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Waste reduction at the source and waste recycle through briquetting of the reduction charge in the black-ash process

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ABSTRACT

Physical losses of material as flue dust in the oil-fired rotary furnaces of black ash process for barite reduction have been arrested using briquetted charge. Similarly fine particles of barium sulphate obtained in the purification of barite could be recycled as a resource by exploiting advantages of catalysis and briquetting techniques.

INTRODUCTION

In the chemical processing of economic mineral resources there are two kinds of wastes generated depending upon the process conditions and the nature of the process. These wastes can be classified into two groups called avoidable and unavoidable wastage of natural mineral resources. The former means that the waste generation limit can be reduced by re-engineering the process or by introducing modifications in the reaction conditions if the causes of waste generation are known precisely. There are many difficulties to scientifically pinpoint trouble spots or the nature and effect of impurities which are the main causes for hampering the yield and generation of large amount of waste by incomplete utilization of valuable natural mineral resources. The processing conditions are often main causes for waste generation and these can be brought under control by suitable remedial measures being incorporated in the process. Unavoidable wastages are dependent on the chemistry of the process and here the process modification will be of no use to reduce the waste due to the prime role of the reaction chemistry in controlling the waste generation. Under such circumstances it is better to attack the problem from a different angle i.e., look at the ways and means of processing or recycling of the waste generated so that ultimate goal of net waste reduction or utilization is realised.

In the present paper we have described briefly our efforts in prevention of avoidable wastage of natural mineral resources and subsequently some study on the recovery/recycle of natural resources from unavoidable wastes has been described.

PREVENTION OF AVOIDABLE WASTES OF NATURAL MINERAL RESOURCES

One of the largest indigenous manufacturers of barium chemicals is located at Cuddapah in Andhra Pradesh and is owned by M/s. Kores (India) Ltd. Chemical Division, Mumbai. The barite used in the rotary furnace for reduction with carbon contains about 93.0% $BaSO_4$, 1.5% Fe_2O_3 and 4.0% SiO_2.

The plant uses fine size barite (<250 μm) and coarser carbon particles. The types of carbons used for reduction are lecofines and LTC sludge. The proportion of barite and carbons used in each batch is as : (i)Barite-2400 kg., (ii) Lecofines - 250 kg. and (iii) LTC - 276 kg.

It may be noted that the carbon content used in the mixed charge is about 65% of theoretical requirement for reduction of barite according to following equation:

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

In the rotary furnaces, furnace oil is fired as a fuel in combination with air as oxidant. The highly viscous and thick nature of furnace oil makes the efficient atomisation of the fuel more difficult and hence always about 10-20% excess air is consumed during combustion. This results in heavy draft in the furnace resulting in blowing up of fine and lighter particles of the charge continuously from the rotary furnace as flue dust. The quantity of flue dust is large in the beginning due to filling of reduction charge to the highest capacity level in the initial stages. On an average, about 10 to 20% of the reduction mass including reduced barite is lost as flue dust and is deposited in the fire box. This is mainly the physical loss of raw materials due to malfunctioning of the rotary furnace system employing the batch operation for reduction purpose. The higher amount of excess air present in the flue gases is harmful in three ways:

1. It takes away most of the energy in the flue gases from the system resulting in more oil consumption.
2. Higher draft of excess air is harmful from the point of view of reduction of barite since carbon and/or CO generated may get turned into CO_2 which otherwise would have been useful in bringing about efficient reduction of barite.
3. Excess oxygen means lower reduction potential, creating an adverse situation towards the end of the reduction process, wherein reverse reaction (reoxidation of barium sulpfide to barium sulphate) is a certain possibility.

For this reason Alekseev and Malakhov (1976) have recommended the use of 1-3% ferrous sulphate based on the weight of barite whereby reduced barium sulphide is protected from the damage due to oxidation in preference to ferrous sulphate. However, this strategy seems to be more difficult from practical point of view since iron salts themselves are known to be responsible for hampering the yield of barium sulphide, forming barium ferrite [Gokarn *et.al.*, 1995].

