

Conversion of natural resources through waste reduction at the processing step by briquetting technique

B.B. KALE, S.S. KULKARNI and A.N. GOKARN

National Chemical Laboratory, Pune 411 008

ABSTRACT

India is gifted by nature by way of large quantities of high grade nonferrous mineral resources like barite containing more than 90% barium sulphate. The processing of barite to win chemicals from it requires its carbothermic reduction at high temperatures being carried out in rotary furnaces. The powdered charge containing barium sulfide is prone to get damaged due to reverse reaction caused by infiltrated oxygen at the end of reduction state. This hampers the yield of water soluble barium sulfide. The paper discusses about the means of achieving favourable kinetics and high recovery of water soluble barium sulphide in the carbothermic reduction of barite at high temperatures. The reaction rate of reduction step was enhanced many folds by using briquetting technique. Even with barite containing large amount of harmful impurities, the yield of barium was improved considerably on pilot plant scale, thus achieving better utilisation of natural resources such as barite and coke.

Keywords : Barite reduction, Briquettes, Rate enhancement.

INTRODUCTION

Black ash process for barite ore (BaSO_4) reduction by carbon is the key step in processing of the mineral for winning various barium chemicals. The reduction is generally carried out in oil-fired rotary kilns which is operated at high temperatures of the order of $1100^\circ\text{-}1250^\circ\text{C}$. Longer exposure of reduced barite viz., BaS, to high temperatures makes it water insoluble, thus hampering the yield of barium^[1]. Besides, impurities such as iron oxide, alumina and silica present in barite form complexes and the barium losses as water insoluble complex accounts to the tune of 1 to 10 times of impurities present^[2].

Prevention of barium losses and for that matter the reduction in losses is the first goal of any barium chemical specialist. Towards this end Jagtap et. al. [3] attempted to bring about reduction in the temperature of black ash process by incorporating gasification catalysts in the carbon matrix. Nishev et. al. [4] suggested the treatment of barite with lime particles which keeps the barite content safe by preferably forming calcium silicates and ferrates. Another methodology to tackle the problem of low yield is the use of calcium carbide as reducing agent [5]. Here the briquettes were made by using the industrial waste as binder and the cylindrical briquettes retained this shape even after exposure to high temperatures. Lowering of the specific area of the reduced barite (BaS) to the harmful oxygen environment and proximity of both the solid reactants ensured better reduction rate and higher content of water soluble barium sulfide in the black ash. The aim of the present work has been to study the kinetics of the briquetted charge for the carbothermic reduction of barite in laboratory scale and also to show with examples how the data can be incorporated on industrial scale.

EXPERIMENTAL

Barite sample used in all the kinetic experiments was obtained from M/s Kores (India) Ltd., Mumbai. The sample containing 96.0% BaSO₄, 0.5% Fe₂O₃, 2.0% SiO₂ was sized into less than 250 μm. As a reducing agent, industrial coke of 353 μm size supplied by the same firm was used.

For laboratory experiments a tubular furnace made of 450 mm long and 75 mm diameter mullite tube covered with kanthal winding was mounted vertically. The temperature of the furnace could be controlled by using chromel-alumel thermocouple sensor and a good temperature controller. For kinetic runs, tubular silica reactor made after fusing two tubes of 500 mm long and 15 mm diameter and 500 mm long and 40 mm diameter was used. The reactor had a 15 mm diameter quartz sintered disc at the central part. The reactor was placed in the furnace in such a way that sintered disc portion was in the hot uniform temperature zone. A standard hydraulic press was used for pelletizing the powdered reaction mixture using a die-punch of 20 mm diameter.

About 9.78 gm barite powder and 2.10 gm industrial coke which is about 62% of standard stoichiometric amount for the system BaSO₄+4C, along with a binder were mixed thoroughly and soaked with 4 to 5 drops of water. The reaction mixture was taken into the die-punch carefully. By applying a load of 1 tonne, 20 mm diameter pellets were prepared. Then the pellets were dried in oven for 3 hours at 120°C. The dried pellets were cooled and then used for reaction.

Precisely weighed sample was placed in a silica sample holder [25 mm dia. and 17 mm height] and then introduced in a preheat zone of tubular reactor mounted in the vertical furnace. After preheating to the desired temperature the sample pan was introduced in a central hot zone maintained at the desired temperature and zero time was noted. After stipulated time interval the reaction could be stopped by removing the sample pan from the hot zone. The cooled sample was weighed, mixed properly and analysed for water soluble barium sulfide (BaS) iodometrically. Runs were taken for powdered charge as well as briquetted charge in the temperature range of 920° to 1000°C.

