EFFECT OF THE TYPE OF CARBON MATERIAL ON THE REDUCTION KINETICS OF BARIUM SULFATE

M. Sh. Bafghi [1,*], A. Yarahmadi [2], A. Ahmadi [3] and H. Mehrjoo [3]

* *msbafghi@iust.ac.ir*

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[1] School of Metallurgy and Materials Engineering, Iran University of Science & Technology, Tehran, Iran.

[2] Department of Mining Engineering, Faculty of Engineering, Yazd University, Yazd, Iran.

[3] School of Metallurgy and Materials Engineering, Iran University of Science & Technology, Tehran, Iran.

Abstract: *The present study deals with the reduction of barium sulfate (Barite) to barium sulfide by use of carbon as the reduction agent. Pellets of barite ore containing about 95% $BaSO_4$ has been reduced under different conditions of temperature, time, ore grain size and the type and grain size of the carbon materials. Graphite, coke and charcoal have been used as the reducing agent and the reduction experiments have been performed in the temperature range of 925-1150 °C. Apart from conducting the experiments using pellets made of ore powder, kinetic analysis of the experimental data by use of the reduced (dimensionless) time method has been another unique feature of the present study. Experimental results show that grain size of either carbon material or barite ore has not appreciable effect on the reaction rate. Kinetic analysis of the experimental data revealed the rate is strongly controlled by the chemical reaction of carbon gasification (Boudouard reaction). The reaction rate is very considerably related to the type of carbon material so that the activation energy varies from 15.6 kcal.mol^{-1} for charcoal to 26.3 kcal.mol^{-1} for graphite and 20.8 kcal.mol^{-1} for coke. This behavior provides further support for the postulated reaction mechanism, i.e., carbon gasification.*

Keywords: *Barite, carbothermic reduction, kinetic analysis, carbon gasification, activation energy.*

1. INTRODUCTION

One of the outstanding uses of barite mineral is its application as a starting material for the production of various barium compounds [1]. Water solubility of barite (barium sulfate) is very limited hence, reduction of this mineral to the water soluble compound of barium sulfide is inevitable [2]. Barite reduction can be performed by use of different reducing agents, such as methane [3], hydrogen [4], carbon monoxide [5] and solid carbon. Although reduction of barite by carbon starts at around 600°C, the rate of reduction is very low even at temperatures around 750°C. The reduction process is practically performed at temperatures between 800 and 1100°C by use of charcoal or coke in the absence of air [6].

Reduction of barite by solid carbon may be presented as follows [7]:

$$BaSO_4 + 2C \longrightarrow BaS + 2\,CO_2 \qquad (1)$$

Nevertheless, the real reducing agent is carbon monoxide (reaction 2) which is regenerated through the well-known Boudouard reaction or carbon gasification by CO_2 (reaction 3). CO_2 is generated as a consequence of the gaseous reduction (reaction2).

$$BaSO_4 + 4CO \longrightarrow BaS + 4CO_2 \qquad (2)$$

$$4CO_2 + 4C \longrightarrow 8CO \qquad (3)$$

Summing reactions (2) and (3) gives the overall reduction reaction [8] in the form of reaction (4):

$$BaSO_4 + 4C \longrightarrow BaS + 4CO \qquad (4)$$

CO which is generated by reaction (4) passes through the solid product layer (BaS) and reacts with $BaSO_4$ (reaction 2) at the surface of unreacted core of the ore particle. CO_2 which is formed by reaction (2) reacts with carbon to produce CO again [9]. With such a reaction mechanism, it seems both the process temperature and energy consumption would be decreased if a carbon material with a higher reactivity (such as charcoal) is used [2].

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Although there is available a relatively considerable number of papers dealing with various aspects of carbothermic reduction of barite, a clear conclusion about the reaction mechanism and its rate controlling step can not be found in the literature. Hence, the present study has been planned and performed to provide reliable data necessary for a methodological kinetic analysis aimed at the clarification of the reaction mechanism.

