OP-59 Revised

~~SECRET~~

3-1891

COPY-1

DECLASSIFIED

PROJECT 9536

Route List

File RECORD CENTER FILE

1. RECORD CENTER
2.
3.
4.
5.

AUTHENTICATED COPY
DO NOT ROUTE OR
DESTROY

Date 2-15-45

Subject SE-IC-3

To Simon-Mackey-Otto

From B. H. Perkins - E. P. S. Black

Copy No. ~~13~~ 4
300 File

BEFORE READING THIS DOCUMENT, SIGN AND DATE BELOW:

AEC RESEARCH AND DEVELOPMENT REPORT

DO NOT CIRCULATE!
REFERENCE COPY ONLY.

UNCLASSIFIED

BEST AVAILABLE COPY

~~SECRET~~

DECLASSIFIED

ORO 95722

DECLASSIFIED

[redacted]

J-,

#1 W.C.Simon-B.L.Mackey-F.A.Otto-TCO A
#2 M.H.Wahl - Wilmington
#3 W.C.Kay - K.W.Millett
#4 J.E.Cole
#5 F.B.Vaughan
#6 P.W.Crane
#7 L.Squires
#8 M.F.Acken - R.H.Beaton
#9 J.E.Willard - S.G.Thompson
#10 300 Area File
#11 300 Area File
#12 300 Area File
#13 300 Area File
#14 300 Area File
#15 Pink Copy
#16 Yellow Copy

COPY

This Document ~~consists~~
10 Pages No.
16 Copies, Series

February 15, 1945

INV. 9-47

Memorandum Report SE-FC-3

Recovery of Product from Lanthanum Fluoride by-product Precipitates

Reviewed and Approved for Public Release by the Hanford Declassification Project
JD Briggs PNNL ADD
6/1/00 Date

CLASSIFICATION CANCELLED
DATE 9-17-58
For The Atomic Energy Commission
H. R. Carroll
Chief, Declassification Branch fn

J E Savely 3-30-00
J Miles, 4-7-00

jd

[redacted]

~~SECRET~~

DECLASSIFIED

DECLASSIFIED [redacted]

2-15-45

Introduction

The possibility that appreciable losses of product at the separations plant might occasionally occur in LaF_3 by-product precipitates prompted a study of methods for the recovery of product lost in this manner. The present report deals with the laboratory development of methods which should provide a satisfactory solution to this problem.

Summary

Practically complete recovery of product from lanthanum fluoride by-product precipitates may be obtained by the use of either of the two methods discussed below. The procedure (Method A) which appears to be preferable because of its greater simplicity, lesser interference with normal production, and better adaptability to existing equipment, involves the following steps:

1) Addition of the product containing LaF_3 by-product precipitate to the oxidized product containing solution after $BiPO_4$ by-product precipitation in the crossover cycle of a subsequent run;

2) Heating with the $KMnO_4$ already present to oxidize the product which was recycled.

3) Carrying the mixed batches through the remainder of the process in the usual way.

In recovery of product by the other method, the product containing precipitate is metathesized with potassium hydroxide (or with hydroxide-carbonate mixture), following which the metathesized precipitate is separated by centrifugation, is washed, and is then dissolved in nitric acid to give a product containing lanthanum nitrate solution which is added to the solution in the D-1 tank prior to permanganate oxidation, (Same as for preferred method above), of a subsequent run.

Details of the two procedures are shown in the accompanying flowsheets.

Experimental Details

Method A

I Recovery of Product by Direct Recycling of the Product-Containing By Product Precipitate.

Satisfactorily complete (>90%) recovery of product from lanthanum fluoride by-product precipitates has been obtained by means of a method which involves direct dissolution of the precipitate. The principal steps of the method are as follows:

1) Mix the lanthanum fluoride slurry which contains the product with the oxidized product-containing solution from the bismuth phosphate precipitation in the crossover cycle of a subsequent batch. The product-containing recycle solution from 231 building may also be added at this point.

DECLASSIFIED [redacted]

[redacted]

2) To the mixture from step 1), after heating to 75°C, add the usual quantities of oxidizing agents and maintain the mixture at 75°C for one hour as specified in the standard flow sheet (except for a slight volume increase resulting from the presence of the LaF_3 slurry) in order to oxidize the product originally in the LaF_3 by-product precipitate. During this step, the lanthanum fluoride largely dissolves owing to its great solubility in the large volume of solution (in the absence of excess hydrofluoric acid*). With solution of the precipitate, product held thereby is released to the solution and is oxidis

3) A lanthanum fluoride by-product precipitation is carried out by the usual flow sheet procedure in the oxidized product containing solution from step(2).

