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Effect of Sodium Nitrate on Carbothermal Reduction of Barites

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ABSTRACT

The paper reports the effect of sodium nitrate on carbothermal reduction of barites. In practice in most industrial reductive operations the extent of reduction seldom exceeds 50 percent. After admixing the sodium nitrate in matrix, the carbothermal reduction of barites has shown encouraging results. Yields have been found to increase of the order of 57 to 60 percent. This may contribute a lot to the economy of the industry.

Keywords: Barite, Coke, Catalyst, Sodium nitrate, Carbothermal reduction.

INTRODUCTION

Barite is one of the major mineral for export among the non-metallic minerals. This indigenous mineral is suitable for the manufacture of barium chemicals. It is mainly used in paints, oil-well drilling [1], rubber, explosives etc. As it is highly insoluble in water only the process of carbothermal reduction can initiate the reaction. 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 leads to a serious loss of such an important mineral and is a great national loss. The author, therefore, became concerned with the problem and studied the impact of different reaction promoting agents on carbothermal reduction of barites 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, discovered various reaction promoting agents which when increased in the matrix improve the yields of the barium sulphide [2-7]. Present investigations are restricted to discuss the effect of sodium nitrate ($NaNO_3$) on carbothermal reduction of barites. By incorporation of sodium nitrate, yields have been found to increase from 50 to 60 percent. Chemically sodium nitrate is $NaNO_3$. At high temperature it 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 [8-17].This makes the reduction process easier and faster too. The experimental investigations with sodium nitrate have been carried out in order to find its effect on carbothermal reduction of barites under anaerobic conditions.

MATERIALS AND METHODS

The raw materials used for study are-

Barite (barium sulphate): Barite was the basic raw material. Barite was in two shades: snow-white ($BaSO_4$ content 98.41%) and pink ($BaSO_4$ content 96.95%). 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 mesh [18].

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

Steam coal - It contained 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 nitrate, starch etc., were used[19].

Iodine solution (0.1N): It was prepared by dissolving 12.7gm of A.R iodine in the conc.solution of potassium iodide (20.0 gm of A.R potassium iodide in 30 -40 ml of distilled water) and was shaken in cold until the whole iodine dissolved. The solution was allowed to acquire room temperature. The volume was made up to one liter with distilled water and kept in a cool and dark place.

Sodium thiosulphate solution (0.1N): 25.0 gm of A.R sodium thiosulphate was dissolved in boiled out distilled water. The solution was made up to one liter.

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 5.0 gm of starch was triturated with 50 ml of water in a mortar. The paste was poured into one liter 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 sodium nitrate on the yield of reduced barites i.e. barium sulphide . 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 nitrate 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 = 0.37 m) both hard and steam coal and clay pots filled with the charge consisting of barites, steam coal in an optimum ratio and sodium nitrate were placed over the furnace gratings in alternating manner and the furnace was fired. After cooling of the furnace the reduced mass was obtained by 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 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

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

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

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

RESULTS AND DISCUSSION

Observed results are summarized in the Table 1.

Table 1. Effect of sodium nitrate on carbothermal reduction of barite*****

S.No	Sodium nitrate by weight of barite (%)	Nature of barite taken	Extent of reduction of barite(in terms of %BaS in black ash)
1.	1	#Pink !White	50.1 57.5
2.	2	#Pink !White	52.2 52.9
3.	3	#Pink !White	52.8 53.4
4.	4	#Pink !White	54.6 57.7
5.	5	#Pink !White	56.2 60.3

* Matrix composition (w/w): (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 nitrate on carbothermal reduction of barites: The catalytic action of sodium nitrate on pink and white variety of barite were shown in the figure 1 and 2.It is clear from figures that by using sodium nitrate the extent of carbothermal reduction of barite increases effectively.

