Removal of calcium from magnesite flotation concentrate by selective leaching and kinetics analysis

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Abstract: Dolomite is the main impurity mineral in magnesite ore, affecting the quality of magnesite products. This study proposed a selective leaching process to reduce the calcium content from the magnesite flotation concentrate using hydrochloride acid (HCl). Laboratory scale tests were conducted to explore the influence of operation factors including HCl concentration, leaching temperature and time, stirring speed on the leaching recovery. The results showed that leaching recovery of CaO and MgO increased with increasing HCl concentration, temperature and time. The CaO leaching recovery is always significantly higher than that of MgO, indicating a good selectivity of HCl to leach dolomite from magnesite. The leaching kinetics of both dolomite and magnesite follow the Avrami model and are diffusion controlled, with an activation energy of 43 ± 1 kJ·mol^{-1} and 25 ± 4 kJ·mol^{-1}, respectively.

Keywords: selective leaching, magnesite, dolomite, leaching kinetics

1. Introduction

Magnesite, as an important non-metallic mineral, is the main source for various magnesium products. Due to its high fire resistance, magnesium oxide is the main raw material for producing basic refractory materials that are widely used in metallurgy, construction, chemical industries, and many other areas (Karaoglu et al., 2016; Yao et al., 2016). In recent years, low-grade magnesite ores with silica and calcium attract increasing attention due to the continuous decline of high-quality magnesite ores. The impurities of silica and calcium could remarkably influence the strength of refractory material produced by magnesite, so the removal of impurity minerals from the low-grade magnesite ore is essential to improve the quality of magnesite. However, the technologies currently applied challenge the industry due to the increase in complexity.

Reverse flotation or direct flotation is usually considered as a classical method to remove impurities from magnesite ore. Silicon containing impurities such as quartz and talc are readily removed by reverse flotation using amine type of cationic collectors, such as dodecylamine, ether amine and cationic gemini surfactants (Santana et al., 2001; Yao et al., 2016; Brezáni et al., 2017). Direct flotation with fatty acid type of anionic collectors is usually adopted to remove calcium-containing impurities such as dolomite. Gence et al. (1995) and Zhang et al. (2018) investigated the adsorption mechanism of oleic acid and sodium oleate in magnesite flotation. Furthermore, researchers have conducted some surface chemistry analysis of magnesite and dolomite including wetting behaviour, electrokinetic behaviour, and solution chemistry to understand the flotation mechanism of these two minerals (Chen and Tao, 2004; Gence, 2006; Gence and Ozbay, 2006). However, in industrial application, it is very difficult to achieve efficient separation only via direct flotation due to the similar crystal structure and surface properties between magnesite and dolomite (Oncek and Kaya, 1994), especially for the intergrowth and inclusions of dolomite in magnesite. Therefore, it is necessary to find an effective deep purification method to further reduce the content of calcium impurities in magnesite flotation concentrate, so as to meet the needs of producing high-performance refractories and functional materials.

Acid leaching is considered as an effective technology for extracting or removing carbonate minerals, and has been widely used in calcareous phosphate ore and copper ore (Ashraf et al., 2005; Gharabaghi et al., 2009; Heydarpour et al., 2011; Shabani et al., 2012). As for leaching of magnesite, the optimum conditions and reaction kinetics for dissolution of magnesite with H_2SO_4 were studied (Abali et al., 2006). In recent years, organic acids such as formic acid, acetic acid, gluconic acid, succinic acid and lactic acid were investigated in leaching kinetics of magnesite as well (Lacin et al., 2005; Bakan et al., 2006; Bayrak et al., 2010; Raza et al., 2014; Raza et al., 2015). However, all above leaching methods for magnesite ore focus on the extraction of magnesium (Fouda et al., 1999; Kaya and Erdogan, 2004), without attention on the removal of calcium carbonate gangue minerals.

As dolomite $(CaMg(CO_3)_2)$ and magnesite $(MgCO_3)$ own similar chemical properties and solubility, the selective leaching of Ca seems difficult to realize. Nevertheless, the research in chemical geology provides a different insight. Chou et al. (1989) studied the dissolution of carbonate minerals (calcite, aragonite, witherite, magnesite and dolomite) by HCl, and the results showed that the solubilities for magnesite were similar to other carbonate minerals. However, the dissolution rates were very different. This indicates that the reactivity of the magnesite and dolomite with HCl might be significantly different. Therefore, this study investigates the leaching kinetics of magnesite flotation concentrate with impurity of dolomite in HCl solution, revealing the possibility of removing dolomite from magnesite by simply using dilute HCl solution.

2.   Materials and methods

2.1. Minerals

The magnesite flotation concentrate used for leaching test was obtained from Subei Mine in Gansu province, China. The chemical composition and the X-ray diffraction patterns were given in Table 1 and Fig. 1, respectively. It can be seen from the results that the MgO and CaO contents in the flotation concentrate are 46.03 and 1.54%, respectively. A majority of magnesite (mass fraction of 94.35%) and a small amount of dolomite (mass fraction of 5.06%) were observed.

