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ChemTech

International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.7, No.01, pp 246-250, 2014-2015

Study of Bone Powder as a Reaction Promoting Agent for the Carbothermal Reduction of Barite

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Abstract: The present paper reports the role of bone powder as reaction promoting agent for the carbothermal reduction of barites. Normally in most industrial reductive operations the extent of carbothemal reduction of barite rarely exceed 40 to 45 percent and a lot of unreacted barite is left behind which is of no use. The results of present experimental investigation indicated that after admixing the bone powder in matrix for the carbothermal reduction of barite the yields (barium sulphide) have been found to increase to the order of 54 percent. Therefore, the study is very important, as it possesses dual benefits in terms of maximum utilisation of barite and more contribution towards national economy.
Keywords: Barite, coke, bone powder, carbothermal reduction, barium sulphide.

Introduction

Barite is one of the major mineral for export among non-metallic minerals. This indigenously mineral widely used in broad range of industries such as paint, rubber, explosive etc. Due to its insolubility in water, non-magnetic nature and inertness towards acids barite is most suitable mineral for the preparation of oil-well drilling mud[1, 2]. It is also used for the manufacture of barium chemicals like barium carbonate, barium chloride etc.

As it is highly insoluble in water, the process of carbothermal reduction can initiate the reaction which is the most common method used in the barium industries. Through this process water insoluble barite converted into water soluble barium sulphide(key material for the manufacture of barium chemicals). Theoretically a pure sample of barite should yield barium sulphide to the extent of about 70% or so. But in most industrial reductive operations the extent of reduction seldom exceeds 45%. This is a serious loss of such an important mineral and a great dent in national economy. The author, therefore, became concerned with the problem. In order to increase the yield of barium sulphide, she studied the impact of different and most probablereaction promoting agents on carbothermal reduction of barites under anaerobic conditions in the pit furnace at high temperatures[3-8].

Present investigations are limited to discuss the effect of bone powder [$Ca_3(PO_4)_2$] on carbothermal reduction of barite under anaerobic conditions. By incorporation of bone powder, yields have been found to increase to the order of 54 percent.

Chemically bone powder is $Ca_3(PO_4)_2$.Thermal decomposition of bones yield porous, friable bone char which is a very good adsorbent. Bone char contains calcium phosphate. At high temperature it reacts with carbon to give carbon monoxide gas which is a good reducing agent and free phosphorus which further sets a chain reactions. All this enhances the reduction process and make it smooth too. The experimental investigations with bone powder have been carried out in order to find its effects on carbothermal reduction of barites under anaerobic conditions.

Materials and Methods

The raw materials used for study are as follows:

Barites (barium sulphate):

Barite is the basic raw material. It was of two shades snow-white ($BaSO_4$ content 98.41%) and pink ($BaSO_4$ content 96.95%). Before the pulverizing of barites of both grades (separately),the powder was checked for reactive impurities like dolomite/limestone and sieved through standard sieves of mesh number 150 mesh[9].

Coal (hard and steam coal):

Hard coal- It contains 64.5% carbon contents and used in the pit furnace as a source of high temperature in the carbothermal studies.

Steam coal - It contains 59.7% carbon contents. It was mixed with barites (both pink and snow white shades separately) for 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, bone powder, starch etc. were used[10].

Iodine solution (0.1N): It was prepared by dissolving 12.7g of A.R iodine in the conc. solution of potassium iodide (20.0 g of A.R potassium iodide in 30 - 40 ml of distilled water). It was shaken in the cold until all iodine dissolved completely. 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): 25.0 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 5.0 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 was decanted.

Experimental Procedure:

Experiments were conducted to investigate the influence of bone powder 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 bone 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 = 1.0 m and diameter = 0.37 m) coal (hard and steam both) and clay pots filled with the charge consisting of barites, steam coal (in an optimum ratio) and bone powder are placed over the furnace gratings in alternating manner. The furnace was then 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 recrushed into the pulveriser. The black powder (BaS) so obtained is called black ash[1, 11]. This powdered black ash was extracted with boiled water for making barium chemicals in subsequent steps. The percentage of barium sulphide (formed from the given amount of barite) in the reduced mass, was found out by the estimation of sulphide ion in accordance with the available Indian Standards[11].

