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CO₂ bubble formation on dolomite surface and its influence on surface wettability and flotation of dolomite

Xianbo Li ^{1, 3, 4}, Qin Zhang ^{2, 3, 4}, Aoao Chen ¹, Xuming Wang ⁵

¹ Mining College, Guizhou University, Guiyang 550025, China

² Guizhou Academy of Sciences, Guiyang 550001, China

³ National and Local Joint Laboratory of Engineering for Effective Utilization of Regional Mineral Resources from Karst Areas, Guiyang 550025, China

⁴ Guizhou Key Lab of Comprehensive Utilization of Nonmetallic Mineral Resources, Guiyang 550025, China

⁵ Department of Metallurgical Engineering, College of Mines and Earth Sciences, The University of Utah, Salt Lake City, UT 84112, USA

Corresponding author: zq6736@163.com (Qin Zhang)

Abstract: Dolomite is a common carbonate mineral that can release CO_2 gas under acidic conditions. The formation of bubbles on the dolomite surface might play a critical role in the flotation separation of dolomite from apatite. In this study, the CO_2 bubbles formation due to CO_2 gas releasing from the dolomite surface under acidic condition was observed using an atomic force microscope (AFM). The influence of CO_2 bubbles on flotation behavior and surface wettability of dolomite was evaluated through micro-flotation test, contact angle measurement and molecular dynamics simulation. The results indicate that no gas phase points were observed on the dolomite surface in deionized water or sodium oleate (NaOL) solution. CO_2 nanobubbles were observed on the dolomite surface treated with NaOL solution at pH 5, with an average size of 44 nm. The presence of CO_2 gas layers has a shielding effect on the adsorption of water molecules on the dolomite surface, potentially enhancing the surface hydrophobicity of dolomite. Therefore, CO_2 bubbles are beneficial for improving flotation recovery of dolomite. This study inspires the idea of utilizing the released CO_2 bubbles in the flotation process of dolomite.

Keywords: dolomite, CO2 bubbles, flotation, surface wettability, adsorption

1. Introduction

Phosphate ore is an important chemical mineral raw material, extensively utilized in agricultural industry, chemical industry, environmental protection, and material science (Ruan et al., 2019). Approximately 85% of phosphorus resources in China can be classified as middle-low grade phosphate ore (Li et al., 2017). Typically, this ore contains various gangue minerals such as dolomite, quartz, calcite (Sis and Chander, 2003; Zhou et al., 2020). As a result, the direct utilization of the raw phosphate ore is hindered. Consequently, beneficiation methods, including froth flotation, heavy media, leaching, and calcination, are necessary to remove these impurities and improve the P_2O_5 grade of concentrate (Liu et al., 2016; Teague and Lollback, 2012).

One of important requirements is limitation of MgO in the phosphate concentrate, therefore removing dolomite is an important and difficult task. The dolomite is a commonly associated gangue mineral in phosphate ore, and it is a typical carbonate mineral (Gong et al., 2024). In the phosphate industry, the reverse flotation method is generally adopted to remove the gangue mineral dolomite and other carbonate mineral from phosphate ore (Aleksandrova et al., 2022). This method has been demonstrated to offer advantages such as high separation efficiency and strong adaptability. However, both dolomite and apatite contain the same lattice ion, Ca^{2+} , leading to a similar surface property and a small difference in floatability (Xie et al., 2018; Yin et al., 2019). Therefore, the reverse flotation technology requires the addition of inorganic acid, such as H₂SO₄, H₃PO₄, HCl to enhance the separation

selectivity (Liu et al., 2017; Mohammadkhani et al., 2011). Specifically, fluorapatite is inhibited under acidic conditions, while dolomite is floated up by adding fatty acid collectors, thereby achieving the separation of dolomite from apatite (Kang and Zhang, 2023).

