FILES CIRCULATING [redacted]
RETURN TO:
TECHNICAL INFORMATION FILES

UNCLASSIFIED

DOCUMENT NO.

HW--30838

DE92 005576

[X] [redacted]

FILE DESIGNATION

300 [redacted]

TITLE

APPLICATION OF THE MERCURY-CATALYZED ALUMINUM JACKET DISSOLVING TECHNIQUE TO THE REDOX PROCESS

[ ] OTHER OFFICIAL CLASSIFIED INFORMATION

THIS MATERIAL CONTAINS INFORMATION AFFECTING THE NATIONAL DEFENSE OF THE UNITED STATES WITHIN THE MEANING OF THE ESPIONAGE LAWS, TITLE 18, U. S. C., SECS. 793 AND 794. THE TRANSMISSION OR REVELATION OF WHICH IN ANY MANNER TO AN UNAUTHORIZED PERSON IS PROHIBITED BY LAW.

AUTHOR

MH Curtis, JL Bradford, and MK Harmon

THIS DOCUMENT MUST NOT BE LEFT UNATTENDED OR WHERE AN UNAUTHORIZED PER[redacted]Y HAVE ACCESS TO IT. WHEN NOT IN USE, IT MUST BE STORED IN AN APPROVED LOCKED REPOSITORY [redacted]HIN AN APPROVED GUARDED AREA. WHILE IT IS IN YOUR POSSESSION AND UNTIL YOU HAVE OBTAINED A SIGNED RECEIPT FROM CLASSIFIED FILES, IT IS YOUR RESPONSIBILITY TO KEEP IT AND ITS CONTENTS WITHIN THE LIMITS OF THIS PROJECT AND FROM ANY UNAUTHORIZED PERSON. ITS TRANSMITTAL TO, AND STORAGE AT YOUR PLACE OF RESIDENCE IS PROHIBITED. IT IS NOT TO BE DUPLICATED. IF ADDITIONAL COPIES ARE REQUIRED, OBTAIN THEM FROM THE RELATED ISSUING FILE. ALL PERSONS READING THIS DOCUMENT ARE REQUESTED TO SIGN IN THE SPACE PROVIDED BELOW.

ROUTE TO:	READ BY:	DATE	ROUTE TO:	READ BY:	DATE
F. H. Woodfield	326 [illegible]	3-15-54			
K. G. Geier ~~via file~~	13240 [illegible] 826	12/8/55			

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

C-3
AEC

DO NOT PRESS

DISTRIBUTION RESTRICTED TO U.S. ONLY

[redacted]

UNCLASSIFIED

COPY NUMBER	DISTRIBUTION
1	R. G. Barnes
2	O. F. Beaulieu
3	R. S. Bell
4	A. P. Boston
5	J. G. Bradley
6	A. H. Bushey
7	J. R. Cartmell
8	V. R. Chapman
9	V. R. Cooper
10	M. H. Curtis
11	O. H. Greager
12	M. K. Harmon
13	O. F. Hill
14	H. H. Hopkins
[illegible]	E. R. Irish
16	L. M. Knights
17	W. N. Mobley
18	R. L. Moore
19	T. Prudich
20	R. J. Sloat
21	R. E. Smith
22	R. E. Tomlinson
23	B. D. Wilson
24	N. G. Wittenbrock
25	F. W. Woodfield
26 - 28	Extra
29	300 File
30	700 File
31	Yellow File

DO NOT PHOTOSTAT

GENERAL ELECTRIC COMPANY

[redacted]

UNCLASSIFIED

HW-30838

RICHLAND, WASHINGTON . . . . . HANFORD ATOMIC PRODUCTS OPERATION

AEC RESEARCH AND DEVELOPMENT REPORT

APPLICATION OF THE MERCURY-CATALYZED ALUMINUM JACKET DISSOLVING TECHNIQUE TO THE REDOX PROCESS

by

M. H. Curtis, J. L. Bradford and M. K. Harmon

Process Chemistry
Chemical Development Unit
Separations Technology Sub-Section

December 11, 1953

Photostat Charge $ 4.93 for Access Permittees

Available from
Technical Information Service Extension
P. O. Box 1001, Oak Ridge, Tennessee

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission to the extent that such employee or contractor prepares, handles or distributes, or provides access to, any information pursuant to his employment or contract with the Commission.

Operated for the Atomic Energy Commission by the General Electric Company under Contract # W-31-109-Eng.-52

Classification cancelled (or changed to UNCLASSIFIED)
Joe R. Dalton, Chief, Br. CRO
authority of Ltr. 7-16-63
by J. C. Ridenour TISOR, date 10-8-63
DISTRIBUTION RESTRICTED TO U.S. ONLY

UNCLASSIFIED

MASTER

INTRODUCTION

Two possible means of removing aluminum jackets from uranium slugs were considered before Hanford start-up in 1944, and have been considered at other sites for processing other types of slugs. The sodium hydroxide-sodium nitrate dissolution, which served well for Bismuth Phosphate plant operation was accepted for use in the Redox plant. The other means of jacket removal, namely, dissolving the jacket in nitric acid with the aid of mercury as a catalyst, has been adapted for use at Arco and offers certain possible advantages for Redox Plant operation.

Several problems related to Redox Plant dissolver operation may possibly be solved by utilization of mercury-catalyzed nitric acid jacket removal, and include:

1. Radioactive contamination of surrounding environment due to ammonium nitrate crystals being discharged from the stack.
2. Routing and disposal of coating wastes.
3. Colloids and solids in IA Column feed which are believed to contribute to build-up of IA Column operating instability (flooding and/or emulsions), to cause Zr-Nb contamination of the uranium and plutonium products, and to be a possible contributing cause of pump, flowmeter, and valve difficulties.
4. Lengthy dissolver time cycle which is becoming the limiting factor in potential plant capacity, and requires round-the-clock chargings with resultant increased costs.

While considerable experimental work has been performed in studying acid coating removal and the effects on subsequent solvent extraction, much of this is of little use for direct application to current Redox Plant operations. The work reported herein (and that yet to be performed) is directed specifically toward the existing Redox Plant and its operation, and will serve as the basis for a survey of the possible application to the Purex process.

OBJECTIVES

The primary purpose of this document is three-fold:

a. To report exploratory experimental work performed to date in the Process Chemistry laboratories on the study of the dissolving reaction and the properties of the resultant feed solution;
b. To present a summary of the status of related work at other sites and by other groups at this site, as determined from a survey of the available literature references;
c. To outline questions yet to be answered before the process may be used in the Redox Plant and a program to be followed to answer these questions.

SUMMARY

The use of mercury-catalyzed dissolving gives promise, based on the experimental work reported and the literature reviewed herein, of relieving the problems set forth in the introduction, because 1) ammonia evolution from the dissolvers is eliminated, 2) coating removal wastes are eliminated and the aluminum jacket material is utilized as process salting agent, 3) a dissolver solution is produced containing easily separated solids and exhibiting favorable disengaging properties, and 4) in laboratory studies dissolver time cycles are substantially reduced.

a. Laboratory-scale dissolvings of non-irradiated slugs have demonstrated a suitable flowsheet for dissolving Hanford 4-inch slugs (see Appendix for the proposed flowsheet). This flowsheet permits coating removal in about 6 hours, with a total of about 8 hours required for the coating removal and first cut of a two-cut dissolving. Solids resulting from these dissolvings have been easily separated from the solutions and the solutions exhibited favorable disengaging properties in the Redox system.
b. A survey has been made of available literature pertaining to mercury-catalyzed dissolving and the hexone system solvent-extraction behavior of its resulting solutions, and those factors pertaining to the possible adaptation to the current Redox process are discussed below.
c. Those items of information required for the evaluation of such a change in the Redox process but for which sufficient data are lacking, are outlined for future study.

