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Kinetics of chlorination and carbochlorination of lead sulfate

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Abstract

The kinetics of chlorination and carbochlorination of $PbSO_4$ with $Cl_2 + N_2$ and $Cl_2 + CO + N_2$ gas mixtures has been studied using thermogravimetric measurements in the range 700–900°C. The chlorination reaction rate of $PbSO_4$ with $Cl_2 + N_2$ increases with rise in the chlorine content in the gas mixture. The reaction order is about 0.66 with respect to chlorine. The chlorination rate of $PbSO_4$ is controlled by a chemical reaction mechanism with an apparent activation energy of about 174 kJ/mol. In the same temperature range, the apparent activation energy of the carbochlorination of lead sulfate by $Cl_2 + CO + N_2$ gas mixture is about 114 kJ/mol. The reaction order is about 0.72 with respect to $Cl_2 + CO$. The maximum reaction rate is obtained by using a carbochlorinating gas mixture having a $Cl_2/(Cl_2 + CO)$ ratio equal to about 0.6. © 1997 Elsevier Science B.V.

Keywords: Kinetics; Chlorination; Carbochlorination; Lead sulfate; Thermogravimetric measurements

1. Introduction

Mineral processing of complex sulfide ores produces either global or selective concentrates. In both cases, lead bearing minerals are present either as major component or a minor one. For example, zinc concentrates contain 0.85 to 2.10% of lead [1]. During the hydrometallurgical processing of these concentrates, the waste solutions' content of lead compounds is not negligible. Lead is precipitated from these solutions as lead sulfate [2] due to its low solubility (0.00425 g/100 cm^3).

For this reason, most of the solid non-ferrous industrial wastes or by-products contain variable amount of lead sulfate [3]. Due to strict environmental regulations concerning waste disposal sites, cheap, efficient, and flexible techniques are investigated to recover valuable metals or to eliminate toxic compounds from these materials [4]. Thermal treatments of industrial wastes or by-products, in controlled atmosphere, for either their decontamination or for valuable elements concentration, or for both, indicate that reduction or decomposition of lead sulfate occurs

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at high temperature during long reaction time [4]. Only, chlorination of lead sulfate can be performed at relatively low temperature.

The present paper deals with the kinetics of chlorination and carbochlorination of $PbSO_4$ by $Cl_2 + N_2$ and $Cl_2 + CO + N_2$ gas mixtures, respectively. This work focuses on determining the effect of flow rate of reactive gas mixture, temperature, time and partial pressure of chlorinating gas mixture on the chlorination rate of lead sulfate. Data analysis is used to propose the eventual reaction mechanism. To our knowledge, the kinetics of $PbSO_4$ chlorination has not been reported.

2. Thermodynamic considerations

The main chlorination and carbochlorination reactions of $PbSO_4$ are given by Eqs. (1)–(8). Fig. 1 summarizes the evolution of the standard free energy changes (ΔG^0) of these reactions as function of temperature 25–1027°C. The data were calculated using the HSC thermochemical data base [5].

It can be seen from Fig. 1 that the chlorination of $PbSO_4$ with Cl_2 in standard conditions is not thermodynamically favorable at temperatures lower than 800°C (Eqs. (1)–(4))

$$PbSO_4 + Cl_2 \rightarrow PbCl_2 + SO_2 + O_2 \quad (1)$$

$$PbSO_4 + Cl_2 \rightarrow PbCl_2 + SO_3 + \tfrac{1}{2}O_2 \quad (2)$$

$$\tfrac{1}{2}PbSO_4 + Cl_2 \rightarrow \tfrac{1}{2}PbCl_2 + \tfrac{1}{2}SCl_2 + O_2 \quad (3)$$

$$\tfrac{2}{3}PbSO_4 + Cl_2 \rightarrow \tfrac{2}{3}PbCl_2 + \tfrac{1}{3}S_2Cl_2 + \tfrac{4}{3}O_2 \quad (4)$$

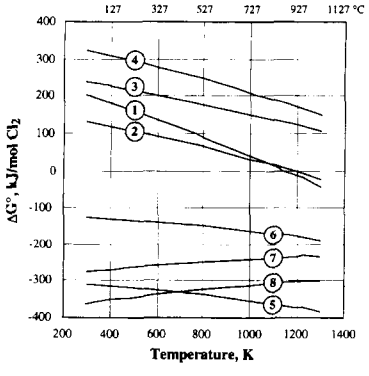

Fig. 1. Evolution of standard free energy changes of $PbSO_4$ chlorination reactions as a function of temperature.

