

Research note

## Kinetic Study of Barite Carbothermic Reduction in Presence of Sodium Carbonate as Catalyst

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### Abstract

The catalytic reduction of barite in the presence of sodium carbonate has been investigated to evaluate the effect of catalyst amount on reaction mechanism. Different amounts of sodium carbonate ranging from 2.5-10.0 wt.% were doped on coke and the test samples containing stoichiometric mixes of barite and coke powders were isothermally heated in air atmosphere. The catalytic effect of sodium carbonate was studied by isothermal experiments performed at different temperatures and reduction times. The conversion-time data were analyzed by using a modified kinetic model and the influence of catalyst content on kinetic parameters was evaluated. The results show that the addition of 7.5 wt.% sodium carbonate significantly decreases activation energy. Finally, the article concludes that catalyst amount has a negligible role on gasification of coke if the reduction process is carried out at high temperature close to 1100 °C. The obtained results can be useful in industrial practice.

**Keywords:** Barite, Coke, Gasification, Catalyst, Sodium Carbonate

### 1- Introduction

The theoretical approaches put forward by different investigators to describe the carbothermic reduction of barite, assume that the initial reaction of barite with carbon takes place where both barite and carbon particles are in contact. The generated CO in this reaction diffuses to the surface of the particles and reacts with barite which is not in contact with carbon [1]. Jagtap et. al., reported that the major reducing agent is gaseous intermediate, CO, which causes the reduction of barite and produces barium sulfide and CO<sub>2</sub>. The CO<sub>2</sub> back diffuses into

the carbon to generate more CO according to the Boudouard reaction as follows [2]:



The kinetic studies carried out by Lozhkin et al., using pure BaSO<sub>4</sub> and barite ore, showed that the reduction takes place through gaseous intermediate [3]. By monitoring the conversion of barite to barium sulfide, they proposed that the reduction of barite is controlled by kinetic of gasification reaction. Though the gasification of carbon is a typical oxidation reaction, popular oxidation

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catalysts like sodium carbonate and sodium chloride have been found to be the catalysts that act as promoters for the reduction process [4]. In developing the reduction rate, Pelovski et al. concluded that incorporation of catalyst to enhance CO generation is reflected in the enhanced rate of barite reduction, and catalyst increases the number of active sites in the Boudouard reaction, which promotes the reduction rate of the barite simultaneously [4].

The study of Gokarn et al., indicated that novel catalyst, namely sodium vanadate, is effective for gasification of active charcoal. Also, they found that isokinetic temperature has vital significance in relation to the anomalous behavior of catalytic and carbothermic reduction of barite at higher temperatures [5].

In our previous investigation on carbothermal reduction of barite in isothermal condition, the effect of particle size distribution on the reduction process was studied by kinetic model. The clear variation in particle size distribution and measuring isothermic conversion-time data indicated that the activation energy decreases only 9 kcal/mol with a decrease in the particle size of the starting material. By using fine particles, -230, +400 mesh, the minimum

activation energy was obtained for catalytic and non-catalytic conditions. Furthermore, the finer particles, -400 mesh, cannot improve the barite reduction process [6].

In the present investigation, a modified kinetic model is used to describe the isothermal reduction of barite, both in the presence and absence of sodium carbonate as catalyst. First, the validity of the model is shown and the effect of catalyst amount on kinetic parameters was then analyzed to better understand the role of sodium carbonate in the reduction of barite in air atmosphere.

## 2. Materials and methods

The effect of sodium carbonate on the reduction of barite ore has been studied according to the following steps. The chemical and mineralogical analyses of barite ore were identified by X-ray diffraction. As reported in Table 1, the main mineral is BaSO<sub>4</sub> and a small quantity of quartz was also found. For all of the experiments, fine-sized barite (-230, +400 mesh) and coarse-sized coke (80% under 140 mesh) were used. The specifications of coke used in the experiments are reported in Table 2.