DISCUSSION OF DATA FROM THE LITERATURE

I. General

The use of nitric acid with mercury as a catalyst for coating removal was initially proposed as a step in the chemical processing of aluminum-jacketed slugs. Some development work was done on the step prior to Hanford Works start-up,(7) and many semi-works dissolvings were made.(10) It was discarded at that time, however, because of lack of information on controlling multiple batch dissolvings and because bonding material solids did not interfere with the bismuth phosphate process.(11) More recently it was proposed for Redox as a possible economy measure;(12) that proposal was not too practical, and contained too many points which were subject to question at that time.(47,48) However, more recent work has led to a better understanding of the factors involved.

Considerable development work on aluminum dissolving has been performed at various sites,(5,19,23,29) and the separations plant at Arco, Idaho, is being put into operation, with the use of mercury catalyst for dissolving various types of reactor fuel elements prior to hexone solvent extraction.(14) Work was done on suppressing radio-iodine evolution with mercury in the Bismuth Phosphate process (32)

Also, a significant preliminary survey was made of the behavior of mercury in the Redox process.[41,46] From these various studies, the problems involved in adapting the HNO_3-Hg technique to the current Redox process may be defined.

II. Dissolving

A. Aluminum

The maximum rate of the aluminum-nitric acid reaction is achieved at a nitric acid concentration of about 23%, either with or without the mercury catalyst, even at boiling temperatures.[29] Since the reaction is difficult to control with excess catalyst present, variations in temperature, catalyst concentration, or nitric acid concentration, may be used as means of controlling the reaction. Two sets of conditions have been proposed for optimum results, the use of 10% acid in one case[10,12] and 45% acid in the other.[7]

The selection of acid concentration is influenced by two factors, viz., off-gas composition and subsequent routing of the jacket removal solution. It has been stated that the 10% nitric acid dissolution gives greater hydrogen concentrations in the off-gases than the more concentrated acid.[12]

If the jacket removal solution were sent to stored waste (as would probably be the case if it were to be used for Purex) the lower acid concentration would be favored, since it would give lower waste volumes when concentrated and neutralized. This procedure has been shown to give from 0.5 to 0.8% uranium loss.[10] If the coating wastes were cribbed, then the dilute acid removal would give the lowest waste losses. However, if the excess acid were to be used subsequently for dissolving uranium, then the dilute dissolving would be disadvantageous since considerable water boil-off would be required prior to use as IAF.

Considerable work has been done on finding an optimum concentration throughout the dissolution of Al-U alloys.[29] A study of the reaction rates in the exploratory work indicated that more rapid coating removal might be obtained by incremental acid addition, and recent Redox Plant experience has shown that the uranium dissolving rate is also increased by this technique. The use of dilute acid imposes a load on the H-4 oxidizer to boil off excess water; thus, the use of acid which averages less than 50% will cause a reduction in the potential head-end processing capacity. This factor should be considered in any study of use of acid recovered in the UO_3 plant.

Since the most convenient temperature for a plant operation of this kind is the boiling point of the solution once the acid concentration has been selected, this then leaves the mercury concentration to be determined for any dissolving rate.

B. Uranium

The presence of mercury does not appreciably affect the rate of dissolving of

uranium in nitric acid.[36] Mercury does not form an amalgam with the uranium under the conditions found in the dissolver.[35] Thus, the uranium dissolving rate would follow the conventional relationships of rates with temperature and acid concentration.[24]

C. Reactions

The following are some of the possible reactions that may take place in this system:

1) $Al + 6\ HNO_3 \longrightarrow Al(NO_3)_3 + 3\ NO_2 + 3\ H_2O$,
2) $Al + 4\ HNO_3 \longrightarrow Al(NO_3)_3 + NO + 2H_2O$,
3) $8\ Al + 30\ HNO_3 \longrightarrow 8\ Al(NO_3)_3 + 3\ N_2O + 15\ H_2O$,
4) $10\ Al + 36\ HNO_3 \longrightarrow 10\ Al(NO_3)_3 + 3\ N_2 + 18\ H_2O$,
5) $2\ Al + 6\ HNO_3 \longrightarrow 2\ Al(NO_3)_3 + 3\ H_2$,
6) $U + 8\ HNO_3 \longrightarrow UO_2(NO_3)_2 + 6\ NO_2 + 4\ H_2O$,
7) $U + 4\ HNO_3 \longrightarrow UO_2(NO_3)_2 + 2\ NO + 2\ H_2O$,
8) $8\ U + 28\ HNO_3 \longrightarrow 8\ UO_2(NO_3)_2 + 6\ N_2O + 14\ H_2O$.

Observed reactions, however, are not the simple ones indicated, and are probably combinations of the above reactions depending on instantaneous acid concentrations and condenser efficiency. While the reactions vary during dissolving as concentrations change,[25,27] the summary of several dissolvings (under a different flowsheet from the one considered here) gives a final equation of:

9) $Al + 3.75\ HNO_3 \xrightarrow{Hg} Al(NO_3)_3 + 0.225\ NO + 0.15\ N_2O + 1.875\ H_2O$.

This reaction produces 400 ml. of off-gas per gram of Al at standard conditions of temperature and pressure, when started with an initial HNO_3 concentration of 4.25 M at the boiling point, with a down-draft condenser on the dissolver and a mercury addition equal to 2% of the weight of aluminum.[27] An overall uranium dissolving reaction, starting with 55% HNO_3 was postulated as follows, on the basis of experimental work at ORNL:[24]

10) $U + 4.5\ HNO_3 \longrightarrow UO_2(NO_3)_2 + 1.22\ NO + 0.33\ NO + 0.33\ NO_2 + 0.26\ N_2O_4 + 0.05\ N_2 + 2.25\ H_2O$.

This reaction gives 47.6 liters of off-gas per mole of U dissolved, at 30°C. and standard pressure.

While the above reactions do not include hydrogen evolution, hydrogen has been found in off-gases. Some interaction of hydrogen with other agents present would be expected to occur, both in solution and in the gas phases, thus:

11) $2H^+ + 2\ HNO_3 \longrightarrow 2\ H_2O + NO_2$,
12) $9H^+ + 3\ HNO_3 \longrightarrow NH_4NO_3 + NO_2 + 4\ H_2O$,
13) $H_2 + NO_2 \longrightarrow NO + H_2O$.

The resultant NH_4NO_3 would be retained in the acid solution, and would, in turn, result in NH_3 evolution in the waste neutralizer. The quantity of NH_4NO_3 formed has not been reported.

Data on H_2 evolution are meager and uncertain and are based on either single-slug or small-scale dissolvings. It was found at KAPL that 8% of the off-gas was H_2 when 10% HNO_3 was used for the dissolving.(12) It was determined that the gases evolved with 45% HNO_3 dissolving could not be exploded, either as evolved or with air dilution.(9) No hydrogen was reported as a product of "J" slug dissolving(27) but up to 5% was reported for EBR slugs,(18) and 0.5% was found in dissolving 2S aluminum(18). Some differences in the results of the various studies could be expected, because some work was done with nitric acid recovery (down-draft condensers) which reduced the percentages of nitrogen oxides present. The fact that the data are in conflict is not surprising, since the summary of many EBR slug dissolving runs showed no hydrogen evolved in several cases, but also showed an occasional gas stream containing a low percentage.(22) It would thus appear that some still unidentified variable not under control was responsible for the hydrogen evolution. Hydrogen has also been reported to result from uranium dissolving.(17)

While the presence of mercury will affect the behavior of iodine during dissolving,(32) a concentration of 10^{-3} M mercury is not sufficient to suppress iodine evolution completely.(34) A second dissolving cut with no mercury present would give the same iodine evolution as present second cuts.

