Process improvement and kinetic study on copper leaching from low-grade cuprite ores

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Abstract: Process improvement and kinetic study on copper leaching from low-grade cuprite ores in sulfuric acid solution are presented in this paper. Effects of major leaching parameters on copper leaching efficiency are determined. The results indicate that copper minerals in the raw ores are mainly cuprites. The reaction rate of this ore increases with an increase in temperature, reaction time, sulfuric acid concentrations and decrease in the particle size of ore. Leaching of about 92.5% of copper is achieved using 0.125-0.074 mm ore particle size at a reaction temperature of 353 K for 180 min reaction time with 150 g/dm^3 sulfuric acid. The solid/liquid ratio was maintained constant at 1:15. Leaching kinetic indicates experimental data complies with shrinking core mode (SCM). It is found in the study that agitation rate is not an influential factor on leaching rate and that the dissolution rate is controlled by surface chemical reaction. The average activation energy of the process is determined to be 45.28 kJ mol^{-1}, and the reaction order of H_2SO_4 is 0.8093.

Keywords: cuprite, dissolution kinetics, sulfuric acid leaching, SCM

1. Introduction

The recovery of metals from nonferrous ores has been widely studied and the process selection depends upon both the composition and the localization of the ore (Akretche et al., 1995; Droppert and Shang, 1995; Fugleberg et al., 1995; Kosyakov et al., 1995). Hydrometallurgical extraction of metals is often used to treat lean and complex ores, especially low-grade ores, waste rocks tailings (Van der merwe and Kasaini, 2011; Ekenes and Caro, 2013; Haghighi et al., 2013) and results in the increase of metal recoveries and the reduction of air pollution. With the gradual depletion of high-grade nonferrous ores, the subsequent shift to low-grade ore bodies has presented a dilemma to the minerals processing industry. In these cases, finer grinds become inevitable to achieve the necessary mineral liberation, which produces particles that are generally below the optimum treatment sizes of current beneficiation practice. The beneficiation of such size particles by conventional processing methods is difficult and inefficient. The main obstacle is attributed to problems posed by their very small mass, large specific area, and the high surface energy (Anastassakis, 2002). Leaching process, which can extract the objective mineral composition under insufficient mineral liberation condition, is therefore the principal operation of the process, and many works are performed to study the composition of run-of-mine ore and dissolution kinetics, to improve extraction yields and economical aspects.

Copper ores can be considered as classical examples which are treated by hydrometallurgical processes. Generally, either copper oxides or roasted sulfides are leached without requiring any further oxidation (Sabba and Akretche, 2006; Marsden and Wilmot, 2007). Sulfuric acid (H_2SO_4) and ammonia ($NH_3 \cdot H_2O$) are usually used as the lixiviant in the leaching copper ores, such as chalcopyrite ($CuFeS_2$), malachite [$Cu_2(CO_3)(OH)_2$]. Sulfuric acid is the most common leaching reagent used for the dissolution of oxidized copper ore because copper oxide ore can be dissolved in H_2SO_4 solution even

at room temperature. Thus, the sulfuric acid consumption dosage is the main economy factor in the leaching process. Depending on the characteristic of the ores, sulfuric acid consumption could range from 0.4 to 0.7 Mg for every Mg of copper recovered (Wu et al., 2013). However, energy consumption can also become an important economy factor when the leaching process runs under the condition of agitation and heating. Study the kinetics of copper leaching is therefore necessary for determining the factors that affect the leaching efficiency.

Related to the kinetics of copper leaching, much work has been performed in laboratory (Grizo et al., 1982; Bingöl and Canbazoğlu, 2004; Habbache et al., 2009; Razavizadeh and Afshar, 2008). Bingöl and Canbazoğlu (2004) concluded that dissolution of malachite during the leaching was described by a logarithmic function, *y=aln(x)+b* and the initial dissolution of malachite was a diffusion controlled reaction. Grizo et al., studied the kinetics of copper leaching from a chalcocite-covellite ore and the rate-determining steps for each period was determined according to both the activation energies and the analytical expressions for each period. Habbache et al. (2009) studied the dissolution kinetics of CuO/Al_2O_3 catalyst in inorganic acid solutions. Razavizadeh and Afshar (2008) showed that the malachite dissolution rate could be modeled in two stages. Stage one was a diffusion-controlled reaction and the dissolution for the stag two was a chemical-controlled reaction. However, few researches were found so far concerning the hydrometallurgy technology for processing low grade cuprite-type copper oxide ore. This kind of ore is usually processed by mill running and then froth floating, but the recovery of copper is lower than 50% using this technology based on our previous researches (Xiong et al., 2012; Feng et al., 2013). For the foregoing reason, further research is still needed for effective exploitation of this kind of ore.

