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The effect of particle size distribution on barite reduction

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ABSTRACT

The present study is a follow-up of investigation on barite reduction to barium sulfide as a function of starting particle size distribution and temperature of reaction. In this work we study the high temperature reduction process of barite from the view point of particle size distribution. Conversiontime data have been obtained using iodometry method in each isothermal condition. A modified kinetic model used to express the carbothermic reduction process. To obtain the values of activation energy and frequency factor, the same expression was selected for each sample at all temperatures. The rate of reaction is found to be related to the particle size distribution and the gasification reaction of coke which has influence on reduction process. The kinetic parameters calculated from standard analysis of isothermal kinetic data indicated that the particle size of barite controlled the reaction when it was coarser than 400 mesh both in presence and absence of catalyst.

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1. Introduction

Barium component such as BaCO₃, BaCl₂ and Ba(NO₃)₂ are important chemical materials that are manufactured from natural barite. These components of barium widely use in ceramic and glass industries, drilling mud composition and nanostructure materials. Conversion of barite to barium sulfide by coke which is "black ash process" is very important reaction in manufacturing above barium components [1]. This reaction frequently performs in rotary kiln or in fluidized bed reactors at high temperature ranging 950–1100 °C in the presence of carbon or methane gas. Reduction of barite by coke can be represented by following reaction [2]:

$$BaSO_4 + 4C \rightarrow BaS + 4CO \tag{1}$$

The major reducing agent is gaseous intermediate CO which influences the reduction of barite as:

$$BaSO_4 + 4CO \rightarrow BaS + 4CO_2 \tag{2}$$

In fact the generated CO diffuses and reacts with barite which is not in contact with carbon. The CO₂ obtained through the reaction diffuses into carbon to generate more CO according to Boudouard reaction:

$$C + CO_2 \rightarrow 2CO \tag{3}$$

Thus, the reduction rate of barite is controlled by the rate of CO generated by Boudouard reaction. Recently, some investigators have been studying the reduction of barium sulfate by carbon in the presence of inorganic materials like sodium carbonate, ferric nitrate and sodium vanadate in which these additives act as promoters for the gasification reaction [3–6].

On the other hand, the particle size distribution of barite influences the activation energy of reactions. In fact two factors are important in reduction process, the particle size of barite and the gasification of coke. In this study firstly a modified kinetic model has been developed for reduction of barite. Various factors affecting on reduction process have been investigated experimentally. The sodium carbonate and ferric nitrate have been selected as catalysts to study the reaction mechanism. In second step, the influence of barite particle size distribution was taken into consideration to investigate its role on reaction kinetic.

2. Materials and methods

The influence of particle size distribution of barite on reduction process has been investigated. At first, an industrial barite ore was selected and the complete chemical and mineralogical analyses were identified by X-ray method. As shown in Table 1, the main mineral was barite and small quantities of quartz were found. Also, an industrial coke was used in reduction process whose chemical analysis was presented in Table 2.

In order to evaluate the effect of the barite particle size on carbothermic process, coarse-sized (-140, +230 mesh) middlesized (-230, +400 mesh) and fine-sized (-400 mesh) were used in stoichiometric mixes of barite and coke (i.e., BaSO₄ + 4C). Also, 5% sodium carbonate and ferric nitrate were doped on coke as

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Table 1

Chem	Chemical and mineralogical analysis of barite ore.									
Chem	Chemical analysis									
SiO ₂	BaO	Na ₂ O	K ₂ O	MgO	CaO	MnO	Al_2O_3	Fe_2O_3	SO ₃	
2.75	60.27	0.67	0.01	0.08	0.08	0.03	0.23	0.33	35.53	
Miner	Mineralogical analysis (calculated by chemical analysis)									
Barite Quartz O									Others	
91.8 2.75 5										

catalyst, based on dry weight of coke. The carbothermic reduction of samples have been performed in laboratory electrical kiln under isothermal conditions at 950, 1000, 1050 and 1100 °C in order to obtain the values of kinetic parameters. The zero point of time scale was defined as starting time at which samples enter the kiln. The cooled samples were weighed and barium sulfide percentage was measured by iodometry method [7]. The producer for determining BaS content is as follow:

