Strengthening the rough selection effect of n-ethyl o-isopropyl thionocarbamate (Dow: Z-200) on chalcopyrite by ultrasonic pretreatment

Yubin Wang, Yan Wang, Bo Yu, Xin Wang, and Xiaoxiao Ma

School of Resource Engineering, Xi’an University of Architecture and Technology, Xi’an, 710055, China

Corresponding author: wy915636557@sohu.com (Y. Wang)

Abstract: In this study, the properties of (CH$_3$)$_2$CHOCSNH$_2$H$_5$ (Dow: Z-200) after the ultrasonic pretreatment was characterized by employing surface tension, viscosity, and Fourier transform infrared (FTIR) spectroscopy, and its influence on chalcopyrite rough selecting was investigated. The results indicate that the pretreated Z-200 can improve the index of chalcopyrite roughing. And, under the same reagent system, the recovery of copper reached 82.84% which was an increase of 24.44% compared with the untreated when Z-200 after ultrasonic pretreatment was applied to the rough separation of chalcopyrite. The reason why ultrasonic can strengthen the flotation effect of Z-200 on chalcopyrite is that ultrasonic pretreatment can decrease the surface tension and viscosity of Z-200 and enhance its foaming performance. Meanwhile, the ultrasonic cavitation destroys the molecular structure of Z-200, so that the relative proportion of methyl absorption peak and amine absorption peak in Z-200 increases. This also further improves the collection performance and foaming performance of Z-200 and strengthens its separation effect on chalcopyrite. The research provides a new idea for Z-200 to act on chalcopyrite and improve its flotation efficiency, reduce the amount of flotation reagent, and its pollution to the environment. It also provides a theoretical basis for expanding the application of ultrasonic technology in the field of flotation.

Keywords: ultrasonic pretreatment, Z-200, action mechanism, chalcopyrite flotation

1. Introduction

In recent years, with the improvement of environmental protection requirements for resource development, research on green and environmentally friendly beneficiation technology has once again become a topical issue of interest to the mineral processing industry again (Liu et al., 2019a; Liu et al., 2019b). How to improve the conventional flotation process to reduce the amount of flotation reagents and the problem of environmental pollution has always been facing by mineral processing researchers (Aharon, 2004). As a physical treatment method, ultrasound has the characteristics of cavitation effect, mechanical effect, thermal effect, etc., it can change the chemical properties and microstructure of the solution and mineral surface properties, and improve the selectivity of the flotation agent to the mineral (Wu et al., 2020; Aitova et al., 2011). It has a good industrial-economic value for improving the grade and recovery of useful minerals and is gradually being applied in various fields of mineral processing (Wang, 2014).

Since ultrasonic waves can produce higher sound wave intensity, it has been studied in the flotation pretreatment, the dispersion, and emulsification of flotation reagents. (1) Flotation pretreatment process: For example, (Lu et al., 2015) studied the effect of ultrasound on the flotation of nickel sulfide ore. The results indicated that ultrasonic can desorb the fine-grained gangue mineral serpentine attached to the surface of the sulfide minerals, which can effectively improve the selection index of nickel. The recovery of nickel concentrate after the ultrasonic treatment reached 79.76%, which was 20.57% higher than that of untreated. To improve the recovery of gold, (Mishra et al., 2004) introduced ultrasonic pretreatment...
technology into arsenopyrite flotation and found that ultrasonic can remove the highly oxidized layer on the surface of arsenopyrite and improve its floatability. (Lu et al., 2019) analyzed the effect of ultrasonic on the surface dissolution, surface properties, and floatability of oxidized pyrrhotite. It was found that ultrasonic can promote the dissolution of oxides on the surface of pyrrhotite, increase the probability of adsorption between pyrrhotite and collector, and improve the flotation index of pyrrhotite. To flotation of magnesite waste with particle size less than 38 µm effectively, (Ozkan, 2002) applied the ultrasonic pretreatment technology to the enrichment test of magnesite slime. And, they found that ultrasonic pretreatment can reduce the flotation foam, increase stability, and prolong the existence time.