The objective of this study was to develop a H_2SO_4 leaching technology for recovering copper from cuprite-type copper oxide ore. The effects of several parameters, including agitation rate, temperature, sulfuric acid concentration and particle size on copper leaching efficiency were evaluated. Finally, the leaching kinetic was examined according to the heterogeneous reaction models and the best fitted equation to the experimental data was determined.

2. Material and methods

2.1 Material

The test material was a tuff-type copper oxide ore from the Dishui Copper Mine of Xinjiang Province, China. The oxidized copper ore was ground into different particle sizes of 0.200～0.125 mm, 0.125-0.074 mm, 0.074-0.05 mm and below 0.05 mm using XMQ 240×90 ball mill for the leaching experiments. The particle size of sample for X-ray diffraction (XRD) and chemical composition analysis was below 20 μm. The chemical composition of raw ore used is shown in Table 1. The phase composition of copper in raw ore indicates that the occupancies of copper oxide and copper sulfide are 92.25% and 6.27%, respectively. The XRD pattern of raw ore is depicted in Fig.1. The copper oxide minerals were cuprites and malachite, and semi-quantitative results of XRD indicated that the contents of cuprite and malachite in the free copper oxide were 80.54% and 11.71%, respectively. H_2SO_4 (wt = 98%, Tianjin chemical reagent) was used as leaching reagent.

Table 1. Chemical composition of raw ore (wt.%).

TCu	Fe	S	CaO	MgO	Al_2O_3	SiO_2
1.29	2.94	0.08	19.73	3.90	9.34	43.69

2.2 Methods

The leaching experiments were carried out in a 1 dm^3 three-necked flask batch reactor. Temperature was controlled by a constant temperature water-bath heater (H-8 digital thermostat water bath pot) and the temperature error was ±0.5 ℃. Agitation rate was controlled by a digital controlled mechanical stirrer (JJ-1 (A) type precision electric mixer) controller. 200 cm^3 solution containing specific lixiviant was added into the reactor. When the desired agitation rate and reaction temperature were reached, the solid sample was added into the reactor. A 2 cm^3 of sample solution was withdrawn

at specific time intervals for analyzing the concentration of copper. At the same time, 2 cm³ of fresh lixiviant was added into the reactor to keep the volume of the solution constant.
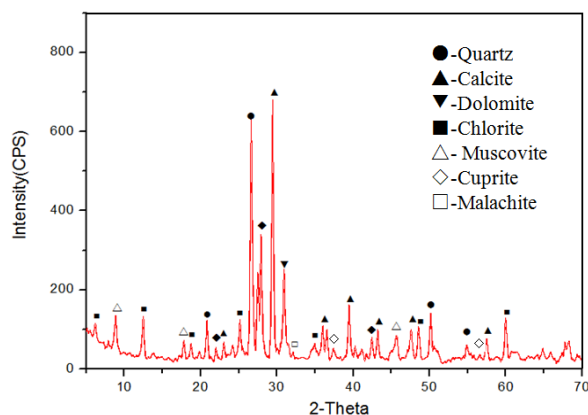

Fig. 1. XRD pattern of raw ore

3. Results and discussion

3.1. Leaching processing of low-grade cuprite ores

3.1.1. Effect of agitation rate

To investigate the effect of agitation rate on the copper leaching efficiency, experiments with five different agitation rates were conducted at leaching time of 60 min and 180 min. During these experiments, the reaction temperature, H_2SO_4 concentration, particle size, and the mass ratio of liquid to solid were kept constant at 353 K, 50 g/dm³, 0.125-0.074 mm, and 4:1, respectively. As shown in Fig. 2 , the copper leaching efficiency increased when agitation rate increasing up to 400 rpm, after which further increasing the agitation rate had little effect on the leaching efficiency. The copper leaching efficiency increases by no more than 15% when the agitation rates increased from 0 to 600 rpm after 180 min leaching. This increase may be attributed to the solid granulates dispersing in the liquid sufficiently. From the principle of hydrometallurgy kinetics (Padilla et al., 2007; Souza et al., 2007), it is well known that the agitation rate has a great effect on the leaching efficiency in a process of leaching reaction (solid-liquid multiphase reaction) if the control step is fluid film diffusion, which can usually improve the leaching efficiency by more than 40 percentage. The fact that the influence of agitation rate on the copper leaching efficiency is not obvious indicates that the diffusion through the fluid film does not act as a rate-controlling step (Levenspiel, 1999). In the following experiments, an agitation rate of 400 rpm was adopted.
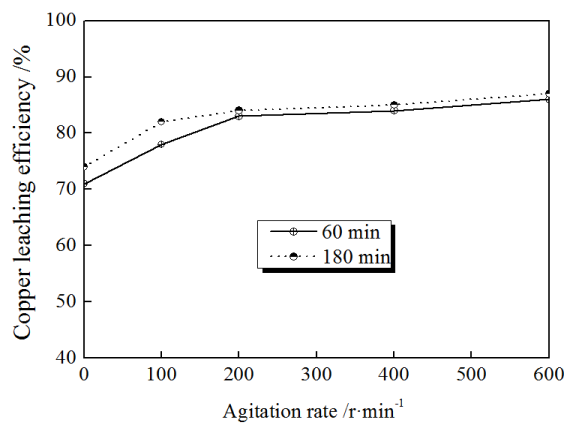

