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Dissolution kinetics of malachite in ethylene diamine phosphate solutions

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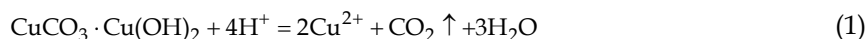
Abstract: Ethylene diamine phosphate (EDP), as a synthetic organic reagent, was used for the first time to leach malachite, and a new method of using organic amine to leach copper oxide ore was developed. The effects of stirring speed, particle size, reagent concentration, and reaction temperature on EDP-dissolution malachite were investigated. Results showed that malachite rapidly dissolved in EDP solution. The malachite-dissolving rate also increased with increased reagent concentration, increased reaction temperature, and decreased particle size. Stirring speed exhibited nearly no effect on EDP-induced malachite dissolution. The leaching kinetics was found to follow the shrinking-core model, and dissolution was controlled by surface chemical reaction with an activation energy of 52.63 kJ·mol⁻¹. A semiempirical rate equation was obtained to describe the dissolution process expressed as $1-(1-X_{Cu})^{1/3}=0.0149(C_{EDP})^{0.7814} \cdot (P_{malachite})^{-0.7982} \cdot \exp(-6.3308/T) \cdot t$.

Keywords: malachite, organic amine, ethylene diamine phosphate, dissolution, kinetic

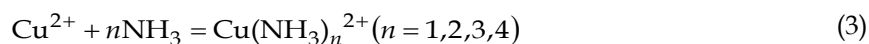
1. Introduction

Because of its excellent physicochemical properties, nonferrous metallic copper is widely used in electronics industries, communication, aviation industries and chemical industries (Habbache et al., 2009; Wang et al., 2010). In the past, the copper was mainly extracted from copper sulfide minerals, such as chalcopyrite (CuFeS₂), chalcocite (Cu₂S), bornite (Cu₅FeS₄), and covellite (CuS). However, with the depletion of sulfide mineral resources the development and utilization of copper oxide minerals, such as malachite (CuCO₃·Cu(OH)₂), azurite (CuCO₃·2Cu(OH)₂), and chrysocolla (Cu_xAl_(2-x)H₂Si₂O₅(OH)₄·nH₂O), have become particularly important. Copper sulfide minerals are hydrophobic, so it can be easily extracted by flotation methods. However, malachite, the most typical copper oxide ore, is a semisoluble salt mineral with a standard solubility product constant of 6.6 × 10⁻⁶ (Ball and Nordstrom, 2001), indicating that a large amount of Cu²⁺ can be dissolved and many hydroxyl ions were adsorbed on the surface of minerals. And more, the adsorption of many polar groups (OH⁻) to the surface of malachite leads to the formation of polar surface, which will decrease mineral surface's hydrophobicity greatly. Thus, it is difficult to float copper oxide minerals directly using xanthates as the collector by flotation methods. Sulfidization - xanthate flotation is often used to recovery copper from copper oxide ore by modifying mineral surface properties to form a hydrophobic surface similar to sulfide minerals (Feng et al, 2017, 2018a and 2018b), but this process is complex and expensive. Therefore, recovery copper from copper oxide ore using leaching method was getting increasing attention. At present, this method deals with copper oxide ore mainly include acids leaching and ammonium/ammonia leaching. Notably, the most widely applied leaching reagents in acid method recovery copper is sulfuric acid and its common chemical reaction equation with

malachite is shown in Eq. (1) (Ata et al., 2001; Bingöl and Canbazoglu, 2004; HSU and MURR, 1975; Lwambiyi et al., 2009; Nicol, 2018). Additionally, Tanaydina and Demirkiranb (2018) investigated the leaching kinetics of copper from malachite ore in aqueous perchloric acid solutions, as a strong oxidant, and obtained good recovery. Its chemical reaction equation could be expressed as Eq. (2).



Although acids like sulfuric acid leach copper from malachite quickly and efficiently, it is noteworthy that these acids also interact with large amounts of gangue material, such as the calcium and magnesium in the ores, which results in an increase in acid consumption. Another more, it was not ignored that strong acids would inevitably corrode equipment and pollute environment. Therefore, alternatives of strong organic acids are used to solve these problems. For example, Deng et al. (2017) investigated the leaching kinetic of malachite by using 5-sulfosalicylic acid. Feng et al. (2015) examined the leaching of copper from malachite with methane-sulfonic acid. Awakura et al. (1991) studied the malachite dissolution in aqueous ethylenediaminetetraacetate solutions. Tanda et al. (2017) investigated the leaching behavior of copper oxide minerals in aqueous alkaline glycine system. In addition to acid methods, another methods widely used for leaching copper oxide ore are ammonia leaching, such as, ammonia, ammonium nitrate, ammonium carbonate, ammonium sulfate, and ammonium chloride. The reason why copper oxide ores can be leached by these inorganics is that Cu^{2+} and ammonia can occur complex reaction as Eq. (3). (Arzutug et al., 2004; Bingöl et al., 2005; Çalban et al., 2005; Ekmekyapar et al., 2012 and 2015; Liu et al., 2010; Wang et al., 2009;). Although ammonia leaching can avoid those problems that acid corrosion equipment and wasted lixiviant, the copper leaching rate is slow.



