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## INVESTIGATION OF LEACHING KINETICS OF CERUSSITE IN SODIUM HYDROXIDE SOLUTIONS

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**Abstract:** The leaching kinetics of cerussite in alkaline medium was investigated with respect to experimental variables such as sodium hydroxide concentration, temperature, particle size and stirring speed. The results showed that leaching reagent concentration and reaction temperature exerted significant effects on the extraction of lead, whereas particle size and stirring speed exhibited a relatively moderate effect on the leaching rate. The leaching process followed the kinetic law of the shrinking core model, and the dissolution rates were controlled by the surface chemical reaction with an apparent activation energy value of 43.79 kJ/mol. A corresponding dissolution kinetic equation was also proposed to describe the dissolution reaction. The results indicated that sodium hydroxide could be used as an effective leaching reagent for extracting lead from cerussite.

**Keywords:** *cerussite, sodium hydroxide, leaching, kinetics, activation energy*

### Introduction

Lead, as an important nonferrous metal, has been widely applied in the electric, chemical engineering, construction, atomic power filed, and other industries because of its excellent physical and chemical properties (Nowak and Laajalehto, 2007; Schroder-Wolthoorn et al., 2008; Zhu et al., 2013). Lead is mainly generated from lead-bearing minerals such as galena, cerussite and anglesite (Nikolic et al., 1996; Herrera-Urbina et al., 1998; Mikhlin et al., 2004), as well as from discarded materials containing lead such as lead-acid batteries, funnel glass and smelting slags (Yuan et al., 2012; Agrawal et al., 2004; Atanasova, 2009; Fedje et al., 2010). In the past, pyrometallurgical processes have been frequently used for smelting lead sulfide and secondary waste containing lead to obtain metallic lead (Okada et al., 2007). However, the disposal of lead using the conventional pyrometallurgical technique is associated

with undesirable emissions of harmful sulfur oxides and lead vapor or dust into the atmosphere (Ettler et al., 2005; Aydogan et al., 2007; Pan et al., 2013). Given these environmental concerns with the pyrometallurgical operation, an increasing number of studies on hydrometallurgical processes have been conducted in the recent years.

Leaching is a key step in the hydrometallurgical process, and the selection of an appropriate leaching reagent is beneficial to this process. Various leaching agents are used in hydrometallurgical processes of lead such as acids, sodium hydroxide and chloride solutions (Baba and Adekola, 2011; Lima and Bernardez, 2013; Nagib and Inoue, 2000; Liao and Deng, 2004; Qin et al., 2012). Lead-bearing minerals can be treated using acidic leaching processes. However the dissolved lead is associated with other metals such as Fe, Ca, Mg and SiO<sub>2</sub>, which results in high acid consumption and complex purification processes (Qin et al., 2007; Feng et al., 2007; Liu et al., 2012). Therefore, a practical and selective reagent for such ores is necessary.

Sodium hydroxide is commonly used as an alkaline reagent in lead extraction. Complex ions are formed between lead cations and hydroxide ions in this leaching system. Nagib and Inoue (2000) compared acid leaching to alkaline leaching, and found that alkaline leaching has more advantages when recovering lead from fly ash generated from municipal incineration plants. In alkaline leaching, some impurities, such as Fe, Mg and Al remained in the solid residue, which facilitated the purification process. Zhao and Stanforth (2000) found that over 85% of lead could be extracted using a cost-effective alkaline leaching process through the addition of sodium sulfide, which produced less than 10% of Al impurities. Similarly, Liu et al. (2011) developed an alkaline leaching process for the production of lead concentrates from lean oxidized ores. In this process the lead concentrations were highly selectively and quantitatively produced from the leaching solution by adding sodium sulfide as precipitant. In addition, Badanoiu et al. (2013) obtained good indexes by treating PbO in waste lead-acid battery with sodium hydroxide solutions. Orhan (2005) employed sodium hydroxide as leaching agent to recover lead from electric arc furnace dust, and showed that 90% of lead was dissolved under the following optimum conditions: S/L ratio of 1/7, 95 °C, 10 M NaOH, stirred at 600 rpm for 2 h.

