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Contract No.-W-35-058-eng.-71

Technical Division

M. D. Peterson, Section Chief
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FINAL REPORT
6/12/47

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THE DEVELOPMENT OF A CHEMICAL PROCESS FOR THE PREPARATION OF Ba^{140}

Problem Assignments: P. A. 263-X60C
P. A. TX1-5

Period Covered: December 23, 1944 to August 11, 1945

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1.0 Summary

It had been demonstrated by members of the Chemistry Division that Ba* was carried from U.N.H. solution by $PbSO_4$ precipitates. The conditions of this carrying have been established within wide limits of the variables tested. The lead carrier was re-dissolved and used repeatedly in successive fresh batches of UNH solution.

The sulfate precipitate was converted to acid soluble carbonate by metathesis with potassium carbonate.

Laboratory and semi-works scale tests indicate the possibility of separating lead from barium by chemical precipitation processes, but electrolysis was recommended for the main-line operation on the basis of semi-works tests that are recorded in another report.

A volume reduction after electrolysis was sought in carbonate precipitation, with various reagents added to complex Fe(III), that was introduced by corrosion, in a soluble form. A more satisfactory volume reduction was found in evaporation.

Further purification and decontamination resulted from the precipitation of $Ba(NO_3)_2$ by the addition of 5 volumes of 23M HNO_3. In the original plant operations the $Ba(NO_3)_3$ so obtained was evaporated and shipped. Several factors made $BaCl_2$ appear to be a more desirable product, so the operation was expanded to include a final precipitation with HCl and ether.

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2.0 Introduction

Kilocurie quantities of La^{140} were desired by the project. A process had been designed and was in production on quantities up to 300 curies of the parent Ba^{140} (1). The scale-up in activity and the attendant development work was undertaken by Section I of the Technical Division. The process that was chosen was based on phase separation by settling and decanting of the supernatant. Changes were made later to filter the precipitates (nitrate and chloride) obtained at the end of the process.

The goal set for this development work was to obtain a product that did not exceed the following specifications.

Lead	50 mg
Iron	10 mg
Chromium	5 mg
Nickel	5 mg
Strontium	50 mg
Inactive Barium	1000 mg

A specific activity that was as high as possible was sought and in some runs has exceded 2,000 curies.

3.0 Flowsheets of the Ba^{140} Separation Process

Three flowsheets are attached to this report. The first (Drawing No. 1784) presents the metal solution, extraction, and metathesis steps in the process and the second (Drawing No. 1785) the electrolysis, and nitrate and chloride precipitation steps. The third flowsheet (Drawing No. 1337) presents the chromate process which was studied as an alternate for separation of barium from the lead carrier. The flowsheets for the mainline process are those issued December 21, 1945, shortly after all development work on the process was concluded. These flowsheets include many changes which were made as a result of the operation of the plant up to that time.

The mainline flowsheet includes the following steps:

1. Metal Solution

   The uranium slugs are dissolved in HNO_3 after the aluminum coating has been removed with NaOH and $NaNO_3$.

2. Extraction

   The Ba^{140} is extracted from the solution by coprecipitation with $PbSO_4$ carrier.

3. Metathesis

   The $PbSO_4$ and $BaSO_4$ are converted to the carbonates by treatment with K_2CO_3 solution.

4. Electrolysis

   The lead is removed from the HNO_3 solution of the metathesis cake by electrolysis to PbO_2.

5. Volume Reduction

   The solution is evaporated to a small volume.

6. $Ba(NO_3)_2$ Precipitation

   The barium as the nitrate is precipitated by adding fuming HNO_3.

7. $BaCl_2$ Precipitation

For further purification from Fe, Pb, Sr, etc., the barium is precipitated as $BaCl_2$ from an HCl-ether mixture. The solution of the $BaCl_2$ precipitate is evaporated to dryness for shipment

8. Waste Disposal

Procedures are given for neutralizing wastes in preparation for storage in appropriate radioactive waste tanks.

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4.0 Experimental

4.1 Extraction Step

The conditions first presented for the carrying of Ba* from UNH on $PbSO_4$ were, in the slurry, 40% UNH (from 50 slugs), 1 g. Pb per liter as nitrate and H_2SO_4 (18M added to 2M H_2SO_4, then 6M H_2SO_4 added to 3.6M) digested, settled and decanted.

A second, third, and fourth extraction were made by pouring the UNH solution from 50 more slugs onto the precipitate (which then dissolved). Enough lead nitrate was added to make up for that lost in the waste, and lead sulfate precipitated again.

In the first test recorded in Table 1 the recommended procedure was employed. Large yellow crystals that formed on the third and fourth precipitations were probably uranyl sulfate precipitating as the result of evaporation.

Further tests (2, 3, 4 and 5, Table 1) varying the proportions of uranyl and sulfate ions demonstrated little difference in Ba* loss between any of the tests.

[redacted]

TABLE 1

Carrying Ba Tracer with $PbSO_4$

Sulfuric added last (18M to conc. of 2M then 6M added to the final concentration)

Test No.	Scale	UNH %	H_2SO_4 M	Pb g/l	Extraction Loss	Washes (6)
1	15 L	40	3.6	0.4	0.2, 0.3 5.0**, 3.5**	0.1
2	1 L	35	3.2	0.4	4.1	11.1
3	1 L	35	3.6	0.4	3.2	8.4
4	1 L	40	3.2	0.4	5.8	1.9
5	1 L	40	3.6	0.4	2.1	2.1

** Large volume of yellow crystalline precipitate formed here. Dissolved in water washes. Probably uranyl sulfate.

[redacted]

Since yellow crystals were observed in test 1, Table 1 and were thought to be uranyl sulfate, qualitative tests on the evaporation (in small increments with cooling between each addition) of an extract solution (0.4 g. Pb per liter 3.4M H_2SO_4) containing 460 g. UNH per liter showed the volume could be reduced 30% before crystals first appeared. A solution containing 330 g UNH per liter lost 45% of its volume under similar test conditions.

Addition of all H_2SO_4 as 6M solution (in two, 1 L. scale tests, 230 and 400 g. UNH/l) resulted in waste losses of 1.3 - 1.6% Ba*, not significantly different from the addition as 18M and 6M H_2SO_4 solutions.

The rate of addition of 6M H_2SO_4 (all added as 6M to a final concentration of 3.2M H_2SO_4) made no significant difference in the amount of Ba* lost in the supernatant (1.2 - 1.5%) when the addition rate varied from 1 min. to 40 min. on 1 L. scale in the laboratory.

