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RECOVERY OF SULPHUR FROM GYPSUM BY REACTION WITH SODIUM CARBONATE: PRODUCTION OF SODIUM SULPHATE

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ABSTRACT

The reaction between gypsum, a waste product of the TSP Factory in Chittagong and solid sodium carbonate was studied under different conditions. The products were sodium sulphate and calcium carbonate. Under optimum conditions about 94% yields of both sodium sulphate and calcium carbonate were obtained at 600 °C within half an hour.

Keywords: *Calcium carbonate, Gypsum, Plaster of Paris, Sodium sulphate.*

1. INTRODUCTION

Sulphur is an important element for commerce and industry. Its world deposit is being exhausted very rapidly day by day due to attempts for the utilization of sulphur containing waste materials into useful products. In Bangladesh, huge amount of gypsum is obtained as a waste product in the TSP Factory at Chittagong. Disposal of this waste product creates an environmental problem in Chittagong. Considering the economic aspect of the industry, this by-product of the industry needs to be utilized into valuable products. Only a small fraction of it is utilized for making hard boards (Leighou, 1953) and plaster moulage in Plastic Surgery (Rana *et al.,* 2003).

Sophia *et al.* (2016) made a review of recent development on gypsum as a construction material and gave an outline of the process of hydration, dehydration and setting of gypsum of the various admixtures on gypsum. William (1968) invented a molding composition consisting essentially of calcium sulfate anhydrite and ammonium alum combined calcium sulfate anhydrite and ammonium alum combined together in water. The molding composition is easily hardenable and is used to form a mold. After it has served this purpose it can be dissolved away by simple contact with water. Oh and Wheelock (1990) made a study on the reductive decomposition of Calcium sulfate with Carbon monoxide and concluded that the reaction of calcium sulfate at 1150°C with gas mixtures containing carbon monoxide, carbon dioxide, and sulfur dioxide is controlled by the reducing potential (Pco/PCOZ). At low reducing potentials of 10 or less, the $CaSO_4$ was completely converted to CaO. At moderate reducing potentials (i.e., 0.20), $CaSO_4$ was converted rapidly to CaO, which was then converted more slowly to CaS. O'Rourke *et al.* (2009) studied development of calcium sulfate - ggbs - Portland cement binders. According to them, the essential properties of cementitious binders containing combinations of gypsum, ground granulated blast furnace slag and other mineral admixtures were reliably assessed. The results of the laboratory tests show that binders manufactured using calcium sulfate as the dominant ingredient develop adequate strengths, but are only suitable for use in dry environments. Malinowski *et al.* (2014) made a study on the utilization of waste gypsum in fertilizer production and concluded that by-product gypsum can be used for the production of the granulated fertilizers. According to the concept, the obtained fertilizers would be of NSCaMg type, with urea as the nitrogen source. The calcium and magnesium sulphates in the waste will be bounded in the fertilizer in the form of adducts of $CaSO_4{\cdot}4CO\ (NH_2)_2$ and $MgSO_4{\cdot}CO\ (NH_2)_2{\cdot}3H_2O$.

De Beer *et al.* (2014) converted calcium sulphide to calcium carbonate during the process of recovery of elemental sulphur from gypsum waste. They obtained the elemental sulphur and calcium carbonate from gypsum waste by thermally reducing the waste into CaS, which is subsequently subjected to a direct aqueous carbonation step for to get H_2S and $CaCO_3$. H_2S is then converted into elemental sulphur by Claus process. De Beer *et al.* (2015) also studied the synthesis of high-purity precipitated calcium carbonate during the process of recovery of elemental sulphur from gypsum waste. They concluded that about 0.37 ton of high-grade PCC can be produced from 1.0 ton of gypsum waste, and generates about 0.19 ton of residue, a reduction of 80% from original waste gypsum mass to mass of residue that needs to be discarded off. The use of gypsum waste as primary material in replacement of mined limestone for the production of $CaCO_3$ could alleviate waste disposal problems, along with converting significant volumes of waste materials into marketable commodities. Ennaciri *et al.* (2016) made a study on the conversion of phosphogypsum to sodium sulfate and calcium carbonate in aqueous solution. They converted