In recent years, research on using organic amine to leach copper oxide ore is gaining interest. Künkül et al. (2013) investigated the leaching kinetics of malachite by using ammonium acetate. Wu et al. (2013) also studied the dissolution kinetic of malachite with ammonium citrate. Bio-leaching technology has also been applied to the recovery of copper oxide minerals (Jain and Sharma, 2004; Lambert et al., 2015). However, the results have not been satisfactory due to the lack of effective and economical autotrophic bacteria, which has limited the industrialization of this method (Hu et al., 2016). Above of these, how to obtain copper leachate efficiently and quickly with little corrosive effect on the leaching equipment is the key to the leaching process. Therefore, we use synthetic ethylene diamine phosphate (EDP) as a neutral leaching agent to study leaching process and its corresponding kinetic.

In previous studies (Shen et al., 2018), EDP has been the activator used in the sulfidation-xanthate flotation (Feng et al., 2017, 2018a and 2018b) of copper oxide ore, obtaining good flotation recovery. During this process, we found that the addition of EDP made more active Cu sites form on the minerals surface, and enhanced the adsorption of sulfide ion on its surface. Moreover, it could be found that the complexation reaction occurred rapidly between the Cu^{2+} and EDP to form copper ammine complex into the slurry solution. Therefore, we have studied the effect of EDP on leaching copper oxide ore. EDP, as a synthesized reagent, which has these advantages of high stability, low corrosivity and low volatilization. In addition, cathodic copper can be easily extracted from copper ammine complex by solvent extraction and electrowinning (Datta et al., 2016; Ghosh et al., 2018).

In this study, we selected malachite as the research object, to investigate its dissolution behavior in EDP solutions, and the dissolution kinetics with the parameters stirring speed, particle size, reagent concentration, and reaction temperature.

2. Materials and methods

2.1. Materials

The malachite-bearing copper oxide ore was collected from Dongchuan, Yunnan Province, China. It was crushed by a hammer, and then pure malachite ($\text{CuCO}_3 \cdot \text{Cu(OH)}_2$) samples were obtained by hand picking, X-ray diffraction (XRD) analysis showed the presence of pure malachite only (Fig. 1).

X-ray fluorescence (XRF) analysis revealed that the sample contained 54.95% Cu (Table 1), indicating that the sample has high purity with a small quantity of mineral impurities. Subsequently, malachite was pulverized in an agate mortar for several minutes and dry-screened using a Tyler sieve to required sizes.

In this study, ethylene diamine phosphate ($C_2H_{11}N_2PO_4$), a white solid analytical grade powder, as the lixiviant, was produced in the laboratory by the chemical reaction between ethylenediamine (Abbr: en, $C_2H_8N_2$) and phosphoric acid. De-ionized water was used in all experiments to prepare the leaching reagent, which was prepared by Mill-Q50 water-purifying device made in America. Fresh chemical solutions were prepared daily for the leach tests.

Table 1. Composition of malachite analyzed by XRF

Elements	Cu	Fe	Mn	Zn	others
Wt (%)	54.95	0.28	0.21	0.05	44.51

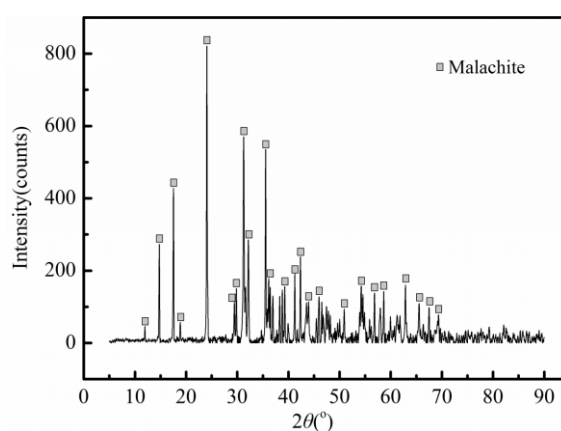


Fig. 1. XRD pattern of a pure malachite sample

2.2. Methods

The malachite leach experiments were conducted in a heat-resistant four-necked flask with a total pulp volume of 600 mL in a thermostatically controlled water bath. For the flask, the mechanical Teflon stirrer was placed in middle neck, a Graham condenser and a thermometer were placed in its any two neck, and the rest one was employed for samples filling and pipetting. 500 mL of leach solution at different concentrations were then added to the four-necked flask. After the temperature of leach solution had stabilized, 0.8 g of pure malachite particles with desired size was added. After every 10 min interval, 2 mL of leach solution sample was withdrawn from the four-necked flask, and 2 mL of fresh EDP solution was added immediately to the leaching system. After the liquid samples were analyzed using inductively coupled plasma atomic emission spectroscopy (ICPS-1000II, Shimadzu, Japan). Then, the dissolved fraction (X_{Cu}) was calculated as follows:

