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Effects of ultrasonic pretreatment on the flotation behavior of galena with and without the presence of pyrite

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Abstract: Utilizing the ultrasonic pretreatment, flotation tests, ICP-OES, and XPS analysis, the effect of the different ultrasonic pretreatment methods on the flotation behavior of galena were investigated. The flotation recovery of galena was improved for pretreated single galena sample, which is mainly attributed to the efficient removal of the oxidized components and contaminants on the surface of galena by the acoustic cavitation. However, the flotation recovery of galena was decreased when pretreated mixture sample of galena and pyrite was used. Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) and X-ray photoelectron spectroscopy (XPS) results reveal that ultrasonic pretreatment facilitates the conversion of PbS to $Pb(OH)_2$ and $PbSO_4$. Besides, the flotation recovery of galena was affected to varying degrees when the galena was mixed with the pyrite of the different particle sizes in the ultrasonic pretreatment process. The reason is that the change in the surface area ratio of these two minerals affects the electrochemical reaction rate between galena and pyrite.

Keywords: galena, ultrasonic pretreatment, flotation, electrochemical reaction

1. Introduction

Ultrasonic is commonly employed during mineral processing to generate two physical phenomena: specific activation of acoustic cavitation and acoustic streaming. Acoustic cavitation occurs in a frequency range of 20-40 kHz, while acoustic streaming dominates at higher frequencies (400 kHz and 1 MHz in the ultrasonic and megasonic systems, respectively) (Aldrich et al., 1999; Cao et al., 2018; Mao et al., 2019). Previous work (Celik et al., 1989; Chen et al., 2015; Fang et al., 2020; Lv et al., 2020) have shown positive effect on flotation in many aspects by applications of acoustic cavitation, including improved attachment of mineral particles to air bubbles, increased flotation recovery, improvement of flotation rate, and selectivity. In addition, the effect of ultrasonic on bubble size, emulsification of reagents, desorption of reagents, and froth control among others have been also reported. The principle is that, as the wave frequency increases reaching high intensities such in ultrasound, the vibroacoustic waves can lead to acoustic cavitation, which causes bubble generation due to progressive pressure drop in each wave cycle as shown in Fig. 1. The bubbles begin to oscillate along the sound field in the first stage after a few cycles the bubbles reach a critical size at which they resonate in a nonlinear regime. This regime makes it difficult for the bubbles to expand to larger sizes, making the medium's response increasingly important, due to the inertial forces that cause shrinkage of the bubble in the compression cycle (Emin et al., 2009). Eventually the bubble collapses under considerable elevated pressure emanating from the medium (Fan et al., 2000). This implosion generates a supersonic micro-jet of fluid in the area where the bubble collapses. It has been shown that this micro-jet possesses great capacity to erode a surface which would remove contaminants on the surfaces of the particles, thus increasing the efficiency of the concentration process.

For example, Gurpinar et al. (2004) found that ultrasonic pretreatment of oily collectors induced

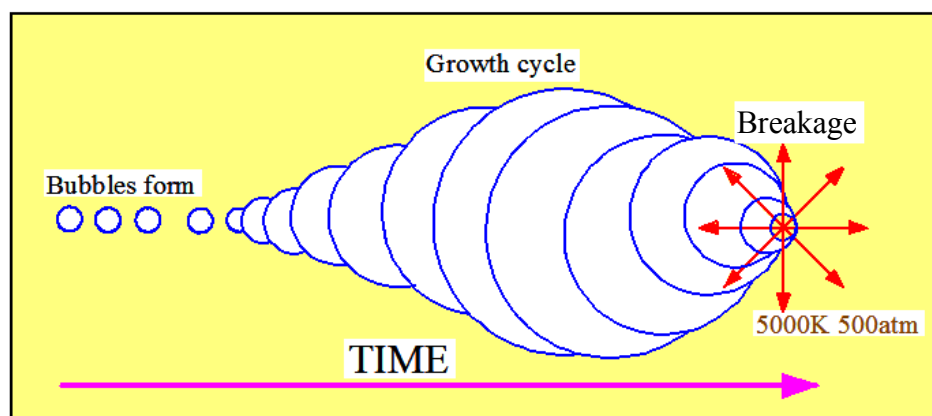


Fig. 1. Growth and breakage of cavitation bubbles

emulsification, which promoted the adsorption of these collectors on the mineral surface and reduced the consumption of collectors. In a study conducted by Kursun (2014), it was shown that both the grade and recovery of zinc concentrates were improved after ultrasound pretreatment. Lv et al. (2015) reported that acoustic cavitation produced by ultrasound could clean the surfaces of sulfide minerals to promote the flotation performance of the nickel sulfide. Compared to conventional flotation, Ozkan et al. (2002) found that ultrasonic pre-condition not only reduced the froth dimension but also improved the froth stability during magnesite flotation. The same group also found that ultrasonic pretreated coal yielded concentrates with higher combustible recovery and lower ash content as compared to that from traditional flotation methods at the same reagent dosages (Ozkan, 2012). Furthermore, Kang et al. (2009) observed that the surface charge properties of arsenopyrite were modified via ultrasound, which increased the floatability of high-sulfur coal.