Estimation of sulphide

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

$$\mathbf{S^{2-} + I_2 \rightarrow S + 2I^-}$$

$$\mathbf{e.g. 2BaS + I_2 \rightarrow 2BaI + 2S^-}$$

Hence sulphideions react with iodine in molar ratio. The latter is estimated conveniently iodimetrically[12].

To estimate the percentage of sulphide ions in reduced black ash, it 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[11]. 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[11].

Results and Discussion

Observed results are summarized in the Table 1.

Table 1: Effect of bone powder in carbothermal reduction of barite*

S.No	Bone powderby weight of barite (%)	Nature of barite taken	Extent of reduction of barite(in terms of %BaS in black ash)
1.	**1**	**#Pink** ***White**	**49.1** **50.3**
2.	**2**	**#Pink** ***White**	**49.9** **51.2**
3.	**3**	**#Pink** ***White**	**50.3** **52.0**
4.	**4**	**#Pink** ***White**	**51.7** **52.8**
5.	**5**	**#Pink** ***White**	**52.0** **53.7**

#Jamrauli origin (Rajgarh, Alwar belt)
***Bhagatka bas origin (Rajgarh, Alwar belt)**

Role of bone powder in carbothermal reduction of barites

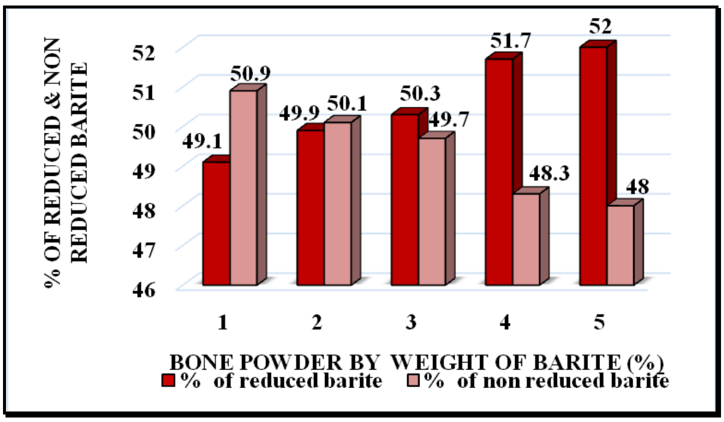

Fig. 1: Relative percentage of reduced and non-reduced pink barite using bone powder

The perusal of Table 1 reveals the percentage of reduced barite by using bone powder. The general impact of bone powder in the carbothermal reduction is to increase the yield of barium sulphide, which can be evidently seen in figure 1 and 2.

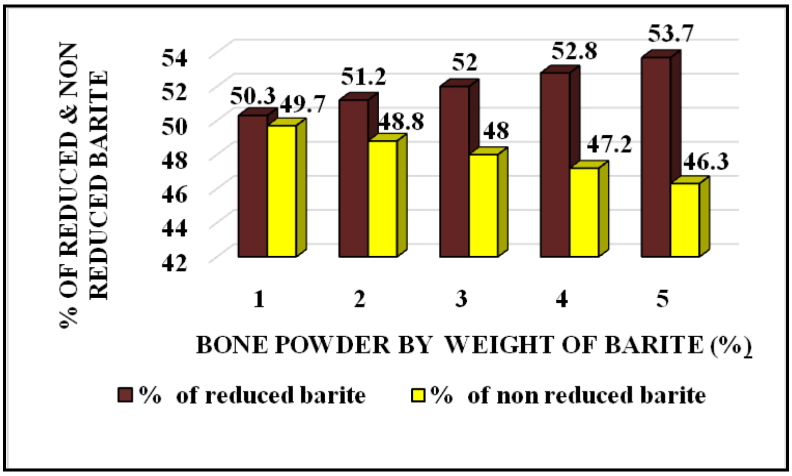

Fig. 2: Relative percentage of reduced and non-reduced snow-white barite using bone powder

The role of bone powder in the carbothermal reduction of barites can be explained as follows:

Bones contain inorganic salts. On heating their thermal decomposition take place and they give porous, friable bone char which is a very good adsorbent. Bone char mainly consist of 70-80% $Ca_3(PO_4)_2$, 3-8% $CaCO_3$ and very little amount of carbon[13, 14]. Calcium phosphate when reacts with carbon it gives carbon monoxide and free phosphorus[15-17].Carbon monoxide being a reducing gas reduces barite to barium sulphide. Phosphorus is knowing to possess very high affinity for oxygen. At high temperature it reacts with barite (barium sulphate) to form oxides of phosphorus and barium sulphide. These oxides are again reduced by available carbon to form phosphorus again and thus a chain process is established. All this promotes the reduction of barite (barium sulphate) and hence supports the reductive process to proceed forward, efficiently and easily.