**Table 1.** Chemical and mineralogical analysis of barite ore

Chemical Analysis									
SiO <sub>2</sub>	BaO	Na <sub>2</sub> O	K <sub>2</sub> O	MgO	CaO	MnO	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>
2.75	60.27	0.67	0.01	0.08	0.08	0.03	0.23	0.33	35.53
Mineralogical Analysis (calculated by chemical analysis)									
Barite	Quartz	Others							
91.8	2.75	5.48							

**Table 2.** Specifications of used coke

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

The particle size of coke and barite is comparable to those used in industrial practice. Different amounts of sodium carbonate, ranging from 2.5-10.0 wt.% were doped on coke. The percentage of sodium carbonate was based on the weight of dry coke. In all cases a stoichiometric composition of reactants, i.e.  $\text{BaSO}_4 + 4\text{C}$  was used. 2.33g barite and 0.48g coke were mixed and isothermal reduction experiments were carried out in a laboratory electrical kiln (Azar Furnace Company, Model F11L, 1500, Iran) at different temperatures between 950 and 1100°C. Each experiment was repeated at least three times. The cooled samples were weighed and in order to analyze barium sulfide percentage the iodometry method was used for each run as in the following steps [7].

The iodine solution and hydrochloric acid solution were prepared by mixing 50 mL of 0.5N iodine solution and 50 mL of 1N hydrochloric acid solution.

The disc sample was crushed and 2 g of black ash powder was mixed with 100 mL distilled hot water and stirred to prevent agglomeration and effective dissolution.

The black ash suspension was added into the iodine and hydrochloric acid solution and stirred for 3 min.

The solution was titrated with 0.1N sodium thiosulfate to obtain a straw color in the presence of the starch indicator. The BaS percentage was calculated by the following equation:

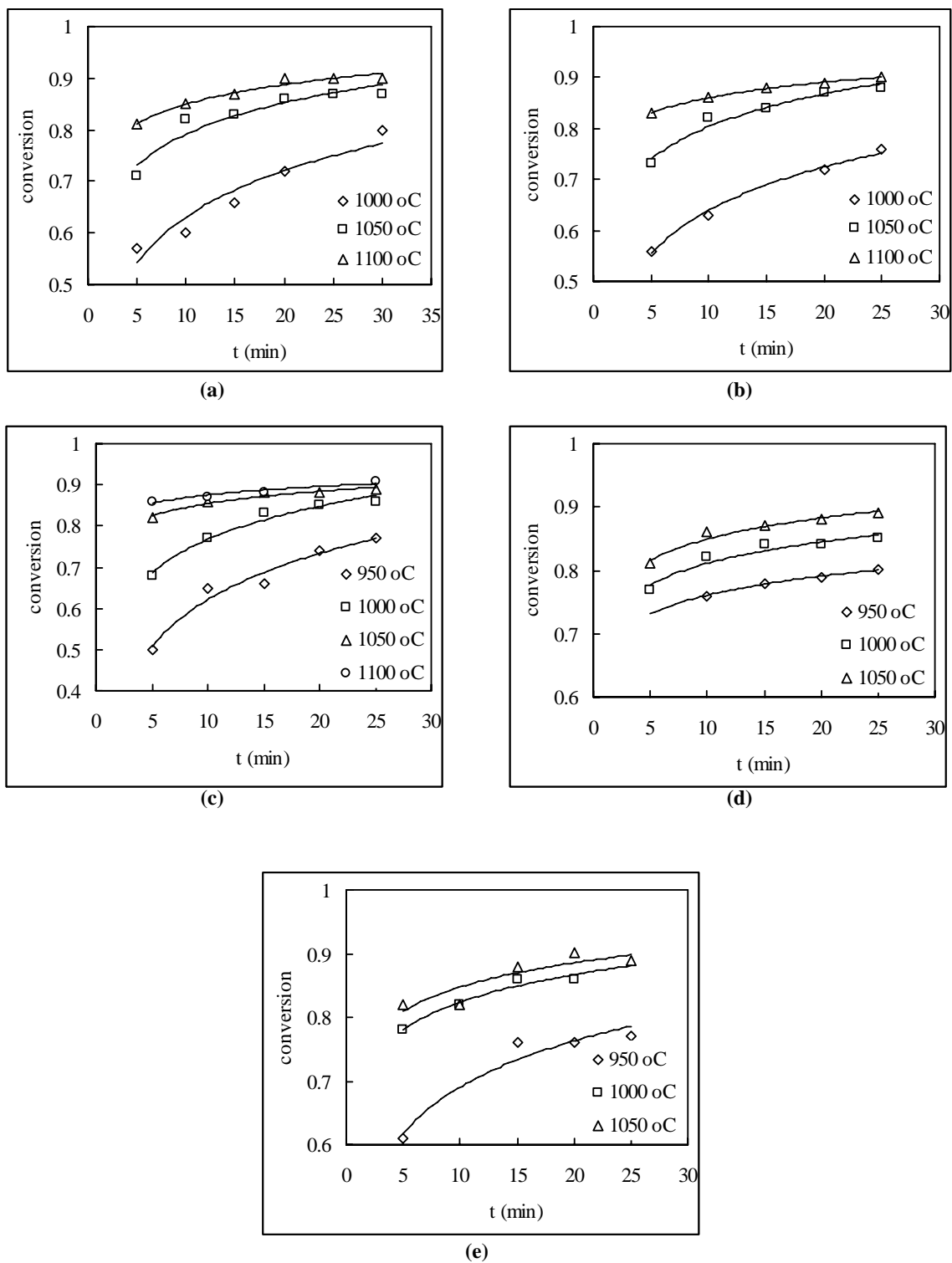
$$C = 8.17 \left( \frac{N_1 V_1 - N_2 V_2}{W} \right) \quad (2)$$