2. EXPERIMENTAL

2. 1. Materials

Barite ore sample used in this study has been delivered from Ardekan Barite Mines (Yazd, Iran). XRD pattern of the ore (Fig. 1) shows that the sample purity is above 90% so that only barite picks can be observed and any impurity is very hardly detectable through XRD procedure. Chemical analysis of the sample has been given in table 1.

Graphite, coke and charcoal were used as carbon material for the reduction. Chemical analysis of these materials has been given in table 2.

Bentonite (about 2%) has been used as binder for making pellets with acceptable strength.

Reduced pellets were dissolved in hot distilled water and barium carbonate was precipitated from solution by the addition of sodium carbonate (analytical grade) solution.

Table 1. Chemical analysis (mass %) of the barite ore sample.

$BaSO_4$	CaO	$SrSO_4$	Al_2O_3	Na_2O	SiO_2	Fe_2O_3
95	2	1.5	0.8	0.5	0.1	0.1

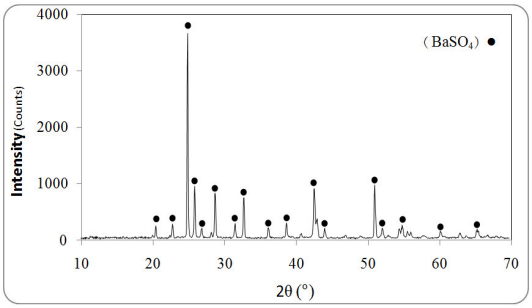

Fig. 1. XRD pattern of the Barite ore sample.

Table 2. Chemical analysis (mass %) of the carbon materials.

Reducing agent	Fixed carbon	Ash	LOI
Graphite	89	6	5
Coke	86.5	11.4	2.1
Charcoal	87	2.3	10.7

2. 2. Procedure

Pellets were made of a mixture containing ore powder (-100 + 200 mesh) with about 2% Bentonite and around 10-15 percent water. Hand-made pellets of approximately 15mm diameter and about 8g weight, were dried at a temperature between 100 and 150°C for about 2 hours.

Dried pellets were weighted with an accuracy of 1mg and then, were put inside a stainless steel crucible on a bed of carbon material. After that, carbon material was added over the pellet so that it was buried completely in carbon. Then, the crucible was placed inside a muffle furnace and kept for the predetermined duration of time at a specific temperature. After the termination of the reduction period, the crucible was pulled out and let to be cooled down. Then, the pellet was pulled out of the remained carbon bed and weighted carefully. Then a portion of the reduced pellets was milled to around -60 mesh and dissolved in 200ml distilled water at around 90°C for about one hour. Undissolved portion of the sample was dried and weighted. Considering that BaS is the sole water soluble compound while remained $BaSO_4$ and gangue material are not, conversion fraction (or the efficiency) was calculated using the sample weight before the reduction experiment and the weight of the residue after leaching the reduced sample.

3. RESULTS AND DISCUSSION

In the present study the effects of temperature, time, ore grain size and the type and grain size of the carbon material have been studied.

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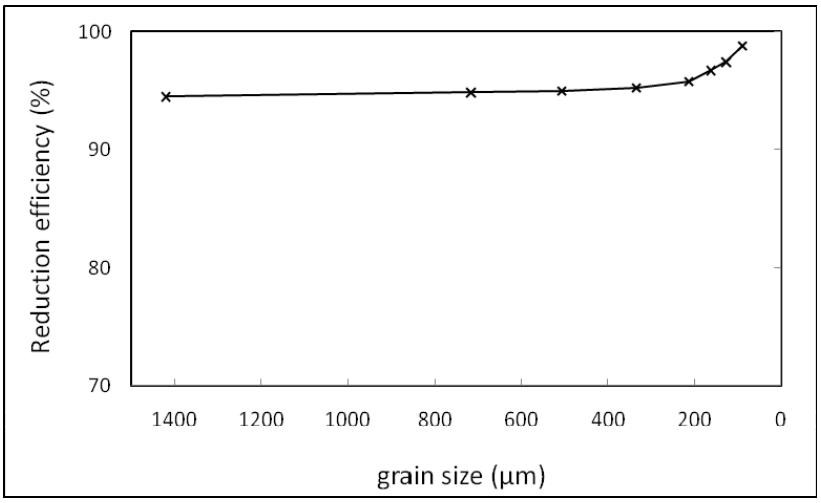

Fig. 2. Reduction efficiency as a function of the coke grain size, (reduction temperature: 1100°C, reduction time: 90 minutes).

