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Solubility of Calcium Sulfate Dihydrate in Nitric Acid Solutions Containing Calcium Nitrate and Phosphoric Acid

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The solubilities of calcium sulfate dihydrate in nitric acid solutions containing different concentrations of calcium nitrate, phosphoric acid, and sulfuric acid have been determined at 25 °C. The equilibria involved in the systems studied were considered. Equations describing the solubility of calcium sulfate dihydrate in these systems are presented. The application of the solubility data to the use of nitric acid solution saturated with calcium sulfate dihydrate in leaching phosphatic iron ore is discussed.

Introduction

In an earlier paper (*1*), a hydrometallurgical process for the removal of phosphorus from iron ore has been suggested. In this process, the ore is leached with nitric acid solution where the apatite contained in the ore dissolves almost completely. The apatite dissolution takes place according to the reaction

$$Ca_5(PO_4)_3X(s) + 10HNO_3 = 5Ca(NO_3)_2 + H_3PO_4 + HX \quad (1)$$

where X is F, Cl, or OH. On the other hand, iron dissolution could be minimized to less than 0.5%. The produced leachate liquors contain mainly phosphoric acid (0.8–1 M) and calcium nitrate (1.5–2 M), as well as excess (unreacted) nitric acid (0.5–1 M). To improve the process economy, the leachate has to be processed for recovery of phosphoric acid and the cycle of nitric acid.

The nitric acid spent in reaction 1 is regenerated via an ionic exchange reaction with, e.g., sulfuric acid:

$$Ca(NO_3)_2 + H_2SO_4 + nH_2O = 2HNO_3 + CaSO_4{\cdot}nH_2O(s) \quad (2)$$

where $n = 0$, $^1/_2$, or 2, depending upon the operating conditions. Since the solubility of hydrated calcium sulfate (gypsum; $CaSO_4{\cdot}2H_2O$) in nitric acid is low, maximum 2.5 wt % at 25 °C (*2*), the regeneration of HNO_3 can be easily achieved by the precipitation of $CaSO_4{\cdot}nH_2O$. After filtration, the acidity of HNO_3 in the regenerated nitric acid can be of sufficiently high concentration that it may be reused in the leaching without further concentration. During the leaching, however, it can be also expected, according to reactions 1 and 2, that further precipitation of calcium sulfate occurs as HNO_3 concentration decreases and $Ca(NO_3)_2$ concentration increases. This will result in an increase of the sulfur content in the ore, which is undesirable with respect to the quality of the iron ore.

Therefore, the determination of the solubility of gypsum in the aqueous systems $H^+–Ca^{2+}–NO_3^-–SO_4^{2-}$ as well as the effect of H_3PO_4 on the solubility is of importance to the process optimization.

The solubility data related to the ternary systems of $CaSO_4–Ca(NO_3)_2$, HNO_3, H_2SO_4, $H_3PO_4–H_2O$ have been reported by many investigators (*2–5*). The multicomponent systems $CaSO_4–HNO_3–H_3PO_4(–H_2SO_4)–H_2O$ were also studied in a certain composition range (*6*, *7*). However, little attention has been paid to the quantitative determination of the effect of $Ca(NO_3)_2$ on the solubility of gypsum in the acid solutions, and few data are available in the composition range of interest. Thus determination of the solubility of calcium sulfate dihydrate in these solutions is very much needed for the process design. In this paper, some results of the solubility of gypsum in solutions related to the process under consideration are presented.

Table I. Solubilities of Gypsum in H_3PO_4–HNO_3 Solutions (M)

no.	$[H_3PO_4]$	$[HNO_3]$	$[CaSO_4]$
1	0	0	0.0155
2	0	1.00	0.1306
3	0	2.01	0.1739
4	0	3.98	0.1996
5	0	7.99	0.1486
6	0	12.01	0.0827
7	0	14.45	0.0556
8	0.102	0	0.019
9	0.099	1.01	0.121
10	0.101	1.99	0.156
11	0.100	4.00	0.188
12	0.099	8.00	0.141
13	0.499	0	0.036
14	0.497	1.00	0.095
15	0.500	2.01	0.134
16	0.502	3.97	0.170
17	0.500	7.98	0.136
18	0.997	0	0.049
19	1.01	0.98	0.086
20	1.00	2.00	0.122
21	0.99	4.00	0.146
22	0.99	8.01	0.118