Table 1. Chemical composition of magnesite flotation concentrate (mass fraction, %)

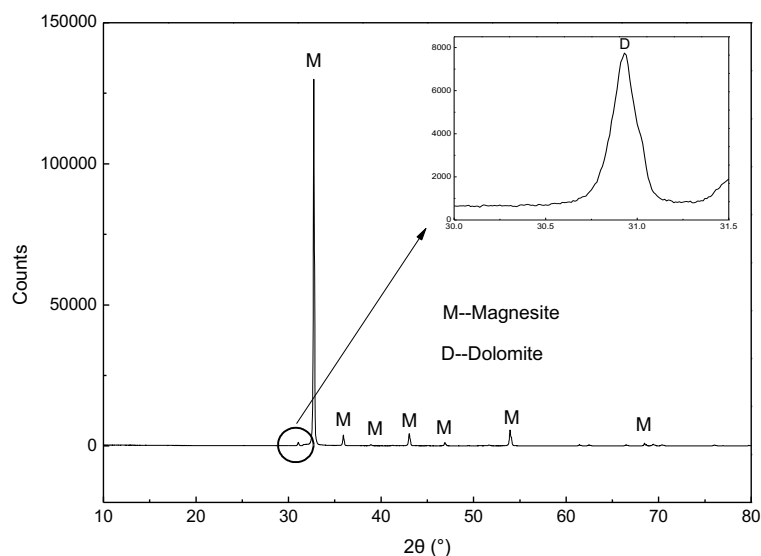| Composition	MgO	CaO	Fe_2O_3	SiO_2	Al_2O_3	K_2O	Na_2O	LOI
Content	46.03	1.54	0.126	0.090	0.027	<0.005	0.010	50.51

Fig. 1. XRD pattern of magnesite flotation concentrate

Fig. 2 shows the mineralogical analysis results based on backscatter scanning electron microscopy (SEM) with EDAX analysis. In the backscatter SEM image, magnesite showed dark gray and dolomite

showed light gray. As shown in Fig. 2, the primary mineral in this sample was magnesite, with a small amount of dolomite. They were closely related to each other and the particle size of dolomite was significantly smaller than that of magnesite. Some dolomite particles were enclosed in coarse magnesite particles while some were associated with magnesite, although some individual dolomite particles with a very small size were observed.
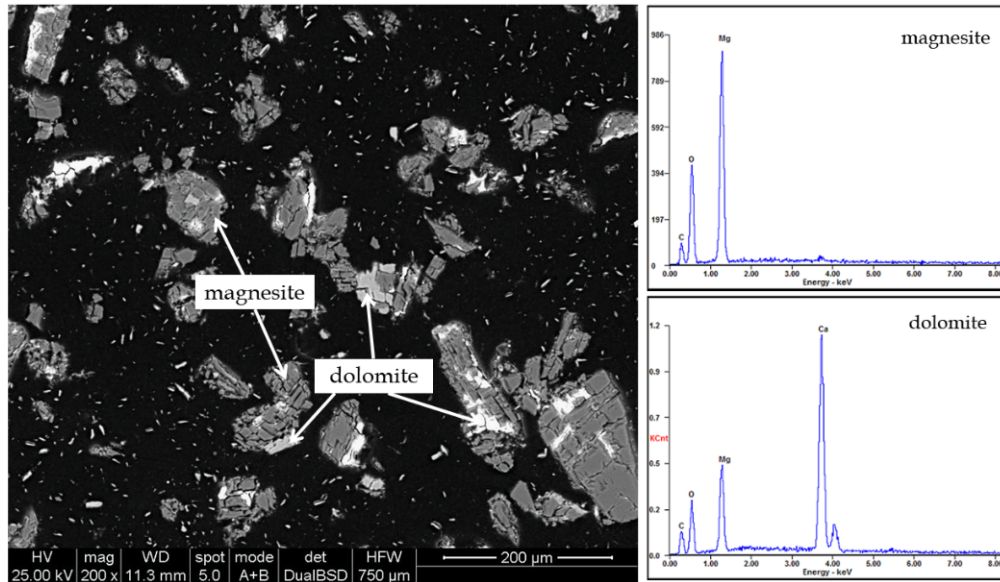

Fig. 2. Backscatter SEM image and EDAX analysis of magnesite flotation concentrate

2.2. Leaching tests

Analytical pure reagent of HCl (36-38%) was used for leaching experiments. The mineral sample (10 g) and 30 mL of HCl solution with a designed concentration were added in a 150 mL conical flask that was placed in a water bath to maintain a constant temperature. Agitation was provided by a magnetic stirrer at a speed range of 100-600 rpm. After leaching, the slurry was filtered and dried for CaO and MgO contents determined by ICP-OES spectrometer (725 model, Agilent Technologies, USA). The mineral samples were digested by HCl, HNO_3, HF and $HClO_4$ solutions with fixed mass ratio before analysis. Each leaching test was repeated at least 3 times, the mean value was reported as the final result.

2.3. X-ray diffractometer analysis

X-ray diffractometer (Ultima IV, Rigaku, Japan, Cu-Kα (λ = 0.15418 nm), 40 kV, 40 mA) was used to analyse the evolution of mineral phase. The scanning 2θ range was 3–80° with a scanning speed was 15°/min. Due to the low dolomite content, the XRD fine scanning patterns was conducted between 30.0–31.5°, with a scanning speed of 2°/min.