Experimental results are presented and discussed hereinafter.

3. 1. Effect of Carbon Material Grain Size

For the study of the effect of carbon material grain size, coke with (-10 +20), (-20 +30), (-30 +40), (-40 +60), (-60 +80), (-80 +100), (-100 +140) and (-140 +200) mesh has been used. This group of experiments was performed at 1100 °C for 90 minutes. Results of this group of experiments have been shown in Fig. 2.

As Fig. 2 shows, the grain size of carbon material has not a pronounced effect on the long term (90 min.) reduction efficiency. Therefore, other experiments of this study have been performed with a constant grain size (-100 mesh) of carbon materials.

3. 2. Effect of Barite ore Grain Size

Three categories of grains, (-100 +140), (-140 +200), and (-200 +270) mesh have been determined to study the effect of the ore particle size on the reduction rate. Experiments were performed at 1100°C and time durations of 15, 30, 45, 60 and 90 minutes. Reducing agent was coke with a grain size of (-100) mesh. Results of this part of experiments have been shown in Fig. 3.

As Fig. 3 shows, barite ore particle size has not a noticeable effect on the reduction rate. This may be an indication that resistance to gas phase mass transfer through the reaction product layer (CO inwards and CO_2 outwards) has not a noticeable contribution in overall reaction rate. Fig. 3 shows that the reaction rate is somewhat smaller in the case of smaller grain sizes. This apparently abnormal behavior is supposed to be related to the higher compactness (and consequently lower diffusivity) of the pellets made by ore powders with smaller particle sizes.

3. 3. Effect of Temperature

With regard to the effect of temperature on the reduction rate, experiments were performed at 925, 1000, 1075 and 1150°C for different time

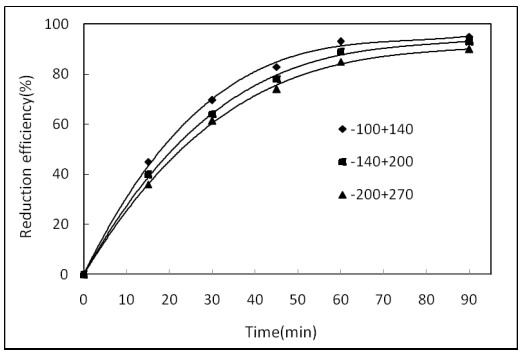

Fig. 3. Effect of Barite ore particle size on the reduction rate (reducing agent: -100 mesh coke).

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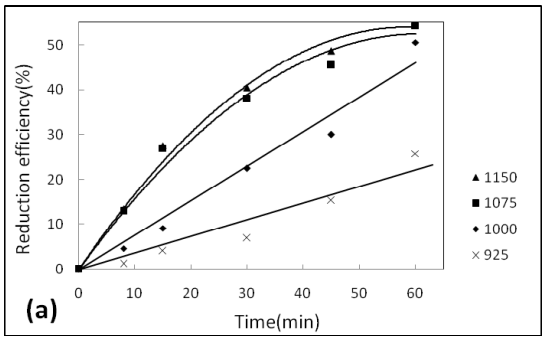
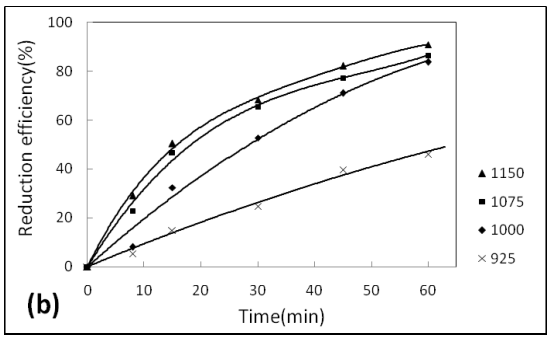