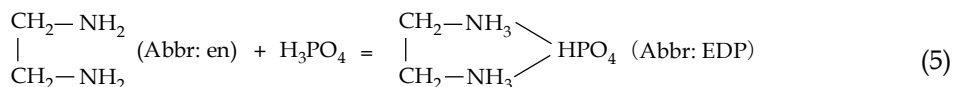
$$X_{Cu} = \text{mass of copper in the solution} / \text{mass of copper in pure malachite}. \quad (4)$$

2.3. Dissolution principle

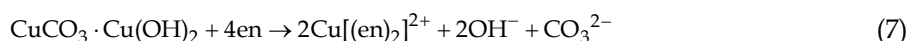
The chemical reaction of ethylenediamine and copper oxide minerals occurred by formation of copper ammine complex. However, ethylenediamine has strong volatility and its emitted gas is highly corrosive, which make it quite difficult that it is served directly as a leaching reagent of copper oxide minerals. Therefore, alternative EDP with high stability was developed and its chemical reaction equation could be expressed as Eq. (5).

Subsequently, it was ionized into ethylenediamine and phosphoric acid after EDP was dissolved in water (as shown in Eq. (6)). The chemical reaction between phosphoric acid and copper oxide minerals is weaker than that of sulfuric acid and copper oxide minerals. And the reaction rate of phosphoric acid with copper oxide is very slow at NPT and it was largely depended on the

concentration of phosphoric acid. Thus, in this study it was not the main chemical reaction and there may exist many other reaction equations in the aqueous solution as well, which need to be further confirmed and deeply researched in future.



Compared to phosphoric acid, ethylenediamine was much easier to react with copper oxide mineral by formation of blue copper ammine complex (Xu, 2000) and its reaction equation could be expressed as Eq. (7).



3. Results and discussion

3.1. Effect of stirring speed

Stirring speed has different effects on different kinetic models. Thus, investigating the effect of stirring speed on the EDP dissolution malachite is important. In this experiment, the EDP concentration, the malachite particle size, and the dissolution temperature were 60 g/L, +150–250 μm , and 40°C, respectively. Stirring speeds of 300, 400, 500, and 600 rpm were used. Fig. 2 shows that the effect of stirring speed on malachite leaching was not obvious at a stirring speed greater than 400 rpm. However, the malachite dissolved fraction was less than that of other stirring speeds at the stirring speed of 300 rpm. This result was because a stirring speed of 300 rpm does not allow the malachite particles to be evenly suspended in the four-necked flask.

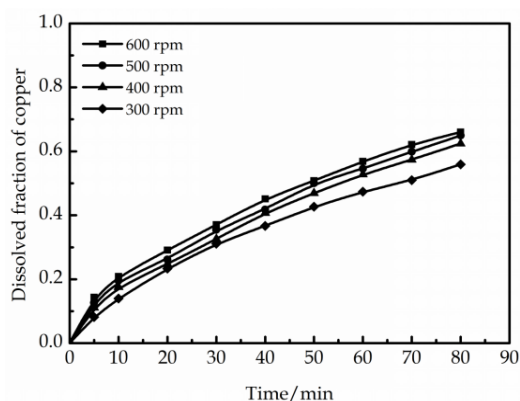


Fig. 2. Effect of stirring speed on malachite leaching

3.2. Effect of particle size.

The copper leaching rates varying with time for malachite with different particle sizes in the EDP solution are seen in Fig. 3, while the stirring speed, the EDP concentration, and the temperature were kept constant at 400 rpm, 60 g/L, and 40°C, respectively. Notably, the leaching rate decreased with increased particle size. Under the same conditions, the dissolved fraction reached 83.62% when +75–96 μm size fraction was used, and that of +250–500 μm size fraction was only 34.18%. The influence of mineral particles size on malachite leaching was mainly attributed to the decreased malachite surface area as the particle size increased. Consequently, the contact area (i.e., the reaction area between the malachite particles and lixiviant) decreased. Therefore, the particle size decrease benefited the dissolution reaction.

3.3. Effect of EDP concentration

Experiments relating to the effect of EDP concentrations on the copper leaching rate were carried out

in the range from 40 to 100 g/L. In these tests, the stirring speed, the malachite particle size, and the temperature were kept constant at 400 rpm, +150–250 μm , and 40°C, respectively. Fig. 4 illustrated the effect of the EDP concentration on the leaching rate and showed that the malachite dissolved fraction increased with increased EDP solution concentration. In addition, when the EDP concentration increased from 40 g/L to 100 g/L, the malachite dissolved fraction increased from 46.95% to 76.21% after 80 min. Therefore, the EDP concentration had an important effect on malachite dissolution.