The grade and recovery of the magnesite concentrate after ultrasonic pretreatment were greatly improved compared with untreated. (2) Dispersion and emulsification process of flotation reagent: For example, (Lertmaser et al., 2002) studied the influence of ultrasonic treatment on foam flotation in different flotation stages from both theoretical and experimental aspects, and discussed the influence of ultrasonic treatment on its flotation by taking graphite as an example. The results confirmed that when ultrasound is used in flotation reagent emulsification, slurry dispersion, slurry, and reagent mixing and flotation, it can speed up the flotation efficiency, increase the concentrate purity, and reduce concentrate ash content under the condition of a fixed concentrate recovery. (Huang, 2019) explored the influence of ultrasonic pretreatment of dodecylamine on the separation of scheelite. The results demonstrated that ultrasonic treatment can destroy the ionization balance of dodecylamine solution, reduce its surface tension, and strengthen its interaction with scheelite. Also, ultrasonic treatment can change the existing form and aggregation state of the dodecylamine solution, increase its specific surface area and the probability of adhesion to scheelite, so that the surface contact angle and adsorption amount of scheelite increase, thus improving the scheelite flotation recovery.

Besides, the high energy density and high-frequency stress of ultrasound can convert high-density surface energy into a small crushing active area, so ultrasound technology is also used in the crushing process of ore. For example, (Ren et al., 2005) combined the advantages of power ultrasonic cavitation dispersion mechanism and mechanical stirring and crushing mechanism, developed a new type of ultrasonic nano powder production equipment and conducted a theoretical analysis. It was found that 80% of the particles with a particle size of <100 nm can be obtained by using this test equipment in one preparation. And, the observation under the scanning electron microscope shows that the nano-particle medium is uniformly dispersed, has no agglomeration phenomenon, and has good sphericity.

Additionally, ultrasonic waves also have a short wavelength, high frequency, small diffraction phenomenon, orientation, bunching, transmission, reflection, and other characteristics, and they are often used in beneficiation testing technology. For example, the ultrasonic level meter uses the reflection properties of ultrasonic to measure the distance of the space in the container, and then calculate the height of the actual material (Zhang et al., 2013).

At present, most of the research on copper flotation has been focused on the pharmaceutical system and mineral processing process (Yan et al., 2019; Han et al., 2017), and the research on the application of ultrasonic energy to the collector to change its nature and existence and improve its collection performance is very much less (Zhang et al., 2017). Based on this context, the research aimed at the effect of ultrasonic pretreatment on the properties of Z-200 and its roughing and separating effect on chalcopyrite, to provide a reference for expanding the application of ultrasonic technology in flotation reagent pretreatment to improve the flotation efficiency of useful minerals, reduce the amount of flotation reagent and its pollution to the environment.

2. Materials and methods

2.1. Materials

The sample used in this study were obtained from a chalcopyrite plant in Xujigou, Shaanxi province, China. To understand the main chemical composition of the ore, the study conducted a chemical multi-element analysis. The chemical analysis of the sample is presented in Table 1.

According to Table 1, the sample was mainly composed of Cu, Fe, S, SiO$_2$, CaO, and Al$_2$O$_3$. Among them, the contents of SiO$_2$ and CaO were 40.61% and 4.53%, respectively, which indicated that the
gangue minerals in the sample were mainly silicate and quartz, and these gangues could affect the quality of copper concentrate. The contents of Cu, Fe, and S in the sample were 1.37%, 17.51%, and 3.18%, respectively. This indicated that copper is a useful element that can be recovered through the flotation process. To determine the main existence method of copper in chalcopyrite, the copper phase analysis of chalcopyrite was carried out, and the result of mineral phase analysis of the chalcopyrite is presented in Table 2.