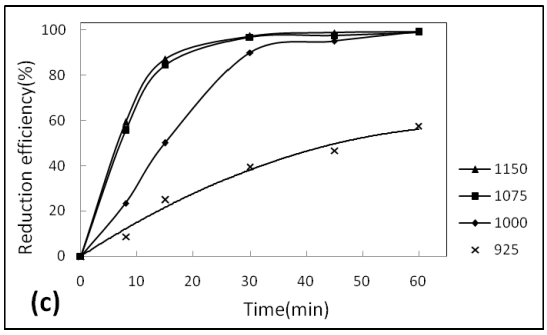
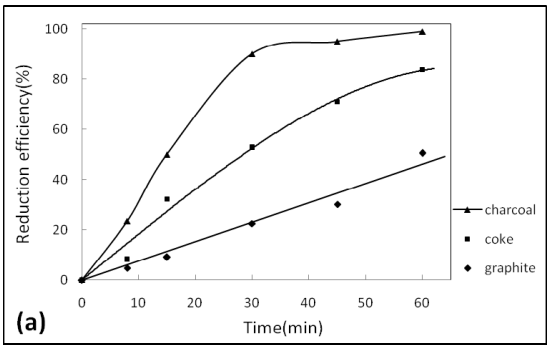


Fig. 4. Effect of temperature on the reduction rate of barite with reducing agent: graphite (a), coke (b) and charcoal (c).

durations of 7, 15, 30, 45 and 60 minutes. Three series of experiments were made using graphite, coke and charcoal as the reducing agent. Results of these experiments have been presented in figures 4(a), 4(b) and 4(c).

As figure (4) shows, increasing the temperature accelerates the reduction reaction noticeably. Due to the high sensitivity of the reaction rate to the experimental temperature, it may be concluded that resistance of the chemical reaction has a predominant role in the reaction kinetics.



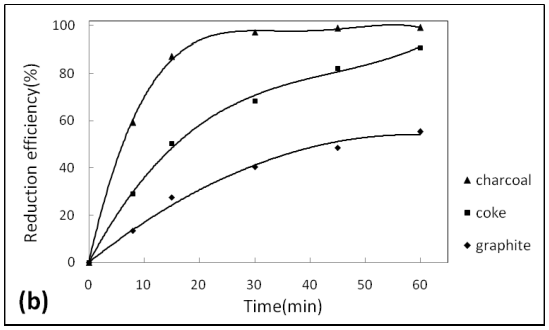


Fig. 5. Effect of the type of carbon material on the reduction rate of barite at 1000°C (a) and 1150°C (b)

3. 4. Effect of Carbon Material Type

In this section effect of the type of carbon material (graphite, coke and charcoal) has been studied. Experimental data relative to 1000 and 1150°C have been shown in Fig. 5.

As shown in Fig. 5, the lowest reduction rate belongs to graphite and the highest to charcoal, while reduction rate with coke stands in-between. Since the reactivity of these carbon materials decreases from charcoal to coke and then to graphite, it may be concluded that carbon gasification (or Boudouard reaction) has a comprehensive role in the overall reaction rate.

3. 5. Kinetic Analysis

The main steps through which barite is reducted by carbon may be considered as follows:

1. Diffusion of CO gas molecules through the

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gas boundary layer towards the sample particles
2. Inward diffusion of CO through the product (BaS) layer
3. Chemical reaction of barite reduction by carbon monoxide (reaction 5) at the surface of the unreacted core of particles

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

4. Outward diffusion of CO_2 molecules through the product layer
5. Diffusion of CO_2 through the gas phase boundary layer
6. Gasification of carbon by CO_2 (reaction 3) and regeneration of CO.

Due to the pronounced effect of the type of carbon material (section 3. 4) it seems that the reaction of carbon gasification (reaction 3) has an outstanding effect on the rate of the overall reaction. Hence, it may be reasonably assumed that chemical reaction of barite ($BaSO_4$) and CO (reaction 2) is sufficiently fast so that its contribution in overall resistance against the reaction can be ignored. This means that this reaction proceeds near the thermodynamic equilibrium. Hence, concentrations of CO and CO_2 at the surface of unreacted core of barite particles are close to their equilibrium levels, while their concentrations at the surface of carbon particles are far from their related thermodynamic values. In other words, in comparison to the equilibrium values, higher CO_2 and lower CO concentrations exist at the surface of carbon particles.

