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Kinetics of carbothermic reduction of zinc sulfide in the presence of calcium carbonate

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Abstract The kinetics of the carbothermic reduction of zinc sulfide in the presence of calcium carbonate was investigated by an atomic absorption spectrometer (AAS) and a thermogravimetric analysis system (TGA). Experimental results indicate that TGA data accompanying with the equation derived from two-stage mechanism can be used to calculate the zinc yield properly. The results of TGA revealed that the rate of reduction in the presence of calcium carbonate was close to that in the presence of calcium oxide. The reduction rate was found to increase with increasing the reaction temperature, the initial molar ratio of C/ZnS, or the initial molar ratio of $CaCO_3$/ZnS and with decreasing the argon flow rate, the sample height, the size of carbon aggregate, the size of calcium carbonate aggregate or the initial bulk density. An empirical rate expression of zinc yield has been regressed based on the experimental data obtained.

Introduction

The carbothermic reduction of zinc sulfide in the presence of calcium carbonate is involved in two chemical processes. One is the zinc extraction from sphalerite through the pyrometallurgical method [1] and the other is the zinc recovery from spent zinc oxide catalyst through the carbothermic reduction process [2]. Carbon acts as a reductant to reduce zinc sulfide and calcium carbonate, as a scavenging agent to trap the sulfur content in the solid sample. Originally, calcium oxide was a commonly used trapping agent and has been studied more extensively [1, 3–6], however studies on the reduction with calcium carbonate are much less frequent [3, 7, 8]. Skopov et al. [3] claimed that $CaCO_3$ decomposed to CaO before carbothermic reduction. Zhang et al. [7] reported that the reduction rate with calcium carbonate was higher than that with calcium oxide, and the fixation of sulfur, in the form of CaS, is excellent during the reduction. Later on, they [8] proposed a reaction mechanism and a rate controlling step to interpret this reaction. Due to the lack of understanding of this reaction, an X-ray diffractometer (XRD), a carbon and sulfur determinator, a scanning electron microscope (SEM), an energy dispersive X-ray analysis (EDX) and a surface area analyzer were employed to study this reaction in this laboratory [9] and the variations of composition and physical properties of the solid sample during reaction have been reported. In addition, a reaction mechanism and a reaction model were proposed to interpret the overall reaction. Continuing the previous investigation [9], a kinetic study on this reaction is presented here. The effects of eight operation variables on the zinc yield are studied and an empirical rate expression for the zinc yield was determined in this work.

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Experimental procedure

Materials

Argon (Yuang-Ron Gas Co., Taipei, Taiwan) with a minimum purity of 99.9995% was employed. Reagent-grade zinc sulfide (minimum purity of 99.99%) and carbon black (minimum purity of 99.99%) were supplied by Acros Organics (Geel, Belgium) and Strem Chem. Co. (Newburyport, MA), respectively. Calcium carbonate (reagent grade, minimum purity of 99.5%) was procured from Wako Pure Chem. Industries (Osaka, Japan). Zinc standard solution of 1,000 ppm (reagent grade) for AAS was produced by Showa Chem. Co. (Tokyo, Japan).

Sample preparation

Powders of zinc sulfide, carbon black and calcium carbonate were dried at 378 K for 43,200 s separately. Zinc sulfide of original size was employed, whereas carbon black and calcium carbonate were screened through a set of Tyler standard screens and then separately dried at 378 K for 43,200 s. These three kinds of powders with known sizes and predetermined proportions were mixed in a V-type blender (S-2, Tsutsui Scientific Instruments, Tokyo, Japan) for 21,600 s. The mixed samples were dried at 378 K for 43,200 s and then stored in a vacuum drier. For reaction, the mixture was transferred to an alumina crucible of 0.02 m diameter and 0.03 m height. The weights of solid samples were in the range of 0.151×10^{-3} to 0.906×10^{-3} kg.

Carbothermic reduction

The carbothermic reduction was carried out in a thermogravimetric analysis system (TGA). The reaction tube of the TGA was heated from room temperature under argon stream. When the temperature of the tube had reached the desired value and had remained stable for 1,800 s, the reaction tube was opened to load the crucible with the sample and then closed. The reaction then started isothermally. The pressure in the system was maintained at 20–40 Pa higher than the atmospheric pressure. When the predetermined reaction time was reached, the solid sample was removed and quenched by an argon stream. The weights of the solid sample during reaction were recorded by a personal computer connected to the TGA.

To check the correctness of the zinc yield obtained from TGA, nine solid samples reacted at 1,303 K for different times were analyzed by an AAS (AA-20, Varian Co., Mulgrave, Australia) following the procedure described below. A solid sample was mixed with 2×10^{-5} m^3 8 N nitric acid at 50 °C for 1,200 s. The slurry thus produced was then filtered using a piece of 5C Adventec filter paper and the filtrate was diluted with distilled water. The zinc content in the liquid sample was analyzed by the AAS, which was operated at a wavelength of 2.139×10^{-7} m, a width of light grid of 1×10^{-9} m and an electric current of 5×10^{-3} A.