Table 1. Results of chemical multi-element analysis of chalcopyrite

<table>
<thead>
<tr>
<th>Elements</th>
<th>Cu</th>
<th>Fe</th>
<th>S</th>
<th>SiO₂</th>
<th>CaO</th>
<th>Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (%)</td>
<td>1.37</td>
<td>17.51</td>
<td>3.18</td>
<td>40.61</td>
<td>4.53</td>
<td>10.68</td>
</tr>
</tbody>
</table>

Table 2. Analysis results of chalcopyrite mineral phase

<table>
<thead>
<tr>
<th>Phase</th>
<th>Copper oxide</th>
<th>Copper sulfide</th>
<th>Bound copper</th>
<th>Total phase sum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (%)</td>
<td>0.0133</td>
<td>1.37</td>
<td>0.0061</td>
<td>1.4043</td>
</tr>
<tr>
<td>Proportion (%)</td>
<td>0.95</td>
<td>98.61</td>
<td>0.44</td>
<td>100</td>
</tr>
</tbody>
</table>

It can be concluded from Table 2 that the copper in the raw ore mainly existed in three ways: Copper oxide, copper sulfide, and bound copper. It can be seen from Table 2 that the ore belonged to sulphide ore, in which the primary copper could be effectively recovered by flotation, while most of the copper oxide and bound copper were difficult to be recovered by flotation, and would be discarded in the tailing, which could have adverse effects on the yield and recovery of copper concentrate.

2.2. Methods

2.2.1. Ultrasonic pretreatment experiments

GS-040A ultrasonic equipment (Shenzhen Geneng cleaning equipment Co., Ltd.) was used to perform ultrasonic pretreatment on Z-200. The parameters for the ultrasonic pretreatment were ultrasonic power 240 W (10%-100% adjustable), heating power 500 W (normal temperature - 60℃), time control 1-99 min, and capacity 10 dm³. During the pretreatment, first, an appropriate amount of Z-200 was put in the beaker and placed in the cleaning tank. Then, according to the experimental design (As shown in Table 3), the output power and pretreatment time were adjusted, and the ultrasonic pretreatment experiments were started (Wang et al., 2020). Finally, the Z-200 after the ultrasonic pretreatment was removed from the cleaning tank for the subsequent flotation experiments and the related solution quality inspection. It should be noted that the study was not focused on the conditional experimen of the decay time, therefore, the solution could be tested immediately after the ultrasonic treatment was completed to reduce the experimental error. The reagent treatment conditions during the flotation experiments were the same as above.

Table 3. Experimental conditions for ultrasonic pretreatment

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Z-200 dosage (cm³)</th>
<th>Ultrasonic pretreatment conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Processing time (min)</td>
</tr>
<tr>
<td>A</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>B₁</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>B₂</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>B₃</td>
<td>5</td>
<td>15</td>
</tr>
<tr>
<td>B₄</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>C</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>D</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>E</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>
2.2.2. Roughing chalcopyrite flotation experiments

In the study, a 1.5 dm³ single-slot flotation machine (China Wuhan lock grinding equipment manufacturing Co., Ltd.) with the rotating speed of 2100 rpm was used for the chalcopyrite rough flotation experiments. In each experiment, the chalcopyrite 500 g and appropriate water were placed into the flotation cell to adjust the pulp concentration to 33%. Then, CaO (Analytical grade), sodium silicate (Analytical pure), and Z-200 (Industrial grade) pretreated by the ultrasonic process were added to the pulp in turn, and the slurry was mixed. Finally, the foam products were filtered and dried, and the recovery after the weighing was calculated. The flowsheet for the flotation experiments is shown in Fig. 1.

![Flowsheet for roughing chalcopyrite flotation experiments](image)

Fig. 1. Flowsheet for roughing chalcopyrite flotation experiments

2.3. Sample characterization

2.3.1. Viscosity measurements

Haake Mars 40 rotary rheometer (Thermo scientific) was used to understand the effect of different ultrasonic pretreatment conditions on the viscosity of Z-200. First, Z-200 after different ultrasonic pretreatment conditions was added to the container, pre-sheared at 150 s⁻¹ for 60 s, and stabilized the slurry for 10 s at 0 s⁻¹. Secondly, the shear rate and shear time were adjusted to 150 s⁻¹ and 60 s, respectively, and then started to measure the shear rate and shear stress. Finally, 100 data was obtained, and the few points with larger errors were removed, and the remaining points were calculated average value.