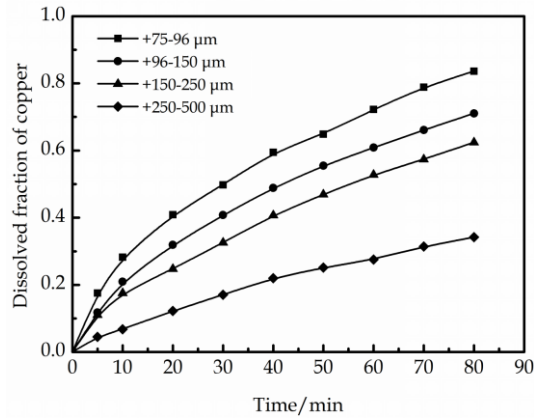


Fig. 3. Effect of particle size on malachite dissolution

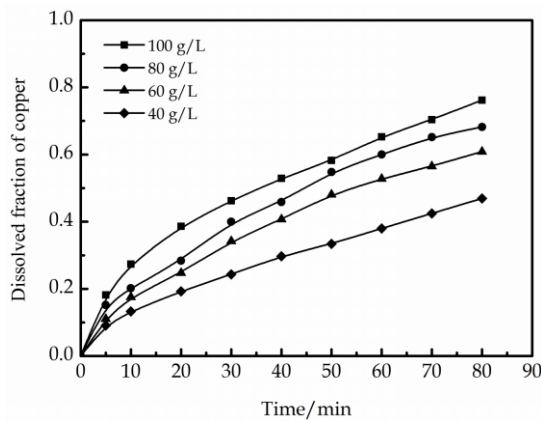


Fig. 4. Effect of EDP concentration on malachite dissolution

3.4. Effect of reaction temperature

The EDP concentration, the malachite particle size, and stirring speed were kept constant at 60 g/L, +150–250 μm , and 400 rpm, respectively. As seen from Fig. 5, the malachite dissolved fraction increased with increased reaction temperature. Malachite was dissolved completely after 70 min at 60°C, and no solid residue was visible in the four-necked flask. This result showed that the shrinking-core model (SCM) was suitable in EDP dissolution malachite. At reaction temperatures of 30°C, 40°C, and 50°C, the malachite dissolved fractions were 36.11%, 62.45%, and 88.41%, respectively. Thus, the reaction temperature had an important effect on malachite dissolution.

3.5. Kinetic analysis

In this study, we found that pure malachite can be completely dissolved at the conditions of 400 rpm stirring speed, 60 g/L EDP concentration, 60°C temperature, and +150–250 μm particle size. Thus, the shrinking-core model (SCM) (Levenspiel, 1999) was suitable in studying the malachite dissolving kinetics in EDP solution. SCM has three possible patterns in determining the rate-controlling step of malachite dissolution in EDP solution as expressed in Eqs. (8), (9), and (10). The step that has the highest fitting to the reaction is then considered to be the rate-controlling step of malachite dissolution.

$$\text{Film diffusion controlled: } k_t = X \tag{8}$$

$$\text{Chemical reaction controlled: } k_r t = 1 - (1 - X)^{1/3} \tag{9}$$

$$\text{Product layer diffusion controlled: } k_d t = 1 - 3(1 - X)^{2/3} + 2(1 - X) \tag{10}$$

where X is the conversion fraction of solid particles, k_t , k_r , and k_d are the apparent rate constants for the different controlling steps, and t is the reaction time.

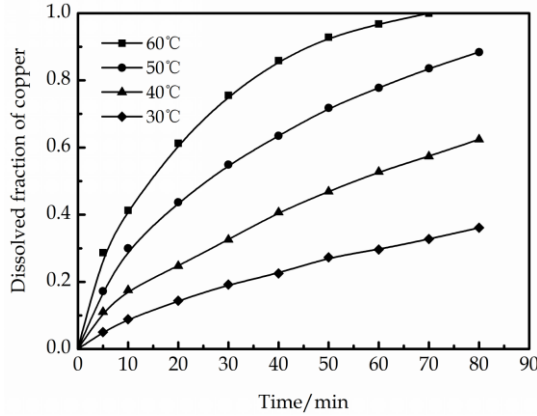


Fig. 5. Effect of reaction temperature on malachite dissolution

To further confirm which pattern was better suitable in EDP dissolution malachite, the SCM with film diffusion, chemical reaction, and product layer diffusion were evaluated. Based on Eqs. (8), (9), and (10), plots of X, $1 - (1 - X)^{1/3}$, and $1 - 3(1 - X)^{2/3} + 2(1 - X)$ versus reaction time t are three straight lines with the slopes of k_t , k_d , and k_r , respectively. The slopes and the kinetic data obtained from these three patterns were evaluated using the correlation coefficient R^2 are shown in Table 2. The statistical data in Table 2 showed that the R^2 values obtained on the basis of the chemical reaction controlling model all exceeded 0.99, and the R^2 values of the other two models were less than 0.99, it could be figured out that the chemical reaction model represented the rate-controlling step of EDP dissolution malachite was better. Moreover, from the experimental results we observed that the effect of stirring speed on EDP dissolution malachite was not obvious as shown in Fig. 2 and the dissolved fraction obtained was very sensitive to reaction temperature as shown in Fig. 5. These two factors are the important characteristic of chemical reaction-controlled model. Subsequently, the activation energy was calculated according to Arrhenius equation and its result as shown in Fig. 6.