Although many researchers have done a lot of research work on the effect of ultrasonic treatment on the flotation system, the main work are focused on a single sulfide mineral and oxide mineral flotation process. While the actual sulfide mineral flotation system often contains a variety of metal minerals, such as galena, chalcopyrite, and other valuable metal minerals associating with pyrite (Cheng et al., 1992; Gardner et al., 1979; Moslemi et al., 2011). Note that most sulfide minerals naturally possess semiconductor characteristics. In a mixture of two sulfides, one with the higher rest potential will act as the cathode while another with the lower rest potential will be the anode (Rao et al., 1988; Qin et al., 2015). For example, according to Hamilton and Rao's (Hamilton et al., 1981; Rao et al., 1989) conclusion, the interactions between a noble mineral such as chalcopyrite and an active mineral such as galena or sphalerite significantly affect the floatability of the noble mineral, and the effect on the active mineral is minimal. While in Ekmekci, Z. and H. Demirel's (1997) study, the interactions between chalcopyrite and pyrite affect the flotation behavior of both minerals, flotation of pyrite is promoted to some extent in the presence of chalcopyrite while chalcopyrite is decreased in the presence of pyrite. In the mixture system of galena and pyrite, galena is electrochemically more active than pyrite and serves as the anode in galvanic combinations with pyrite (Trahar et al., 1994; Qin et al., 2015). Although it did not change the oxidative and reductive products of galena when galena coupled with pyrite but increased the current density during the oxidation process (Eslami Andargoli et al., 2012; Qin et al., 2016). Flotation results showed that the presence of pyrite leads to an influence on the floatability of galena, which correlate with proportion of each mineral in the composition of sample (Jones et al., 2007; Kang et al., 2008).

As known, ultrasonic pretreatment in an aqueous solution can decompose the components in the solution (Kingman et al., 2004). It is well established that dissolved gas and water vapor in the cavitation bubble undergo thermal decomposition, resulting in the formation of OH^- and H^+ radicals (reaction 1). Such radicals can be involved in secondary reactions (reactions 2-5) (Ozkan et al., 2006; Shu et al., 2019). The occurrence of H_2O_2 and nascent oxygen can accelerate the galvanic interaction between the minerals. The effect of the electrochemical reaction is related to the increased dissolution of the active mineral. The metal ions hydrolyze forming hydroxo-complexes or precipitated hydroxides, which adsorb on the mineral surface, rendering the mineral hydrophilic (Ozkan et al., 2007). Besides, the high-temperature and high-pressure environment generated by the ultrasound in the solution may also lead

to chemical reactions that are difficult to trigger at normal temperature and pressure (Waters et al., 2007). Therefore, when the ultrasonic wave is applied to the slurry containing more than two kinds of metal sulfide minerals, the ultrasound may not only clean the oxide film on the mineral surface to facilitate flotation but also may harm flotation efficiency due to the acceleration of the electrochemical reaction which might trigger unknown chemical reactions. This may be one of the important reasons why ultrasonic technology is difficult to be successfully applied in the flotation system of the poly-metallic sulfide minerals.



To investigate the difference in the effect of ultrasonic pretreatment on flotation performance between single sulfide and the poly-metallic sulfides, microflotation experiments were carried out using single mineral sample and mixed binary minerals sample. In addition, the effect of ultrasonic treatment on the electrochemical reaction as well as surface properties were also studied by using ICP-OES (Inductive coupled plasma-optical emission spectrometry) and XPS (X-ray photoelectron spectroscopy) analysis.

2. Materials and methods

2.1. Sulfide mineral samples and reagents

Galena and pyrite samples obtained from Fankou (Guangzhou province, China) were pre-processed by a series of physical upgrading processes, such as hand selection, crushing, grinding, chemical analysis, and screening (Lu et al., 2020; Zheng et al., 2020; Xue et al., 2020). The chemical composition of galena and pyrite sample is shown in Table 1. Results of chemical composition show that the purity of the galena used is 97.41% and that it contains 84.36% Pb. The purity of the pyrite used is 93.07%, which contains 43.47% Fe. Pure minerals with different size fractions were obtained by the screening process. Galena with the particle size of 38-74 μm , pyrite with the particle size of -38 μm , 38-74 μm and 74-150 μm were used for flotation tests. ICP-OES and XPS analyses were conducted on galena with a particle size of 38-74 μm and pyrite with a particle size of -38 μm .

Table 1. Chemical composition of Galena and Pyrite (in mass fraction %)

Sample	Pb	Fe	Zn	S
Galena	84.36	0.25	0.29	13.05
Pyrite	0.05	43.47	0.01	49.60

Sodium diethylthiocarbamate (DDTC) ($\text{C}_5\text{H}_{10}\text{NNaS}_2$) and methyl isobutyl carbinol (MIBC) ($\text{C}_6\text{H}_{14}\text{O}$) purchased from Zhuzhou Chemical Reagent Co., Ltd., were used as the collector and the frother respectively. Calcium oxide (CaO) was used as the regulator. Deionized (DI) water (resistivity: 18.3 M Ω cm) was used in all experiments.

