Electrolytic and Ionexchange Studies on Gypsum

S. Nageswar and A. Suresh

Department of Chemistry, Central College Bangalore University, Bangalore, India

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A process of utilising Gypsum as a raw material was studied using ion exchange and electrolytic method to obtain sulphuric acid, sodium sulphate, potassium sulphate and ammonium sulphate, etc.

Gypsum is a very common form of $CaSO_4 2H_2O$ which occurs in many parts of India. The utilisation of gypsum as a raw material for the manufacture of ammonium sulphate, sulphuric acid, sodium sulphate and potassium sulphate is of industrial importance.

Although the manufacture of sulphuric acid was studied by various workers,[1,2,3,4,5] there is no satistactory method for the production of sulphuric acid and other related products from gypsum. In the present communication the studies on the production of sulphuric acid and other related products are accomplished by an integrated cross cycle of ion exchange and electrolytic methods. In the above method, an aqueous solubrought in contact with a cation exchange resin in its tion of gypsum is ionic form of H^+, Na^+ and K^+ to remove calcium ion and replace them with the respective ions. The calcium ions are obtained in the form of calcium chloride when the cation exchanger is eluted with hydrochloric acid, sodium chloride, and potassium chloride to get back the original forms. The ion exchange process is carried out as an integrated cross cycle singal phase method.

EXPERIMENTAL

In the electrolytic method the saturated solution of Gypsum was electrolysed in a glass vessel of $1\frac{1}{2}$ litre capacity, kept in a thermostat maintained at required temperatures. In the cell platinum foils were used as electrodes. The anode and the cathode compartments were separated by a porous pot. The solution was constantly stirred to maintain uniform concentration and temperature of the electrolytic solution.

The electrolysis of gypsum was carried out with different amounts of sodium hexameta phosphate to increase the solubility of gypsum in water. One litre of the solution was electrolysed and the acid produced in the cathode compartment was estimated at every time interval of 30 minutes. The results obtained are tabulated in table—I. The current and the voltage were noted down using a sensitive ammeter and voltmeter.

TABLE I

Electrode : Platinum — Temperature : 26°C
Surface area = 26.52 sq cm — Voltage : 4 volts.

Duration of electrolysis in hours	Current in Amps.	Formation of acid in weight% H_2SO_4	H_3PO_4	Amount of sodium Hexametaphosphate used (g)
1	0.03	0.08	1.7	1.0
2	0.04	0.11	2.3	
3	0.04	0.2	3.1	
1	0.6	0.2	4.0	5.0
2	0.6	0.3	5.2	
3	0.6	0.4	8.2	
1	0.5	0.4	9.1	10.0
2	0.6	0.6	11.6	
3	0.6	0.6	13.2	

The electrolytic reaction is,

$$CaSO_4 2H_2O \longrightarrow Ca^{++} + SO_4^{--} + 2OH^- + 2H^+ \longrightarrow H_2SO_4 + Ca(OH)_2$$

The acid formed was taken out and the porous pot was washed with Nitric acid and water by applying suction for the next experiment.

In the ionexchange process, the saturated solution of gypsum was passed through an ion exchange coloumn consisting of DOWEX 50×4 (Baker analysed reagent) in the ionic form of H^+. The ion exchange coloumn was, constructed using a long water condenser where the resin

can be maintained at different temperatures. The saturated solution of gypsum from aqueous suspension of gypsum from an aspirator bottle kept at the top of the coloumn was passed through the ion exchange coloumn of length 50 cm containing 125 gm of resin at the rate 20 ml per minuite (fig. 1.). Sulphuric acid formed during the ion exchange process was estimated and the results obtained are tabulated in the table III. The sulphuric acid solution along with the slurry was recycled for about ten times and again estimated. The results obtained are tabulated in the table IV. Similar experiments were carried out by passing gypsum solution on sodium and potassium forms of cation exchange resins to produce sodium sulfate and potassium sulfate in separate coloumns.