2.3.2. Surface tension measurements

QBZY-2 series automatic surface tension meter (Shanghai Fangrui Co., Ltd.) was used to understand the effect of different ultrasonic pretreatment conditions on the surface tension of Z-200. To reduce the measurement error, the average value of five recorded data was taken as the final result during the measurements.

2.3.3. Fourier transform infrared (FTIR) spectroscopy analysis

To understand the changes of functional groups of Z-200 after different ultrasonic pretreatment conditions, the liquid film method was used to detect Z-200 by using a tensor27 Fourier transform infrared spectrometer (Bruker, Germany). First, two infrared window tablets were taken, and the Z-200 sample after the ultrasonic pretreatment was dripped on one window tablets. Secondly, covered it by another window tablets, moved back and forth slightly, and capillary action was used to form a uniform bubble-free liquid film. Finally, the prepared infrared window tablets were fixed to the sample holder for scanning test. The scanning range of the instrument was 400 ~ 4000 cm⁻¹, the minimum resolution was 0.09 cm⁻¹, and the precision of the wavenumber was 0.01 cm⁻¹ (Sun et al., 2020).

3. Results and discussion

3.1. Effect of ultrasonic pretreatment Z-200 on the flotation performance of chalcopyrite

The flotation experiments on the collection performance of Z-200 to chalcopyrite under different ultrasonic pretreatment conditions were carried out, and the results are shown in Fig. 2.
Fig. 2a shows that the recovery of roughing chalcopyrite flotation increased and then slowly decreased with the increase of ultrasound time. This indicated that the collector performance of Z-200 to chalcopyrite first strengthen and then weaken with the increase of ultrasound time. And, the recovery of roughing chalcopyrite flotation reached the maximum value of 75% when the ultrasound time was 5 min. At this time, Z-200 showed the best collector performance for the flotation of chalcopyrite. According to Fig. 2b, the recovery of roughing chalcopyrite flotation increased gradually with the increase of output energy. This showed that the collection performance of Z-200 for the chalcopyrite flotation increased with the increase of output energy. And, the recovery of roughing chalcopyrite flotation reached the maximum, and increased 24.44% compared with the untreated while the output power was 90%. Therefore, the ultrasonic pretreatment of Z-200 improve its collection performance for chalcopyrite significantly.

3.2 Effect of ultrasonic pretreatment on properties of Z-200 and mechanism analysis

3.2.1 Effect of ultrasonic pretreatment on the surface tension of Z-200

During the flotation process, the surface tension of the foaming agent will affect its foaming performance (Ding et al., 2013). The cavitation is accompanied when ultrasound act on liquid and the cavitation can produce high temperature and high pressure, which will affect the surface tension of the liquid (Wang et al., 2020). To understand the effect of different ultrasonic pretreatment conditions on the surface tension of Z-200, the surface value of Z-200 was measured as a function of ultrasound time, and the results are shown in Fig. 3.

![Fig. 2. Effect of Z-200 on the recovery of roughing chalcopyrite flotation before and after the ultrasonic pretreatment (The amount of chalcopyrite: 500 g, the pulp in solids ratio: 33 %, the mixing speed 2100 rpm, the dosage of CaO dosage: 500 g/Mg, the dosage of sodium silicate 500 g/Mg, the dosage of Z-200 30 g/Mg, output energy 70%, ultrasound time 5 min).](image)

![Fig. 3. Effect of ultrasonic pretreatment on the surface tension of Z-200 (Output energy 70%, ultrasound time 5 min).](image)
According to Fig. 3, the surface tension of Z-200 decreased first and then tended to be gentle with the increase of ultrasound time and the output energy. Compared with the untreated, the surface tension of Z-200 after ultrasonic pretreatment decreased. This was due to the high temperature, high pressure, and shock wave generated by cavitation when the ultrasonic propagates in the solution, which breaks the balance of the interaction between the molecules in the solution, reduces the inter-molecular gravitation and decreases the surface tension of the Z-200 (Wang et al., 2001).