Results and discussion

Comparison of results of AAS and TGA

If Reaction 1 is considered as the overall reaction proceeded

$$\mathrm{ZnS(s)} + 2\mathrm{C(s)} + \mathrm{CaCO_3(s)} = \mathrm{Zn(g)} + \mathrm{CaS(s)} + 3\mathrm{CO(g)} \tag{1}$$

in the process of reduction, data obtained by the TGA can be employed to calculate the percentage of zinc yield Y_{Zn} according to Eq. 2

$$Y_{\mathrm{Zn}}(\%) = \frac{(W_o - W)/(\mathrm{MW_{Zn}} + 3\mathrm{MW_{CO}})}{N^o_{\mathrm{ZnS}}} \times 100 \tag{2}$$

where $\mathrm{MW_{CO}}$ = molecular weight of carbon monoxide (28 kg kmol^{-1})
$\mathrm{MW_{Zn}}$ = molecular weight of zinc (65.39 kg kmol^{-1})
N^o_{ZnS} = total moles of zinc sulfide in solid sample at $t = 0$ (kmol)
W = weight of solid sample at $t = t$ (kg)
W_o = weight of solid sample at $t = 0$ (kg)

Our previous investigation [9] proposed that in the initial stage (0–450 s), the calcium carbonate decomposition

$$\mathrm{CaCO_3(s)} = \mathrm{CaO(s)} + \mathrm{CO_2(g)} \tag{3}$$

and the carbothermic reduction

$$\mathrm{ZnS(s)} + \mathrm{C(s)} + \mathrm{CaO(s)} = \mathrm{Zn(g)} + \mathrm{CaS(s)} + \mathrm{CO(g)} \tag{4}$$

proceeded simultaneously, and after the initial stage only the carbothermic reduction, Reaction 4, occurred.

If this two-stage reaction mechanism is accepted, the zinc yield after 450 s can be calculated according to Eq. 5

$$Y_{\mathrm{Zn}}(\%)=\frac{(W_{\mathrm{o}}-0.44x_{\mathrm{CaCO_3}}W_{\mathrm{o}}-W)/(\mathrm{MW_{Zn}}+\mathrm{MW_{CO}})}{N^{\mathrm{o}}_{\mathrm{ZnS}}}\times 100 \tag{5}$$

where $x_{\mathrm{CaCO_3}}$ is the initial weight fraction of calcium carbonate in solid sample.

Either Reaction 1 or two-stage reaction mechanism, Reactions 3 and 4, is accepted as the overall reaction, the reactant ZnS transforms to zinc vapor, which will vaporize, during reaction. Therefore, the percentage of zinc yield Y_{Zn} can be calculated from the data of AAS according to Eq. 6

$$Y_{\mathrm{Zn}}(\%)=\frac{N^0_{\mathrm{Zn}}-N_{\mathrm{Zn}}}{N^0_{\mathrm{Zn}}}\times 100 \tag{6}$$

where N^0_{Zn} and N_{Zn} are the total moles of zinc in solid sample at $t = 0$ and $t = t$, respectively.

The results of TGA with two calculation methods and those of AAS are depicted in Fig. 1. It can be seen that the zinc yields calculated according to Eq. 5 are very close to those of AAS. This finding verifies our previous postulation of two-stage mechanism [9]. It also implies that the conclusion drawn by Zhang et al. [7, 8], that the carbothermic reduction with $\mathrm{CaCO_3}$ is faster than that with CaO, is not correct, since their zinc yield was calculated according to Eq. 2.

AAS analysis of the zinc content in a solid sample is a direct and accurate method to obtain the zinc yield. However, the experiments of carbothermic reduction and the analyses of zinc compositions in the solid samples are time-consuming. On the other hand, TGA is more convenient since it continuously records the weights of solid sample at different reaction times. However, care should be taken in converting the weight of solid sample to zinc yield. For convenience, TGA data and Eq. 5 will be employed hereafter to obtain the zinc yield.

Comparison of rate of carbothermic reduction with $\mathrm{CaCO_3}$ and that with CaO

To compare the rate of carbothermic reduction with $\mathrm{CaCO_3}$ and that with CaO, three sets of experiments were carried out at 1,253, 1,303 and 1,353 K under the following conditions. $\mathrm{CaCO_3}$ of 11.40×10^{-6} m was employed to replace CaO of 17.90×10^{-6} m, as used by Huang [6]; and other experimental conditions used were same as those of Huang [6] (Argon flow rate $= 0.50 \times 10^{-5}$ $\mathrm{m^3\ s^{-1}}$; sample height $= 0.50 \times 10^{-2}$ m; initial molar ratio of C/ZnS = 2.0; initial molar ratio of CaO/ZnS = 1.5; average size of ZnS aggregate $= 5.98 \times 10^{-6}$ m; size of carbon aggregate $= 67.7 \times 10^{-6}$ m). The initial bulk densities of these two cases, which can not agree with each other, are 388 and 429 kg $\mathrm{m^{-3}}$, respectively. The results of the present study (with $\mathrm{CaCO_3}$) and those of Huang [6] (with CaO) are shown in Fig. 2, which reveal that the rates of reduction with $\mathrm{CaCO_3}$ are close to those with CaO. This finding, again, supports the two-stage mechanism mentioned before and indicates the error of the conclusions by Zhang et al. [7, 8]. It also implies that $\mathrm{CaCO_3}$ is preferable to CaO as a scavenging agent in the carbothermic reduction, since it is cheaper and the rates of both reactions are similar.