D. Conditions

1. Time

Using 10% nitric acid, the coating has been removed from Hanford-type 4-inch slugs in 1 hour.(10) Aluminum jackets have been removed from thorium slugs in 30 minutes with 40% acid.(15) The time of dissolving jacketed EBR slugs in 40% HNO_3 was 3.5 hours, while the same slugs without jackets required 4.0 hours in 55% acid. The metallurgy of "J" type slugs was found to influence the time required to dissolve them(18); thus cast slugs required 10 hours to dissolve in 4.25 M acid with a mercury concentration equal to 5% of the alloy weight, while extruded slugs required only 4 hours to dissolve in the same strength of acid and a mercury concentration of only 2% of the alloy weight.

The time required should be a function, chiefly, of rate of heat evolution and the ability of the dissolver cooling coils to dissipate this heat. No data have been found in the work reviewed on the heat evolution of this type of reaction. The Redox plant dissolvers have a heating capacity of about 10^6 BTU per hour and a cooling capacity of about 6×10^5 BTU per hour.

2. Temperature

The rate of reaction is a function of temperature, for both uranium(24) and aluminum(29). While some flowsheets require maintaining a fixed temperature by the

use of steam or cooling water,[11] it is more in accord with present dissolver operation to allow the reaction to proceed at the solution boiling point and apply steam or cooling water in a manner which will give a constant pressure drop across the dissolver tower and a constant pot vacuum.

3. Chemical Addition

While some experimental work included the soaking of the material to be dissolved in mercuric nitrate solution prior to dissolution in order to make short term experiments reproducible,[8,30], this was not shown to be of sufficient aid in long dissolvings to attempt in plant operation.[30] Mercuric nitrate, the most feasible reagent for this process, requires that a stock solution contain appreciable amounts of nitric acid to prevent the precipitation of the basic nitrate; a solution 6 M $Hg(NO_3)_2$ and 3 M HNO_3 has been proposed.[28]

The sequence of initial chemical addition is dictated by the relationship between acid concentration and dissolving rate. When the optimum dissolving rate occurs at an acid concentration greater than that which gives the maximum rate (ca. 23% HNO_3), as is the case for a 45% acid dissolving, then 60% acid must be added first, followed by water. This sequence insures that the desired rate condition is approached from the slow rate side rather than through a rapid rate region prior to completion of the acid addition.

Also, once a set of conditions of acid concentration, catalyst concentration, and temperature, has been selected to give a controllable reaction rate, consideration should be given to maintaining these conditions beyond the start of the reaction. Thus, a small initial charge of 45% HNO_3 is soon depleted by reaction, and as it is reduced in strength the reaction rate will increase. The initial charge of acid must therefore be large to maintain a constant controllable rate, or incremental acid additions should be used to prevent the free acid concentration from being depleted.

The work with "J" type slugs[29] showed that an optimum acid concentration exists which gives a maximum dissolving rate for any aluminum nitrate concentration. This condition exists when K, in the expression, $K = 1.5\ H^+ + NO_3^-$, is equal to 6.45. It is possible that a similar relationship holds for the coating removal operation and a suitable incremental acid addition technique may be derived.

4. Rate Control

Once the catalyst has been added, temperature and chemical addition offer means of controlling the dissolution rate. As indicated in the above paragraph 2 on temperature, control may be achieved by cooling or heating. Further control may also be achieved by controlled acid and water additions, as indicated in the preceding comments on chemical additions. Drowning of the aluminum reaction, if required, would be accomplished by the addition of nitric -- never with water. Such acid drowning would increase the rate of uranium dissolving, but this is much slower than the aluminum reaction.

Care should be taken when approaching the operating rate at the start of the reaction, or any time the vessel has been cooled, since mercury plated out on the aluminum in the cold will give a very vigorous initial reaction on re-heating. (See the remarks in paragraph 3, above, on chemical addition which discusses soaking the slugs in catalyst.)

5. Metal Heel

The size of the uranium heel of partially dissolved slugs affects the rate of uranium dissolving.(26) Since the uranium reaction is in competition with the aluminum reaction for the nitric acid, it may be seen that the heel size should be defined for any set of conditions for the dissolving.

Mercury does not form an amalgam with uranium(37), nor does it plate out on the stainless steel(37) under the conditions in the dissolver and therefore it is not expected that any mercury will stay in the dissolver between cuts. However, if any aluminum is left at the end of the first cut, mercury should plate out on it, on cooling, to such an extent that the aluminum acid dissolving will continue in the second cut.

6. Other Considerations

Even incremental acid addition will not insure a uniform reaction rate. As the aluminum surface is decreased, the amount of mercury per unit of aluminum will increase and accelerate the dissolving of the remaining aluminum. Also, preferential attack of the aluminum has been observed(31), probably due to different metallurgical forms of aluminum.(23) Any change of structure of aluminum under irradiation may also affect the dissolving rate of irradiated slug jackets.

Foaming of the mercury-catalyzed aluminum dissolving has been observed to be great, and continuous dissolver design for "J" slugs is considerably affected by it.(31) However, the foaming is about the same order of magnitude as that occurring in dissolving uranium and no special difficulties are foreseen in carrying out such aluminum dissolving in a vessel that has been successfully used for dissolving uranium.

Control of final solution acidity may be more difficult than with current dissolving procedures if specific gravity is used as the control means. Each dissolver, depending on its loss of nitric acid due to condenser efficiency, leakage of air, etc., will produce a solution having a characteristic final specific gravity. A proposal made for dissolving FER slugs to control final acidity by the pot vapor temperature, offers promise of being an adequate means of controlling the reaction.(20) The vapor temperature reflects the boiling point of the free acid in the pot. Vapor temperatures are observed to be initially high and to decrease until they reach that of water, when all free acid is gone.(21)

E. Effects

1. Solution Composition

The dissolving of a Hanford-type 4-inch slug (1783 grams of uranium, 58.84 grams

of aluminum and 1.15 grams of silicon, gives 0.29 mole of aluminum for each mole of uranium in solution. Table XXX shows the density and freezing point relationships of solutions having such a ratio. It appears that the highest uranium concentration which may be safely transferred and stored is 2.0 M.

The composition of each cut required to give a final feed composition of 2 M UNH, 0.58 M ANN, may be predicted. A first cut (1.16 M ANN, 1.3 M UNH, 0.0 M HNO_3) that takes all of the aluminum and 32.5% of the uranium will have a freezing point of 25°C. and a specific gravity of 1.5943 at that temperature. A second cut (2.7 M UNH, 0.0 M HNO_3) with a volume equal to the first, which takes the remaining uranium will have a freezing point of 25°C. and a specific gravity of 1.8590 at that temperature.

2. Bonding Agent

Hanford 4-inch slugs contain an average of 1.15 grams of silicon and 0.01 gram of tin. These amphoteric elements, used to bond the can to the slug, are the major source of insoluble residues from the nitric acid dissolvings, since on alternate contact with caustic and acid, they form the acid-insoluble silicic and metastannic acids, which may cause emulsification and entrainment during subsequent solvent extraction. Moreover, under these conditions they tend to form colloids, and thus their complete removal during feed preparation is all but impossible. Even silicon that has been dissolved in caustic is a potential source of gelatinous solids, inasmuch as slug rinses do not completely remove all such materials from the slugs and the vessel.(43) This heel contamination is often overlooked by laboratory workers investigating solids behavior.(44)

The solids remaining after mercury-catalyzed dissolvings are "very finely divided and cause no trouble in jetting."(12) Other known properties (discussed under EXPERIMENTAL, below) appear to offer distinct advantages over the current method.