Table II. Solubilities of Gypsum in H_2SO_4–HNO_3 Solutions (M)

no.	$[H_2SO_4]$	$[HNO_3]$	$[CaSO_4]$
1	0.101	0	0.016
2	0.100	1.02	0.097
3	0.100	1.98	0.132
4	0.099	3.97	0.152
5	0.098	8.00	0.101
6	0.500	0	0.020
7	0.498	1.00	0.035
8	0.501	1.98	0.053
9	0.500	3.98	0.055
10	0.499	8.02	0.026
11	1.002	0	0.021
12	4.010	0	0.005

Experimental Section

Materials. All chemicals, Merck's GR grade, were used as such without further purification. The solutions were prepared by dissolving the following chemicals in bidistilled water: nitric acid (minimum 65%), phosphoric acid (minimum 85%), sulfuric acid (95–97%), and calcium nitrate (minimum 98.5% $Ca(NO_3)_2{\cdot}4H_2O$).

All experiments were carried out under thermostatic conditions at 25 °C. Gypsum precipitate was produced by mixing the solutions of calcium nitrate and sulfuric acid and used for the preparation of solutions saturated with the sulfate.

Precipitation. An aliquot of 20–100 mL of aqueous solution of known composition was mixed with a certain amount of

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Table III. Solubilities of Gypsum in HNO_3–$Ca(NO_3)_2$ Solutions (M)

no.	$[Ca(NO_3)_2]$	$[HNO_3]$	$[CaSO_4]$
1	0.099	0	0.022
2	0.100	0.99	0.094
3	0.101	2.01	0.128
4	0.099	3.98	0.148
5	0.101	8.00	0.098
6	0.502	0	0.0090
7	0.499	1.00	0.0491
8	0.500	2.00	0.0661
9	0.498	4.02	0.0743
10	0.501	8.00	0.0378
11	1.000	0	0.0070
12	1.000	1.01	0.0311
13	0.998	2.01	0.0401
14	0.999	3.99	0.0413
15	0.998	7.97	0.0188
16	2.010	0	0.0052
17	2.003	1.00	0.0184
18	2.001	1.99	0.0208
19	1.997	3.97	0.0191
20	1.998	7.98	0.0063
21	4.010	0	0.0020

Table IV. Solubilities of Gypsum in H_3PO_4–HNO_3–$Ca(NO_3)_2$ Solutions (M)

no.	$[H_3PO_4]$	$[Ca(NO_3)_2]$	$[HNO_3]$	$[CaSO_4]$
1	0.98	0.104	0	0.029
2	0.99	0.097	1.00	0.084
3	1.01	0.103	2.02	0.122
4	1.01	0.098	4.01	0.140
5	1.02	0.102	7.99	0.088
6	1.02	0.502	0	0.026
7	0.99	0.504	1.00	0.042
8	0.98	0.499	2.00	0.056
9	1.00	0.495	3.98	0.062
10	1.01	0.501	8.01	0.028
11	0.98	1.01	0	0.016
12	0.97	1.02	1.00	0.025
13	0.98	0.99	1.98	0.032
14	1.00	1.00	4.02	0.034
15	0.99	1.02	8.03	0.015
16	0.99	2.02	0	0.010
17	0.97	2.03	1.01	0.014
18	0.98	1.98	2.00	0.017
19	0.99	1.99	4.02	0.015
20	1.00	2.01	8.02	0.004

Table V. Solubilities of Gypsum in H_3PO_4–HNO_3–H_2SO_4 Solutions (M)

no.	$[H_3PO_4]$	$[H_2SO_4]$	$[HNO_3]$	$[CaSO_4]$
1	0.99	0.103	0	0.037
2	1.02	0.102	1.01	0.079
3	1.03	0.097	2.02	0.117
4	1.00	0.096	4.00	0.135
5	0.98	0.101	7.99	0.085

sulfuric acid overnight and then allowed to settle for 3–4 weeks. The resulting suspension was centrifuged and filtered. The filtrate was analyzed. The precipitate was washed with the bidistilled water, dried, and stored for use in further experiments.