It is well known that carbonate minerals can dissolve and release CO_2 gas in an acidic medium. The differential solubility of dolomite in slightly acidic solution is utilized to generate micro- CO_2 bubbles at the dolomite/water interface. Dolomite particle/bubble aggregates float to the surface, leaving phosphate concentrate with low MgO content (El-Midany et al., 2009a). The CO_2 flotation is a non-equilibrium condition in which CO_2 dissolves in water, reacts with the surfaces of carbonate minerals (calcite and dolomite), competes with the anionic collector species, and decrease the hydrophobicity of the surface state. Consequently, selective separation of apatite from the carbonate gangue minerals is achieved (Wang et al., 2013). Freitas et al. (2020) indicated that the process based on the application of CO_2 for the separation of calcite and apatite may be a technical alternative that causes less impact on flotation performance for the phosphate concentration ores with carbonated gangue. Saldi et al. (2021) investigated the dissolution mechanisms of dolomite at acidic pH by high resolution pH-stat and mixed-flow reactor experiments, in conjunction with AFM and TEM observations.

The utilization of this phenomenon for separation of dolomite from phosphate is limited by the need for a surface-active agent that can maintain such gas adhered to the particle surface. El-Midany et al. (2011) found that polymers and surfactants, specifically Polyvinyl Alcohol (PVA) polymer, showed promising results in forming stable bubbles of CO₂ gas at the dolomite surface. Nanobubbles on dolomite surface were observed under water, depressant and collector solutions, the observed bubble density was highest under collector conditions, with 0.656 bubbles per μ m², compared to 0.342 nanobubbles per μ m² under water conditions, this is because because the collector has affected the pinning of the bubbles (Owens et al., 2018). Vaziri Hassas et al. (2018) found that bubble attachment and pyrite flotation is improved with CO₂ due to the formation of nano-bubbles and the spreading of these CO₂ molecules at the pyrite surface.

The above research results indicate that the impact of CO_2 bubbles on the flotation of mineral, especially carbonate minerals, has received attention. However, the presence of CO_2 bubbles on dolomite surface has not been observed, and their impact on surface wettability and flotation remains unclear. Generally, flotation of dolomite from phosphate ore is carried out in a slurry at pH about 5 (Amirech et al., 2018; Gao et al., 2023). Therefore, in this study, the CO_2 bubbles released from the dolomite surface were detected by AFM in a pH 5 solution. Meanwhile, the deionized aqueous solution was serves as a reference. The influence of CO_2 bubbles on flotation behavior and surface wettability of dolomite was clarified by micro-flotation test, contact angle measurement, and molecular dynamics simulation (MDS).

2. Materials and methods

2.1. Materials

The dolomite sample was obtained from Guizhou Province, China. The X-ray diffraction (XRD, D8 Advance, Bruker, Germany) pattern of dolomite is shown Fig. 1, and the characteristic diffraction peaks of the mineral sample matched well with the standard pattern of $CaMg(CO_3)_2$ (PDF#36-0426), no obvious impurity peaks were observed. This indicates that the dolomite sample was pure. The chemical composition of the mineral sample was analyzed by the X-ray fluorescence (Axios, Panalytical Company, Netherlands), and the results are listed in Table 1. The results showed that the dolomite contained 21.90% of MgO.

Sodium oleate (NaOL), used as the collector, was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. The pulp pH was adjusted with a 0.1 mol/L hydrochloric acid (HCl) solution, which was purchased from Chongqing Chuandong Chemical (Group) Co., Ltd. All the reagents used in this study were of analytical grade.

Table 1. Chemical composition of mineral sample (wt%)

Chemical composition	CaO	MgO	SiO ₂	P_2O_5	Fe ₂ O ₃	Al_2O_3	Other
Content	32.33	21.90	1.14	0.52	0.11	0.15	43.85



Fig. 1. XRD pattern of dolomite sample

2.2. Micro-flotation experiments

Micro-flotation tests were conducted in an XFGCII flotation machine (mechanical agitation) with a volume capacity of 40 mL. Initially, 2.0 g of dolomite samples were placed in a plexiglass cell with 40 mL of distilled water. After agitation for 1 min at 1992 rpm, an HCl solution was added to adjust the pH of the slurry. The collector was then added into the cell with conditioning time of 1 min, and flotation was conducted for an additional 3 min. The froth and sink products were separately filtered, dried, weighed. Each micro-flotation experiment was conducted three times, and the average reported as the final value.