RESULTS AND DISCUSSION

The kinetic runs were carried out at temperatures 920°C, 960°C and 1000°C using barite ore both in powder as well as pellet form. The conversion time plots for powder form and pellet form are shown in Fig. 1(a) and Fig. 1(b) respectively. The sigmoidal behaviour of the plots indicate the slow initial rate followed by accelerated rate and ending with deceleration. This kind of behaviour is generally observed in the reaction involving decomposition of solids and mostly gasification reactions. This typical trend can be attributed to the rate of CO generation contributing mainly to the reaction rate. This fact is also clear from the observed linear relationship between the fractional conversion of barium to barium sulfide and weight of the reduced mass.

To obtain the kinetic parameters, modified volume reaction model (MVR) developed by Kasaoka et. al. has been applied to the conversion time data [6]. The linearised equation for the MVR model can be written as,

$$\ln [-\ln (1-x)] = \ln a + b \ln \theta \quad \dots \quad (1)$$

where x is the fractional conversion, θ is the time in minutes and a, b are model parameters. For given x (fraction conversion), model plots were drawn as shown in Fig. 2(a) and Fig. 2(b) for powder and pellete forms respectively. Rate constants K were calculated and tabulated in Table 1. Here for conversion x,

$$k(x) = a^{1/b} b[-\ln (1-x)]^{b-1/b} \quad \dots \quad (2)$$

$$\text{and for } x = 0.5, K_{\text{avg}} = K a^{1/b} b(-\ln 2)^{b-1/b} \quad \dots \quad (3)$$

From Table 1 it is observed that when the reaction mixture is in the pellet form the value of K are higher then in case of powder form. The reaction rate in case of pellet is higher because of the easy heat transferred in the pellet form and due to perfect solid-solid contact between the reactants [7]. This helps in the enhanced direct reduction between the carbon particles and sulphate although the

Table 1 : Kinetic runs of reduction of barite by industrial coke

Temperature °C	Rate constant, k (sec ⁻¹)	
	Powder	20 mm dia pellet (load : 1 tonne)
920	2.6532 x 10 ⁻⁴	1.0098 x 10 ⁻³
960	4.1478 x 10 ⁻⁴	1.508 x 10 ⁻³
1000	5.2682 x 10 ⁻⁴	2.333 x 10 ⁻³

major portion of the reaction is due to Bourdourd reaction. The CO₂ generated gets reduced by carbon in the vicinity to form carbon monoxide which is responsible for enhanced rate of reduction. The compact form of briquettes also support the endothermic reduction reaction system by ensuring better heat transfer. Moreover, due to endothermic nature of reduction reaction, the temperature in briquettes never exceeds outside temperature and hot spot generation is prevented even in the plant scale. The pellets were found to retain their shape and size even after reduction. This helps in protecting the inner portion of the reduced sample

Table 2 : Laboratory experiments with Barite briquettes.
Charge composition (kg) : Barite-2400, Lecofines-250,
LTC sludge-276, and binders: Briquette size = 25 mm dia.

Run No.	Wt. of charge (g)	Wt. of product (g)	Time (hrs)	BaS Content (%)	BaS in product (g)	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	1.5	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	1241.9	1933
12**	686	468	2	48.65	227.6	265.3	2120