Dissolution. An aliquot of 20 mL of the aqueous solution of HNO_3, or another acid and salts, at various concentrations was used to dissolve gypsum that was obtained earlier. The solutions with small amounts of solid were continuously stirred for 2–3 days and then allowed to settle for 3–4 weeks. After centrifugation and filtration, the filtrate was analyzed.

Analysis. The total concentration of acids, as well as that of H_3PO_4, was determined by potentiometric titration of the aqueous mixture of acids with a standard solution of sodium hydroxide. During the titration, the interfering ion Ca^{2+} was precipitated as oxalate by adding a certain amount of $K_2C_2O_4$. The total concentration of sulfates was determined gravimetrically by barium sulfate method (*8*). The calcium content was determined by EDTA titration or atomic absorption spectrophotometry. However, both calcium and sulfur contents in a sample were not experimentally determined when one of them could be derived from another. The concentrations of nitric acid or nitrates were computed by the mass balance conditions (*1*).

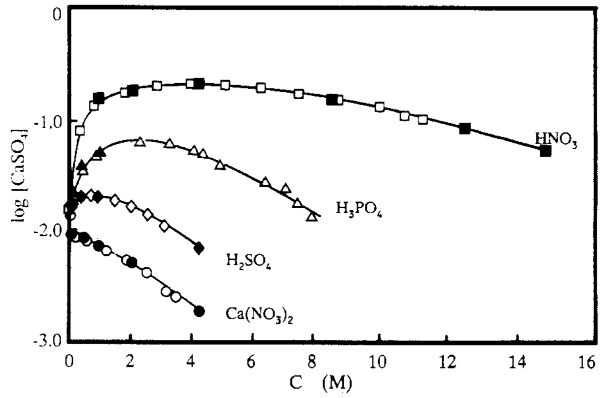

Figure 1. Solubility of $CaSO_4{\cdot}2H_2O$ in various aqueous solutions at 25 °C (full points are obtained in the present work; open points are literature data (*2*–*5*)).

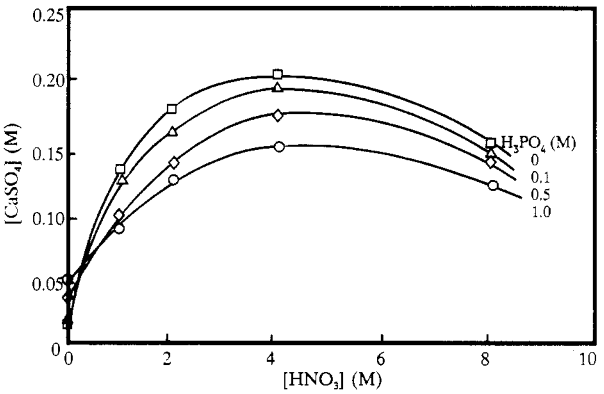

Figure 2. Effect of H_3PO_4 concentration on the solubility of $CaSO_4{\cdot}2H_2O$ in nitric acid at 25 °C.

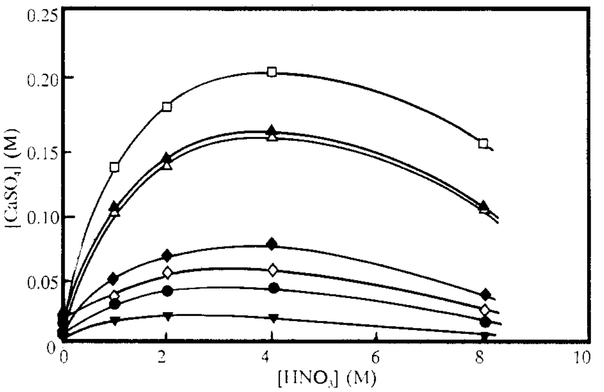

Figure 3. Effect of $Ca(NO_3)_2$ and H_2SO_4 on the solubility of $CaSO_4{\cdot}2H_2O$ in nitric acid at 25 °C. $[H_2SO_4]$: (□) 0, (△) 0.1, (◇) 0.5 M. $[Ca(NO_3)_2]$: (▲) 0.1, (◆) 0.5, (●) 1, (▼) 2 M.

