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The Study of Carbothermal Reduction of Barite in Presence of Calcium Chloride

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Abstract: In present study the effect of calcium chloride as a reaction promoting agent on carbothermal reduction of barite was investigated. After admixing calcium chloride in matrix for the carbothermal reduction of barite, the result shows that yields of barium sulphide have been found to increase to the order of 52 percent. This may contribute a lot to the economy of the barium industry.
Keywords: Barite, fluxing agent, calcium chloride, iodometry.

Introduction

Barite is one of the major mineral for export among non-metallic minerals. It finds its main uses in paints, rubber, explosives, in drilling mud for exploration of oil[1], etc. Barite ore is the indigenous natural starting material for producing various barium chemicals like barium chloride, barium carbonate, barium nitrate etc. which are the important materials in chemical, ceramic and oil industries. But as barite is highly insoluble in water, it deters the process. In industrial practice, barium sulphide (water soluble) is prepared by the carbothermal reduction of barite. Theoretically a pure sample of barite should yield barium sulphide to the extent of about 70 % or so. But in actual practice the extent of reduction hardly ever exceeds 50 %. The author, therefore, studied the impact of different reaction promoting agents on carbothermal reduction of barite under anaerobic conditions in the pit furnace at high temperatures in order to increase the yield of barium sulphide and she discovered various reaction promoting agents which when admixed in the matrix improve the yield of barium sulphide[2-4]. Present investigations are reserved to confer the effect of calcium chloride on carbothermal reduction of barite. The basis of its selection as a promoting agent was its capacity to act as a comparatively low melting ionising solvent and because of this property calcium chloride may also serve as a fluxing agent for barite. Such a situation might be beneficial physically for effective reduction of barite.

Materials and Methods

Barite (barium sulphate):

Barite the basic raw material of snow-white shade was pulverized separately. The powder was checked for reactive impurities like dolomite/ limestone and sieved through standard sieves of mesh number 150 meshes[5]. Chemical analysis of barite sample has been given in Table 1.

Table 1. Chemical analysis (mass %) of the used barite ore sample

Shade of barite	$BaSO_4$	SiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O
# Snow white	98.41	0.53	0.09	0.25	0.10	0.07	0.03

 # Snow white [Bhagat ka bas origin, Rajgarh, Alwar, (Raj.)]

Coal (hard and steam coal):

Hard coal was used in the pit furnace as a source of high temperature in the carbothermal studies. Steam coal was mixed with barite in the carbothermal reduction of barite. It was pulverized and graded through 80 mesh number standard sieves.

Clay Pots:

Clay pots of 250 ml were used for carbothermal reduction of barite.

Chemical reagents:

Iodine, sodium thiosulphate, calcium chloride, starch etc. were used.

Required reagents for the estimation are discussed below[6, 7].

Iodine solution (0.1N):

It is prepared by dissolving 12.7g of A.R iodine in the conc. solution of potassium iodide (20 g of A.R potassium iodide in 30 -40 ml of distilled water).It was shaken in the cold until all iodine dissolved. The solution was allowed to acquire room temperature. The volume was made up to one litre with distilled water and kept in a cool and dark place.

Sodium thiosulphate solution (0.1N):

25 g of A.R sodium thiosulphate was dissolved in boiled out distilled water. The solution was made up to one litre.

Dilute hydrochloric acid (5N apporx.):

45 ml of pure conc. hydrochloric acid was poured into 30 ml of distilled water. The solution was made up to 100 ml and shaken to ensure thorough mixing.

Indicator solution:

0.01 g of mercuric iodide and 5 g of starch was triturated with 50 ml of water in a mortar. The paste was poured into one litre of boiling water with constant stirring and boiled for 5 minutes .After cooling, the clear solution obtained was decanted.

Experiments were conducted to investigate the influence of calcium chloride on the yield of reduced barite i.e. barium sulphide as follows:

For the carbothermal reduction, powdered heterogeneous mixture of barite (white grade) and steam coal were prepared in optimum ratio. In this matrix calcium chloride in different proportions (1, 2, 3, 4, and 5% by weight of barite) was mixed thoroughly and filled in clay pots of 250 ml. In the pit furnace (depth = one m and diameter = 0.37m) both coal (hard and steam both) and clay pots filled with the charge consisting of barite, steam coal (in an optimum ratio) and calcium chloride were placed over the furnace gratings in alternating manner and the furnace was fired. After cooling of the furnace the reduced mass was obtained after breaking the clay pots carefully in the form of lumps. The entire process took about 48 hours. Reduced crude lumps of barium sulphide were recrushed in the pulveriser. The black powder (BaS) so obtained is called black ash[7, 8]. This powdered black ash was extracted with boiled water for making barium chemicals in subsequent steps. The amount of barium sulphide (formed from the given amount of barite) percentage in the reduced mass was found out by the estimation of sulphide ion in accordance with the available Indian standards[7].

Entire experimental investigations with calcium chloride have been carried out under anaerobic conditions in order to find its effects on carbothermal reduction of barite.

Estimation of Sulphide

Sulphide ion in the presence of hydrochloric acid reacts with iodine ions as follows:

$$S^{-2} + I2 \rightarrow S + 2I^{-}$$

e.g. $2BaS^{+} I2 \rightarrow 2BaI + 2S^{-}$

Hence S^{-2} ion reacts with iodine in molar ratio. The latter is estimated conveniently iodimetrically[9].

