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TECHNOLOGY-FEED MATERIALS

THE SALTING-IN AND SUPERSATURATION
OF BARIUM AND LEAD SULFATES IN
URANYL NITRATE SOLUTIONS DERIVED
FROM PITCHBLEND

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THE SALTING-IN AND SUPERSATURATION OF BARIUM AND
LEAD SULFATES IN URANYL NITRATE SOLUTIONS DERIVED
FROM PITCHBLEND

I. INTRODUCTION

Uranyl nitrate solutions derived from pitchblende are treated with sulfate to remove most of the lead, and then treated with a barium salt to remove excess sulfate. They are, therefore, saturated with barium sulfate and also contain some lead ion. During ether extraction of such solutions a precipitate frequently appears which tends to clog the spaces between the column packings. Analysis of this precipitate shows it to be largely barium sulfate plus some lead sulfate. As a step toward eliminating the difficulty, it was necessary to know whether the sulfates were being salted-in or were merely supersaturating, and to find out what other factors might affect the observed precipitation. Both natural liquors from pitchblende and synthetic uranyl nitrate solutions were used for tests which were designed to study separately the properties of barium sulfate and of lead sulfate.

II. DISCUSSION

Supersaturation was studied by seeding the liquors with weighed quantities of barium sulfate and filtering the suspended material thru weighed fritted glass crucibles after shaking overnight. After washing, the residue was dried and weighed, the increase in weight representing precipitated BaSO_4 . Salting-in by uranyl

nitrate was studied by extracting the uranyl nitrate with ether and filtering the precipitated BaSO_4 after an overnight stand.

As will be seen from the data given below salting-in was by far the more important factor in the observed precipitation. If another salting-in agent of potency equal to or greater than that shown by the uranyl nitrate could be added to the solutions, the BaSO_4 would be held in even after the uranyl nitrate was removed. Calcium nitrate, normally added to increase the extraction efficiency of uranyl nitrate into ether, was found to have very little salting-in action on BaSO_4 . Ferric nitrate, however, which is a possible alternative to calcium nitrate as an extraction salting agent⁽¹⁾ was found to be similar to uranyl nitrate in its salting-in action on both barium and lead sulfates. While some precipitation was still observed on standing, it occurred at a sufficiently slow rate to permit the raffinate to leave the extraction column before an appreciable deposit would appear on the column packing.

While substitution of ferric nitrate for calcium nitrate effectively prevents the unwanted deposit in the column, it involves other changes in the system which require further study. Another alternative would, therefore, be of interest. A partial solution was found in a buildown procedure. In considering this possibility it was thought the salting-in effect of uranyl nitrate might not vary linearly with concentration, and might even go thru a maximum, whereas the volume effect on the total amount of BaSO_4 in solution would of necessity be linear. Therefore a buildown of the barium

treated liquors before filtration of the BaSO_4 , followed by dilution of the filtrate to the original volume might leave less BaSO_4 in solution at equilibrium. Furthermore, the attainment of equilibrium in the BaSO_4 precipitation should be more nearly complete. Both of these effects were realized in the actual experiments. In spite of considerable improvement, however, some precipitation still occurred. If desirable these two treatments could be used to complement each other.

III. EXPERIMENTAL

An artificial feed solution was prepared from 800 grams of uranyl nitrate hexahydrate dissolved in water, 60 ml concentrated nitric acid added, and made up to 1 liter. Sodium sulfate was added to this solution and the sulfate ion precipitated by adding a slight excess of BaCO_3 , boiling, and filtering. A natural feed solution was prepared from pitchblende by dissolving in nitric acid, precipitating lead with sulfate, and removing excess sulfate with barium carbonate. The uranium concentrations in the resulting solutions were approximately the same.

One hundred ml portions of each of these solutions were seeded with 0.5000 g BaSO_4 and shaken overnight in a Fisher Gyrosolver. Similar portions were salted with 20 g $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ per 100 ml of solution and similarly seeded and shaken. Similar calcium nitrate salted and unsalted portions were extracted with four successive 200 ml portions of ether containing one mol of nitric acid per liter. The raffinate from the extraction were allowed to stand overnight before filtering in weighed fritted glass crucibles. The results follow:

TABLE I

Salting-in and Supersaturation of BaSO_4 in $\text{UO}_2(\text{UO}_3)_2$ Solutions

Conditions	Salted in BaSO_4 (mg/l)	Supersaturated BaSO_4 (mg/l)
Artificial feed shaken seeded		37
Artificial feed extracted	665	
Artificial feed + calcium nitrate shaken seeded		15
Artificial feed + calcium nitrate extracted	562	
Natural feed shaken seeded		34
Natural feed extracted	842	
Natural feed + calcium nitrate shaken seeded		72
Natural feed + calcium nitrate extracted	1324	

In experiments on similar, but not identical, solutions in which 220 g/l of ferric nitrate was substituted for calcium nitrate, there was no precipitate present immediately after extraction. On standing overnight, however, precipitation occurred in the raffinates, but these precipitates amounted to less than 60% of those obtained from unsalted feeds.

An artificial feed solution containing 1 gram per ml of uranyl nitrate hexahydrate was acidified with nitric acid, and added sulfate was precipitated with BaCO_3 as above. A 250 ml portion of the unfiltered solution was boiled down until a temperature of 118°C was reached. The volume was then 135 ml. While still hot the BaSO_4 precipitate was filtered off and washed. The combined washings and filtrate were diluted to 250 ml, cooled, and extracted with four 500 ml portions of ether. Approximately 60% of the original barium sulfate was precipitated in the raffinate on standing, as compared to 90% from a similar solution which was boiled at constant volume for the same length of time.

Less work was done on lead sulfate, but enough measurements were made to show similar behavior to that of barium sulfate. The salting-in was very strong, more than 30 g/l of PbSO_4 being retained in a 500 g/l uranyl nitrate solution even on standing as long as 48 hours. This explains the otherwise surprising fact that appreciable amounts of lead are left in feed solutions which have been treated with a three to six fold excess of sulfate, and that lead sulfate precipitates out of such solutions on extraction of the uranyl nitrate. In one experiment using ferric nitrate salting in an artificial feed saturated with PbSO_4 67% of the PbSO_4 present was prevented from precipitating immediately after extraction, although another 50% was precipitated on long standing. In a natural feed

the immediate precipitation was zero due to the fact that such solutions are not saturated with lead sulfate after the removal of sulfate ion by barium. The effect of the boildown treatment was not tried on lead sulfate.

IV. SUMMARY

The supersaturation of barium sulfate is less than 5% as great as the salting-in of barium sulfate by uranyl nitrate. Lead sulfate is salted-in very strongly by uranyl nitrate, its solubility in concentrated solutions being as much as 500 times its solubility in water. Ferric nitrate is much more effective than calcium nitrate in holding barium sulfate and/or lead sulfate in solution on extraction of the uranyl nitrate with ether. A boildown procedure is helpful in reducing the amount of barium sulfate dissolved in uranyl nitrate solutions.

V. LITERATURE CITED

- (1) Barnes Et. al. - Mallinckrodt Chemical Works Research Report No. 18 of this group.

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