RI 7990

Bureau of Mines Report of Investigations/1974

Recovery and Separation of Rare-Earth Elements, Barium, and Strontium From Bastnäsite With Sulfuric Acid

UNITED STATES DEPARTMENT OF THE INTERIOR

Report of Investigations 7990

Recovery and Separation of Rare-Earth Elements, Barium, and Strontium From Bastnäsite With Sulfuric Acid

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March 3, 1849

UNITED STATES DEPARTMENT OF THE INTERIOR
Rogers C. B. Morton, Secretary

Jack W. Carlson, Assistant Secretary–Energy and Minerals

BUREAU OF MINES
Thomas V. Falkie, Director

This publication has been cataloged as follows:

Eisele, Judith A

Recovery and separation of rare-earth elements, barium, and strontium from bastnäsite with sulfuric acid, by J. A. Eisele and D. J. Bauer. [Washington] U.S. Bureau of Mines [1974]

10 p. illus., tables. (U.S. Bureau of Mines. Report of investigations (7990)

Includes bibliography.

1. Earths, Rare. 2. Alkaline earth metals. 3. Strontium. 4. Barium. 5. Bastnäsite. I. U.S. Bureau of Mines. II. Bauer, Donald J., jt. auth. III. Title. (Series)

TN23.U7 no. 7990 622.06173

U.S. Dept. of the Int. Library

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RECOVERY AND SEPARATION OF RARE-EARTH ELEMENTS, BARIUM, AND STRONTIUM FROM BASTNÄSITE WITH SULFURIC ACID

by

J. A. Eisele[1] and D. J. Bauer[2]

ABSTRACT

The Bureau of Mines conducted a bench-scale investigation of a concentrated H_2SO_4 reaction for recovering and separating rare-earth elements, barium, and strontium from a bastnäsite ore and byproduct. Barium and strontium were dissolved in the concentrated acid and precipitated as a mixed product by water dilution. Separation of strontium from barium was effected by reaction with Na_2CO_3 solution, followed by a dilute acid leach of the $SrCO_3$ formed.

After removing the barium and strontium from bastnäsite ore, the rare-earth elements were roasted to water-soluble sulfates. The rare-earth sulfate solution was subsequently processed by solvent extraction to produce rare-earth oxides low in lead and magnesium.

INTRODUCTION

Bastnäsite, a rare-earth fluocarbonate containing predominantly light rare-earth elements La through Nd is the main source of rare-earth elements in the United States; the largest known deposit in the world is at Mountain Pass, Calif. Bastnäsite occurs in close association with barite, celestite, strontianite, calcite, and silica gangue. The material is processed by flotation concentration of the rare-earth elements, followed by hydrochloric acid leaching and roasting, to give a high-grade rare-earth oxide concentrate, which can then be further processed into commercial products (3).[3] The flotation step generates a large quantity of tailings containing barium, strontium, and calcium.

The barium and strontium are not presently being separated because of economic considerations. Strontium minerals are not produced in the United States because it is cheaper to import high-grade foreign material than to beneficiate the lower grade domestic resources. (However, if consumption

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[1] Research chemist.

[2] Supervisory chemical engineer.

[3] Underlined numbers in parentheses refer to items in the bibliography at the end of this report.

increases as predicted, a shortage could develop in the coming years, and the increased price for strontium chemical would make their domestic production more favorable.) Barite is used mainly for drilling-mud formulations and, although produced domestically from extensive United States deposits, large quantities of it are imported.

This study was originally undertaken by the Bureau of Mines to develop a method for converting domestic barite tailings into potentially marketable products. The method developed to treat the tailings was then extended to the bastnäsite ore to provide an integrated process offering the following advantages: (1) the rare-earth oxide product is lower in lead and phosphorus content than is obtainable in the present method of processing, (2) recovery of rare-earth elements is improved, and (3) potentially marketable byproducts are produced.

MATERIALS AND PROCEDURES

Materials

The barite concentrate used in this study was obtained from Molycorp's Mountain Pass mine and mill, and was made by floating $BaSO_4$, $SrSO_4$, and $SrCO_3$ away from $CaCO_3$ and gangue in the barite tailings. Composition of a typical barite concentrate is given in table 1. The tailings are generated at the rate of approximately 280,000 tons per year.

TABLE 1. - Composition of barite flotation concentrate

	Percent
$BaSO_4$	72.1
$SrSO_4$[1]	22.4
$CaCO_3$	2.5

[1] A small amount of the strontium is present as carbonate.