3. Results and discussion

3.1. Effect of initial HCl concentration

Fig. 3 shows the leaching results at different HCl concentrations for 30 min, 25 °C, with a stirring speed of 300 rpm. The leaching recoveries of both CaO and MgO increased with increasing HCl concentration until 1.0 mol/L, but with different rates. For instance, the MgO leaching recovery gradually increased from approximate 3.89% to around 6.82% when HCl concentration increased from 0.2 to 1.0 mol/L. Differently, the CaO leaching recovery dramatically increased from around 53.48 to 81.23% and then to 82.93% when HCl concentration increased from 0.2 to 0.8 mol/L, then to 1.0 mol/L. It should be noted that the leaching recovery of CaO was significantly higher than that of MgO, i.e., more than 82% versus less than 7%, indicating a good selectivity for dolomite due to the addition of HCl. In addition, the grade of CaO decreased from around 0.77 to 0.29% when HCl concentration increased from 0.2 to 1.0 mol/L. In contrast, the MgO grade increased from 46.89 to 47.30%. The results indicate that the addition of HCl

is not only beneficial to reducing CaO content, but also beneficial to increasing MgO grade, with limited MgO loss during leaching process. Therefore, 1.0 mol/L HCl was applied for further leaching experiments.
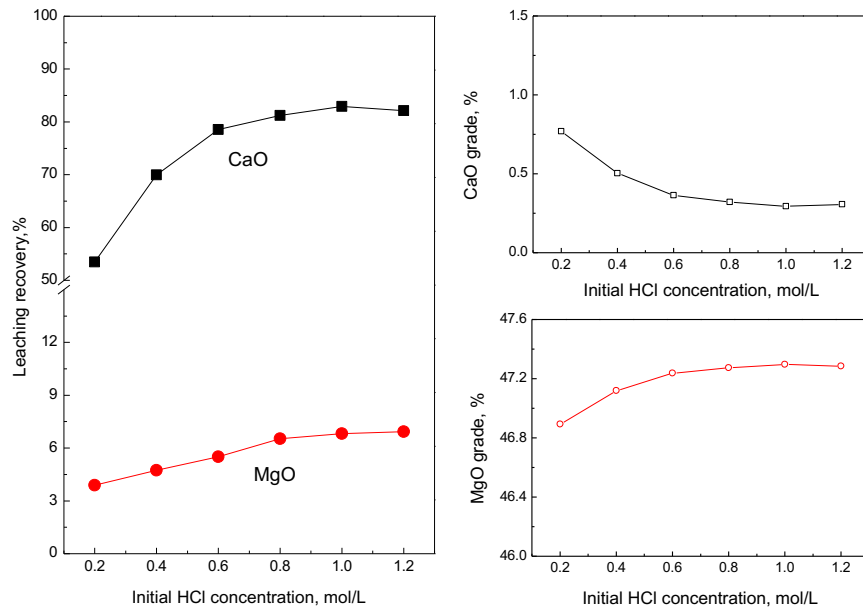

Fig. 3. Effect of initial HCl concentration on CaO/MgO leaching from magnesite flotation concentrate (leaching at 25 °C, 300 rpm for 30 min)

The dolomite remained in the magnesite flotation concentrate was further investigated by XRD (Fig. 4). A clear dolomite diffraction peak at 30.9° was observed in the unleached sample. However, the diffraction peak for dolomite gradually decreased or even disappeared at increased HCl concentration, consistent with the leaching results shown in Fig. 3. This suggests that dolomite could be dissolved and Ca^{2+} was selectively released into HCl solutions during the leaching process, thus reducing the impurity CaO in the concentrate.
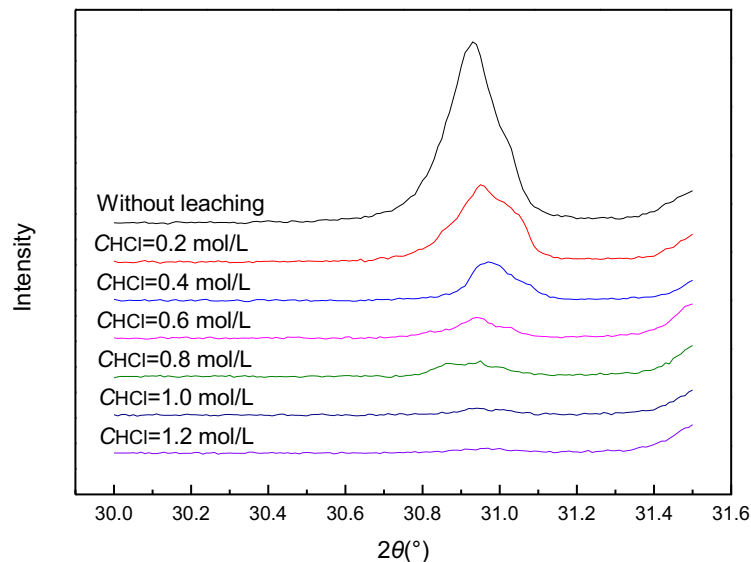

Fig. 4. XRD patterns of magnesite flotation concentrate leached in HCl with different concentrations