Fig. 1 Comparisons of the results of TGA and AAS

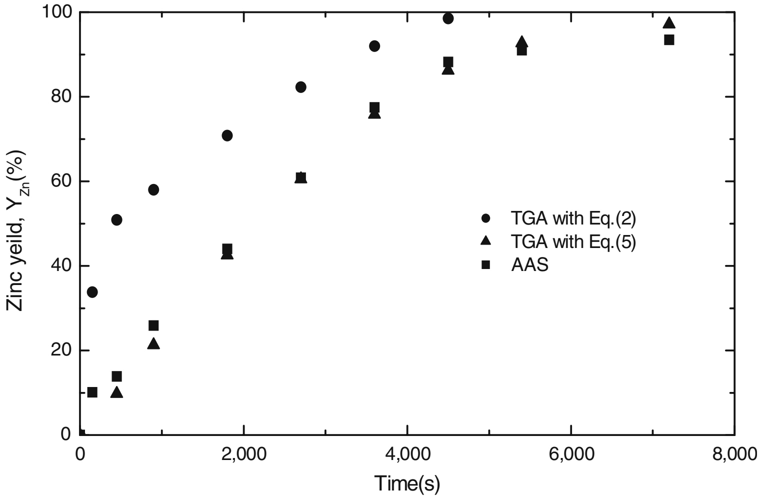
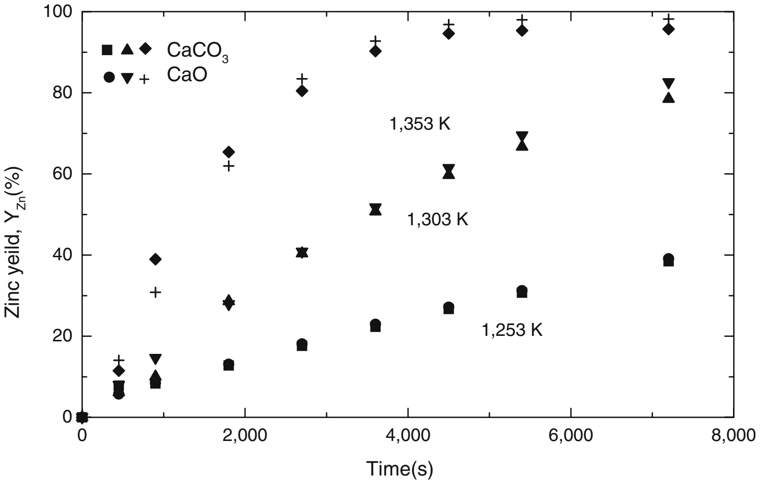


Fig. 2 Comparisons of the rates of zinc yield in the presenc of $CaCO_3$ (present study) with those of CaO [6]



Effects of experimental variables on rate of carbothermic reduction

Before the experimental results of this series are presented, the detailed reaction mechanism proposed in our previous study [9] will be presented here, since it will be employed to interpret the experimental results obtained.

The two-stage mechanism mentioned above is actually a simplification of the following mechanism.

Initial stage:

$$2ZnS(s) + 3O_2(g) = 2ZnO(s) + 2SO_2(g) \tag{7}$$

$$(1+n)C(s) + \frac{1+2n}{2}O_2(g) = CO(g) + nCO_2(g) \tag{8}$$

$$ZnS(s, \beta\text{-type}) = ZnS(s, \alpha\text{-type}) \tag{9}$$

$$CaCO_3(s) = CaO(s) + CO_2(g) \tag{10}$$

$$ZnS(s) + CaO(s) = ZnO(s) + CaS(s) \tag{11}$$

$$ZnO(s) + C(s) = Zn(g) + CO(g) \tag{12}$$

$$ZnO(s) + CO(g) = Zn(g) + CO_2(g) \tag{13}$$

$$C(s) + CO_2(g) = 2CO(g) \tag{14}$$

Propagation stage:

$$ZnS(s) + CaO(s) = ZnO(s) + CaS(s) \tag{11}$$

$$ZnO(s) + C(s) = Zn(g) + CO(g) \tag{12}$$

$$ZnO(s) + CO(g) = Zn(g) + CO_2(g) \tag{13}$$

$$C(s) + CO_2(g) = 2CO(g) \tag{14}$$

Final stage:

The reaction slows when the contact area between ZnS(s) and CaO(s) becomes small.

Termination stage:

The overall reaction ceases when one of the reactants, ZnS, C or $CaCO_3$ is exhausted.

The consumptions of ZnS(s) and C(s) due to Reactions 7 and 8 are not significant while "Reaction 9" is only a physical transformation involving a crystal structure change. Reaction 10 is the decomposition of calcium carbonate. Reactions 11–14 are the reaction steps of the carbothermic reduction, Reaction 4. If the points discussed above are taken into account, this four-stage mechanism can be simplified to the two-stage mechanism mentioned before, Reactions 3 and 4.