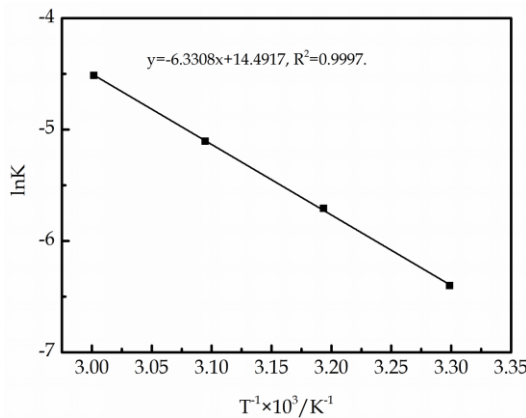


Fig. 6. Arrhenius curve for dissolution reaction of malachite in EDP solution

Plot of $T^{-1} \times 10^3$ versus $\ln k$ is a straight with the slope of $-E/R$ is -6.3308 and the activation energy was calculated as $E = 6.3308 \times 8.314 = 52.63 \text{ kJ mol}^{-1}$. Another important characteristic of chemical reaction-controlled model is the activation energy more than 42.0 kJ mol^{-1} (Yang and Qiu, 2011). Thus, the reaction process of EDP dissolution malachite was controlled by surface chemical reaction.

Fig. 7 was the results of plot of $1 - (1 - X_{Cu})^{1/3}$ versus time for the experimental parameters and its

data are presented in Table 2. The results in Fig. 7 and Table 2 indicated that the EDP dissolution malachite follows the kinetic model resented in Eq. (9).

Table 2. Values of k_l , k_d , k_r , and R^2 of three kinetic models.

Parameters	Film diffusion		Surface chemical reaction		Product layer diffusion	
	X_{Cu}		$1-(1-X_{Cu})^{1/3}$		$1-3(1-X_{Cu})^{2/3}+2(1-X_{Cu})$	
	K_l	R^2	K_r	R^2	K_d	R^2
T /°C						
60	0.0130	0.8615	0.0110	0.9935	0.0131	0.9887
50	0.0102	0.9180	0.0061	0.9901	0.0065	0.9834
40	0.0074	0.9600	0.0033	0.9906	0.0024	0.9719
30	0.0043	0.9619	0.0017	0.9913	0.0007	0.9798
C_{EDP} /g/L						
100	0.0086	0.9330	0.0358	0.9907	0.0040	0.9812
80	0.0081	0.9443	0.0277	0.9908	0.0031	0.9811
60	0.0072	0.9497	0.0227	0.9913	0.0023	0.9836
40	0.0053	0.9505	0.0022	0.9901	0.0011	0.9671
$P_{malachite}$ /μm						
375	0.0095	0.9261	0.0016	0.9912	0.0006	0.9774
200	0.0084	0.9413	0.0033	0.9906	0.0024	0.9841
123	0.0074	0.9512	0.0041	0.9905	0.0033	0.9719
85.5	0.0042	0.9711	0.0053	0.9902	0.0053	0.9737