The good selectivity of HCl to leach dolomite from magnesite may be due to the difference of dissolution rate towards the two minerals. According to Busenberg and Plummer (1982), the reaction occurred between HCl and dolomite displayed as a two-step reaction, and the $CaCO_3$ component dissolved faster than $MgCO_3$. The reaction could be presented as follows (Eqs. 1 and 2):

$$CaMg(CO_3)_2 + H^+ \rightarrow MgCO_3 + Ca^{2+} + HCO_3^- \qquad (1)$$

$$MgCO_3 + H^+ \rightarrow Mg^{2+} + HCO_3^- \qquad (2)$$
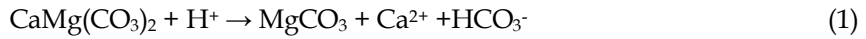
Among these reactions, the first step is very rapid and the overall rate of reaction is controlled by the rate of the second step. The study of Chou et al. (1989) confirmed this reaction process, and pointed out that the forward rate constants of magnesite were 3-4 orders of magnitude lower than those for $CaCO_3$, although they had similar solubilities. The much lower rate constants of magnesite were probably due to the fact that it is very difficult to hydrate the $MgCO_3$ and to dehydrate the Mg^{2+} ion (Chou et al., 1989).

3.2. Effect of stirring speed

Fig. 5 shows the effect of stirring speed on CaO/MgO leaching from magnesite flotation concentrate. The results indicated that the leaching recoveries of both CaO and MgO increased with increasing stirring speed at 100 to 200 rpm at 25 °C, 1.0 mol/L HCl, and the stirring speeds did not play a significant role on the leaching recoveries when increasing the stirring speed from 200 to 600 rpm. In addition, the MgO grade of residue remained at 47.16-47.30%, while the CaO grade fluctuated between 0.29 and 0.43%, obtaining the lowest CaO grade and highest MgO grade at 300 rpm. Thus, a stirring speed of 300 rpm was adopted for further experiments.
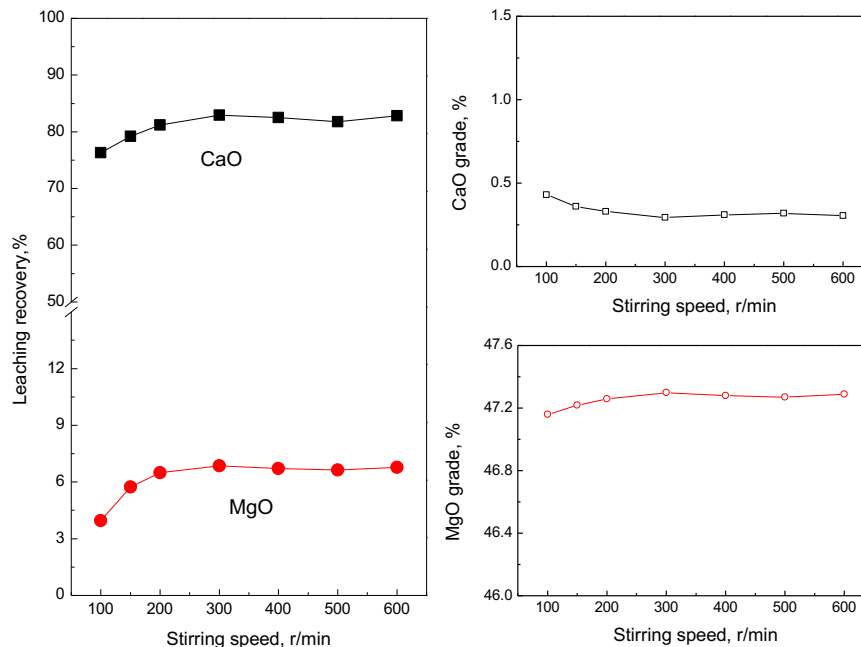

Fig. 5. Effect of stirring speed on CaO/MgO leaching from magnesite flotation concentrate
(leached in 1.0 mol/L HCl solution controlled at 25 °C for 30 min)

3.3. Effect of leaching temperature

Fig. 6 shows that the leaching recoveries of both CaO and MgO increase with increasing temperature, with the CaO leaching recovery being more sensitive to temperature than that of MgO. For instance, the CaO leaching recovery increased rapidly from 56.67 to 82.81% when temperature increased from 5 to 25 °C. Further increase in temperature to 45 °C changed the CaO leaching recovery insignificantly. However, the MgO leaching recovery gradually increased from 3.36 to 11.38% when temperature increased from 5 to 45 °C. It should be noted that the maximum difference in leaching recovery between CaO and MgO was achieved at 25 °C. In addition, the CaO grade dramatically decreased from 0.71 to 0.29%, while MgO grade increased significantly from 46.94 to 47.30%, when temperature increased from 5 to 25 °C. However, further increase in temperature (to 45 °C) did not change the grades of MgO and CaO apparently. Previous study shows the magnesium extraction from magnesite ore at high temperature (greater than 50 °C) (Lacin et al., 2005; Bayrak et al., 2006), which would however result in significant CaO removal but more MgO loss. Therefore, this study indicates that the selective leaching of dolomite can be optimized at room temperature.
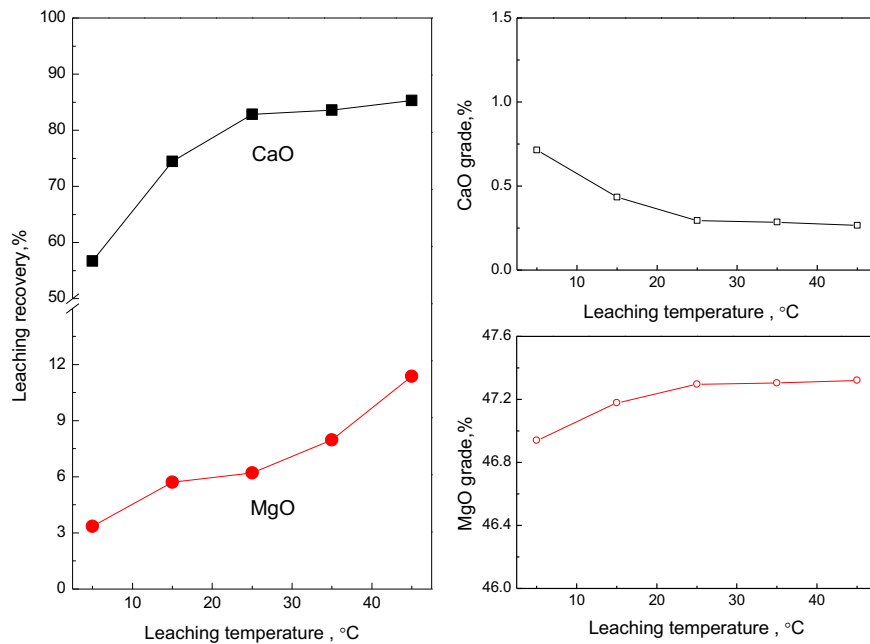
Fig. 6. Effect of leaching temperature on CaO/MgO leaching from magnesite flotation concentrate
(leached in 1.0 mol/L HCl solution, stirred at 300 rpm for 30 min)