4) The (LaF_3) product precipitation of the crossover cycle and subsequent operations of the separations process are carried out with the product solution from step (3) in the usual manner.

The solution from (2) contains more than the usual quantity of product, (if much product is in the recycled LaF_3 by-product) and also contains dissolved lanthanum fluoride not normally present. However, these differences have presented no difficulties in laboratory experiments and none are anticipated under plant conditions. Approximately three times the usual quantity of lanthanum fluoride is precipitated in the first shot of the by-product precipitation** (step 3) but this has not resulted in excessive product losses in the laboratory; the available information indicates that the larger quantity of precipitate can be handled satisfactorily in the available equi

As is evident from the data of Table I, practically complete recovery (>90%) of the product originally present in lanthanum fluoride by-product precipitates has been recovered in solution for the subsequent by-product precipitation and product precipitation steps in nine out of the ten investigated cases (there is no apparent explanation for the one failure indicated).

It is worthy of note that product recovery by this method was as complete using actual plant material of low product concentration for testing, as it was with synthetic material, prepared in the laboratory, containing a higher product concentration. The data also show that the process is satisfactorily operable in the presence of recycled lanthanum nitrate solution containing reduced product, such as is customarily recycled from the 231 Buildi

Investigations of the distribution of radioactive lanthanum between precipitate and solution indicate that product enters solution during step (2) of the process described here as a consequence of solution of the lanthanum fluoride (Tables III and IV). The proportion of radioactive lanthanum originally present in the precipitate which enters solution during this step is essentially the same as the proportion of the product which enters the solution. When flow sheet amounts of LaF_3 by-product precipitate are recycled to the oxidized solution after $BiPO_4$ by-product precipitation, complete dissolution of LaF_3 and product occurs. If a high ratio of LaF_3 to volume of solution is used, however, the proportion of the product entering solution is similar to the proportion of LaF_3 dissolved. These findings are in accor with the available data regarding the solubility of lanthanum fluoride (Tabl

---

* Care should be taken to insure complete removal of any "heels", containing HF, from the vessel before addition of the LaF_3 slurry.

** The dissolved LaF_3 is insoluble in the presence of the excess HF used f the precipitation.

[redacted]

[redacted]

Bulk Reduction

LaF_3 By-Product Precipitation Including Recovery of Product From Prior LaF_3 By-Product Precipitation

Method A

Building 224, Section D

A First Precipitation

1. Receive about 20,000 lbs. of oxidized filtrate from A-3 into D-1.
2. Jet LaF_3 by-product slurry containing product to be recovered from D-4 to D-1, 1500 lbs. (180 gal.) (A)
3. Heat to 75°C.
4. Add 620 lbs. (70 gal.) of 5% $KMnO_4$ solution.
5. After 30 minutes, cool to 35°C.
6. Add 85 lbs. of anhydrous HF. (B)
7. Add 105 lbs. (12 gal.) of La salt solution (10% La salt, 10% HNO_3) Rate of addition - 5 lbs./min. (B)
8. Agitate for 1-hour at 35°C.

B First Centrifuging and Second Precipitation

Centrifugation in D-2 is made at the normal feed rate.

Succeeding steps in the process are made according to standard flow sheet conditions.

(A) If recycle solution is involved, it is added at the same point as the LaF_3 by-product slurry. Order of addition is not important.

(B) If recycle solution is added, the addition of HF (step 6) is made at the standard rate of 3 lbs. per minute. When lanthanum is added at step 2 as a recycle solution, step 7 is omitted.

[redacted]

II Recovery of Product by Metathesis of the Product-Containing Precipitate

Satisfactorily complete recovery of product from lanthanum fluoride by-product precipitates was obtained by a procedure involving metathesis of the precipitate as a first step prior to recycling. In the two investigated cases (Table II) 96.0 and 87.6*%, respectively, of the product initially present in the precipitate was recovered as lanthanum nitrate solutions of product suitable for recycling in the manner currently used for similar solutions from the 231 building.

This recovery process is operable without any unusual difficulty under laboratory conditions, and there appears to be no reason why it cannot be operated similarly successfully in the appropriate plant equipment. However, the present arrangement of plant equipment does not permit operation of the process without construction of an additional transfer line to permit removal of the lanthanum fluoride slurry (and product) from vessel D-4 to Cell B in which it would be advisable to carry out the metathesis recovery process. In operation of this recovery process, present plans call for the following steps.

1) Transfer of the product-containing slurry from D-4 to B-1. (Requires installation of new transfer line).

2) Metathesis of the slurry in B-1 in the usual way (as applied in Cell F), using increased quantities of the hydroxide and carbonate solutions on account of the increased volumes.

