

MANUFACTURE OF BARIUM CHEMICALS FROM INDIGENOUS BARITE

NAZIR AHMED CHOCHAN, M.H. QURESHI, AZIZUL HAQ and F.A. FARUQI

PCSIR Laboratories, Lahore 16

(Received July 31, 1972; revised March 19, 1973)

Abstract. A successful attempt has been made to manufacture barium carbonate from indigenous barite by a process involving reaction between barite and an aqueous solution of soda ash under atmospheric pressure. The effects of such variables as particle size, temperature, time and concentrations of the reactants on the reaction yield were studied. Highest conversion obtained was 95.80%.

Barium carbonate is the parent barium salt being used for the production of barium compounds which find a variety of industrial applications.¹ The ceramic and oil industries use a considerable amount of its carbonate and sulphate. Barium chloride finds its usage as a purifying agent for salt brines used in the manufacture of sodium hydroxide. It is also employed as a water softener in boiler compounds and in medicinal preparations. Barium nitrate finds its use in the pyrotechnics and explosives and also, to a small extent, in medicinal preparations. Barium oxide is used both as an industrial drying agent and in the case-hardening of steel. Barium chromate, lemon chrome or chrome yellow is used in yellow pigments and safety matches. Recently, barium compounds have started finding their increasing usage in the ferro-electric industry for the production of barium titanate as a dielectric material.

Barium chemicals are usually manufactured either by the carbon-reduction process at elevated temperatures or fusing barite with soda-ash and leaching the product with hot water. Recently, attempts have been made to react barite either with potassium^{2,3} carbonate in aqueous solution or fusing it with a mixture⁴ of soda-ash and sodium chloride and leaching the product with water. Reaction between powdered barite and zirconium nitrate⁵ has also been tried at low temperatures. A process involving reaction between barite and soda-ash in aqueous solution under high pressure⁶ has been developed and patented in Pakistan.⁷

In the present work barite has been made to react with sodium carbonate in aqueous solution at the atmospheric pressure. The method is simpler both in terms of equipment and handling operations and has the advantages over the widely used carbon-reduction process of yielding barium carbonate free from objectionable sulphur compounds.

Materials and Method

Large deposits⁸ of barite are available in West Pakistan in the Hazara, Khudzar and Lasbela districts. In the present work a representative sample of the Hazara barite was chemically analysed according to standard methods⁹ and was found to contain 95.70% barium sulphate. The barium sulphate contents were, however, increased to 96.83% by boiling the sample

with dilute hydrochloric acid. This upgraded barite was used during the present work.

Technical grade soda-ash of Lever Brothers (Pakistan) containing 98% sodium carbonate was used throughout the work.

Experimental

In each of the experiments 100 g upgraded barite of various mesh sizes ($-72+100$ to $-200+250$) was heated in a steel beaker with varying quantities of Na_2CO_3 in 400 ml distilled water. The contents of the beaker were heated for 60 min at the atmospheric pressure. Frequent stirring was done during digestion. The contents were then allowed to stand for sometime and the supernatant liquid containing Na_2CO_3 and Na_2SO_4 was decanted off. The residue containing BaCO_3 and the unreacted BaSO_4 was repeatedly water-washed till free from Na_2CO_3 and Na_2SO_4 . The residue was then treated with a sufficient quantity of $\text{HCl}(\text{dil})$ to convert BaCO_3 into BaCl_2 and the mixture was heated to ensure complete conversion of BaCO_3 to BaCl_2 . The solution was filtered and the residue was washed with water. The filtrate was then treated with $\text{H}_2\text{SO}_4(\text{dil})$ to convert BaCl_2 into BaSO_4 which was filtered, washed, dried and ignited to see the percentage conversion of BaSO_4 . Alternatively, BaCl_2 could be either crystallised by concentrating the filtrate or it could be converted into BaCO_3 by treating it with Na_2CO_3 solution. The basic BaCO_3 thus produced may be utilised for the production of many industrially important barium salts.

Results and Discussion

The data concerning the effect of particle size on the efficiency of reaction is presented in Table 1. It may be observed from here that the particle size of barite significantly effects the conversion yield of barium sulphate. The conversion obtained was only 10.5% when barite of mesh size $-72+100$ was used. However, the percentage conversion improved as the mesh size decreased till it was maximum (28.75) when mesh size was reduced to $-175+200$ or $-200+250$. It was due to the fact that finer particles have greater surface area exposed to a substrate and hence the chemical reaction between barite and soda ash proceeded to completion.