2.3. AFM measurement

A polished dolomite surface was used as the substrate. The in-situ topography of dolomite surface in HCl and NaOL solutions was characterized using an MFP-3D bio-AFM instrument (Asylum Research, Santa Barbara, CA, USA). The probe was produced by Oxford PNP-TR-Au with a spring constant of 0.32 N/m. The AFM imaging was conducted using liquid phase module with AC tapping mode. The polished dolomite block was placed on the AFM sample stage, and a drop of deionized water or deionized water with pH 5 was applied to the dolomite surface. For the dolomite surface treated with NaOL solution at pH 5, the dolomite block was immersed in 1×10⁻³ mol/L NaOL solution for 10 min, then washed by deionized water and dried with N₂. Thereafter, a drop of deionized water or deionized water of pH 5 was dropped on the treated dolomite surface, and the dolomite surface was imaged to observe the morphology of CO₂ bubbles. The apparent phase difference was used to help distinguish the nanobubbles formed on the dolomite surfaces. The image analysis software Image-Pro Plus was used to measure the size of CO₂ bubbles manually. The two-dimensional AFM image of dolomite surface in air is shown in Fig. 2, and the root-mean-square (rms) roughness is 2.58 nm.



Fig. 2. AFM topographic image of the polished dolomite surface

2.4. Contact angle measurements

The contact angle measurements were carried out using a contact angle measuring instrument (HARKE-SPCAX3, Beijing Hake Testing Instrument Factory, Beijing, China) with sessile drop method. The dolomite block was ground and polished before measurement. The polished surface was immersed in different concentrations of NaOL collector solution for 3 min at pH 5. Then, the block was air-dried. A water-droplet of approximately 2 μ L was placed onto the dolomite surface to create the three-phase contact line. Each sample was measured three times, and the most representative value was reported.

2.5. Molecular dynamics simulation

Molecular dynamics simulation calculation was performed using Materials Studio software. The (104) surface is the cleavage plane of dolomite, representing the most stable surface with the lowest surface energy (Higgins et al., 2007; Cao et al., 2020). Therefore, the (104) surface was selected as the adsorption surface. Water molecules and reagent solution models were constructed under the Amorphous Cell. The models were geometrically optimized using the Smart method under the COMPASS II force field of Forcite module. Build Layers function was utilized to combine the water box or reagent solution model with the (104) surface, constructing the water molecules/reagent solution dolomite system in the presence of CO_2 gas layer. The initial configuration is shown in Fig. 3. The MDS were performed using the COMPASS II force field, NVT ensemble, and Velocity Scale thermostat method. The Atom based method and Ewald method were used to calculate the van der Waals interaction and the electrostatic interaction, respectively. The calculation accuracy was set as fine, the simulation time step was 1.0 fs, and the total time was 500 ps. The trajectory file was analyzed after successful simulation.



Fig. 3. Initial configuration of water molecules/reagent solution on the (104) surface of dolomite in the presence of CO₂ gas layer

2.6. Zeta potential measurements

The zeta potentials of dolomite under various NaOL concentrations were measured using a zeta potential analyzer (Delsa[™] Nano C, Beckman Coulter, USA). 40 mg of dolomite powder was added into 40 mL of a 1 mM KCl background electrolyte solution with different NaOL concentrations. The suspension was agitated for 2 min with a magnetic stirrer to ensure full dispersion of mineral particles. Zeta potential measurements were conducted three times for each sample, and the average value was reported as the final value.

