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Catalytic Effect of Sodium Nitrite in Carbothermal Reduction of Barites

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ABSTRACT

The paper reports the effect of sodium nitrite on carbothermal reduction of barites. In practice, in most industrial reductive operations the extent of reduction seldom exceeds 50 percent. After admixing the sodium nitrite in matrix the carbothermal reduction of barites has shown encouraging results. Yields have been found to increase to the order of 57 percent. This may contribute a lot to the economy of the industry.

Keywords: Barite, coke, catalyst, sodium nitrite, carbothermal reduction.

INTRODUCTION

India occupies a very prominent position in the world map of barite, ranking third in reserves and second in production. It is one of the major mineral for export among non-metallic minerals. Barite finds its principle utility in drilling mud for exploration of oil [1] because of its high specific gravity, inertness to acids, insolubility in water and above all its low cost compared to many other available heavy materials. It is also used in paints, rubber, explosives etc.

This indigenous mineral is suitable for the manufacture of barium chemicals like barium chloride, barium carbonate, barium nitrate etc. As it is highly insoluble in water, very few methods are available for converting water insoluble barite into water soluble barium sulphide which is the key material for initiation of the reaction. In practice, barium sulphide is prepared by the process of 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 industrial reductive operations the extent of reduction seldom exceeds 50 %. This is a serious loss of such an important mineral and a great national loss too. The author, therefore, became concerned with the problem. She 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 [2-8]. Present investigations are restricted to discuss the effect of sodium nitrite ($NaNO_2$) on carbothermal reduction of barite. By incorporation of sodium nitrite yields have been found to increase from 50 to 57 percent.

Chemically sodium nitrite is $NaNO_2$.At high temperature it changes to sodium nitrate in the presence of barium sulphate. Sodium nitrate decomposes and gives nascent oxygen, nitrites and other oxides of nitrogen. This nascent oxygen reacts with carbon and produces an active reducing gas i.e. carbon monoxide [9-17]. All this enhances the reduction process and makes it easier too. Entire experimental investigations with sodium nitrite have been carried out under anaerobic conditions in order to find its catalytic effects on carbothermal reduction of barites.

MATERIALS AND METHODS

The raw materials used for study are as follows:

Barite (barium sulphate)
Barite is the basic raw material. It was of two shades, snow-white and pink. 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.)]
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[18].

Coal (hard and steam coal)
Hard coal- It contains 64.5% carbon contents. It was 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 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 [19, 20].

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.

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.

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 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.

Experiments were conducted to investigate the influence of sodium nitrite 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 sodium nitrite 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 sodium nitrite 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 [20, 21]. 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 [20].

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 S^{-2} ion reacts with iodine in molar ratio. The latter is estimated conveniently iodimetrically [22].

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 [20]. 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 [20].

(a) Barite (150 mesh) – 2parts,
(b) Coal – (80 mesh) – 1 part,
(c) Colour of black ash - Blackish grey

#Jamrauli origin (Rajgarh, Alwar belt)

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

Catalytic effect of sodium nitrite on carbothermal reduction of barites: The catalytic action of sodium nitrite on pink and white variety of barite are shown in the Figure 1 and 2.It is clear from

RESULTS AND DISCUSSION

Observed results are summarized in the Table 2.

Table 2: Effect of sodium nitrite on the carbothermal reduction of barite

S.No	Sodium nitrite by weight of barite (%)	Nature of barite taken	Extent of reduction of barite(in terms of %BaS in black ash)
1.	1	#Pink ##White	49.2 50.9
2.	2	#Pink ##White	51.1 53.6
3.	3	#Pink ##White	53.0 54.7
4.	4	#Pink ##White	54.8 55.1
5.	5	#Pink ##White	55.7 56.8

Matrix composition (W/W):

Figure 1 and 2 that by using sodium nitrite the extent of carbothermal reduction of barite increases commendably.

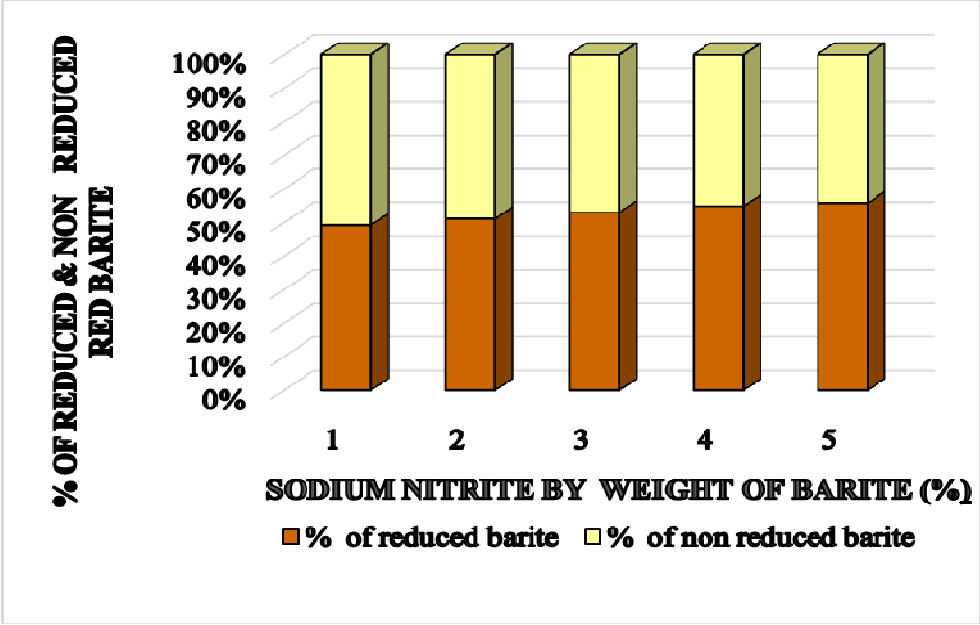

Figure 1: Extent of reduction on pink variety of barite using sodium nitrite.

