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RaLa Process Research

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I. PRESENT PROCESS RESEARCH

A. Precipitation of Lanthanum Oxalate

A detailed study of the precipitation of $La_2(C_2O_4)_3$ was made during this quarter in an effort to gain a better understanding of the current process at Bayo.

Five reagents were used as precipitants for this investigation. The crystal size was observed, and the per cent lanthanum yield was determined in each run at two different temperatures. Ten cubic centimeters of saturated reagent was added to 30 cc. of solution containing 12 mg. lanthanum, La^{140} tracer and enough HNO_3 to give 40 cc. of solution 0.34N in HNO_3.

Reagent	Excess C_2O_4 = (x theoretical required)	% Yield 23°	% Yield 65°
Oxalic Acid	55	97.0	86.7
Sodium Oxalate	21	97.6	88.3
Potassium Oxalate	129	94.7	95.9
Sodium Acid Oxalate	10.2	96.1	27
Mixed Oxalate (1.7 g. $NaHC_2O_4$ and 1.3 g. $H_2C_2O_4$/100 cc.H_2O)	17.7	95.1	79.8

With the exception of sodium and potassium oxalates which produced flocculent precipitates, the other precipitants gave fine to medium crystals which were filterable. Since higher yields are obtained at Bayo where HF is used to metathesize the precipitate, it is logical to assume that the HF has some action as a scavenger. Moreover, the slurries at Bayo have appeared milky, which would not be the case if the lanthanum were present as LaF_3 metathesized from $La_2(C_2O_4)_3$ crystals.

B. Per Cent Barium Impurity Studies

Since past results indicate that only a partial separation is obtained by successive precipitations with ammonia, a clean-up milking was made in which the lanthanum and other impurities were precipitated from a solution 2N in [illegible]. In the table below are found the results obtained for s[illegible]

Milking	Precipitant	% Ba carried with $La(OH)_3$
1st	2N NaOH	17.2
2nd	ca. 0.4N NH_4OH	0.25
3rd	" " "	1.06
4th	" " "	1.06
5th	" " "	less than 0.03

(For comparison, the % Ba associated with the La in the first step was 10.1, 10.8 and 11.4 for the first, second and third milkings respectively of shipment No. 42. Dilute ammonia was used as the precipitant in each case).

These data seem to indicate that even though considerable barium is lost in the first milking, a solution remains in which the impurities are negligible. For the 10,000-curie shipments anticipated in the future, it is advisable to insist on a clean product or perform a clean-up milking after receipt of the shipment.

C. Impurities in the Present Shipments

The sample, submitted for spectrochemical analysis in March, was examined by CMR-1. This specimen represented contaminants which were precipitated with NaOH during the clean-up milking of shipment No. 46. In decreasing order of abundance the analytical report was as follows: La (carrier), Ca, Ba, Fe, Mg, Al, Si, Cr.

As soon as the barium has decayed (about three curies at present) to a safer level, the material will be analyzed gravimetrically.

II. THE GROWTH OF La^{140} FROM Ba^{140} AS FOLLOWED BY THE β COUNTER

A Ba-La equilibrium solution was stripped of the La^{140} by a multiple fuming HNO_3 separation using additional lanthanum carrier in each step. The pure barium was then mounted on copper discs and counted every half hour for several hours. Counting was continued twice daily for two weeks. Ba_o was obtained by extrapolating the initial counts to separation time. The maximum count was that taken at 5.65 days (at this point the Ba and La are equal, and the Ba has decayed to 73.7% of the original).

Ratio of Ba/La counting efficiencies = $\frac{0.737 \times Ba_0}{\text{Max. count} - 0.737\ Ba_0} = 0.676^{\gamma\Delta}$

$^{\Delta}$With the γ counter about 5% of the counts in an equilibrium solution are due to barium.

$^{\gamma}$End window type β counter used. Sample was 3.5 cm. (third shelf) from window, 4.7 mg./cm.^{2}.

The interesting feature about this study was that the β growth-curve for lanthanum very closely resembled the temperature curves obtained at Bayo when the lanthanum grows to equilibrium with the barium parent. (See "Temperature Measurements" below).

III. TEMPERATURE MEASUREMENTS

A Weston thermometer was sheathed in platinum, calibrated and adapted to the process plug. With this arrangement measurements can be taken at any time the solution is not being processed. After milking off the lanthanum a series of readings was taken while the daughter was growing. The increase in temperature after the apparatus had reached equilibrium was attributed to the growth of lanthanum.

The temperature rise closely parallels the β growth-curve for La'^{40}; an increase of about 100% was observed during the growth to maximum which occurs at 5.65 days.

Recent results further substantiate that the temperature for 10,000 curies will be about 90° above room temperature. At this time it appears that cooling requirements in the new cell are more significant than was first believed.

IV. EXCHANGE OF LANTHANUM IN HNO_3 SOLUTIONS

Data which have been obtained to date on the problem of determining the rate of exchange of La'^{40} between crystals of $Ba(NO_3)_2$ and the solution phase are summarized in the table below. The HNO_3 concentration of the solutions was held constant at 16N.