Reduced (dimensionless) time method is an effective procedure for the determination of the rate controlling mechanism [10]. In this method, experimental data are presented in the form of an equation like $g(\alpha)=kt$ with α being the fraction reacted and t presenting the time. This equation is simply converted to $g(\alpha)=A(t/t_{0.5})$, where $t_{0.5}$ is the time for 50 percent conversion and A is a parameter with a constant value, dependent only to the type of $g(\alpha)$ function and independent to the experimental conditions. By this method, all data obtained under different conditions can be presented in a single curve of α-$t/t_{0.5}$.

Since gas phase mass transfer is sufficiently high at elevated temperature, this step is not believed to be of a noticeable importance in the rate controlling mechanism. On the other hand, due to small size of the pellets, it is believed that heat transfer is not also important. Hence, either gas diffusion through the product layer or chemical reaction (or the combination of both) could be the rate controlling step(s).

Using reduced time method, equation (6) is obtained for chemical reaction and equation (7) for mass transfer rate controlling situations:

$$1-(1-\alpha)^{\frac{1}{3}} = 0.2063\frac{t}{t_{0.5}} \quad (6)$$

$$1-\frac{2}{3}\alpha-(1-\alpha)^{\frac{2}{3}} = 0.0367\frac{t}{t_{0.5}} \quad (7)$$

Comparison of the experimental data (black circle symbols) and values calculated (solid line) by using equations (6) and (7) has been shown in figures (6) and (7).

As seen in the figures (6) and (7), experimental data show a better correlation with the chemical reaction control model (fig. 6) compared to that of mass transfer. Therefore, it may be concluded that the overall reaction is predominantly governed by the chemical reaction. Further support for this conclusion could be provided by comparison of the values of the activation energy.

For this purpose, plots of $g(\alpha)$ values against time should be drawn for various experimental temperatures. Slopes of the lines obtained in this

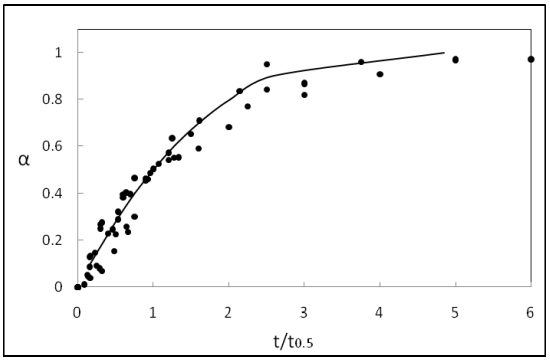

Fig. 6. Presentation of α vs. $t/t_{0.5}$ for chemical reaction rate controlling situation.

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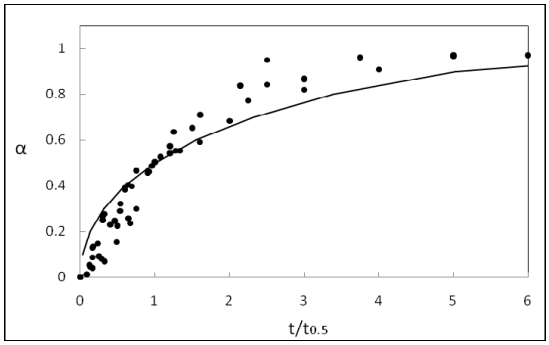

Fig. 7. Presentation of α vs. $t/t_{0.5}$ for mass transfer rate controlling situation.