Given that lead resources have been continuously exploited and lead sulfide ores have gradually become depleted, oxidized lead minerals have been developed as important sources of lead metal to meet future demands. Cerussite is the most popular and common mineral among these oxidized lead minerals. Although a number of studies have indicated that alkaline leaching is a favorable method to extract lead from various lead-bearing materials, no information on alkaline leaching of cerussite and its corresponding kinetics studies has been reported so far. Therefore, this study aims to investigate the extraction of lead from pure cerussite using aqueous sodium hydroxide solutions as leaching reagents and the kinetics of this leaching process. The effect of sodium hydroxide concentration, reaction temperature, particle size and stirring speed on the dissolution ratio of cerussite are also evaluated.

## Materials and methods

### Materials and reagents

Samples of cerussite from the Yunnan province of China were obtained after the manual removal of gangue minerals. X-ray fluorescence (XRF) and X-ray diffraction (XRD) analyses of materials showed that the cerussite contained 76.70% Pb, 4.48% C and 18.30% O with only  $\text{PbCO}_3$  crystals. The pure cerussite sample was manually ground in a mortar, and then sieved through standard test sieves to produce the desired particle sizes for the leaching experiments. Analytical-grade sodium hydroxide was used as the leaching reagent. Pure deionized water was used for all experimental works.

### Leaching experiments

The leaching process was performed in a 500 cm<sup>3</sup> three-necked flask batch reactor in a thermostatically controlled water bath, equipped with a digital mechanical stirrer, a thermometer and a condenser to prevent evaporation loss. Typically, 500 cm<sup>3</sup> of freshly prepared sodium hydroxide solutions with various concentrations were added into the reactor and heated until the required temperature was reached. A five g sample of cerussite with the required particle size was added at a certain stirring speed, and then 5 cm<sup>3</sup> of the resulting solutions was accurately withdrawn at specific time intervals and filtered prior to the lead concentration analysis, using an atomic absorption spectrophotometer (AAS).

## Results and discussion

Cerussite can be dissolved in alkaline solution of sodium hydroxide. In this study, high concentration of aqueous sodium hydroxide was used to dissolve cerussite to form a soluble complex. The basic leaching reaction between cerussite and sodium hydroxide may be described as in Eq.(1)



### Effect of sodium hydroxide concentration

Several experiments, each lasting for 30 min, were carried out to investigate the effect of sodium hydroxide concentration on the dissolution of cerussite with an average particle size of 126  $\mu\text{m}$  at 333 K, stirring speed of 500 rpm and solid to liquid ratio of 1/100 g/cm<sup>3</sup>. The results in Fig.1a showed a direct relationship between the lead leaching fraction and sodium hydroxide concentration. The leaching fraction of lead reached the maximum in about 15 min of dissolution when the concentration of sodium hydroxide was 5 mol/dm<sup>3</sup>, while additional leaching time was required to obtain the same leaching fraction of lead at lower sodium hydroxide concentration.

