

Effect of temperature on the leaching of copper oxide ore in phosphoric acid solution and kinetics

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10 **Abstract:** In this study, copper extraction from copper oxide ore using phosphoric acid solution as leaching agent was investigated, wherein the effects of the main factor temperature on the leaching of the copper oxide ore was researched, together with the leaching kinetics. It was experimentally demonstrated that the copper leaching rate increased with the increasing reaction temperature. Moreover, the leaching process can be described by the shrinking core model for surface chemical reaction. The activation energy of the leaching process was determined to be 30.65kJ/mol..

15 **Key words:** Copper oxide ore; phosphoric acid; temperature; kinetics

0 Introduction

Copper, one of the most popular and the most valuable metals applied in human life and industry, generally appears in the forms of sulfides and oxides in nature, such as chalcopyrite, bornite, chalcocite, malachite and chrysocolla, etc.^[1,2], wherein the copper sulfide ore has better floatability, which can be separated from the gangue and recovered by flotation. However, for the high-grade copper sulfide resources are increasingly depleted, researches on the separation and extraction of copper from copper oxide ores containing carbonate and silicate earn much attention^[3-6].

25 Among these copper oxide ores, malachite, a significant copper-bearing mineral existing in the oxidized zone of the copper deposits, has been extensively applied to industrial production for copper extraction, with the chemical formula of $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, wherein the theoretical compositions of CuO , CO_2 and H_2O account for 71.95%, 19.90% and 8.15%, respectively.

30 Hydrometallurgy is generally employed for copper extraction from copper oxide ores, wherein copper solution is firstly obtained, and then copper can be gained by solvent extraction and electrowinning^[7]. Copper recovery by leaching has the advantages of low cost, short period, easy manipulation, favorable performance and environmental protection, etc.. Currently, the principal leaching technologies include acid leaching and ammonia leaching, wherein strong acids, such as sulfuric acid, hydrochloric acid and nitric acid, etc. are commonly used for the former^[6-9], while ammonium carbonate^[10,11], ammonium hydroxide^[1,12], and ammonium nitrate^[13], etc. for the latter.

40 So far, no research on the metallurgical extraction of copper from copper oxide ore using phosphoric acid (PA) has been reported. Whether the PA has a favorable leaching effect on the copper oxide ore, it is well worthy to be studied. While PA has the potential to be employed for ore leaching, but unfortunately, it has not yet been applied to the non-ferrous metal extraction area. In this work, the main factor (temperature) and leaching kinetics of copper oxide ore were studied with PA as a leaching reagent, which also provided a reference for its application in leaching of other carbonate ores.

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1 Experimental

1.1 Materials

Experimental samples were obtained from Yunnan Province, China. Ore samples were crushed, ground, and sieved using standard test sieves to obtain the desired particle sizes. XRD experiments were performed using a Japan Science D/max-R diffractometer apparatus with CuK α radiation ($\lambda = 1.5406 \text{ \AA}$) at an operating voltage of 40 kV and a current of 40 mA. The diffraction angles (2θ) ranged from 10° to 90° . Fig. 1 shows the results of X-ray analysis, which indicate that the samples consist of malachite, quartz, and calcite. As could be seen from Fig. 1, the main mineral composition of the raw materials were malachite, quartz and calcite. Chemical analysis of the experimental sample was conducted, as shown in Table 1, which indicated that CuO accounted for 47.32 % and SiO₂ accounted for 11.45 % of the sample, with other gangues containing calcium and magnesium, consistent with the XRD analysis result.

De-ionized water was employed as the leaching solvent in the experiment, which was prepared by Mill-Q50 water-purifying instrument made in the USA, with the resistivity of 18MQ; additionally, the experimental sulfamic acid was analytically pure, produced by JHYT Chemical Reagents Co., Ltd. in Tianjin, China.