The effects of eight operating variables on the rate of zinc yield are depicted in Figs. 3–10. The eight variables studied are: argon flow rate, sample height, reaction temperature, initial molar ratio of C/ZnS, initial molar ratio of $CaCO_3$/ZnS, size of carbon aggregate, size of $CaCO_3$ aggregate and initial bulk density. The values of these variables studied are listed

Fig. 3 Plot of zinc yield against time. Effect of argon flow rate

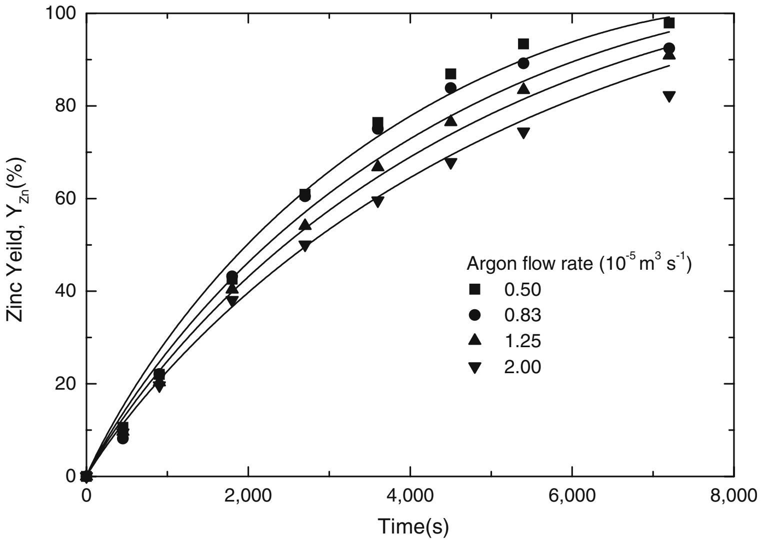


Fig. 4 Plot of zinc yield against time. Effect of sample height

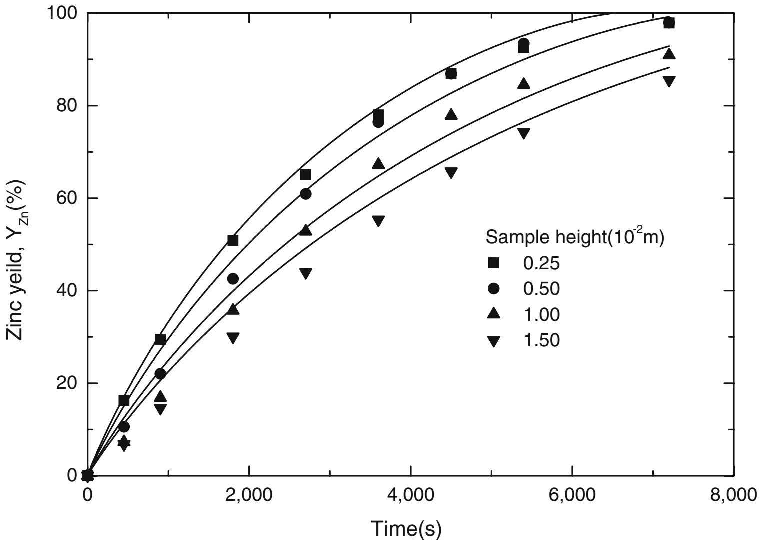


Fig. 5 Plot of zinc yield against time. Effect of reaction temperature

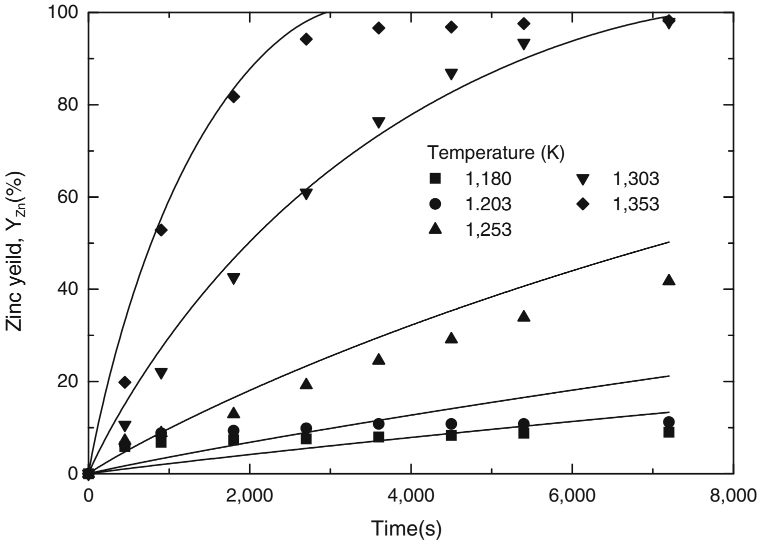


Fig. 6 Plot of zinc yield against time. Effect of initial molar ratio of C/ZnS

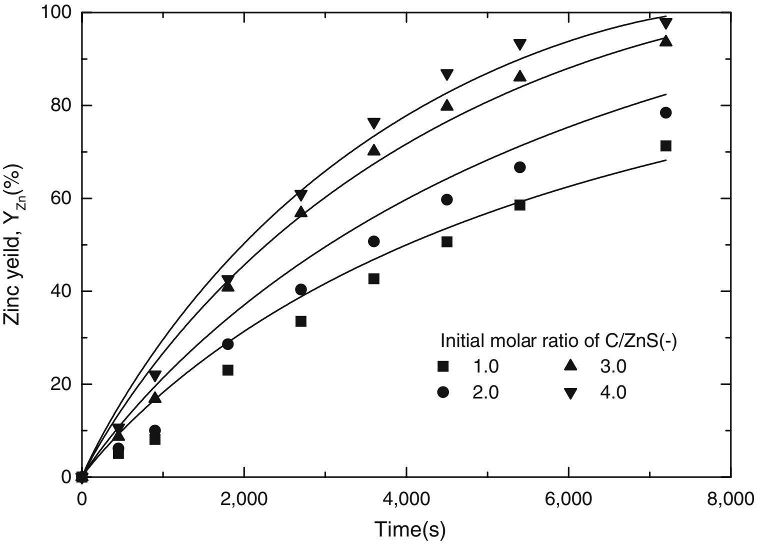


Fig. 7 Plot of zinc yield against time. Effect of initial molar ratio of $CaCO_3$/ZnS