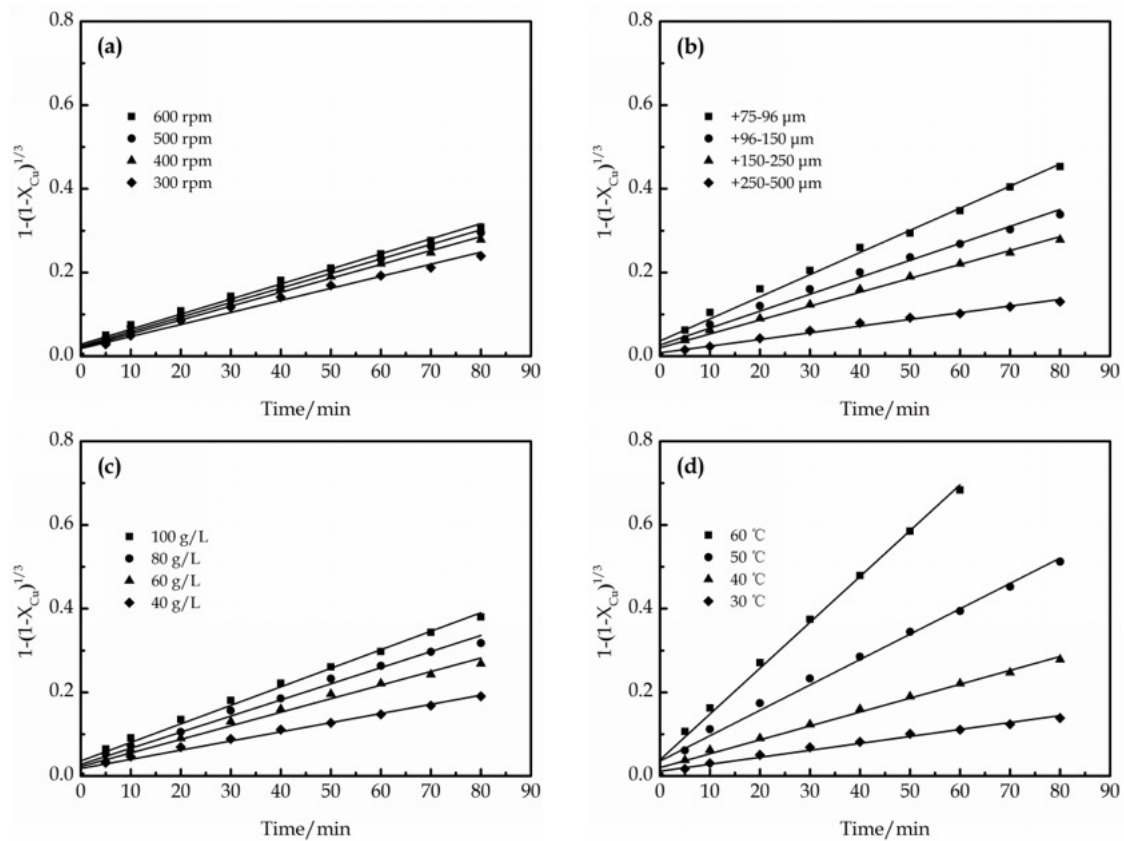


Fig. 7. Plot of $1-(1-X_{Cu})^{1/3}$ versus time for the experimental parameters (a) Stirring speed; (b) Particle size; (c) Reagent concentration; (d) Reaction temperature

Therefore, the semi-empirical kinetic model of EDP dissolution malachite can be expressed as

$$1 - (1 - X_{Cu})^{1/3} = A \cdot (C_{EDP})^\alpha \cdot (P_{malachite})^\beta \cdot \exp(-E/RT) \cdot t \quad (11)$$

where A , C_{EDP} , $P_{malachite}$, E , R , and T represent the frequency or pre-exponential factor, the EDP concentration, malachite particle average size, the activation energy, the universal gas constant, and reaction temperature, respectively. The constants α and β are related parameters.

As shown in Eq. (11), given the C_{EDP} , $P_{malachite}$, and T we can calculate the dissolved fraction X_{Cu} if we know the values of A , α , and β . In this study, monofactor analysis method was applied to investigate the effect of the stirring speed, reagent concentration, the particle size, and temperature on EDP dissolution malachite. Thus, setting C_{EDP} as the independent variable and X_{Cu} as the dependent variable, the other parameter, A , $P_{malachite}$, and T , were regarded as constants. Thus, Eq. (11) can be expressed as

$$d[1 - (1 - X_{Cu})^{1/3}]/dt = k \cdot (C_{EDP})^\alpha \Rightarrow \ln[d[1 - (1 - X_{Cu})^{1/3}]/dt] = \ln k + \alpha \ln C_{EDP} \quad (12)$$

Further derivation, Eq. (12) is expressed as

$$d[1 - (1 - X_{Cu})^{1/3}]/dt = k \cdot (P_{malachite})^\beta \Rightarrow \ln[d[1 - (1 - X_{Cu})^{1/3}]/dt] = \ln k + \beta \ln P_{malachite} \quad (13)$$

where $k = A \cdot (P_{malachite})^\beta \cdot \exp(-E/RT)$ is a constant.

Thus, plot of $\ln[d[1 - (1 - X_{Cu})^{1/3}]/dt]$ versus $\ln C_{EDP}$ is straight with a slope of α and the slope α was calculated as 0.7814 as shown in Fig. 8. Similarly, when set $P_{malachite}$ as the independent variable and X_{Cu} as the dependent variable, the Eq. (11) can be expressed as

$$1 - (1 - X_{Cu})^{1/3} = k \cdot (C_{EDP})^\alpha \cdot t \quad (14)$$

where $k = A \cdot (C_{EDP})^\alpha \cdot \exp(-E/RT)$ is a constant.

And, plot of $\ln[d[1 - (1 - X_{Cu})^{1/3}]/dt]$ versus $\ln P_{malachite}$ is straight with a slope of β and β was calculated as -0.7982 as shown in Fig. 9.

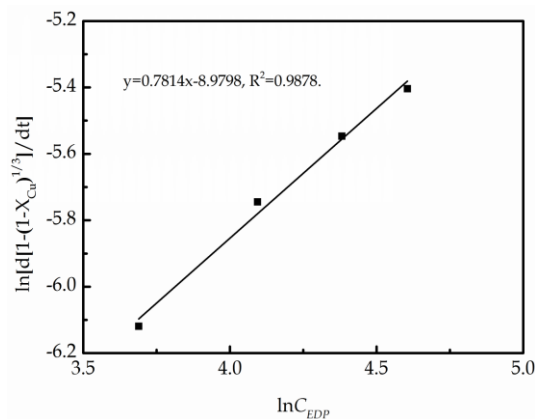


Fig. 8. Plot of $\ln[d[(1 - (1 - X_{Cu})^{1/3})]/dt]$ versus $\ln C_{EDP}$

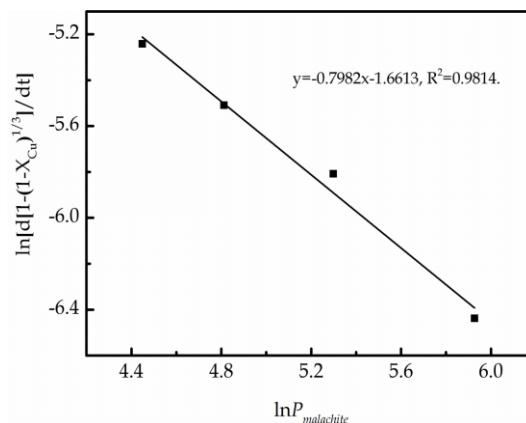


Fig. 9. Plot of $\ln[d[(1 - (1 - X_{Cu})^{1/3})]/dt]$ versus $\ln P_{malachite}$

Finally, using all the data shown in Figs. 3-5, one can estimate a value for A and it was calculated to be approximately 0.0149 min^{-1} .