* Nitrogen flow absent

** Powder charge

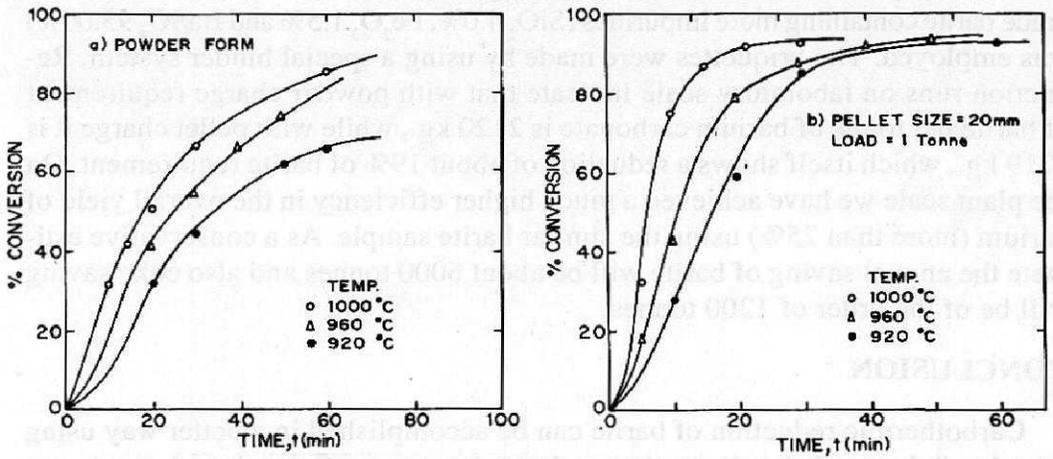


Fig. 1 : Conversion-time plots for reduction of barite by inudustrial carbon (62% stoichiometric).

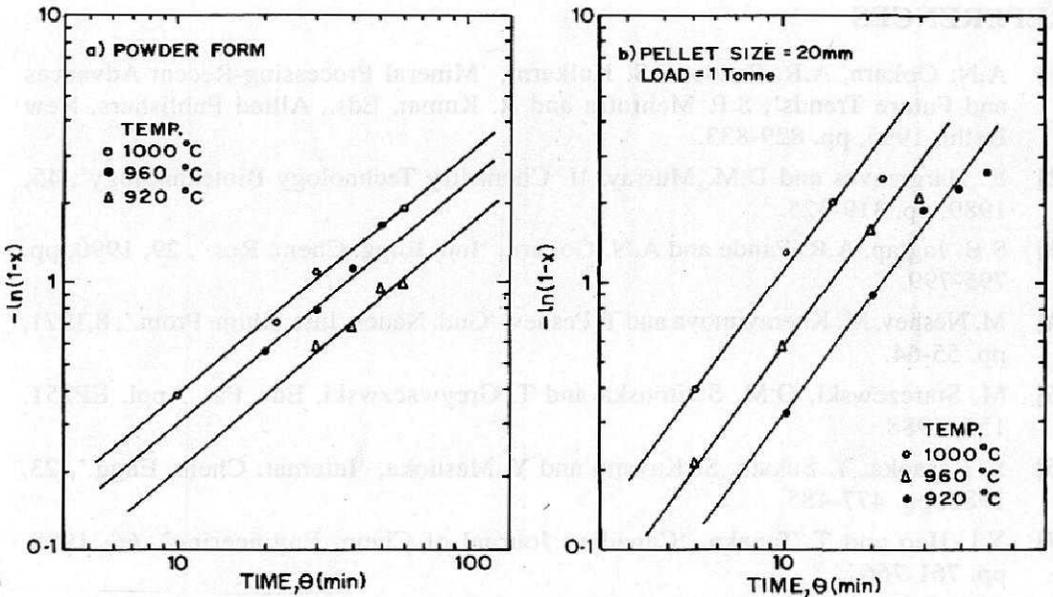


Fig. 2 : Model plots for reduction of barite by industrial carbon (62% stoichiometric).

containing barium sulfide from the attack of oxygen infiltrated into the system. This helps to arrest reverse reaction resulting in loss of barium sulfide. Thus enhanced rate of reaction observed in the particular system using briquettes has been responsible in achieving higher extent of recovery of barium using sample from industries. Table 2 gives a comparative data of conversion efficiency of

powder and pellet form of reduction charge in the laboratory^[8]. Here lower grade barite containing more impurities (SiO_2 4.0%, Fe_2O_3 1.5% and BaSO_4 93.00%) was employed. The briquettes were made by using a special binder system. Reduction runs on laboratory scale indicate that with powder charge requirement of barite per tonne of barium carbonate is 2120 kg., while with pellet charge it is 1719 kg., which itself shows a reduction of about 19% of barite requirement. On the plant scale we have achieved a much higher efficiency in the overall yield of barium (more than 25%) using the similar barite sample. As a conservative estimate the annual saving of barite will be about 6000 tonnes and also coke saving will be of the order of 1200 tonnes.

CONCLUSION

Carbothermic reduction of barite can be accomplished in a better way using briquetted charge. It has been shown that briquette configuration shows better kinetics and can be applied advantageously on the plant scale also. This fact has been shown clearly with examples in present work.

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