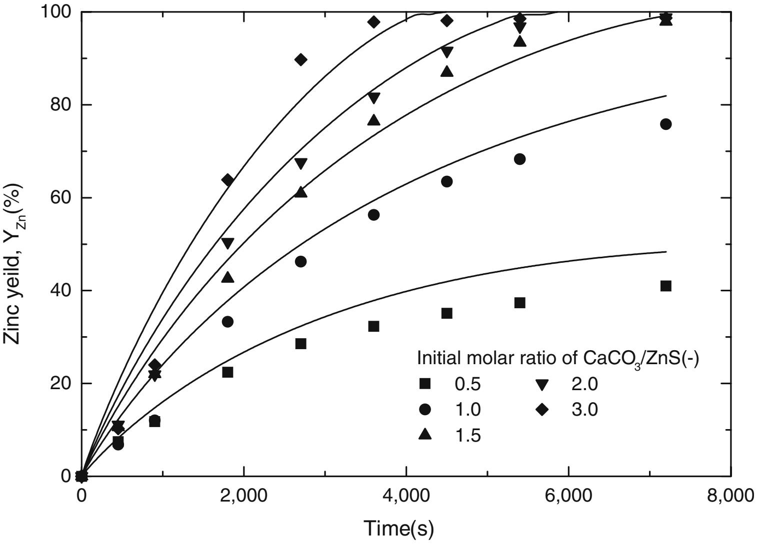


Fig. 8 Plot of zinc yield against time. Effect of size of carbon aggregate

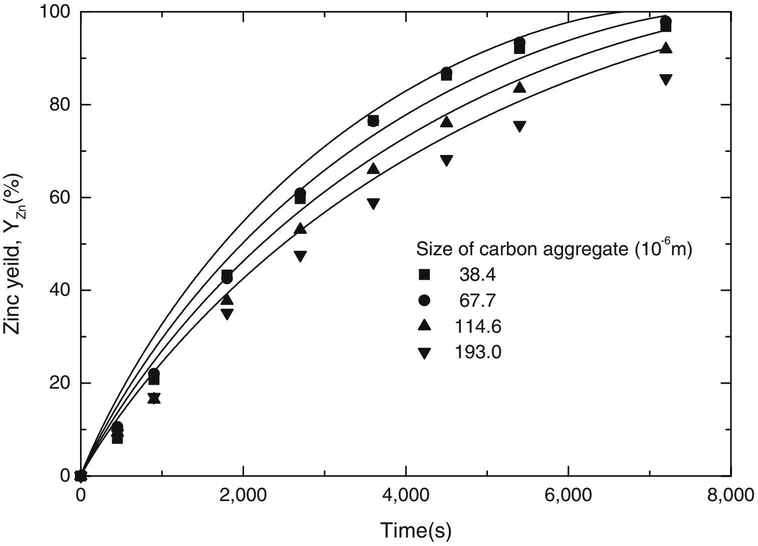


Fig. 9 Plot of zinc yield against time. Effect of size of $CaCO_3$ aggregate

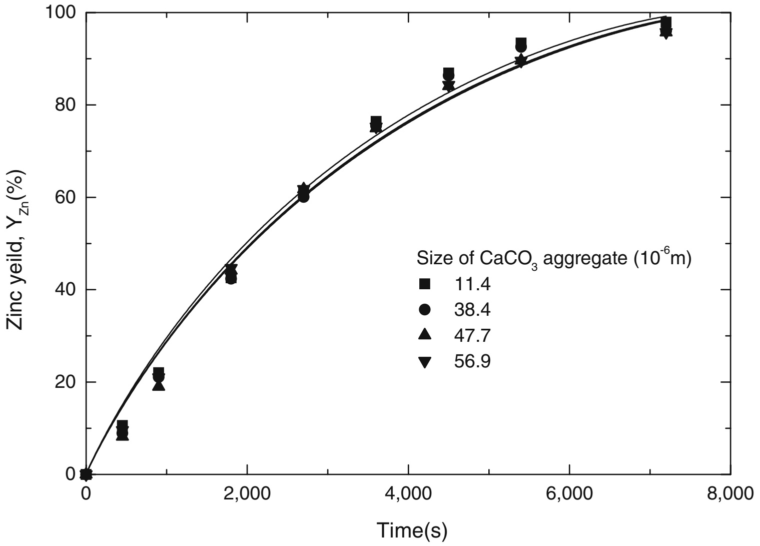


Fig. 10 Plot of zinc yield against time. Effect of initial bulk density

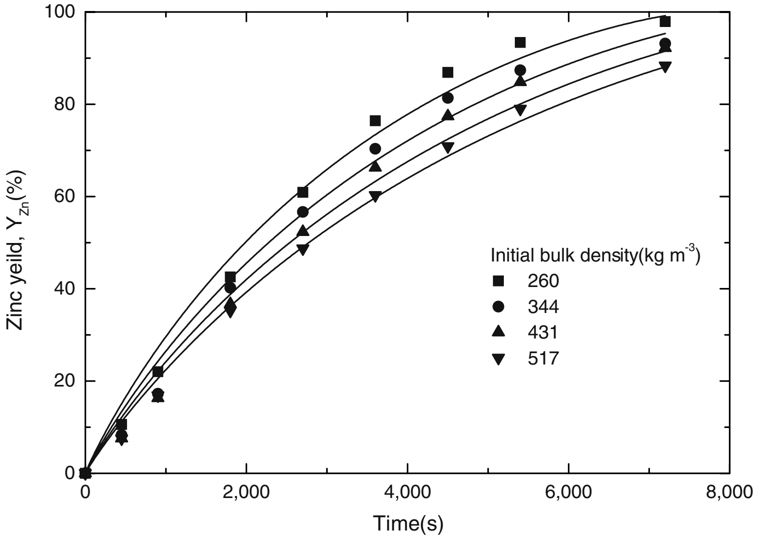


Table 1 Values of experimental variables in carbothermic reduction experiments

Variable	Value[a]
Argon flow rate (10^{-5} m^3 s^{-1})	0.50, 0.83, 1.25, 2.00
Sample height (m)	0.0025,0.005, 0.010, 0.015
Sample diameter (m)	0.02
Reaction temperature (K)	1,180, 1,203, 1,253,1,303, 1,353
Initial molar ratio of C/ZnS (–)	1.0, 2.0, 3.0,4.0
Initial molar ratio of $CaCO_3$/ZnS (–)	0.5, 1.0,1.5, 2.0, 3.0
Size of ZnS aggregate (10^{-6} m)	5.98
Size of carbon aggregate (10^{-6} m)	38.4,67.7, 114.6, 193.0
Size of $CaCO_3$ aggregate (10^{-6} m)	11.4, 38.4, 47.7, 56.9
Initial bulk density (kg m^{-3})	260, 344, 431, 517

[a] Underlined values are standard operating variables

in Table 1. The standard operating variables are underlined, indicating that when the effect a variable is not studied, its value is held at the underlined value in that series of experiments.

The effect of argon flow rate on the zinc yield is shown in Fig. 3, clearly indicating that the faster the argon flow, the slower the reaction. This can be explained as follows. When the argon flow rate is higher, the easier the produced gases CO(g), CO_2(g) and Zn(g) diffuse out, which causes the low concentrations of CO(g), CO_2(g) and Zn(g) in the solid matrix. The low concentrations