3.4. Effect of leaching time

Fig. 7 shows the effect of leaching time on the leaching recovery and grade of CaO and MgO. The CaO leaching recovery increased dramatically from 46.89 to 85.20%, and the MgO leaching recovery only increased from 3.06 to 10.68%, when leaching time increased from 5 to 120 min. Considering the leaching of CaO nearly equilibrated at 30 min but MgO recovery increased linearly after 30 min, the 30 min was selected to avoid more MgO loss. Under these leaching conditions, the residual CaO grade was only 0.27% (85% removal from the concentrate), with a 6.22% loss for MgO. CaO leaching rate reached equilibrium in a short time, while that of MgO continued increased with the extension of leaching time, which also proved the difference of reaction rate between the two minerals with HCl.
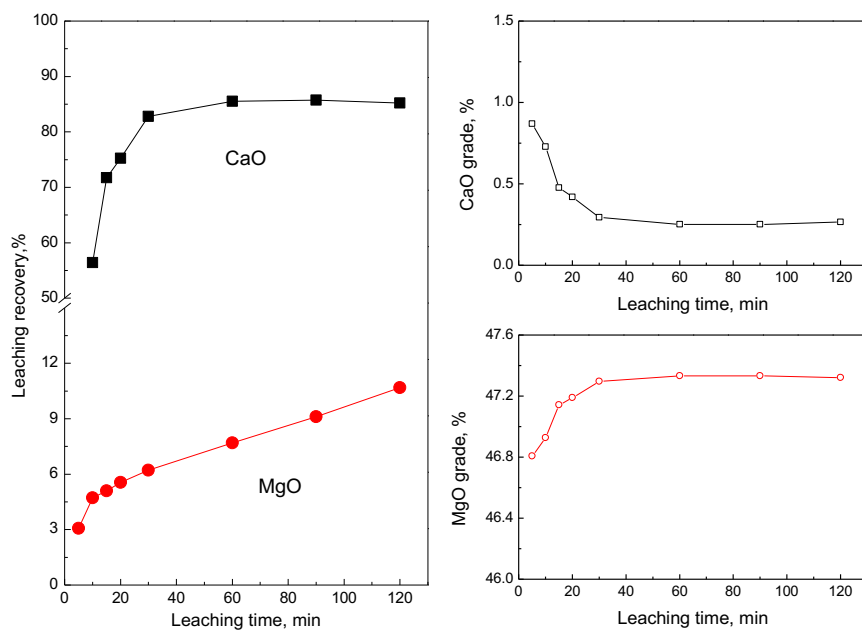

Fig. 7. Effect of leaching time on CaO/MgO leaching from magnesite flotation concentrate
(leached in 1.0 mol/L HCl solution controlled at 25 °C, stirred at 300 rpm)