3. Results and discussion

3.1. AFM image analysis of dolomite surface

AFM imaging can be used to directly measure the number and size of CO_2 bubbles on dolomite surface. The contrast phase images over an area of 5 × 5 µm² are presented in Fig. 4, and the size distribution of CO_2 bubbles on the surface of dolomite is shown in Fig. 5. As shown in Fig. 4a, the surface of dolomite in deionized water was relatively smooth, and no gas phase was observed. However, in deionized water at pH 5, a large number of gas phases were detected on the surface of dolomite (Fig. 4b). As shown in Fig. 5a, the size distribution of CO_2 bubbles follows a normal distribution, ranging from 20 to 120 nm with an average size of 53 nm. This observation indicates that the surface of dolomite was dissolved and CO_2 bubbles were released under acidic condition (pH 5).

Similarly, no gas phase was displayed on the surface of dolomite treated with 1×10^{-3} mol/L NaOL solution (Fig. 4c). However, under the acidic condition at pH 5, the gas phase composition was detected, with the CO₂ bubble size ranging from 10 to 90 nm (an average size of 44 nm). Compared with the case of pristine dolomite in deionized water at pH 5, the gas phases on the surface of dolomite treated with 1×10^{-3} mol/L NaOL solution at pH 5 are more uniform and denser, which could be attributed to the enhanced hydrophobicity on the dolomite surface after NaOL adsorption, resulting in the stronger hydrophobic interaction between CO₂ bubbles and dolomite. This is consistent with previous results by Owens et al., (2018) who investigated the nanobubbles on dolomite surface and found that the bubble density was highest under collector conditions. The presence of the surfactant or polymer adsorbed at either the gas-liquid or liquid-liquid interface affect the bubble stability at the interface, the rate of CO₂ evolution is very low which keeps the polymeric membrane at its highest elasticity (El-Midany et al., 2009b). Thus, the dolomite will generate CO₂ gas that is trapped by the surfactant (El-Midany et al., 2009a). Clearly, it can be concluded that the surface of dolomite could release CO₂ bubbles under the acidic condition.

In addition to the CO₂ nanobubbles detected by AFM, a small number of large CO₂ bubbles in pH 5 solution were also observed using an optical microscope, the results are shown in Fig. 6. In deionised water of pH 5, bubbles of various sizes were observed gathering on the surface of dolomite, with an average diameter of about 11 μ m. For the dolomite surface treated with 1×10-3 mol/L NaOL solution at pH 5, a small number of uniformly sized bubbles are distributed on the surface, with an average diameter of about 8 μ m.



Fig. 4. AFM phase contrast image of dolomite surface (a) in deionized water, (b) deionized water at pH 5, (c) 1×10^{-3} mol/L NaOL solution, (d) 1×10^{-3} mol/L NaOL solution at pH 5



Fig. 5. Size distribution of CO₂ bubbles on the surface of dolomite in (a) deionized water at pH 5, (b)1×10-3 mol/L NaOL solution at pH 5



Fig. 6. Microscopic images of dolomite surface (a) in pH 5 deionised water and (b)1×10⁻³ mol/L NaOL solution at pH 5

3.2. Micro-flotation experiments

To investigate the effect of CO_2 bubbles produced by the dissolution of dolomite with HCl on flotation of dolomite, the order of adding flotation reagent was designed as HCl+NaOL and NaOL+HCl. Specifically, HCl+NaOL represents first adjusting the pulp pH to 5 with an HCl solution, and stirring to remove CO_2 bubbles, followed by adding NaOL to continue stirring for 1 min before flotation. Conversely, NaOL+HCl means first adding NaOL and stirring for 1 min, followed by immediate flotation after adding HCl. This approach is beneficial for the flotation utilization of the generated CO_2 bubbles.