TABLE 1. BARITE-Na₂CO₃, 1:1; TIME OF DIGESTION, 60 MIN.

Mesh size	Conversion (%)
1. -72 +100	10.50
2. -100 +120	12.60
3. -120 +140	15.30
4. -140 +150	18.70
5. -150 +175	22.50
6. -175 +200	28.70
7. -200 +250	28.75

TABLE 2. PARTICLE SIZE, -200+250; TIME, 60 MIN.

Barite-Na ₂ CO ₃	Conversion (%)	$K = \frac{[\text{BaCO}_3][\text{Na}_2\text{SO}_4]}{[\text{BaSO}_4][\text{Na}_2\text{CO}_3]}$
1:1	31.10	0.0738
1:2	47.90	0.117
1:3	60.90	0.156
1:4	70.75	0.213
1:5	78.86	0.281
1:6	87.52	—
1:7	95.80	—
1:8	95.61	—

The concentration dependence of the reaction is shown in Table 2. It may be noted from here that the rate of reaction between barite and soda-ash is directly proportional to the concentration of soda-ash. The maximum conversion yield obtained was 95.80% when barite and soda-ash were used in the ratio of 1:7. Barium sulphate, being sparingly soluble in water, is only slightly ionised and an equilibrium is soon established between the two phases. It is assumed that the reaction between CO₃²⁻ and Ba²⁺ ions takes place in instantaneous successive stages till an equilibrium is set up between the product and the reactants. Some equilibrium constants of the reaction are given in Table 2. It is clear from here that the equilibrium constant of the reaction at a certain concentration of sodium carbonate differs by only 0.04-0.06 from that in the successive experiment. Since the equilibrium constant of a chemical reaction directly varies with temperature, the change in the equilibrium constants may be attributed to the experimental error either in temperature or time of heating. However, these constants are fairly comparable with those for an analogous reaction given in the literature.⁴ It was observed that by maintaining other conditions, the rate

of conversion is directly proportional to temperature or the duration of heating the reaction mixture. Maximum conversion obtained was 95.80% when the mixture was heated for 60 min. First period of low-reactivity can probably be attributed to low temperature of the mixture.

It was also noted that the quantity of water used also effected the rate of conversion of barite. However, a constant volume of 400 ml water maintained was found to be optimum for a mixture of 100 g barite and 700 g sodium carbonate. In case of a paste of the above mixture with water, the percentage conversion was found to be depressingly low. On the other hand the addition of too much water also adversely effected the conversion yield. The cause of the slow rate of reaction in the first case is obviously due to the restricted mobility of the ions while the slow rate of reaction in the latter case may be the result of lower concentration of the reactants per unit volume of the mixture.

Conclusions

1. Abundantly available domestic barite can be successfully used in the process which is simple and economical.
2. The maximum reaction yield obtained is 95.80% when barite of mesh size -200+250 is heated for 60 min with BaSO₄-Na₂CO₃ as 1:7.
3. Separation of sodium carbonate and sodium sulphate from the mother liquor can be made by different methods and sodium sulphate thus recovered as a by-product may be used in paper, textile and leather industries as well as in the manufacture of sodium sulphate.

Acknowledgement. Thanks are due to Dr. K.A. Shahid for giving valuable suggestions and Mr. Ghulam Farid for his assistance in carrying out the experiments.

References

1. H. Remy, *Treatise on Inorganic Chemistry* (Elsevier, New York, 1956), vol. I, pp. 78, 271, 73.
2. J.R. Partington, *General Inorganic Chemistry* (Macmillan, London, 1954), second edition, p. 382.
3. Svetozar Milicev and Joze Siftar, *Monatsh. Chem.*, **63**, 941(1965).
4. H.S. Booth and E.F. Pollard, *Ind. Eng. Chem.*, **40**, 1984(1948).
5. A.H. Angerman, U.S. Patent 2,514,115 (1950).
6. J.W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry* (Longmans Green, London, 1952), vol. III, p. 699.
7. R.A. Shah and S.M.H. Naqvi, *Pakistan Patent* 114721 (1965).
8. *Directory of Mineral Deposits of Pakistan*, vol. 15, part 3, p. 55 (Geological Survey of Pakistan).
9. W. Scott, *Standard Methods of Chemical Analysis* (D. Van Nostrand Company, New York, 1954) fifth edition, vol. I, p. 130.