

## Effects of Temperature and Particle Size Distribution on Barite Reduction by Carbon monoxide Gas

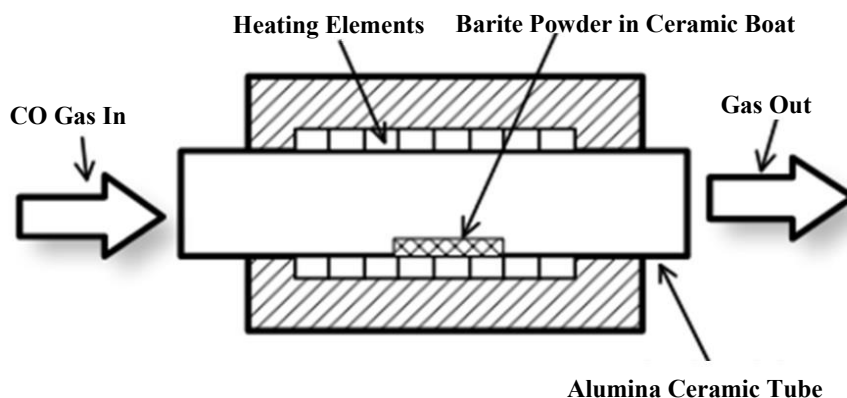
Saeed Vakilpour, Ahmad Ghaderi Hamidi\*

Department of Metallurgy and Materials Engineering, Hamedan University of Technology, Hamedan, Iran.

### HIGHLIGHTS

- Reduction of barite particles with different particle sizes by CO gas.
- Study of a technical grade barite with relatively low BaSO<sub>4</sub> content (82%).
- Kinetic relations of reduction of BaSO<sub>4</sub> to BaS.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

*Article history:*

Received 06 November 2016  
Received in revised form  
10 December 2016  
Accepted 26 February 2017

*Keywords:*

Barite  
Carbon monoxide  
Activation energy

### ABSTRACT

In this research, a mineral barite powder was reduced by carbon monoxide gas and the effects of reduction time and temperature was investigated as well as barite particle size. Results showed that the best result would be feasible when the barite particle sizes are between (-70 +100) in mesh scale. The barite reduction could reach the maximum level (98%) after reduction by carbon monoxide at 850°C for one hour. Meanwhile, the same amount of reduction could have been achieved in shorter time intervals at higher temperatures. The kinetics model for reduction process was also determined and activation energy was calculated.

## 1. Introduction

Barite is the most abundant mineral of barium. Crude barite is widely used in drilling fluids for oil and gas exploration. Barite with quite high purity can be raw material for synthesis of barium and its compounds [1]. Barite (mainly barium sulfate) reduction to barium sulfide that is dissolvable in water is an imperative step in synthesis of barium compounds [2]. In industrial plants, charcoal is usually used to reduce barite [3]. Nevertheless the high consumption of charcoal besides producing impure barium sulfide with longer reduction times and higher rate of pollution makes the gases more favorable reduction agents [4]. Carbon monoxide, hydrogen or reformed methane can be used in the process of reduction by gases. Some researchers investigated the possibilities of using hydrogen gas for barite reduction in temperature ranges of 800 to 1100°C [5, 6]. The hydrogen has shown strong reducing ability but with higher cost in comparison with others [7, 8]. Although there would be a difficulty for methane reformation, reduction of barite with methane has been also investigated [9]. Barite can also be reduced by CO bearing nitrogen and the reduction rate of barite in temperature ranges of 850 to 1000°C can be increased either by increasing the CO concentration or the temperature [10]. In the process of reduction by gas, the burning gas also can provide needed heat and fluid bed. These advantages decrease the reduction temperature to lower

than 1000 °C and time to lower than one hour. This also is favorable energetically but still using gas as a reduction agent for barite has not been industrialized [11].

There is no report about reduction of barite by pure CO. there is only one article that have used nitrogen gas with partially CO (carbon monoxide fractions of 2.4–9.6%) [10]. In this research the effects of some parameters of reduction in CO atmosphere has investigated. The aim of this research is to determine the start temperature for barite reduction by carbon monoxide gas, fulfilling the conditions for lowering the temperature and energy consumption and keeping the reduction rate at the highest simultaneously.

