DECLASSIFIED

HW-22557

ILLUSTRATION UNIT 11

-1-

HW-22557

Classification Canceled and Changed To

DECLASSIFIED

1. R. B. Richards	9. J. G. Bradley
2. C. A. Rohrsman	10. E. R. Irish - R. B. Lemon
3. J. O. Ludlow	11. R. E. Tomlinson
4. K. C. Vint	12.-15. Extra
5. F. W. Woodfield	16. 700 File
6. O. F. Hill	17. 300 File
7. V. R. Cooper	18. Pink Copy
8. R. E. Smith	19. Yellow Copy
- By Authority of CG-PR-2
RM Item 3-11-92
By PM Eick 12-14-93
Verified By J. N. Wells-12-15-93

RECEIVED

October 29, 1951

COPY 1 OF 1

300 AREA
CLASSIFIED FILES

Process Considerations
Additional Product Concentration
Facilities in 202-S

The Document contains

Page No. 1

TO: File

FROM: R. E. Tomlinson R.E.T.

Summary

Investigations concerning the coupling step required to adapt a Redox IIBP to a 234-5 feed have indicated that a single peroxide strike from a solution 50 - 60 g./l. in product and about 2 M in nitric acid is adequate. Additional work is planned to demonstrate both peroxide and Pu(IV) oxalate strikes under these conditions. The present Redox PR cage product contains 10 g./l. in product and over 500 g./l. in nitric acid, and probably requires two peroxide strikes; in addition, the operating capacity of the PR cage may be inadequate to process the throughputs desired in the Redox plant.

A two stage continuous concentration process for Redox IIBP is jointly suggested by Design and Development and Chemical Development personnel, and is described in this document. This process is believed to be simple and easily operable. Acid is removed from the product solution adequately for the single peroxide strike coupling procedure. Batch size appears to be easily controllable.

This unit might be installed in the present PR cage in lieu of the existing equipment, or in a new cage to be built adjacent to the existing cage.

Introduction

Economic studies⁽¹⁾ have established the desirability of processing the highest feasible fraction of the total plant throughput in a solvent extraction separations unit. Early evaluations of the capacity of the Redox production plant⁽²⁾⁽³⁾ indicate that additional product concentration facilities will probably be required to process the desired throughputs. Data concerning the actual processing capacity of the Redox facilities as constructed are currently being obtained.

MASTER

DISTRIBUTION RESTRICTED TO U.S. ONLY

DECLASSIFIED

DECLASSIFIED

Experiments directed toward the development of a coupling step to facilitate the processing of product from the Redox unit in the 234-5 unit have been described by the Chemical Research Section⁽⁴⁾⁽⁵⁾ and by the 234-5 Process Development Section⁽⁶⁾⁽⁷⁾. These data indicate that a peroxide precipitation from the concentrated IIBP solution (about 10 g.Pu/l.) is unsatisfactory in that product losses to the supernate are excessive.⁽⁴⁾ Partial neutralization of the acid by KOH addition reduced the waste losses satisfactorily, but produced an undesirable low-density precipitate.⁽⁴⁾ If, however, acid were removed from the IIBP solution by further concentration to 250 to 300 g.Pu/l. and the resultant solution diluted to 50 g.Pu/l. (about 100 to 120 g.HNO₃/l.) a peroxide precipitate could be formed with acceptable supernate losses and bulk density.⁽⁵⁾⁽⁶⁾ A peroxide precipitate prepared in this manner was used to produce a button in the 234-5 experimental facilities.⁽⁶⁾ Spectrographic analysis of this button revealed equal or better purity than a button produced from comparable solutions by a two-peroxide-strike procedure.⁽⁷⁾ These results are inconclusive in that aluminum separation was incomplete in all runs, indicating possible recontamination.

This memo assumes that it is desirable to remove acid from the Redox IIBP solution by concentration, and that the concentrated solution will permit coupling with the 234-5 process via a single peroxide strike.

Discussion

Process Aims

Based on data concerning later coupling steps, the process aims of the concentration step have been tentatively set as a hexone-free solution which, when diluted, will produce a solution containing 50 to 60 g.Pu and about 120 g.HNO₃ per liter. The instantaneous inventory of product in the unit should be held as low as practicable, and the product in the end stream should be held to 375 grams per batch (± 25 grams) without reliance on laboratory analysis. All vessels must meet plant standards for criticality safety.

Suggested Process

A two stage continuous concentration unit is jointly suggested by Design & Development and Chemical Development personnel to meet the process aims. See Figure I. The first unit would concentrate the feed to about 12 molar HNO₃, thereby reducing the volume to about 7% of the feed. The feed to, and vapors from, this unit would be passed countercurrently through a fractionating tower, returning aqueous HNO₃ and product to the concentrator and vaporizing the hexone from the 2BP feed. This unit is essentially the same as that proposed by Design and Development.⁽⁸⁾ The concentrate from this first unit would be cascaded to a second concentrator having a working volume of 0.8 to 1.5 liters. This concentrator would vaporize nitric acid and water as required to maintain a constant volume. When the specific gravity of the second evaporator contents rises to a predetermined value, the flow from the first unit would be temporarily discontinued and the contents of the second unit transferred to the PR can. This product solution may be diluted as desired to meet later process conditions.

DECLASSIFIED

DECLASSIFIED

Control Mechanisms

The control of the first concentrator is based on the nitric acid content of the system, the concentration of product and other ions being too small to affect the solution's physical characteristics appreciably. Assuming the first concentrator is controlled to a boiling point of $119^\circ \pm 0.5^\circ\text{C}$, the concentrate would be held to $56 \pm 1.5\%$ HNO_3 . See Figure II. Assuming the characteristics of solution 321-2(5) to be typical of Redox II BP solutions, and assuming the plutonium concentration parameters to be parallel to the X-Y curve for zero plutonium concentration, the nitric acid concentration may be estimated in the second concentrator concentrate. These values are given below.