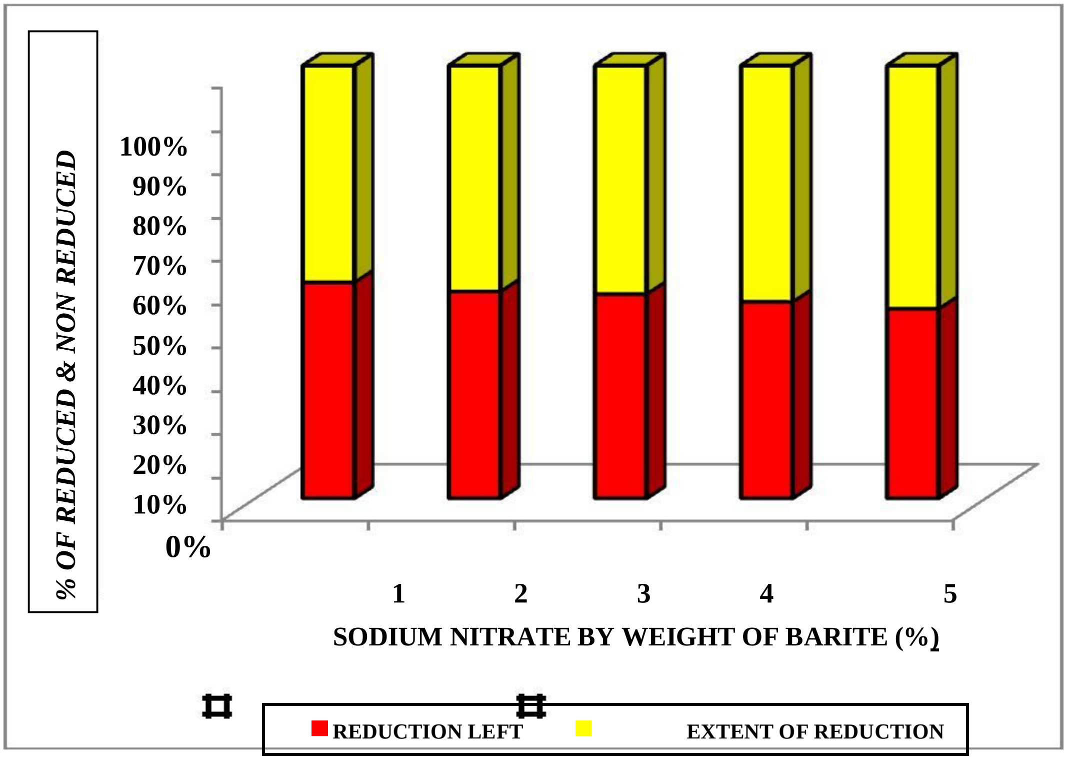

Figure 1. Extent of reduction on pink variety of barite using sodium nitrate.

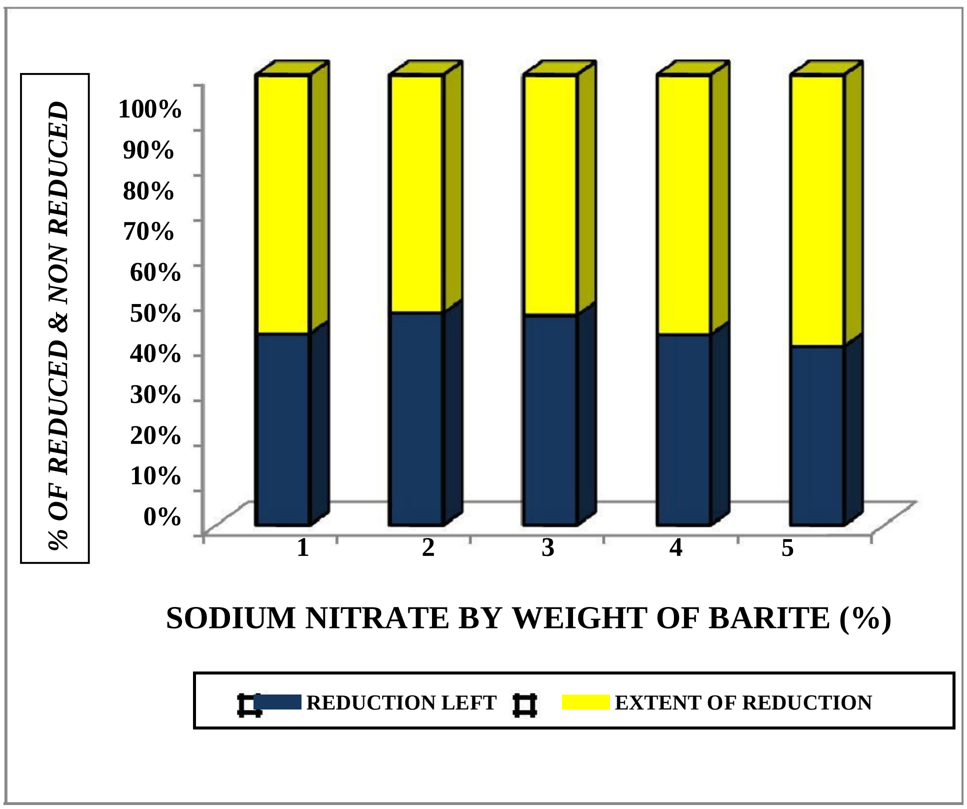

Figure 2. Extent of reduction on white variety of barite using sodium nitrate.

The effect of sodium nitrate (used as reaction promoting agent) on the carbothermal anaerobic solid phase reduction of barites is shown in table1. The obtained results show that the general impact of sodium nitrate in the carbothermal reduction of barite increases the yield of barium sulphide. This may be ascribed to the role of catalyst played by sodium nitrate in the carbothermal reduction of barites. The sodium nitrate decomposes readily at higher temperature to produce nascent oxygen, which in turn reacts with coal particles to form carbon monoxide. Carbon monoxide being a reducing gas reduces barites to barium sulphide as usual at high temperatures. Proposed reactions are as follows:
Carbothermal reduction without sodium nitrate:

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

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

Carbothermal reduction in presence of sodium nitrate:

$$NaNO_3 \rightarrow NaNO_2 + O \quad ......(3)$$

$$C + O \rightarrow CO \quad ......(4)$$

$$BaSO_4 + 4CO \rightarrow BaS + 4CO_2 \quad ...... (5)$$

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

APPLICATIONS

Since barium sulphate is highly insoluble in water only by carbothermal reduction of barite (barium sulphate) it changes into water soluble barium sulphide. Use of sodium nitrate as a catalyst to enhance the percentage of reduced barium sulphide is quite encouraging. It is a simple industrial method and affects the economy of the industries.

CONCLUSIONS

Based on the above investigations and results from table 1 it is concluded that up to the extent of experimental limits, sodium nitrate is a good catalyst where sodium ions seem to play no role in the heterogeneous carbothermal reduction of barites and carbothermal reduction of barites seems to be indifferent to the presence of any alkali metal cation.

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