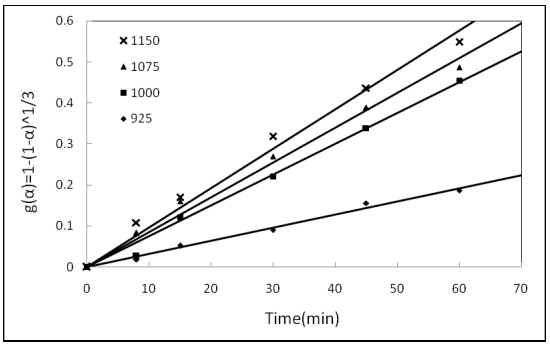

Fig. 8. g(α) vs. time plot for chemical reaction control model. (Reducing agent: coke)

way are equal to the apparent rate constant (k). For example, fig. 8 shows the plots of g(α) for chemical reaction model vs. time for the experiments performed by using coke as the reducing agent.

Values of the apparent rate constant (k) obtained in this way for different reducing carbon materials and various temperatures have been presented in table 3.

Activation energy can be obtained by application of the Arhenius equation to the calculated values of the apparent rate constant (k) delivered at various temperatures.

Plots of *lnk vs. 1/T* for different carbon materials are shown in Fig. 9. From slopes of the lines (-E/R) activation energy of the reduction reaction can be computed. Values of the activation energy obtained in this way have been presented in table 4 for graphite, coke and charcoal.

Comparison between the values of activation energy obtained in the present work to those

Table 3. Values of the apparent rate constant for graphite, coke and charcoal obtained at various temperatures.

Temperature (˚C)	$k\times10^3$ (min^{-1})		
	graphite	coke	charcoal
925	1.22	3.20	9.10
1000	2.47	5.51	15.00
1075	4.22	8.50	19.00
1150	4.56	9.52	21.77

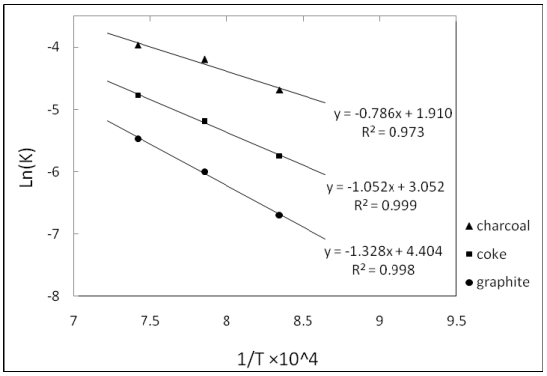

Fig. 9. Plots of Lnk vs. 1/T for different type of carbon material. (k: apparent rate constant related to the chemical control model)

Table. 4. Values of the activation energy.

Reducing agent	Activation Energy (kJ/mol)	Activation Energy (kcal/mol)
Graphite	110.5	26.3
Coke	87.5	20.8
Charcoal	65.4	15.6

reported by other authors for similar studies is very interesting. Gokarn and co-workers [11] have obtained an energy activation of 86.4 kJ/mol (about 20.2 kcal/mol) for the reduction by coke which is very close to that of the present study. Activation energy for the reduction by charcoal reported by Jagtap et. al. [2] is around 17 kcal/mol, i.e., only about 1.4 kcal/mol higher than that of this work.

As seen in table (4) reaction with graphite has the highest value of activation energy and that

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with charcoal has the lowest, while that of coke stands in-between. This is in accordance to the reactivity of these carbon materials. Dependence of the rate of carbothermic reduction of barite on the carbon gasification reaction has been observed and reported by other authors [2, 9, 11].

Based on the above information and judgment, strong dependence of the overall reaction of barite carbothermic reduction on the resistance of carbon gasification reaction becomes very clear.

4. CONCLUSIONS

1. The reaction of carbothermic reduction of barite is very strongly dependent on the process temperature which is an indication of the outstanding function of the chemical reaction as a rate controlling step.
2. Particle size of the reducing agent (coke) has a small effect on the long term efficiency.
3. Kinetic analysis of experimental data through the application of reduced time method shows that the overall rate is predominantly under the control of the chemical reaction.
4. By increasing the reactivity of carbon material (graphite, coke and charcoal) reduction rate increases. This is believed to be an indication of the important effect of carbon gasification reaction on the overall rate.
5. Considerable difference of the values of activation energy obtained for the reduction by various carbon materials (26.3 kcal/mol for graphite, 20.8 kcal/mol for coke and 15.6 kcal/mol for charcoal) provides further support for the postulated reaction mechanism.

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