Fig. 2. Effect of agitation rate on copper leaching efficiency

3.1.2. Effect of reaction temperature

H_2SO_4 concentration of 150 g/dm³ and a mass ratio of liquid to solid of 15:1 were used to investigate the effect of reaction temperature on copper leaching efficiency. This amount of H_2SO_4 concentration has greatly exceeded the theoretical amounts. Thus, the concentrations of the leaching reagents could be regarded as constants before and after the reaction occurs. When the sample granularity was 0.125-0.074 mm and agitation rate was 400 rpm, the influence curve of reaction temperature is presented in Fig. 3. It can be seen that the influence of temperature on the leaching efficiency of copper is obvious. The leaching efficiency increases with an increase in temperature, which is especially obvious between 323 and 353 K. Specifically, the copper leaching efficiency increased from 68.3 to 92.5% when the temperature was increased from 303 to 353 K after 180 min leaching.
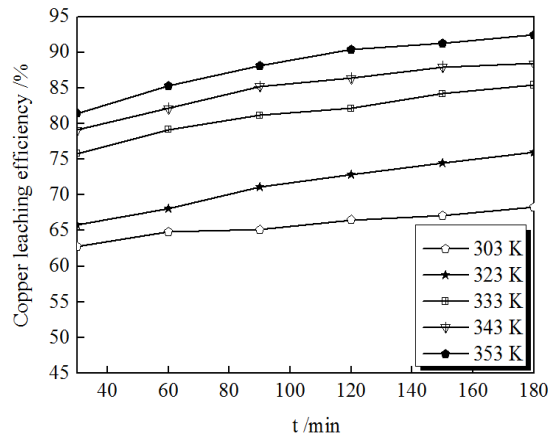

Fig. 3. Effect of temperature on copper leaching efficiency

3.1.3. Effect of particle size

Four different particle sizes were used in the experiments with a H_2SO4 concentration of 150 g/dm³, a reaction temperature of 333K, a mass ratio of liquid to solid of 15:1 and a stirring speed of 400 rpm. The results are given in Fig. 4. Data from Fig. 4 indicates that smaller particle sizes result in higher copper leaching efficiency. In the particle size range of 0.125-0.074 mm, the leaching efficiency of copper after 180 min leaching reached a high level and further increase in particle size, little change in copper leaching efficiency was observed. Thus, the desirable size distribution range for the present sample was in the range of 0.125-0.074 mm.
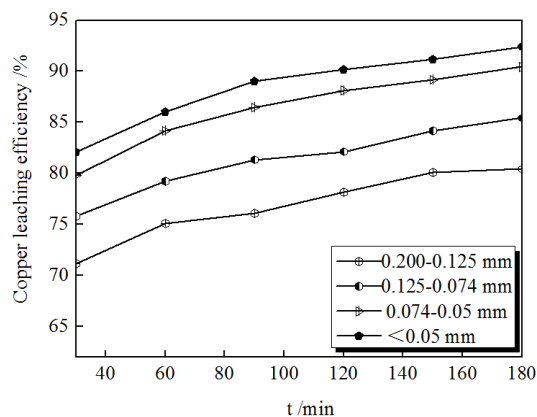