Table 1 Chemical analysis result of the experimental sample

Element	CuO	SiO ₂	CaO	MgO
Content (%)	47.32	11.45	1.31	0.10

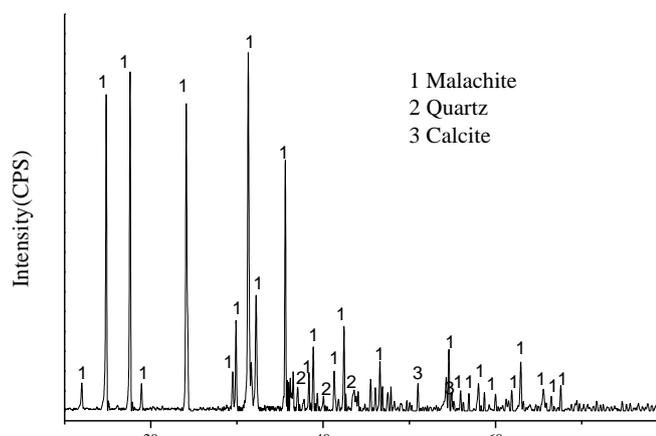


Fig. 1 X-ray diffraction pattern of the experimental sample

1.2 Procedure

Throughout the experiment, the scientificity and accuracy in terms of experimental scheme design, experimental operation and data analysis were paid special attention so as to avoid experimental and analytical errors as much as possible. As a result, a set of compound device for leaching, defined as CDL, was particularly self-designed, wherein 8 reactor units were placed into a thermostatic water bath with each connected by a three-necked flask as shown in Fig. 2, for each flask, a graham condenser and a mechanical stirrer were placed in two necks, respectively, and the third was used for sample filling and pipetting, blocked off with a ground stopper. In the CDL, the eight graham condensers were connected end to end with rubber tubes, and respectively connected to the water inlet and outlet to condensate the steam generated during the experiment. Thus, the

75 whole CDL was composed of one water bath, eight three-necked flasks, eight mechanical stirrers and eight graham condensers, wherein a number of non-stop magnetic stirrers were placed at the bottom of the water bath to get the liquid homogeneous. Moreover, the water bath temperature could be automatically controlled, and the rotational speeds of the mechanical stirrers could be adjusted. By the way, this device was customized from Jiangsu ZBR Instrument Co., Ltd. in China.

80 After the temperature and rotating speed were well adjusted, 5g ore sample and 1000mL de-ionized water were respectively added to each three-neck flasks to carry out the leaching kinetic experiment, wherein the temperature on the PA leaching copper oxide ore was mainly investigated. For each time, 5mL solution was pipetted and filled into a sealed chemical bottle, and subsequently, inductively coupled plasma atomic emission spectroscopy (ICP-AES, ICP-1000
85 II SHIMADZU) was applied to test the copper concentration in the solution at a certain moment, and the leaching rate x was further calculated..

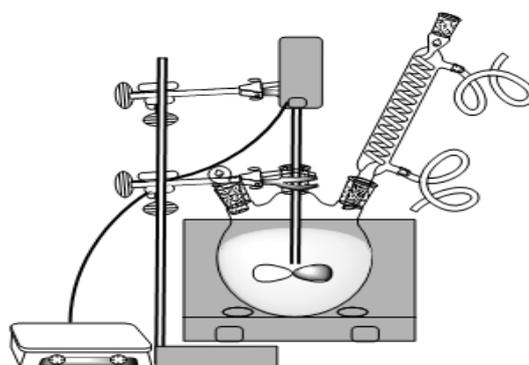


Fig. 2 Structural unit of compound device for leaching

2 Results and discussion

90 2.1 Effect of reaction temperature

A series of tests, each lasting for 60 min, were conducted to determine the effects of temperature on copper extraction. The experiments were carried out at five different temperatures in the range of 20 °C to 60 °C. In these experiments, the phosphoric acid concentration, solid-to-liquid ratio, particle size, and stirring speed were kept constant at 1 mol/L, 5 g solid/1 L solution, 85.5 μm, and 800 rpm, respectively. The results plotted in Fig. 3 show that the leaching rate of malachite increased considerably with increasing reaction temperature. At a reaction temperature of 20 °C, 31.98% of copper was leached, whereas at 60 °C, 86.27% of copper was extracted. Results from the temperature experiments indicate that the reaction temperature has a significant effect on the extraction of copper from malachite.