3.5. Leaching kinetics analysis

Fig. 8 shows the leaching recovery of CaO and MgO at different temperatures within 90 min. It is clear that CaO (Fig. 8a) leaching recovery is different to that of MgO (Fig. 8b). For instance, CaO leaching recovery within the first 5 min was higher than 29% at 5 °C, and even over 83% at 45 °C, indicating a very fast leaching rate of CaO in the initial stage. However, after 5 min, CaO leaching recovery showed a parabolic trend at 5 to 35 °C, suggesting a gradually decreased leaching rate. The single diffusion ($kt=1-2x/3-(1-x)^{2/3}$) and surface chemical reaction ($kt=1-(1-x)^{1/3}$) models, or a mixture of them (Safari et al., 2009; Li et al., 2013) have been tried but failed to fit the leaching kinetics, e.g. not a liner trend or low R^2 values.
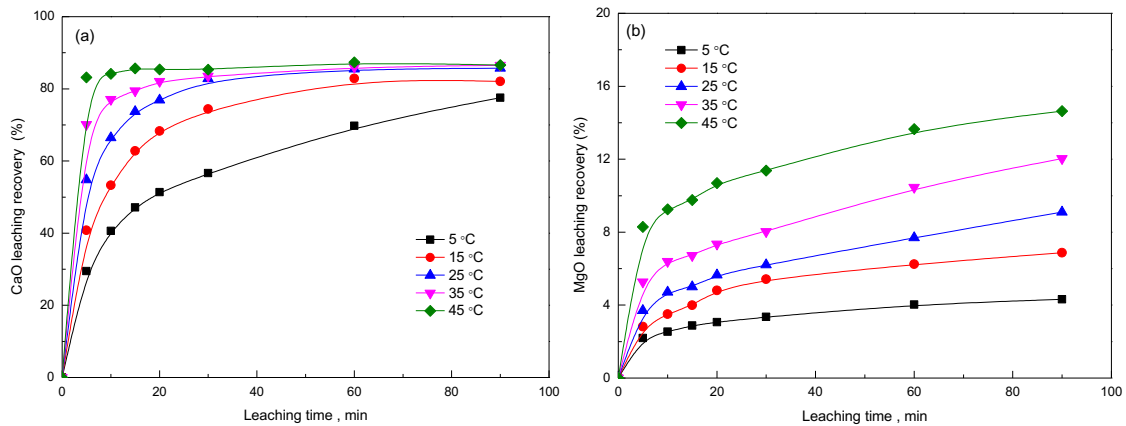

Fig. 8. Leaching recovery of (a) CaO, (b) MgO at different temperatures (leached in 1.0 mol/L HCl solution, stirred at 300 rpm)

However, the Avrami equation (Eq. 3) (Avrami, 1939; Sheibani et al., 2008; Sokic et al., 2009) can fit the leaching trend.

$$-\ln(1-x) = kt^n \tag{3}$$

where k is the rate constant, n is the time exponent, x is the fraction reacted.

The parameters k and n could be obtained via plotting a linear plot of $\ln(-\ln(1-x))$ as a function of $\ln t$ to determine the reaction rate controlling step (Fig. 9). A good linear fit was observed for all the temperatures examined, indicating that the Avrami model can accurately demonstrate the leaching process of dolomite and magnesite. `
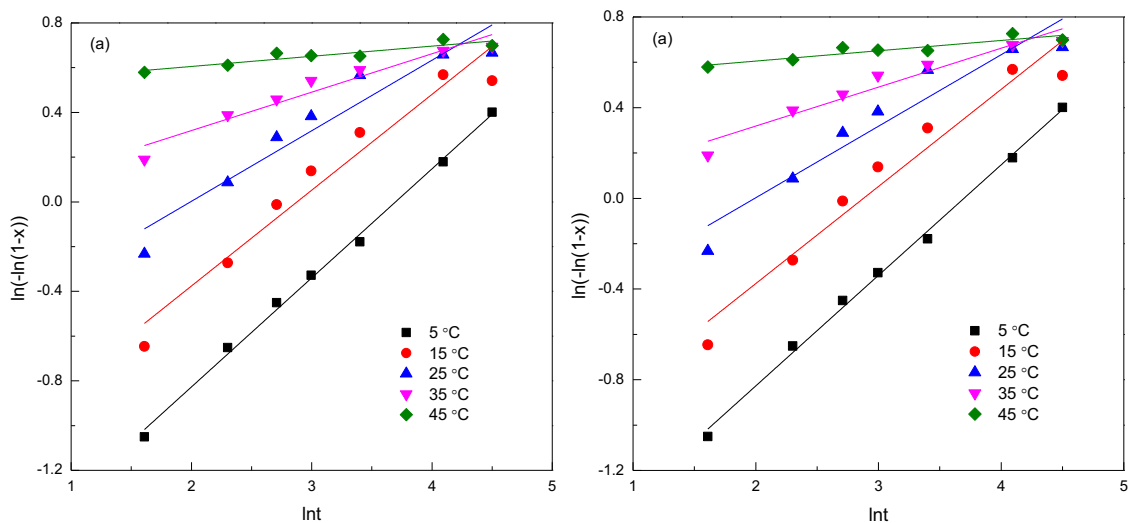

Fig. 9. The plots of $(\ln(-\ln(1-x)))$ vs. $\ln t$, for (a) CaO, (b) for MgO

The fitted parameters were shown in Table 2. And the n values indicate the information on the mechanism of the reaction. For instance, when $0.5<n<1$ indicates a chemical reaction mechanism.

A smaller n value (n≤0.5) suggests a diffusion controlled leaching mechanism even a high activation energy might be calculated (Sokic et al., 2009). The n values shown in Table 2 indicate that the leaching of CaO and MgO is diffusion controlled. It should be noted that the n values for MgO remain within 0.2160-0.3229, with an average value of 0.2780. However, the n values for CaO decrease dramatically, especially at temperature greater than 25 °C.

