



Thermal reduction of barium sulphate with carbon monoxide— A thermogravimetric study

P.S. Hlabela^{a,b}, H.W.J.P. Neomagus^{a,*}, F.B. Waanders^a, O.S.L. Bruinsma^a

^a School of Chemical and Minerals Engineering, Chemical Resource Beneficiation, North-West University, Private Bag X6001, Potchefstroom 2520, South Africa

^b Scientific Capacity Unit, National Intelligence of South Africa, PO Box 8854, Pretoria 0001, South Africa

ARTICLE INFO

Article history:

Received 22 June 2009

Received in revised form

29 September 2009

Accepted 5 October 2009

Available online 13 October 2009

Keywords:

Barium sulphate

Barium sulphide

Carbon monoxide

Thermal reduction

ABSTRACT

The kinetic parameters of the reduction of barium sulphate to barium sulphide using carbon monoxide fractions of 2.4–9.6% and temperatures of 850–1000 °C, using an isothermal thermogravimetric method, were obtained. This reaction has shown to be temperature and carbon monoxide concentration dependent. By variation in temperature, at constant CO fractions, an average activation energy of 149 (±10) kJ/mol was observed. By changing the CO fraction at constant temperature, it is suggested that the reduction reaction is first order in CO. An overall reaction rate equation is proposed.

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1. Introduction

The search for sulphate removal technologies from sulphate rich water has led to the discovery of the use of BaCO₃ and BaS in these processes. BaCO₃ and BaS can be effectively used for the removal of sulphates from sulphate rich industrial waste waters and have exhibited a number of advantages over the use of other chemicals [1,2]. The removal of sulphates in these technologies is via precipitation of BaSO₄ when either BaCO₃ or BaS is dosed into sulphate rich water. The precipitation of BaSO₄ is favoured due to the low solubility of BaSO₄ in water (0.0015 g/L).

The use of BaCO₃ and BaS in mine water treatment for sulphate removal results in the production of a BaSO₄ sludge. As it is the case with many chemical water treatment processes, the conversion of the resultant sludge into a commercially valuable product increases the viability of the process and adds to the environmental awareness.

Besides its numerous existing uses, BaSO₄ can also be thermally reduced back to BaS, which then can be reused directly in the BaS process or be used as a starting material for the production of BaCO₃. Another process in which BaS has found use is the production of elemental sulphur via the PipCo process [3]. In this technology BaS is dissolved in water, from which the sulphide is

stripped and with further processing oxidized into elemental sulphur.

This process forms the downstream step of the integrated BaCO₃/BaS process for sulphate removal from mine waste water, making it commercially viable. This step requires collection, drying and thermal decomposition of the precipitated BaSO₄ to BaS in the presence of a reducing agent. As a precursor for the industrial production of elemental sulphur, optimisation of reaction conditions for the production of BaS is important.

Although successful reduction of BaSO₄ (up to 90%) was obtained when this reaction was carried out in a tube furnace with solid carbon as reducing agent [1,2] reaction kinetics thereof were not thoroughly explored. The knowledge about the reaction kinetics of BaSO₄ reduction is crucial for the design and up-scaling of the reactor to a full scale operation.

Thermal reactions of solids are most easily studied quantitatively using thermal analysis techniques, i.e., thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). The development and readily availability of reliable and accurate electronic microbalances in TG have led to the wide application of this technique in kinetic studies of the decomposition of solids [4].

The reduction of BaSO₄ using solid carbon-containing reducers have been investigated under various experimental conditions [5,6]. It is generally accepted that the solid reducers are initially gasified to CO which then interacts with BaSO₄ to produce BaS [7,8]. By using TGA-methods, the kinetics of the BaSO₄ reduction using

* Corresponding author. Tel.: +27 18 2991991; fax: +27 18 2991535.

E-mail address: hein.neomagus@nwu.ac.za (H.W.J.P. Neomagus).

Nomenclature

E_{act}	activation energy (J mol ⁻¹)
m	mass (mg)
m_0	initial mass (mg)
m_f	mass after reaction (mg)
m_t	mass at time t (mg)
n	order of carbon monoxide
p_{CO}	partial pressure of CO (Pa)
R	universal gas constant (8.3144 J mol ⁻¹ K ⁻¹)
t	time (min)
T	temperature (K, °C)
r_0	initial reaction rate (s ⁻¹)
X	conversion

solid carbon as a reducer and the effect that the partial pressure of oxygen has on the kinetics of this reaction have been demonstrated [7]. These studies have supported the assumption of gasification of the solid carbon reducer to CO gas prior to BaSO₄ reduction to BaS.