where C is the BaS percentage,  $N_1 V_1$  and  $N_2 V_2$  are total moles of iodine and sodium thiosulfate solutions respectively. W is the initial weight of the sample. The fractional conversion of  $\text{BaSO}_4$ , x, was calculated according to the stoichiometric reaction presented in Equation 3.



### 3. Results and discussion

The values of conversion versus reduction time have been plotted in Fig. 1 in the absence and presence of different amounts of  $\text{NaCO}_3$ . As is evident, conversion increases with reduction time and the rate of the reaction drops as the barite is reduced to barium sulfide.



**Figure 1.** Conversion – time plots for the reduction of barite in the presence of (a) 0.0%, (b) 2.5%, (c) 5.0%, (d) 7.5% and (e) 10% sodium carbonate

From isothermal experiments it can be seen that there is a slight increase in the gasification rate with an increment in the catalyst quantity, except for the case in which a 7.5 wt.% catalyst was used. To compare the effects of catalyst content on kinetic of reduction, a modified kinetic model has been developed by Kasoaka et al. [8]. It is related to isothermal gasification and has been applied for conversion – reduction time data. Since structural changes take place in the matrix of coke during the gasification, application of the proposed equation by Kasoaka et al. is justified. The model was presented as follows:

$$x = 1 - \exp(-kt^m) \quad (4)$$

where  $x$  is the fractional conversion,  $t$  is reduction time,  $k$ , and  $m$  are constants of the equation respectively. To verify the validity