- (i) the iodine solution and hydrochloric acid solution was prepared by mixing 50 ml of 0.5N iodine solution and 50 ml of 1N hydrochloric acid solution.
- (ii) 2 g of black ash was mixed with 100 ml deionized hot water and stirred to prevent agglomeration and effective dissolution.
- (iii) the black ash suspension was added into the iodine and hydrochloric acid solution and stirred for 3 min.
- (iv) the solution was titrated with 0.1N sodium thiosulfate to obtain straw color in presence of starch indicator. The BaS percentage was calculated by following equation:

$$C = 8.17 \left(\frac{N_1 V_1 - N_2 V_2}{W} \right)$$
(4)

where *C* is the BaS percentage, N_1V_1 and N_2V_2 are total moles of iodine and sodium thiosulfate respectively. W also is the initial weight of sample. The fractional conversion of BaSO₄ was calculated according Eq. (1).

3. Results and discussion

The experiments, which lead to the exponential construction plots of conversion versus time, enable us to elaborate on the mechanism of reduction process and to estimate the values of activation energy. To compare the effect of particle size distribution on reduction of barite a modified kinetic model, which is related to carbothermic reduction, was applied for all conversion-time data [3]. The kinetic model can be represented as following:

$$x = 1 - \exp(-kt^m) \tag{5}$$

where *x* is the fractional conversion, *t* is reduction time, *k* and *m* are constant rate and power of equation, respectively.

The conversion-time variations were plotted in Fig. 1 for three groups of barite particle size distribution in absence of catalyst. As can be observed in this figure, the conversion values increase

Table	2
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Materials	Percentage	Particle size distribution (mesh)	Percentage
Fixed carbon	70	+16	0
Ash	10	-16, +140	20
Volatile matter	16	-140	80
Moisture	4		



Fig. 1. Conversion-time plots for the reduction of barite at different particle size distribution in absence of catalyst.

with the rise in reduction temperature in all conditions. These are due to gasification promotion of Boudouard reaction at higher temperature. The conversion-time plots show that the rate of reaction increases as particle size of barite was finer. As previously discussed, the values of kinetic parameters obtained by the logarithmic method allow the assessment of the modified kinetic model and choice of kinetic expression for the reduction of barite in all cases. To obtain the values of activation energy, it is necessary to find the values of rate constants at different temperatures. The choice of the kinetic equation allows the calculation of the rate constant values, *k*, from the logarithmic form of general kinetic expression as follows:

$$\ln[-\ln(1-x)] = \ln k + m \ln t$$
 (6)

Fig. 2 shows the logarithmic plots of Eq. (5) and the calculated values of k and m were reported in Table 3 for each isothermal runs. The values of rate constant are then used in the plot of $\ln k$ versus 1/T which is logarithmic form of Arrhenius equation:

$$k = k_0 \exp\left(-\frac{E_a}{RT}\right) \tag{7}$$



Fig. 2. Application of modified kinetic model to the isothermal reduction of barite at different particle size distribution in absence of catalyst.

Table 3							
The constant	rate a	ind m	values	of	modified	kinetic	model.

Catalyst type	Particle size distribution (mesh)	т			k			r					
		950	1000	1050	1100	950	1000	1050	1100	950	1000	1050	1100
Without catalyst	-140, +230		0.50	0.35	0.24		0.31	0.66	1.16		0.99	0.98	0.97
	-230, +400		0.39	0.30	0.20		0.44	0.84	1.25		0.98	0.97	0.99
	-400		0.36	0.28	0.20		0.44	0.83	1.21		0.96	0.96	0.98
5% Na ₂ CO ₃	-140, +230	0.52	0.40	0.26		0.29	0.66	1.19		0.99	0.99	0.99	
	-230, +400	0.50	0.46	0.31		0.37	0.57	1.17		0.98	0.99	0.98	
	-400	0.48	0.36	0.30		0.36	0.69	1.17		0.99	0.99	0.97	
5% Fe(NO ₃) ₃	-140, +230		0.53	0.42	0.25		0.31	0.63	1.16	0.99	0.99	0.98	
	-230, +400		0.46	0.28	0.23		0.41	0.96	1.20	0.98	0.99	0.98	
	-400		0.34	0.30	0.16		0.47	0.83	1.36	0.99	0.99	0.99	



