CANADA

SOME SOLUBILITY STUDIES IN THE SYSTEM THORIUM CARBONATE-SODIUM CARBONATE-SODIUM BICARBONATE-SODIUM SULPHATE-WATER

by

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ABSTRACT

The solubility of the thorium pentacarbonate complex has been determined in aqueous solutions containing about 10% total carbonate (carbonate: bicarbonate ratio varied from 7:3 to 3:7) and 0 to 10% sodium sulphate at 25° and at 53°C. The ThO_2 solubility in all cases is of the order of 15 g/l at 25°C and 35 g/l at 53°C. At room temperature, it is slightly decreased as the sodium sulphate concentration is increased. The solid phase in equilibrium with these solutions is $Na_6\ Th(CO_3)_5 \cdot X\ H_2O$.

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INTRODUCTION

Thorium can be extracted from acid sulphate leach liquors by primary and secondary alkylamines in an inert hydrocarbon diluent (1, 2). Typical secondary amines used are di(tridecyl P) amine (Carbide and Carbon Chemicals), Amine 9D 178 (Rohm and Haas Co.), and Armeen 2-12 (Armour and Co.). A typical primary amine is Primene JM-T (Rohm and Haas Co.). The structure of the complex thorium sulphate species extracted is not established, but it involves six sulphate molecules per thorium atom, so that the extraction reaction may be tentatively written:

$$(R_2\,NH_2)_2\,SO_4 + Th(SO_4)_6^{8-} \rightleftharpoons (R_2\,NH_2)_8\,Th(SO_4)_6 + SO_4^{2-}$$

The thorium is then stripped from the amine by contacting the organic solution with a 10% aqueous solution of sodium carbonate (3, 4, 5). This reaction is represented as:

$$(R_2\,NH_2)_8\,Th(SO_4)_6 + 17\,CO_3^{2-} \rightleftharpoons$$
$$8\,R_2\,NH + Th(CO_3)_5^{6-} + 6SO_4^{2-} + 8\,HCO_3^-$$

Thus, on completion of the stripping step, the strip solution contains the thorium complex, carbonate, bicarbonate and sulphate ions. Moreover, since the thorium is recovered by precipitation of thorium with sodium hydroxide, followed by recycle of the barren solution to stripping, the sulphate content will build up rapidly and then level off at a value determined by the amount of solution bled off or $Na_2\,SO_4$ crystallized out by cooling. Up to 155 g/l $Na_2\,SO_4$ has been reported (6).

A knowledge of the solubility relationships in the system thorium carbonate - sodium carbonate - sodium bicarbonate - sodium sulphate would therefore be of value in determining what the optimum concentration and temperature conditions for the strip solution are. Since this information is not readily available, experimental work was carried out to establish, in a general way, the effect of the major variables.

APPARATUS AND REAGENTS

Room temperature equilibrations were carried out using 8-oz screw cap bottles and an Eberbach shaker. Equilibrations at 53°C were carried out in a constant temperature water bath, using 12-oz citrate of magnesia bottles.

The stock solutions of sodium carbonate, sodium bicarbonate and sodium sulphate were prepared from CP reagents.

A large batch of sodium thorium pentacarbonate dodecahydrate was prepared in the following way. A 200-g portion of $Th(NO_3)_4 \cdot 4H_2O$ was dissolved in 400 ml water, ammonium hydroxide was added, and the precipitated thorium hydroxide was centrifuged and washed by repeated repulping, centrifuging and decanting until free of ammonia. To the semi-solid paste were added 120 g sodium bicarbonate and 40 g of sodium carbonate. The paste dissolved to give an almost clear solution, which was decanted into a 1-litre beaker. The contents were evaporated to half volume on the steam bath, then allowed to stand 2 days. The crystals were separated on a sintered glass Buchner funnel

and allowed to air dry for a week. The sodium, carbon dioxide (acid evolution) and thorium contents were determined. These are given in Table 1.

TABLE 1

Analysis of Sodium Thorium Pentacarbonate

Used for Solubility Measurements.

	Theor. for $Na_6\ Th(CO_3)_5.12H_2O$	Found %
ThO_2	29.8	30.0
CO_2	24.8	25.3
Na	15.6	15.6

PROCEDURE

All the solutions used contained approximately 10% sodium carbonate + sodium bicarbonate.

Two sets of experiments were carried out, one at room temperature and one at 53°C. Each set consisted of three series of carbonate-bicarbonate ratios (7:3, 5:5 and 3.7), and each series consisted of five solutions covering the range 0 to 100 g/l $Na_2\ SO_4$.