Since the addition of lead nitrate before each sulfuric acid strike to replace lead lost in the supernatant did entail certain operational risks it was considered advisable to test the effect of adding all of the lead before the first precipitation. No significant differences in barium losses were noted when all the lead was added before the first precipitation (Table 2).

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TABLE 2

Extraction and Metathesis with all Lead added Before

The First Precipitation

3 l. scale in stainless steel. Extraction (1) 50% UNH (1.5M H_2SO_4 to 2M, 6M H_2SO_4 to 3.4M), digested 1 hr. at 90°C, settled, decanted, washed. (2), (3), (4) UNH added to the cake then H_2SO_4).
Metathesis: Twice by 4M K_2CO_3 at 90°C for one hour diluted to 0.5M K_2CO_3, settled, decanted and washed.

	Extraction Wastes Strike				Extraction Washes	Metathesis Waste	Metathesis Cake Solution	Material Balance
	1	2	3	4				
Ba*(%)	0.6	0.9	0.7	0.3	1.0	0.1	73.0**	75.6
Pb (%)	6.8	7.8	8.9	8.3	0.6	2.3	62.5	96.9

** Also contained 7 mg. Fe.

[redacted]

[redacted]

The amount of lead carrier added was varied from 0.08 to 0.8 g. Pb(II) per liter. The solution with 0.08 gm Pb(II) formed no visible precipitate while 0.12 and 0.16 gm Pb(II) did not form a visible precipitate. Extractions with 0.2, 0.4, 0.64 and 0.8 gm Pb(II) did not vary significantly among themselves (Table 3).

TABLE 3

Variations in the Amount of Lead (0.2 to 0.8 g/l) in the Extraction Step (3 L. scale in S.S.)

Extraction: to 50% UNH solution added 18M H_2SO_4 to 2M, then 6M H_2SO_4 to 3.2M (30 min. at 80 - 90°C). Heating was continued for one hour, settled one hour, decanted, washed 4 times.

Metathesis: treated twice with 4M K_2CO_3 (20 ml/gm Pb) at 80 - 90°C. for 15 minutes, diluted to 0.5M K_2CO_3, digested 1/2 hour, settled 1 hr., decanted, dissolved in 25 ml 20% HNO_3.

	Extraction		Metathesis		Material Balance
	Wastes (One Extraction only)	Washes	Wastes	Cake Solution	
Ba*(%)	0.8-2.1	0.5-1.4	0.2-0.6	64-81	63-83
Pb (%)	3.3 6.7	0.2-1.2	1.8-2.0	75-116	122-129

[redacted]

The presence of HNO_3 in the UNH employed for extraction had little effect on the Ba* lost in the supernatant. Ba* losses were less than 1% when the HNO_3 concentration varied from 1.8% to 20% of the 50% UNH solution.

Characteristics of the reaction vessel have an effect on the crystallization of lead sulfate. In glass vessels crystals had formed when sufficient 18M H_2SO_4 was added to attain a concentration of 2M (no precipitate was visible at 1.8M). In a repetition of the above test in stainless steel (25-12) crystals appeared at 1.4M H_2SO_4 but not at 1.2M.

The cessation of agitation after all reagents had been added (i.e. digested without agitation) raised the Ba* losses in the waste to 9% (control experiment 2).

The method of washing the extraction precipitates, either (a) three times with 28% H_2SO_4 and once with water or (b) once with 28% H_2SO_4 and three times with water made no difference in Ba* lost in the wash (both below 1%).

4.11 <u>High Production Extraction</u>

To obtain the maximum amount of barium per extraction it was considered possible to dissolve 67 slugs per batch and precipitate Pb from three batches to obtain a total of 200 slugs (limited by size of extraction vessel in the final plant). The results summarized in Table 4 show the minimum acid concentration in the slurry to be 2.4M H_2SO_4 and because of high lead solubility, 0.8 grams of Pb(II) per liter are required in extraction.

[redacted]

[redacted]

TABLE 4

Wash precipitation reduction (in Stainless Steel)

[illegible] (87 slugs full scale) was added Pb and H_2SO_4 (6-18%) [illegible] H_2O, final concentration at 95°C, digested one hour, settled one hour, then decanted.

No. Scale**	H_2SO_4 Conc. added (%)	H_2SO_4 Conc. final (%)	Lead g/l	Ba* in supn't. after 60 min. settling As Rec'd. (%)	Ba* in supn't. after 60 min. settling Lab Cent'fd. (%)	Pb in Supernatant
0.5 l.	6	2	0.4	75.4		
10 l.	6	2	0.4	75	35	
0.5 l.	6	2	0.53	28	18	
10 l.	6	2	0.6	15 (hot), 4 after 16 hr. settling, 60 at r.t.		
0.5 l.	6	2	0.8	4.1	3.9	
0.5 l.	9	2	0.4	21.5	2.1	
10 l.	12	2	0.4	18		
10 l.	18	2	0.4	4		20
10 l.	18	2	0.6	2		90
10 l.	18	2	0.8	4		105
0.5 l.	18	2.4	0.8	6.6	3.2	57
0.5 l.	18	2.4	0.93	2.5		48

**Full scale - 250 l.

[redacted]

The conditions considered optimum, 2.4M H_2SO_4 and 0.8 g Pb(II) per liter, (Table 5) produced losses that were no greater than those encountered in the process originally proposed (50 slugs per batch, 3.4M H_2SO_4 and 0.4 g Pb(II) per liter.

TABLE 5

High Production Extraction and Metathesis (1 L. scale in stainless steel)

90% UNH (67 slugs full scale) containing 0.8 g Pb per liter plus 1.2M H_2SO_4 to 2.4M H_2SO_4, three times. Metathesized by 4M K_2CO_3 diluted to 0.5M K_2CO_3.

Extraction Waste	Ba* Losses Wash (%)	Ba* Metathesis Waste (%)	Ba* recovered Metathesis Cake (%)	Material Balance (%)
1.4, 1.6, 2.5	0.3	0.2	89	95.0
1.4, 1.7, 3.4	1.0	0.0	80	87.5

4.12 Carrying by Other Precipitates

A laboratory tracer test was conducted wherein Ba(II) 4 mg/l. was precipitated from UNH solution by making it 3.2M in H_2SO_4. Settling was visually poor and after centrifuging 32% Ba* remained in the supernatant.