On the other hand, reactions of carbochlorination of $PbSO_4$ (Eqs. (5)–(8)) are thermodynamically feasible:

$$PbSO_4 + Cl_2 + 2CO \rightarrow PbCl_2 + SO_2 + 2CO_2 \quad (5)$$

$$PbSO_4 + Cl_2 + CO \rightarrow PbCl_2 + SO_3 + CO_2 \quad (6)$$

$$\tfrac{1}{2}PbSO_4 + Cl_2 + 2CO \rightarrow \tfrac{1}{2}PbCl_2 + \tfrac{1}{2}SCl_2 + 2CO_2 \quad (7)$$

$$\tfrac{2}{3}PbSO_4 + Cl_2 + \tfrac{8}{3}CO \rightarrow \tfrac{2}{3}PbCl_2 + \tfrac{1}{3}S_2Cl_2 + \tfrac{8}{3}CO_2 \quad (8)$$

Further, according to thermodynamic data and at temperatures higher than 427°C, the carbochlorination of $PbSO_4$ generating $PbCl_2$, SO_2 and CO_2 as products, is the most probable reaction (Eq. (5)).

3. Materials and experimental procedure

The kinetic studies of chlorination and carbochlorination of $PbSO_4$ were carried out using thermogravimetric (TG) experimental set. The thermogravimetric chlorination tests were realized with 100 mg of sample, using the CAHN D100 microbalance schematized in Fig. 2. It has a sensibility of 10 μg. A data acquisition system records, in-line, the sample weight and temperature directly as functions of time. The chlorination gas mixtures were purified from humidity through a $CaCl_2$ column before their introduction in

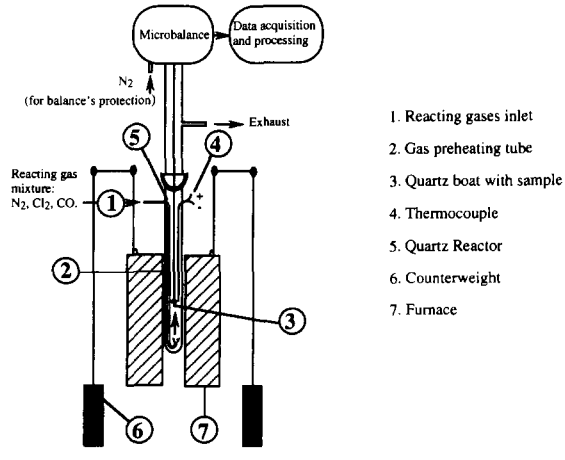

Fig. 2. Thermogravimetric apparatus.

the reactor through inlet 1. They were transported and preheated through the reactor 2 and released upward from the bottom-end through a porous fused silica for uniform gas distribution. For TG tests in non-isothermal conditions, the sample was heated directly in the chlorination gas flow. The furnace heating rate was about 11°C/min. For isothermal TG experiments, the sample was first heated in a nitrogen flow to the desired temperature. Nitrogen was then replaced by the chlorinating gas mixture at the initial chlorination time. The unreacted chlorine present in the exhaust gases is eliminated by NaOH solution before their release to the atmosphere.

The sample used in this study was a $PbSO_4$ powder supplied by PROLABO (Paris, France) having a purity higher than 99.9%. The particle size was determined using Mastersize X laser analyzer of Malvern instruments (Malvern, Worcestershire, UK). The average particle size (d_{50}) was about 8 μm. The specific surface area was measured by analyzer Beta 4210 of Beta Scientific Corporation (Albertson, New York, USA). It was equal to 0.60 ± 0.02 m^2/g. This sample is probably composed of non-porous particles.