Results

The solubility data obtained in the present study are given in Tables I–V and compared in Figures 1–4. The solubility of gypsum is determined as a function of the composition of the solutions. The last digit of the experimental data indicates the precision. The results are presented below.

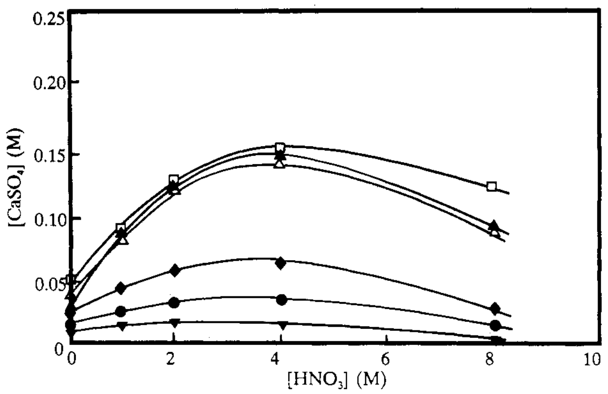

Figure 4. Effect of H_3PO_4 (1 M), $Ca(NO_3)_2$, and H_2SO_4 on the solubility of $CaSO_4 \cdot 2H_2O$ in nitric acid at 25 °C. [H_2SO_4]: (□) 0, (△) 0.1 M. [$Ca(NO_3)_2$]: (▲) 0.1, (◆) 0.5, (●) 1, (▼) 2 M.

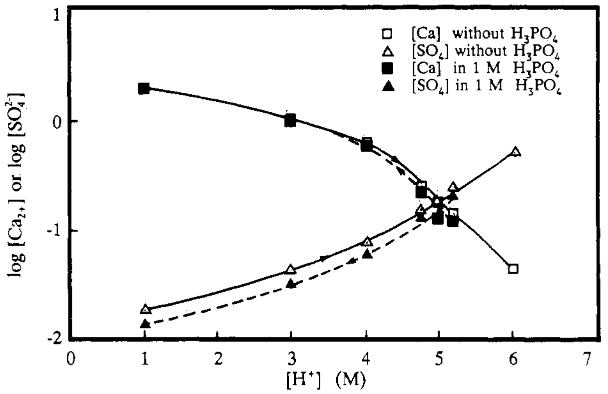

Figure 5. Prediction of solubility of $CaSO_4 \cdot 2H_2O$ during the regeneration of nitric acid by H_2SO_4 and during leaching of iron ore with regenerated nitric acid solutions.

Effect of Acids or Ca(NO$_3$)$_2$. Figure 1 gives the solubility of gypsum at 25 °C as a function of the concentrations of different solutes studied, i.e., $Ca(NO_3)_2$, HNO_3, H_2SO_4 or H_3PO_4. Some of the literature data (*2–5*) are also included for comparison. As can be seen, gypsum has the highest solubility in nitric acid solutions and decreases in the order of $HNO_3 > H_3PO_4 > H_2SO_4 > Ca(NO_3)_2$.

Combined Effect of HNO$_3$ and One of H$_3$PO$_4$, H$_2$SO$_4$, and Ca(NO$_3$)$_2$. Figure 2 shows the combined influence of nitric and phosphoric acids on the solubility of gypsum, while Figure 3 shows the combined influence of nitric acid and either calcium nitrate or sulfuric acid. The solubility of gypsum in HNO_3 solutions is generally reduced with increasing the content of another solute in the solutions, except at low acidity. This salting-out (including common-ion) effect is in the order of $H_2SO_4 > Ca(NO_3)_2 > H_3PO_4$.