Tests have been made, using solutions with uranium complexed by carbonate and peroxide to carry Ba* with $PbCO_3$ or $PbCrO_4$. In those solutions where yields have been high, the dilution has been so high as to require more than four batches per 200 slugs.

[redacted]

4.2 Metathesis

The conditions recommended for metathesis in the 706-D process included the addition to the extraction cake (100 g Pb plus Ba* as sulfates) of 20 ml. 4M K_2CO_3 per gram of Pb(II), digestion at 90 - 100°C for one-half hour, dilution with water (one-half hour) to 0.5M K_2CO_3, cooling, settling and decanting. The entire procedure was repeated. The results from such runs are included in Table 6.

TABLE 6

Metathesis in Glass Equipment

Ba Carrier added g. (full scale equivalent)		Scale Pb(g)	Waste Solution		Product Solution	
			Ba*(%)	Pb(%)	Ba* %	Pb %
I	0	10	1.0	4.4	99.0	89
II	1.0	5	1.6	1.8	106	74

Since difficulty was experienced in the solution of the metathesis cake, qualitative tests were made on relative solubility (Table 7). Two treatments were found to be better than one.

TABLE 7

Solubility Behavior of Metathesis Cake

Number of Treatments	K_2CO_3 Conc. After Dilution	Relative Solubility in 1M HNO_3 (1.5 times theoretical amount)
One	0.5M	Foamed, still cloudy after 60 min.
One	1 M	Same
Two	0.5M	Less foaming, solution complete in 45 minutes r.t.
Two	1 M	Same

4.21 Residues from Dissolution of the Cake

Semi-works metathesis solutions usually contained some black, insoluble residue. Spectrographic analysis showed this material to be rich in Fe, Ni, and Cr (elements to be expected from the corrosion of stainless steel). The insoluble residue from semi-works run Ba-10 contained less than 1% of the Ba*.

4.22 Variations from the Flowsheet Procedure

4.221 Metathesis with 1M K_2CO_3 without Further Dilution

For each treatment, there was used 150 ml. 1M K_2CO_3 per g. Pb at 90-100°C for 15 minutes. After the second treatment the cake was washed free from carbonate and dissolved in 25 ml. 0.5M HNO_3 per gram Pb. Of the total Ba* added 2.5% was found in the waste (0.6% floating) and 97.5% in the cake solution.

4.222 Metathesis with 4M Na_2CO_3

Laboratory tests were carried out to study the possibility of re-placing K_2CO_3 with Na_2CO_3. The supernatants contained 3.9% Ba* and 0.4% Pb when settled at room temperature, 10 minutes in glass, 3 g. total Pb and contained 2.0% Ba* and 2.6% Pb when settled hot (90 - 100°C). More data are summarized in Table 8. Because of the higher losses in metathesis with Na_2CO_3, this carbonate was not recommended for plant use.

[redacted]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible] (%) in [illegible] Na_2CO_3 washed (24 min. settling)	[illegible]	[illegible]
[illegible]	3.0	[illegible]	[illegible]	5.2	93	[illegible]
2	2.0	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	3.5	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	1.1	[illegible]	[illegible]
5	[illegible]	[illegible]	3.3	1.3	98.2	[illegible]
6	[illegible] Na_2CO_3					
	1.8	[illegible]	0.6	4.6	96.2	[illegible]

[redacted]

[illegible] Metathesis Flowsheet

[illegible] Flowsheet operation conducted at [illegible] [illegible] Metathesis [illegible] results compared [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] respectively after laboratory [illegible]

[illegible] based on the basis of both economics and chemistry [illegible] the metathesis step could be carried out at room temperature or at elevated temperatures.

4.2.1 Metathesis in One Step

The single step metathesis with either 4M K_2CO_3 or [illegible] at room temperature or at 90°C resulted in incomplete metathesis [illegible] the fact that one half of the Ba could be removed from the cake solution by batch centrifugation.

4.2.2 Metathesis of Inactive $BaSO_4$

In the interest of designing a process for using inactive barium as carrier it was shown that barium sulfate did not settle well from the [illegible] solution (section 4.1.12). The following test showed that $BaSO_4$ [illegible] g./125 ml. 4M K_2CO_3) was not completely metathesized by K_2CO_3.

Five g. Ba (as $BaSO_4$) with tracer added was metathesized twice with 125 ml 4M K_2CO_3 at 90°C according to flowsheet conditions. The residual cake was treated with 1M HCO_3 and centrifuged. The centrifugate contained [illegible] of the Ba.

4.2.4 Metathesis and Separation

Laboratory tests on 1/10th scale were made using 40 ml 20% KCO_3-[illegible]

[redacted]

[redacted]

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[illegible] HNO_3 per gram Pb to $PbCO_3$ (plus Ba*) at 75°C for one-half hour, cooled and centrifuged. The supernatant contained 10% Ba* with or without one [illegible] of Ba carrier (10 mg Ba per gram Pb). The addition of Ba carrier [illegible] the nitric acid, nitrate metathesis did not significantly change the results.

[illegible] Acetate Metathesis

The nitrate cake (10 g. Pb, in glass, in the laboratory) was treated with 10 ml 6M ammonium acetate per g Pb at 75°C for 30 minutes, cooled and centrifuged. The acetate digestion was repeated using one-half the volume of 6M ammonium acetate. The residue was washed with 5 ml 23M HNO_3 (fuming) per gram Pb then three times with one-half volume of 6M HNO_3 and then dissolved in water. Results (Table 9) indicate highest losses in the 6M HNO_3 washes. These losses could have been reduced by using a higher concentration of HNO_3 in the washing step.

TABLE 9

Metathesis with Ammonium Acetate

Acetate Metathesis Solution	Ba* (%)
Acetate wastes	1.1
23M HNO_3 wastes	4.5
6M HNO_3 wastes	25.0
Dissolved cake	68.5

[redacted]

[redacted]

[illegible]

4.3 Volume Reduction after Metathesis

4.31 [illegible] Carbonate

[illegible] as the metathesis cake was dissolved in a [illegible] large volume and would be diluted further by jet [illegible] [illegible] a volume reduction step was considered desirable. One of the [illegible] methods proposed for volume reduction was the addition of carbonate [illegible] precipitate lead carbonate that would carry the Ra^{2+}. Sodium carbonate gave higher Ra^{2+} losses in the waste (19%) than did potassium carbonate (5.6%), Table 10.

4.32 Evaporation

The volume reduction method that was chosen by the [illegible] group on the basis of simplicity of operation was evaporation.