4. Results and discussion

4.1. Non-isothermal thermogravimetric analysis (TGA) of $PbSO_4$ under different atmospheres

The TGA of $PbSO_4$ was carried out under different atmospheres, viz., N_2, $Cl_2 + N_2$ and $Cl_2 + CO + N_2$ to determine the behavior of the sample toward these gases. The total gas-flow rate was maintained at 30 l/h. Fig. 3 gives the obtained percent weight loss (% W.L.) curves as a function of temperature for different gas mixtures.

In presence of nitrogen, the decomposition of $PbSO_4$ starts at temperatures higher than 950°C. On the other hand, the chlorination of lead sulfate begin at about 600 and 650°C using $Cl_2 + CO + N_2$ and $Cl_2 + N_2$ gas mixtures, respectively. The reactivity of $PbSO_4$ with respect to the carbochlorinating gas mixture was higher than that obtained by the chlorinating one. This agrees with the thermodynamic calculations. Examination of the non-isothermal data indicates that chlorination of $PbSO_4$ occurs in the range 600–900°C. Hence, kinetic studies under isothermal conditions were carried out in this temperature range.

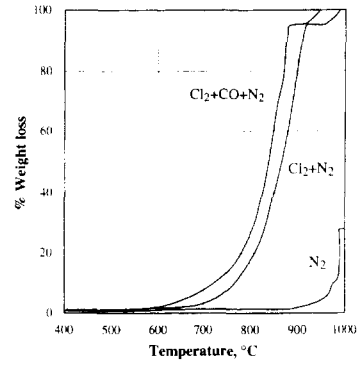

Fig. 3. TGA of $PbSO_4$ in N_2, $Cl_2 + N_2$ and $Cl_2 + CO + N_2$ gas atmospheres.

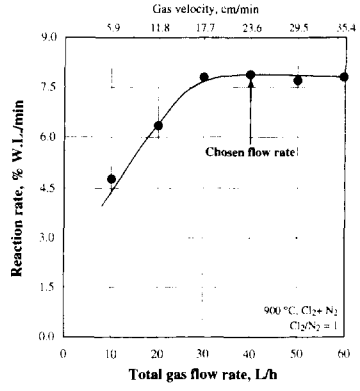

Fig. 4. Effect of the gas-flow rate on the chlorination rate of $PbSO_4$ with $Cl_2 + N_2$.

4.2. Kinetics of chlorination of $PbSO_4$ by $Cl_2 + N_2$

4.2.1. Effect of gas-flow rate

The influence of gas-flow rate on the $PbSO_4$ chlorination rate was studied at 900°C, with an equimolar gas mixture of $Cl_2 + N_2$. Fig. 4 shows the evolution of the chlorination rate as a function of the gas-flow rate of the chlorinating gas mixture. Clearly, the chlorination rate is almost independent of the gas-flow rate for gas velocities higher than 23.6 cm/min or 40 l/h. In such case, the effect of mass transfer at 900°C is minimized [6]. The determination of the different kinetic parameters was carried out using this gas velocity.

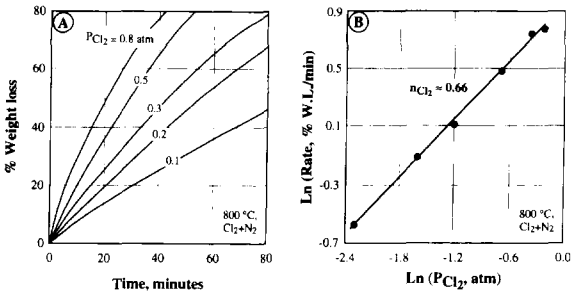

Fig. 5. Effect of chlorine partial pressure on the chlorination rate of $PbSO_4$ with $Cl_2 + N_2$.

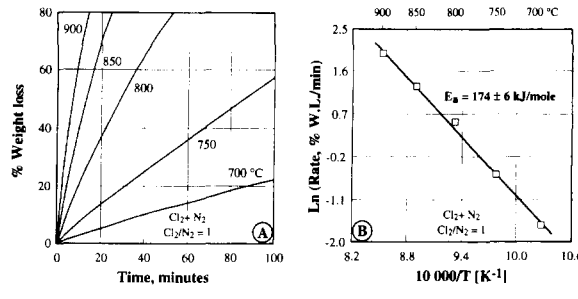

Fig. 6. Effect of temperature and Arrhenius plot for chlorination of $PbSO_4$ by $Cl_2 + N_2$.