Part of the solid residue resulting from the bonding material, is now slurried out with the coating wastes; all of the solids removed from the system, however, if mercury-catalyzed dissolving is used, will leave via the centrifuge. This will change the centrifuge waste picture somewhat. Also, it must be pointed out that everything which enters the dissolver must go out "through process." Thus it will be highly desirable that slug buckets be free of foreign materials.

3. Uranium and Plutonium Loss

One advantage of the mercury-catalyzed dissolving procedure is that it eliminates the problem of disposal of coating wastes. This, of course, eliminates the loss of plutonium and uranium to these wastes, but their loss to centrifuge wastes under mercury-dissolving conditions is not known.

4. Fission Product Behavior

The presence of mercury will affect the evolution of iodine from the dissolvers by reducing the amount evolved, from the current average of 50%, to less than 0.05%,

if 10^{-4} M mercury is present.(33) This effect would not be noticed for second cuts, unless additional mercury were added (see under D.5, above). The use of this suppression effect might be quite desirable in the case of silver reactor difficulties, to allow processing at maximum rates at times when the silver reactor is not functioning.

The use of mercury dissolving may affect Zr-Nb decontamination in both the head-end and solvent extraction steps by altering the characteristics of the gelatinous bonding layer-hydrated oxide type of solids (see paragraph E.2, above) which adsorb these radio-elements and influence their behavior.

5. Corrosion

Mercury will not plate out on stainless steel under dissolver conditions, and corrosion studies have shown that 10^{-3} M Hg in dissolver solution causes no increased corrosion in 309 SCb stainless steel.(35) Similar results are reported for 10^{-2} and 10^{-3} M Hg in similar solutions on the same type of stainless.(38) Type 347 stainless steel showed a corrosion rate of .5 mils/year in a 2 M aluminum solution containing 0.085 weight per cent $Hg(NO_3)_2$.(42) It has been reported that heliarc-welded 347 is corroded by 2.0 M aluminum nitrate and 5% $Hg(NO_3)_2$ in acid waste storage tanks.(45) In the initial development of the Bismuth Phosphate process, 181 coating removal runs were made using Hg-10% HNO_3 solutions; there is no record of corrosion of the dissolver having been observed.(10)

III. Feed Preparation

A. Adjustment

The problem of blending cuts to give a uniform feed composition might be solved in the Redox Plant in two ways. The no-longer-needed rinse tanks could be replaced by larger tanks, and the coating removal-first cut solution could be stored therein, to be returned to the dissolver after the second cut. This would provide the blending of cuts prior to transfer to the storage tanks. Another possibility would be for all coating removal-first cuts to be routed to H-10, with subsequent cuts to be routed to H-8 and H-9, followed by batch blending into H-7 from appropriate tanks, using weight factor for control of size of batches to be transferred. Either procedure would allow the dissolvers to operate independently of each other. Routings would be scheduled to allow maximum use of all storage tanks.

Due to the solids present, it would be important for agitators to be in operation in the storage tanks at the time of transfer. (These solids are fine and easily dispersed, but will settle on standing.) Thus, to prevent deposition of solids in the tanks and to insure a uniformity of solids content in the batches sent to the centrifuge, satisfactory agitator operation would be mandatory.

Some dilution of solutions would occur during jet transfer from dissolvers to storage tanks to oxidizer. This dilution water would have to be boiled off during the operation of the oxidizer. A 2.0 M UNH solution represents the most concentrated solution that might be processed safely, due to 25°C freezing point considerations.

Sampling of dissolver solution in the H-7 blend tank would be required, as at present, so that acidity adjustments could be made in the oxidizer. No change in adjusting procedure would be required.

B. Oxidation

No difficulty should be experienced with oxidation by dichromate. Mercuric dichromate is only slightly soluble, but in the reported work with mercury dissolving and dichromate oxidation no mention was found of solubility difficulties.(2)

C. Centrifugation

The change of centrifuge conditions is mentioned above, and includes an expected increase in the amount of solids to be centrifuged out as well as improved centrifugation properties of these solids. The density of the solution to be centrifuged will be less, thus also aiding separation of the solids. Preliminary laboratory studies indicate that these solids are more easily removed by centrifugation than the MnO_2 from permanganate head-end treatment. Fission product and plutonium scavenging by these solids is yet to be determined.

D. Permanganate Head-End

Mercury has been shown to be a catalyst for the reduction of permanganate by X-rays.(1) Its effect on the current head-end treatment in the presence of high-level radioactivity has yet to be determined.

Mercury is 65% adsorbed on MnO_2 when present in a concentration of 10^{-3} M, and 20% adsorbed when the concentration is 10^{-2} M Hg.(46) The effect of such adsorbed mercury on Zr-Nb has not been determined.

No change is foreseen in the actual volatilization of Ru from solutions prepared by mercury dissolving. Experiments conducted to determine $KMnO_4$ reduction rates and MnO_2 scavenging behavior will permit determination of volatilization effects also.

It has been shown that considerable iodine is adsorbed on MnO_2 in the absence of mercury and is not appreciably volatilized during cake dissolution.(39) The influence of mercury on such behavior still has to be determined.

IV. Solvent Extraction

A. Flowsheet

If a 2.0 M UNH solution is the most concentrated solution that can leave the oxidizer because of freezing point considerations, then jet dilutions will reduce this to about 1.8 M UNH by the time it enters the 1A Column as feed. Thus, the 1A flowsheet will be determined by a feed of 1.8 M UNH, 0.52 M ANN and -0.18 M HNO_3, from which several alternate flowsheets may be proposed, incorporating such possibilities as dual-scrub, single-scrub, waste-backcycle, etc. A tabulation of three

possible flowsheets is given in Table II with current flowsheets for comparison. Selection of the flowsheet will be made on the basis of plant operating economy, decontamination, waste losses, and limiting capacity. No flowsheet changes are indicated for columns other than the IA Column.

B. Decontamination

Expected solvent extraction decontamination will be influenced both by the changed feed preparation and the changed solvent extraction flowsheet. The changed dissolving procedure will increase the amount of iodine retained in the column feed.

It was shown that iodine was the major contaminant in IAP (mercury present, hexone system), but constituted only 10% of the activity of the aqueous IBP, having been retained largely with the solvent leaving the IB Column (oxidizing first cycle, no partitioning).(6)

The solvent extraction behavior of Zr-Nb may be influenced by the absence of silicic acid in the mercury dissolved feeds, but no information appears appears to be available on this. The effect of changing IA flowsheets, however, is expected to alter decontamination, since the change from single to dual-scrub flowsheets was shown in the Process Chemistry laboratory to give a greater decontamination across the IA system, and to affect the partitioning in the IB system by reducing the proportion of activity leaving with the IBP.

C. Waste Losses

The greatest impact on waste losses will be due not to the presence of mercury in the system but rather to IA flowsheet changes. Flowsheet conditions (see the proposed flowsheets in Table II) would be chosen with an adequate salting strength and solvent flow to control the IAW waste losses to desired low values.

D. Path of Mercury in Process

Batch extraction data exist for mercury distribution coefficients in the Redox process, which indicate an expected distribution of mercury in the first cycle of 10% in IBP, 35% in ICU and 55% in the ICW.(41,46) Final concentrations of mercury in the product streams are predicted to be 35 ppmp U and 2000 ppmp Pu, from a IAF initially 2×10^{-3} in mercury. It is predicted that a substantial reflux of mercury will occur in the IA and IB systems. Indications are, however, that dynamic extraction work will show little mercury in product streams.(13)

The solubility of Hg under IB Column conditions is limited. This is probably due largely to the fact that mercurous ion is very insoluble(13), although the basic mercury sulfamate has also been reported to be insoluble.(3) The basic nitrate salts also are only slightly soluble(4) and require excess nitric acid to keep them in solution.(28) It was found that ferrous sulfamate could not be added to the IA Column of the "25" process because of the precipitation of mercury, present at a

0.002 M concentration.[16] In the Idaho Chemical Processing Plant it was found that precipitation of mercury would occur with ferrous sulfamate in the second cycle of HFR fuel processing.[13] It is recorded that 0.33 g./l. Hg formed a slight precipitate with 0.05 M ferrous sulfamate.[49] Thus, the build-up of mercury in Redox II by reflux may lead to some precipitation. Depending on the path of mercury, this limitation may influence the flowsheet to be used for back-cycle; e.g., the No. 6 Flowsheet in Table II may be preferred over No. 5 Flowsheet, if appreciable quantities of Hg are in the plutonium cycle wastes.

