A-85-012
6-7

~~UNCLASSIFIED~~

REF: CMR-10-96

Project Authorization No. CMR-10-10

VERIFIED UNCLASSIFIED
6/25/91

PUBLICLY RELEASABLE
LANL Classification Group
6/25/91

THIS DOCUMENT CONSISTS OF 6 PAGE(S)
NO 1 OF 2 COPIES, SERIES A

RaLa PROCESS RESEARCH

~~CAUTION~~

This do[illegible] affecting the Na[illegible] Its [illegible] in any m[illegible] prohibited and m[illegible] criminal penalties under applicable Federal laws.

Date:

February 1950

CLASSIFICATION CANCELLED
PER DOC REVIEW JAN. 1973

Work done by:
J. Schulte
L. LaMar
H. Newbury
S. Krainock
E. Herrera

UNCLASSIFIED

I. PREVIOUS STATUS OF PROJECT

The development of chemical processes for the separation of La^{140} from its parent Ba^{140} at high activity levels had proceeded through several alternative proposed methods to the selection of two most promising processes for final development. Both of these methods utilize centrifugation and a final precipitation as fluoride. Both had been shown satisfactory in general for yield, purity, bulk, volume of solutions, and effect of impurities, but the optimum combination of conditions had not been obtained.

II. PRESENT PROCESS RESEARCH

A. Determination of Per Cent Ba Impurity

This work has been carried out for shipments Nos. 44, 45 and 46 and will be discontinued after shipment No. 46 has been finished.

The results obtained verify those of past shipments; viz., when visible amounts of impurities are present, then high Ba losses are sustained in the early milkings. It has been felt that a safe policy is to make a "clean-up" milking before any attempt is made to deliver a source.

B. Determination of Impurities

The clean-up milking from shipment No. 46 in which 17% Ba was lost is being saved for further study. This material represents the contaminants which are precipitated as the hydroxide. An attempt will be made to isolate and identify these impurities which frequently cause difficulty.

A process chimney containing about 45 curies was allowed to decay to a safe laboratory working level. A barium-strontium separation was then made on the sample. The results from this test should show the approximate Sr^{89} present in the RaLa sources delivered to GMX-5. At the present time both fractions are decaying with a barium half-life.

CLASSIFICATION CANCELLED PER DOC REVIEW JAN. 1973

C. Effect of $NaNO_3$ on the Precipitation of $Ba(NO_3)_2$

This study was carried out with the idea that $Ba(NO_3)_2$ could be precipitated from a solution high in nitrate which is not completely supplied by HNO_3.

However, when 0.5 g of barium was precipitated from solutions 4N in HNO_3 and containing from 0-10 g of $NaNO_3$, the yield dropped consistently from 68% with no $NaNO_3$ present to 54% when 10 g of $NaNO_3$ was added. It is apparent that the extra nitrate ion added in the form of $NaNO_3$ actually increases the solubility of $Ba(NO_3)_2$ in 4N HNO_3.

III. STUDIES OF THE NEW PROCESSES

A. Fuming HNO_3 Process

It was at first believed that the HNO_3 concentration should not exceed 4N during the LaF_3 precipitation step. However, it was shown that 80% yields were obtained when this dilution was made. Contrary to previous results, 96% yields were obtained when the LaF_3 was precipitated from solutions which were as high as 10.5N in HNO_3. It is evident that volume effects are more important than acid concentration during LaF_3 precipitations. However, a possible increase in barium contamination may modify this improvement.

It was shown that slowing down the centrifuge too quickly during runs caused the precipitates to be stirred up by the disturbance of the supernatant liquid. Data were obtained for the construction of an automatic control to give a uniform acceleration and deceleration rate.

The centrifuge in the DP mock-up has been moved to H building and rebuilt to give better performance at higher speeds.

B. Hydroxide Process

It was shown that the centrifugation time for the LaF_3 precipitate must be greater than ten minutes, but need not exceed twenty minutes.

