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RaLa PROCESS RESEARCH

Date:
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Work Done By:
H. Elliott
J. W. Schulte
J. F. Suttle

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SUMMARY:

Process development for the preparation of RaLa sources has continued, with final abandonment of all proposed one-step processes. Of the two-step processes remaining, those considered fully adequate and subject only to high activity-level testing are the fuming nitric acid process and the multiple hydroxide process. In both of these the final step is a fluoride step. Other processes considered promising but requiring further investigation are the hydroxide-fluooxalate process, the TTA extraction process, and two ion exchange processes using Dowex 50.

The nitric acid process is considered most reliable in the presence of impurities and least susceptible to loss of the barium parent under such conditions. Also it does not depend upon pH measurements at any point in the process. The multiple hydroxide process is subject to the foregoing criticisms, none of which are considered insurmountable, but is somewhat simpler to engineer (pH measurements in radiation fields being the principal difficulty).

A. One-Step Processes

These processes were reinvestigated using more active solutions. The results obtained are listed below.

1. HNO_3 -HF

	% Ba impurity	Previous results % Ba impurity
a. 5 mg.La, 60 mg.Ba	0.62, 0.61	1.8, 4.6
b. 5 mg.La, 60 mg.Ba, typical impurities	25.6	----

2. $HClO_4$-HF

	% Ba impurity	Previous results % Ba impurity
a. 5 mg.La, 250 mg.Ba	1.4, 1.4	4.0, 4.7
b. 5 mg.La, 250 mg.Ba, typical impurities	7.0, 7.0	----

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Because of the high Ba impurity and other difficulties previously stated, these processes are still not applicable to the preparation of pure La sources.

B. Double Hydroxide Precipitation

Essentially the same procedure was used as described in the previous Quarterly Report. The objective was to determine the effect of impurities on the per cent Ba impurity when single and double precipitations were used. Approximately 10^6 c/m of equilibrium solution was used in an attempt to minimize the counting discrepancies.

1. Precipitation of La with NH_4OH

	% Ba impurity	Previous results % Ba impurity
a. No impurities, single precipitation	0.04, 0.04	<0.1
b. Typical impurities, single precipitation	0.16, 0.12	0.08-2.4
c. Typical impurities, double precipitation	0.02, 0.02	2.2, 4.7

From these data it is quite apparent that precipitation of La with NH_4OH is a very convenient and satisfactory method for separating Ba from La.

2. Precipitation of La with NaOH

An attempt was made to prepare carbonate-free NaOH for a study similar to the one above. However, since about 10% Ba impurity was carried with the La, it was concluded that the NaOH still contained carbonate. It is not unlikely though that virtually the same results as those with NH_4OH could be obtained.

3. Second Step for Proposed Hydroxide Process

It has been previously stated that $La(OH)_3$ is far too bulky to serve as a source. Consequently, as a second step to the hydroxide separation, precipitation of the La with HF appears most promising. Of the several precipitants studied HF appears superior. This choice is based on the small vol[illegible]

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obtained; and the fact that precipitation of LaF_3 from a slightly acid solution offers another separation from Ba due to the solubility of BaF_2.

4. Optimum Conditions for Precipitating LaF_3

Several runs have been made to determine the optimum normalities of HF and HNO_3 from which to precipitate LaF_3. In all cases ten mg. of La carrier plus active La were used in a total volume of 45 cc. All reactions were carried out in ceresin lined containers.

a. Variable HNO_3 (HF maintained at 4 N)

N HNO_3	% La precipitated
0-1	>99
1.2	98.9
1.8	98.6
2.5	96.4
3.5	96.2
5.0	91.8

b. Variable HF (HNO_3 maintained at 0.75 N)

N HF	% La precipitated
0.1	Ppt. did not centrifuge down
0.3	65.4
0.6	90
1.0	97.2
1.5	98.3
2.1	98.6
2.8	98.8
4.0	99.0

From these results it is apparent that 0.75 N HNO_3 and 3-4 N HF offer the best conditions for precipitating LaF_3.