To estimate the percentage of sulphide ions in reduced black ash was added into hot water and boiled for 4 to 5 minutes. After filtering, the residue was washed with hot water for say about 3 – 4 times. The filtrate was made up to the required volume.

From the above prepared solutions the sulphide ions were estimated in accordance with the available Indian standards[8].

Results and discussion

Observed results are summarized in the Table 2.

Table 2: Effect of calcium chloride on the carbothermal reduction of barite

S.No	Calcium chloride by weight of barite (%)	Nature of barite taken	Extent of reduction of barite(in terms of %BaS in black ash)
1.	1	#White	48.2
2.	2	#White	49.4
3.	3	#White	51.0
4.	4	#White	51.9
5.	5	#White	52.3

#Bhagat ka bas origin (Rajgarh, Alwar belt)

Effect of calcium chloride on carbothermal reduction of barite:

The effect of calcium chloride on white variety of barite is shown in the figure 1. It is clear from figure 1 that by using calcium chloride the extent of carbothermal reduction of barite increases commendably.

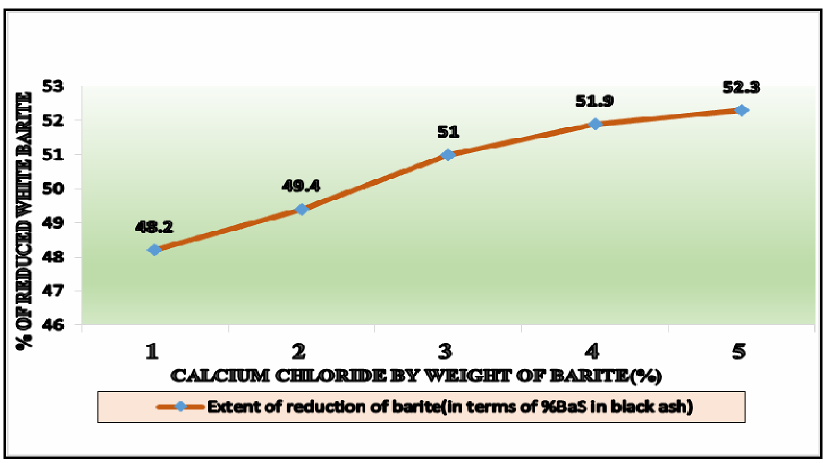

Figure 1: Extent of reduction on white shade of barite using calcium chloride.

The Table 1 reveals the effect of calcium chloride on heterogeneous solid phase of carbothermal reduction of barite under anaerobic conditions. The general impact of calcium chloride in the reduction is to increase the yield of barium sulphide. This may be due to the fact that when calcium chloride is allowed to react with the heterogeneous mixture of barite and coal it produces sulphide, chloride and carbon monoxide (reducing gas). Production of carbon monoxide enhances the reductive process and makes its easier too. Although at the same time some amount of calcium sulphide is also formed along with barium sulphide and barium chloride. As calcium sulphide is sparingly soluble in water it remains unextracted during the extraction of black ash. Resulting this reduces the soluble contents of the black ash[10, 11]. Consequently relatively lower barium sulphide percentage of black ash is expected.

Proposed reactions are as follows:

Carbothermal reduction without calcium chloride:

$BaSO_4 + 4C \rightarrow BaS + 4CO$ …… (1)

$BaSO_4 + 4CO \rightarrow BaS + 4CO_2$ …… (2)

Carbothermal reduction in presence of calcium chloride:

$BaSO_4 + CaCl_2 + 4C \rightarrow BaCl_2 + CaS + 4CO$ …… (3)

$BaSO_4 + 4CO \rightarrow BaS + 4CO_2$ …… (4)

$BaS + CaCl_2 \rightarrow BaCl_2 + CaS$ …… (5)

In role of reaction (3) and (4) are quite favourable in promotion of the carbothermal reduction and reaction (5) is not so favourable. This in fact is observed by the experimental results.

Conclusion

Calcium chloride gives favourable results in the heterogeneous carbothermal reduction of barite within the experimental limits.

References

1. Robert Kresse; Ulrich Baudis; Paul Jäger; H. Hermann Riechers; Heinz Wagner; Jochen Winkler; Hans Uwe Wolf, Ullmann's Encyclopaedia of Industrial Chemistry, Wiley-VCH, Weinheim, 2007.
2. K.Hargreaves; D.M.Murray, Journal of Chemical Technology and Biotechnology, 1989, 45 (4), 319-325.
3. Krik-Othmer, Encyclopaedia of Chemical Technology, John Wiley.New York, 1991, Vol 3, 902.
4. Y.Pelovski; I. Gruchavov; I. Dombalov, J.Thermal Anal. 1987, 32.barites
5. A Salem; Y O Tavakkoli, Mater. Res. Bull., 2009, 44, 1489.
6. IS: 1070 - Specification for Water, Distilled Quality (ISI, New Delhi), 1971.
7. IS: 5877- Specification for Barium Sulphide. Technical (Black ash) (ISI, New Delhi), 1971.
8. Barites A market survey, MSI (Indian Bureau of Mines, Nagpur), 1988.
9. Arthur, V. I., A text Book of quantitative Inorganic analysis, 3rd Ed, ELBS and Long mans Green and Co Ltd, London, 1962.
10. I Ilic; K Cerovick, Scand. Jour. of Metal. 1997, 26, 14-17.
11. M Randell; FR Bichowsky, Journ. Amer. Chem. Soc., 1918, 40, 368.

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