V. Product Handling

A. Uranium

If the above prediction of a final mercury concentration of 35 ppmp uranium in the end-stream is substantiated, then consideration should be given to the fate of this mercury. Since it has been shown that mercury does not increase corrosion under dissolver conditions, it is not expected to increase corrosion of the uranium concentrators. Due to its vapor pressure and to the nature of its oxides, which decompose on heating, mercury would be expected to be volatilized during calcination of UNH to UO_3.[41] Efficient fume recovery would then obviously be mandatory. Its presence in the UO_3 product is not desirable but might possibly be tolerated if the concentration is not excessive.

B. Plutonium

A final mercury concentration of 2000 ppmp plutonium, as predicted above, would make mercury a major contaminant. No study has been made of the fate of this mercury in, or its effect on, subsequent plutonium processing steps.

VI. Waste Processing

As previously indicated, both iodine and mercury would be found in organic waste streams, e.g., IOW, but their fate in the IO Column and the solvent distillation step is not known. It has been shown by batch contactings that the IO Column should not remove all of the iodine in the solvent[40], and although present plant operation does not result in continued iodine build-up in the solvent, it is possible that the increased concentration of iodine (as a result of the use of mercury) may result in a build-up of this fission product to a finite steady-state value in the retreated hexone.

The behavior of iodine in the aqueous waste concentrators has been determined, but in the absence of mercury.[39] Although considerable iodine does volatilize, very little fails to condense. Mercury-catalyzed dissolving will decrease iodine evolution from the dissolvers and so will put more iodine in the waste system. If the magnitude of this increased concentration is great enough, some increase of iodine in the off-gas system may be noted, but is not expected to reach significant proportions.

EXPERIMENTAL

I. Conditions

Two series of runs were made in the laboratory on a one-slug basis, using unirradiated Hanford 4-inch, jacketed, reject slugs. Some of the runs were performed in a glass resin flask, but most were performed in a stainless steel beaker. Both dissolver vessels were fitted with covers and condensers and were heated by electrical jackets. All runs except one were made with the standard up-draft type of condenser.

A. First Series

This series of runs was made using acid additions that would give a coating removal cut volume of about one-quarter of the final solution volume per charge; hence, two uranium dissolving cuts were required after the coating removal-first cut dissolving. For these coating removal cuts, half of the total acid volume used was charged initially at either 30 or 45 weight per cent concentration; the remainder was added slowly as 60% acid when the initial reaction had slowed down.

Heating was required to initiate the reaction, but once the temperature reached 100°C., sufficient heat was generated to sustain the reaction without the application of additional external heat. Since the stainless steel vessel used in this series of runs had no coil or jacket suitable for cooling, sparging with cold air was the only available means for controlling the reaction. This proved only partially effective. After the initial vigorous reaction had subsided, the application of external heat was required to keep the dissolver contents boiling.

A brief tabulation of this series of runs is given in Table IV, and the sequence of operations and resulting run data for a successful run are shown in Table V.

B. Second Series

Based on the data from the first series of runs, conditions were altered for the second series. Although not all runs were made with sufficient acid, data were sought in this series to permit defining the conditions for a two-cut dissolving. All initial acid concentrations were 45% HNO_3 with the subsequent continuous addition of 60% acid made at the optimum rate as determined by the acid profiles of the previous series. The dissolver vessels used were equipped with cooling coils and provisions for reading pot vapor temperatures.

II. Results

A. First Series

From the first series of runs, information was obtained which could be applied to the second series, including the following items:

1. The optimum concentration of $Hg(NO_3)_2 \cdot H_2O$ (the commonly available salt) is approximately 1 per cent by weight of the aluminum. (This corresponds to about 0.6 per cent on the basis of Hg rather than $Hg(NO_3)_2 \cdot H_2O$).

2. The optimum initial acid concentration is 45% HNO_3.

3. Acid concentration profiles as a function of time indicate that the initial depletion of acid is very rapid and that early addition of concentrated acid is necessary to keep the concentration at 45% for as long as possible while the aluminum is being dissolved.

Run I-D, Table V, shows a suitable flowsheet for the first cut of a 3-cut dissolving. This cut, completed in about 5-1/2 hours, dissolved all of the aluminum in 3-1/2 hours and about 15% of the charged uranium. Two more cuts each of about the same volume would have removed the rest of the charged uranium to be blended with the first cut to give a feed of the desired composition.

B. Second Series

The second series confirmed the optimum catalyst and initial acid concentrations and defined the conditions for continuous acid addition. A tabulation of the runs is given in Table VI, and data for the final run are shown in Table VII. Other points established were:

1. Foaming during the aluminum-nitric acid reaction was of the same order of magnitude as for the uranium-nitric acid reaction.

2. With the recommended amount of catalyst, the first cut was completed in about 7 hours, the first 6 of which were required to complete the aluminum removal.

3. Doubling the amount of catalyst reduced the aluminum removal time to 3 hours but made little difference in total dissolving time for the cut.

4. Rate control was easily achieved by the use of the cooling coils. A temperature drop of 1°C. from the boiling point (ca. 110°C.) was sufficient to quench the observable aluminum-nitric acid reaction nearly completely.

5. A total of 2-1/2 gallons of cooling water (in at 13°C., out at 100°C.) was sufficient to control the reaction with twice the recommended 1% catalyst used, in the laboratory equipment.

6. Vapor temperature appeared to be a satisfactory control criterion for following the progress of the reaction.

7. The first cut solutions contained less than 0.1 gram per liter of ammonium ion (analytical lower limit).

8. Observation of down-draft dissolving techniques indicated that altering the air-sweep rate to compensate for varying off-gas composition during the reaction would be desirable.

9. The solids resulting from the runs were finely divided and granular, lending themselves to improved ease of separation by centrifugation.

There was no indication of any gelatinous solids being present, as was the case with solutions prepared by conventional caustic coating removal followed by acid uranium dissolution. (Such slime formation is chiefly due to incomplete rinsing of the caustic from the slugs and vessel prior to acid addition.) The fineness of these solids was such that they were readily slurried by air sparging and removed through the decant line. Centrifugation for 10 minutes at 1000 x G was sufficient to remove all visible solids from the solutions. Following Run I-D, the balance of the uranium charged was removed in two additional cuts and these cuts were blended and adjusted to a 2.0 M UNH IAF composition. After centrifugation for 20 minutes at 1700 x G the solution gave a vibrational disengaging time of 30 seconds, compared with 28 seconds for C.P. IAF, 54 seconds for the uncentrifuged first cut solution, and 32 seconds for uncentrifuged IAF prepared by the conventional de-jacketing and dissolving techniques. While these disengaging times show little difference between caustic and acid coating removals, the cumulative effects may be quite different. Unfortunately, no completely satisfactory laboratory method has been found to indicate tendencies of solutions to cause solvent extraction column operating instabilities.