3) Separation of the metathesized precipitate in centrifuge B-2. (Waste to B-3 and discard.)

4) Solution of the precipitate in HNO_3 and transfer to B-4 by washing.

5) Transfer of the solution-containing the recovered product from B-4 to D-1, where it is mixed with the effluent in D-1 from the $BiPO_4$ by-product precipitation of a subsequent run, and processing in the usual manner, with oxidation and lanthanum fluoride by-product precipitation, etc.

Maximum use is made of existing equipment in the process as outlined here; the only new construction required is installation of the transfer line from D-4 to B-1. However, the proposed scheme represents an improvisation rather than the ideal process, as the equipment in Cell B is too large for proper processing of the small volumes involved, so that considerable washing is necessary to avoid loss of a considerable proportion of the product in the "heels" left in the various vessels. With care, however, it is believed that the process can be operated satisfactorily. The equipment in Cell F in which the usual metathesis step takes place is better suited for carrying out the recovery process than is that in Cell B; however, the use of Cell F for product recovery necessitates the installation of at least two additional transfer lines, and might result in contamination of the equipment in the cell, which would seriously interfere with the scheduled processing of the usual runs. For these reasons, the use of Cell B is preferred to that of F.

[*] In this case only 88.4% of the product initially present was accounted for. The 87.6% of the initial product recovered represents 99.1% of the product accounted for.

DECLASSIFIED

[redacted]

Bulk Reduction

Recovery of Product From LaF_3 By-Product

Method B (Metathesis)

The procedure as outlined below should be considered as a guide for the process rather than a final operating log. Since the process involves use of equipment not normally used in the metathesis and subsequent centrifugation steps, certain changes may be necessary due to equipment limitations. The procedure represents the process as visualized on the basis of laboratory experience.

1. Receive about 1500 lbs. (180 gal.) of LaF_3 slurry in B-1 from D-4. (A)
2. Wash D-4 with 83 lbs. (10 gal.) H_2O and jet to B-1.
3. Add 1850 lbs. (165 gal.) of 35% KOH solution.
4. Add 960 lbs. (78 gal.) of 45% K_2CO_3 solution.
5. Heat to 80°C and agitate for two hours.
6. Cool to 35°C.
7. Jet to B-2.
8. Centrifuge at 870 RPM with rate of 40-60 lbs./min. (B)
9. Skim to 10 gallon heel. (C)
10. Add 250 lbs. (30 gal.) of 1% KOH solution to B-2 and wash cake.
11. Skim to 10 gallon heel.
12. Add 46 lbs. (4.0 gal.) of 60% HNO_3 to B-2 and rotate bowl to dissolve cake. (D)
13. Jet to B-4.
14. Jet to D-1 from B-4.
15. Wash B-2 bowl with 86 lbs. (10 gal.) of 6% HNO_3.
16. Jet to B-4.
17. Jet to D-1 from B-4.
18. Wash B-2 bowl with 86 lbs. (10 gal.) of 6% HNO_3.
19. Jet to B-4.
20. Jet to D-1 from B-4.

Initial Precipitation on subsequent run

1. Receive about 20,000 lbs. of oxidized filtrate from A-3 into D-1 which contains the $La(NO_3)_3$ solution from B-4.
2. Heat to 75°C.
3. Add 620 lbs. (70 gal.) of 5% $KMnO_4$ solution.
4. After 30 min., cool to 35°C.
5. Add 85 lbs. of anhydrous HF slowly over 1/2 hour period. Rate of addition - 3 lbs./min.
6. Agitate 1-hour at 35°C.
7. Jet to centrifuge D-2.

First centrifuging, final precipitation, and remainder of process steps are made according to standard flow-sheet procedure.

(A) Use of this method requires construction of a transfer line from D-4 to B-1.

(B) This centrifugation is made in a 40 inch instead of the 26 inch centrifuge which is normally used for the metathesis slurry. Feed rates and centrifuge speed were calculated to correspond with conditions pertaining in the centrifugation of the metathesis slurry in the 26 inch centrifuge. Actual experience may be necessary to establish best conditions.

~~SECRET~~

DECLASSIFIED

DECLASSIFIED [redacted] J-1

2-15-45

(C) In view of the comparatively large capacity of tank B-1 and lack of specific data as to the volume of heel which would remain in this tank, it may be advisable to recycle effluent from the centrifuge through B-3 to B-1 as a wash of this tank.

(D) Volumes required for cake removal can only be had by experience with the equipment. The procedure for dissolving the $La(OH)_3$ and for washing the bowl may require modification.

