UNCLASSIFIED

NYO-1320

Subject Category: METALLURGY-RAW MATERIALS

UNITED STATES ATOMIC ENERGY COMMISSION

THE SOLUBILITY OF CALCIUM SULFATE
IN SOME RAFFINATES

By
O. J. Buckheim
R. M. Paine
A. E. Ruehle

CLASSIFICATION CANCELLED
DATE FEB 28 1957 *DE*
For The Atomic Energy Commission
H. F. Canale
Chief, Declassification Branch

Price \$ *0.25*

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

March 9, 1951

Mallinckrodt Chemical Works
St. Louis, Missouri

Technical Information Service, Oak Ridge, Tennessee

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission to the extent that such employee or contractor prepares, handles or distributes, or provides access to, any information pursuant to his employment or contract with the Commission.

UNCLASSIFIED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

[REDACTED]

This report has been reviewed under the Declassification Guide of 1955.

The Atomic Energy Commission makes no representation or warranty as to the accuracy or usefulness of information or statements contained in this report, or that the use of any information, apparatus, method or process disclosed in this report may infringe privately-owned rights. The Commission assumes no liability with respect to the use of, or for damages resulting from the use of, any information, apparatus, method or process disclosed in this report.

This report has been reproduced directly from the best available copy.

Printed in USA, Charge 25 cents. Available from the Technical Information Service, P. O. Box 1001, Oak Ridge, Tennessee. Please direct to the same address inquiries concerning the procurement of classified AEC reports.

[REDACTED]

0312281031

AEC, Oak Ridge, Tenn.

UNCLASSIFIED

NYO-1320

The Solubility of Calcium Sulfate in Some Raffinates

by

O. J. Buckheim

R. M. Paine

A. E. Rushle

Classification cancelled (or changed to) UNCLASSIFIED

by authority of NYO AEC-381 2/28/57

by Jack Redenow TIE, date 3/14/57

Kallinckrodt Chemical Works

St. Louis, Mo.

March 9, 1951

This document is
PUBLICLY RELEASABLE

H. K. Kinsman
Authorizing Official
Date: 12/21/09

- 3 -

UNCLASSIFIED

~~CONFIDENTIAL~~

NYO-1320

- 4 -

Summary:

The approximate solubility of calcium sulfate in several ether-saturated raffinates was measured as equilibrium was approached from the high side. The effect of varying concentrations of iron, calcium, sulfate, and nitric acid on the solubility of calcium sulfate was determined.

Conclusions:

1. The solubility of calcium sulfate in raffinates containing 30 g/l of excess HNO_3 is strongly dependent on the Fe^{+++} concentration.
2. The solubility probably is influenced by other ions present in varying amounts in MgX and pitchblende.
3. For a single raffinate the solubility goes through a flat maximum at about 3 N excess acid.
4. Typical, approximate solubility limits are: 5 g/l Ca at 20 g/l SO_4 ; 10 g/l Ca at 12 g/l SO_4 ; others may be read from the curves in Figure 1.

Introduction:

The formation of scale in tanks, lines, pumps, etc., has been a serious problem in the operation of the uranium refinery. An especially bad trouble-maker has been gypsum. Calcium sulfate is salted-in strongly by uranyl nitrate, due to the complexing of sulfate ion by uranium. As uranium is extracted from the aqueous phase, the latter may become supersaturated with calcium sulfate, and a gypsum scale then deposits. Since other nitrates also salt-in calcium sulfate, and since feeds vary in both calcium and sulfur content, it has been our practice to remove most of the SO_4 with Ba^{++} . It is presently hoped to save part of the cost of the barium by controlling the sulfate at a higher, but still safe, level. To this end the present study was undertaken to provide a basis for setting a safe sulfate limit.

Experimental:

- A. A sample of ether-saturated plant raffinate derived from a pitchblende feed (Lots A249, A256 and A258) was clarified by filtration and analyzed for sulfate (9 g/l) and nitric acid (30 g excess acid/l). Varying amounts of Na_2SO_4 , $\text{Fe}(\text{NO}_3)_3$, and HNO_3 were added to 250 ml portions of the filtrate.

~~CONFIDENTIAL~~

- 5 -

Samples were stirred until dissolution was complete. Aqueous $\text{Ca}(\text{NO}_3)_2$ was added to the samples until a precipitate of CaSO_4 became visible in each. Stirring was continued for approximately forty hours. The raffinates were filtered and analyzed for Ca, SO_4 , and Fe. The data are shown in Table I and Figure I.