TABLE 10

Volume Reduction with Carbonate

To a synthetic cake solution (400 ml. containing 10 g. Pb) was added 25% carbonate solution to a final concentration of 0.5M carbonate. [illegible] separation was made by decantation after settling.

Carbonate Used	Waste Loss		Cake Solution	
	Ra^{2+} (%)	Pb (%)	Ra^{2+} (%)	Pb (%)
Sodium	19.1, 19.3	1.6, 1.8	80.8, 81.1	98.2, 98.5
Potassium	5.2, 5.4	3.6, 3.3	97.2, 108	95.5, 97.4

[redacted]

[redacted]

4.40 [illegible]

The process [illegible] electrolysis, was investigated in the past work. Since no work was done on this in the laboratory it was not considered in this report but will be discussed in another report to be issued later.

4.41 Hydroxide

To a synthetic metathesis cake solution containing Ba* and a full scale equivalent of 1 g. Ba carrier was added 10 ml 2M NaOH solution per g. Pb and then heated to 75°C for 30 minutes, cooled and centrifuged. The process was repeated once more. The Ba* loss was 14%.

4.42 $PbBr_2$ and $BaHPO_4$ Precipitation

A solution of 10 ml containing 0.05 mols NaBr was added to 130 ml of 0.2M HNO_3 containing 4 g. Pb and Ba*. After 1 hour of agitation the slurry was centrifuged. To the supernatant was added 0.1 g. Ba carrier and 1 g. $(NH_4)_2HPO_4$ in 5 ml. of solution and NaOH was added until a pH of 7 was reached. While 110% of the starting Ba* was found in the barium phosphate, 22% of the Pb was also found here.

4.43 Phosphate Precipitation

Pb(20 g) was precipitated at a pH2 in the presence of 0.7M phosphate in 200 ml solution. By adjusting the pH to 7, Ba was precipitated as the phosphate in 1.2 liters of solution.

The analysis of the solutions is given below:

	% Ba*	Pb, mg. full scale equivalent
Loss in lead phosphate	8.8	
Yield in supernatant	93.8	15
Yield in barium phosphate	66.3	0.5

[redacted]

4.44 Lead Tartrate Complex

In three 1/10 scale runs the sulfate cake after extraction was treated with 2M NaOH, 2M K_2CO_3 and 0.8 sodium tartrate. The slurry was centrifuged; the separated precipitate was washed and dissolved in HNO_3. The product solution contained 97, 88, 79 and 79%. of the barium tracer and the full scale volume equivalent of 112, 115, 25 and 16 mg Pb respectively (tolerance was set at 50 mg Pb). Barium losses in the waste solutions were 9.4, 9.7, 14.6 and 10.2% respectively.

4.45 PbS and $BaCO_3$ Precipitation

Preliminary scouting tests revealed that PbS precipitated from 0.5M HNO_3 carried 0.5% Ba* and higher losses resulted when the solution was made in 1M in NaOH. Colloidal sulfur was formed when H_2S was bubbled through the solution (0.5M HNO_3) at 90°C. Solutions neutralized with NaOH (after H_2S treatment) before the addition of K_2CO_3 did not precipitate $BaCO_3$.

The recommended procedure was tested in glass equipment. One liter of solution containing 100 g Pb, 500 mg Ba and Ba*, 100 mg Fe in 0.5M HNO_3 was treated over a 30 minute period with freshly prepared $(NH_4)_2S$ solution (made by adding 1M H_2S to concentrated NH_4OH) to obtain a final concentration of 1M ammonium ion. The slurry was settled, the supernatant decanted and the precipitate washed. To the supernatant was added 40% K_2CO_3 (over a 30 minute period) to obtain 0.5M K_2CO_3. The slurry was settled for one hour and decanted. The precipitate was dissolved in dilute HNO_3 and $Ba(NO_3)_3$ precipitated by the addition of 5 volumes of 23M HNO_3 (fuming)

An advantage of this method is the decontamination from iron in the PbS precipitation. Lead removal, also, was better than the goal sought (50 mg final product). Three times out of four the Ba* yield was 85% or better. A problem remaining for development, however, is the one of the removal of the

[redacted]

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	0.8	90	[illegible]	8.2
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	84	[illegible]	0.9
[illegible]	[illegible]	[illegible]	[illegible]	0.3	78	[illegible]	1.2
[illegible]	[illegible]	[illegible]	0.9	[illegible]	114	[illegible]	[illegible]

[illegible] Chromate separation

[illegible] Precipitation of Lead and Barium

Lead chromate can be precipitated from nitric acid solution (0.5 to [illegible] while barium chromate is soluble. However, the barium can be made to precipitate above pH 7, by the addition of NaOH to the supernatant from the lead chromate precipitation. Barium losses in wastes (table 12) can be kept below 7% and the lead in the product was kept below 20 mg (tolerance 50 mg Pb).

[redacted]

[redacted]

TABLE 14

Separation of Lead from Barium by Chromate Precipitation

30 g Pb(II) and 0.4 g Ba(II)/l

Test Number	Scale Liter	Waste Loss(1) Pb ppt.	Ba Supernatant	Product (2) Pb gm full scale
1	0.1	16%	22%	1
2	0.1	13	0	15
3	0.1	6	1	20
4	1	6	1	0
5	1	2	1	20
6	1	2	3	10
7	0.1	1.5	0.4	12
8	0.1	1.1	-	-
9 (3)	1	3.3	0.3	7
10 (3)	1	2.2	0.2	6

(1) 0.5 to 2M HNO_3 for $PbCrO_4$ precipitation, settled well and re-dissolved in 4M HNO_3 containing 1M $NaNO_2$.

(2) pH 12-14 for $BaCrO_4$ precipitation, did not settle, centrifuged. Did not dissolve completely in HNO_3 with or without $NaNO_2$ added.

(3) Dichromate used instead of chromate. No significant difference in physical behavior or yield between dichromate and chromate.

[redacted]

A test was made (Table 13) to study the effect of pH on the precipitation of Pb and Ba as chromate. It is apparent that complete precipitation of Ba occurred at a pH of 7 or higher. It is significant that the lead was not re-dissolve on the addition of more NaOH indicating that the lead carried by the $BaCrO_4$ was probably not in solid solution.