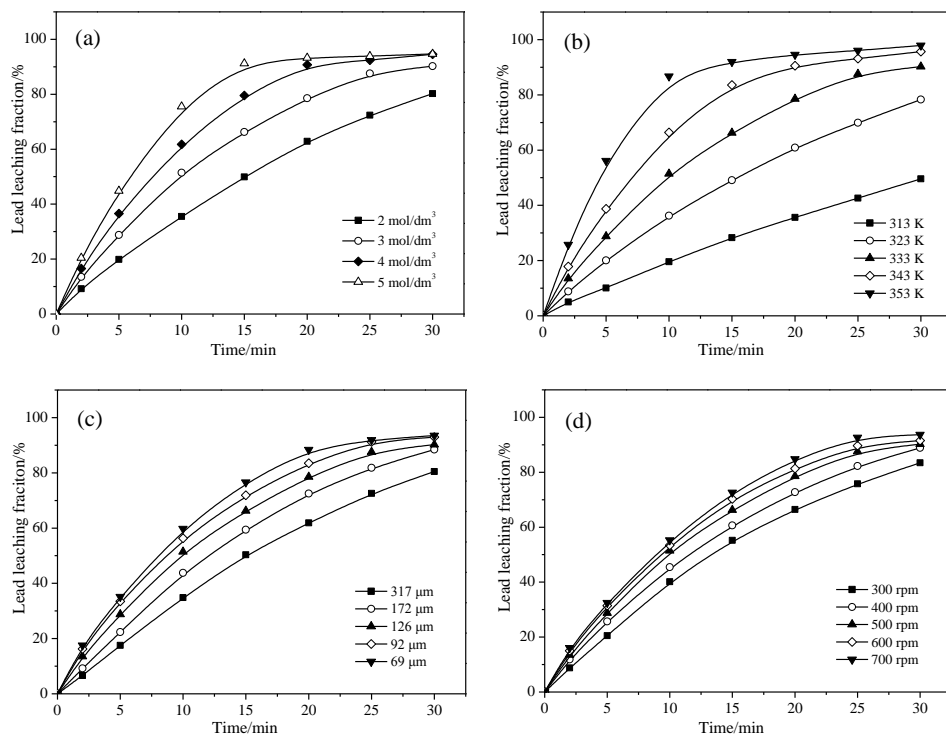


Fig. 1. Effect of operation parameters on the leaching efficiency of lead: (a) sodium hydroxide concentration, (b) temperature, (c) particle size, and (d) stirring speed

### 3.2. Effect of temperature

Figure 1b showed the effect of temperature between 313 K and 353 K on the dissolution of cerussite. Samples with 126  $\mu\text{m}$  average particle size were dissolved in 3  $\text{mol}/\text{dm}^3$  of sodium hydroxide. The solid to liquid ratio was kept constant at 1/100  $\text{g}/\text{cm}^3$  with a stirring speed of 500 rpm. The results showed that the reaction temperature clearly exerted significant effects on lead extraction. The lead leaching fraction increased with elevating temperature because of the active molecular motion. At high temperature (353 K) the leaching fraction of lead reached 86.72% in 10 min of dissolution, whereas less than 20% of lead was extracted within the same dissolution time at 313 K.

### Effect of particle size

Samples with average particle sizes of 317, 172, 126, 92 and 69  $\mu\text{m}$  were used in dissolution experiments at 500 rpm stirring speed, 3  $\text{mol}/\text{dm}^3$  sodium hydroxide, 333 K and 1/100  $\text{g}/\text{cm}^3$  solution. The results are given in Fig. 1c. Within the coarser particle size range of 126  $\mu\text{m}$  to 317  $\mu\text{m}$ , the leaching fraction of lead was affected by particle size, which may be attributed to the increase in cerussite surface area. The exposure of

the sample to the solution increased with the decrease in particle size. In the finer range (69–126  $\mu\text{m}$ ) the difference of lead extraction was not so great that fine grinding would not be required due to the high operation cost. Based on these results, an average particle size of 126  $\mu\text{m}$  was sufficient for the leaching experiments.

### Effect of stirring speed

The effect of stirring speed on the dissolution performance of cerussite samples was evaluated by regulating the stirring speed to 300, 400, 500, 600 and 700 rpm. The average particle size, initial sodium hydroxide concentration, reaction temperature and solid to liquid ratio were kept constant at 126  $\mu\text{m}$ , 3 mol/dm<sup>3</sup>, 333 K and 1/100 g/cm<sup>3</sup>, respectively. The results are given in Fig.1d. Results demonstrated that no significant impact on the leaching fraction of lead using the given stirring speed range. The stirring speed of 500 rpm was sufficient to bring mineral particles into adequate contact with leaching reagents.