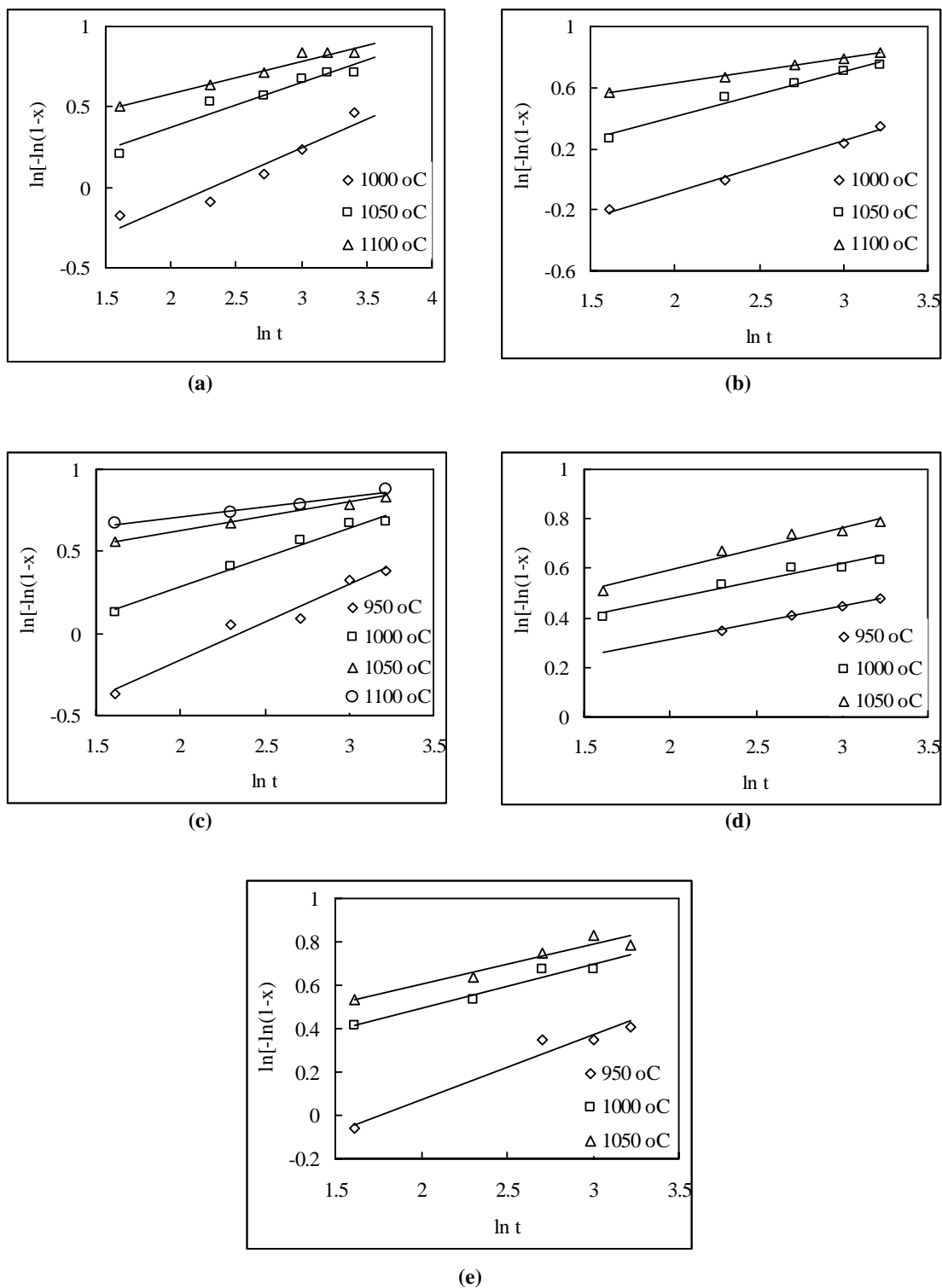
of the proposed model for the reduction of barite in the studied conditions, the kinetic model was put into the logarithmic form:

$$\ln[-\ln(1-x)] = \ln k + m \ln t \quad (5)$$

Fig. 2 indicates the variation of conversion versus reduction time in logarithmic scale to clarify the validity of the presented model by Kasoaka et al. The model satisfactorily fitted the conversion data for all studied conditions. Also, Table 3 details the values of slopes,  $m$ , and  $k$  values obtained by the ordinates from the origin of straight lines. It can be observed that the constant rates increase considerably when reduction temperature rises, whilst the value of  $m$  does not indicate a regular variation with temperature except for a few cases, therefore, we considered the average value for this parameter.