Fig. 3. Arrhenius plots for reduction of barite in absence of catalyst for different particle size distribution.

where k_0 is the frequency factor, E_a is the activation energy, R is the gas constant, and T is the absolute temperature. Fig. 3 presents the Arrhenius plots for three groups of particle size in absence of catalyst. Also the values of activation energy and exponential factor were reported in Table 4.

The values of activation energy are not significantly different for each group of samples containing different particle size distribution. It is observed that the value of activation energy decreases as particle size distribution of barite is shitted to finer sizes. Activation energy falls down, approximately 9.0 kcal, when the barite particle range changes from (-140, +230 mesh) to (-230, +400 mesh), but more decrease in particle size has little effect on activation energy. The trends of kinetic parameters show an overall positive effect in the rate enhancement of reduction when particle size is coarser than 400 mesh. The difference can be tentatively explained by two factors that control the reduction of barite. One of them is the effect of particle size of barite which increases the reaction rate due to an increase in surface area and the second is



Fig. 4. Conversion-time plots for the reduction of barite at different particle size distribution in presence 5% Na₂CO₃ as catalyst.

the gasification of coke. As a matter of fact, in the case of finer size of barite particles, the activation energy of reduction reaction is approximately 9.0 kcal less than coarse size and the trends of activation energy and frequency factor show an overall positive effect in the rate constants. This phenomenon shows that reaction was controlled by the particle size of barite when it is coarser than 400 mesh.

In the first part of the investigation it was inferred that the carbothermic reaction of barite is physically related to gasification process of coke throughout the Boudouard reaction and intermediate gaseous phase diffusion i.e. CO is the rate limiting step in overall reaction. The formation of barium sulfide involves with value of CO that is controlled by gasification of coke. Therefore, decreasing particle size of barite less than -400 mesh has no effect on rate constants and activation energy consequently.

Figs. 4 and 5 present the plots of conversion-time data for barite reduction in presence of 5% sodium carbonate and ferric

Table 4				
The values of kin	etic parameters i	n absence a	nd presence of	f catalyst.

Catalyst type E_a (kcal/mol)				ko		r			
	-140, +230	-230, +400	-400	-140, +230	-230, +400	-400	-140, +230	-230, +400	-400
Without catalyst 5% Na ₂ CO ₃ 5% Fe(NO ₃) ₃	45.5 45.1 46.1	36.6 37.1 37.9	35.3 37.6 37.0	$\begin{array}{c} 2.0 \times 10^{7} \\ 3.4 \times 10^{7} \\ 2.5 \times 10^{7} \end{array}$	$\begin{array}{c} 8.5 \times 10^5 \\ 1.6 \times 10^6 \\ 1.4 \times 10^6 \end{array}$	$\begin{array}{c} 5.1 \times 10^5 \\ 1.9 \times 10^6 \\ 1.1 \times 10^6 \end{array}$	0.99 0.99 0.99	0.99 0.99 0.99	0.99 0.99 0.96



Fig. 5. Conversion–time plots for the reduction of barite at different particle size distribution in presence of 5% Fe(NO_3)_3 as catalyst.

nitrate. Also, the values of m and rate constants are reported in Table 3. As may be observed the rate constants of carbothermic reaction increases with addition of sodium carbonate, but it obviously seems that ferric nitrate has negligible effect on k values of reaction. To verify the influence of catalysts on activation energy the values of $\ln k$ are plotted versus 1/T in Figs. 6 and 7 for all particle size distribution. Also, the values of kinetic parameters in presence of catalysts were reported in Table 4. As previously discussed particle size distribution changes the values of activation energy only 8.0 kcal both in presence of sodium carbonate and ferric nitrate when the particle size distribution decreases from (-140, +230 mesh) to (-230, +400 mesh). The decreasing particle size less than 400 mesh changes the value of activation energy negligibly. This effect is because of controlling reduction process by the surface area of barite.