5. Solubility of LaF_3

To remove the last vestiges of Ba in the LaF_3 it is advisable to wash the precipitate. Previous work has shown that considerable La is lost in this operation. Therefore, studies were carried out to determine the extent of this loss with various wash solutions.

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Forty milligrams of La were precipitated as the fluoride from 45 cc. of solution which was 0.75 N in HNO_3 and 4 N in HF. After centrifuging, the supernate was decanted and the precipitate was washed with 25 cc. of HF, HNO_3 or water.

HF Wash		HNO_3 Wash	
N of HF	% Ppt. Dissolved	N HNO_3	% Ppt. Dissolved
0.14	0.29	0.1	9.6
0.7	0.20	0.5	10.8
1.4	0.02	1.0	62.6
2.8	0.10	2.0	62.0

H_2O Wash 1.4, 2.1% La dissolved*

*In this case some of the LaF_3 precipitate may have been in suspension and could not be centrifuged.

It is evident that the LaF_3 should be washed with either dilute HF or with the same solutions used for precipitation, viz., 4 N HF, 0.75 N HNO_3.

6. Volume of Anticipated Source

In the future process a source of 10 kilocuries would represent about 20 mg. of La and equally as much cerium. Consequently an experiment was carried out in which 40 mg. of La (representing 20 mg. La and 20 mg. Ce) was precipitated with HF in Lusteroid tubes and centrifuged. The supernate was decanted and the precipitate transferred to a calibrated glass centrifuge tube. After an additional centrifuging the volume was found to be 0.3 - 0.4 cc.

This precipitate would represent the minimum volume in which this source could be prepared since the presence of impurities and additional cerium would necessarily cause an increase in the quantity of precipitate.

C. Fuming Nitric Acid Process

1. Solubility of Barium Nitrate

This matter is quite significant in the tentative future process. As mentioned in the preceding Quarterly Report, the excess HNO_3 could possibly be

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These experiments have now been carried out, and the volumes to be handled have been calculated on the basis of the data obtained.

In parallel experiments one gram and five grams of Ba were precipitated as $Ba(NO_3)_2 \cdot 2H_2O$ from cold fuming HNO_3. The precipitates were then washed with iso-propyl alcohol three times or evaporated to dryness three times with water to remove the nitric acid left after decantation. After drying, the precipitates were then dissolved by adding increments of water while vigorously stirring.

Method	cc. of H_2O necessary to dissolve ppt.	
	1 g. Ba	5 g. Ba
HNO_3 not removed	48	---
Isopropyl alcohol	24	120
Evaporation	38*	115

*HNO_3 probably not completely removed.

2. Calculations for Volumes

Assuming that future shipments will contain 5 g. of Ba (as barium nitrate) and that 115 cc. will completely dissolve this residue, the volumes, based on optimum conditions, which will be handled are as follows:

Step	Volume of Solution
1. Dissolving residue	115 cc. H_2O
2. Add 201 cc. fuming HNO_3 to ppt. Ba	316 cc. app. 14 N HNO_3
3. Dilute supernate from step 2 with 939 cc. H_2O and 218 cc. 48% HF	1473 cc., 4 N in HF and 4 N in HNO_3

These volumes have been determined without taking into account any rinses, which would obviously increase these values. It is quite [illegible] that the

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quantity of water required in the first step greatly influences the final volume of solution from which La is precipitated and centrifuged. Therefore, it is imperative that the quantity of inert Ba present in the shipments be held to a minimum.

D. Evaluation of Present Process

Samples are now being taken at different steps during the preparation of the present sources. In this manner it is hoped that reliable values of Ba impurity present at each step will be obtained. The results from this procedure should be far more accurate than corresponding results from laboratory tracer experiments.