Fig. 4. Effect of particle size on copper leaching process

3.1.4. Effect of H_2SO_4 concentration

Keep the temperature at 333 K, original particle size in the range of 0.125-0.074 mm, agitation rate of 400 rpm and mass ratio of liquid to solid of 15:1, the influence of H_2SO_4 concentrate on copper

leaching efficiency was evaluated. The results are shown in Fig. 5. It is obvious that the concentration of H_2SO_4 had a pronounced effect on copper leaching efficiency. The experiments showed that the leaching efficiency of copper tended to increase with increasing of H_2SO_4 concentration, the copper leaching efficiency obtained after 180 min of reaction could be improved by 10% when the H_2SO_4 concentration increased from 100 to 250 g/dm³.
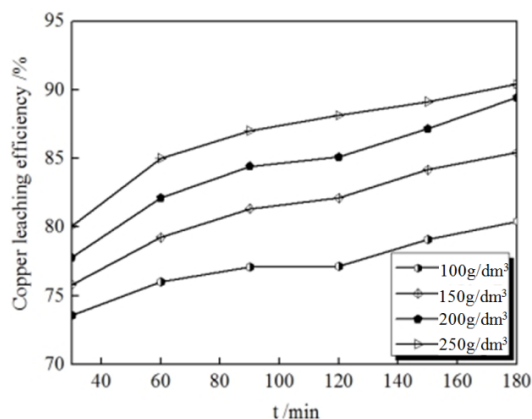

Fig. 5. Effect of H_2SO_4 concentration on copper leaching efficiency

3.2. Kinetic analysis

The rate of a reaction between a solid and a fluid such as the system considered here can be expressed by heterogeneous models. To interpret the results of low-grade cuprite ores dissolution in the sulfuric acid media, the kinetic has been assessed on the basis of the shrinking core model (SCM). SCM is chosen because it approximates real particles more closely than does the other conversion models in a wide variety of situations (Levenspiel, 1999; Habbache et al., 2009). In this model, the reaction between solid and fluid reactants is believed to occur on the outer surface of the solid. The solid reactant is initially surrounded by a fluid film through which mass transfer occurs between the solid and the bulk fluid. As the reaction proceeds, a product layer forms around the unreacted core. With the increase of the conversion, the unreacted core of the particle shrinks and the layer of the product thickens (Habbache et al., 2009; Künkül et al., 2013).

If the reaction rate is controlled by diffusion through a product layer, the integrated rate equation is as follows (Baba and Adekola, 2010):

$$1 - 3(1-x)^{2/3} + 2(1-x) = K_d t . \tag{1}$$

If the reaction is controlled by a surface chemical reaction, the integrated rate equation of this step can be written as follows (Ekinci et al., 1998; Jena et al., 1999):

$$1 - (1-x)^{1/3} = K_r t \tag{2}$$

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 the surface chemical reaction, and t is the reaction time.

3.2.1. Test the validity of SCM

The experiments of agitation rate have indicated that the diffusion through the fluid film does not act as a rate-controlling step. Thus, when the SCM in which the rate limiting step is the chemical reaction (Eq. (2)) was applied to the data shown in Fig. 3, good linear fits were obtained as shown in Fig. 6. The slope of the straight line is the constant of apparent reaction rate K_r. Obviously; the straight lines in Fig. 6 do not go through the origins. This phenomenon attributes to that the reaction rate of initial stage (0-30 min) is too fast to be sampled, and the kinetic model for initial stage is not established. Similar results had been obtained by other researcher (Sun et al., 2009). Fig. 7 shows the ln$k$ vs. 10^3 T^{-1} curves, which are the Arrhenius curves for leaching copper from low grade cuprite ores. The average activation energies were calculated from the slopes $-E_a/RT$. Calculations yielded E$_a$=45.28 kJ mol^{-1}. The

activation energy of processes controlled with diffusion is characterized to be from 4.18 to 12.55 kJ mol^{-1}, while for a chemically controlled process it is usually greater than 41.84 kJ mol^{-1} (Abdel-Aal, 2000). It can be therefore concluded that the chemical reaction is the rate limiting step during the leaching process, which is in agreement with the results of the agitation rate effects.
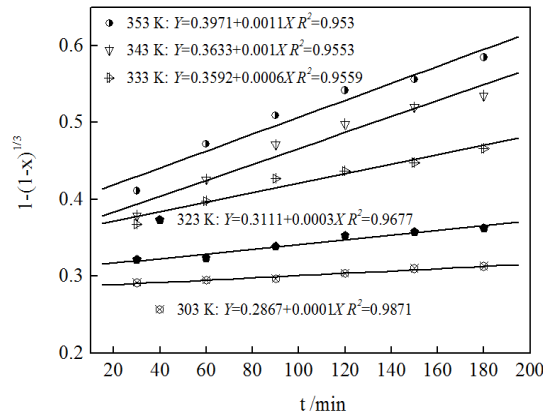