### 3.2.3. Effect of ultrasonic pretreatment on the viscosity of Z-200

Viscosity has a great influence on the foaming performance of the surfactant. The increase of viscosity helps to improve the stability of the foam, and the decrease of viscosity is helpful to enhance the foaming property (Shi et al., 2011). To understand the effect of ultrasonic pretreatment on the viscosity of Z-200, the viscosity of Z-200 under different ultrasonic conditions was measured, and the results are shown in Fig. 4.

![Viscosity vs. Ultrasound Time](image)

**Fig. 4. Effect of ultrasonic pretreatment on the viscosity of Z-200 (Output energy 70%, ultrasound time 5 min)**

The viscosity of the solution is closely related to the internal energy of the liquid. The internal energy of the liquid is greater, the intermolecular attraction is lower, and the viscosity is lower (Huang et al., 2014). According to Fig. 4a, the viscosity of Z-200 decreased first and then increased slowly with the increase of ultrasound time. And, the viscosity of Z-200 was the smallest when the ultrasound time was 5 min. And, as seen from Fig. 4b that the viscosity of Z-200 gradually decreased with the increase of output energy. Compared with the untreated, the viscosity of Z-200 after the ultrasonic pretreatment was reduced. This was because the cavitation bubble generated when the ultrasonic cavitation effect in solution will generate instantaneous high temperature and high pressure inside the bubble when it collapses, and shock waves will be generated outside the bubble so that the internal energy of the liquid in the microscopic area around the hot spot increases, that is, the viscosity decreases (Huang et al., 2019).

### 3.2.4. Infrared spectrum analysis of ultrasonic pretreatment Z-200

When ultrasonic waves act on a liquid, cavitation will occur to form cavitation bubbles, and the high temperature and high pressure, shock waves, and microjets generated during the adiabatic collapse of cavitation bubbles will have a certain effect on the solution medium so that the solution state, composition and function or structural changes, etc. (Xue et al., 2008). To understand the effect of ultrasonic pretreatment on Z-200, the infrared spectrum of Z-200 before and after the ultrasonic pretreatment was characterized, and the results are shown in Fig. 5.

According to Fig. 5, it is known that the absorption peaks at wavenumber 2978 cm$^{-1}$ and 2875 cm$^{-1}$ in *Sample A* correspond to the C-H antisymmetric stretching vibration peaks and symmetric stretching vibration peaks of a methyl group in Z-200 respectively, the absorption peaks at wavenumber 2935 cm$^{-1}$ correspond to the C-H asymmetric stretching vibration peaks of the methylene group in Z-200, the absorption peaks at wavenumber 3450 cm$^{-1}$ represent the intramolecular hydrogen bond, the absorption peaks at wavenumber 3270 cm$^{-1}$ represent the amine stretching vibration peaks, and the infrared adsorp-
Fig. 5. The infrared spectrum of Z-200 under different ultrasonic pretreatment conditions (Output energy 70%, ultrasound time 5 min)

Optation peaks at wave numbers 1383 cm\(^{-1}\) and 1374 cm\(^{-1}\) represent the symmetric bending vibration peaks of methyl (Zhang, 2013). Compared with the untreated Sample A, it was found that the strength of methyl stretching vibration peak and amino stretching vibration peak of each sample after the ultrasonic pretreatment was enhanced, also, the amine absorption peak showed a trend of broadening, which indicated that the ultrasonic pretreatment of Z-200 could change its chemical environment. It is known from the literature that the methyl content will affect the collection performance of Z-200, and the amino content will affect the foaming performance of Z-200 (Gao et al., 2019). To further understand the influence of ultrasonic pretreatment on the collection performance and foaming performance of Z-200, and the research performed peak separation processing on the methyl stretching vibration peak and amine vibration peak of Z-200 before and after the ultrasonic pretreatment. The peak fitting diagrams of the Z-200 methyl group and amine group are shown in Figs. 6 and 8, respectively, and the result for the analyses are presented in Tables 7 and 9, respectively.

As shown in Fig. 6, the total absorption peak of Z-200 was composed of three peaks of C-H antisymmetric stretching vibration peak and symmetric stretching vibration peak in the methyl group and C-H asymmetric stretching vibration peak of the methylene group. Comparing with the untreated Sample A, it was found that the peak intensity of the methyl vibration absorption peak in Z-200 after the ultrasonic pretreatment increased.