Set A, at room temperature, was carried out by measuring 100-ml portions of each solution into an 8-oz screw cap bottle. Fifteen-gram portions of $Na_6\ Th(CO_3)_5.\ 12H_2O$ were added and the bottle was capped and shaken for 24 hours. The solution was then allowed to stand for a further 24 hours. The room temperature was recorded and the

solid was separated from the solution by filtering under suction, using a sintered glass Buchner funnel. The solid phase was allowed to air-dry and was then bottled and assayed for ThO_2, CO_2, and Na.

The solution phase was assayed for ThO_2, Na_2CO_3, $NaHCO_3$, Na_2SO_4, and CO_2. The results are given in Table 2.

Set B, at 53°C, was carried out by measuring 110-ml portions of each solution into a 12-oz glass citrate of magnesia bottle. Twenty-five grams of $Na_6Th(CO_3)_5 \cdot 12H_2O$ was added to the bottle and the bottle was stoppered. The bottles were suspended in a constant-temperature bath at 53°C for 48 hours, then removed from the bath. A 100-ml portion of the clear solution was withdrawn rapidly and transferred to an 8-oz screw cap bottle. (The solid phase in the citrate of magnesia bottles was not retained or analyzed.)

The bottles were capped and allowed to stand one week. The solid phase which had crystallized out was separated, air-dried, and weighed. Solid and solution phases were bottled and analyzed as before. The sum of the thorium content of the solid and solution phases in each bottle was taken as the solubility of thorium at 53°C. The results are given in Tables 3 and 4.

It should be pointed out that in the case of the solutions that had been equilibrated at 53°C and cooled to room temperature for a week, a further quantity of complex salt separated during the period between the separation and the analysis of the solution phase. The problem was overcome, in so far as the analysis was concerned, by warming the

TABLE 2

Solubility of Sodium Thorium Pentacarbonate Dodecahydrate

in Sodium Carbonate - Sodium Bicarbonate - Sodium Sulphate

Solutions at 25°C.

(Approaching equilibrium from unsaturation)

Equilibrium Solution Phase Assays					Equilibrium Solid Phase Assays			
Na_2SO_4 (g/l)	Na_2CO_3 (g/l)	$NaHCO_3$ (g/l)	CO_2(ev.) (g/l)	ThO_2 (g/l)	ThO_2 (%)	CO_2(ev.) (%)	Na (%)	SO_4 as S (%)
Set No. 1, Base Solution 7% Na_2CO_3 - 3% $NaHCO_3$								
<.02	69.8	30.2	58.4	18.8	30.6	25.2	15.3	<.01
9.9	67.6	30.4	58.0	18.4	30.5	25.0	15.3	<.01
19.5	69.3	30.3	58.2	17.8	30.7	25.0	15.1	<.01
48.8	67.9	30.0	57.0	16.9	30.1	25.0	14.9	<.01
96.7	69.0	30.0	54.7	15.2	30.6	24.9	15.0	<.01
Set No. 2, Base Solution 5% Na_2CO_3 - 5% $NaHCO_3$								
<.02	51.8	47.0	58.1	17.4	31.0	25.4	14.8	<.01
10.2	50.4	47.5	58.3	17.0	30.6	25.3	15.2	<.01
19.8	50.1	48.3	58.0	16.6	30.8	25.3	15.2	<.01
49.2	50.4	48.5	56.2	15.4	30.6	25.4	15.4	<.01
97.3	49.8	45.5	55.8	14.4	30.3	25.5	15.5	.04
Set No. 3, Base Solution 3% Na_2CO_3 - 7% $NaHCO_3$								
<.015	33.8	65.4	57.3	13.7	31.1	25.4	15.2	<.01
9.9	36.0	61.7	55.9	13.3	30.7	25.5	14.9	<.01
19.5	41.0	63.0	56.8	13.2	30.8	25.6	15.3	<.01
48.5	33.2	65.0	56.7	12.8	31.0	25.4	14.7	.02
97.0	35.6	61.9	56.1	12.0	31.3	25.3	14.1	<.01

TABLE 3

Solubility of Sodium Thorium Pentacarbonate Dodecahydrate

in Sodium Carbonate - Sodium Bicarbonate - Sodium Sulphate

Solutions at 25°C.