Table 2. Values of kinetic parameters of n and lnk obtained via Avrami equation

T (°C)	CaO			MgO		
	n	lnk	R^2	n	lnk	R^2
5	0.4875	-1.8024	1.00	0.2441	-4.2045	1.00
15	0.4284	-1.2328	0.94	0.3229	-4.0498	0.98
25	0.3154	-0.6282	0.91	0.3115	-3.7818	0.99
35	0.1717	-0.0245	0.93	0.2956	-3.4280	0.98
45	0.0455	0.5145	0.85	0.2160	-2.8255	0.99

In order to determine the activation energy, the Arrhenius equation (Eq. 4) can be used (Cao et al., 2012):

$$k = k_0 \, e^{-E_a/RT} \tag{4}$$

where k_0 is the frequency or pre-exponential factor, R is universal gas constant, E_a is activation energy, and T is temperature in Kelvin.

Fig. 10a shows the plot of lnk versus 1000/T, with a slope of $-E_a/(RT)$ and an intercept of lnk_0. By using the Arrhenius equation, the following values were determined, E_a = 43±1 kJ/mol for dolomite while 25±4 kJ/mol for magnesite.
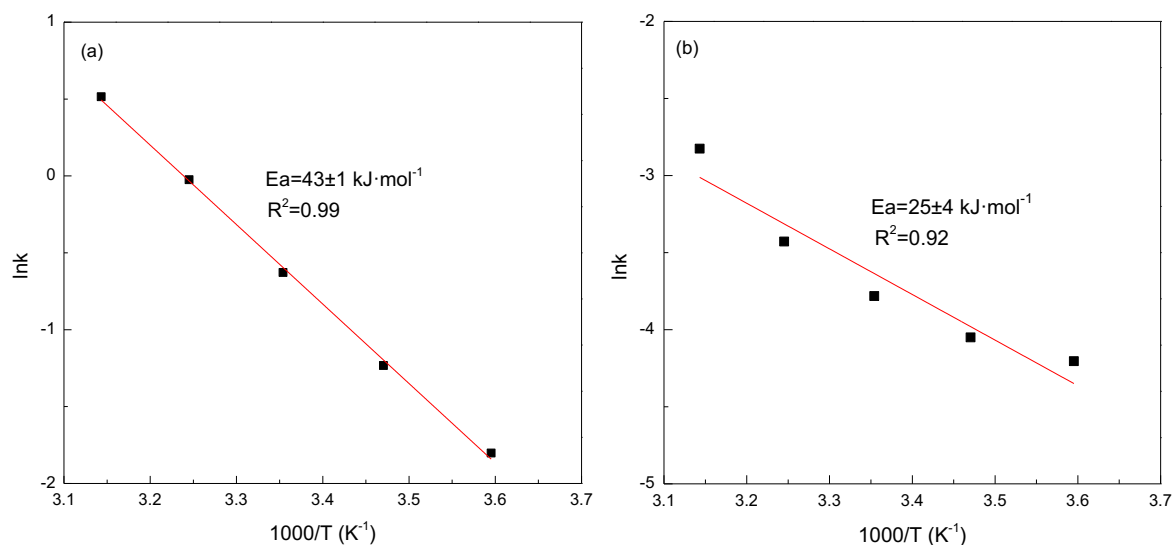

Fig. 10. Arrhenius plots for (a) CaO (dolomite) and (b) MgO (magnesite) leaching

4. Conclusions

In this study, HCl leaching was utilized to remove CaO from magnesite flotation concentrates, and was demonstrated to display a good selectivity for CaO removal. From the experiments and analysis results, the following conclusions can be obtained:

(1) HCl leaching can reduce calcareous material from magnesite flotation concentrate to improve its grade. The increase in HCl concentration and leaching time is beneficial to CaO leaching, with leaching temperature of 25 °C for optimized selectively leaching of dolomite from magnesite.

(2) The HCl leaching process was diffusion controlled for both dolomite and magnesite, with an activation energy of 43±1 kJ/mol and 25±4 kJ/mol, respectively.

References

AVRAMI, M., 1939. *Kinetics of phase change. I. General Theory.* J. Chem. Phys.7, 1103-1112.

ASHRAF, M., ZAFAR, Z.I., ANSARI, T.M., 2005. *Selective leaching kinetics and upgrading of low-grade calcareous phosphate rock in succinic acid.* Hydrometallurgy. 80, 286-292.

ABALI, Y., COPUR, M., YAVUZ, M., 2006. *Determination of the optimum conditions for dissolution of magnesite with H_2SO_4 solutions.* Indian J. Chem. Technol.13, 391-397.

BUSENBERG, E., PLUMMER, L.N., 1982. *The kinetics of dissolution of dolomite in CO_2-H_2O systems at 1.5 to 65℃ and 0 to 1 atm P_{CO2}.* AM. J. Sci. 282, 45-79.

BAKAN, F., LACIN, O., BAYRAK, B., SARAC, H., 2006. *Dissolution kinetics of natural magnesite in lactic acid solutions.* Int. J. Miner. Process. 80, 27–34.

BAYRAK, B., LACIN, O., BAKAN, F., SARAC, H., 2006. *Investigation of dissolution kinetics of natural magnesite in gluconic acid solutions.* Chem. Eng. J. 117,109-115.

BAYRAK, B., LACIN, O., SARAC, H., 2010. *Kinetic study on the leaching of calcined magnesite in gluconic acid solutions.* J. Ind. Eng. Chem.16, 479-484.

BREZANI, I., SKVARLA, J., SISOL, M., 2017. *Reverse froth flotation of magnesite ore by using (12-4-12) cationic gemini surfactant.* Miner. Eng. 110, 65-68.