Microprobe analysis of the barite concentrate showed strontium to be present with barium in almost continuous series from barite to celestite. No other barium minerals were present; however, some strontium is present as strontianite. The barite concentrate received from Molycorp was leached with dilute HCl[4] to remove the remaining calcium, which also dissolved the strontium present as strontianite and resulted in a product containing 75 pct barium sulfate and 22 pct strontium sulfate. This was used as a starting material for experiments to recover pure barium and strontium compounds.

The bastnäsite ore used was rod-mill feed from the Mountain Pass operation and had the composition presented in table 2. Microprobe analysis of this material showed a small amount of the rare-earth elements to be present as monazite, which is also the main source of phosphorus. The small amount of lead is present as galena, and the iron is present as oxides. Barium,

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[4] All chemicals used were reagent-grade, except H_2SO_4, which was technical-grade.

strontium, and calcium are found in the same mineral assemblages as reported for the barite tailings concentrate.

TABLE 2. - Composition of bastnäsite ore, percent

	Rod-mill feed	HCl-leached feed
Rare-earth oxide[1]	7.05	12.4
Calcium..........	15.5	.1
Strontium........	8.5	6.7
Barium...........	13.6	21.6
Fluorine.........	.9	([2])
Iron.............	1.8	3

[1] Rare-earth oxide consists of 32 pct La, 48 pct Ce, 35 pct Pr, 12.3 pct Nd, and 0.7 pct Sm.

[2] Not determined.

Procedures

The bastnäsite ore was leached with 10 pct HCl to remove calcium prior to reaction with H_2SO_4; otherwise, the calcium would report with the barium-strontium fraction, where it was difficult to remove. The composition of the leached bastnäsite is given in table 2.

Both the barite concentrate and the HCl-leached ore were reacted with concentrated H_2SO_4 at 150° C for 4 hours. The slurry was stirred during the entire reaction period. The mixture was cooled, and the acid was separated from the residue by centrifugation. The residue was repulped with fresh acid, and centrifuged again to wash it. Barium and strontium were recovered from the concentrated H_2SO_4 by carefully adding the acid to an equal volume of water; $BaSO_4$ and $SrSO_4$, which are soluble in concentrated H_2SO_4, are insoluble in dilute acid and precipitate.

In experiments where the barium and strontium sulfates were to be further reacted with Na_2CO_3, it was necessary to keep the precipitates damp in order to obtain a good reaction because the dried sulfates formed lumps that were difficult to break up. The moist sulfates were reacted with Na_2CO_3 solutions at the boiling point for 30 min, filtered, then leached with dilute HCl to dissolve the $SrCO_3$ formed by metathesis. To change all the strontium into CO_3 form, it was necessary to use conditions that also converted some of the barium. This left a relatively pure (98 to 99 pct) $BaSO_4$ residue, but the HCl solution contained both strontium and barium. A controlled amount of Na_2SO_4 was added to precipitate the barium.

The residue remaining after reacting the barite concentrate with concentrated H_2SO_4 was discarded. When using rod-mill feed, the residue contained the rare-earth elements. This residue was mixed with enough additional H_2SO_4 to give a thick paste and roasted at 650° C for 2 hours to convert the rare-earth elements into sulfates. The cooled calcine was water-leached to recover the soluble rare-earth sulfates.

RESULTS AND DISCUSSION

Barite Tailings Concentrate

Barium and strontium are difficult to separate efficiently because of their close chemical similarity. The solubility products of the sulfates and carbonates of these elements follow:

$BaSO_4$	9×10^{-11}
$BaCO_3$	1.2×10^{-8}
$SrSO_4$	3.8×10^{-7}
$SrCO_3$	5.5×10^{-9}

From these, it can be seen that $SrSO_4$, although relatively insoluble, has a solubility product condiderably greater than that of $BaSO_4$, and the solubility of $SrCO_3$ is even less than that of $SrSO_4$. For this reason, it is expected that when a mixture of $BaSO_4$ and $SrSO_4$ is reacted with a carbonate solution, strontium will be preferentially metathesized to the carbonate.

Some initial experiments were carried out with barite concentrate containing calcium, but it was discovered that, because it followed the strontium, the 1 pct calcium remaining in the concentrate was difficult to remove. Hydrochloric acid was used to leach the calcium. Dilute acid of pH 2 and a reaction time of 1 min were sufficient to remove calcium from the concentrate.