**Table 3.** The constant rate and  $m$  values of modified kinetic model

Na <sub>2</sub> CO <sub>3</sub> (%)	k				m			
	950 °C	1000 °C	1050 °C	1100 °C	950 °C	1000 °C	1050 °C	1100 °C
0		0.45	0.83	1.21		0.36	0.28	0.20
2.5		0.47	0.83	1.36		0.33	0.29	0.16
5.0	0.34	0.65	1.33	1.59	0.46	0.36	0.17	0.12
7.5	1.04	1.21	1.29		0.17	0.14	0.14	
10.0	0.59	1.08	1.27		0.30	0.20	0.18	



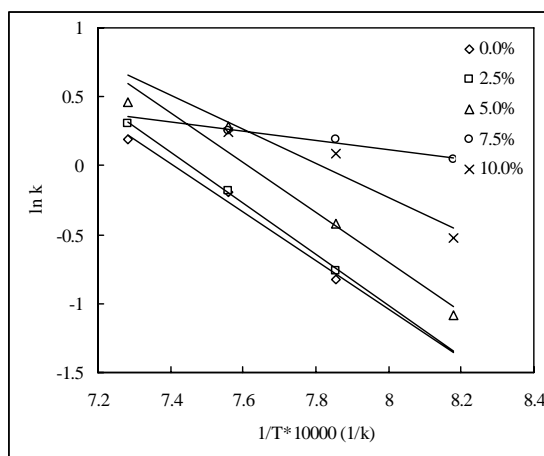
**Figure 2.** Application of modified kinetic model to the isothermal reduction of barite in the presence of 0.0%, (b) 2.5%, (c) 5.0%, (d) 7.5% and (e) 10% sodium carbonate

The constant rates values have been plotted versus the inverse of temperature in Fig. 3 on a semi-logarithmic scale for non-catalyzed and catalyzed conditions. The plots are observed to fit straight lines well, which indicates the variation of this parameter with temperature may be represented by Arrhenius equation as follows:

$$k = k_0 \exp\left(-\frac{E_a}{RT}\right) \quad (6)$$

where  $k_0$  and  $E_a$  are frequency factor and activation energy respectively.  $T$  is absolute temperature and  $R$  is ideal gas constant. The following equation, which relates the conversion to reduction time and temperature, was obtained by taking Arrhenius equation into Equation 4 and average value of  $m$ :

$$x = 1 - \exp\left(-k_0 \exp\left(-\frac{E_a}{RT}\right) t^{0.24}\right) \quad (7)$$



**Figure 3.** Arrhenius plots for reduction of barite in the presence of different values of sodium carbonate

**Table 4.** The values of kinetic parameters as functions of sodium carbonate percentage

$\text{Na}_2\text{CO}_3$ (%)	$E_a$ (kcal/mol)	$k_0$
0.0	35.3	$5.0 \times 10^5$
2.5	37.0	$1.1 \times 10^6$
5.0	36.0	$9.6 \times 10^5$
7.5	6.8	17
10.0	24.6	$1.6 \times 10^4$

The addition of 7.5 wt.% sodium carbonate results in minimum activation energy by a corresponding decrease in frequency factor. The trends of kinetic parameters show an overall positive effect on the rate of gasification reaction in the presence of 7.5 wt.% catalyst, especially at low temperatures. The pattern of variation in kinetic parameters shows a special phenomenon called by Gokarn et al., the compensation effect [5]. The existence of compensation or isokinetic effect is proved by the linear relationship between  $E_a$  and  $k_0$  as in the following equation:

$$\ln k_0 = \ln k_{\text{iso}} + \frac{E_a}{RT_{\text{iso}}} \quad (8)$$

where  $k_{\text{iso}}$  and  $T_{\text{iso}}$  are isokinetic rate constant and isokinetic temperature respectively. The isokinetic temperature has been suggested to characterize the temperature at which the rate constants within the group of related reactions have the same values. It means that the rate constant will be unaffected by the quantities of catalyst at isokinetic temperature [5].