4.2.2. Effect of partial pressure of chlorine

This effect was determined at 800°C using a $Cl_2 + N_2$ gas mixture having a chlorine partial pressures of 0.1 to 0.8 atm. Fig. 5(A) summarizes the evolution of the percent weight loss of the sample as a function of time for different chlorine partial pressures. Fig. 5(B) shows the influence of the partial pressure of chlorine on the reaction rate. The apparent reaction order deduced from this curve is about 0.66. This value is a non-integer, thus, it seems that the mechanism of chlorination of $PbSO_4$ in $Cl_2 + N_2$ gas mixture is complex [7]. The dissociation of chlorine to monoatomic could be one of the possible intermediate steps.

Thermodynamic study indicates that the reactions of $PbSO_4$ chlorination were more favorable with Cl than with Cl_2 (Eqs. (9) and (10)). However, Reaction 11 shows that the dissociation of Cl_2 is thermodynamically unfavorable in the explored temperature range. Besides, photo dissociation of chlorine could be favored by artificial or natural light.

$$PbSO_4 + Cl_2 \rightarrow PbCl_2 + SO_3 + \tfrac{1}{2}O_2, \quad \Delta G^0_{600°C} = 54.6\,\text{kJ}, \quad \Delta G^0_{900°C} = 79\,\text{kJ} \tag{9}$$

$$PbSO_4 + 2Cl \rightarrow PbCl_2 + SO_3 + \tfrac{1}{2}O_2, \quad \Delta G^0_{600°C} = -90.8, \quad \Delta G^0_{900°C} = -102.1 \tag{10}$$

$$Cl_2 \rightarrow 2Cl, \quad \Delta G^0_{600°C} = 145.4, \quad \Delta G^0_{900°C} = 100.0 \tag{11}$$

4.2.3. Effect of temperature

The effect of temperature on the chlorination of $PbSO_4$ was studied between 700 and 900°C. An equimolar gas mixture having a total flow rate of 40 l/h (or 23.6 cm/min) was used. Fig. 6(A) groups the evolution of the percent weight loss of samples versus time obtained at different temperatures. As expected, the rate of reaction increases as the temperature augments. The apparent activation energy (E_a) of the $PbSO_4$ chlorination is about 174 kJ/mol as shown by Fig. 6(B). Such a value suggests that the chlorination rate is probably controlled by that of the chemical reaction.

To check this hypothesis, the mathematical formulation of experimental data was tried using the following equations deduced from J. Szekely et al. [6]:

$$kt = 1 - (1 - X)^{1/F_p} \tag{12}$$

$$kt = X \quad (\text{for } F_p = 1) \tag{13}$$

$$kt = 1 - (1 - X)^{1/2} \quad (\text{for } F_p = 2) \tag{14}$$

$$kt = 1 - (1 - X)^{1/3} \quad (\text{for } F_p = 3) \tag{15}$$

where k is the constant, t the reaction time, X the extent of reaction (ratio of weight of the reacted fraction to initial weight), and F_p the particle shape factor (1 for infinite slabs, 2 for cylinders and 3 for spheres).

These equations describe a process controlled by the chemical reaction in case of the shrinking nonporous particles (with or without a solid porous product) and porous particles with unchanged overall particle size having a particle shape factor of 1 to 3. They are also applied for pore diffusion control in the case of complete gasification of porous solids. The used lead sulfate sample can be considered as nonporous solid as mentioned in Section 3.

The best fitting of the experimental data was obtained by Eq. (14) in the explored temperature range. Results are shown in Fig. 7 where the average

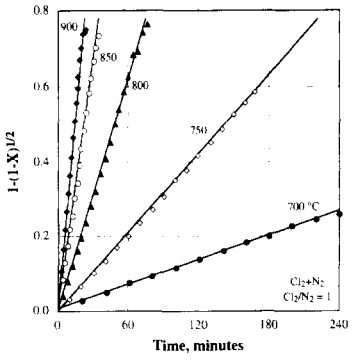

Fig. 7. Mathematical fitting of the chlorination data using Eq. (14).

correlation coefficient is 0.997. This result combined to the high value of the apparent activation energy confirm that the chlorination rate is controlled by the chemical reaction.

