Study of Effect of Iron powder in Carbothermal Reduction of Barites

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ABSTRACT
In present study the catalytic reduction of barite in the presence of iron powder has been investigated for the high retrieval of water soluble barium sulphide. Iron powder ranging from 1.0 to 5.0 wt. % was admixed in matrix for the carbothermal reduction of barites at high temperatures. Yields of barium sulphide have been found to increase considerably thus achieving better use of barite.

Keywords: *Barite, coke, catalyst, iodometry, iron powder.*

1. INTRODUCTION

Barite is one of the major mineral for export among non-metallic minerals. It is the indigenous natural starting material for producing various barium chemicals such as barium chloride, barium carbonate, barium nitrate etc. which are very important in chemical, ceramic and oil industries. Carbothermal reduction of barite at high temperature by carbon is the key step to convert highly insoluble barite to water soluble barium sulphide. 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 exceeds 40 %, due to many reasons like the presence of impurities in barite, lack of research work, dearth of technical knowledge etc. [1].

The author, therefore, worked on different factors to enhance the yield of barium sulphide obtained after the carbothermal reduction of barite under anaerobic conditions in the pit furnace at high temperatures.[2-4]. Present paper is limited to discuss the effect of iron powder on carbothermal reduction of barite. Iron is naturally occurring element. It was selected as a trial catalyst by author because iron in its finely powdered state is a known reducing agent. [5].

2. MATERIALS AND METHODS

2.1. Barite (barium sulphate)
Barite the basic raw material of snow-white shade, was pulverized and powder was checked for reactive impurities like dolomite/ limestone and sieved through standard sieves of mesh number 150 meshes [6].

2.2. 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.

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

2.4. Chemical reagents- Iodine, sodium thiosulphate, iron powder, starch etc. were used.
Required reagents for the estimation are discussed below [7].

2.4.1. Iodine solution (0.1N)
It is prepared by dissolving 12.7gm of A.R iodine in the conc. solution of potassium iodide (20 gm 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.

2.4.2. Sodium thiosulphate solution (0.1N)
25 gm of A.R sodium thiosulphate was dissolved in boiled out distilled water. The solution was made up to one litre.

2.4.3. 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.

2.4.4. Indicator solution
0.01 gm of mercuric iodide and 5 gm 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.
For the carbothermal reduction, powdered heterogeneous mixture of barite (snow-white grade) and steam coal was prepared in optimum ratio. In this matrix iron powder 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 barites, steam coal (in an optimum ratio) and iron powder 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 iron powder 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].

3. RESULTS AND DISCUSSION

The Table 1 reveals the effect of iron powder on heterogeneous solid phase of carbothermal reduction of barite under anaerobic conditions.

Table 1: Effect of iron powder on the carbothermal reduction of barite

S.No	Iron powder by weight of barite (%)	Extent of reduction of barite(in terms of %BaS in black ash)
1.	1	45.8
2.	2	44.2
3.	3	42.8
4.	4	40.1
5.	5	38.0

3.1. Effect of iron powder on carbothermal reduction of barites:

The effect of iron powder on white variety of barite is shown in the Fig. 1 It is clear from Fig. 1 that the carbothermal reduction of barite in the presence of increasing proportion of iron powder decreases the yield of reduced barite gradually.

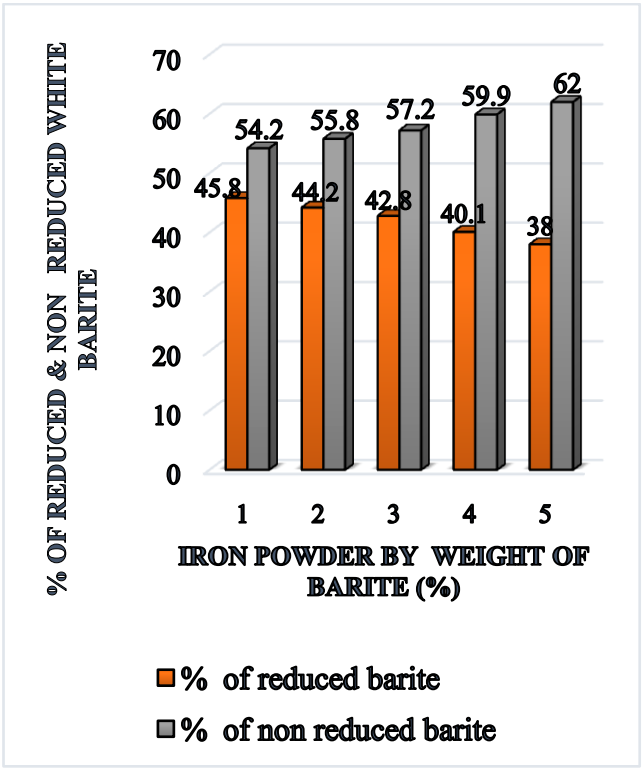

Figure 1: Extent of reduction on white variety of barite usingiron powder.

It may be assumed that during the anaerobic reduction of barite in the presence of iron powder at high temperature there may be formation of some ferrous sulphite. In addition carbon from steam coal may also react with molten iron to form metal carbide which is not good a reducing agent. Once the sulphate has been reduced to sulphide in presence of iron, both iron and barium sulphides are formed in the black ash. The former being water insoluble is not extracted under the usual conditions resulting in lower percentage of sulphide (barium sulphide) in the black ash as expected.

Proposed reactions are as follows:

Carbothermal reduction without iron powder:

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

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

Carbothermal reduction in presence ofiron powder:

Major

$3BaSO_4 + 8Fe \rightarrow 3BaS + 4Fe2O3$… (1)

Minor

$BaSO_4 + 3Fe \rightarrow BaO + Fe2O3 + FeS$….(2)

450-900º

$FeO + CO \rightarrow Fe + CO_2$ …… (3)

$3Fe + 2CO \rightarrow Fe_3C + CO_2$ …… (4)

On the basis of above proposed reactions, (2) and (3)reactions are posing adverse effects on the carbothermal reduction of barite.

4. CONCLUSIONS

- Iron powder (in less percentage) increases the extent of carbothermal reduction of barites up to certain limit.
- Formation of iron carbide is not favorable for carbothermal reduction of barite.
- Iron powder during the reaction forms water insoluble ferrous sulphide.

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