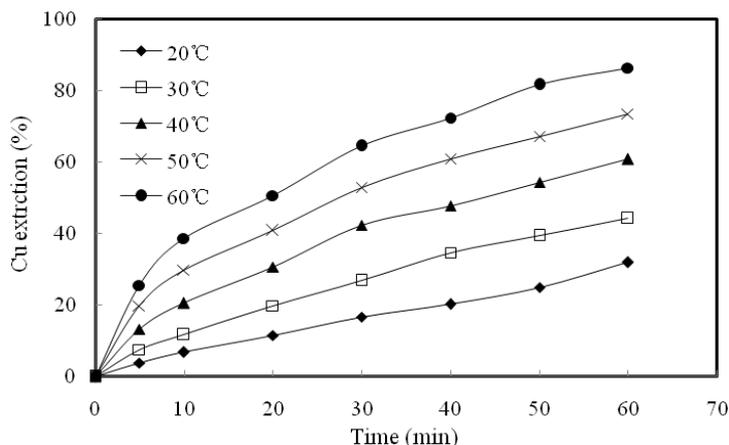


Fig. 3 Effect of temperature on malachite dissolution

2.2 Kinetic analysis

The leaching reaction of mineral particles by a reagent (a solid–fluid reaction) is represented by the following reaction:



where a , b , A , and B represent the stoichiometric coefficient, the fluid reactant, and the solid undergoing dissolution, respectively.

Generally, the liquid-solid reaction of the leaching process can be divided into three forms: the first is one type of shrinking core model, wherein the products are soluble in water, and the solid particle size gradually decreases until completely disappear with the reaction progressing; the second is another shrinking core model, wherein the products are solid and adhere to the unreacted core; and for the last one, the solid reactant disperses in the indissoluble gangues generally with pores and cracks, through which the liquid reactant can diffuse into the ores, thus the leaching reaction will simultaneously take place on both the surface and the interior.

The pore diffusion model can be grouped into regular pore model, homogeneous model, random pore model, particle pore model, etc., with three basic steps included, i.e. liquid phase mass transfer, pore diffusion and chemical reaction on the pore surface of the solid^[14-17].

For leaching process without any solid product layer and with the leaching reagent concentration kept constant during the reaction, the kinetic equation can be generally expressed as^[14,17]:

$$1 - (1-x)^{1/Fp} = [bk' C_{A0} / (a\rho_B r_0)] t \quad (2)$$

Wherein x is the leaching rate; k' is the apparent speed constant; C_{A0} is the initial concentration of leaching reagent A; ρ_B , r_0 and Fp are the molar density, the original radius and the shape factor of the ore particle, respectively; a and b are the reaction coefficients of the leaching reagent A and the ore B, respectively. Then, the speed Eq.(2) is applicable to the leaching process controlled by either diffusion or chemical reaction. When the leaching reagent concentration varies during the leaching process, the leaching kinetic equation of the single-grading can be generally expressed as^[14,17]:

$$[dx]/[dt] = [(3bk' C_{A0}) / (a\rho_B r_0)] (1-x)^{2/3} (1 - a\sigma x/b) \quad (3)$$

Wherein σ is a constant associated with single-grading, average-grading or multiple-grading, and $\sigma = n_{B0} / (C_{A0} V)$.

Therein, the value of n is related to the particle size of the initial solid reactant B_0 .

For leaching reactions with solid products, the rate equation of leaching kinetics can be

classified into the following types.

135 The total leaching rate is controlled by the diffusion of the liquid boundary layer, with the kinetic equation as follows^[14,17]:

$$x = 3bD_L C_{A0} / (a\bar{\rho}_B r_0)] t \tag{4}$$

Wherein D_L is the effective diffusion coefficient of the liquid boundary layer, and $\bar{\rho}$ is the thickness of the liquid boundary layer.

140 If the total rate is determined by the interior diffusion rate of the solid product layer, the kinetic equation is^[14,17]:

$$1 - 2/3x - (1-x)^{2/3} = 2bD_S C_{A0} / (a\rho_B r_0^2)] t \tag{5}$$

Wherein D_S is the effective diffusion coefficient of the solid product layer.