Figure 7a shows that the relative proportion of the methyl in Z-200 increased first and then decreased slightly with the increase of ultrasound time. When the ultrasonic time was 5 min, the relative proportion of the methyl was the largest, which increased by 2.76% compared with the untreated Sample A. As can be seen from Fig. 7b that the relative content of the methyl of Z-200 increased gradually with the increase in the output energy. Compared to Sample A, the relative proportion of the methyl increased by 4.80% and 5.33%, respectively, when the output powers were 80% and 90%. This was due to the high temperature, high pressure, shock waves, and micro-jets generated by the formation of cavitation bubbles accompanied by ultrasonic cavitation during adiabatic collapse (Kowalski et al., 1978; Kang., 2008; Zheng., 2018), which destroyed the balance of interactions between Z-200 molecules, changes the solution properties of Z-200 and made the relative proportion of the methyl that play the role of collecting in Z-200 increase, that was, the collecting effect become better and the flotation performance was enhanced.

From Fig. 8 that the total absorption peak of Z-200 was composed of the amine group vibration absorption peak and the hydrogen bond vibration absorption peak. Compared with the untreated Sample A, it was found that the peak intensity of the amine group absorption vibration peak in Z-200 after the ultrasonic pretreatment increased.

As shown in Fig. 9a, the relative proportions of the amine group of Z-200 increased firstly and then tended to remain unchanged with the increase of ultrasound time. Compared with the untreated Sample A, the relative proportion of the amine groups increased by 14.23% and 13.74%, respectively, when the ultrasound time were 10 min and 20 min. According to Fig. 9b, the relative proportion of the amine group in Z-200 increased gradually with the increase of output energy. Compared to Sample A, the rela-
Fig. 6. Peak-fitting graph of the effect of ultrasound time and output power on Z-200 methyl group

Fig. 7. Effect of ultrasonic pretreatment with different conditions on the relative proportion of methyl area in Z-200 peak fitting graph (Output energy 70%, ultrasound time 5 min)
Fig. 8. Peak fitting diagram of the effect of ultrasonic time and output power on Z-200 amine groups

Fig. 9. Effect of ultrasonic pretreatment on relative proportions of amino groups in Z-200 peak fitting diagram under different conditions
tive proportion of the amine groups increased by 16.97% when the output power was 90%. This was due to the high temperature, high pressure, shock waves, and micro-jets generated by the formation of cavitation bubbles accompanied by ultrasonic cavitation during adiabatic collapse (Kowalski et al., 1978; Kang., 2008; Zheng., 2018), which destroyed the balance of interactions between Z-200 molecules, changed the solution properties of Z-200 and made the relative proportion of the amine groups that play the role of foaming in Z-200 increase, that was, the foaming performance become better and the flotation performance was enhanced.

4. Conclusions
In summary, the effect of ultrasonic pretreatment on the properties of Z-200 and its effect on the chalcopyrite rough selection was investigated. The following conclusions were drawn:

(1) Under the conditions of flotation machine rotation speed of 2100 rpm, CaO dosage of 500 g/Mg, sodium silicate dosage of 500 g/Mg, and Z-200 dosage of 30 g/Mg, ultrasonic pre-treatment of Z-200 under certain conditions treatment can significantly enhance the effect of sorting chalcopyrite.

(2) Ultrasonic pretreatment under certain conditions can reduce the surface tension and viscosity of Z-200, improve its foaming performance, and the greater the ultrasonic output power, the lower the surface tension and viscosity, the better the foaming performance.

(3) Ultrasonic pretreatment can enhance the rough separation effect of Z-200 on chalcopyrite. This is because the ultrasonic pretreatment can change the ratio of effective groups in Z-200 and increase the relative ratio of methyl and amine groups in Z-200, that is, the collection performance and foaming performance of Z-200 is enhanced.

(4) The research provides a new idea for improving the performance of Z-200 flotation and its separation effect on chalcopyrite and also provides a certain theoretical basis for expanding the application of ultrasonic technology in the field of flotation.

Acknowledgments
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