A first approach to producing pure barium and strontium products was to react the calcium-free tailings concentrate with Na_2CO_3 solution under various conditions, in an attempt to change the $SrSO_4$ to $SrCO_3$. Approximately half the strontium was easily converted and could, after filtration, be removed by dilute acid leaching; the other half resisted metathesis, even under severe conditions. Microprobe analysis of the barite concentrate and of a metathesized-leached sample showed that the high-ratio celestite-barite and strontianite particles were gone; however, where celestite was enclosed by barite, it had not reacted. To make a clean barium-strontium separation, the entire crystal structure was disrupted by dissolving the barium and strontium sulfates in hot concentrated H_2SO_4. Table 3 presents the results of studies to determine the reaction temperature and amount of acid needed to achieve complete dissolution. An earlier test had shown that 30 min was sufficient time for reaction and that, even in 10 min, most of the sample had reacted.

From table 3, it can be seen that a large excess of H_2SO_4 (500 ml H_2SO_4/ 75 g barite concentrate, or 12 lb H_2SO_4/lb barite) must be used. As this acid is diluted with an equal volume of water to recover the barium and strontium sulfates, provision must be made for evaporating the water and recovering the acid for recycling. Temperatures below 150° C resulted in decreased recovery of barium and strontium.

TABLE 3. - Dissolution of mixed barium and strontium sulfates in concentrated H_2SO_4

Concentrated H_2SO_4, ml[1]	Temperature, ° C[2]	Composition of dissolved material			Tailings	
		Total, g[3]	$BaSO_4$, pct	$SrSO_4$, pct	Total, g	Major component(s)[4]
125	150	22.5	54.0	42.3	52.0	Ba
250	150	45.9	68.0	28.6	30.1	Ba
350	150	60.6	74.2	24.1	16.4	Ba
500	150	70.2	75.3	22.3	6.5	Si, Mg, Fe
1,000	150	69.2	77.6	22.0	6.4	Si, Mg, Fe
500	125	57.1	70.5	24.7	19.6	Ba
500	100	61.1	72.5	26.4	15.9	Ba
500	75	64.3	72.4	22.9	13.3	Ba

[1] Per 75-g charge.

[2] Charge held at reaction temperature for 30 min.

[3] Measured by precipitating the Ba and $SrSO_4$ by water dilution and drying.

[4] Spectrographic analysis.

The sulfates, when dried and roasted to remove occluded H_2SO_4, have a specific gravity of 4.15 to 4.23, marginally acceptable for drilling-mud formulations. American Petroleum Institute specifications call for a minimum specific gravity of 4.20 for barites intended for drilling mud.

To further separate the mixed sulfates into individual barium and strontium products, the damp sulfates were metathesized with Na_2CO_3. Table 4 gives the results of using various amounts of Na_2CO_3 with the sulfates obtained from 75 g of barite concentrate. To convert all the strontium, large amounts of Na_2CO_3 must be used, and much of the barium is also reacted. The Na_2CO_3 solution separated from the Ba-Sr-SO_4-CO_3 residue can be made up to the desired strength and reused. The reacted solids were leached with HCl solution (pH 0.5) to dissolve barium and strontium carbonates and leave a residue of 98 pct $BaSO_4$. Barium sulfate of this purity meets the specification for barium content for "blanc fixe," a relatively high-priced barium compound.

TABLE 4. - Metathesis of $SrSO_4$ and $BaSO_4$ with Na_2CO_3

Na_2CO_3, g[2]	HCl soluble[1]		Residue		
	$BaSO_4$, g	$SrSO_4$, g	$BaSO_4$, g	$BaSO_4$, pct	$SrSO_4$, g
10	0.02	0.02	36.1	73.7	11.1
20	.02	.15	37.1	74.2	12.4
30	.02	.59	37.2	75.9	10.6
60	.03	4.4	40.9	87.1	6.4
90	15.3	11.0	34.8	96.8	1.19
150	24.8	10.6	21.7	98.5	.51

[1] After reacting the mixed sulfates for 30 min at 97° C, the mixture was leached with dilute HCl (pH 0.5) to remove metathesis products.

[2] Per 75-g starting charge of barite tailings. The Na_2CO_3 was dissolved in 500 ml of H_2O.

A relatively pure strontium product can be recovered from the HCl solution by adding Na_2SO_4 to precipitate the barium. The results of adding various amounts of Na_2SO_4 are shown in table 5. Here again, to obtain a clean strontium product, some of it must be sacrificed in order to precipitate all the barium. Strontium can then be recovered from the barium-free solution by precipitation or evaporation. The mixture of barium and strontium sulfates resulting from the Na_2SO_4 precipitation step can be returned to the Na_2CO_3 metathesis step.