TABLE 13

Effect of pH on the Precipitation of Lead and Barium with Chromate

A mixture of Pb(II), Ba tracer, and chromate corresponding to the supernatant from the precipitation of lead chromate was made alkaline with NaOH solution. Samples were removed, centrifuged and tested periodically.

pH	Analysis of Supernatant	
	Pb(mg/l)	Ba^{2} (cts./min./ml)
1	23	1184
2	19	1029
5	22	59
7	13	7
9	66	6
11	10	7
12-14	8	5

[redacted]

TABLE 14

Barium Losses and Lead Separations

In the Lead Chromate Precipitation

DEPARTURE FROM FLOWSHEET

	a		b	c		d
	Pb Content			$Na_2Cr_2O_7$ Equiv. Pb		Pb-Ba added to $Na_2Cr_2O_7$
	20 g	200 g	70-80°C	1.1	1.5	
% Ba in $PbCrO_4$ cake	0.7	4	0.9	0.3	0.3	13
% Ba in Supernatant	99.0	95.5	101	98	80	-
Mg Pb in Supernatant (full scale equivalent)	324	283	280	656	322	290

March 3, 1945 flowsheet values: (a) 100 g Pb
(b) room temperature
(c) 2.0 equiv. $Na_2Cr_2O_7$ per equiv. Pb.
(d) dichromate added to Pb-Ba solution

$BaCrO_4$ precipitates did not settle any better when the precipitation was made hot, when trivalent chromium was present, or when the chromate was reduced in the acid solution with H_2O_2, or when the solution was made alkaline and oxidized with H_2O_2 to precipitate $BaCrO_4$.

Yields in this latter process are indicated by 1.7 and 0.4% Ba* in the supernatant from the product solution (7.8 and 17.6% Ba* respectively unaccounted for) with 13 and 7 mg Pb (full scale equivalent) associated with the product.

[redacted]

Lead Chromate Precipitation

Large variations from flowsheet values in (a) amount of Pb used, (b) temperature of precipitation, and (c) amount of dichromate added resulted in large increases in Ba losses in 1 liter lab tests on stainless steel, [illegible] Ba carrier. However, a significant increase in Ba loss occurred when the Pb-Ba metathesis cake solution was added to the dichromate for $PbCrO_4$ precipitation, in place of the flowsheet dichromate addition to the Pb-Ba solution. (Table 14).

1.462 Single Precipitation of Barium Chromate

It was believed that the precipitation of lead chromate was an unnecessary step, that the lead could be kept in solution during the barium chromate precipitation by adding NaOH first. A test devised to determine the separation from lead was made using a synthetic solution of the metathesis cake with varying amounts of lead, 0.5 g total barium in 5 liters 1M HNO_3 by adding 2.5 liters of 50% NaOH. The barium chromate was precipitated with 1 liter of sodium dichromate (150 g/l) and digested for one half hour at 70°C. The product precipitate was centrifuged and dissolved in 2M HNO_3. Lead separation was below the desired limit (50 mg total) when 10 grams or less lead (tests 2 to 5, table 15) was present but at 100 grams of lead the residue was 7 times higher than the limit (test 1, Table 15). Barium losses were below 2% in all tests.

Tests were made to study the effect of dichromate concentration on the precipitation of barium chromate. A synthetic metathesis cake solution (100 g lead, 0.5 g barium in 5 liters of 1.7M HNO_3) was treated with 2 liters of 50% NaOH. Varying amounts of sodium dichromate solution were added to aliquots (20 min. addition) digested one hour at 90°C, centrifuged and separated. The product precipitate was dissolved in 5 liters 2M HNO_3 and re-precipitated as before. Barium losses were lower at the higher dichromate concentration

and while the lead carrying was below tolerance it was less than a factor of 2 (table 16).

TABLE 15

Lead and Barium Yields in the Single Step Precipitation with Chromate (200 ml scale)

Test No.	Full Scale Equivalent of Lead (mg.) Starting Solution	Product Solution	Ba* Loss %
1	10^5	388	1.2
2	10^4	35	1.2
3	10^3	15	2.0
4	10^2	7.5	1.4
5	10	7.5	1.6

TABLE 16

Precipitation of Barium Chromate (200 ml. 0.02 full scale; results calculated to full scale)

Test Number	$Na_2Cr_2O_7$ (g)	Ba* Loss First Precipitation	Ba* Loss Second Precipitation	Products Ba* %	Products Pb (mg)
1	38	10.1	3.4	85.5	30
2	75	4.5	1.8	93.3	35
3	150	1.6	0.6	97.3	28

A semi-works trial of the step as outlined in test 3, Table 16 was made at one-half scale and included centrifuging through a 5-inch solid bowl. After the first precipitation the waste solution contained 0.3% of the Ba* and the product carried 2 g lead. After the second precipitation 50 mg lead remained with the product that accounted for 90% of the barium. Waste from the second precipitation contained 0.6% of the barium.

An attempt was made to improve the settling characteristics of barium chromate by using 2 g. strontium (on the full scale). In such a test with only one product precipitation but other conditions similar to those of test 3, Table 16 and settling of the product precipitate, the Ba* losses were 4.9% with a yield of 93.1%. Strontium would follow barium through the nitrate precipitation but would be discarded in the waste from the chloride precipitation.

4.5 Volume Reduction after Electrolytic Separation of Lead

After the separation of lead by electrolysis a volume reduction step was considered necessary. Barium carbonate is crystalline (settles well) and has a low solubility (0.5 to 5% loss, tests 1 and 2 Table 17. Since it was fairly certain that iron would be present in the process solutions, the process was checked with iron present and this seemed to interfere with the settling of the precipitate (tests 3 and 4 Table 17).

TABLE 17

Volume Reduction after Electrolysis

250 ml electrolyzed solution (0.5 g Ba) was made 0.5M in K_2CO_3 by the addition of 4M K_2CO_3. Settled 30 minutes and the supernatant decanted.

Test Number	Remarks	Ba* Loss in Supernatant (%)
1	1 gm. Ba.	0.6
2		5.4, 0.5, 1.5
3	200 mg Fe	3.5
4. a b c d	In stainless steel, Ba. accumulated and dissolved in next batch of electrolyte, Fe likewise accumulated	8.2 11.7 4.8 13.1

4.6 Barium Nitrate Precipitation

4.61 Precipitation of $Ba(NO_3)_2$

Further purification of barium resulted from the precipitation of barium nitrate (a crystalline solid that settled well) from a solution that was 18 to 20M in HNO_3 (made by adding 5 volumes of 23M HNO_3 to 1 volume of aqueous solution containing barium). Losses in the waste, after settling, were below 3.6% when the barium concentration was greater than 130 mg per liter (table 18).