Close coordination with the production group should lead to a better understanding of problems in the present process; moreover information gained from this cooperation may be of value in selecting the new process.

E. Ion Exchange Process Using Mineral Acid

This process differs from the usual buffered citrate process in that no accurate pH measurements need be made, so that the effect of radiation on the pH of the solutions need not be considered. As noted below, nitric acid solutions approximately 4.5 normal will not remove lanthanum from Dowex 50 columns, while barium in preliminary tests seems to be completely removed at this strength.

1. Preparation of Columns

Dowex 50 columns of approximately 1 cm^2 cross-section and of various heights were prepared. Fine particles of resin were removed by screening and backwashing. In each experiment the resin was then washed by the appropriate acids before placing activity on the column. Calculations were based on comparison with blank counting solutions.

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2. Effect of HNO_3 Strength on Lanthanum Retention

Eight normal and 6 N HNO_3 were observed to react noticeably with Dowex 50. Using normalities of 4.5 and less, it was found that over 99% of the La was held on columns 12 cm. long. At 5 N, 96% of the La remained on the resin.

3. Removal of Lanthanum from Resin

Various solutions of ammonium citrate were tested, with the following results:

Increment No.	Vol. eluting increment	$\frac{A_1^{\bullet}}{A_2^{\bullet}}$	% original La yield	% original Ba yield
1	20 cc.	0	16.3	0
2	5	.04	9.93	.46
3	5	.097	35.71	4.00
4	5	.60	19.60	13.59
5	5	1.89	10.22	22.27
6	5	4.04	3.84	17.95
7	5	11.93	1.17	14.02
8	5	20.23	.31	7.17
9	5	18.1	.16	3.29

4. Effect of HNO_3 Strength on Barium Retention

Known amounts of inactive Ba were placed on columns in 1 N HNO_3 solution and eluted with successively higher concentrations of HNO_3. The barium removed from the column was precipitated with sulfuric acid and compared with a blank precipitate containing the full amount of barium. This rough test showed that nearly all Ba was removed from the column at and above a normality of 3.5 in HNO_3.

5. Effect of Perchloric Acid

Experiments in which perchloric acid was substituted for nitric acid showed that both lanthanum and barium are retained by the column even at high normalities.

F. Ion Exchange Process Using Citrate Solutions

This is the standard process and is being tested to determine the effect of inert barium, radiation, etc.

G. TTA Benzene Process

In this process an aqueous solution of barium and lanthanum is adjusted to the proper pH and agitated with a solution of TTA in benzene, the pH being selected so that lanthanum is selectively extracted from the barium. The benzene solution of lanthanum is then re-extracted with acid to remove the lanthanum, which is finally precipitated with fluoride.

The study of this process is being carried on by Suttle as a consultant research problem. At present tracer solutions of lanthanum free from barium are being used to determine the constant K of the following equilibrium:

$$K = \frac{[LaT_3]_b \cdot [H]^3_a}{[La]_a \cdot [HT]^3_b}$$

After various experimental variables had been removed, quite consistent results were obtained. The results at 25°C are indicated below, and compared with results on the same equilibrium obtained by Broido and others at Oak Ridge. The reason for the discrepancy in the two series is not known. The same assumptions as to activity coefficients were made in both cases.

Sample	pH	$\frac{La_a}{La_b}$	K x 10^{10}
55	3.53	.0047	1.05
59	3.58	.0086	1.38
61	3.59	.0079	1.17
56	3.60	.0109	1.40
63	3.68	.0201	1.62
57	3.72	.0177	1.08
62	3.81	.0427	1.40
60	3.82	.0474	1.44
66	4.10	.305	1.34
64	4.59	9.61	1.43

Oak Ridge Values

	3.02	.00105	8
	3.18	.0031	7
	4.07	1.55	8.4
	4.09	1.53	

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Similar studies for barium are planned, and the effect of temperature on both constants will be determined.

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