So far as we are aware, no literature has reported any work on the reduction of BaSO₄ using CO gas as a reducing agent, instead of solid carbon. However, results on the decomposition of the calcium analogue of BaSO₄, i.e., CaSO₄ in the CO atmosphere have been previously reported [9]. This study concentrated on the effect of the CO gas concentration, temperature and the heating rate on the reduction of CaSO₄. It was elucidated from this study that the decomposition of CaSO₄ to CaS and CO₂, in the presence of CO, begins at 780 °C, reaches a maximum at 865 °C and is complete at 955 °C. The DTA curves indicated that this reaction is exothermic with a measured ΔH value of 171(±33) kJ/mol.

It was concluded from these studies that by slow heating, in a gaseous medium containing 20–100% of CO, CaSO₄ is completely reduced to CaS with maximal rate just below 865 °C. With CO content lower than 20% in the gas phase and at temperatures above 1050–1100 °C, the formation of CaO, SO₂ and CO₂ becomes dominant and, correspondingly, the overall exothermic effect becomes an endothermic effect [10]. It was further concluded that application of inhibitors such as CO₂ or O₂ in the gas phase would prevent the formation of CaS and hence promote the formation of CaO and SO₂.

The aim of this study was to investigate the reaction kinetics of the reduction of barium sulphate with different concentrations of CO at different temperatures, and to find a kinetic relation of the reduction reaction. This information forms the basis on which the optimisation of the full scale operation of the BaSO₄ reduction to BaS process will be based.

2. Experimental

2.1. Materials

A chemically pure BaSO₄ (specially purified to >99.7%), from BDH chemicals was used in all TGA experiments. The average particle size of the BaSO₄ range was 5 (±1) μm. A specialised prepared CO/N₂ gas mixture (9.6 (±0.3)% CO in N₂) and UHP N₂-gas (>99.999%), supplied by Afrox South Africa, were used.

2.2. Methods

The TGA measurements of the samples were performed by recording the isothermal TG curves on a 2050 Du Pont TGA. The BaSO₄ samples (12–13 mg) were placed in a standard platinum crucible (6 mm diameter and 5 mm depth). In all experiments the sample was heated with a heating rate of 20 °C/min to the desired

temperature in a N₂ atmosphere. If isothermal conditions were obtained, the CO/N₂ mixture was introduced in such a way that the total flow rate was 200 N mL/min. This was achieved by using 2 Brooks 5850 Mass Flow Controllers. All experiments were carried out at a total pressure of 87.5 (±1) kPa.

The isothermal runs were performed with different CO concentrations (2.4%, 4.8% and 9.6%), at different temperatures (850, 900, 950 and 1000 °C) for each concentration.

3. Results and discussion

3.1. Experimental data and processing of data

An example of the raw data that is obtained from the TGA in the conversion of BaSO₄ to BaS at a final temperature of 850 °C in a 4.8% CO in N₂ mixture is given in Fig. 1.

Initially the gas atmosphere consisted of N₂ only, and the temperature was raised linear to the desired temperature, in this case 850 °C. During heating, the mass of the sample decreased slightly, possible due to the release of moisture and other impurities. As the temperature reached a constant value, the gas supply was shifted to a CO/N₂ mixture, in this case 4.8% CO. The shift in gas-supply caused an abrupt but small change in both mass and temperature, which can be seen in Fig. 1. Since the mass of the BaSO₄ sample was not exactly the same for all samples and some mass loss was observed during heating, a comparison between different experiments was done, by comparing the relative mass (m/m_0), where m_0 was taken at the time of the change in gas atmosphere. A comparison of three experiments, all carried out at 950 °C is given in Fig. 2.

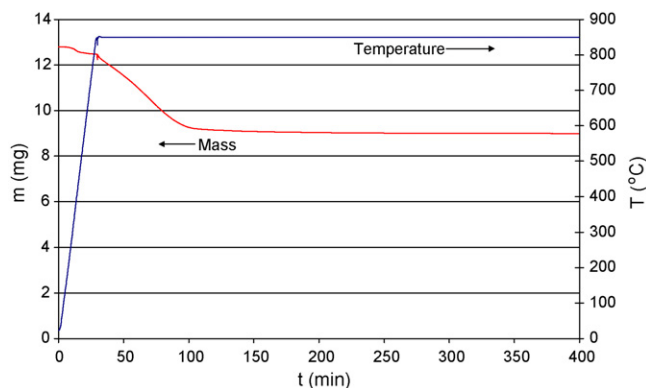


Fig. 1. Reduction of BaSO₄ in a 4.8% CO/N₂ mixture at 850 °C.