C. Coagulation of LaF_3 Precipitate

The coagulating effect of various ions upon LaF_3 precipitate was determined by small-scale runs with the following results:

CLASSIFICATION CANCELLED
PER DOC REVIEW JAN. 1973

Electrolyte Used	Number of Equivalents Used (1/4 g)	% La Remaining in Solution
$Fe(NO_3)_3 \cdot 9H_2O$	1.8	8.7
$K_2C_2O_4 \cdot H_2O$	2.8	10.6
KNO_3	2.5	14.6
$MgSO_4$	4.2	14.8
$AlCl_3$	5.7	21
- - -	- -	45.4

It was also shown that the amount of lanthanum coagulated by addition of ferric ion is partially dependent upon the ratio of ferric ion to lanthanum ion. The results are listed below:

Equivalents of Fe^{+3} Added per Equivalent of La^{+3} Present	% Yield
- - -	82.5
3.468	92.5
6.86	97.6
25.76	95

The amount of iron remaining in the precipitate was estimated to be approximately 1 mg.

IV. SUMMARY OF NEW PROCESSES

Considerable work has been carried out in developing two processes, either of which can be used satisfactorily in the new hot cell. Although there are a few minor points that are still under investigation, the general procedures to be used are listed below:

A. Fuming HNO_3 Process

1. The active residue (about 10-15 kilocuries) received will contain about 2 g barium (3.8 g $Ba(NO_3)_2$), 20 mg La^{140} and 20 mg inactive cerium. This will be dissolved in 50 cc H_2O.

2. 60 cc of cold fuming HNO_3 will then be added to precipitate the barium. The reaction mixture, 12N in HNO_3, will then be agitated to assure complete barium precipitation.

3. After centrifugation the supernate containing the lanthanum and cerium is decanted into the "screw tip" cup. The $Ba(NO_3)_2$ is then washed with 10 cc

12N HNO_3 and centrifuged. This supernate is added to the "screw tip" cup. The $Ba(NO_3)_2$ is redissolved and stored for the next run.

4. At this point 21 cc of 48% HF is added to the "screw tip" cup. The LaF_3 is precipitated from 141 cc of solution which is 4N in HF and 10.2N in HNO_3.

5. After agitating thoroughly the LaF_3 is collected in the source tip by centrifugation. The supernate at this point contains small amount of barium and lanthanum. It is decanted to waste.

6. The source tip is then disengaged from the centrifuge cup and is screwed on the plug provided by GMX-5.

B. Hydroxide Process

1. The same residue, described under "Fuming HNO_3 Process", will be dissolved in 60 cc H_2O, and the pH adjusted to 2.0 with HNO_3 or HCl.

2. To this will be added 12 cc of concentrated NH_4OH to give 72 cc of solution which is 2N in NH_4OH.

3. After stirring and centrifuging, the supernate containing the barium will be decanted, re-acidified, and stored for the next run.

4. The precipitate is then slurried up with 20 cc 2N NH_4OH and recentrifuged. It may be advisable to add this decantate to the barium solution.

5. The $La(OH)_3$ is dissolved in 20 cc of 2N HNO_3 and the solution transferred to a screw tip cup.

6. To the solution is then added 3.5 cc of 48% HF to give 23.5 cc of solution, 4N in HF and 1.7N in HNO_3.

7. The reaction mixture is stirred to assure complete precipitation of the LaF_3, centrifuged and the supernate is decanted.

8. The source tip containing the LaF_3 is disengaged from the centrifuge cup and screwed on the plug provided by GMX-5.

CLASSIFICATION CANCELLED
PER DOC REVIEW JAN. 1973

Future plans include such studies as determining the optimum conditions for centrifuging, pH measurements, determination of impurity specifications, the effect of temperature on limiting the time for certain operations and methods for obtaining high yields when LaF_3 is precipitated from large volumes.