[redacted] DECLASSIFIED

DECLASSIFIED

[redacted]

3-1

2-15-45

Table III

Solubilities of LaF_3 in HNO_3*

HNO_3 Normality	La^{3+} mg/l
1.05‡	474
2.53	920
3.94	1460
5.06	1420
6.15	1540
7.95	1700
8.09	1660

* CN-1214 - Page 12

‡ Solution for oxidation prior to LaF_3 by-product precipitation is ca. 1.3M with respect to HNO_3.

Table IV

Relation Between Dissolution of Product Containing LaF_3 Precipitates and Recovery of Product Therefrom

				Product Distribution*			
				After Oxidation Step			
				Before LaF_3 By-Product Ppt.		After LaF_3 By-Product Ppt.	
Exp't.	Method Of Recovery		Initial Precipitate	Sol'n.	Pp't.	Sol'n.	Pp't.
1	Method A	Product	100	92.9	1.1	94.0	0.5
		La^{3+} **	100	88.5	3.2	2.7	87.4
2	Method A Except only 0.1 specified Vol.***	Product	100	33.6	66.4	34.5	65.5
		La^{3+} **	100	34.1	65.9	0.9	98.3

* Results of analyses on basis content of initial simulated by-product precipitate = 100. Small quantities of material not accounted for.

** La distribution as indicated by observing distribution of γ activity from 40 hr. La tracer which was initially incorporated into the simulated LaF_3 by-product precipitate along with product.

*** Volume of A-3-OS solution is 0.1 of the proportionate volume to which the amount of LaF_3 used here would be recycled under process conditions. Hence, the LaF_3 did not completely dissolve.

[redacted]

DECLASSIFIED

DECLASSIFIED

[redacted]

2-15-45

Table I

Recovery of Product from Lanthanum Fluoride By-Product Precipitates by Direct Recycling of the By-Product Precipitates[b]

Exp't.	Initial Product* Conc. (%)	Initial 231 LaF$_3$ Ppt.	Initial 231 Recycle Sol'n.	Product Distribution (%) After Oxidation Step: Before LaF$_3$ By-Prod. Ppt. Solution	Before LaF$_3$ By-Prod. Ppt. Precipitate	After LaF$_3$ By-Prod. Ppt. Solution	After LaF$_3$ By-Prod. Ppt. Precipitate
[illegible]	20	100	0	98.3	0.3	--	--
[illegible]	20	100	0	0.6	95.7	--	--
[illegible]	20	100	0	99.8	0.7	93.8	1.1
[illegible]	40	51.4	48.6	99.5**	0.5**	111	0.5
[illegible]	20	0	100	--	--	97.4	0.4
[illegible]	11	100	0	92.9	1.1	94.0	0.5
[illegible]	[illegible]	100	0	99.5**	0.5**	90.5	1.4
8	[illegible]	100	0	--	--	95.4	2.8
[illegible]	0.1[a]	100	0	--	[illegible]	97.7	2.3
10	0.1[a]	100	0	--	1.5	99.3	[illegible]

* Product content of the LaF$_3$ Ppt. to be reworked, calculated as % lost from runs involving initial product concentration of 250g/T c[illegible].

** Product distribution in small sample (ca. 1ml.)

a D-4-BP slurry from T-5-01-B-3.

b All experiments listed were conducted in 25-12 Cb stainless steel containers on a scale corresponding to a volume of 500 ml. for lanthanum fluoride by-product precipitation.

[redacted]

DECLASSIFIED

DECLASSIFIED [redacted] 34

Table II

Recovery of Product from Lanthanum Fluoride By-Product Precipitates by the Metathesis Process (Method B)[a]

Exp't.	Product Distribution % Total*		
	Metathesis Waste	Oxidized Solution After LaF_3‡ Precipitation	LaF_3 By-Product Ppt.‡
1	0.3	87.6	0.5
2	0.2	96.0	1.1

* The initial LaF_3 precipitate from which product was recovered contained a quantity of product corresponding to a loss of 20% from a run involving an initial product concentration of 250 g/T of U.

‡ After metathesis of product-containing LaF_3 precipitate, solution of the metathesized precipitate, oxidation of resulting solution and precipitation of a LaF_3 by-product precipitate.

[a] All experiments carried out in 25-12 Cb stainless steel containers on a scale corresponding to a volume of 500 ml. for LaF_3 by-product precipitation.

L. Squires - Chief Supervisor fd.
S.G.Thompson-Senior Supervisor

B. H. Perkins RPS Black
R.P.S.Black and B.H.Perkins
Separations Engineering
Technical Department

RPS:BHP:jd

~~SECRET~~ **DECLASSIFIED**