In such circumstances the only solution liked by the plant people is, slight modification of the plant or modification of the feed (charge) to overcome the adverse effects of excess oxygen in the rotary furnace. In the plant practice, the first strategy of controlling the excess oxygen by using efficient imported burners did not yield expected results, due to the viscous nature of furnace oil used as fuel. It is known that minimum use of excess air in the burner is possible, if the fuel used is thin like diesel oil and for that matter natural gas. The prohibitive cost factors of both discouraged the plant personnel in adapting any new modification from point of view of burner operation. As an alternative and easily adaptable solution to tackle oxygen problem, we suggested the technique of shaping the charge in the form of briquettes incorporating special type of binders.

Experimental

A number of trial experiments were carried out to prepare 25 mm dia., and 50-70 mm long cylindrical briquetes using binders like molasses, lignosulfonates, starch, etc. Ultimately a combination binders was used for making briquettes having strong impact resistances.

We have carried out trial experiments in the laboratory using the above briquetted charge sample ranging from 25 gm to 3000 gms in a static bed using muffle furnace at 1000°C with varying duration simulating the conditions in the plant practice [1.5 hrs to 3.0 hrs of reaction period]. The results have been tabulated in Table 1. In all the experiments a slow stream of nitrogen is employed, except in run No. 11.

Results and Discussion

In all the experiments it was observed that reduced barite retained its cylindrical shape and remained very hard during the reduction process including in run No. 11. This of course should result in combating harmful effects of oxygen, hampering the yield of water soluble BaS. If the briquettes are strong during and after the reduction, the reduced material (black ash) will be saved from the danger of oxidation due to infiltered oxygen. Since the reduction is endothermic in nature, the temperature of the reaction mass inside the briquette is always lower, helping in prevention of side reactions (silicate formation).

Table 1 : Laboratory experiments with barite briquetts Charge composition (kg): barite 2400, lecofines 250, LTC sludge 276, and binders: briquette size = 25mm dia

Run No.	Wt. of Charge (g)	Wt. of product (g)	Time (hrs)	(%) Bas	Bas in product	$BaCO_3$ expected in product (g)	Barite/ tonne $BaCO_3$ kg.
1.	1000	657.4	3	59.75	392.7	457.8	1747
2.	1000	656.2	3	57.98	380.5	443.5	1804
3.	1000	648.2	2	64.30	417.2	486.3	1645
4.	1000	663.0	$1^1/_2$	57.03	378.1	440.8	1815
5.	1000	658.3	2	64.88	427.1	497.9	1609
6.	3000	1969	2	62.48	1230.2	1434.1	1674
7.	3000	2165	2	58.48	1266.1	1475.8	1626
8.	61.1	40.4	2	63.67	25.72	29.99	1630
9.	64.6	42.7	2	61.45	26.24	30.59	1689
10.	54.3	36.2	2	59.03	21.37	24.91	1744
11.*	3000	1960	2	54.35	1065.8	1241.8	1933
12.**	686	468	2	48.65	227.6	265.3	2120

* Nitrogen flow absent   Average of runs 1–11 = 1719

** Powder charge

In the plant practice, using the briquetted charge, there has been an improvement of overall yield of more than 25% in comparison to the normal powder charge performance. As a conservative estimate, by implementing our briquetting technique, the company can save natural barite to the tune of more than 5000 tonnes per annum. The same logic can be applied to the savings in carbon reductants (upto 1000 tonnes per annum).

RECOVERY/RECYCLE OF NATURAL RESOURCES FROM UNAVOIDABLE WASTES

In the previous section, we have dealt with in detail how valuable natural resources can be conserved by avoiding wastage of them by achieving enhanced efficiency of conversion of mineral resources like barite into a useful product. The damage to the barium sulphide product due to oxygen infiltered into the rotary furnace was the cause of reduced yield of water soluble barium sulphide due to reverse reaction taking place during the final stages of the batch reduction process in the rotary furnace. Our technique of briquette reduction helped in overcoming the barium loss which was an avoidable damage [wastage]. In the following paragraphs we deal with another real life problem concerning to the recovery of natural resources from unavoidable wastage in a chemical factory.