[redacted]

[redacted]

[illegible] Precipitate

[illegible]

[illegible]

[illegible] Precipitation

In nitric acid (15%) solutions containing RbO_3 up to 1.75M no precipitation occurred even when the solutions were seeded with solid RbO_3.

[illegible] Lead

The combination of carbonate and nitrate precipitations separated lead by factors as large as [illegible] In another experiment where [illegible] and [illegible] mg Pb in [illegible] ml of solution was treated with [illegible] M RbO_3 [illegible] the lead.

[redacted]

4.624 Iron, Chromium and Nickel

The separation of barium from Fe by the carbonate volume reduction and nitrate precipitations was shown to be sufficient to meet the requirements imposed, i.e. 10 mg in final product (see Table 19).

In another test where 200 mg each of Cr and Ni was added to 1 g. Ba in 100 ml solution and precipitation caused by the addition of 5 volumes 23M HNO_3, no detectable amounts of Cr and Ni were found in the product.

4.625 Strontium

The fuming HNO_3 step produced no significant separation of strontium from barium under the conditions employed. A solution (250 ml) containing 50 mg strontium with tracer and 500 mg inactive barium was treated with 5 volumes of 23M HNO_3, and agitated at room temperature for 30 minutes. The supernatant was decanted after allowing the precipitate to settle. The solid dissolved in 250 ml of water was re-precipitated twice more in the same manner. Analyses of waste solutions reveal 1.5, 4.3 and 3.5 mg Sr* lost in the supernatants and 49.8, 37.5 and 34.2 mg Sr* respectively in the dissolved product cakes.

4.63 Dissolving the $Ba(NO_3)_2$ Precipitate

It is difficult to dissolve the barium nitrate precipitate in a small volume of water unless the supernatant (18M HNO_3) were well separated from the crystals. Settling and decanting did not separate the supernatant sufficiently well to produce a readily soluble precipitate (1 gram total barium as nitrate and 200 ml. water).

[redacted]

[redacted]

TABLE 19

Separation from Lead and Iron

Test Number	Carbonate Waste	Ba* losses 18M HNO_3 Waste	Wash*	% Ba in Final Solution	Pb		Fe	
					Added mg	Residual mg	Added mg	Residual mg
1	3.4	3.4	0.3	90	25	8	-	1
2	1.9	2.5	0.8	96	25	5	-	1
3	4.6	1.5	3.5	118	50	7	50	1
4	4.0	2.0	3.5	92	50	1	50	1
5	3.7	1.8	1.1	85	50	26	100	1
6	4.8	3.0	1.4	93	50	88	100	1
7	3.6	1.7	0.4	89	50	17	200	7
8	3.5	0.6	0.5	87	50	99	200	7
9	2.5	0.8	0.5	72	28	16	250	2
10	3.8	1.0	0.6	86	28	9	250	2
11	2.7	0.2	0.4	83	200	43	25	3
12	3.7	0.5	0.4	94	200	26	25	3
13	-	0.3	0.1	107	—		-	-
14	-	0.2	0.2	107	—		-	-

*12 thru 17A one 10M HNO_3 wash.
18 thru 18A two washes with dioxane.
Runs 16 and 16A were from semi-works run Ba-27.

[redacted]

4.631 Washing with Dioxane

It was proposed that the nitric acid be removed by washing with dioxane (a water soluble organic solvent). Dioxane, however, does not appear satisfactory since there is a reaction between nitric acid and dioxane. Reaction with fuming nitric acid at room temperature gave voluminous brown fumes and a white solid (in 25% yield) that was identified as oxalic acid (by melting point, neutralization equivalent and permanganate titration).

4.632 Filtration

In the process that was finally adopted by the plant, the barium nitrate precipitate was filtered on a sintered glass disc to provide separation of solid from supernatnant with low hold-up of supernatant.

4.7 Chloride Precipitation

Operating experience in building 706-D proved the barium nitrate precipitation to be insufficient to provide the required decontamination from other metallic ions. Since 706-C had employed barium chloride precipitation with HCl-ether to good advantage, certain variables were checked in the laboratory before submitting the process to 706-D. The flow-sheet process has been outined in Table 20 along with the quantitative data obtained in several tests.

(1) Control tests on half and full scale revealed 2.6 and 3.4% Ba* lost in the supernatant; at the same time decontamination factors of 25 for Pb(II) and over 1000 for Fe(III) resulted (Tests 1 and 2).

(2) Doubling the volume of the aqueous solution containing tracer and carrier approached the limit of operability. At higher dilutions (3 and higher) waste losses amounted to 15% and more. (Tests 3 - 8).

(3) Little difference in the loss of Ba* in the waste resulted from a

variation of the ratio of volumes of HCl/ether between 0.1 and 6. At higher HCl concentrations, however, Pb(II) decontamination was better by a factor of 3. (Tests 9 and 10).

(4) The use of 3 or 4 times the flowsheet volume ratio of HCl-ether per tracer solution produced apparent higher losses in the supernatant. (A factor of 2 in tests 19 - 24 inclusive.)

(5) No significant difference in waste loss was noted by varying the temperature from 0 to 30°C. At the higher temperatures lead decontamination was better (factor 3 - 8) (Tests 25 - 28).

(6) Other organic solvents (namely dioxane, etheylene glycol, n-butanol and isopropanol were substituted for ether without significant changes in the waste losses (Tests 29 - 32).

(7) One-tenth scale tests with only alkali metal chlorides in the aqueous solution precipitated solid from a solution containing 10% KCl or 3% NaCl, no precipitate was formed with 20% NH_4Cl.

The precipitation of $BaCl_2$ by HCl-ether offers a convenient method for decontaminating the product precipitate. The range of conditions, in which the waste losses were reasonably low, was broad enough to permit remote control operation.

TABLE 20

Precipitation by the HCl-Ether Process

Full scale experiments utilized 50 ml barium (II) tracer solution containing 500 mg barium (II) carrier and 250 mg each of Pb(II) and Fe(III), to which was added 500 ml of a solution containing 5 volumes of 37% HCl and 1 volume diethyl ether. The mixture after agitation with air for 10 minutes at room temperature was filtered through a sintered glass disk and washed twice with 50 ml of ethyl alcohol solution containing 4% HCl.