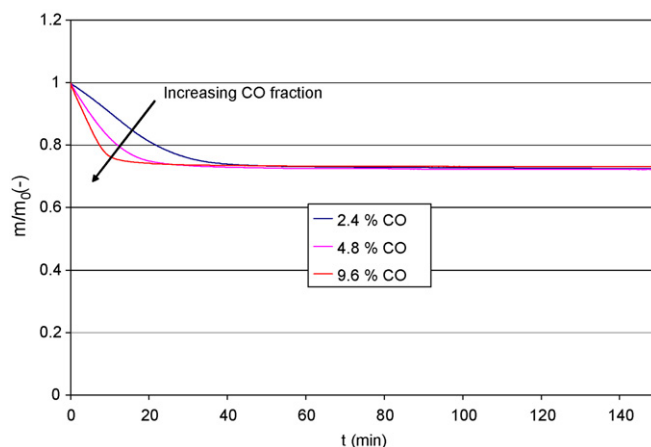


Fig. 2. Reduction of BaSO₄ with CO at 950 °C for different CO concentrations.

Table 1
Observed m/m_0 -values for all experiments.

$T(^{\circ}\text{C})$	X_{CO}		
	9.6%	4.8%	2.4%
850	0.749	0.757	0.716
900	0.729	0.702	0.693
950	0.730	0.719	0.722
1000	0.712	0.719	0.684

From Fig. 2, it can be seen that the mass loss, and hence the reaction rate, increases with the CO partial pressure. It can also be determined that the equilibrium m/m_0 -value converge to 0.730, 0.719 and 0.722 for the 9.6%, 4.8% and 2.4% CO experiments respectively. These values are in good agreement with the theoretical final value of 0.726, which is the ratio of molecular weight of BaS and BaSO₄. These and other values of m/m_0 are given in Table 1.

From Table 1, it can be concluded that the experiments are all carried out between a final value of m/m_0 of 0.072 (± 0.04). The differences in observed m/m_0 could mainly be ascribed to the noise that was introduced by the switching of the gases. To overcome this, and to specifically look at the conversion of BaSO₄, X was defined, for each experiment, as:

$$X = \frac{m_0 - m_t}{m_0 - m_f}$$

The values of the conversion as a function of time and temperature are given in Fig. 3a–c for 2.4%, 4.8% and 9.6% CO respectively.

From all three figures, it can be seen that the conversion rate increases with temperature, and by comparing the three figures, it can again be concluded that the conversion rate increases with the CO partial pressure. From Fig. 3a to c, it can also be seen that the conversion increases initially linear, and flattens abruptly at

Table 2
Determined r_0 values (in s^{-1}).

$T(\text{K})$	$p_{\text{CO}}(\text{Pa})$		
	8400	4200	2100
1123	0.000568	0.000266	0.000134
1173	0.001184	0.000453	0.000339
1223	0.001841	0.001204	0.000562
1273	0.003690	0.001701	0.000896

higher conversion, especially at high reaction rates. As a measure of the reactivity, the initial reaction rate (r_0) has been determined graphically and are given for all experiments in Table 2.

3.2. Proposed reaction kinetic equation

The reaction kinetic equation that is proposed is based on the Arrhenius equation, which accounts for the effect of temperature, in combination with a power rate law, which accounts for the effect of partial pressure of CO, according to:

$$r_0 = k_0 \exp\left(\frac{-E_{\text{act}}}{RT}\right) p_{\text{CO}}^n \quad (1)$$

The activation energy was found by plotting $\ln(r_0)$ as a function of $(1/T)$ for the different CO fractions and is given in Fig. 4.

From the slopes, activation energy of 148, 156 and 144 kJ/mol were obtained for the 2.4%, 4.8% and 9.6% CO values respectively. From these values an activation energy of 149 (± 10) kJ/mol is proposed. The Arrhenius figure presented in Fig. 4 does not show significant deviations from linearity at higher temperature and the relative large value that is obtained for the activation energy indicate that the measurements are carried out in the reaction controlled regime.