### Kinetics study

Leaching rate facilitates practical operation conditions and enhances the productivity of lead extraction. Thus, extracting lead economically is important. However, no information on the leaching kinetics of cerussite in sodium hydroxide solutions has been published yet. A discussion of the leaching kinetics of cerussite in sodium hydroxide solutions is necessary to investigate the reaction course and the dissolution rates.

The dissolution of cerussite in sodium hydroxide is a heterogeneous reaction, and the relevant kinetics follows the shrinking core model which was described by Liddell (2005) in detail. According to this model, the dissolution process is controlled by either diffusion through the solution boundary, diffusion through the solid product layer, or surface chemical reaction (Liu et al., 2010; Ekmekyapar et al., 2012; Habbache et al., 2009). Assuming that the solid has a spherical appearance and the process is controlled by diffusion through the product layer, the integrated equation of the shrinking core model can be described as follows:

$$k_d t = 1 - (2/3)x - (1-x)^{2/3}. \quad (2)$$

When the process is controlled by surface chemical reaction, the integrated equation of the shrinking core model can be given as

$$k_r t = 1 - (1-x)^{1/3}, \quad (3)$$

where  $x$  is the conversion fraction of solid particles,  $k_d$  is the apparent rate constant for diffusion through the product layer,  $k_r$  is the apparent rate constant for surface chemical reaction, and  $t$  is the reaction time.

Table 1. The apparent rate constants  $k_r$  and  $k_d$  for the kinetic model and their corresponding correlation coefficient values  $R^2$ 

Parameter	Surface chemical reaction		Diffusion through the product layer	
	$1-(1-x)^{1/3}$ $k_r$ (min <sup>-1</sup> )	$R^2$	$1-(2/3)x-(1-x)^{2/3}$ $k_d$ (min <sup>-1</sup> )	$R^2$
Particle size (μm)				
317	0.0139	0.9992	0.0036	0.9125
172	0.0173	0.9997	0.0051	0.9350
126	0.0202	0.9988	0.0059	0.9419
92	0.0227	0.9973	0.0070	0.9550
69	0.0257	0.9991	0.0076	0.9406
Stirring speed (rpm)				
300	0.0152	0.9994	0.0041	0.9343
400	0.0175	0.9992	0.0052	0.9420
500	0.0202	0.9988	0.0059	0.9419
600	0.0216	0.9981	0.0065	0.9499
700	0.0234	0.9995	0.0073	0.9436
NaOH concentration (mol/dm <sup>3</sup> )				
2	0.0139	0.9997	0.0036	0.9189
3	0.0202	0.9988	0.0059	0.9419
4	0.0274	0.9999	0.0084	0.9394
5	0.0371	0.9998	0.0116	0.9372
Temperature (K)				
313	0.0068	0.9994	0.0010	0.9075
323	0.0134	0.9994	0.0033	0.9255
333	0.0202	0.9988	0.0059	0.9419
343	0.0303	0.9999	0.0085	0.9309
353	0.0488	0.9998	0.0145	0.9232

Values of  $1-(2/3)x-(1-x)^{2/3}$  and  $1-(1-x)^{1/3}$  versus the reaction time were plotted to investigate effects of experimental variables such as sodium hydroxide concentration, temperature, particle size and stirring speed, on the dissolution kinetic model presented in Eqs. (2) and (3). The kinetics data including apparent rate constants and corresponding correlation coefficient values obtained from these two models were provided in Table 1. Low correlation coefficients were obtained for the diffusion through the product layer model, indicating that this model can not represent the rate-controlling step. Higher regression coefficient values were obtained for the surface chemical reaction model, indicating that the the surface chemical reaction acted as the rate-controlling step in this dissolution system. This hypothesis was supported by the experimental results as shown in Fig. 2, which were plots of  $1-(1-x)^{1/3}$  versus time as a function of sodium hydroxide concentration, temperature, particle size and stirring

speed. In addition, it is known that if the dissolution reaction is controlled by the surface chemical reaction, then the dissolution rate should be sensitive to the reaction temperature. Combining these results as shown in Fig.1b, the dissolution rates were fairly sensitive to temperature, which further demonstrated that the dissolution process was controlled by the surface chemical reaction.