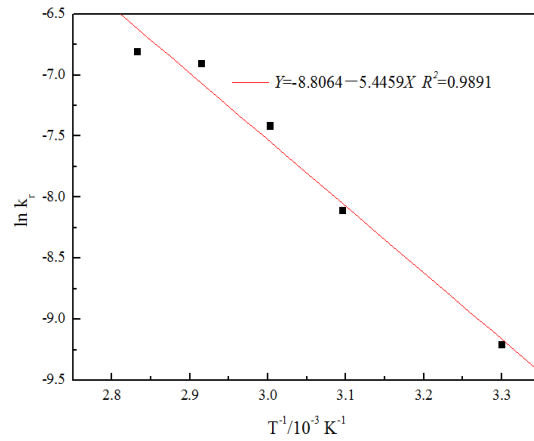Fig. 6. Plots of $1-(1-x)^{1/3}$ vs. leaching time at different temperatures
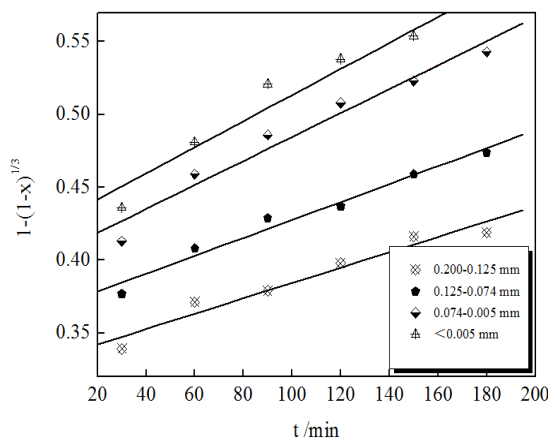

Fig. 7. Plots of ln$k$ vs. $10^3/T$

Fig. 8. Plot of $1-(1-x)^{1/3}$ versus time for various particle sizes

The results for copper leaching shown in Fig. 4 are reploted according to Eq. (2). As Fig. 8 shows, there is also a linear relationship between panicle sizes and $1-(1-x)^{1/3}$. This proves again that the process proceeds in accordance with the model strictly. Moreover, the relationship between the

constant of apparent reaction rate (K_r) and the reciprocal of average particle size of ore d_0^{-1} is shown in Fig. 9. Thus, parameter K_r can be represented as $K_r = 3.13556 \times 10^{-4} + 2.9537\ d_0^{-1}$ for the leaching process. It can be clearly seen that the reaction rate constant is inversely proportiona1 to the initial size.
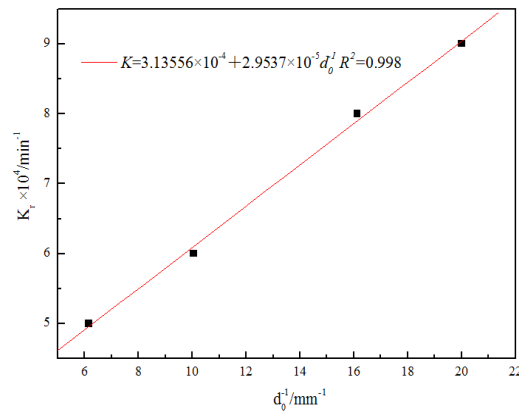

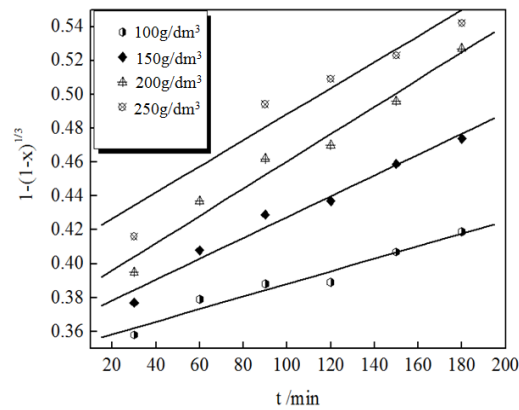Fig. 9. Plot of constant apparent reaction rate (K_r) versus reciprocal of particle size of ore (d_0^{-1})

Fig. 10. Plot of $1-(1-x)^{1/3}$ versus time for various H_2SO_4 concentrations

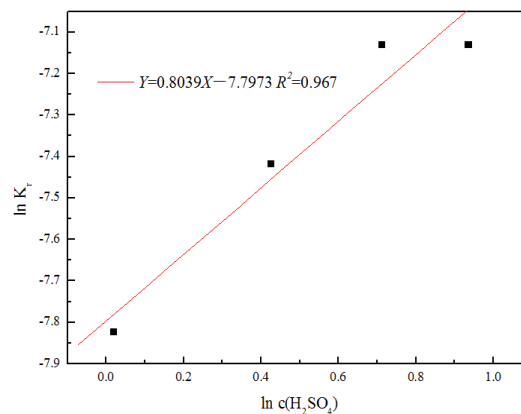Fig. 11. Plot of ln K_r versus ln c(H_2SO_4)

Meanwhile, to test the validity of the model in Eq. (2), $1-(1-x)^{1/3}$ versus time was plotted for the H_2SO_4 concentration according to the data shown in Fig. 5. As shown in Fig. 10, the slope of the straight line is the constant of apparent reaction rate (K_r), the linear relationship between H_2SO_4 concentrations and $1-(1-x)^{1/3}$ indicated that the leaching kinetics can also be explained by the SCM at these H_2SO_4 concentrations. Moreover, the K_r tends to increase with increasing of H_2SO_4 concentration.