Further information about the residual solids was obtained by studying those resulting from Run II-E. The first and second cuts were combined and centrifuged at 1000 x G. About 9 ml. of solids were centrifuged from 3700 ml. of solution, and this 0.24 volume per cent represented essentially all of the solids associated with one 4-inch slug. The apparent density of this cake was 1.77 g./ml. The solution density was 1.63 g./ml. These solids were shown by spectrographic analysis to contain more than 1% Al, approximately 0.01% U, less than 0.01% Cu and Sn, and no detectable quantity of Hg.

III. Discussion

Study of the experimental results has led to the proposal of the dissolving flowsheet shown in the Appendix. It is expected that only the rate of continuous acid addition will have to be adjusted for any given dissolver since the rates of reaction will determine the rate of depletion of nitric acid. Variables such as the use of updraft or downdraft condensers, vessel air leaks, efficiency of heating and cooling, etc., will affect the rates of reaction. A glance at the acid concentrations during the two runs tabulated (Runs I-D and II-E in Tables V and VII) shows that optimum acid concentrations were not maintained in these laboratory runs.

FUTURE WORK

I. General

The preceding summary of preliminary laboratory work and discussion of data

from the literature has pointed out some of the pertinent factors to be investigated further. While considerable information has been obtained on mercury-catalyzed dissolving of various types of slugs, and some is available on the behavior of mercury and iodine in hexone solvent extraction processes, it is not believed that the process is ready for testing in the Redox plant. A specific flowsheet must be developed for dissolving, and data should be obtained on all subsequent processing steps as practiced in the present continuous Redox plant operation, with particular emphasis on those factors which may have detrimental effects on operations or product quality.

A program is currently under way to develop a mercury-catalyzed dissolving procedure for the present Redox plant, and to answer questions of process importance. This program involves considerable laboratory "cold" and "hot" work, plus "cold" semi-works scale studies in the 321 Building dissolver which is a 1/20th scale model of the production plant dissolvers. It should be noted here that although 1% catalyst (based on the weight of Al) was adequate for satisfactory jacket removal in these single-slug laboratory experiments, it was found necessary to increase this concentration 3- to 5-fold to obtain the same results in the 321 Building Cold Semi-Works dissolver as indicated by preliminary data. A complete presentation of these 1/20-scale results will be made in a forthcoming document. The program may be separated into three phases.

II. First Phase -- Development of Flowsheets

It is desired to:

A. Develop and demonstrate a mercury-catalyzed dissolving flowsheet that will give controllable dissolver operation with a minimum dissolver time cycle. The emphasis will be placed on down-draft dissolver operation.

B. Develop and demonstrate a IA Column solvent extraction flowsheet which will permit adequate processing of the feeds resulting from the mercury-catalyzed dissolvings. The emphasis will be placed on dual-scrub flowsheets with waste back-cycled as scrub.

III. Second Phase -- Providing Process Information

It is desired to:

A. Obtain data on off-gas compositions and volumes.

B. Obtain nitric acid consumption data.

C. Obtain heat evolution data.

D. Provide data for reaction control criteria, including specific gravities, boiling temperatures, and vapor temperatures.

E. Determine ammonium ion content of feeds.

F. Determine the behavior of solids, including centrifuge requirements, (residence times, cake volumes, cake washing and removal), adsorption of Pu and fission products.

IV. Third Phase -- Investigation of Process Complications

It is desired to:

A. Investigate effects on head-end treatment, including $KMnO_4$ stability, ruthenium volatilization, MnO_2 scavenging, and iodine evolution.

B. Investigate the path of mercury in continuous counter-current solvent extraction including over-all uranium and plutonium cycles, and during start-up and shut-down.

C. Determine the fate of mercury in, and its effect on, subsequent processing if solvent extraction leaves appreciable quantities of mercury in the product streams.

D. Determine the path of iodine during solvent extraction and waste concentration in the presence of mercury.

E. Determine the fate of iodine and mercury in solvent treatment.

M. H. Curtis
M. H. Curtis

J. L. Bradford
J. L. Bradford

M K Harmon
M. K. Harmon

MHC:JLB:MKH/meb

REFERENCES

(1) Clark and Coe, J. Chem. Phys. 5, 97 (1937).

(2) Ephraim, Inorganic Chemistry, 5th Edition (revised) Interscience Publishers, p. 490 (1948)

(3) Ibid., p. 654.

(4) Ibid., p. 708.

(5) ANL-4110 "Studies in Counter Current Solvent Extraction for Decontamination of Enriched Uranium from the Proposed High Flux Research Pile." H. Evans, S. Vogler, and H. H. Hyman. 1-28-48.

(6) Ibid., p. 28.

(7) CN-544-B Report for Month Ending March 27, 1943, Technology, Separation Processes Section. J. B. Sutton. 3-27-43. pp. 16-18.

(8) Ibid., p. 16.

(9) Ibid., p. 18.

(10) CN-1879 Progress Report, First Nine Months Operation of Separations Plant. A. C. Cox. 10-9-44. pp. 28, 29.

(11) CN-2021 "Recommendations for Process Conditions at Hanford Engineer Works and Review of Separations Process Chemistry." M. F. Acken. 10-1-44. p. 12.

(12) GEH-19,220 "Coating Removal Report." B. V. Coplan, J. K. Davidson, A. C. Schafer. KAPL. 12-11-51.

(13) IDO-14242 "Mercury in the "25" Process." A. E. Erhard, R. H. Perkins. 5-5-53.

(14) IDO-14250 "Revised Feed-Preparation and Solvent-Extraction Flowsheets for the Idaho Chemical Processing Plant." E. J. Fuller, R. B. Lemon. 5-11-53.

(15) MonN-125 Separation of U-233 from Thorium, Progress Report, July 1945 to June 1946. F. L. Steahly. 7-25-46. p. 9.

(16) ORNL-676 "Terminal Report of ORNL Pilot Plant Development of the MTR "25" Recovery Process." A. M. Rom. 5-23-50. p. 21

(17) ORNL-1061 Chemical Technology Division Quarterly Progress Report for Period Ending May 20, 1951. W. K. Eister, ed. 9-24-51. pp. 12-19.

(18) Ibid., pp. 57-62.

(19) ORNL-1137 "Solution of Experimental Breeder Reactor Slug." E. M. Sampson, Jr. 5-11-52.

REFERENCES (Cont.)

(20) Ibid., p. 8.

(21) Ibid., p. 20.

(22) Ibid., Tables 13.1.8 to 13.1.12, inclusive.

(23) ORNL-1195 "Dissolution of Uranium-Aluminum Alloys." D. L. Foster, E. O. Nurmi. 7-22-52

(24) ORNL-1208 "Recovery of Nitrogen Oxides and Rare Gas Fission Products from the Nitric Acid Dissolution of Irradiated Uranium." A. T. Gresky. 4-30-52.

(25) Ibid., p. 25.

(26) Ibid., p. 36.

(27) Ibid., p. 70.

(28) ORNL-1431 "Laboratory Development of the Thorex Process, Progress Report, Sept. 30, 1952." A. T. Gresky, et al. 4-6-53. p. 27.

(29) HW-18414 "Nitric Acid Dissolution of Uranium-Aluminum Alloy." R.E. Burns, C. H. Holm. 8-12-52

(30) Ibid., p. 11.

(31) Ibid., p. 18.

(32) HW-21103 "Retention of Iodine in Process Solutions by Mercuric Salts." C. H. Holm. 6-15-51.

(33) Ibid., p. 6.

(34) Ibid., p. 11.

(35) Ibid., p. 21.

(36) Ibid., p. 22.

(37) Ibid., p. 23.

(38) HW-22779 "Corrosion of Stainless Steel Type 309 SCb in 200 Area Dissolver Solution Containing Mercuric Ion." K.L. Sanborn. 11-20-51.

(39) HW-23342 "Behavior of Iodine in the Redox Process." J. S. Kane, R. E. Burns, 1-21-52. p. 13.