Proposed reactions are as follows:

<u>Reduction in absence of bone powder</u>

$BaSO_4 + 4C \rightarrow BaS + 4CO$ …… (1) (Slow reaction)
$BaSO_4 + 4CO \rightarrow BaS + 4CO_2$ ……(2)

<u>Reduction in presence of bone powder</u>

(Onheating)
Bone powder$\rightarrow$ $Ca_3(PO_4)_2 + CaCO_3$ + salts + bone char (adsorbent) …… (3)
$Ca_3(PO_4)_2 + 3C \rightarrow 2CaCO_3 + CO + 2P + CaO$ …… (4)
$BaSO_4 + C + 2P \rightarrow BaS + CO + P_2O_3$ …… (5)
$2BaSO_4 + 3C + 2P \rightarrow 2BaS + 3CO + P_2O_5$ …… (6)
$3BaSO_4 + 8P \rightarrow 3BaS + 4P_2O_3$ ……(7)
$5BaSO_4 + 8P \rightarrow 5BaS + 4P_2O_5$ ………(8)
$P_2O_5 / P_2O_3 + 5/3\ C \rightarrow 2P + 5/3\ CO$ ……(9)
$BaSO_4 + 4CO \rightarrow BaS + 4CO_2$ ……(10)

In role of reactions (3) to (9) are quite favourable in promotion of the carbothermal reduction. This in fact is witnessed by the experimental results. Increase in yields of barium sulphide with increasing amounts of bone powder (up to the experimental limits) is quite expected on similar accounts.

Conclusion

Up to the extent of experimental limits, bone powder is a good reaction promoting agent. It gives good yields of barium sulphide by carbothermal reduction of barite. Calcium ions seems to play no role in the heterogeneous carbothermal reduction of barites. Carbothermal reduction of barites seems to be in-different in the presence of alkali metal cations.

References

1. Barites A Market Survey, IBM Nagpur, MSI, 1988.
2. Kresse Robert; Baudis Ulrich; Paul Jäger; Riechers H. Hermann; Heinz Wagner; Jochen Winkler; Wolf Hans Uwe., Ullmann's Encyclopaedia Of Industrial Chemistry, Wiley-VCH, Weinheim2007.
3. Hargreaves K; Murray D.M, J. Chem. Tech. And Biotech.1989, 45 (4) 319-325.
4. Lozhkin A.F; Pashcenko V.N; Povar F.V, J. Appl. Chem. USSR, 1974, 47 (5),1031-1034.
5. Jagtap S.B; .Pande A.R; Gokarn A.N, Ind.Eng.Chem.Res. 1990, 29, 795-799.
6. Pechkovski V.V; Ketov A.N, Zh.Prkl.Khim. 1960, 33, 1719-1723.
7. Pelovski Y; Gruchavov I; Dombalov I, J.Thermal Anal. 1987, 32, 1743-1745.
8. Kirk-Othmer, Encyclopedia Of Chemical Technology, Vol. 3, New York, John Wiley.1991.
9. Salem A; Tavakkoli Y O, Mater. Res. Bull., 2009, 44,1489-1493.
10. Specification For Water, Distilled Quality, IS: 1070, 1971, New Delhi: BIS.
11. Specification For Barium Sulphide. Technical (Black Ash), IS: 5877, 1971, New Delhi: BIS.
12. Arthur, V. I., "A Text Book Of Quantitative Inorganic Analysis", 3rd Ed., London, ELBS Andlongmans Green And Co Ltd, 1962.
13. Deitz, V. R., Bibliography Of Solid Adsorbents, United States Cane Sugar Refineries And Bone Charmanufacturers And The National Bureau Of Standards,Washington, D.C., 1944.
14. Taggart W G. Louisiana Planter, 1917, 58, 381.
15. Lassieur A., International Cong. App. Chem., 1912, 8.Ii, 171.
16. Wazer Van, "Encyclopedia Of Chemical Technology," Edited By Kirk And Othmer, Interscience publishers, New York, 1953, 10, 403- 510.
17. Wazer Van, "Phosphorous And Its Compounds," Interscience Publishers, New York, 1958.

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