Fig. 11 presents the relationship between $\ln K_r$ and $\ln c(H_2SO_4)$. According to the slope of line, the chemical reaction order of H_2SO_4 can be calculated, which is $n(H_2SO_4) = 0.8039$ during the whole stage of 30-180 min.

3.2.2. Macro-kinetic equation of the SCM

The apparent reaction rate equation (K_r) of leaching copper from the complex multi-metal copper oxide ore can be described by the following equation (Mo, 1998; Sun et al., 2009):

$$K_r = k_0 d_0^{-1} c^n (H_2SO_4) \exp[-E_a / RT] \tag{3}$$

where k_0 is the constant. For deducing the constant value of k_0 from Eq. (3), a linear relationship of K_r against the value of $d_0^{-1} \times c^n (H_2SO_4) \times \exp[-E_a/RT]$, designated as 'multiple' can be set up; the slope of the line is k_0. At the core sample granularity of 0.1250-0.074 mm, the reciprocal of average particle size (d_0), values of K_r, the order of reaction n (H_2SO_4) and activation energy (E_a) at different temperature against the 'multiple' have been obtained (shown in Table 2, the values of K_r and 'multiple' are magnified 1000 times).

Table 2. The values of K_r and $d_0^{-1} \times c^n$ (H_2SO_4)$\times \exp[-E_a/RT]$ designated as 'multiple'

Temperature, K	Apparent reaction rate (K_r), min^{-1}	Reciprocal of average particle size (d_0), mm	Order of reaction (n)	Activation energy (E_a), kJ mol^{-1}	Multiple
303	0.1				2.210E-04
323	0.3				6.730E-04
333	0.6	0.0995	0.8093	45.28	1.117E-03
343	1.0				1.799E-03
353	1.1				2.820E-03

Fig. 12 shows the linear relationship of 'K_r' against 'multiple'. As can be seen, the apparent reaction rate equation of this leaching process is as follows:

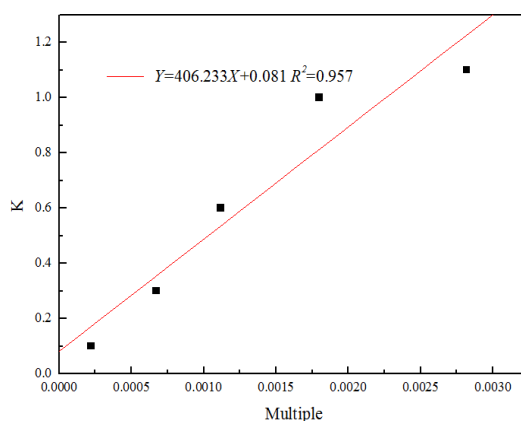$$K_r = 406.233 d_0^{-1} c^{0.8039} (H_2SO_4) \exp[-45.28 / RT] . \tag{4}$$

Fig. 12. The linear relationship of 'K' against 'multiple' (i.e. $d_0^{-1} \times c^n$ (H_2SO_4)$\times \exp[-E_a/RT]$)

Considering Eq. (2), the equation representing the kinetic of present copper ores can be expressed as:

$$1 - (1-x)^{1/3} = 406.233 d_0^{-1} c^{0.8039} (H_2SO_4) t \exp[-45.28 / RT] + A , \tag{5}$$

where A is a constant. Eq. (5) is the leaching models of the stage of 30$\sim$180 min. Thus, the curves corresponding to the equation will not go through the origin of coordinate.

3.3. Discussion

In this paper, process improvement and kinetic study on copper leaching from low-grade cuprite ores by H_2SO_4 was investigated. Finally, Leaching of about 92.5% of copper was achieved under the optimum leaching parameters. This therefore makes it possible for copper industries to leach copper from similar copper oxide ore and improve the utilization efficiency of copper resource. Generally speaking, the reaction rate of upper stage is relatively slow compare with the initial stage reaction rate, studying this stage's kinetic of copper ores will more significant for their utilization efficiency. The schematics of SCM for copper leaching from low-grade cuprite ores in sulfuric acid solution is shown in Fig. 13.