TABLE 5. - Amount of Na_2SO_4 needed to precipitate barium from acidic chloride solution

Grams of Na_2SO_4 per gram of Ba	Remaining in solution	
	Barium, g/l	Strontium, g/l
0 (head solution)..	3.1	3.0
0.32...............	2.4	3.0
.65...............	1.6	3.0
.97...............	1.0	2.7
1.29...............	.4	2.7
1.61...............	.05	2.3
1.94...............	.03	2.0

Bastnäsite

The foregoing studies proved the feasibility of utilizing a concentrated H_2SO_4 reaction as a basis for separating barium and strontium from a mixed byproduct of bastnäsite. A logical extension of this work was to react the bastnäsite ore itself with concentrated H_2SO_4. The latter reaction could have the additional advantage of eliminating grinding and flotation, and could result in high recovery of rare-earth sulfates at lower cost.

It became evident that the concentrated H_2SO_4 treatment would break down the coarse ore. But, as explained for the barite tailings, it was necessary to remove calcium prior to H_2SO_4 treatment. One liter of 10 pct HCl was used to remove the calcium from 100 g of crusher material. Once the calcium was removed, the material was reacted with H_2SO_4 in the same manner as the barite concentrate, using 500 ml of H_2SO_4/75 g of ore. Table 6 shows the composition of leached rod-mill feed and the recovery of barium and strontium by H_2SO_4 treatment. The small amount of rare-earth elements present in the acid-soluble product is due to the monazite present in the bastnäsite; the rare-earth phosphates are soluble in concentrated H_2SO_4 and are precipitated with barium and strontium on water dilution. The barium-strontium product has a specific gravity of 4.17 ±0.05 and is marginally acceptable for drilling mud without further treatment. Alternately, it may be subjected to Na_2CO_3 metathesis to produce separate barium and strontium products as already described.

TABLE 6. - Recovery of barium and strontium from calcium-free rod-mill feed

	Calcium-free feed[1]			Acid-soluble product		
	Rare-earth oxide	Barium	Strontium	Rare-earth oxide	Barium	Strontium
Weight-percent........	12.4	21.6	6.7	1.3	43.7	10.7
Grams.................	18.6	32.4	10.1	.9	30.0	7.3
Recovery.........pct..	-	-	-	-	93	73.0

[1] 150-g charge; treated with 1 liter concentrated H_2SO_4

The residue from the concentrated H_2SO_4 treatment was roasted with additional H_2SO_4 at 650° C for 2 hours to completely convert the rare-earth fluocarbonates to sulfates. A lower temperature roast did not give complete conversion. When the cooled calcine was water-leached, 97 pct of the total rare-earth elements were dissolved. The leach solution also contained 0.6 g/l Fe, 0.8 g/l Mg, 1 ppm Pb, and no detectable P. Rare-earth elements can be directly precipitated from this solution by oxalic acid or base, and roasted to the oxide. However, when the oxides are to be used as cell feed to produce misch metal, lead is undesirable because it concentrates in the electrolyte bath. When phosphorus is present in rare-earth oxide cell feed, it forms phosphine, which is slowly released from the metal and constitutes a health hazard. The rare-earth oxides produced by the current commercial process contain from 0.5 to 2 pct P_2O_5. Presumably, magnesium would also build up in the cell bath. At this point, the sulfate solution was processed by solvent extraction to separate the rare-earth elements from some of the impurities.

The leach solution was contacted with 20 pct Primene JMT[5] (a commercial primary amine) in kerosine to extract the rare-earth elements, which were subsequently stripped from the organic phase with acid. Lead and magnesium impurities in the rare-earth oxide product were reduced to the levels shown in table 7. Iron is evidently extracted and stripped with the rare-earth elements as it is concentrated in the solvent-extraction purified product. This should cause no problem when the rare-earth oxides are used as cell feed to produce misch metal, which is then added to iron or steel to modify its properties. On a long-term basis, however, it could build up in the cell bath and spoil the electrolyte.

TABLE 7. - Impurities in rare-earth oxides. Precipitates made directly from leach solution and from solution purified by SX

	Directly precipitated	SX purified
RE_2O_3............wt-pct[1]..	98.8	98.6
Mg..............wt-pct[2]..	0.061	0.002
Pb.................ppm[2]..	65	(3)
P...............wt-pct[2]..	0.016	(3)
Fe..............wt-pct[2]..	0.035	0.47

[1] Determined by X-ray analysis of individual rare-earth elements.

[2] Determined by wet-chemical methods.

[3] Not detected spectroscopically.

The rare-earth sulfate solution could also be used as feed for a solvent-extraction circuit to recover individual rare-earth elements (1, 4).

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[5] Reference to specific brands is made for identification only and does not imply endorsement by the Bureau of Mines.