## 2. Materials and Methods

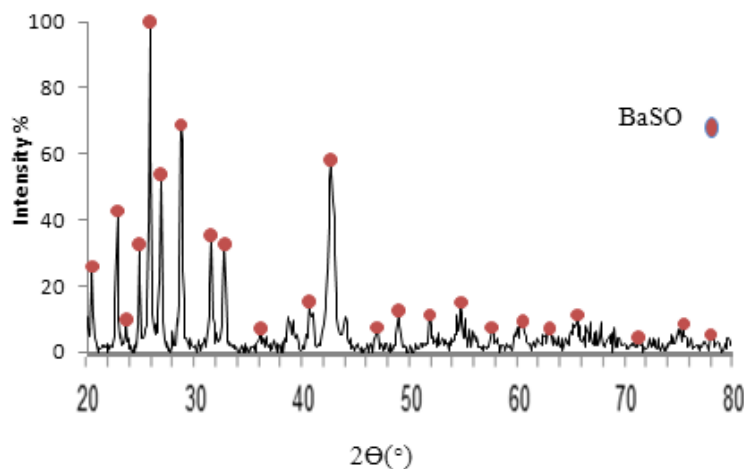
Milled mineral barite was used as raw material. Chemical analysis of the barite that was determined by X-ray florescence (XRF) is shown in Table 1. X-ray diffraction results (Fig.1) also shows that barium sulfate is dominant phase in primary specimen.

The barite samples with specific particle size distributions were used for gas reduction. Reduction cycles were examined at temperature range of 600 to 1000°C. Heating rate was 15 °C/min and 99.9% purity carbon monoxide gas flow was kept during the reduction cycle with flow rate of 0.1 L/min.

Samples with weight of 1.000 g were reduced in a tube furnace and weight reductions were measured

**Table 1.**  
Chemical analysis of mineral barite

Compound	BaSO <sub>4</sub>	SrSO <sub>4</sub>	Fe	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>
Wt.%	81.52	2.05	0.28	3.75	7.91	4.47



**Fig. 1.** XRD patterns of milled primary barite.

tube furnace and weight reductions were measured as the criterion for reduction. Using equations 1 and 2, it is possible to calculate the reduction levels. The parameters in equation 1 and 2 are defined in Table 2.

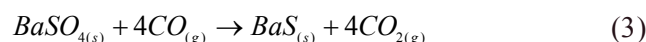
$$\Delta m_{\text{BaSO}_4\text{-red}} = \Delta m_{\text{tot}} - (\Delta m_{\text{SrSO}_4\text{-red}} + \Delta m_{\text{BaSO}_4\text{-vol}} + \Delta m_{\text{BaSO}_4\text{-moi}}) \quad (1)$$

$$\text{Reduction Percentage} = (\Delta m_{\text{BaSO}_4\text{-red}} / \Delta m_{\text{Sto}} - \Delta m_{\text{BaSO}_4\text{-red}}) * 100\% \quad (2)$$

### 3. Results and discussion

#### 3.1. Thermodynamics of barite reduction by CO

Reaction 3 demonstrates the barite reduction by CO gas. The Gibbs free energy of supposed reaction versus temperature is shown in Fig.2.



As is evident in Fig.2, barite reduction by CO gas should be possible from 500 °C but experimental results are not in agreement with the above thermodynamic predictions. As is demonstrated in Fig.3, barite

isothermal reduction started from 600 °C and reached to a significant amount at 850 °C. The increasing of reduction temperature above 950 °C did not lead to further reduction. Therefore temperature range of 850-950 °C as optimized temperature was selected for study of other parameters.

#### 3.2. Effect of barite particle size

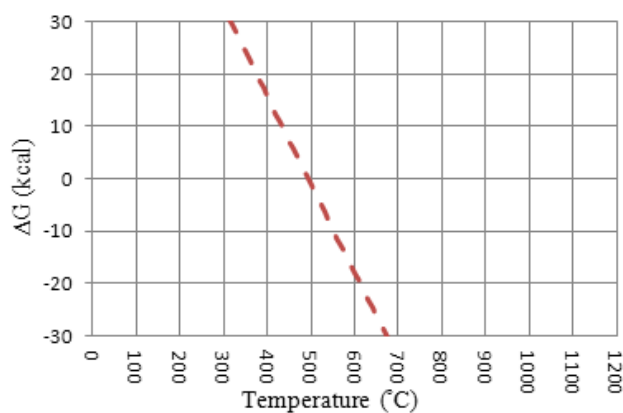
Three different ranges of particle size of milled barite as: (-20, +50), (-70, +100) and (-140, +170) were chosen to be reduced at 900 °C. The reduction times were also set at 15, 30, and 45 minutes. The reduction results versus time are demonstrated in Fig.4.