[redacted]

No.	Scale	Departure from Procedure	Be* % Combined Supernatants	Be* % Products Solutions	Decontamination Factors Pb	Decontamination Factors Fe
1	0.5	None	2.6	97.2	25	1000
2	1	None	3.4	-	-	-
3	0.5	10 ml water added to tracer solution	3.0	94.5	35	1000
4	0.5	50 ml Ditto	3.6	-	33	1000
5	1	50 ml Ditto	6.8	-	33	-
6	1	100 ml Ditto	15.0	-	-	-
7	1	150 ml Ditto	28.8	-	-	-
8	0.5	200 ml Ditto	26.2	-	100	1000
9	1	Volume ratio 37% HCl/ether - 0.1	4.0	-	-	-
10	0.5	1	1.7	91	10	-
11	1	1	2.7	-	-	-
12	0.5	2	2.8	91	13	-
13	0.5	3	2.9	89	18	-
14	1	3	2.1	-	-	-
15	0.5	4	3.5	94	27	-
16	0.5	5 No Departure	3.2	89	28	-
17	1	5 Do	3.2	-	-	-
18	0.5	6	3.3	85	27	-
19	0.5	Volume ratio HCl-ether/tracer solution 5	4.0	100	17	-
20	0.5	10 Do	3.2	-	-	-
21	0.5	15	4.3	96	23	-
22	0.5	20	4.4	97	53	-
23	0.5	30	7.6	90	67	-
24	0.5	40	8.7	96	15	-
25	0.5	Digestion Temperature 0°C.	1.4	102	15	-
26	0.5	10°C	1.8	90	15	-
27	0.5	20	2.2	91	40	-
28	0.5	30 (Bpt ether 34 - 35°C)	2.8	89	125	-
29	0.5	Dioxane substituted for ether	2.9	92	36	1000
30	0.5	Ethylene glycol " " "	3.3	100	59	1000
31	0.5	N-Butanol " " "	2.5	90	21	1000
32	0.5	Iso-Propanol " " "	2.8	92	24	1000

[redacted]

4.8 Freezing Points of Process Solutions

No solidification or crystallization occurred on cooling the following solutions to -15°C; 60% HNO_3, coating removal waste solution, 95% H_2SO_4, 50% K_2CO_3, extract slurry, extraction waste, unwashed extraction cake, 50% H_2SO_4 (+ 2% HNO_3), 25% H_2SO_4 (1% H_2SO_4) and 48% UNH.

The 50% NaOH solidified at 20°C; the cooling curve shows a break at 6°C. 75% UNH freezes at 45°C; 6% $Pb(NO_3)_2$, at -1°C; $PbSO_4$ extraction cake slurry, at -3°C; metathesis waste, at -6°C; Na_2CO_3-Na_3PO_4 neutralizing solution for extraction waste, at 35°C; and the neutralized extraction waste, at -6°C.

5.0 Waste Disposal

Waste solutions from the process had to be alkaline for transporting through the waste system. The pipes are steel and the storage tanks are concrete; acid solutions might well cause serious damage that would be difficult to repair because of the radio activity. Since all of the solutions did contain large quantities of radioactive isotopes it was necessary to remove them through the regular hot waste system.

The solution containing aluminum from the jacket removal is alkaline and can be discarded without further treatment.

The waste metal solution from which has been precipitated lead sulfate carrying barium was made alkaline with sodium carbonate and tri-sodium phosphate. The composition of the solution then approaches the waste metal solution from the plutonium process.

Carbonate waste solutions from metathesis can be handled without further treatment.

The process chosen for the separation of lead from barium being electrolysis, one of the wastes for disposal was PbO_2 that had been plated on a platinum screen. This material dissolved readily in a mixture of HNO_3 and H_2O_2 and was neutralized with NaOH.

The concentrated HNO_3 waste was poured into 30% NaOH for neutralization.

Hydrochloric acid waste solutions were transferred from glass equipment and dropped onto a large volume of 1% NaOH to make alkaline and dilute.

The chromate waste disposal tests were made at 1/10 full scale. The amounts are given in full scale equivalents.

[redacted]

The $PbCrO_4$ by-product cake was slurried in 2 liters 8M HNO_3, 1 liter 4M $NaNO_2$ was added and 0.6 liters H_2O wash. Agitated with air for 1 hour at 90°C. (reduction of chromate). The reaction was complete in 20 minutes.

[redacted]

[redacted]

CN-2196

MonT-155
6/13/47

6.0 Bibliography

1. CN-2196 Kubsch - Preparation of Radioactive Barium - Lithium

2. MonT-155 Rodger - Summary of 706D Ba^{140} Production Runs 1-13.

MonT-155

[redacted]

7.0 Appendix

7.1 Microscopic Examination of Precipitates

Microphotographs were made of some of the precipitates prepared under varying conditions. All photographs were taken using the same magnification, about 150 diameters.

Lead sulfate crystals made in glass at increasing temperatures are shown in figures 1, 2 and 3. Larger crystals resulted from precipitation at higher temperatures; these larger crystals are more desirable for this precipitate that is separated by settling. The lead sulfate crystals shown in figures 4, 5, 6 and 7 were made under conditions more nearly approximating those recommended in the flowsheet. Large crystals resulted from high digestion temperatures in stainless steel also.

Lead chromate precipitate, shown in figure 8, contained large crystals which fact was reflected in the rapid settling rate of all similar lead chromate precipitates.

In figures 9 and 10 the small particle size is apparent. Poor settling (incomplete in 6 hours) was characteristic of most of the barium chromates prepared. None of the tricks employed made this precipitate settle any more rapidly.

Barium carbonate, in the concentration step, and barium nitrate shown in figures 11 and 12 respectively, were composed of large particles that settled well.

Figure 1. $PbSO_4$ crystals made by precipitating Pb from a 27% UNH solution at 3.4M in H_2SO_4 in glass at 20-30°C.

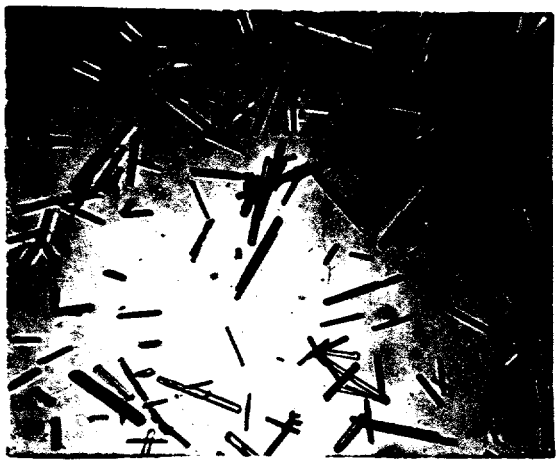

Figure 2. $PbSO_4$ crystals made as those in Figure 1 except at 50°-60°C.