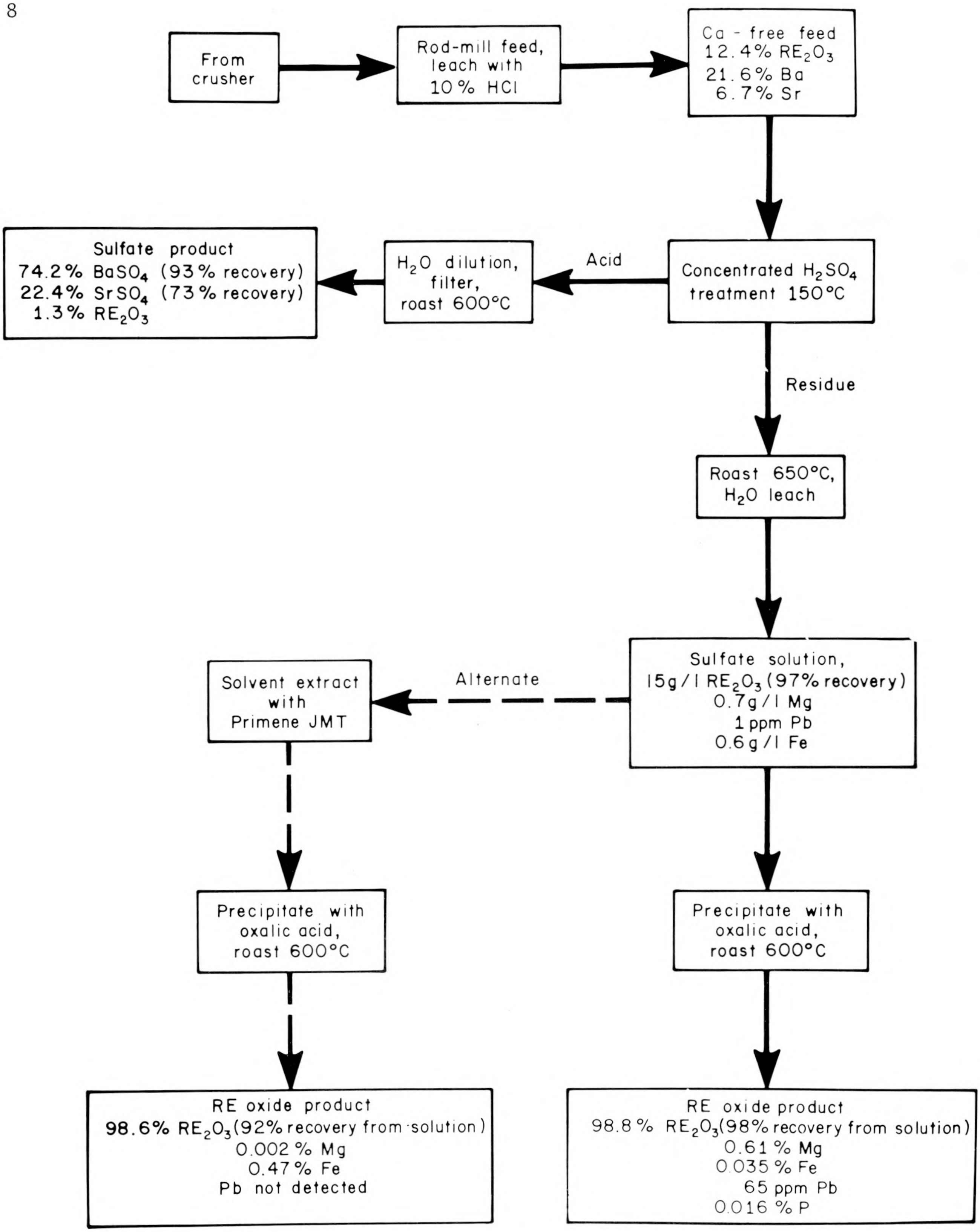

FIGURE 1. - Flow diagram for treatment of bastnäsite with concentrated H_2SO_4.

Figure 1 is a flow diagram of the sulfuric acid process for treating bastnäsite for recovery of rare-earth elements, barium, and strontium. The final recovery of rare-earth elements from bastnäsite using H_2SO_4 is probably higher than can be obtained by any process using a flotation concentration step.

CONCLUSIONS

A process has been described that yields a high recovery of rare-earth elements from bastnäsite, as well as recovering usuable byproducts of barium and strontium either as combined sulfates for drilling-mud formulations or as pure barium and strontium chemicals. The rare-earth oxide products obtained from such a process would be low in phosphorus and lead impurities, which are presently a problem in rare-earth oxide cell feed used to produce misch metal.

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U.S.G.P.O.—1974-606-064/543

INT.-BU.OF MINES,PGH.,PA. 19813