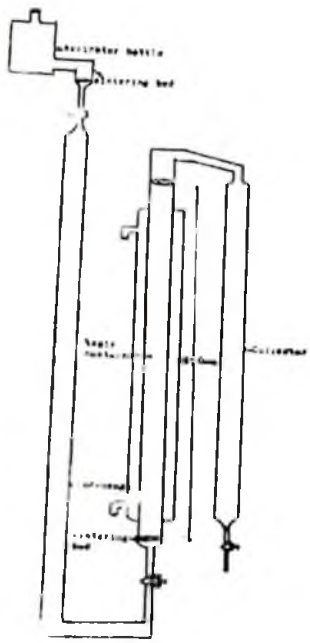


Fig.-1 Ion Exchange Coloumn.

TABLE II Ion exchange resin DOWEX 50×4 in hydrogen ionic form 125 g.

Contact time in sec.	Formation of acid in wt %	Temperature in C°
45	0.009	25
45	0.4	30
45	1.0	40
45	1.0	50

TABLE III Ion exchange Resin DOWEX 50×4 in the hydrogen form 125 g.

Number of circulations	Formation of acid in %
2	0.8
4	1.0
6	2.6
8	3.5
10	4.1
12	5.0

The reactions are as follows:

1) $2H^{+}R + CaSO_4.2H_2O \longrightarrow H_2SO_4 + Ca^{++}R_2 + 2H_2O$

2) $2Na^{+}R + CaSO_4.2H_2O \longrightarrow Na_2SO_4 + Ca^{++}R_2 + 2H_2O$

3) $2K^{+}R + CaSO_4.2H_2O \longrightarrow K_2SO_4 + Ca^{++}R_2 + 2H_2O$

4) $Ca^{++}R_2 + NaCl \longrightarrow CaCl_2 + 2Na^{+}R + 2H_2O$

Sodium sulphate and potassium sulphate obtained from integrated ion exchange method were also electrolysed and the results are shown in Table II.

TABLE IV

Electrolysis of saturated sodium sulphate.

Electrode: Platinum of surface area 21.284 sq cm Carbon cathode

Voltage: 6 volts

Temperature: 30°C

Duration in minutes	Current in Amps.	Formation of acid in wt.%
30	1.5	0.4
60	1.5	1.1
90	1.4	1.5
120	1.4	1.9
150	1.4	2.2
180	1.3	3.6
210	1.3	4.0
240	1.3	4.6

The electrolytic reaction is

1) $Na_2SO_4 + H_2O \longrightarrow 2Na^+ + SO_4^{--} \longrightarrow 2NaOH + H_2SO_4$

2) $K_2SO_4 + H_2O \longrightarrow 2K^+ + SO_4^{--} \longrightarrow 2KOH + H_2SO_4$

DISCUSSION

From the results of the electrolytic studies it can be seen that the current efficiency is about 35% to 45% and the concentration of sulphuric acid obtained is also low. This is due to the low solubility of calcium sulphate in water The calcium hydroxide formed during the electrolysis also hinders the flow of current. Further the solubility,[4] decreases with the increase of concentration of calcium hydroxide. At higher temperatures part of the current, is utilised for the liberation of hydrogen and oxygen.

In the electrolysis of calcium sulphate with sodium hexametaphosphate there will be an increase in the yield of sulphuric acid owing to the increase in the solubility of calcium sulphate. It can be seen from Table I that more the amount of phosphate used, the yield is also greater.

In the ion exchange process the reaction is quick and recycling gives better yield. It is advantageous to utilise hydrochloric acid, sodium chloride and potassium chloride as regenerating eluent. The ion exchange process utilising potassium chloride and sodium chloride can be carried out at any convenient temperature. When large availability of sulphuric acid exists, potassium sulphate and sodium sulphate can be advantageously produced from potassium chloride and sodium chloride.

The above results indicate that gypsum could be utilised for the production of potassium sulphate, sodium sulphate.

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