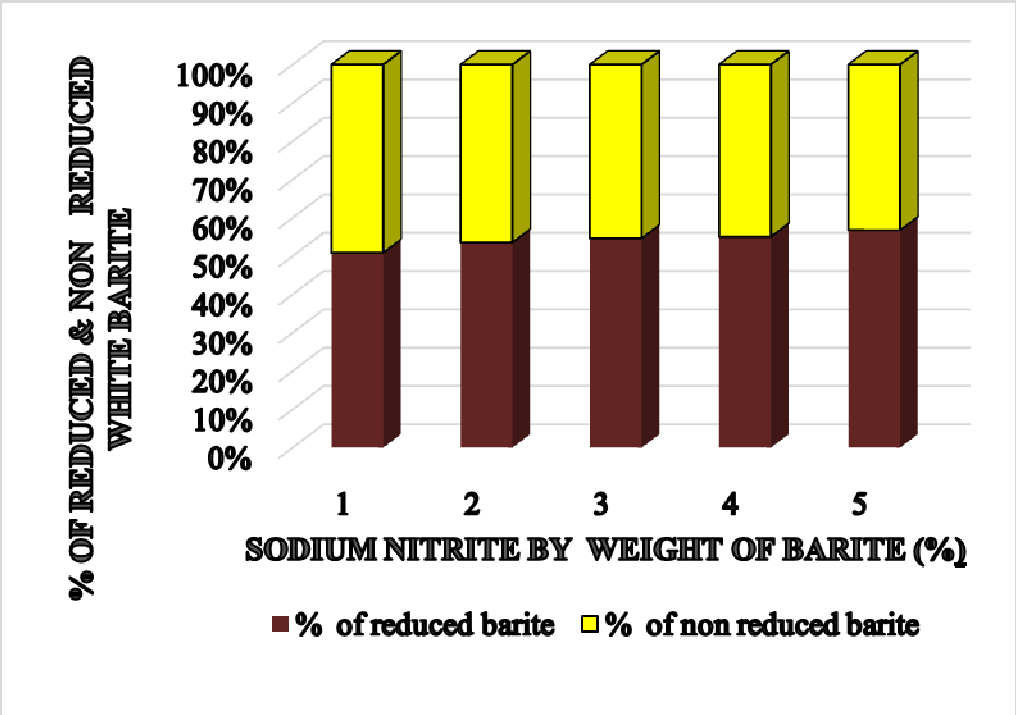

Figure 2: Extent of reduction on white variety of barite using sodium nitrite.

The effects of sodium nitrite (used as reaction promoting agent) on the carbothermal anaerobic solid phase reduction of barites are shown in the Table 2. The general impact of sodium nitrite in the reduction is to increase the yield of barium sulphide. This may be ascribed to the role of a catalyst played by the sodium nitrite in the carbothermal reduction of barites. On heating sodium nitrite melts. In molten state it reacts with barium sulphide and gives sodium nitrate.

At higher temperature sodium nitrate decomposes as usual and gives other oxides of nitrogen and nascent oxygen. Carbon reacts with nascent oxygen to form carbon monoxide. Carbon monoxide being a reducing gas reduces barites to barium sulphide and makes the reductive process to proceed forward efficiently.

Proposed reactions are as follows:

Carbothermal reduction without sodium nitrite:

$$BaSO_4 + 4C \rightarrow BaS + 4CO \quad \ldots\ldots (1)\ \text{(Slow reaction)}$$

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

Carbothermal reduction in presence of sodium nitrite:

$$NaNO_2\ \text{(on heating)} \rightarrow \text{MELT} \quad \ldots\ldots (3)$$

$$4NaNO_2 + BaSO_4 \rightarrow 4NaNO_3 + BaS \quad \ldots. (4)$$

$$NaNO_3 \rightarrow NaNO_2 + O \quad \ldots\ldots (5)$$

$$C + O \rightarrow CO \quad \ldots\ldots (6)$$

$$BaSO_4 + 4CO \rightarrow BaS + 4CO_2 \quad \ldots\ldots (7)$$

In role of reactions (3), (4) and (5) are quite favourable in promotion of the carbothermal reduction .This in fact is witnessed by the experimental results. Increasing amounts of sodium nitrite is also quite expected on similar accounts.

CONCLUSIONS

- Up to the extent of experimental limits sodium nitrite is a good catalyst.
- Sodium ions seem to play no role in the heterogeneous carbothermal reduction of barites.

- Carbothermal reduction of barites seems to be indifferent to the presence of alkali metal cations.

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