(40) Ibid., p. 10.

REFERENCES (Cont.)

(41) HW-24139 Chemical Research Quarterly Report for January through March, 1952. O. F. Hill, F. J. Leitz. 4-15-52. p. 56.

(42) HW-26650 "Report of Discussions at ORNL." A. M. Platt, D. P. Granquist. 12-24-52. p. 4.

(43) HW-26769 Progress Report, Chemical Development, Separations Technology, December, 1952. F. W. Woodfield. 12-31-52. p. 8.

(44) HW-29619 Quarterly Progress Report, Chemistry Unit, July, August, September, 1953. A. H. Bushey. 11-16-53. p. 16-18.

(45) TID-2011 "Design of the Idaho Chemical Processing Plant," F. L. Culler, Reactor Sci. Technol., 3(4): 171, December, 1953.

[redacted]

APPENDIX

RECOMMENDED MERCURY-CATALYZED DISSOLVING FLOWSHEET

Method: Two-cut dissolving; first cut, mercury catalyzed, removes all aluminum and 32.5% of charged uranium; second cut removes 67.5% of charged uranium. Heel maintained of 50% of uranium charged.

Control: The coating removal cut operation will be controlled by heating or cooling to maintain a constant vacuum and tower differential pressure, with vapor temperature as the criterion for determining completion of dissolving.

Charge: Total uranium weight charged will be such that the second cut (67.5% of that charged) may be safely dissolved with sufficient freeboard as determined by previous experience.

Acid: Equal volumes to be used for each cut as determined by the second cut volume. First cut acid is added in two parts. The initial addition as 45% acid is to be half of the total acid volume, and the second half is to be added continuously as 60% acid.

Catalyst: $Hg(NO_3)_2 \cdot H_2O$, 1% of weight of Al, for 4-inch slugs.

FLOWSHEET

A Coating Removal - First Cut

1. Charge jacketed 4-inch slugs.
2. Add catalyst, as 1 M $Hg(NO_3)_2$ in 45% HNO_3.
3. Add 45% acid.
4. Turn on off-gas jet, condenser cooling water, pot heating steam. (Adjust air sweep if down-draft dissolvings are used.)
5. When pot temperature reaches 100°C., start continuous acid addition at a rate which will complete the addition in 75 minutes.
6. Control reaction by the use of steam or cooling water as required, to maintain constant pot vacuum and tower differential pressure at values commonly used for uranium dissolving.
7. When pot vapor phase temperature drops to 101°C., turn off steam, turn on cooling water, cool to 40°C.
8. Dilute to sp. gr. of 1.59 with water.
9. Transfer to storage tank.
10. Turn off condenser cooling water, off-gas jet.

B Second Cut

Follow conventional uranium dissolving flowsheet.

TABLE I

APPLICATION OF MERCURY CATALYZED NITRIC ACID SLUG DISSOLVING TO THE REDOX PLANT — EVALUATION OF INTRODUCED CHANGES

CHANGE	ADVANTAGES	DISADVANTAGES
Changes physical properties of solids in feed to IA Column.	1. Easier removal of solids from feed solutions. 2. Possible elimination of build-up of IA Column operating instability. 3. Possibility of eliminating (or reducing) break-through of Zr-Nb to uranium and plutonium cycles.	
Introduces mercury to process.	Effects not evaluated.	1. Mercury as a possible contaminant in both products. 2. Introduces a poisonous chemical.
Reduces dissolver time cycle.	1. Helps eliminate possible limitation on plant capacity.	
Changes behavior of radio-iodine.	Effects unknown.	Effects unknown.
Eliminates caustic coating removal.		
1. No coating wastes.	1. No losses of product to coating wastes. 2. Eliminates equipment and time required for separate waste handling. 3. Reduces volume of waste to be stored.	1. Cribbing of coating wastes not possible under present proposal. 2. Equipment and operation gains probably off-set by requirement for proper blending of cuts.
2. No caustic used by	1. Simplifies operation, frees	

TABLE II

PROPOSED REDOX IA-COLUMN FLOWSHEETS
MERCURY CATALYZED DISSOLVING

		Flowsheet Number(1)					
		1	2	3	4	5	6
Stream	Component	Single-Scrub	Dual-Scrub(3)	Dual Scrub(2,3)	Single-Scrub	Dual-Scrub(2,3)	Dual Scrub(2,4)
IAF	UNH, M	2.0	2.0	2.0	1.8	1.8	1.8
	HNO_3, M	-0.2	-0.2	-0.2	-0.18	-0.18	-0.18
	$Na_2Cr_2O_7$, M	0.10	0.10	0.10	0.09	0.09	0.09
	ANN, M	--	--	--	0.52	0.52	0.52
	Density, G./Ml.	1.68	1.68	1.68	1.62	1.62	1.62
	Flow(5)	100	100	100	111	111	111
IAS	ANN, M	2.06	2.51	2.50	1.63	2.51	2.51
	HNO_3, M	-0.2	-0.2	-0.2	-0.2	-0.2	-0.2
	$Na_2Cr_2O_7$, M	0.01	0.005	0.005	0.01	0.005	0.005
	Density, G./Ml.	1.32	1.40	1.40	1.27	1.40	1.40
	Flow(5)	115	110	111	110	110	82
IAA	ANN, M	--	0.5	0	--	--	--
	HNO_3, M	--	-0.2	0.04	--	0.04	0.04
	$Na_2Cr_2O_7$, M	--	0.01	0.01	--	0.01	0.01
	Density, G./Ml.	--	1.08	1.00	--	1.00	1.00
	Flow(5)	--	35	35	--	35	35
IAX	Density, G./Ml.	0.80	0.80	0.80	0.80	0.80	0.80
	Flow(5)	420	420	460	420	420	420
IAP	UNT, M	0.45	0.45	0.41	0.45	0.45	0.45
	HNO_3, M	0.015	0.015	0.014	0.015	0.015	0.015
	Density, G./Ml.	0.96	0.96	0.95	0.96	0.96	0.96
	Flow(5)	445	445	485	445	445	445
IAW	ANN, M	1.25	1.33	1.25	1.25	1.44	1.30
	HNO_3, M	-0.2	-0.2	-0.2	-0.19	-0.18	-0.17
	$Na_2Cr_2O_7$, M	0.05	0.06	0.06	0.05	0.05	0.05
	Density, G./Ml.	1.22	1.23	1.22	1.22	1.25	1.23
	Flow(5)	190	220	184	184	231	202
L/V Extraction Section		0.427	0.494	0.379	0.413	0.519	0.454

(1) Flowsheets 1 through 3 are for current dissolving, and 4 through 6 are for the Hg-catalyzed dissolving.
(2) "Saltless" IAA.
(3) Maximum salting strength, back-cycle of 2DW, 2AW and 3AW.
(4) Limited back-cycle, plutonium cycle wastes not back-cycled.
(5) Relative to IAF rate for Flowsheet 1.

TABLE III

SOLUBILITY OF SOLUTIONS PREPARED BY MERCURY-CATALYZED DISSOLVING

Test Solutions: Prepared by diluting following stock solutions with water to desired concentration.

Component	Solution A	Solution B
UNH, M	2.00	2.00
ANN, M	0.58	0.58
HNO_3, M	0.10	-0.20
$Na_2Cr_2O_7$, M	0.10	0.10
$NaNO_3$, M	0.00	0.30

Saturation Temperature: Temperature at which first solids appear on cooling. (Found to be nearly identical with temperature at which solids re-dissolved on heating.)