of CO(g) and CO_2(g) hinder Reactions 13 and 14, respectively, while low concentration of Zn(g) may reduce the resistances of the diffusing CO and CO_2 gases to solid ZnO and C, which speeds up Reactions 13 and 14, respectively. The effects of the first two are stronger than the latter, so the overall reaction is hindered.

No similar reports can be compared in the system of ZnS/C/$CaCO_3$, while present results are different from those of Huang [8] who studied the system of ZnS/C/CaO.

Figure 4 shows the effect of sample height on the zinc yield, indicating that the higher the sample, the slower the reaction. A high sample increases the gaseous concentrations of CO(g), CO_2(g) and Zn(g). The first two accelerate the overall reaction and the latter one slows it. The effects of the sample height on the former two are less than that of latter one, so the overall reaction is slowed down.

Present results agree with those in the system of ZnS/C/CaO [1, 6].

In the next series of experiments, the carbothermic reductions were conducted at five temperatures within the range of 1,180–1,353 K, with the results as shown in Fig. 5. It can be observed that an increase of reaction temperature accelerates the reaction. When the reaction temperature is below 1,203 K, the zinc yield is very low. These results agree with previous findings both in the system of ZnS/C/$CaCO_3$ [2] and ZnS/C/CaO [1, 3, 4, 6].

The effect of the initial molar ratio of C/ZnS on the rate of zinc yield is shown in Fig. 6. A high carbon content in the solid sample provides more surface area for Reaction 14 and accelerates it, so the overall reaction is speeded up.