4.3. Kinetics of carbochlorination of $PbSO_4$ by $Cl_2 + CO + N_2$

4.3.1. Effect of gas-flow rate

The influence of total gas-flow rate on the carbochlorination of $PbSO_4$ was studied at 900°C using an equimolar $Cl_2 + CO + N_2$ gas mixture. Fig. 8 shows the evolution of the reaction rate as a function of the gas-flow rate. The reaction rate is almost independent of the gas-flow rate for gas velocity equal to 35.4 cm/min (60 l/h). This gas-flow rate was used for determining the kinetics parameters of carbochlorination of $PbSO_4$.

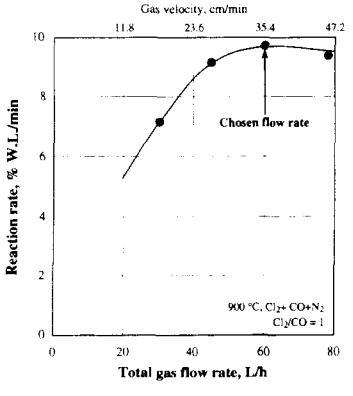

Fig. 8. Effect of gas-flow rate on the carbochlorination rate of $PbSO_4$ with $Cl_2 + CO + N_2$.

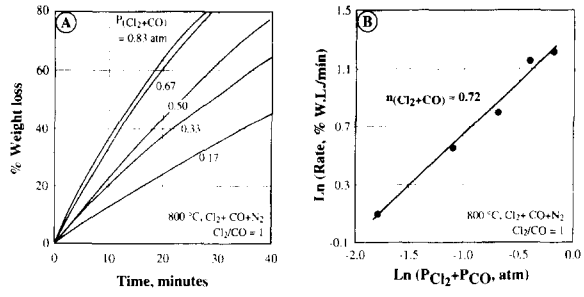

Fig. 9. Effect of Cl_2 + CO partial pressure on the carbochlorination rate of $PbSO_4$.

4.3.2. Effect of partial pressure of $Cl_2 + CO$ gas mixture

The effect of the partial pressure of $Cl_2 + CO$ in the carbochlorinating gas mixture on the reaction rate of $PbSO_4$ was studied at 800°C. The molar ratio Cl_2/CO was kept constant and equal to 1. Fig. 9(A) summarizes the evolution of the percent weight loss as a function of time for $Cl_2 + CO$ partial pressures between 0.17 and 0.83 atm. The reaction rate increases as the partial pressure of $Cl_2 + CO$ augments in the reactive gas mixture. According to Fig. 9(B), the apparent reaction order of $PbSO_4$ carbo-chlorination is equal to 0.72 with respect to $Cl_2 + CO$. This value is also non-integer indicating a complex reaction mechanism involving probably several intermediate steps [7].

4.3.3. Effect of $Cl_2/(Cl_2 + CO)$ ratio

The influence of this ratio (r) on the carbochlorination reaction rate was studied at 800°C. The proportion of $Cl_2 + CO$ in the $Cl_2 + CO + N_2$ gas mixture was kept constant and equal to 66.7% Fig. 10(A) gives the evolution of percent weight loss versus time for a $Cl_2/(Cl_2 + CO)$ ratio of 0.25 to 1. Fig. 10(B) shows that the reaction rate of carbochlorination of $PbSO_4$ passes by a maximum corresponding to a carbochlorinating gas mixture having a $Cl_2/(Cl_2 + CO)$ ratio of about 0.6. On both sides of this value, the reaction rate decreases as a result of either the decrease of chlorine partial pressure or that of carbon monoxide.