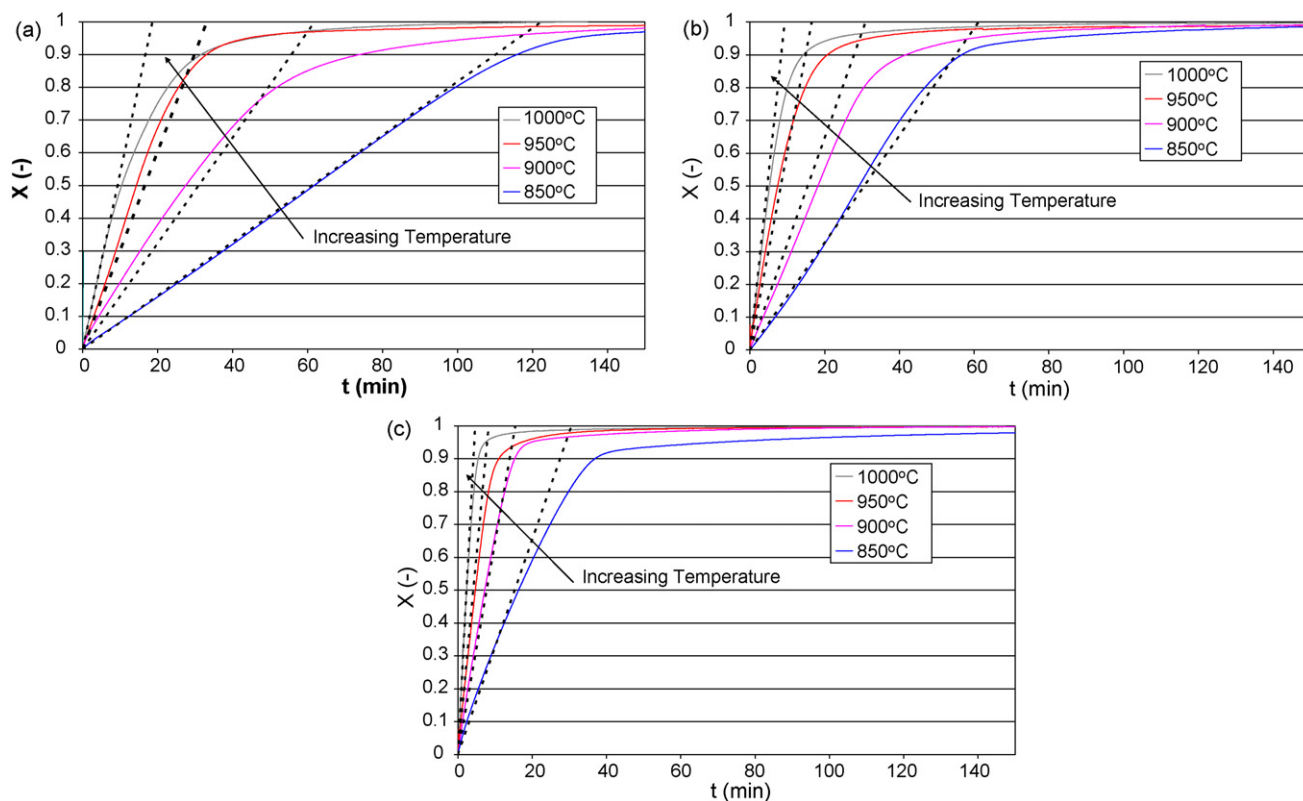


Fig. 3. (a) Reduction of BaSO₄ with 2.4% CO as a function of time and temperature (dotted lines represent initial reaction rate according to Eq. (2)). (b) Reduction of BaSO₄ with 4.8% CO as a function of time and temperature (dotted lines represent initial reaction rate according to Eq. (2)). (c) Reduction of BaSO₄ with 9.6% CO as a function of time and temperature (dotted lines represent initial reaction rate according to Eq. (2)).

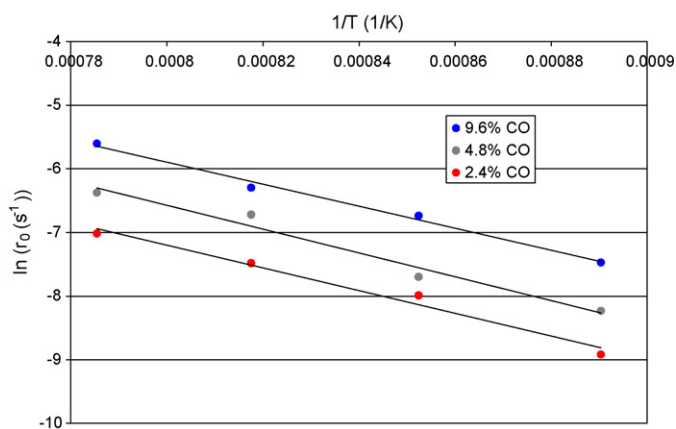


Fig. 4. Arrhenius plot of the reduction of BaSO₄ for different CO fractions.

