and 125 p.s.i., give a conversion of only ca. 95%.)
5. Devising satisfactory analytical methods and techniques for ClF_3 systems. (Chlorine trifluoride can be hydrolyzed "safely" only in the vapor phase.)

The only experimental work in progress on this process at ORNL at the present time consists of lab-scale studies being carried on by R. E. Leuze and C. J. Schilling. Their main effort at present is devoted to operating a lab-scale "continuous" dissolver designed to simulate the operation of the proposed plant unit. This apparatus has been in operation only a short time and no data have been obtained as yet. It is planned to study the effect of composition variables and temperature on the kinetics of the reaction of uranium with ClF_3-HF mixtures under conditions approximating to those which would exist in the proposed plant dissolver. The dissolution in the lab-scale unit will not actually be "continuous" but will involve essentially dissolution to a uranium heel.

Previous batch dissolution studies have shown that the rate of dissolution of uranium in ClF_3-HF mixtures is markedly dependent on the previous history of the metal. It is hoped that this effect can be eliminated as a variable by carrying out the rate studies on a single "batch" of metal. The rate data obtained should then be self-consistent but may not be directly applicable to dissolution of irradiated uranium.

It was originally planned at ORNL to use as a basis for the economic study of the chlorine trifluoride process a flowsheet employing an extractive distillation with a perfluorocarbon compound to separate the UF_6 from the PuF_3 and solid fission product fluorides. With this flowsheet the slurry of PuF_3 and fission product fluorides

withdrawn continuously from the bottom of the dissolver would be fed continuously to a distillation tower in which a high boiling perfluorocarbon compound would reflux. The overhead product from this column would be purified UF_6. The bottoms product would be a slurry of PuF_3 and fission product fluorides in the perfluorocarbon compound. This slurry would be fed continuously to a scrubbing unit where the solids would be dissolved in aqueous aluminum nitrate solution. The resultant aqueous solution would be processed and the plutonium recovered by solvent extraction. The perfluorocarbon compound would be dried and recycled to the distillation column.

Some laboratory studies have been made employing perfluorocarbon compounds which might be used in such an extractive distillation, e.g., a perfluorotributyl amine, a perfluoro cyclic ether, and a cyclic perfluorocarbon compound used at K-25, "C-816".

The radiation stability of such compounds has been studied and found to be about the same as for hydrocarbons.

The chemical stability of such compounds has been studied also. It is found that a polymer is formed on contacting the perfluoro tributyl amine with UF_6. Contacting "C-816" with UF_6 at 100°C leads to formation of lower fluorides at an appreciable rate (e.g., 0.08 g of lower fluorides formed from 100 g "C-816" in 4 hours at 100°C). Leuze believes that the chemical stability of these materials could be improved by a pre-conditioning treatment with elemental fluorine.

Some studies have also been made of the scrubbing step in which PuF_3 and other solids would be dissolved in aqueous aluminum nitrate. Uranium tetrafluoride was employed as a stand-in for PuF_3 in these studies. Dissolution was found to be rapid if vigorous agitation is employed or if the scrubbing is carried out with boiling aluminum nitrate solutions. Phase separation is poor, however, and some water is retained by the organic phase. (The perfluorocarbon phase is cloudy after separation.)

Use of an extractive distillation step employing a perfluorocarbon compound has now been abandoned on the advice of K-25 personnel that a process employing such compounds in operations where they might conceivably come in contact with ClF_3 would be too hazardous to be considered for a large scale plant. As mentioned earlier, the cost study will now be based on a flowsheet in which the PuF_3 and fission product fluorides will be transported by slurrying with UF_6 only.

II. Wet Preparation of Uranium Tetrafluoride

Higgins and Roberts at ORNL are continuing studies on a process which gives promise of reducing the cost of preparation of UF_4 from the aqueous nitrate products of solvent extraction plants. This process involves an ion exchange step in which the uranyl ion is adsorbed out of a nitrate solution on a Dowex-50 resin column. The uranium is then eluted off the resin with an aqueous HF solution. The ion exchange step thus serves to eliminate nitrate from the uranium solution. The solution of UO_2F_2 in aqueous HF is then subjected to an electrolytic reduction (at the boiling point of the solution) in which solid $UF_4 \cdot 3/4\ H_2O$ is formed.