The activation energy estimated for reduction of barite in presence of catalysts in three groups of particle size distribution is only slightly different from the values reported in absence of



Fig. 6. Arrhenius plots for reduction of barite at different particle size distribution in presence of 5% Na_2CO_3 as catalyst.



Fig. 7. Arrhenius plots for reduction of barite at different particle size distribution in presence of 5% Fe(NO₃)₃ as catalyst.

catalyst. Furthermore, the rate of reaction in all cases increases with addition of Na₂CO₃. According to Hamilton et al. [8], in catalyst gasification, the rate is proportional to both the number of active sites and pores development in the carbon matrix where reaction takes place. However, an increase in the surface area alone is not sufficient to increase the reaction rate. The presence of active sites is more important. Thus the catalysts play a beneficial role in increasing the number of active sites generated in carbon matrix. This is evident from the fact that the value of frequency factor, k_0 , which is a measure of the number of active sites, is more in presence of ferric nitrate compared to the non-catalytic case. However, the sodium carbonate increases the values of frequency factor in reduction of barite more than ferric nitrate.

The trend of kinetic parameters shows an overall positive effect in rate enhancement of barite reduction when particle size of barite ranges -230, +400 mesh. The pattern of variation in kinetic parameters show special phenomenon called isokinetic effect [6]. The existence of isokinetic effect has been proved by linear



Fig. 8. The effect of particle size on isokinetic parameters in absence and presence of catalyst.

Table 5

The values of isokinetic parameters for catalytic and non-catalytic conditions.

Catalyst type	T _{iso} (°C)	k _{iso}
Without catalyst	1140	1.82
5% Na ₂ CO ₃	1033	0.98
5% Fe(NO ₃) ₃	1173	2.73

relationship between E_a and k_0 as following equation:

$$\ln k_0 = \ln k_{\rm iso} + \frac{E_{\rm a}}{RT} \tag{8}$$

where k_{iso} and T_{iso} are isokinetic rate constant, respectively. Isokinetic temperature is described as temperature in which rate constants at different particle size distribution have the same values. It means that at isokinetic temperature the rate constants are unaffected by the particle size of barite. To evaluate isokinetic effect, the plot of $\ln k_0$ versus E_a in semilogarithmic scale was made as shown in Fig. 8. These plots show to be straight line, in agreement with isokinetic equation which predicts a relationship between frequency factor and activation energy. In Table 5, the values of k_{iso} and T_{iso} are reported for catalytic and non-catalytic conditions. The values of T_{iso} are close to each other in absence and presence of ferric nitrate and are around 1155 °C. This indicates that the particle size of barite has no role in the reduction of barite when process was performed at around this temperature. Table 5 data indicates that presence of sodium carbonate as a catalyst in initial composition may be able to decrease isokinetic temperature considerably.

4. Conclusion

In the present study, the possible use of different particle sizes of barite in reduction process was investigated in presence and absence of catalyst. From the results obtained by using a modified kinetic model, the following conclusions can be drawn:

- The presence of 5 wt.% sodium carbonate in the barite composition strongly favors reaction rate compared to the same value of ferric nitrite.
- The clear variation in particle size distribution and measuring isothermic conversion-time data indicated that the activation energy decreases only 9.0 kcal. By using a particle size distribution range of -230, +400 mesh the minimum activation energy was obtained for catalytic and non-catalytic condition. Further, the use of barite with particle size between -230 and +400 mesh allows reaching the best results in presence of sodium carbonate due to the modification in active site and kinetic parameters. The finer size of barite, -400 mesh, could not improve the barite reduction.
- The addition of ferric nitrate to mixtures of barite and coke could raise the number of active sites of coke. The reason for the increase in of active sites number is the difference in frequency factor of Arrhenius equation.

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