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phosphogypsum to calcium carbonate and sodium sulfate. The reaction for chemical decomposition of phosphogypsum is made at room temperature in aqueous solution and studied at various concentrations and times. According to the obtained results, we concluded that the reaction is complete only after half an hour. It also presents other advantages: it is reproducible, ecological and not expensive. Bhuiyan *et al.* (2017) prepared CS_2 by reaction of by-product gypsum with CCl_4 vapour and obtained 98.32% CS_2 and 93.49% $CaCl_2$ at 800°C.

Gypsum, the waste product of the TSP Factory, has been produced industrially and is a problem for its disposal. It is important for an industry to use the waste by-product, which motivated the authors to undertake the study for its better utilization into valuable chemicals which have also demand in other industries. The main objective of this study is to utilize industrially gypsum waste of the TSP Factory by conversion of its sulphur and metal components into useful products economically. Most of the processes mentioned above are lengthy, time consuming and less cost effective. The reaction between gypsum and sodium carbonate was chosen for the production of Na_2SO_4, which is an important chemical for the paper industry and $CaCO_3$ which is used in the cement and lime industries; the reaction is less time consuming and cost effective. Pilot Plant Study was made with higher amounts of the reactants so that the production can be made industrially.

2. EXPERIMENTAL

2.1 Purification of gypsum

A weighed amount of gypsum was treated with 100 ml of 0.5 M sulphuric acid solution. It was stirred thoroughly and the supernatant liquid was decanted off. The process was repeated for five times. The residue left was washed with distilled water repeatedly until it was free from acid. It was then treated with rectified spirit and finally dried at 110°C in an electric oven for 2 hours. The gypsum was then converted to Plaster of Paris by heating the sample at 120-150°C for 2 hours (Shreve, 1956). After analysis, Plaster of Paris was found to have a purity of 99.56%. The dehydration reaction is:

$$CaSO_4.2H_2O \rightarrow CaSO_4.1/2H_2O + 3/2H_2O \quad \text{at } 120\text{-}150°C$$

All the reactions were carried out with this sample of gypsum thus purified.

2.2 Reaction procedure

A weighed amount of Plaster of Paris, $CaSO_4.\frac{1}{2}H_2O$, was thoroughly mixed with a definite proportion of anhydrous sodium carbonate and transferred on to a silica boat. The boat was placed in the middle part of a reaction tube which, in turn, was introduced into an electric furnace. The reaction tube was then connected to a nitrogen cylinder on one hand and to a bubbler containing water on the other hand. Nitrogen gas was passed through the system for some time. The temperature of the furnace was raised to the desired point and the reaction was carried out for a certain period. The furnace was then switched off and allowed to cool down to the room temperature in a slow stream of nitrogen. The reaction boat was taken out, and the solid reaction products were leached with boiling water, cooled and filtered. Sulphate present in the filtrate was quantitatively estimated (Vogel, 1962) and the amount of sodium sulphate was calculated. No trace of calcium sulphate was found in the filtrate. The amount of carbon-di-oxide evolved from the residue by the action of hydrochloric acid and the total amount of calcium carbonate were also calculated. The experimental set up is shown in Figure 1.