The effect of addition order of HCl and NaOL on the flotation recovery of dolomite is presented in Fig. 7. Fig. 7 displays that the recovery of dolomite increased with the NaOL concentration ranging from 1×10^{-5} to 1×10^{-3} mol/L, and the recovery reached the maximum value at a NaOL concentration of 1×10^{-5} 3 mol/L. However, upon further increasing the concentration to 1×10^{-2} mol/L, the recovery of dolomite actually decreased. This is because the critical micelle concentration (CMC) of NaOL is 1×10^{-3} mol/L, the spherical micelles are formed when the CMC is reached (Ye et al., 2018), resulting in a decrease in the effective concentration of the collector. This finding is consistent with the results reported by Cao et al. (2015). Therefore, when NaOL is used as a collector during flotation, there is a suitable concentration. It is noteworthy that the recovery of dolomite with the adding order of NaOL+HCl is higher than that of HCl+NaOL. This indicates that CO₂ bubbles are beneficial for flotation of dolomite, which can improve the recovery. The result is consistent with our previous research, where nanobubbles enhanced the reverse flotation of dolomite from a mid-low grade phosphate ore (Zhang and Zhang, 2021). This can be attributed to that the capturing the CO_2 gas at the dolomite particle surface into bubbles using a coating agent can be used to selectively separate dolomite by flotation, and the presence of an acidic medium and a coating agent are basic requirements (El-Midany et al., 2009b). Besides, increasing the NaOL concentration would weaken the effect of CO₂ bubbles on the flotation recovery of dolomite.

The adsorption of flotation reagent and flotation behavior of minerals can be well explained by the zeta potential measurement. The zeta potentials of dolomite treated with different NaOL concentrations are shown in Fig. 8. NaOL can dissociate into carboxylic anions (RCOO-), and NaOL is negatively charged. As shown in Fig. 8, with the increase of NaOL concentration from 0 to 1×10^{-3} mol/L, the absolute value of zeta potential of dolomite increased significantly in deionized water and pH 5 solution, which indicates that NaOL was adsorbed onto the surface of dolomite. This is consistent with the result that the zeta potential of the dolomite surface was negative after the addition of NaOL, indicating the adsorption of NaOL on the dolomite surface (Yin et al., 2024). Interestingly, upon further increasing the NaOL concentration to 1×10^{-2} mol/L, the zeta potential of dolomite remained almost unchanged. This suggests that increasing the concentration did not improve the adsorption of NaOL on the surface of dolomite. The results are in good agreement with micro-flotation experiment.



Fig. 7. Effect of the addition order of HCl and NaOL on the recovery of dolomite



Fig. 8. Zeta potentials of dolomite in deionized water and pH 5 solution under different NaOL concentrations

3.3. Contact angle measurement results

The contact angle can quantitatively characterize the surface wettability of mineral. Generally, a larger contact angle of mineral surface indicates a better floatability (Gao et al., 2023). The effect of the addition order of HCl and NaOL on contact angles of dolomite is shown in Fig. 9. Obviously, NaOL could enhance the surface hydrophobicity of dolomite, as the contact angle of dolomite improved with the increase of NaOL concentration from 1×10^{-5} to 1×10^{-3} mol/L. When the NaOL concentration is 1×10^{-3} mol/L, the maximum contact angle reached 71.8° and 79.1° for HCl+NaOL and NaOL+HCl,

respectively. However, the contact angle significantly reduced in the presence of 1×10^{-2} mol/L NaOL, indicating enhanced surface hydrophilicity. Furthermore, the contact angle of dolomite with the adding order of NaOL+HCl is higher than that of HCl+NaOL; these results are in agreement with the flotation results. The contact angle measurement also proves that the presence of CO₂ bubbles could improve the surface hydrophobicity of dolomite.



