ChemTech

International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.7, No.6, pp 2769-2772, 2014-2015

# Influenceof Sulphur in Carbothermal Reduction of Barites

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**Abstract:** In present study the effect of sulphur on carbothermal reduction of barite was investigated. The results show that after admixingsulphur in matrix for the carbothermal reduction of barites, yields have been found to increase to the order of 57 percent. This may contribute a lot to the economy of the barium industry.
**Keywords*:*** Barite, catalyst, sulphur, iodometry.

## Introduction

Barite is one of the major mineral for export among non-metallic minerals. It finds its main uses in drilling mud for exploration of oil[1], in paints, rubber, explosives etc.Barium compounds such as barium chloride, barium carbonate, barium nitrate etc. are the important materials in chemical, ceramic and oil industries and barite ore is the indigenous natural starting material for producing various barium chemicals. But water insolubility of barite deters the process. Hence in 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 most reductive operations 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.In course of the experimental investigations, she discovered various reaction promoting agents which when increased in the matrix improve the yield of barium sulphide[2-5]. Present investigations are restricted to discuss the effect of sulphur on carbothermal reduction of barite.

The chemical composition of sulphur in commercial grade is $S_8$. Author has chosen it for trial purposefully on account of its affinity for oxygen atoms to form sulphur dioxide readily. In this way it reacts with bonded oxygen of barite i.e. barium sulphate and the object of conversion to barium sulphate to barium sulphide would be saved.

## Materials and Methods

### Barite (barium sulphate):

Barite the basic raw material was of two shades, snow-white and pink. Barites of both grades were pulverized separately. The powder was checked for reactive impurities like dolomite/limestone and sieved through standard sieves of mesh number 150 meshes[6].Chemical analysis of both samples has been given in Table 1.

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

| Shades of barite | $BaSO_4$ | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MgO | $Na_2O$ | $K_2O$ |
|---|---|---|---|---|---|---|---|
| # Pink shade | 96.95 | 0.92 | 0.19 | 0.84 | 0.18 | 0.13 | 0.06 |
| ## Snow white | 98.41 | 0.53 | 0.09 | 0.25 | 0.10 | 0.07 | 0.03 |

# **Pink shade** [Jamrauli origin, Rajgarh, Alwar, (Raj.)]
## **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 coalwas mixed with barites in the carbothermal reduction of barites. It was pulverized and graded through 80 mesh number standard sieves.

**Clay Pots:**

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

**Chemical reagents:**

Iodine, sodium thiosulphate, sodium nitrite, starch etc. were used. Required reagents for the estimation are discussed below[7, 8].

**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 sulphur on the yield of reduced barites i.e. barium sulphide as follows:

For the carbothermal reduction, powdered heterogeneous mixture of barites (pink and white grades both separately) and steam coal were prepared in optimum ratio. In this matrix sulphurin 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 barites, steam coal (in an optimum ratio ) and sulphur 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[8, 9]. 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[8].

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

**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[10.]

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 sulphur on the carbothermal reduction of barite**

| S.No | Sulphur by weight of barite (%) | Nature of barite taken | Extent of reduction of barite(in terms of %BaS in black ash) |
|---|---|---|---|
| 1. | 1 | #Pink<br>##White | 48.2<br>51.3 |
| 2. | 2 | #Pink<br>##White | 51.0<br>53.1 |
| 3. | 3 | #Pink<br>##White | 52.8<br>54.7 |
| 4. | 4 | #Pink<br>##White | 53.6<br>55.1 |
| 5. | 5 | #Pink<br>##White | 54.1<br>56.2 |

**#Jamrauli origin (Rajgarh, Alwar belt)**
**##Bhagat ka bas origin (Rajgarh, Alwar belt)**

**Effect of sulphur on carbothermal reduction of barites:**

The effect of sulphur on pink and white variety of barite are shown in the figure 1 and 2. It is clear from figure 1 and 2 that by using sulphur the extent of carbothermal reduction of barite increases commendably.

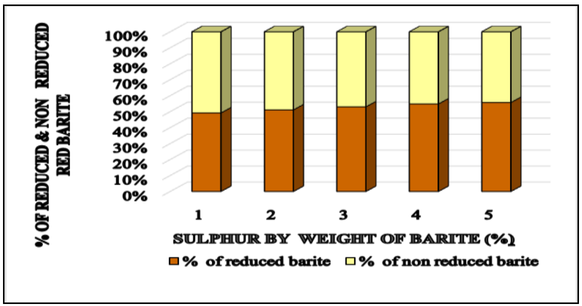


**Figure 1: Extent of reduction on pink variety of barite usingsulphur.**

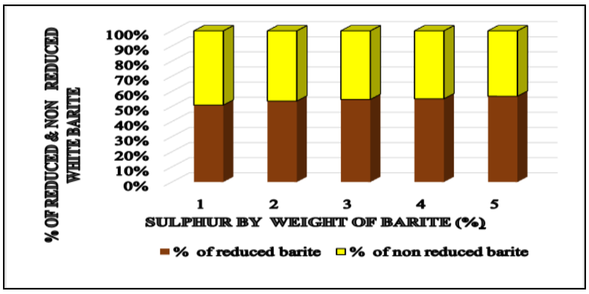


**Figure 2: Extent of reduction on white variety of barite usingsulphur.**

The Table 1 reveals the effect of sulphur on heterogeneous solid phase of carbothermal reduction of barite under anaerobic conditions. The general impact of sulphurin the reduction is to increase the yield of barium sulphide. It may be assumed that barite when reacts with sulphur it produces barium sulphide and sulphur di-oxide. In that way because of its low melting point, sulphur would be available in vapour phase under the situations of carbothermal reduction of barite. Sulphur vapour should be better reducing agent than solid carbon. Accordingly, it is noted that the presence of sulphur is exerting favourable effects on the reduction of barite into barium sulphide.

Proposed reactions are as follows:

**Carbothermal reduction without** sulphur**:**
**$BaSO_4 + 4C \rightarrow BaS + 4CO$ …… (1) (Slow reaction)**
**$BaSO_4 + 4CO \rightarrow BaS + 4CO_2$ …… (2)**
**Carbothermal reduction in presence of** sulphur**:**
**$BaSO4 + 2S \rightarrow BaS + 2SO_2$ …… (3) (Fast reaction)**

In role of reaction (3) is quite favourable in promotion of the carbothermal reduction .This in fact is witnessed by the experimental results. Increasing amounts of sulphur is also quite expected on similar accounts.

## Conclusion

Sulphur gives favourable results in the heterogeneous carbothermal reduction of barites within the experimental limits.

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