Thus, the reaction kinetic equation of malachite in EDP solution can be described as:

$$1 - (1 - X_{Cu})^{1/3} = 0.0149(C_{EDP})^{0.7814} \cdot (P_{malachite})^{-0.7982} \cdot \exp(-6.3308/T) \cdot t \quad (15)$$

The experimental results are plotted against the calculated results for verification of this model, as shown in Fig. 10. The correlation coefficient calculated for this regression was 0.96 and it shows that the model is acceptable for this system.

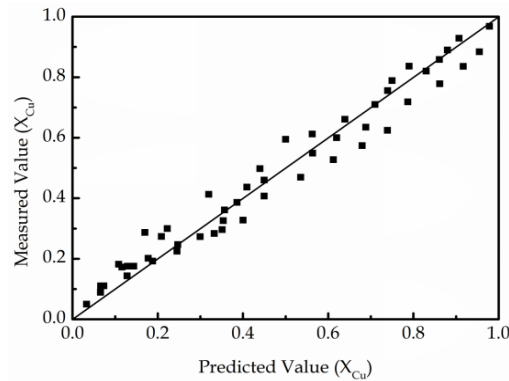


Fig. 10. Predicted value vs measured value of copper dissolved fraction

4. Conclusions

The effects of the stirring speed, the particles size, the EDP concentration, the reaction temperature, and dissolution time on the EDP dissolution pure malachite were investigated. It was found that the copper dissolved fraction was increased with increasing the EDP concentration, increasing the reaction temperature, and decreasing the particles size. The stirring speed showed nearly no effect on EDP dissolution malachite. The reaction kinetics model of EDP dissolution pure malachite was eventually established as $1 - (1 - X_{Cu})^{1/3} = 0.0149(C_{EDP})^{0.7814} \cdot (P_{malachite})^{-0.7982} \cdot \exp(-6.3308/T) \cdot t$, which followed the shrinking-core model and were controlled by the surface chemical reaction with the dissolution reaction activation energy of $52.63 \text{ kJ mol}^{-1}$.

Acknowledgments

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References

- ARZUTUG, M.E., KOCAKERIM, M.M., ÇOPUR, M., 2004. *Leaching of malachite ore in NH₃-saturated water*. Ind. Eng. Chem. Res. 43, 4118-4123.
- ATA, O.N., ÇOLAK, S., EKINCI, Z., ÇOPUR, M., 2001. *Determination of the optimum conditions for leaching of malachite ore in H₂SO₄ Solutions*. Chem. Eng. Technol. 24, 409-413.
- AWAKURA, Y., HIRATO, T., KAGAWA, A., YAMADA, Y., Majima, H., 1991. *Dissolution of malachite in aqueous ethylenediaminetetraacetate solution*. Metall. Trans. B. 22, 569-574.
- BALL, J.W., NORDSTROM, D.K., 2001. *User's manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural waters [R/OL]*. Menlo Park, California: U.S. Geological Survey. https://wwwbrr.cr.usgs.gov/projects/GWC_chemtherm/pubs/wq4fdoc.pdf.
- BİNGÖL, D., CANBAZOĞLU, M., AYDOĞAN, S., 2005. *Dissolution kinetics of malachite in ammonia/ammonium carbonate leaching*. Hydrometallurgy 76, 55-62.
- BİNGÖL, D., CANBAZOĞLU, M., 2004. *Dissolution kinetics of malachite in sulphuric acid*. Hydrometallurgy 72, 59-165.
- ÇALBAN, T., ÇOLAK, S., YEŞİYURT, M., 2005. *Optimization of leaching of copper from oxidized copper ore in*