Time-hours	Fraction of La'^{40} Remaining in Precipitate
25$^{\Delta}$	0.895
50	0.863
91	0.865
92	0.805
169	0.848

$^{\Delta}$The $Ba(NO_3)_2$ crystals were dried after separation and kept in a vacuum dessicator 144 hours before being placed in HNO_3.

In order to have a better understanding of the exchange reaction, the kinetics of the exchange was considered. An equation was derived in collaboration with R. P. Hammond and P. C. Hammer, which can be used to predict the rate of exchange of La'^{40}. This equation is as follows:

$\frac{L}{L'} = \frac{e^{-(\lambda_2-\lambda_1)t} - e^{-\lambda_3 t}}{(1 + \frac{\lambda_3}{\lambda_2-\lambda_1})(e^{(\lambda_2-\lambda_1)t} - 1)}$ where $\frac{L}{L'}$ is the fraction of La'^{40} remaining in the crystals of $Ba(NO_3)_2$ after time t, and λ_3 is a rate constant, assumed to be proportional to the amount of La'^{40} in the crystals. Other symbols are those conventionally used in radiochemistry. It is seen that when t is large, $\frac{L}{L'}$ approaches the value of $\frac{1}{1 + \frac{\lambda_3}{\lambda_2-\lambda_1}}$. Thus λ_3 can be determined accurately from this simple relation.

The value of λ_3 was estimated to be about $2 \times 10^{-3} hr^{-1}$ from data listed in the table above. More data are needed to determine λ_3 accurately. The exchange reaction should be allowed to proceed at least 200 hours.

V. SEPARATION OF BA AND LA WITH VERSENE

Experiments for finding the optimum conditions for separating Ba and La with Versene were carried out. The La was precipitated from solutions, which contained 20 mg. La, 50 mg. Ba, Versene and fluoride ion, by lowering the pH with HCl. Although the La yields were quite high, the per cent Ba carried with the La ranged from 20 to 65%. It appears very doubtful if this method could be used to produce La sources containing less than 0.1% Ba'^{40}.

Other experiments were then carried out to determine if BaF_2 precipitated independently of LaF_3 at pH values of 3 and 4. Large crystals of BaF_2 were observed after forty hours; whereas a fine precipitate formed immediately at a pH of 5.

From equilibria considerations high fluoride ion, high hydrogen-Versene ion and low Versene anion concentrations would seem to minimize the Ba carriage.

VI. PROPOSED PROCESSES

A. Determination of Yield and Barium Carriage

Experiments were continued to determine the yield and barium carriage of the proposed processes under the mechanical conditions to be expected in the new building. The procedures used were essentially those given in the quarterly report dated February 1950. Results showed an overall yield of 97.7% for the hydroxide process and 94.1% for the fuming HNO_3 process. Barium carriage averaged 0.74% for the hydroxide process (with single hydroxide precipitation) and 0.36% for the fuming HNO_3 process.

B. Effect of Impurities

Experiments were begun to determine the effect of impurities upon the yield, volume of precipitate and barium carriage in these processes. The present specifications for shipments to be processed by the fuming HNO_3 method are as follows:

Fe 500 mg.

Ni 10 mg.

Pb 200 mg.

Cr 10 mg.

Active Sr 100 curies

The net result when all of these impurities, except the active Sr, were added to the starting solution for the fuming HNO_3 process was a 100% volume increase and an increase in yield from 94 to 97%. Further experiments indicated that no single impurity was the cause of this volume increase. Other runs showed that either iron plus chromium or iron plus lead must be present for an increased volume, but that all three metals must be present to account for the total increase. The precipitate will be analyzed quantitatively for more information about the compounds precipitating with the LaF_3, barium carriage studies are not yet complete.

VII. DEVELOPMENT OF A LINE SOURCE

In anticipation of a need for a source approximating a line instead of a point, a cylindrical tip three inches long was designed and experiments made to

determine the feasibility of using a tip with a small inside diameter. Results showed that tips with inside diameters of 1/16" can be used to obtain essentially complete yields when LaF_3 is centrifuged. The distribution of the precipitate along the axis of the source was determined to be uniform in the 1/8" I.D. tips. In the 1/16" I.D. tips approximately 40% of the precipitate was evenly distributed in the lower 1/3 of the tip, the remaining 60% being evenly distributed through the upper 2/3 of the tip. It is believed that a slightly longer centrifugation time would give a uniform distribution throughout the tube. The apparent practical limit upon the inside diameter of the tip appears to be the volume of the precipitate. Using 0.25 cc. the average of previous measurements for the volume of 40 mg. of La-CeF_3 makes necessary a tip length of at least 1.3 inches for the 1/8" I.D. tip and 5 inches for the 1/16" I.D. tip.

VIII. BARIUM COUNTING EFFICIENCY

Experiments are being carried out to redetermine the relative γ counting efficiency of barium in an equilibrium solution. The technique used is being refined to obtain precise results.

IX. CORROSION TESTS ON 316 STAINLESS STEEL

Tests were made on 316 stainless steel to determine whether or not a high concentration of HNO_3 would passivate it, so that it would not be attacked by HF during a fluoride precipitation. The results showed a weight loss of 1262 mg./decimeter^2/day, indicating that these conditions are quite corrosive.