Hydrofluoric acid will be recovered by distillation. It is also considered economically feasible to recover nitric acid from the waste from the ion exchange step by distillation.

It is considered that the ion exchange step has been fully demonstrated on the lab-scale and is ready for pilot plant testing. Some decontamination is possible in the ion exchange step, and it is believed that such a step could be substituted for the last uranium solvent extraction cycle. Decontamination factors of 25 have been obtained for Ru, Zr, and Nb, and it is believed that these could be improved by factors of perhaps 2 to 4. Decontamination factors for light contaminants are lower, of the order of 5 to 10. Iron is perhaps the worst contaminant since it will deposit with the UF_4.

Selecting suitable materials of construction for the electrolytic cell is the major unsolved problem remaining in this work. Platinum anodes were used in the early work, but these are considered too expensive for a full-scale plant. Current studies are being made with carbon anodes. These deteriorate rapidly in the boiling HF solution, giving a suspension of carbon particles which must be separated from the UF_4. Various techniques have been employed for this. One involves wrapping the carbon anodes with a suitable resistant cloth. This suffices to retain the carbon particles but increases the resistance of the cell. Compartmented cells have also been employed where the carbon can be filtered off between compartments. It is planned to study vertical cells where there is a possibility of removing the carbon suspension by a flotation process.

Current efficiencies of the order of 90% are obtained in the reduction step and 95-98% conversion to $UF_4 \cdot 3/4\ H_2O$ is apparently easily obtained. Recycle of the residual UO_2F_2 apparently presents no problems.

An economic study has been made of this process. The capital cost is estimated at $5,031,090 for a 20-ton per day plant. The total cost for conversion of aqueous UNH to solid $UF_4 \cdot 3/4\ H_2O$ is estimated to be 23¢ per pound, of which 5¢ per pound is plant amortization (over 6 2/3 years) and 18¢ per pound is operating cost. The estimated operating cost includes a charge of 3¢ per pound for replacement of anodes.

No work has yet been done on the drying and fluorination of the $UF_4 \cdot 3/4\ H_2O$ product produced in this process.

A report summarizing the present status of this process is in preparation.

J. E. Moore at K-25 is studying other methods of reducing the UO_2F_2 product from the ion exchange step. A process involving preparation of a double salt of UO_2F_2 with NH_4F which can be dried in a spray drier and reduced to UF_4 by NH_3 at high temperatures is regarded as offering promise. Such a reduction step would have the advantage that it would not require extensive handling of aqueous HF solutions.

III. Pyrometallurgical Processes

A program of investigation of high temperature processing methods has been initiated in the Chemical Engineering Division at ANL. The techniques which it is proposed to explore are as follows:

A. Extraction of Plutonium Out of Molten Uranium by Treatment with Molten Metals Immiscible with Uranium

Extractant metals to be tested include silver, cerium, and lanthanum.

B. Decontamination of Uranium by Electrical Transport Through Fused Salts

Decontamination of uranium by electrical transport through a bath consisting of the eutectic mixture of LiCl and KCl has been attempted. The decontamination obtained was poor, but it is hoped that it can be improved by increasing the concentration of uranium in the electrolyte. Considerable difficulty has been encountered also in obtaining an adherent deposit of uranium on the cathode.

C. Decontamination of Uranium by Direct Electrolytic Generation of UF_6

Apparatus is being set up to explore the possibility of generating UF_6 directly by employing a solution of UF_4 in KF·HF as the electrolyte in a high temperature fluorine cell. The hope is that the uranium in the system will depolarize the anode so that UF_6 rather than F_2 will be generated at the anode.

D. Recovery of Plutonium from Molten Uranium by Slagging Techniques

Techniques to be explored include slagging with mixtures of UF_4 and BeF_2 and perhaps with oxides.

IV. Solvent Extraction Processes

A. Solvent Extraction Studies at ANL

The work on the Halex process has been concluded, and the final report is in preparation. Future work on solvent extraction at ANL will be confined to studies of contactors and small-scale scouting work on application of solvent extraction to systems other than the nitrate system.