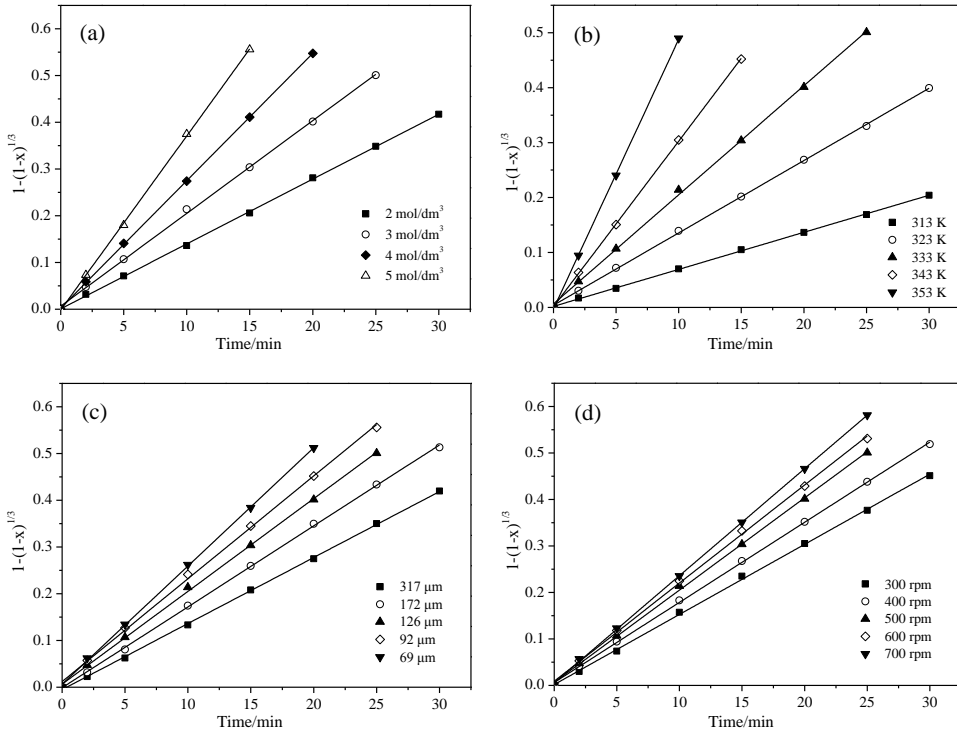


Fig. 2. Plot of  $1-(1-x)^{1/3}$  versus time for different operation parameters: (a) sodium hydroxide concentration, (b) temperature, (c) particle size, and (d) stirring speed

The kinetic equation of lead extraction from cerussite can be expressed as follows:

$$1-(1-x)^{1/3}=k_0 \cdot (C)^\alpha \cdot (PS)^\beta \cdot (SS)^\gamma \cdot \exp(-E_a/RT) \cdot t, \quad (4)$$

where  $C$ ,  $PS$ ,  $SS$ ,  $E_a$ ,  $R$ , and  $T$  represent the sodium hydroxide concentration, particle size, stirring speed, activation energy, universal gas constant and temperature, respectively. The constants  $\alpha$ ,  $\beta$  and  $\gamma$  are the reaction orders for the related parameters, and  $k_0$  is the frequency or pre-exponential factor.

