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Effect of zinc on the carbothermal reduction of barite

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ABSTRACT

Present paper discusses about the effect of zinc powder on the yield of water soluble barium sulphide, obtained after the carbothermal reduction of mixture of snow white barite with zinc powder in different optimum ratio. Experimental results show that low proportion of zinc powder enhances the yields of barium sulphidethus attaining better utilization of natural resource and contributing positively towards national economy.

Keywords: Barite, zinc powder, coke, black ash, pyrochromic.

INTRODUCTION

Barite an indigenous, non-metallic mineral is one of the major mineral for export. In the world map of barites, India ranks second in production and third in reserves [1].

Barite is in demand due to its insolubility in water, high specific gravity, non-magnetic nature, and inertness towards acids etc. and mainly used for the preparation of oil-well drilling mud, paints, rubber, explosives, nuclear waste management etc. [2-4]. Barite is only most suitable and commonly used material for manufacturing of a variety of barium chemicals such as barium chloride, barium carbonate, barium nitrate etc. with wide applications. In practice carbothermal reduction of barite using carbon is the key step to convert water insoluble barite to water soluble barium sulphide. When both barite and carbon are in contact, reduction of barite takes place according to the following equation:

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

During the reduction, generated carbon monoxide reacts with remaining barite and produces more CO thus enhances the rate of reduction.

 $\begin{array}{rcl} BaSO_4 &+& 4CO &\rightarrow & BaS &+& 4CO_2.....(2) \\ \\ & C+CO_2 \rightarrow 2CO.....(3) \end{array}$

But in most reductive operations yield is very poor due to many reasons like the presence of impurities in barite, lack of research work, dearth of technical knowledge etc.

Therefore, to tackle the problem of low yield, author worked on different factors to influence the efficiency of carbothermal reduction of barite under anaerobic conditions in the pit furnace at high temperatures. The aim of the

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present work has been to study the action of zinc powder (as a reaction promoting agent) on carbothermal reduction of barite under anaerobic conditions.

MATERIALS AND METHODS

Following raw materials were used for the study:

Barite (barium sulphate)

Basic raw material for investigation was barite of snow-white shade. Chemical analysis of snow white barite is given in Table 1.

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

Shade of barite	BaSO ₄	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	Na ₂ O	K ₂ O
# 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.)]

Snow white barite was pulverized and checked for reactive impurities like dolomite/limestone and sieved through standard sieves of mesh number 150 mesh [5].

Coal

As a source of high temperature hard coal of 64.5% carbon was used in the pit furnace whereas steam coal of 59.7% carbon was first pulverized then graded through 80 mesh number standard sieves and mixed with snow white barite for the carbothermal reduction.

Clay pots

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

Chemical reagents

Iodine solution (0.1N)

It was prepared by dissolving 12.7g of A.R iodine in the conc. solution of potassium iodide and was shaken in cold until iodine dissolved completely. The solution was allowed to acquire room temperature and volume was made up to one liter with distilled water. Stored 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 and solution was made up to one liter.

Dilute hydrochloric acid (5N apporx.)

45 ml of pure conc. hydrochloric acid was transferred 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. With constant stirring prepared paste was poured into one liter of boiling water and further boiled for 5 minutes. After cooling, the clear solution was decanted.

Experimental Procedure

To find out the role of zinc powder as a reaction promoting agent on the yield of reduced barite, experiments were conducted as follows: In an optimum ratio, powdered white grade barite mixed with steam coal for the purpose of carbothermal reduction. Zinc powder in different proportions (1, 2, 3, 4, and 5% by weight of barite) was mixed thoroughly in this matrix and filled into clay pots of 250 ml. Clay pots filled with the charges were placed over the furnace gratings in alternating manner with hard and steam coal. The furnace was then fired. The entire process took about 48 hours. After cooling of the furnace the reduced mass i.e. barium sulphide lumps was obtained by breaking the clay pots carefully. Reduced crude lumps of barium sulphide were recrushed in the pulveriser. The obtained black ash after the extraction with boiled water, is used for making barium chemicals in the succeeding steps. The

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percentage of barium sulphide in the reduced mass obtained after the carbothermal reduction of barite, was calculated by the estimation of sulphide ion as per the available Indian Standards [6-8].

Estimation of sulphide

In the presence of hydrochloric acid, sulphide ion reacts with iodine ions as follows:

$$\mathbf{S}^{-2} + \mathbf{I}_2 \longrightarrow \mathbf{S} + 2\mathbf{I}^{-} \dots \dots (4)$$

e.g. 2BaS+
$$I_2 \rightarrow 2BaI + 2S^{-}$$
..... (5)

Hence S^{-2} ion reacts with iodine in molar ratio which was estimated iodimetrically [9].

RESULTS AND DISCUSSION

Role of zinc powder

Figure 1 is revealing the impact of zinc powder on carbothermal reduction of snow white barite i.e. up to the experimental limits increasing proportion of zinc powder decreases the yield of reduced barite gradually.

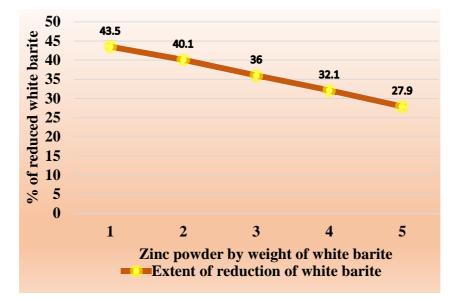


Fig. 1: Extent of carbothermal reduction of snow white barite using zinc powder

It could be explained on the basis that anaerobic carbothermal reduction of barite in presence of zinc powder at such a high temperature leads to the formation of sulphides and oxides of barium and zinc resulting black ash contains both i.e. barium sulphide as well as zinc sulphide. Since zinc sulphide is sparingly soluble in water thus it cannot be extracted under usual conditions of aqueous extraction which decreases the percentage of soluble sulphide (or barium sulphide) in the black ash. At the same time the colour of reduced mixture was found oddly reddish brown in place of usual blackish grey. This may be ascribed to the pyrochromic characteristics of sulphides and oxides of zinc.

Chemically the possible reactions involved in presence of zinc in the clay pots at the temperatures of the pit furnace are as follows:

Reduction in presence of zinc powder

BaSO ₄ +	4Zn	\rightarrow	BaS + 4ZnO	(6)
BaS +	ZnO	\rightarrow	BaO + ZnS	(7)
BaSO ₄ +	4C	\rightarrow	BaS + 4CO	(8)
BaSO ₄ +	4CO	\rightarrow	$BaS + 4CO_2$	(9)
Zn	+ CO ₂	\rightarrow	ZnO + CO	(10)

Formation of zinc oxide and zinc sulphide in reaction.6, 7 and 10have adverse effects on the yield of water soluble barium sulphide after the carbothermal reduction of white barite.

CONCLUSION

Zinc powder (in less percentage) increases the extent of carbothermal reduction of barites up to certain limit. Zinc powder during the carbothermal reduction at high temperature forms water insoluble zinc sulphide/oxide which are not favorable to obtain high yield of barium sulphide.

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