- $NH_3-(NH_4)_2SO_4$ medium. Chem. Eng. Commun. 92, 1515-1524.
- DATTA, A., DATTA, D., CHANDRA, A., 2016. Separation and recovery of copper from aqueous solutions using tri-n-butyl phosphate in benzene. J. Mol. Liq. 221, 139-148.
- DENG, J.S., WEN, S.M., YIN, Q., WU, D.D., SUN, Q.W., 2017. Leaching of malachite using 5-sulfosalicylic acid. J. Taiwan. Inst. Chem. E. 71, 20-27.
- EKMEKYAPER, A., AKTAŞ, E., KÜNKÜL, A., DEMİRKIRAN, N., 2012. Investigation of Leaching Kinetics of Copper from Malachite Ore in Ammonium Nitrate Solutions. Metall. Trans. B. 43B, 764-772.
- EKMEKYAPAR, A., DEMİRKIRAN, N., KÜNKÜL, A., AKTAŞ, E., 2015. Leaching of malachite ore in ammonium sulfate solutions and production of copper oxide. Braz. J. Chem. Eng. 32, 155-165.
- FENG, Q.C., WEN, S.M., ZHAO, W.J., LV, C., BAI, X., 2015. Leaching of copper from malachite with methane-sulfonic acid. Solvent. In: Solvent Extraction Research and Development, Japan. 22(2). pp. 159-168.
- FENG, Q.C., ZHAO, W.J., WEN, S.M., 2017. Copper sulfide species formed on malachite surfaces in relation to flotation. J. Ind. Eng. Chem. 48, 125-132.
- FENG, Q.C., ZHAO, W.J., WEN, S.M., 2018a. Surface modification of malachite with ethanediamine and its effect on sulfidization flotation. Appl. Surf. Sci. 436, 823-831.
- FENG, Q.C., ZHAO, W.J., WEN, S.M., 2018b. Ammonia modification for enhancing adsorption of sulfide species onto malachite surfaces and implications for flotation. J. Alloy. Compd. 744, 301-309.
- GHOSH, A., DATTA, D., USLU, H., BAMUFLEH, H.S., KUMAR, S., 2018. Separation of copper ion (Cu^{2+}) from aqueous solution using tri n butyl phosphate and di 2 ethylhexyl phosphoric acid as extractants. J. Mol. Liq. 258, 147-154.
- HABBACHE, N., ALANE, N., DJERAD, S., TIFOUTI, L., 2009. Leaching of copper oxide with different acid solutions. Chem. Eng. J. 152, 503-508.
- HSU, P., MURR, L.E., 1975. A simple kinetic model for sulfuric acid leaching of copper from chrysocolla. Metall. Trans. B. 6, 435-440.
- HU, K.J., WU, A.X., WANG, H.J., WANG, S.Y., 2016. A new heterotrophic strain for bioleaching of low grade complex copper ore. Minerals 2016, 6 (1), 12.
- JAIN, N., SHARMA, D., 2004. Biohydrometallurgy for nonsulfidic minerals – A review. Geomicrobiol. J. 21, 135-144.
- KÜNKÜL, A., GÜLEZGIN, A., DEMİRKIRAN, N., 2013. Investigation of the use of ammonium acetate as an alternative lixiviant in the leaching of malachite ore. Chem. Ind. Chem. Eng. Q. 19, 25-34.
- LAMBERT, F., GAYDARDZHIEV, S., LEONARD, G., LEWIS, G., BAREEL, P.F., BASTIN, D., 2015. Copper leaching from waste electric cables by biohydrometallurgy. Miner. Eng. 76, 38-46.
- LEVENSPIEL, O., 1999. Chemical Reaction Engineering. Third ed. John Wiley & Sons, Inc.
- LIU, W., TANG, M.T., TANG, C.B., HE, J., YANG, S.H., YANG, J.G., 2010. Dissolution kinetics of low grade complex copper ore in ammonia-ammonium chloride solution. T. Nonferr. Metal. Soc. 20, 910-917.
- LWAMBIYI, M., MAWEJA, K., KONGOLO, K., LWAMBIYI, N.M., DIYAMBI, M., 2009. Investigation into the heap leaching of copper ore from the Disele deposit. Hydrometallurgy 98, 177-180.
- NICOL, M.J., 2018. The kinetics of the dissolution of malachite in acid solutions. Hydrometallurgy 177, 214-217.
- SHEN, P.L., LIU, D.W., XU, X.H., JIA, X.D., ZHANG, X.L., LIU, D., LIU, R.Z., 2018. Effect of ethylene diamine phosphate on the sulfidization flotation of chrysocolla. Minerals 8, 216.
- TANDA, B.C., EKSTEEN, J.J., ORABY, E.A., 2017. An investigation into the leaching behaviour of copper oxide minerals in aqueous alkaline glycine solutions. Hydrometallurgy 167, 153-162.
- TANAYDIN, M.K., DEMİRKIRAN, N., 2018. Investigation of selective leaching and kinetics of copper from malachite ore in aqueous perchloric acid solutions. Sep. Sci. Technol. Published online.
<https://doi.org/10.1080/01496395.2018.1512619>
- XU, X.J., 2000. The Theory of Oxidized Mineral Flotation Using Organic Chelating Agents as Activators. Yunnan Science & Technology Press, Kunming, China.
- YANG, X.W., QIU, D.F., 2011. Hydrometallurgy. Second Ed. Metallurgical Industry Press, Beijing, China.
- WANG, X., CHEN, Q.Y., HU, H.P., YIN, Z.Y., XIAO, Z.L., 2009. Solubility prediction of malachite in aqueous ammoniacal ammonium chloride solutions at 25 °C. Hydrometallurgy 99, 231-237.
- WANG, Z.K., CHE, J.T., YE, C.L., 2010. Application of ferric chloride both as oxidant and complexant to enhance the dissolution of metallic copper. Hydrometallurgy 105, 69-74.
- WU, D.D., WEN, S.M., YANG, J., DENG, J.S., JIANG, L., 2013. Dissolution kinetics of malachite as an alternative copper source with an organic leach reagent. J. Chem. Eng. Jpn. 46, 677-682.