(Approaching equilibrium from supersaturation)*

Equilibrium* Solution Phase Assays					Equilibrium* Solid Phase Assays			
Na_2SO_4 (g/l)	Na_2CO_3 (g/l)	$NaHCO_3$ (g/l)	CO_2(ev.) (g/l)	ThO_2 (g/l)	ThO_2 (%)	CO_2(ev.) (%)	Na (%)	SO_4 as S (%)
Set No. 1, Base Solution 7% Na_2CO_3 - 3% $NaHCO_3$								
0.22	**	**	57.17	18.5	30.0	25.29	15.6	.15
10.34	72.3	32.2	67.10	26.0	29.8	25.42	15.8	.07
20.81	76.2	27.7	58.94	18.0	30.0	25.13	15.5	.12
50.9	74.3	**	59.07	18.2	30.0	25.28	15.5	.12
100.1	72.7	31.6	**	15.7	30.2	25.16	15.6	.07
Set No. 2, Base Solution 5% Na_2CO_3 - 5% $NaHCO_3$								
0.22	55.1	46.7	66.90	25.1	29.8	25.36	15.8	.05
10.53	55.6	46.5	66.77	25.0	29.9	25.22	15.6	.05
20.76	54.0	49.5	63.11	20.6	29.8	25.17	15.7	.06
51.1	51.8	49.4	62.92	20.5	29.9	25.65	15.5	.06
99.1	53.6	54.4	58.49	15.8	30.2	25.56	15.8	.05
Set No. 3, Base Solution 3% Na_2CO_3 - 7% $NaHCO_3$								
0.75	38.9	61.4	67.20	24.8	30.2	25.47	15.7	.05
10.3	43.9	61.1	61.60	19.1	30.0	25.58	15.7	.05
21.7	**	**	52.00	13.3	30.0	25.98	15.9	.20
49.7	40.8	59.9	61.32	18.2	30.0	25.39	15.9	.08
96.1	38.0	64.0	63.13	19.0	30.0	25.45	15.7	.08

* Equilibrium not fully obtained

** Insufficient sample

TABLE 4

Solubility of Sodium Thorium Pentacarbonate Dodecahydrate

in Sodium Carbonate - Sodium Bicarbonate - Sodium Sulphate

Solutions at 53°C.

Equilibrium Solution Phase Assays				
Na_2SO_4 (g/l)	Na_2CO_3 (g/l)	$NaHCO_3$ (g/l)	CO_2(ev.) (g/l)	ThO_2 (g/l)
Set No. 1, 7% Na_2CO_3 - 3% $NaHCO_3$				
0.22	*	*	73.3	37.6
10.34	72.3	32.2	76.2	36.7
20.81	76.2	27.7	69.5	30.7
50.9	74.3	*	75.7	37.9
100.1	72.7	31.6	*	37.7
Set No. 2, 5% Na_2CO_3 - 5% $NaHCO_3$				
0.22	55.1	46.7	74.6	34.1
10.53	55.6	46.5	75.4	34.0
20.76	54.0	49.5	75.6	35.3
51.1	51.8	49.4	75.7	35.3
99.1	53.6	54.4	75.0	35.2
Set No. 3, 3% Na_2CO_3 - 7% $NaHCO_3$				
0.75	38.9	61.4	74.5	33.6
10.3	43.9	61.1	74.4	34.8
21.7	*	*	56.7	18.7
49.7	40.8	59.9	74.8	34.2
96.1	38.0	64.0	76.3	34.6

* Insufficient sample

solution sufficiently to redissolve the precipitate and cooling to room temperature just before carrying out the determination. This experience indicated that one week is not sufficient time to permit attainment of equilibrium in the case of the supersaturated solution.

DISCUSSION

The results given in Table 2 are believed to represent the equilibrium saturation of sodium thorium pentacarbonate dodecahydrate fairly well, although the equilibration time was short (24 hours). The data in Table 3, for the tests where equilibration was approached from high temperature saturation, were obtained inevitably as a result of the method used in obtaining the saturation data at 53° (see page 4) and are merely presented to show the tendency to supersaturation in the system, and, more important, to show that the same equilibrium solid phase is deposited from a saturated solution as results from adding excess of the complex salt at room temperature.

CONCLUSIONS

The solubility of sodium thorium pentacarbonate in sodium carbonate - bicarbonate solutions at 25°C corresponds to 18.8 g/l ThO_2 for 7% sodium carbonate - 3% sodium bicarbonate; 17.4 g/l for 5% sodium carbonate - 5% sodium bicarbonate; and 13.7 g/l for 3% sodium carbonate - 7% sodium bicarbonate. It is decreased by not more than 19% by up to 100 g/l sodium sulphate. At 53°C the corresponding figures are 37.6 g/l, 34.1 g/l and 33.6 g/l ThO_2, and the presence of up to 100 g/l sodium sulphate has no effect on solubility at this tempera-

ture. In no case did the equilibrium solid phase contain other than traces of sulphate, and the stable solid phase corresponded to $Na_6 Th(CO_3)_5 . XH_2O$. The solid phase was air-dried in all cases prior to analysis, so it is not possible to define the equilibrium moisture content.

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