The values of  $\alpha$ ,  $\beta$  and  $\gamma$  were determined to be 1.0583,  $-0.4059$  and 0.5130, respectively, according to Fig. 3a–3c. The activation energy may be calculated using the Arrhenius equation, and the Arrhenius plot of the dissolution process was shown in Fig. 3d. According to the data from Fig. 3d, the activation energy was determined to

be 43.79 kJ/mol. Substituting the value of  $\alpha$ ,  $\beta$  and  $\gamma$  and  $E_a$  into Eq.(4), the value of  $k_0$  was calculated to be about  $1.36 \times 10^4$ . Thus, the equation representing the dissolution kinetics of cerussite in sodium hydroxide solutions can be expressed as follows:

$$1-(1-x)^{1/3} = 1.36 \times 10^4 \cdot (C)^{1.0583} \cdot (PS)^{-0.4059} \cdot (SS)^{0.5130} \cdot \exp(-43.79/RT) \cdot t. \quad (5)$$

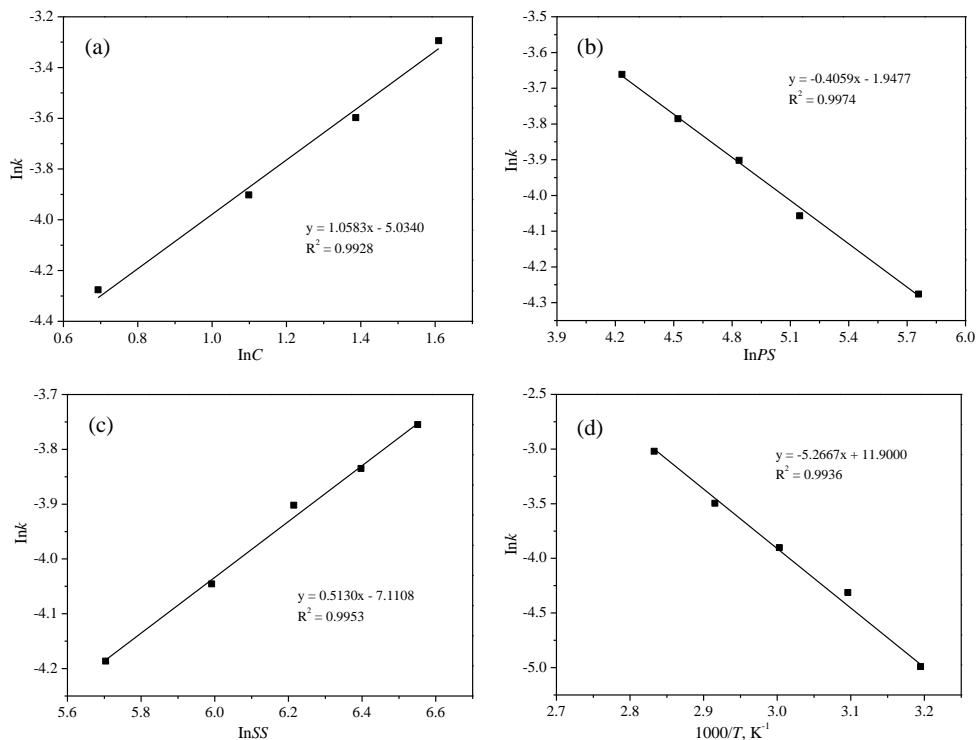


Fig.3. Plot of  $\ln k$  versus operation parameters: (a) sodium hydroxide concentration, (b) particle size, (c) stirring speed, and (d) temperature

## Conclusions

The dissolution rate of cerussite in sodium hydroxide solutions was mainly dependent on leaching reagent concentration and reaction temperature, while particle size and stirring speed had no pronounced effect on the extraction of lead. The dissolution process followed a shrinking core model with the surface chemical reaction as the rate-controlling step. The activation energy of the dissolution reaction was 43.79 kJ/mol. The dissolution kinetics of cerussite in sodium hydroxide solutions can be expressed by the following equation:

$$1-(1-x)^{1/3} = 1.36 \times 10^4 \cdot (C)^{1.0583} \cdot (PS)^{-0.4059} \cdot (SS)^{0.5130} \cdot \exp(-43.79/RT) \cdot t.$$



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