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THE DISTRIBUTION OF BORON AND MOLYBDENUM IN THE RECOVERY OF
NITRIC ACID AND CALCIUM NITRATE FROM RAFFINATES ORIGINATING
WITH PITCHBLLENDE

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WITH PITCHBLEND

I. INTRODUCTION

Every impurity present in the ore must find some point in the process where it can separate at the rate it enters the system or else it will build up to undesirable concentrations. Some of the impurities are insoluble, some are precipitated, and others remain in the raffinate from the ether extraction. Since it is planned to recover nitric acid and calcium nitrate from the raffinate for recycling, care must be exercised that no impurity is returned to the system with them in significant quantities. Boron seems the most likely source of danger, especially since boric acid is known to steam distill and therefore might appear in recovered nitric acid. Molybdenum is also a special case since it tends to extract into ether under the same conditions as uranyl nitrate.

II. DISCUSSION

This work consists of three parts: a) A study of the boron distribution between distilled nitric acid and the residual raffinate concentrate containing most of the impurities originally present; (b) a study of the conditions for precipitation of most of the cations from this concentrate, using lime as the precipitant, and of the

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distribution of boron and molybdenum under optimum precipitation conditions; and (c) a study of the distribution of boron in crystallization of calcium nitrate from the filtrate obtained from the lime precipitation.

a) The major difficulty was analytical, in that the determination of traces of boron is difficult in the presence of both nitric acid and the cations present in pitchblende raffinates. Furthermore the nitric acid precludes separation of the boron as methyl borate. It was found possible, however, to determine the boron in the presence of calcium nitrate and smaller amounts of nitric acid by application of a potentiometric mannitol titration method ⁽¹⁾. This, coupled with the practice of adding known amounts of boron to solutions under investigation, enabled the obtaining of limiting percentages in the distribution sought, even though establishing a complete boron balance was not feasible. By solving two simultaneous equations involving two unknowns, it is possible to estimate the boron originally present, from determination of the amounts distilled and comparison with the amounts added. Such estimates give lower and more probable values than the limiting values, but even the latter are sufficiently low to prove that serious proportions of boron will not be returned to the system via recovered nitric acid.

b) The same difficulties in analysis also apply here, and a similar approach is applicable. Actually, however, the results on early tests showed such a low boron value in the filtrate, and the results in section (c) were so favorable that extensive experiments were not attempted. The molybdenum balance presented no problem.

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c) Since recovered calcium nitrate will probably be used without washing, the centrifuged crystals will be covered with a layer of mother liquor which will be richer in boron than the crystals themselves. This makes it difficult to obtain a boron balance representing the true distribution, but for practical application the figures given below should be representative. No analytical difficulty was present here except that the precision was only fair, though satisfactory for the small amounts involved.

III. EXPERIMENTAL

a) In a typical experiment one liter of raffinate, to which 65 mg of boron as boric acid was added, was distilled until a temperature of 126°C was attained. Four cuts were taken of the distillate which were analyzed for HNO_3 and B. The results given in Table I show 2.25 mg., or 3.6%, of the added boron in the combined distillate.

TABLE I

Distillation of HNO_3 and Boron from a Pitchblende Raffinate

<u>Cut #</u>	<u>g HNO_3</u>	<u>mg B</u>
1	1.14	0.10
2	12.6	0.30
3	23.4	1.64
4	13.4	0.21

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b) To each of several 500 ml. portions of raffinate different amounts of lime were added and the solutions boiled for 30 minutes, filtered, cooled, and the pH measured. The maximum filter rate was found at pH 10.5. At this point precipitation is complete as shown by a potentiometric titration and by spectrographic analysis of the filtrate. Based also on spectrographic analysis of precipitates obtained in a fractional precipitation, the order of precipitation is V, Fe, Cu, Ni, Mg. Molybdenum and boron balances were made for the precipitation at pH 10.5. It was found that 99.2% of the molybdenum and 67% of the boron were in the precipitate.

c) In a typical experiment, 3 kg. of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ was dissolved in water and sufficient boric acid added to make the boron content 100 p.p.m. The resulting solution was boiled down to 125°C, cooled, and the crystals centrifuged out. The mother liquor was again boiled down to 125°C and a second crop of crystals obtained. Approximately 75% of the $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ was recovered as crystals. These were combined and analyzed for boron. Twelve percent of the original boron appeared in the crystals. In another experiment where less boron (10 p.p.m.) was added, 32% appeared in the crystals. As pointed out above, most of this can probably be accounted for by adhering mother liquor.

III. SUMMARY

In processing pitchblende raffinates for recovery of nitric acid and calcium nitrate, approximately 99% of the molybdenum is precipitated with the metallic hydroxides by a lime treatment. The

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limiting quantities of boron returned to the system are approximately 32% with the recovered nitric acid, and 32% of 33% of the remainder, or 8%, with the recovered calcium nitrate. The estimated most probable values are 2% with the nitric acid and 7% with the calcium nitrate, or less than 10% overall. This figure could be cut further by means of a quick wash of the centrifuged calcium nitrate crystals.

IV. LITERATURE CITED

- (1) Ruehle, A.E. and Shock, D.A., J. Ind. Eng. Chem. (Anal. Ed.) 17 453 (1945)

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