4.3.4. Effect of temperature

This effect on the reaction rate was studied between 700 and 900°C using an equimolar $Cl_2 + CO + N_2$ gas mixture. Fig. 11(A) gives the evolution of percent

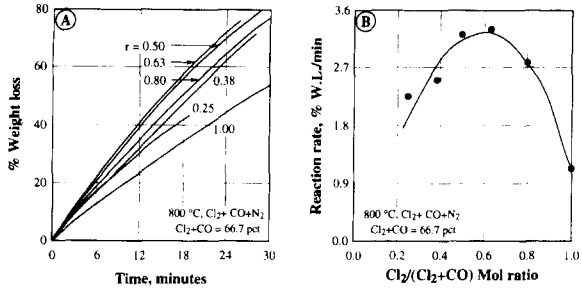

Fig. 10. Effect of $Cl_2/(Cl_2 + CO)$ ratio on the carbochlorination reaction rate of $PbSO_4$.

weight loss as function of time for different reaction temperatures. The reaction rate increases monotonously with the temperature rise.

In the explored temperature range, Fig. 11(B) indicates that the apparent activation energy is about 114 kJ/mol. This value suggests that the process is probably controlled by the chemical reaction rate. As indicated in the case of the chlorination of $PbSO_4$ by $Cl_2 + N_2$, the best mathematical formulation of the reaction's progress is obtained using Eq. (14) as shown in Fig. 12. The average correlation coefficient is about 0.999. This favors the hypothesis that the carbochlorination rate is controlled by the chemical reaction.

The Arrhenius plots of the chlorination and carbochlorination of $PbSO_4$ are shown in Fig. 13. This figure indicates that the carbochlorination reaction rate is systematically higher than that of chlorination. However, at temperatures higher or equal to 900°C, the reaction rate of lead sulfate carbochlorination and that of chlorination of $PbSO_4$ are almost equal.

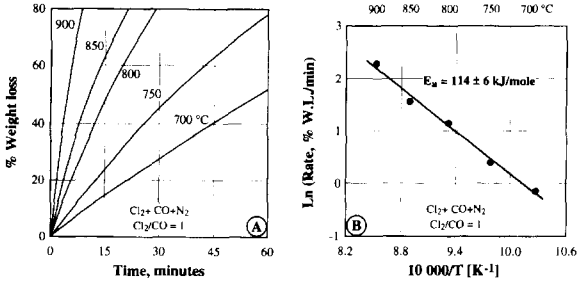

Fig. 11. Effect of temperature and Arrhenius plot of $PbSO_4$ carbochlorination by $Cl_2 + CO + N_2$.

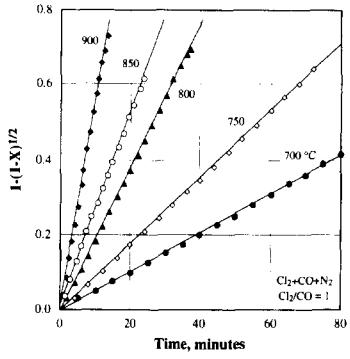

Fig. 12. Mathematical fitting of the carbochlorination data using Eq. (14).

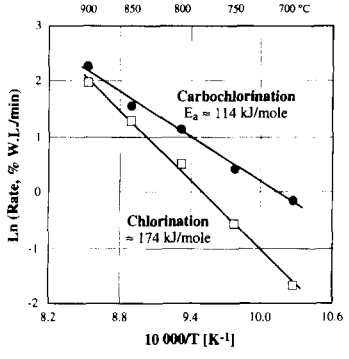

Fig. 13. Comparison of Arrhenius plots of carbochlorination and chlorination of $PbSO_4$.

5. Conclusions

The reactivity of lead sulfate to the carbochlorinating gas mixture is systematically higher than that toward the chlorinating gas mixture for the explored temperature range of 700–900°C.

At 800°C, the apparent reaction order for the chlorination and carbochlorination of lead sulfate is about 0.66 and 0.72 with respect to Cl_2 and $Cl_2 + CO$, respectively. The maximum carbochlorination rate is obtained with a chlorinating gas mixture having a $Cl_2/(Cl_2 + CO)$ molar ratio of about 0.6.

In the range 700–900°C, the apparent activation energy for the chlorination and carbochlorination of $PbSO_4$ are 174 and 114 kJ/mol, respectively. These values suggest that the global rate is controlled by the chemical reaction in two cases. Mathematical fitting is best made with the shrinking cylinder model and

supports the hypothesis that the chemical reaction is the rate controlling step.

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