145 If the total rate is determined by the interface chemical reaction rate, the kinetic equation is^[14,17]:

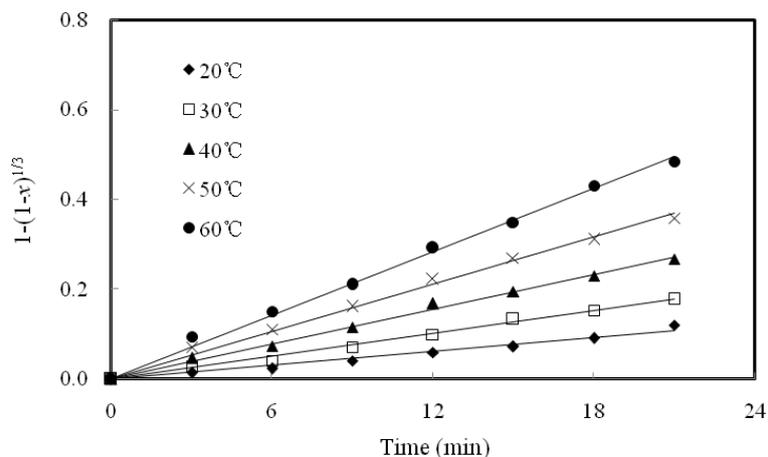
$$1 - (1-x)^{1/3} = bkr C_{A0} / (a\rho_B r_0)] t \tag{6}$$

Wherein kr is the speed constant of the interface chemical reaction.

If the reaction is controlled by a surface chemical reaction, the integrated rate equation of this step is written as follows:

150 To test the validity of the model in Equation (6) firstly, the left side of Equation (6) was plotted versus time, for the temperature. The graph obtained is shown in Fig. 4. The results show that the kinetic model in Equation (6) is an appropriate representation of the leaching process of malachite.

The Arrhenius plot of the leaching process is shown in Fig. 5. Calculations yielded $E = 30.65$ kJ/mol.



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Fig. 4 Plot of $1-(1-x)^{1/3}$ versus time for various temperatures

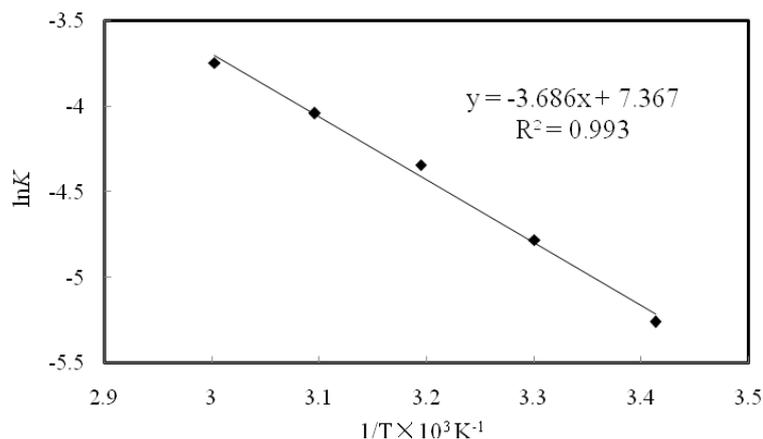


Fig. 5 Arrhenius plot for the leaching of copper oxide ore

3 Conclusions

160 In this study, copper extraction from copper oxide ore using phosphoric acid solution as
 leaching agent was investigated, wherein the effects of the main factor temperature on the leaching
 of the copper oxide ore was researched, together with the leaching kinetics. The optimum leaching
 conditions was determined to be 60 °C temperature. In addition, 60 min was found to be the
 sufficient time to achieve over 80% copper extraction. The leaching kinetics of copper oxide ore
 165 in phosphoric acid solution was found to be controlled by the shrinking core model for surface
 chemical reaction. The apparent activation energy was calculated as 30.65kJ/mol at temperatures
 that ranged from 20 °C to 60 °C.

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