TABLE I

Sample	g/l SO_4	g/l Ca	Initial g/l HNO_3	g/l Fe
1	3.3	24.4	30	9.7
2	11.0	10.3	30	10.3
3	26.5	3.5	30	10.2
4	49.2	1.6	30	10.2
5	47.5	2.6	30	21.9
6	47.2	3.7	30	29.7
7	48.8	5.2	30	40.1
8	16.7	4.7	10	10.3
9	18.0	5.5	30	10.3
10	19.6	5.5	50	10.2
11	20.6	5.5	70	9.9
12	23.5	7.4	30	22.2
13	18.0	12.3	30	29.1
14	15.6	16.9	30	38.0

- B. A sample of ether-saturated plant raffinate derived from a mixed MgX-pitchblende feed (Lots A249, A256, A258, P34, P35, F36, F37, P40, P42, P43, P44 and P46) was filtered and analyzed for sulfate (30 g/l) and nitric acid (25 g excess acid/l). The same procedure of aliquoting, salting, and stirring was followed as in Section A. Analyses of the filtered raffinate samples are:

TABLE II

Sample	g/l SO_4	g/l Ca	Initial g/l HNO_3	g/l Fe
15	8.6	15.1	25	11.
16	21.2	6.1	25	11.
17	33.1	3.6	25	11.
18	58.4	1.7	25	11.
19	34.4	8.1	25	24.
20	28.2	9.7	25	24.
21	29.6	13.6	25	48.

These data are plotted in Figure I.

DECLASSIFIED

- 6 -

- C. Raffinate from an MgX feed, being unobtainable from the plant, was produced in the laboratory. MgX (Lot P88) was slurried in hot HNO_3 for one hour, concentrated to 56°Be ; adjusted to 30 g/l excess HNO_3 , and slurry-extracted with 1N HNO_3 - ether. Additional sulfate was added followed by sufficient $\text{Ca}(\text{NO}_3)_2$ to cause precipitation of CaSO_4 . Stirring was maintained forty hours after which the filtrates were analyzed as follows:

TABLE III

Sample	g/l SO_4	g/l Ca	Initial g/l HNO_3	g/l Fe
22	6.3	13.8	30	16.
23	10.5	9.4	30	16.
24	20.2	4.6	30	16.
25	26.6	3.5	30	16.

These data are plotted in Figure I.

- D. A second sample of ether-saturated, mixed-feed raffinate (Lots A260-A264 incl.; P58, P59, P61, P70, P71, P81, P83) was filtered and analyzed for Ca (3.4 g/l), SO_4 (15.7 g/l), and HNO_3 (30 g/excess/l). An aliquot of this raffinate was boiled to reduce excess acid to 16 g/l. Additional acid was added to other aliquots to increase the acid concentrations to the values shown in Table IV. All samples were diluted or concentrated to 250 ml to insure identical salt concentration. Stoichiometric quantities of $\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$ and anhydrous Na_2SO_4 were added to each sample to produce a concentration of 75 g CaSO_4 /l, in 16 g/l excess SO_4 initially present. Solutions were stirred about forty hours, filtered, and analyzed.

TABLE IV

Sample	g/l CaSO_4 from Ca Analyses	moles Ca/l	moles SO_4 /l	calculated solubility g/l Ca SO_4 $\sqrt{[\text{Ca}] \times [\text{SO}_4]} \times 136.13$	N HNO_3
26	16.7	.123	.178	20.1	0.23
27	17.1	.126	.195	21.4	0.45
28	19.6	.144	.198	22.9	0.94
29	20.8	.153	.220	24.9	1.83
30	22.3	.164	.232	26.5	2.71
31	21.3	.157	.232	25.9	3.58
32	20.8	.153	.229	25.5	4.60
33	20.6	.151	.221	24.8	5.04

These data are plotted in Figure II.

007029.000

- 7 -

Discussion:

It will be noted from the curves that, while the solubilities in a single raffinate are self consistent, there is not complete agreement among the solubilities found in different raffinates even though the effects of iron and acidity are taken into consideration. This is probably due to the influence of other ions which complex sulfate, and which are present in varying concentration from batch to batch. That such is the case has also been indicated by variability in the effect of sulfate on the extraction of uranium, as shown by unpublished work in this laboratory.

It should be realized that because of probable lack of equilibrium even after 40 hours stirring, the values found in this study are only approximate. They do serve as a reasonably reliable guide to plant operation, however, since the solutions are probably nearer to equilibrium than are plant raffinates by the time the latter are past the point where they could cause trouble in the process.

DECLASSIFIED

DECLASSIFIED