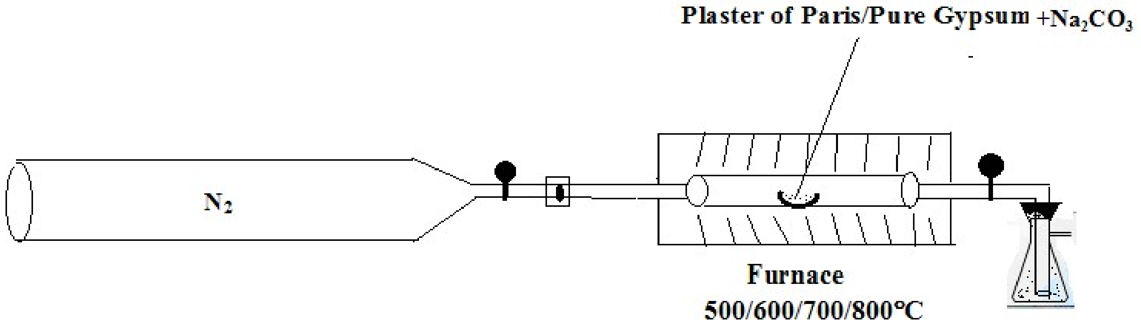

Figure 1: Experimental Set up

The reaction between Plaster of Paris and sodium carbonate is given below:

$$\left[CaSO_4 \cdot \frac{1}{2} H_2O + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4 + \frac{1}{2} H_2O\right]$$

It may be mentioned that the products obtained by reaction were dissolved in water and the aqueous solution was prepared for detecting sulphate and carbonates. Sulphate in the solution was detected by adding barium chloride when white precipitation of BaSO4 was formed, indicating the presence of sulphate in the solution:

$Na_2SO4 + BaCl_2 = 2\ NaCl + BaSO_4$ (White ppt. of Barium Sulphate)

The solution of the product when treated with hydrochloric acid gave effervescence of CO_2 gas which turned lime water milky. The presence of Ca ion was tested by adding Sodium Oxalate, which formed a white precipitation of Calcium oxalate, indicating the presence of calcium:

$CaCl_2 + Na_2C_2O_4 = CaC_2O_4$ (White ppt.) + 2 NaCl

3. RESULTS AND DISCUSSION

Reaction between Plaster of Paris obtained from gypsum and sodium carbonate was studied under various conditions. The results are given in Tables 1-3.

3.1 Effect of Temperature

It is seen from Table 1 that the percentage yield of calcium carbonate and sodium sulphate increases with temperature. Thus at 500°C, the yield is about 89% whereas at 600°C the yield is about 94% in both the cases. The percentage yield does not improve with further rise of temperature. Optimum temperature is thus found to be 600°C.

Table 1: Effect of temperature on the reaction

$CaSO_4.\frac{1}{2}H_2O$ taken =1.0 g, Na_2CO_3 (anhy.) taken = 0.78 g

Reaction time = 1.5 hrs.

Temperature (°C)	Amount of $CaCO_3$ formed (g)	% yield of $CaCO_3$	Amount of Na_2SO_4 formed (g)	% yield of Na_2SO_4
500	0.6140	89.00	0.8711	88.08
600	0.6470	93.76	0.9190	93.77
700	0.6490	94.05	0.9215	94.03

3.2 Effect of Time

From Table 2 it is clear that the reaction is very rapid and 93.47% of Na_2SO_4 is obtained within 15 minutes. Further increase of time even up to 1.5 hrs does not increase the % yield of Na_2SO_4 to a considerable degree.

Table 2: Effect of time on the reaction

$CaSO_4.\frac{1}{2}H_2O$ taken =1.0 g, Na_2CO_3 (anhy.) taken = 0.78 g

Temperature = 600°C

Time	Amount of $CaCO_3$ formed (g)	% yield of $CaCO_3$	Amount of Na_2SO_4 formed (g)	% yield of Na_2SO_4
15 min.	0.6380	92.46	0.9160	93.47
30 min.	0.6494	94.11	0.9222	94.10
1 hr.	0.6503	94.24	0.9235	94.23
1.5 hr.	0.6470	93.76	0.9190	93.77

3.3 Effect of Na_2CO_3 - input

It is found from Table 3 that with 0.5g of Na_2CO_3, 72.23% of Na_2SO_4 and 72.29% of $CaCO_3$ are obtained. When the amount of Na_2CO_3 is increased to 0.78g as much as 94.2% of both Na_2SO_4 and $CaCO_3$ are obtained in 30 minutes at 600°C.