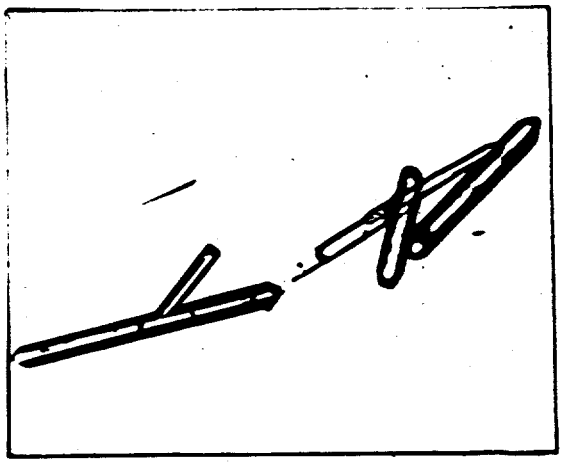

Figure 3. $PbSO_4$ crystals made as those in Figure 1 except at 90-100°C.

[redacted]

[redacted]

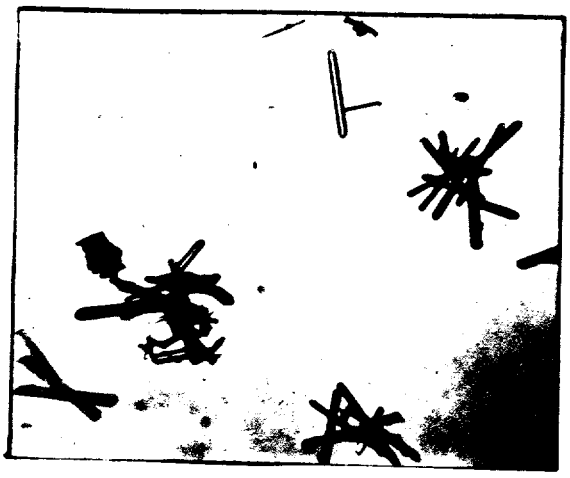

Figure 4. $PbSO_4$ crystals made by precipitating Pb from a 27% UNH solution at 2M H_2SO_4 at 20-30°C. in stainless steel.

Figure 5. $PbSO_4$ crystals made as those in Figure 4 except solution made 3.4M in H_2SO_4 and digested at 90°C.

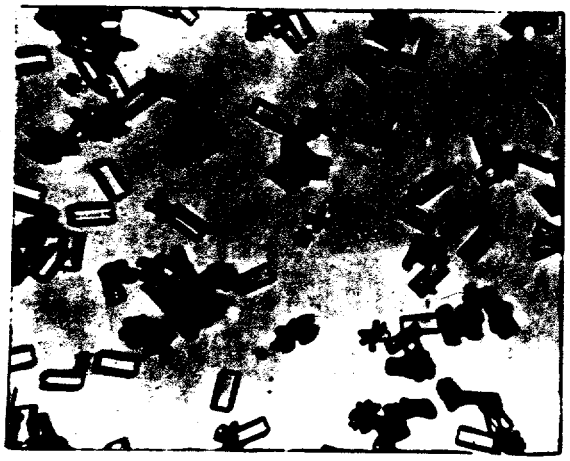

Figure 6. $PbSO_4$ crystals made by precipitating Pb from a 27% UNH solution at 2M H_2SO_4 at 90-100°C. in stainless steel.

[redacted]

[redacted]

Figure 7. $PbSO_4$ crystals made as those in Figure 6 except solution made 3.4M in H_2SO_4 and digested at 90°C.

Figure 8. $PbCrO_4$ crystals made at room temperature by adding 960 ml. 0.5M $Na_2Cr_2O_7$ solution over one hour to 625 ml. of solution containing 100 g. Pb, 0.5 g. Ba, 1.4M HNO_3.

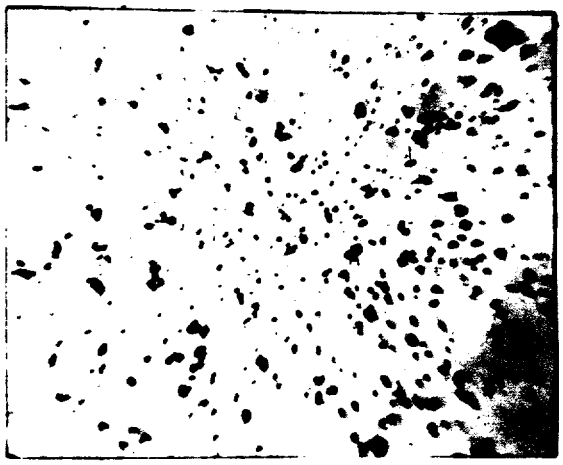

Figure 9. Ba CrO_4 crystals made by adding 800 ml. 10M NaOH over 1/2 hour at room temperature to the clear effluent remaining over $PbCrO_4$ precipitate of Figure 4.

[redacted]

[redacted]

Figure 10. $BaCrO_4$ crystals made by adding to the clear effluent remaining over $PbCrO_4$ precipitate of Figure 4, 25 ml. 3% H_2O_2, then adding at 70-80°C. over 0.5 hours 800 ml. 10M NaOH and digesting 0.5 hours.

Figure 11. $BaCO_3$ crystals, carbonate concentration step, made by adding 50% K_2CO_3 solution to the electrolyzed solution at room temperature until 0.5M in K_2CO_3.

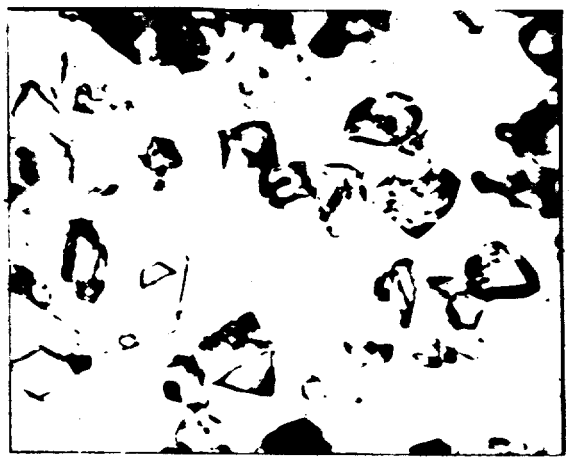

Figure 12. $Ba(NO_3)_2$ crystals made by adding fuming HNO_3 to $Ba(NO_3)_2$ solution until 16M in HNO_3.

[redacted]