To evaluate the compensation effect, the plot

of  $\ln k_0$  versus  $E_a$  was plotted in semi – logarithmic scale as shown in Fig. 4. This plot is shown to be a straight line, in agreement with the isokinetic equation which predicts a relationship between frequency factor and activation energy. From the ordinate at the origin of straight line, the value of 1.53 was obtained for  $k_{iso}$ . Also,  $T_{iso}$  was predicted to be equal to 1101°C, in which the catalyst content has no role on coke gasification.

In order to evaluate the effect of isokinetic temperature on reduction rate, the reaction was isothermally carried out at 950 and 1050°C in the absence and presence of 7.5 wt.% catalyst in which the conversion–reduction time plots were shown in Fig. 5. It is clearly seen that the conversion values are significantly higher in the presence of the catalyst than those in absence of sodium carbonate at 950°C. Moreover, the significant difference is not observed for catalytic and non – catalytic cases at 1050°C. In fact, the catalyst has a negligible role in the reduction of barite at a higher temperature than is frequently considered for the reduction of barite in industrial practice. The isokinetic temperature calculated by kinetic parameters is 1101°C, i.e. close to the temperature that sodium carbonate is not able to promote gasification and reduction rate consequently.

The values of conversion computed by kinetic model were plotted versus those determined experimentally in Fig. 6. To compare the experimental data with model predictions, the percent deviations,  $D_v$ , were calculated between experimental data points and theoretical predictions by the following equation:

$$D_v = \left[ \frac{X_{cal} - X_{exp}}{X_{exp}} \right] \times 100 \quad (9)$$

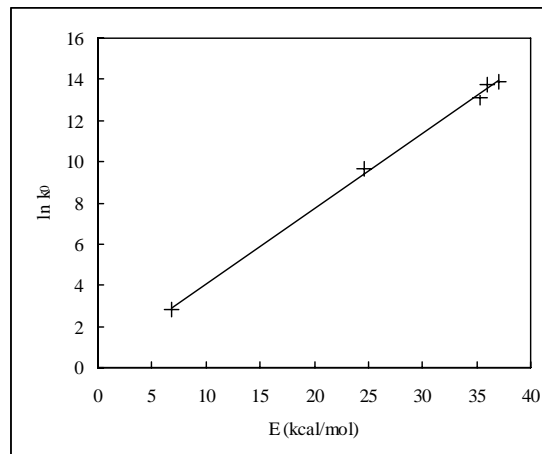


Figure 4. Isokinetic effect plot for sodium carbonate gasification of coke

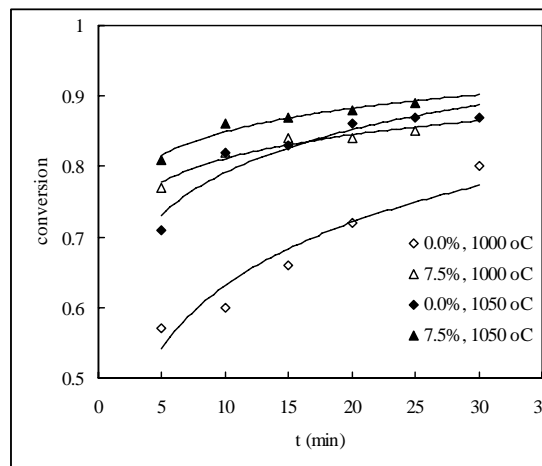


Figure 5. Compensation effect of sodium carbonate

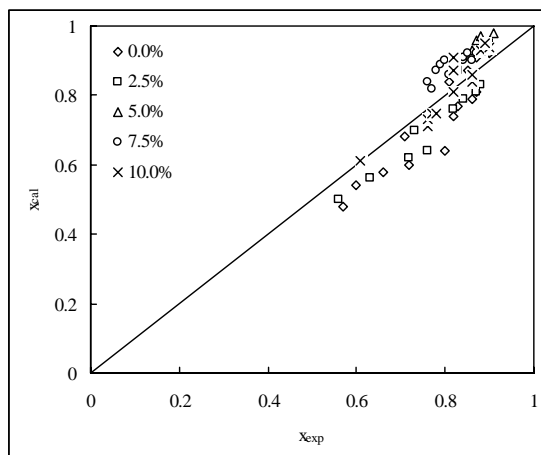
From these percent deviations, an overall root mean square, rms, was then calculated as follows:

$$rms = \left[ \sum_{i=1}^N \frac{D_v^2}{N} \right]^{\frac{1}{2}} \quad (10)$$

Approximately good agreement can be observed between the experimental data and the calculated values with a rms of 3.05



which substantiates the validity of modified kinetic model.



**Figure 6.** Evaluation of modified kinetic model for estimation of conversion

#### 4. Conclusions

The effect of sodium carbonate on the reduction of barite was studied by modified kinetic model presented by Kasoaka et al. to describe the conversion of barite to barium sulfide throughout the gasification reaction of coke. The kinetic results lead to the following conclusions:

It was found that 7.5 wt.% of catalyst effectively improves the rate constant due to a significant decrease in activation energy. It was also observed that the addition of catalyst has a negligible role in the reduction rate of barite at high temperatures (above 1050°C). This phenomenon is due to the compensation behavior in catalytic gasification of coke and was confirmed by calculation of isokinetic temperature. The validity of the kinetic model presented by Kasoaka et al. to describe the reduction process in air atmosphere was substantiated in the presence and absence of catalyst.

#### 5- Acknowledgment

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#### 6- Nomenclature

$k$	reaction rate constant, $\text{min}^{-0.24}$
$k_0$	frequency factor, $\text{min}^{-0.24}$
$m$	the constant of conversion equation
$C$	BaS percentage
$D_v$	conversion deviation
$E_a$	activation energy, kcal/mol
$N$	number of experimental data
$N_1V_1$	moles of iodine solution, mol
$N_2V_2$	moles of sodium thiosulfate, mol
$R$	ideal gas constant, kJ/mol.K
rms	root-mean-square
$T$	absolute temperature, K
$t$	reduction time, min
$W$	initial weight block ash, g
$x$	fractional conversion of barite

#### Subscribe

cal	calculated value
exp	experimental value
iso	isokinetic

#### Reference

- [1] Ravdel, A. A., Novikova, N. A., "Reduction of barite with carbon", *J. Appl. Chem., USSR*, 36 (7), 1384 (1963).
- [2] Jagtap, S. B., Pande, A. R., Gokarn, A. N., "Effect of catalysts on the kinetics of the reduction of barite by carbon", *Ind. Eng. Chem. Res.*, 29, 795 (1990).
- [3] Lozhkin, A. F., Pashchenko, V. N., Povar, F. V., "Kinetics of reduction of barite with carbon", *J. Appl. Chem. USSR*, 47 (5), 1031(1974).

- [4] Pelovski, Y., Gruchavov, Ir., Dombalov, I., "Barium sulfate reduction by carbon in presences of additives", *J. Thermal Anal.*, 32, 1743(1987).
- [5] Gokarn, A. N., Proghan, S. D., Pathak, G., Skulkarni, S. S, "Vanadium-catalyzed gasification of carbon and its application in the carbothermic reduction of barite", *Fuel*, 79, 821(2000).
- [6] Salem, A., Tavakkoli Osgouei, Y., "The effect of particle size distribution on barite reduction", *Mater. Res. Bull.*, 44, 1489 (2009).
- [7] Sell, F.D., Hilton, L., *Encyclopedia of industrial chemical analysis*, Wiley, New York, 6, p.569 (1984).
- [8] Kasaoka, S., Sakata, Y., Shimada, M., "The sulfur tolerance of various catalysts for the gasification of coal char", *Int. Chem. Eng.*, 2, 705 (1986).
- [9] Kenney, J.F., Keeping, E.S., "Root mean square in mathematics of statistics", Pt. 1, 3<sup>rd</sup> ed., Van Nostrand, Princeton, NJ, p. 59 (1962).