Table 3: Effect of Na_2CO_3 - input on the reaction

$CaSO_4.\frac{1}{2}H_2O$ taken =1.0 g, Temperature = 600°C

Reaction time = 30 min.

Na_2CO_3 input (g)	Amount of $CaCO_3$ formed (g)	% yield of $CaCO_3$	Amount of Na_2SO_4 formed (g)	% yield of Na_2SO_4
0.500	0.4987	72.29	0.7082	72.23
0.780	0.6502	94.24	0.9233	94.23
0.836	0.6492	94.11	0.9221	94.01

3.4 Reaction under different conditions of introducing the boat

All the above experiments were carried out by introducing the silica boat containing the reactants first in the reaction tube of the electric furnace and thereafter the temperature was raised to the desired point. Here some experiments were carried out by raising the temperature first and then introducing the boat with its contents directly at the central zone of the electric furnace. The results are given in Table 4.

Table 4: Reaction under different conditions of introducing the boat

$CaSO_4.\frac{1}{2}H_2O$ taken =1.0 g, Na_2CO_3 (anhy.) taken = 0.78 g

Temperature = 600°C

Time	Amount of $CaCO_3$ formed (g)	%yield of $CaCO_3$	Amount of Na_2SO_4 formed (g)	%yield of Na_2SO_4
15 min.	0.6472	93.65	0.9191	93.79
30 min.	0.6452	93.50	0.9162	93.49
1 hr.	0.6502	94.24	0.9235	94.23

The Table 4 shows that the results are the same as obtained by introducing the boat first and then raising the temperature. It shows that the reaction requires very short time for completion.

3.5 Reaction with larger amount of reactants

An experiment was carried out taking 10 times the amount of substances under the same conditions for pilot plant study. The results are given below:

Amount of $CaCO_3$ formed = 6.49 g
% yield of $CaCO_3$ = 94.05
Amount of Na_2SO_4 formed = 9.2163 g
% yield of Na_2SO_4 = 94.04

The above results are in good agreement with the results obtained earlier.

3.6 Reaction in Nickel Crucible

Two other experiments were also conducted in nickel crucible in presence of air. Roasting was done with the help of Bunsen burners for 30 minutes. The results are:

(a) $CaSO_4.\frac{1}{2}H_2O$ taken =10.0 g
Na_2CO_3 (anhy.) taken = 7.8 g

Results:

Amount of $CaCO_3$ formed = 6.49 g
% yield of $CaCO_3$ = 94.12
Amount of Na_2SO_4 formed = 9.2226 g

%yield of Na_2SO_4 = 94.11

(b) $CaSO_4.\frac{1}{2}H_2O$ taken =15.0 g

Na_2CO_3 (anhy.) taken = 11.70 g

Results:

Amount of $CaCO_3$ formed = 9.6855 g
% yield of $CaCO_3$ = 93.58
Amount of Na_2SO_4 formed = 13.7550 g
% yield of Na_2SO_4 = 93.59

The above results show that the percentage of yield in the case of experiments conducted in presence of nitrogen gas is the same as that of experiments carried out in open air. The yields of the products such as sodium sulphate, calcium carbonate are very high and are 93-94%. The results are very encouraging and can be used industrially for manufacturing the important chemicals Na_2SO_4 and $CaCO_3$. It may be mentioned Beer *et al.* (2015) about 0.37 ton of high-grade PCC can be produced from 1.0 ton of gypsum waste.

4 CONCLUSIONS

From the study of the present work it is clear that the reaction between Calcium sulphate hemihydride obtained from gypsum and anhydrous sodium carbonate takes place very rapidly even in presence of air. The reaction is very simple and takes short time to complete and requires no costly apparatus, and the yield is very high. About 94% sodium sulphate can be obtained by heating a mixture of purified gypsum and sodium carbonate in 30 minutes. Thus, gypsum, a waste product of the TSP Factory, can be utilized for making calcium carbonate and sodium sulphate both of which are important raw materials for many industries in Bangladesh.

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