Estimated HNO_3 in
Second Concentrator Concentrate
Assuming Feed is $56 \pm 1.5\%$ HNO_3

<u>Pu, g/l</u>	<u>Concentrate HNO_3:Wt %</u>	<u>SG_{HNO_3}¹¹</u>
10	$63 \pm 0.6\%$	$.832 \pm .003$
100	$59.9 \pm 0.6\%$	$.366 \pm .003$
200	$55.9 \pm 0.6\%$	$.345 \pm .003$
300	$53.7 \pm 0.6\%$	$.331 \pm .003$
400	$52.5 \pm 0.6\%$	$.325 \pm .003$
500	$51.3 \pm 0.6\%$	$.318 \pm .003$

* Assumes Sp. Gr. of final solution is the sum of $1.0 + \text{SG}_{\text{HNO}_3} + \text{SG}_{\text{Pu}} + \text{SG}_{\text{misc}}$

The estimated nitric acid concentration of the concentrated and diluted product stream are given in the table below.

Estimated Acid content after Dilution of
Concentrated II BP
(The control point of the first concentrator assumed as 119°C .)

<u>Concentrated to g/l Pu</u>	<u>HNO_3, g/l after dilution</u>	
	<u>at 50 g/l Pu</u>	<u>at 60 g/l Pu</u>
300	119	142
400	87	104
500	67	81

Fluctuations in the HNO_3/Pu ratio in the II BP stream are automatically compensated by the proposed control mechanisms, the varying nitric acid loads being evaporated as required by the second evaporator with no effect on the nitric concentration in the concentrate.

DECLASSIFIED

DECLASSIFIED

-4-

HW-22507

In Figure III, the significance of specific gravity measurements is graphically examined. The effect of nitric acid on specific gravity is plotted from the above estimates. The effect of plutonium on specific gravity was estimated from data in the B₂PO₄ Technical Manual; the specific gravities given were corrected for HNO₃ contribution on the assumption that the concentration step was comparable to that reported in HW 21679, solution 321-2. The specific gravity contribution due to plutonium estimated in this manner agrees closely with the known contribution due to uranium. The contribution of miscellaneous ions to the specific gravity was estimated from the ionic concentrations found in solution 321-2, except that the U/Pu ratio was assumed to be 0.001 instead of the 0.47 reported.

Examination of Figure III indicates that, for solutions containing up to 400 g/l Pu, more than 80% of the specific gravity increase will be contributed by the plutonium and nitric acid. These effects are predictable and are believed to be reproducible in the process outlined. The magnitude of specific gravity increase due to miscellaneous ions is not precisely known, its magnitude and fluctuations being determined by the operation of the solvent extraction cycles. Based on experience in the 321 Building operation, it is believed that these ions are present mainly by solubility and little by entrainment. This consideration is the basis of the prediction that the specific gravity increase due to miscellaneous ions will be relatively small (see Figure 3) and effectively reproducible. Assuming the specific gravity measurement is reproducible to ± 0.01 unit, the product content per batch can probably be held to ± 15 grams and possibly to ± 5 grams. Greater deviations, such as caused by flooding in the solvent extraction columns, would result in a smaller batch size; the specific gravity increase due to the increased miscellaneous ions would result in a reduced plutonium content when the specific gravity control point is reached.

Development Work Required

No development work appears to be required to allow the construction of the concentrator units. The equipment postulated is standard and has known operating characteristics.

The precipitation of product from the concentrate should be demonstrated further by both the peroxide and Pu⁺⁴ oxalate processes, where miscellaneous ion rejection is not adequately known. This work is planned by Process Assistance, Separations Technology.

DECLASSIFIED

DECLASSIFIED

HW-22001

References

- (1) HW-21949 Economic Comparison: BiPO_4 - TBP Combination vs. a Second Redox Installation, by C. A. Rohrmann, 8-14-51.
- (2) HW-20958 Increase in Redox Capacity (Part II - Additional PR Cage), by F. W. Woodfield, et.al., 5-3-51.
- (3) HDC-2290 Potential Capacity of the Redox and BiPO_4 Plants, by C. A. Rohrmann and R. E. Tomlinson, 8-7-51.
- (4) HW-21614 Precipitation of Plutonium Peroxide from Concentrated IIRP Solution, by K. M. Harmon, 7-11-51.
- (5) HW-21679 Evaporation of Redox Solutions, by P. J. Richardson, 7-13-51.
- (6) HW-21456 Progress Report for May, 1951, by V. B. Cooper.
- (7) HW-21792 Progress Report for June, 1951, by V. B. Cooper, 7-30-51.
- (8) SK-2-5642 Engineering Flow Diagram Revising PR Cage.

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.

DECLASSIFIED

- 6 -

HW-22557
FIA 11

FIGURE 15 HNO₃ VAPOR-LIQUID EQUILIBRIA

DATA FROM FINEY, PR 162170
TEMPERATURES ARE BOILING POINTS
OF HNO₃-H₂O MIXTURES AT 760 MM HG

EFFECT OF CO AND NITROGEN
VOC'S IN REPRO. MAY BE
ESTIMATED FROM DATA IN
HW 21425, SECTION 15-2.
NUMBERS GIVE THE PV
CONCENTRATION IN GRAMS/LITER

Y = Weight Fraction H₂O in Repro

DECLASSIFIED

114-22001

DECLASSIFIED

END

DATE

FILMED

5/9/94