The present results agree with those of Huang [6] and are somewhat different from Skopov et al. [3] and Zhang et al. [7] for the system of ZnS/C/CaO.

The effect of the initial molar ratio of $CaCO_3$/ZnS is depicted in Fig. 7 showing that the higher the ratio, the faster the reaction. The reason for this is that when the ratio is high, more calcium carbonate is present in the sample, which generates more calcium oxide due to the decomposition of calcium carbonate, Reaction 10. Consequently, Reaction 11 is accelerated, which furthermore speeds up the overall reaction.

The present results agree with those of Huang [6] for the system of ZnS/C/CaO, although our results do not coincide with those of Zhang et al. [7] in the whole range of the ratio.

It is generally known that small grains in the solid sample of a gas–solid reaction system result in a high reaction rate. In the present study, two series of experiments were performed. In one series, the average sizes of ZnS and $CaCO_3$ were fixed at 5.98×10^{-6} m and 11.40×10^{-6} m, respectively and the size of carbon was varied to be 38.4×10^{-6}, 67.7×10^{-6}, 114.6×10^{-6}, 193.0×10^{-6} m. In the other series, the average size of ZnS and C were held constant at 5.98×10^{-6} m and 67.7×10^{-6} m, respectively and the size of $CaCO_3$ was varied: 11.4×10^{-6}, 38.4×10^{-6}, 47.7×10^{-6}, 56.9×10^{-6} m. After comparing the sizes obtained here and those observed in electron micrographs [9], it is clear that sizes of the powders mentioned here are the sizes of aggregates instead of grains. Present experimental results, shown in Figs. 8 and 9, indicate that the smaller the aggregate size of either C or $CaCO_3$, the faster is the reaction. However, the effect of $CaCO_3$ size is not significant. These results agree with those of Huang [6].

In the final series of experiments, four experimental runs with different initial bulk densities were carried out: 260, 344, 431, and 517 kg m^{-3}. The results, as shown in Fig. 10, indicate that, when the initial bulk density was increased, the rate of zinc yield was decreased. The effect of initial bulk density was found to be similar to that of sample height. The reasoning employed in that case can be applied here too.

The trend of the present results is close to Huang [6] and somewhat different from Abramowitz and Rao [1].

Empirical rate equation for zinc yield

The data shown in Figs.3–10, indicate that the rates of zinc yield are influenced by the argon flow rate, sample height, reaction temperature, initial molar ratio of C/ZnS, initial molar ratio of $CaCO_3$/ZnS, size of carbon aggregate, size of $CaCO_3$ aggregate and initial bulk density. If exact values of zinc yield are needed, one has to construct a mathematical model considering the intrinsic reaction rate, diffusing rate in solid matrix and mass transfer rate in artificial gas film outside the solid sample. Then the zinc yield can be predicted based on this model. However, this is a rather tough task and beyond the scope of this study. Before this model is developed, a simple empirical rate equation, shown in Eq. 15, may be helpful for this purpose.

$$\frac{\mathrm{d}N_{\mathrm{Zn}}}{\mathrm{d}t} = k_{\mathrm{o}}\exp(-\mathrm{E/RT})d_{\mathrm{C}}^{n_1}d_{\mathrm{CaCO_3}}^{n_2}h^{n_3} Q^{n_4}\rho_{\mathrm{o}}^{n_5}N_{\mathrm{ZnS}}^{n_6}N_{\mathrm{CaCO_3}}^{n_7}N_{\mathrm{C}}^{n_8}N_{\mathrm{CaS}}^{n_9} \tag{15}$$

where d_C is the size of carbon aggregate (m); d_{CaCO3} is the size of calcium carbonate aggregate (m) ; E is the activation energy (kJ $kmol^{-1}$) ; h is the sample height (m) ; k_o is the frequency factor ($m^{n_1+n_2+n_3+3n_4+3n_5}$ $kmol^{n_6+n_7+n_8+n_9}$ kg^{n_5} s^{1+n_4}) ; N_C, N_{CaCO3}, N_{CaS}, N_{Zn} and N_{ZnS} are the instantaneous number of moles of C, $CaCO_3$, CaS, Zn and ZnS, respectively (kmol) ; Q is the argon flow rate (m^3 s^{-1}) ; R is the universal gas constant (8.314 kJ $kmol^{-1}$ K^{-1}) ; T is the reaction temperature (K) ; t is the reaction time (s), and ρ_o is the initial bulk density (kg m^{-3}).

The relationships between N_C, N_{CaCO_3}, N_{CaS}, N_{Zn} as well as N_{ZnS} and zinc yield Y_{Zn} can be written as

$$N_C = N_C^o - N_{ZnS}^o Y_{Zn} \tag{16}$$

$$N_{CaCO_3} = N_{CaO} = N_{CaCO_3}^o - N_{ZnS}^o Y_{Zn} \tag{17}$$

$$N_{CaS} = N_{ZnS}^o Y_{Zn} \tag{18}$$

$$N_{Zn} = N_{ZnS}^o Y_{Zn} \tag{19}$$

$$N_{ZnS} = N_{ZnS}^o - N_{ZnS}^o Y_{Zn} \tag{20}$$

where N_C^o, $N_{CaCO_3}^o$, and N_{ZnS}^o are the number of moles of C, CaCO$_3$ and ZnS in the solid sample before reaction, respectively.