Results showed that barite samples with coarse, medium and fine particle size revealed the lowest, the highest, and the medium reduction rates, respectively. The finest particles showed the lowest amount of reduction rate. The fine particle powder mass had narrow channels for gas diffusion and has exposed more resistance against gas exchange. Although the fine powder had the highest surface/mass ratio but deficiency of gas transportation decelerated the reduction process. On the other hand, the coarse particles had the lowest surface/mass ratio therefore the

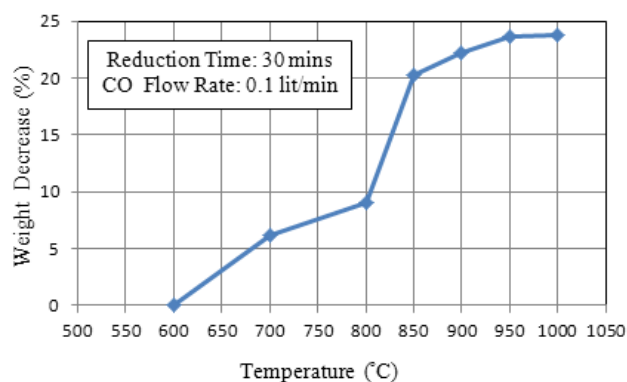
**Table 2.**

Defining the parameters of equations 1 and 2

Calculated weight reduction due to stoichiometric reduction of whole BaSO <sub>4</sub> to BaS	$\Delta m_{\text{Sto}}$
weight reduction due to barite reduction	$\Delta m_{\text{BaSO}_4\text{-red}}$
Weight reduction due to volatiles elimination	$\Delta m_{\text{BaSO}_4\text{-vol}}$
Weight reduction due to moisture elimination	$\Delta m_{\text{BaSO}_4\text{-moi}}$
Weight reduction due to full reduction of SrSO <sub>4</sub> to SrS	$\Delta m_{\text{SrSO}_4\text{-red}}$
Measured total weight reduction of specimen	$\Delta m_{\text{tot}}$



**Fig. 2.** Gibbs free energy changes of barite reduction reaction versus temperature [12].



**Fig.3.** Weight decrease due to barite reduction by CO at different temperatures for 30 min.

reducing agent (CO gas) needed to diffuse across a thick reacted surface layer (BaS) to complete reaction of the reduction. The specimen of medium particle size barite (-70 +100) showed the highest reduction rate and a better balance between two above effective parameters has been established. Therefore it is predictable that barite powders with particles bigger than tested coarse powder and smaller than tested fine powder would have lower reduction rate. XRD results for primary barite and the reduced sample are shown in Fig.5 and demonstrates that BaS (barium sulfide) is dominant phase of reduced sample.

### 3.3. Time effect on barite gas reduction

To investigate the effect of time on reduction process, four different timings was set at 15, 30, 45, and 60 minutes. The reduction temperatures were arranged at 850, 900, and 950°C, other parameters were also kept constant. Results are demonstrated in Fig.6.

According to Fig. 6, at reduction temperature of 850°C, reduction is more sensitive to time changes in comparison to others. Results are suggesting that the biggest portion of reduction process has been

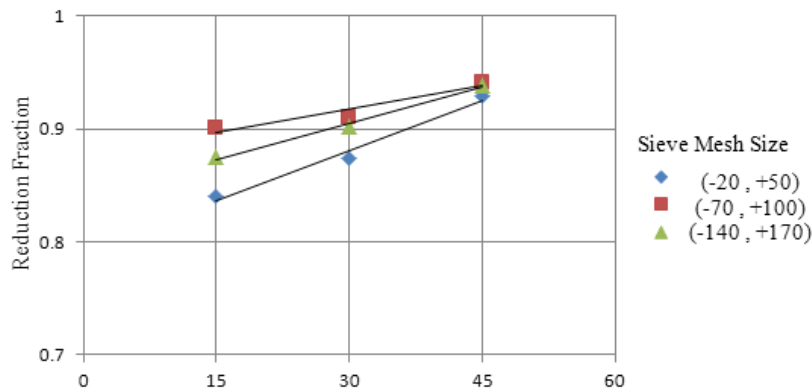


Fig. 4. Effect of barite particle size on reduced mass fraction at 900°C.