Simultaneous Effect of HNO$_3$, H$_3$PO$_4$, and Ca(NO$_3$)$_2$ or H$_2$SO$_4$. Figure 4 shows the combined influences of 1 M H_3PO_4 and either H_2SO_4 or $Ca(NO_3)_2$ on the solubility of gypsum in HNO_3 solutions. The present results are obtained mainly from the precipitation experiments, in which the initial solutions consisted of HNO_3, H_3PO_4, and $Ca(NO_3)_2$ at various concentrations. The composition of the solutions is chosen so that they are comparable to those obtained in the process under consideration. As seen from Figure 4, the presence of H_3PO_4 reduces the salting-out effects of H_2SO_4 and $Ca(NO_3)_2$, especially at low concentrations. However, the combined effects tend to suppress further the solubility.

Discussion

The solubility data obtained may be interpreted by considering the different equilibria involved in the systems studied.

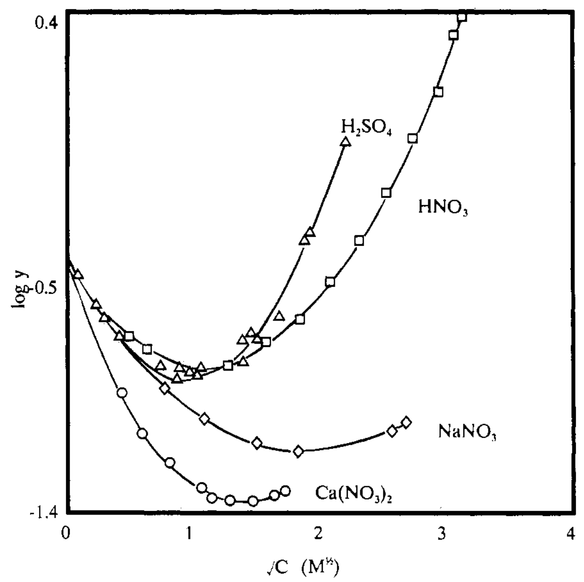

Figure 6. Effect of various bulk solutions on the mean ion activity coefficient (data for $NaNO_3$ taken from ref *5*).

The solubility of calcium sulfates can be simply expressed as

$$CaSO_4 \cdot nH_2O \overset{K_{so}}{=} Ca^{2+} + SO_4^{2-} + nH_2O \qquad (3)$$

where K_{so} is the solubility product. In the present experiments the formed solid phase was analyzed and found to consist only of calcium sulfate dihydrate. It is apparent that the addition of a souble calcium salt, e.g., $Ca(NO_3)_2$, will result in a decrease of the solubility of calcium sulfate dihydrate due to the common-ion (Ca^{2+}) effect. In acidic solutions the formation of HSO_4^- is pronounced with increasing the acidity of the solution. This will result in further dissolution of the gypsum, i.e.

$$CaSO_4 \cdot 2H_2O(s) + H^+ = Ca^{2+} + HSO_4^- + 2H_2O \qquad (4)$$

with the reaction constant

$$K = K_{so}/K_2 \qquad (5)$$

where K_2 is the second ionization constant of H_2SO_4. The concentration of the species H_2SO_4 is negligible as long as the acidity is not very high (4).

In a system H^+–Ca^{2+}–HSO_4^-–NO_3^-(–$H_2PO_4^-$), the solubility of gypsum, S, will be governed by the following relationships:

when $[SO_4]_T < [Ca]_T$

$$S = [SO_4]_T = K(K_2 + [H^+])/[Ca]_T \qquad (6)$$

when $[SO_4]_T = [Ca]_T$

$$S = ([SO_4]_T[Ca]_T)^{1/2} = (K(K_2 + [H^+]))^{1/2} \qquad (7)$$

when $[SO_4]_T > [Ca]_T$

$$S = [Ca]_T = K(K_2 + [H^+])/[SO_4]_T \qquad (8)$$

The above equations offer a qualitative description of the experimental data shown in Figures 1–5.

This indicates that a strong acid such as HNO_3 dissolves more gypsum than a weak acid such as H_3PO_4. On the other hand, H_2SO_4, though it is considered as a strong acid, will decrease the solubility of gypsum more than H_3PO_4 due to the contribution of H^+ and HSO_4^- species as can be seen from eq 8.