Concentration of UNH, M	Specific Gravity, 25°C.		Saturation Temperature, °C.	
	A	B	A	B.
2.0	1.738	1.728	24.5	19.0
1.9	1.700	1.695	16.9	16.0
1.8	1.660	1.650	13.0	8.7
1.7	1.625	1.625	8.7	2.3
1.6	1.592	1.588	1.5	13.0

[redacted]

TABLE IV

LABORATORY-SCALE DISSOLVING OF "COLD" SLUGS
MERCURY CATALYSIS

SERIES I

Run Conditions: (Coating removal plus first cut)

Initial charge: 1) Canned slug (1780 grams of U; 59 grams of Al)
2) Heel of partially dissolved slug.

Initial chemical addition: 500 ml. of acid and catalyst as shown.

Continuous chemical addition: 500 ml. of 60% HNO_3 added at rate of 5 ml. per minute.

Catalyst: 1 M $Hg(NO_3)_2$ in 45% HNO_3; amount used expressed as weight of $Hg(NO_3)_2 \cdot H_2O$ as per cent of weight of Al.

Temperature: Maintained at about 110°C. Cooling required for a period during initial reaction.

Results:

	Run Designation			
	A	B	C	D
Initial Acid Concentration, Wt.%.	30	45	45	45
Catalyst Added, Wt.% of Al.	4.7	4.7	0.47	1.16
Time Continuous Chemical Addition Started, Minutes after Beginning of Run.	120	90	120	75
Total Run Time, Minutes.	240	270	360	450
Coating Removal Time, Minutes.	240	90	360	270
Run Completed to 0.0 M HNO_3.	No	No	No	Yes
Uranium Dissolved, Grams.	48	79	219	262
Rate of Aluminum Dissolving Reaction.	Too Rapid	Too Rapid	Too Slow	Optimum

UNCLASSIFIED

TABLE V

RUN DATA

LABORATORY-SCALE DISSOLVING OF "COLD" SLUGS
MERCURY CATALYSIS

RUN I-D, SERIES I, TABLE IV

Operation	Time, Min.	Solution Temp., °C.	Solution Composition HNO_3, M	UNH, M	ANN, M	Sp.Gr., 25°C.	Coating Removal, %
Charge 1180 g. "heel".	--						
Charge canned slug (4-inch).	--						
Charge 500 ml. of 45% HNO_3, 0.005 M in $Hg(NO_3)_2.H_2O$.	--		9.2	0.0	0.0	1.278	0
Start heating.	0	25					
Turn heat off.	33	101					
Air sparge to cool solution.	35	110					
Sample solution.	40	116	4.5	0.4	1.6	1.484	55
Turn sparge off.	52	111					
Turn heat on and sample.	60	111	0.6	0.4	1.9	1.460	62
Start adding 60% HNO_3, 5 ml./min.	75	111					
Sample	90	111	1.3	0.5	2.4	1.493	76
Sample	150	113	1.8	0.5	2.2	1.513	90
Finish acid addition.	175	113					
Sample	210	112	1.6	0.7	1.8	1.559	97
Sample	270	112	0.6	0.9	1.75	1.580	100
Sample	330	112	0.0	1.1	2.05	1.620(1)	100
Sample	390	112	-0.2	1.1	2.05	1.625(1)	100
Turn heat off (end of run).	450	112	-0.4	1.1	3.1	1.666(1)	100

(1) Calculated values. Samples had to be diluted to prevent freezing at room temperature.

[redacted]

UNCLASSIFIED

UNCLASSIFIED

TABLE VI

LABORATORY-SCALE DISSOLVING OF "COLD" SLUGS
MERCURY CATALYSIS

SERIES II

Run Conditions:

Initial Charge: 1) Canned slug (1780 grams of U; 59 grams of Al).
2) Heel of partially dissolved slug.

Acid Addition: Both starting and additional acid as shown. Where acid was added other than the initial charge, it was added incrementally at a rate of 10 ml. per minute as 60% HNO_3, starting when solution temperature reached 100°C.

Catalyst: 1 M $Hg(NO_3)_2$ in 45% HNO_3; amount used expressed as weight of $Hg(NO_3)_2 \cdot H_2O$ as percent of weight of Al.

Final Composition: Every 30 minutes, 30 ml. samples were taken. Results are not corrected for these samples, in some cases final volumes reported were achieved by dilution.

Temperature: Maintained about 110°C. Cooling water (12°C.) was applied to cooling coils when foaming was observed to be excessive; water exit temperature was about 100°C.

Results:

		Run Designation				
		II-A	II-B	II-C	II-D	II-E
Catalyst Added, Wt.% of Al.		0.59-1.04(1)	0.86	1.13	2.3	2.3
Heel, Grams of U Metal.		---	1150	211	868	534
Volume of Initial Acid Added, Ml. of 45%..		1000	1000	750	750	750
Volume of Additional Acid, Ml. of 60%.			1000	750	750	750
Total Run Time, Minutes.		180	360	360	360	495
Coating Removal Time, Minutes.		180	360	360	180	240
Time to Reach 0.0 M Final Acidity, Minutes(2)			420	450	420	545
Composition of Final Solution.	Desired					
AlN, M	1.16	2.0	0.81	1.12	1.65	1.74
UNH, M	1.3	0.01	1.27	0.66	0.86	0.76
HNO_3, M	0.0	3.6	0.7	1.60	0.15	0.54
Volume, Ml.(3)	1000	1000	1800	1500	1350	1100
Final Vapor Temperature, °C.		104	101	102	100.5	101
Condenser Operation.		Up-draft	Up-draft	Up-draft	Up-draft	Down-draft

(1) Reaction slow for first hour of run; catalyst concentration was increased.
(2) Estimated
(3) In some cases, final dilution was made.

UNCLASSIFIED

UNCLASSIFIED

UNCLASSIFIED

TABLE VII

RUN DATA
LABORATORY-SCALE DISSOLVING OF "COLD" SLUGS
MERCURY CATALYSIS

RUN II-E, SERIES II, TABLE VI

Operation	Time Min.	Temperature, °C. Pot	Temperature, °C. Vapor	Solution Composition HNO_3 M	Solution Composition ANN, M	Solution Composition UNH, M	Volume, Ml. (1)	Cooling Water
Charge 534 g. "beel".								
Charge canned slug (4-inch)								
Charge 4 ml. of 1 M $Hg(NO_3)_2 \cdot H_2O$								
Charge 750 ml. of 45% HNO_3.								
Start heating pot.	0	25	25	9.2	0.0	0.0	750	
Reduce heat	15	113	101				750	
Start adding 60% HNO_3, 10 ml./min.	20	114	107				750	Intermittent
Take 10 ml. sample (1)	45	112	107	5.30	0.75	0.19	1000	"
Take 10 ml. sample (2)	75	110	106	5.80	0.77	0.38	1250	"
Finish acid addition.	90	111	105				1470	"
Take 10 ml. sample (3)	105	110	105	5.20	0.82	0.41	1400	"
" " " (4)	135	111	104	3.98	0.80	0.54	1370	"
" " " (5)	165	111	104	3.77	1.75	0.62	1340	"
" " " (6)	195	112	103	3.39	1.75	0.71	1310	"
" " " (7)	225	109	103	2.53	1.79	0.84	1280	
" " " (8)	255	112	103	2.36	1.84	0.92	1250	"
" " " (9)	285	113	102	1.61	1.85	0.99	1220	"
" " " (10)	315	113	102	1.50	1.86	1.03	1190	"
" " " (11)	345	114	101	1.35	1.68	1.07	1160	"
" " " (12)	375	114	101	1.07	1.77	1.00	1130	"
" " " (13)	405	114	101	0.81	1.77	1.14	1100	"
Add 100 ml. H_2O. Sample. (14)	495	114	101	0.54	1.74	0.78	1200	
Turn cooling H_2O on.								
Turn cooling H_2O off (end of run).	510	35	65					

(1) Calculated

END

DATE FILMED

2/28/92