Fig. 9. Effect of the addition order of HCl and NaOL on contact angles of dolomite (a) HCl+NaOL, (b) NaOL+HCl

3.4. Molecular dynamic simulation

The adsorption equilibrium configurations of the water molecules on dolomite surface in the absence and presence of CO_2 gas layer are shown in Fig. 10. As shown in Fig. 10a, water molecules can spread on the surface of dolomite, with the water molecules closest to the surface arranged more tightly. This indicates that the natural dolomite surface is hydrophilic, which aligns with previously studies (Du and Li, 2023). It can be seen that the CO_2 gas layer could prevent the water molecules from diffusing towards the dolomite surface to form a stable hydrated layer. Only a small amount of water molecules could break through the obstruction of the CO_2 gas layer and interact with the surface of dolomite. Tao et al. (2021) also demonstrated that CO_2 is physically adsorbed on the surface of dolomite because there is no overlap of electron clouds. Therefore, CO_2 gas layers precipitated on the mineral surface have a certain shielding effect on the adsorption of water molecules.

The relative concentration distribution of water molecules on the (104) surface of dolomite along the z-axis direction is shown in Fig. 11. For the adsorption of water molecules on the dolomite surface without CO_2 gas layer, the closer to the surface, the higher the relative concentration of water molecules. This indicates a strong hydration effect on the surface of dolomite. Each peak in the concentration curve presents a water molecule layer, and the hydration film on the mineral surface is composed of these water molecule layers. The thickness of the hydration film is equal to the value on x-axis of the last peak in the curve minus the corresponding value on the crystal surface. Without CO_2 gas layer, there are two peaks in the relative concentration curve of water molecules. The hydration film on the surface of dolomite is composed of two layers of water molecules, with a thickness of 0.68 nm. For the adsorption



Fig. 10. Adsorption configuration of the water molecules on dolomite surface in the (a) absence and (b) presence of CO₂ gas layer

of water molecules on the dolomite surface in the presence of CO_2 gas layer, there is no significant peak in the relative concentration curve of water molecules, indicating weakened hydration. By comparing the relative concentration distribution curve of water molecules on the surface of dolomite with or without a CO_2 gas layer, it can be concluded that the CO_2 gas layer acts as a barrier for the adsorption of water molecules on the surface of dolomite.

The adsorption configuration of water molecules and oleic acid ions on the dolomite surface in the presence of CO_2 gas layer is shown in Fig. 12. As shown in Fig. 12, oleic acid ions can penetrate the barrier effect of the CO_2 gas layer and interact with the surface of dolomite. However, the number of oleate molecules breaking through the CO_2 gas layer is relatively small, and the coverage of CO_2 on the surface can, to some extent, shield the Ca, Mg active sites on the dolomite surface. This will have a certain impact on the interaction between oleate and the dolomite surface. A comparison of the number of water molecules on the CO_2 gas layer in Fig. 10 shows that after adsorbing oleate molecules, the number of water molecules adsorbed on the dolomite surface decreased, thereby enhanced the surface hydrophobicity of dolomite. This analysis is consistent with the results of contact angle measurement and flotation experiment that presence of CO_2 could improve the surface hydrophobicity and recovery of dolomite.



Fig. 11. Relative concentration of water molecules on the (104) surface of dolomite along the z-direction



Fig. 12. Adsorption configuration of the water molecules-NaOL on dolomite surface in the presence of CO_2 gas

4. Conclusions

The purpose of this study is to confirm the CO₂ bubbles formation due to CO₂ gas releasing from the dolomite surface under acidic condition and evaluate its influence on surface wettability and flotation behavior. It was found that no gas phase points were observed on the dolomite surface in deionized water or NaOL solution. CO₂ nanobubbles formation on dolomite surface treated with NaOL solution at pH 5 were observed, presenting a normal distribution with an average size of 44 nm. MDS calculation shows that CO₂ gas layer acts as a barrier for the adsorption of water molecules on the surface of dolomite, enhancing the surface hydrophobicity of dolomite, this is also confirmed by the contact angle measurement. As a result, CO₂ bubbles are beneficial for improving the flotation recovery of dolomite. This study provides an insight into utilization of CO₂ bubbles released from dolomite surface in the acidic condition during flotation. Changing the addition order of acid and collector, such as adding NaOL collector first and then adding acid for immediate flotation, may be an alternative approach.

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