The expression for the rate of zinc yield r_{Zn} can be obtained by substituting Eqs. 16–20 into Eq. 15

$$\begin{aligned} r_{Zn} = \frac{dY_{Zn}}{dt} &= k_o \exp(-E/RT) d_C^{n_1} d_{CaCO_3}^{n_2} h^{n_3} \\ &Q^{n_4} \rho_o^{n_5} N_{ZnS}^{o\,(n_6+n_7+n_8+n_9-1)} \\ &(1 - Y_{Zn})^{n_6} \left(\frac{N_{CaCO_3}^o}{N_{ZnS}^o} - Y_{Zn}\right)^{n_7} \left(\frac{N_C^o}{N_{ZnS}^o} - Y_{Zn}\right)^{n_8} Y_{Zn}^{n_9} \end{aligned} \tag{21}$$

The data shown in Figs. 3–10 were correlated by Eq. 21 utilizing the nonlinear regression method of DRNLIN subroutine of IMSL [10] and the final expression obtained is

$$\begin{aligned} r_{Zn} = \frac{dY_{Zn}}{dt} &= 2.320 \times 10^8 \exp(-274,487/RT) \\ &d_C^{-0.219} d_{CaCO_3}^{-0.025} h^{-0.813} Q^{-0.231} \rho_o^{-0.999} N_{ZnS}^{o\;0.511} \\ &(1 - Y_{Zn})^{0.291} \left(\frac{N_{CaCO_3}^o}{N_{ZnS}^o} - Y_{Zn}\right)^{0.686} \\ &\left(\frac{N_{C^o}}{N_{ZnS}^o} - Y_{Zn}\right)^{0.599} Y_{Zn}^{-0.065} \end{aligned} \tag{22}$$

No rate expression has been found in literature report, hence, it is not possible to compare Eq. 22 with others. However, comparisons of the values of parameters of Eq. 22 with those of Huang [6], who employed CaO as the scavenging agent, are interesting. The parameter values of these two cases are listed in Table 2. The effect of the size of calcium oxide has not been examined in previous studies [6]. Therefore, the value of the related parameter can not be depicted. It can be observed that the activation energy of the system of ZnS/C/CaCO$_3$ is close to that of ZnS/C/CaO. This finding indicates indirectly that reactions of these two systems follow the same reaction equation, Eq. 4, most of the time. Table 2 also shows that the signs of n_4 of both systems are different while those of n_1 to n_3 and n_5 to n_6 are the same, which means that the effects of argon flow rate of these two system are opposite and those of other variables are the same. The sensitivities of the effects of operating variables can be known by comparing the absolute values of these parameters. It can be found that the sensitivities of the effects of sample height, initial molar ratio of CaCO$_3$/ZnS and size of carbon aggregate of these two cases are close to each other; whereas those of initial molar ratio of C/ZnS, initial bulk density and zinc yield are quite different.

Table 2 Parameter values of rate equations of zinc yield for carbothermic reduction in presence of CaCO$_3$ and that in presence of CaO

	In presence of CaCO$_3$ (this study)	In presence of CaO [6]
Activation energy (kJ mol^{-1})	274.487	298.228
Exponent of d_C, n_1 (–)	–0.219	–0.199
Exponent of d_{CaCO_3}, n_2 (–)	–0.025	–
Exponent of h, n_3 (–)	–0.813	–0.528
Exponent of Q, n_4 (–)	–0.231	0.052
Exponent of ρ_0, n_5 (–)	–0.999	–0.557
Exponent of (1–Y_{Zn}), n_6 (–)	0.291	0.408
Exponent of $\left(\frac{N_{CaCO_3}^0}{N_{ZnS}^0} - Y_{Zn}\right)$, n_7 (–)	0. 686	0.458
Exponent of $\left(\frac{N_C^0}{N_{ZnS}^0} - Y_{Zn}\right)$, n_8 (–)	0.599	0.361
Exponent of Y_{Zn}, n_9 (–)	–0.065	–0.012

The zinc yields, calculated by integrating Eq. 22, are plotted as solid lines in Figs. 3–10. Fair agreements exist between the calculated and the experimental results. This equation is, therefore, believed to be helpful for reactor design for this reaction system.

Conclusions

1. A two-stage mechanism has been established to interpret the carbothermic reduction of zinc sulfide in the presence of calcium carbonate.
2. The rate of carbothermic reduction of zinc sulfide in the presence of calcium carbonate has been found to be close to that in the presence of calcium oxide.

3. The rate of carbothermic reduction can be increased by increasing reaction temperature, initial molar ratio of C/ZnS, or initial molar ratio of $CaCO_3$/ZnS. It can also be increased by decreasing the argon flow rate, sample height, size of carbon aggregate, size of $CaCO_3$ aggregate, or initial bulk density.
4. Based on the experimental data obtained, an empirical rate expression for the zinc yield has been determined.

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