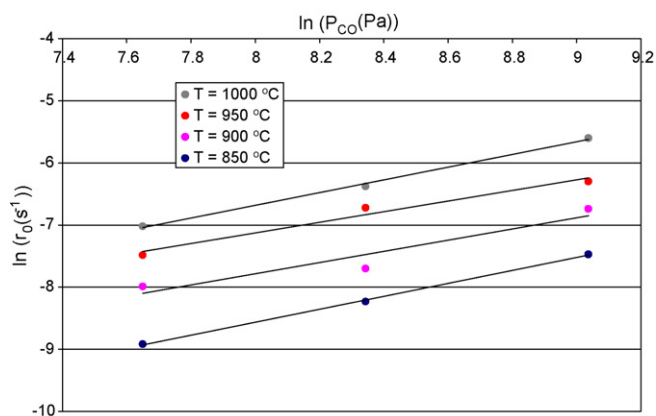


Fig. 5. $\ln(r_0)$ as a function of $\ln(p_{CO})$ for different temperatures.

To obtain the kinetic dependency of the partial pressure of CO (m), a plot of $\ln(r_0)$ as a function of $\ln(p_{CO})$ is drawn for different temperatures and is given in Fig. 5:

From the slopes of Fig. 5, the value of n can directly be obtained and was found to be 0.99, 0.90, 0.86 and 1.02 for 850, 900, 950 and 1000 °C respectively. From these values, an average value of 0.94 (± 0.12) is obtained, which suggests that the reduction of BaSO₄ with CO is a first order reaction in CO. A value for k_0 was regressed based on the proposed values of E_{act} and m and was found to be 0.57 (± 0.10). All errors were obtained from a 95% confidentiality interval. So the overall rate equation for the reduction of BaSO₄ with CO in the temperature range of 850–1000 °C, 2.4–9.6% CO, is given in Eq. (2):

$$r_0 = 0.57 \exp\left(\frac{-149,000}{RT}\right) p_{CO} \quad (2)$$

With this rate equation, the initial reactivity is also given in Fig. 3a–c in the form of dotted lines. From a comparison, it can

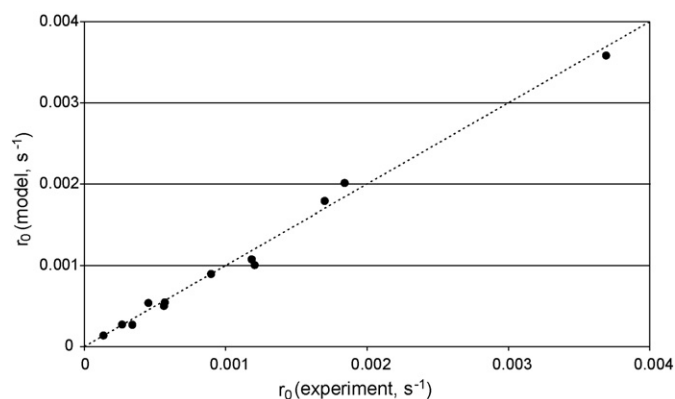


Fig. 6. Parity plot of experimental and modelled data.

be seen that the prediction of the initial reaction rate is adequate. Also, the experimental obtained r_0 data (as given in Table 2) are confronted with the modelled data (as calculated with Eq. (2)), using a parity plot as given in Fig. 6:

From Fig. 6 it can also be seen that Eq. (2) gives an accurate quantification of the initial reaction rate.

4. Conclusions

The results from this study have shown that the thermal reduction of barium sulphate to barium sulphide using CO, as reducing agent, is dependent on both the partial pressure of CO and the temperature. This reaction is a first order reaction in CO with an average activation energy of 149(± 10) kJ/mol in the region of 850–1000 °C. A further study is undertaken to investigate the possible retarding effect of CO₂ on the reaction rate.

Acknowledgements

Technological and Human Resources Industrial Program (THRIP) and Council for Scientific and Industrial Research (CSIR) are acknowledged for funding this research.

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