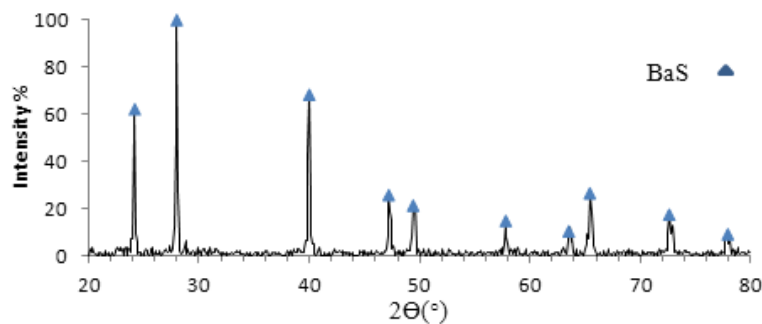


Fig. 5. XRD patterns of reduced barite specimen.

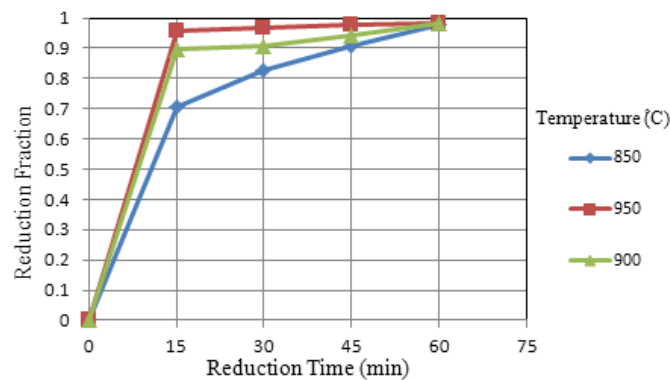


Fig. 6. Reduced barite mass fraction versus of isothermal holding time.

completed in the first time period (less than 15 minutes), specially for the higher temperatures as 950°C. Therefore, it is worth mentioning that the reduction rate will change slightly at higher temperatures. For different temperatures, the maximum levels of reduction were almost same.

### 3.4. The kinetics of barite reduction by gas

#### 3.4.1. The kinetics model

Reduction progress at all three temperatures i.e. 850, 900 and 950°C were considered as the first order reactions as are proven in Fig.7. Results showed that theoretical and experimental data are highly matched when the assumption is based on first order reactions. Therefore, it would be safe to say that the barite reductions in all three temperatures were according to first order reaction [13].

As mentioned in section 3.1, the barite reduction with CO gas is done according to equation 3. Therefore the reduction products were the Barium sulfide and CO<sub>2</sub> gas. It means reacting a solid with a gas produced another solid and another gas. In this condition and by assuming that the barite particles were spherical, the properties of reduction product formed on primary barite particles (BaS) is determining of the reduction progression. There would be two kinetic models which could be offered to investigate the reaction mechanism [14,15].

To determine the kinetic model, reduced (dimensionless) time method has used. This is an applicable method to determine the speed controlling mechanism of a reaction [16]. In this method, the general equation is  $g(x)=kt$ , where;  $x$  is the reaction fraction,  $k$  is the speed constant and  $t$  is the time. As mentioned

before, for this reduction reaction, two types of equations are suggested as equations 4a and 4b:

$$1 - (1 - x)^{1/3} = kt \quad (4a)$$

$$1 - \left(\frac{2}{3}\right)x - (1 - x)^{2/3} = kt \quad (4b)$$

For the relation 4a, the reduction rate is controlled by the rate of reduction chemical reaction and for relation 4b, the diffusion rate across reduction products is speed controller. Results showed that experimental data is matched with kinetics model b (98.45%) comparing to another model. Consequently, the diffusion rate of gaseous species (CO&CO<sub>2</sub>) through reduction products (BaS layer) had been the controlling mechanism of reduction rate. Fig.8 shows full compliance between the kinetics model and experimental data.

#### 3.4.2. Activation energy calculation of reduction reaction

For calculating the activation energy, relation 5 exponential equation is used where, the  $k$  is speed constant,  $k_0$  is the frequency factor,  $R$  is the gases constant,  $T$  is the temperature and  $E$  is activation energy [16]:

$$k = k_0 \exp(-E/RT) \quad (5)$$

First, the speed constant for model 4.b at 850, 900, 950, and 1000 °C has determined and then Fig. 9 has been draw according to above exponential equation. Results from Fig.9 show that  $(E/R)$  ration is 1.9943 and activation energy is 165.81 kJ/mol.