In the concentrated acid solutions, however, the solubility of gypsum has been shown to decrease with increasing the acidity. This is explained by the salting-out effect, which increases the mean activity coefficients, as shown in Figure 6. The maximum solubility observed for gypsum at a certain acidity (Figure 1), is in fact a combined influence of the common-ion effect and salting-out effect.

Application of Solubility Data to Leaching. Figure 5 gives an example for the concentrations of Ca^{2+} and SO_4^{2-} in a solution saturated with gypsum precipitate. The results simulate the regeneration of HNO_3 by increasingly adding H_2SO_4, as represented in reaction 2. As seen, the addition of H_2SO_4 decreases $[Ca^{2+}]$ in solution but it increases $[SO_4^{2-}]$ as well as the solubility of gypsum. The maximum solubility of gypsum is when $[Ca]/[SO_4] = 1$, which represents the complete regeneration of HNO_3. At this condition, the corresponding concentration of SO_4^{2-} is ca. 0.19 M for a solution containing 5 M NO_3^-. If such a solution is used directly for leaching (reaction 1), gypsum will precipitate as the equilibrium concentration is expected to be approximately 0.01 M when the solution contains 1 M H_3PO_4 and 2 M $Ca(NO_3)_2$. Under these conditions, the use of 1 L of regenerated nitric acid solution may introduce ca. 5.6 g of sulfur into the leached ore.

In order to avoid the precipitation of gypsum during the use of regenerated nitric acid, a partial regeneration of the acid is recommended. In this way a certain amount (a steady-state concentration) of calcium nitrate will be maintained in the solution, thus reducing the solubility of gypsum.

The above method seems to be the simplest method to overcome problems with introducing sulfur to the leached ore. Other options are (1) selective separation of nitric acid, e.g., by solvent extraction with minimum or no coextraction of sulfates, and (2) evaporation of the completely regenerated nitric acid. This will produce concentrated nitric acid solution with very little sulfate present.

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Solubility and Density Isotherms for Potassium Sulfate–Water–2-Propanol

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The solubility of potassium sulfate in water and in aqueous 2-propanol has been determined over the temperature range 20–50 °C, and the densities of the resulting saturated solutions have been measured. In all cases, the presence of 2-propanol significantly reduces both the solubility and density of potassium sulfate in aqueous solution. The solubility data may conveniently be expressed by a relationship of the form $\ln(w_{eq}) = A + Bx + Cx^2$ with an accuracy of +2%, where w_{eq} is the equilibrium saturation concentration of potassium sulfate, expressed as kilograms of potassium sulfate per kilogram of water, and x is the concentration of 2-propanol expressed as kilograms of 2-propanol per kilogram of water.

Introduction

The drowning-out precipitation of soluble inorganic salts from aqueous solution by the addition of an organic second solvent has a number of advantages. These generally lie in the possibility of carrying out the operation at ambient temperature and obtaining crystals of high purity. The technique is attracting the increasing attention of technologists in the chemical and pharmaceutical industries (*1*, *2*).

Recent complementary investigations of the continuous drowning-out precipitation of potassium sulfate have clearly shown that it is possible to retrieve a crystal product which is close to that obtained by cooling crystallization (*3*). The aim of the present work was to provide accurate solubility and density data for solutions of potassium sulfate in water and aqueous 2-propanol mixtures as an aid toward the assessment of the potential of drowning-out precipitation using alcohol as a separation technique.

Experimental Section

The solubility of the system potassium sulfate–water–2-propanol has been determined by equilibrating crystals and solution in an agitated solubility cell (*1*). The apparatus used for the solubility measurements was a 150-mL glass vessel closed by a ground glass stopper and fitted with a magnetic stirrer. The cell was immersed in a thermostatic water bath controlled to ±0.05 °C. The procedure was as follows. Volumetric quantities of saturated aqueous potassium sulfate solution and 2-propanol were charged to the solubility cell and agitated for a minimum of 1 h at a temperature at least 5 °C lower than the saturation temperature. The temperature of the water bath was then increased to that corresponding to the

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