Macro-kinetic equation:

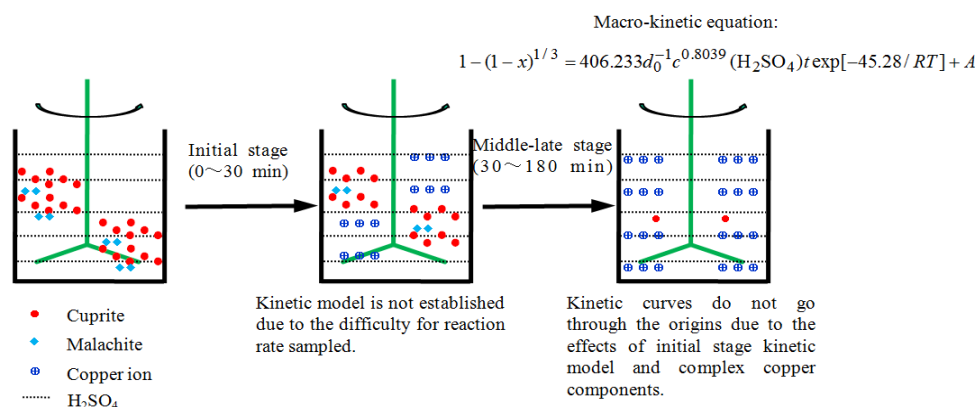$$1-(1-x)^{1/3} = 406.233 d_0^{-1} c^{0.8039} (H_2SO_4) t \exp[-45.28/RT] + A$$

Fig. 13. Schematics of SCM for copper leaching from low-grade cuprite ores in sulfuric acid solution

During testing the validity of SCM, the kinetic curves do not go through the origins. This phenomenon attributes to that the reaction rate of initial stage (0-30 min) is too fast to be sampled, and the kinetic model for initial stage is not established. Similar results had been obtained by Sun et al., and their results indicated that the process of leaching copper can be divided into three stages. Because the reaction rate of the first stage (0-2 min) is very fast and difficult to be sampled, the kinetic model for this stage is not established, and thus the second and third stage's kinetic curves do not go through the origin (Sun et al., 2009). Also, complex copper components will make the kinetic curves do not go through the origin (Yan and Cai, 2000). Thus, experimental data of leaching kinetic in present study is agreed with the results of SCM and can provide some technical supports for the effective exploitation of cuprite-type copper oxide ore.

4. Conclusions

Copper minerals in the raw ores are mainly cuprites. Leaching kinetic indicates that the process of leaching copper from the present sample by H_2SO_4 can be described with shrinking core model (SCM). The apparent average activation energy is 45.28 kJ mol^{-1}, and the reaction order of H_2SO_4 is 0.8093. Chemical reaction at the new particle surface is the rate controlling steps. The macro-kinetic equation for the process of leaching copper from low grade cuprite ores in sulfuric acid solution is as follows：

$$1-(1-x)^{1/3} = 406.233 d_0^{-1} c^{0.8039} (H_2SO_4) t \exp[-45.28/RT] + A . \tag{5}$$

The reaction rate of this copper oxide ore increases with an increase in temperature, reaction time, sulfuric acid concentrations and a decrease in the particle size of ore. The leaching efficiency of copper can be more than 92%, which exhibits better economic value. This therefore makes it possible for copper industries to leach copper from similar copper oxide ores and improve the utilization efficiency of copper resource.

References

ABDEL-AAL, E. A., 2000. *Kinetics of sulfuric acid leaching of low-grade zinc silicate ore*. Hydrometallurgy, 55, 247-254.

AKRETCHE, D.E., KARA SLIMANE, S., KERDJOUDJ, H., 1995. *Selective leaching of a polymetallic complex ore by sulphuric acid and thiourea mixed with sea water*. Hydrometallurgy, 38, 189-204.

BABA, A. A., ADEKOLA, F. A.., 2010. *Hydrometallurgical processing of a nigerian sphalerite in hydrochloric acid: characterization and dissolution kinetics*. Hydrometallurgy, 101, 69-75.

BINGÖL, D., CANBAZOĞLU, M., 2004. *Dissolution kinetics of malachite in sulphuric acid*. Hydrometallurgy, 72, 159-165.

DROPPERT, D.J., SHANG, Y., 1995. *The leaching behaviour of nickeliferous pyrrhotite concentrate in hot nitric acid*. Hydrometallurgy, 39, 169-182.