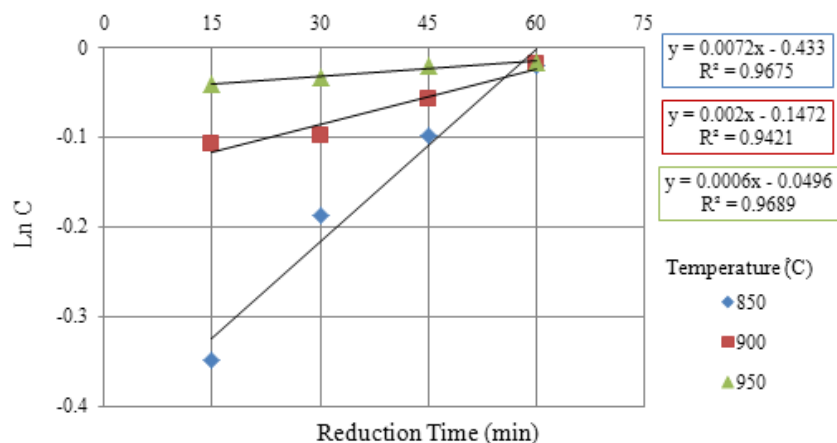


Fig. 7. Determining the barite reduction reaction order.

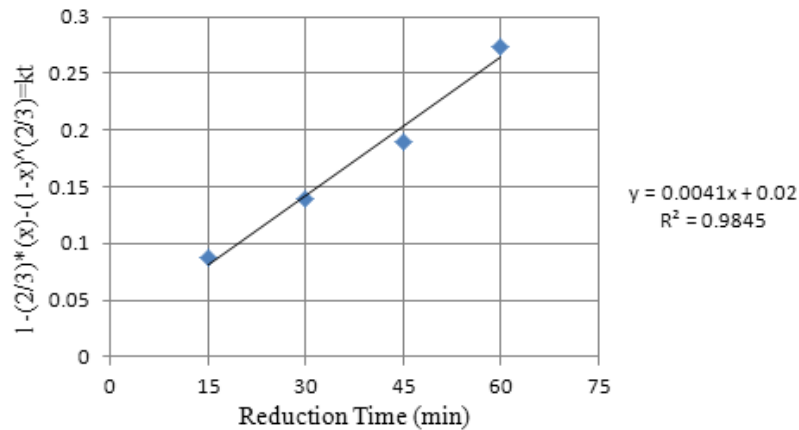


Fig. 8. Kinetics model of barite reduction process with gas at 850 °C.

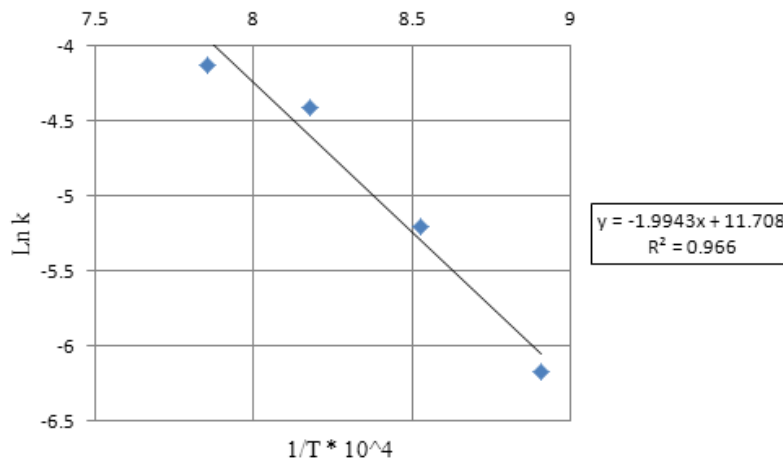


Fig. 9. Calculating activation energy for barite reduction with gas.

#### 4. Conclusions

The barite reduction with CO gas should have been thermodynamically feasible from 500 °C, but practically it started at 600 °C because at lower temperatures the reaction was very slow. The reduction rate was improved considerably at 850 °C and its reduction was completed in one hour. By increasing the reduction temperature to 950 °C, reduction rate continued to increase and the maximum reduction level was achievable in 15 minutes. Medium particle size barite (-70 +100) has highest reduction rate in comparison to fine and coarse powder. Activation energy of barite reduction by CO was 165.81 kJ/mol.

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