George Bernstein is studying the operation of the stacked stage extractor with the CCl_4-TBP system. This unit is operated as a compound extraction column plus a stripping column. Bernstein feels that the stacked stage extractor has advantages as a research tool because of the ease of sampling at intermediate points but probably would have no advantage over pulse columns as a production unit.

Laboratory studies are in progress on solvent extraction of HCl systems. It is believed that the corrosion difficulties with such systems could be minimized by using ceramics in regions of low activity levels.

Studies of electrolytic dissolution of uranium in H_2SO_4 are in progress at the present time. A fumeless dissolving is employed in which a metal ion is discharged at the cathode, so the uranium dissolution is accomplished without generating hydrogen at the cathode. It is planned to study the processing of such solutions by solvent extraction.

B. Purex Laboratory Studies at ORNL

The semiworks Purex testing program has been concluded. Some additional laboratory studies have been carried on by Flanary. These have been devoted mainly to the solvent clean-up problem and to the problem of ruthenium distillation in the waste concentration and acid recovery steps.

Iodine retention by the solvent is believed to arise from addition of iodine to unsaturates present in the diluent. Some work was done on removal of activity from the solvent by adsorption on solids. Of the adsorbents tested, activated alumina showed the most promise, giving a gross beta-gamma d.f. of 50-100. The decontamination decreases markedly with throughput, however, beginning to tail off after 15 bed volumes. The desorption of activity off the bed is difficult also.

Exchange of the iodinated solvent with other iodine compounds was found to be slow. Decontamination was poor in those exchange reactions tested.

Further studies on the ruthenium behavior in the acid recovery step indicate that the ruthenium d.f. is dependent on the time of retention of ruthenium in the still pot. The ruthenium d.f. remains relatively constant for about the first twenty-four hours and then begins to tail off rather rapidly. Ruthenium distillation is very rapid out of nitric acid solutions of concentration greater than ca. 8 M.

Little work has been done on the UX_1 separation. The pilot plant runs were generally of 2-3 days' duration. These were made by first establishing steady state for the bulk constituents with cold feeds and then switching to hot feeds. It was found that a steady state activity distribution was generally obtained in 3-5 column changes.

It is admitted that a long term effect arising from slow reflux of UX_1 could have escaped notice in the semiworks runs.

In the last series of semiworks runs it was found that the water wash of the recovered solvent was giving no additional decontamination, and since the centrifugate step was giving satisfactory phase separation, the water wash was dispensed with.

V. Separation of Plutonium Isotopes at Y-12 (ORNL) - Electromagnetic Method (1)

The objective in the plutonium isotope separation program is to prepare samples of the "pure" isotopes for research purposes. The emphasis was placed on optimizing separation factors rather than recoveries. Thus, resolution factors for plutonium isotopes are about the same as for uranium isotopes, i.e., a depletion by a factor of ca. 10, but recoveries are only about one-fourth as high for plutonium isotopes, i.e., ca. 4% for plutonium as compared with ca. 15% for uranium. The lower recovery efficiency for plutonium arises from two factors; a lower arc efficiency for plutonium and a lower retention of plutonium on the collector.

Most of the work done to date has been with feeds containing ca. 0.7% Pu-240. The products obtained with these feeds are 1-2 g of a Pu-239 product containing ca. 700 ppm Pu-240, and ca. 200 mg of a Pu-240 product consisting of 50-75% Pu-240, the remainder being Pu-239. The advantage of the latter product (and presumably the reason for employing a low level feed) is that it contains no Pu-241.

It is planned in the near future to begin running feeds containing 5% or more of Pu-240 and collect both Pu-240 and Pu-241.

Within about a year it will be possible to begin processing feeds of irradiated plutonium. With these feeds it will be possible to collect Pu-240, Pu-241, and Pu-242, all of purities of 80-90%.

No good performance figures are available as yet, so no cost estimates are possible at the present time. However, the opinion of personnel engaged in this work is that calutron separation of plutonium isotopes on a production scale is not likely to be economically feasible.

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Reference

(1) Prog. Report, Electromagnetic Research Div., CRNL-1269, 1/15/51, pp. 44-50.