M/s. Grasim Industries Ltd., Chemical Division, Nagda in Madhya Pradesh has a 450 tonne per day capacity caustic soda plant using Membrane Process. In the brine purification section of the plant, sodium chloride solution containing sodium sulphate impurity to the extent of 0.45% is got rid of by treating it with a 15% solution of barium chloride. Here the double decomposition reaction takes place according to following equation :

$$Na_2SO_4 + BaCl_2 \rightarrow 2\ NaCl + BaSO_4 \qquad \ldots \quad (2)$$

Thus in the plant, about 4 tonnes of barium sulphate as a waste product is generated per day and since it is not finding economic outlet, it is considered as a waste. Management of the company have realised recently that by way of using barium chloride, they are infact converting processed barite mineral into a waste barium sulphate sludge.

The management of the company approached us to help them for the conversion of barium sulphate into barium sulphide using black ash process. Since the particle size of precipitated barium sulphate was about 5–10 μm, it could not be used directly into the rotary furnace for reduction along with carbon, since the high blast prevailing in the furnace made most of the fine particles to fly away from the furnace. We have studied the reduction of fine sized barite containing 97% $BaSO_4$ using briquette technique.

Experimental

By applying the same briquetting technique, a number of laboratory experiments were carried out. Exactly weighed fine $BaSO_4$ powder (3.50 gms) and Lecofines (1.12 gms) were mixed thoroughly and this charge was introduced in the preheated horizontal reactor and runs were taken at 920–1000°C for various durations. After stipulated time, the samples were analysed for water soluble BaS.

For catalytic runs, 5% sodium carbonate (Na_2CO_3) was doped on lecofines by incipient wetting technique. Runs were taken in both catalytic and noncatalytic mode in the temperature range of 880°C to 1000°C. In addition to this, briquettes of size 12 mm dia and 25 mm length were made and runs were taken under identical conditions. Conversion time data of reduction with lecofines are given in Table 2. For making briquettes on the laboratory scale, there was no need of any binder.

Table 2 : Laboratory studies on the reduction of fine $BaSO_4$ powder form and pellets with lecofines [5% soda ash as catalyst]

Temp. °C	Mode of reaction	Time (min)	(%) BaS (water sol.)	(%) Conversion
920	Non-catalytic (powder)	90	53.99	57.75
920	Catalytic (pellets)	90	67.00	70.00
920	Catalytic (pellets)	120	71.75	78.30
960	Non-Catalytic (powder)	60	52.23	62.57
960	Non-Catalytic (powder)	90	55.18	62.18
1000	Non-Catalytic (powder)	60	52.79	62.42
1000	Catalytic (pellets)	60	69.11	77.39

Results and Discussion

The barium sulphate obtained as a byproduct was very fine in nature, and purity was always above 97.0% suggesting absence of impurities. Absence of impurities in barium sulphate ensures lower reactivities necessitating drastic conditions (high temperature) for reduction. Reduction of fine barite powder with the industrial coke sample, i.e., lecofines were tried both in powder, briquetted forms as well as catalytic powder and catalytic pellet form, in the temperature range of 920°C to 1000°C. Here the extent of reduction was higher than that with petroleum coke. Moreover when powder charge was pressed in to pellet, the extent of conversion improved to the extent of 10 to 12% and finally when the catalyst was introduced into the matrix of lecofines, followed by use of briquetted charge, the extent of reduction was quite significant. These data have been tabulated in Table 2.

From the data of Table 2 it can be concluded that even fine and pure barium sulphate powder can be reduced satisfactorily by using the combination of briquetting and catalyst doping techniques as shown in the present study.

CONCLUSIONS

The problem associated with reduction of natural barite and fine precipitated barium sulphate has been solved by the use of briquetting technique. Good improvement in the yield of water soluble barium sulphide has been achieved in both the cases. Thus, by using our special technique, the generation of both the wastes - avoidable and unavoidable – can be minimized.

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