CHOU, L., GARRELS, R.M., WOLLAST, R., 1989. *Comparative study of the kinetics and mechanisms of dissolution of carbonate minerals.* Chem. Geol. 78, 269-282.

CHEN, G.L., TAO, D., 2004. *Effect of solution chemistry on flotability of magnesite and dolomite.* Int. J. Miner. Process. 74, 343-357.

CAO, Z., ZHONG, H., JIANG, T., WANG, S., LIU, G.Y., XIA, L.Y., 2012. *A novel hydrometallurgy of molybdenite concentrate and its kinetics.* J. Chem. Technol. Biotechnol. 87, 938-942.

FOUDA, M.F.R., ABD-ELZAHER M.M., AMIN R.S., 1999. *Exploitation of Egyptian dolomite and magnesite ores for the preparation of magnesium compounds I. Kinetics of the reaction with hydrochloric acid.* S. Afr. J. Chem. 52, 84-89.

FOUDA, M.F.R., ABD-ELZAHER M.M., AMIN R.S., 1999. *Exploitation of Egyptian dolomite and magnesite ores for the preparation of magnesium compounds Ⅱ. Kinetics of reaction with nitric and sulphuric acids.* S. Afr. J. Chem. 52, 90-94.

GENCE, N., OZDAG, H., 1995. *Surface properties of magnesite and surfactant adsorption mechanism.* Int. J. Miner. Process. 43, 37-47.

GENCE, N., 2006. *Wetting behavior of magnesite and dolomite surfaces.* Appl. Surf. Sci. 252, 3744-3750.

GENCE, N., OZBAY, N., 2006.*Ph dependence of electrokinetic behavior of dolomite and magnesite in aqueous electrolyte solutions.* Appl. Surf. Sci. 252, 8057-8061.

GHARABAGHI, M., NOAPARAST, M., IRANNAJAD, M., 2009. *Selective leaching kinetics of low-grade calcareous phosphate ore in acetic acid.* Hydrometallurgy. 95, 341-345.

HEYDARPOUR, T., REZAI, B., GHARABAGHI, M., 2011. *A kinetics study of the leaching of a calcareous phosphate rock by lactic acid.* Chem. Eng. Res. Des. 89, 2153-2158.

KARAOGLU, H., YANMIS, D., GURKOK, S., 2016. *Magnesite enrichment with pseudomonas oryzihabitans isolated from magnesite ore.* Geomicrobiol. J. 33, 46–51.

LACIN, O., DONMEZ, B., DEMIR, F., 2005. *Dissolution kinetics of natural magnesite in acetic acid solutions.* Int. J. Miner. Process. 75, 91-99.

LI, Y., KAWASHIMA, N., LI, J., CHANDRA, A.P., GERSON, A.R., 2013. *A review of the structure, and fundamental mechanisms and kinetics of the leaching of chalcopyrite.* Adv. Colloid Interface Sci. 197-198, 1-32.

KAYA, M. ERDOGAN, N., 2004. *Production of magnesium compounds from KUMAS (Turkey) electro-filter magnesite dust waste.* Global Symposium on Recycling, Waste Treatment and Clean Technologies, Madrid, Spain, pp. 563-572.

ONCEK, S., KAYA, M., 1994. *Concentration of magnesite by column flotation.* 5th International Mineral Processing Symposium, Cappadocia, Turkey, pp. 211-218.

RAZA, N., Zafar, Z.I., NAJAM-UL-HAQ, M., 2014. *Utilization of formic acid solutions in leaching reaction kinetics of natural magnesite ores.* Hydrometallurgy 149,183-188.

RAZA, N., ZAFAR, Z.I., NAJAM-UL-HAQ, KUMAR, R.V., 2015. *Leaching of natural magnesite ore in succinic acid solutions.* Int. J. Miner. Process. 139, 25-30.

SANTANA, A.N., PERES, A.E.C., 2001. *Reverse magnesite flotation.* Miner. Eng. 14, 107-111.

SHEIBANI, S., ATAIE, A., HESHMATI-MANESH, S., 2008. *Kinetics analysis of mechano-chemically and thermally synthesized Cu by Johnson–Mehl–Avrami model.* J. Alloy. Compd. 455, 447-453.

SAFARI, V., ARZPEYMA, G., RASHCHI, F., MOSTOUFI, N., 2009. *A shrinking particle-shrinking core model for leaching of a zinc ore containing silica.* Int. J. Miner. Process. 93, 79-83.

SOKIC, M.D., MARKOVIC, B., ZIVKOVIC, D., 2009. *Kinetics of chalcopyrite leaching by sodium nitrate in sulphuric acid.* Hydrometallurgy. 95, 273-279.

SHABANI, M.A., IRANNAJAD, M., AZADMEHR, A.R., 2012. *Investigation on leaching of malachite by citric acid.* Int. J. Min. Met. Mater. 19, 782-786.

YAO, J., YIN, W., GONG, E., 2016. *Depressing effect of fine hydrophilic particles on magnesite reverse flotation.* Int. J. Miner. Process.149, 84-93.

ZHANG, H., LIU, W.G., HAN, C., HAO, H.Q., 2018. *Effects of monohydric alcohols on the flotation of magnesite and dolomite by sodium oleate.* J. Mol. Liq. 249, 1060–1067.