EKENES, J.M., CARO, C.A., 2013. *Improving leaching recovery of copper from low-grade chalcopyrite ores*. Minerals & Metallurgical Processing, 30, 180-185.

EKINCI, Z., COLAK, S., CAKICI, A., SARAC, H., 1998. *Leaching kinetics of sphalerite with pyrite in chlorine saturated water*. Minerals Engineering. 19, 279-283.

FUGLEBERG, S., HUTHOLM, S.E., ROSENBACK, L., HOLOHAN, T., 1995. *Development of the hartley platinum leaching process*. Hydrometallurgy, 9, 1-10.

ANASTASSAKIS, G.N., 2002. *Separation of Fine Mineral Particles by Selective Magnetic Coating*. Journal of Colloid and Interface Science, 256, 114-120.

GRIZO, A., PACOVIĆ, N., POPOSKA, F., KONESKA, Ž., 1982. *Leaching of a low-grade chalcocite-covellite ore containing iron in sulphuric acid: The influence of pH and particle size on the kinetics of copper leaching*. Hydrometallurgy,
8, 5-16.

HABBACHE, N., ALANE, N., DJERAD, S., TIFOUTI, L., 2009. *Leaching of copper oxide with different acid solutions*. Chemical Engineering Journal., 152, 503-508.

HAGHIGHI, H. K., MORADKHANI, D., SEDAGHAT, B., NAJAFABADI, M. R., BEHNAMFARD, A., 2013. *Production of copper cathode from oxidized copper ores by acidic leaching and two-step precipitation followed by electrowinning*. Hydrometallurgy, 133, 111-117.

JENA, P. K., BARBOSA, O., VASCONCELOS, I. C., 1999. *Studies on the kinetics of slurry chlorination of a sphalerite concentrate by chlorine gas*. Hydrometallurgy, 52, 111-122.

KOSYAKOV, A., HAMALAINEN, M., GROMOV, P., KASIKOV, A., MASLOBOEV, V., NERADOVSKY, YU., 1995. *Autoclave processing of low grade copper-nickel concentrates*. Hydrometallurgy, 39, 223-234.

KÜNKÜL, A., GÜLEZGIN, A., DEMIRKIRAN, N., 2013. *Investigation of the use of ammonium acetate as an alternative lixiviant in the Leaching of malachite ore*. Chemical Industry and Chemical Engineering Quarterly, 19, 25-34.

LEVENSPIEL, O., 1999. *Chemical Reaction Engineering*. Industrial and Engineering Chemistry Research, 38, 4140-4143.

MARSDEN, J. O., WILMOT, J. C., 2007. *Medium-temperature pressure leaching of copper concentrates-Part 1: Chemistry and initial process development*. Minerals & Metallurgical Processing, 24, 193-204.

PADILLA, R., VEGA, D., RUIZ, M.C., 2007. *Pressure leaching of sulfidized chalcopyrite in sulfuricacid-oxygen media*. Hydrometallurgy, 86, 80-88.

RAZAVIZADEH, H., AFSHAR, M.R., 2008. *Leaching of Sarcheshmeh copper oxide ore in sulfuric acid solution*. Minerals & Metallurgical Processing, 25, 85-90.

SABBA, N., AKRETCHE, D.E., 2006. *Selective leaching of a copper ore by an electromembrane process using ammonia solutions*. Minerals Engineering, 19, 123-129.

SOUZA, A.D., PINA, P.S., LIMA, E.V.O., DA SILVA, C.A., LEÃO, V.A., 2007. *Kinetics of sulphuric acid leaching of a zinc silicate calcine*. Hydrometallurgy, 89, 337-345.

SUN, X.L., CHEN, B.Z., YANG, X.Y., LIU, Y.Y., 2009. *Technological conditions and kinetics of leaching copper from complex copper oxide ore*. J. Cent. South Univ. Technol., 16, 936-941.

VAN DER MERWE, R., KASAINI, H., 2011. *Leaching characteristics of copper refractory ore in sulfate media*. Minerals & Metallurgical Processing, 28, 208-214.

WU, D.D., WEN, S.M., DENG,J.S., LIU, J., 2013. *Dissolution kinetics of malachite as an alternative copper source with an organic leach reagent*. Journal of Chemical Engineering of Japan, 46, 677-682.

XIONG, K., WEN, S.M., ZHENG, G.S., BAI, S.J., SHEN, H.Y., 2012. *Flotation research on cuprite-type oxide copper in Xin Jiang*. Advanced Materials Research, 524-527, 987-992.

YAN, W., CAI, W.L., 2000. *Reaction Kinetics of Acidic Leaching of Composite Copper ore*. Engineering Chemistry and Metallurgy, 21, 298-301.