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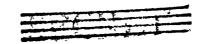
Rala PROCESS RESEARCH

Date: February, 1949 Work Done By: H. Elliott J. W. Schulte J. F. Suttle

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SUMM!ARY:

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).

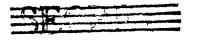
A. One-Step Processes

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

1. HNO3 -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.	HC104-HF		CLASSIFICATION CANCELLED
	a. 5 mg.La, 250 mg.Ba	1.4, 1.4	4- PER DOC REVIEW JAN. 1973
	b. 5 mg.La, 250 mg.Ba, typical impurities	7.0, 7.0	and the state of the







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 10⁶ c/m of equilibrium solution was used in an attempt to minimize the counting discrepancies.

1. Precipitation of La with NHLOH

	% Ba impurity	Previous results 8 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

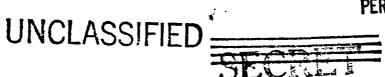
From these data it is quite apparent that precipitation of La with NH40H is a very convenient and satisfactory method for separating Ba from La.

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 NH4OH 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 volcassification CANCELLED PER DOC REVIEW JAN. 1973



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obtained; and the fact that precipitation of LaF3 from a slightly acid solution offers another separation from Ba due to the solubility of BaF2.

4. Optimum Conditions for Precipitating LaF3

Several runs have been made to determine the optimum normalities of HF and HNO3 from which to precipitate LaF3. 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 HNO3 (HF maintained at 4 N)

N HNO3	% 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 (HNO3 maintained at 0.75 N)

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

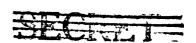
From these results it is apparent that 0.75 N HNO3 and 3-4 N HF offer the best conditions for precipitating LaF3.

5. Solubility of LaF3

To remove the last vestiges of Ba in the LaF3 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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rorty milligrams of La were precipitated as the fluoride from 45 cc. of solution which was 0.75 N in HNO3 and 4 N in HF. After centrifuging, the supernate was decanted and the precipitate was washed with 25 cc. of HF, HNO3 or water.

HF Wash		HI	HNO ₃ Wash		
N of HF	% Ppt. Dissolved	N HNO3	% Ppt. Dissolved		
0.14 0.7	0.29 0.20	0.1 0.5	9.6 10.8		
1.4 2.8	0.02 0.10	1.0	62.6 62.0		
H ₂ O Wash	1.4, 2.1% La dissolved		32.0		

^{*}In this case some of the LaF3 precipitate may have been in suspension and could not be centrifuged.

It is evident that the LaF3 should be washed with either dilute HF or with the same solutions used for precipitation, viz., 4 N HF, 0.75 N HNO3.

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.

 $^{\mathrm{T}}$ his 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 HNO3 could possibly because CLASSIFICATION CANCELLED PER DOC REVIEW JAN. 1973

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removed by washing with an organic solvent or evaporating to dryness. This scheme would decrease the quantity of water necessary to dissolve the precipitate, which must be completely in solution for maximum La yield.

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.

<u>Method</u>	cc. of H ₂ O necessary	to dissolve ppt.
	<u>l g. Ba</u>	5 g. Ba
HNO3 not removed	48	
Isopropyl alcohol	24	120
Evaporation	38*	115

*HNO3 probably not completely removed.

2. <u>Calculations for Volumes</u>

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 ₂ 0
2.	Add 201 cc. fuming HNO3 to ppt. Ba	316 cc. app. 14 N HNO ₃
3.	Dilute supernate from step 2 with 939 cc. H ₂ O 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 ASSISICATION CANCELED PER DOC REVIEW JAN. 1973



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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

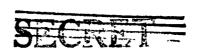
This process differs from the usual buffered citrate process in that no accurate pH measurements need be made, so that the effect of radiation on the pH of the solutions need not be considered. As noted below, nitric acid solutions approximately 4.5 normal will not remove lanthanum from Dowex 50 columns,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

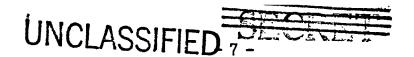
1. Preparation of Columns

Dowex 50 columns of approximately 1 cm² 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 HNO3 Strength on Lanthanum Retention

Eight normal and 6 N HNO₃ were observed to react noticeably with Dowex 50. Using normalities of 4.5 and less, it was found that over 9% 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	$\frac{A_1}{A_2}$	% original <u>Ia yield</u>	% 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 HNO3 Strength on Barium Retention

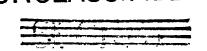
Known amounts of inactive Ba were placed on columns in 1 N HNO₃ solution and eluted with successively higher concentrations of HNO₃. The barium removed from the column was precipitated with sulfuric acid and compared with a blank precipitate containing the full amount of barium. This rough test showed that nearly all Ba was removed from the column at and above a normality of 3.5 in HNO₂.

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 CLASSIFICATION CANCELLED PER DOC REVIEW JAN. 1973





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:

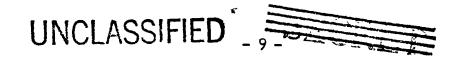
$$K = \frac{\left[\text{LaT}_3\right]_b \cdot \left[\text{H}\right]_a^3}{\left[\text{La}\right]_a \cdot \left[\text{HT}\right]_b^3}$$

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	<u>рН</u>	Ia _a Ia _b	$K \times 10^{10}$
55 59 61 56 63 57 62 60 66 64	3.53 3.58 3.59 3.60 3.68 3.72 3.81 3.82 4.10	.0047 .0086 .0079 .0109 .0201 .0177 .0427 .0474 .305	1.05 1.38 1.17 1.40 1.62 1.08 1.40 1.44 1.34
	3.02 3.18 4.07 4.09	Oak Ridge Values	8CLASSIFICATION CANCELLED 7PER DOC REVIEW JAN. 1973 8.4



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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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