2.2. Ultrasonic pretreatment

Before the flotation tests, minerals were pretreated by ultrasound. The ultrasonic oscillators were equipped at the bottom of the glass beaker as showed in Fig. 2(a). The frequency of the ultrasonic transducer is 40 kHz. The power of the transducer is 80 W. With this transducer, the highest ultrasonic intensity in the pulp inside the beaker is 0.82 W/cm². During the ultrasonic pretreatment, the temperature of the pulp was controlled below 40°C to prevent minerals from being oxidized by limiting the pretreatment time as 5 min (Cao et al., 2017; Gungoren et al., 2017). The specification of the ultrasonic instrument is show in Table 2.

Table 2. Details of the ultrasonic instrument

Instrument	Model	Operating frequency(kHz)	Output power (W)	Highest ultrasonic intensity(W/cm ²)	Company
Ultrasonic cleaning tank	JP-010S	40	80	0.82	Jiemeng

To investigate the difference in the effect of the single galena and the galena with the presence of pyrite ultrasonic pretreated on flotation performance of galena, the different methods of ultrasonic pretreatment were adopted before flotation processes. Two different methods were used to pre-treat the single galena and a mixture of galena and pyrite, respectively, as showed in Fig. 2(b).

Method A: the Method A is about a single mineral treatment. 1 g of galena and 1 g of pyrite were weighed firstly and placed separately in a beaker filled with 50 mL of DI water. The galena and pyrite size depends on specific experimental requirements. The single galena and pyrite are pretreated by ultrasound in separate beakers. After ultrasonic pretreatment for 5 minutes, the pulp was filtered and washed three times with DI water to avoid interference of dissolved components on flotation, and then pyrite and galena were placed in a flotation cell for flotation experiments.

Method B: the Method B is about the mixed of binary minerals treatment. Galena with the particle size of 38-74 μm and pyrite with the particle size of -38 μm , 38-74 μm and 74-150 μm were employed. 1 g of galena and 1 g of pyrite were weighed firstly and placed together in a beaker filled with 100 mL of DI water. After ultrasonic pretreatment for 5 minutes, the mixture was filtered and washed three times with DI water, and then the flotation process was carried out on this mixture of pyrite and galena.

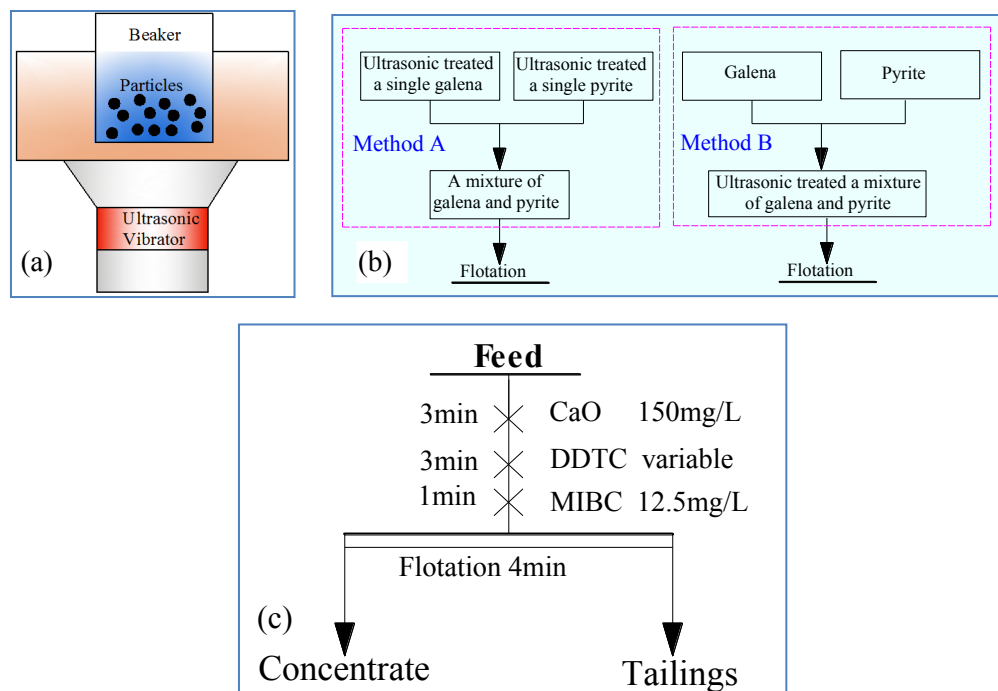


Fig. 2. Processes of the ultrasonic pretreatment and flotation tests (a - schematic diagram of the ultrasonic pretreatment device, b - the different methods of the ultrasonic pretreatment; c - flotation process)

2.3. Flotation tests

As shown in Fig. 2(c), the flotation tests were carried out in an XFG flotation machine with a 40 mL plexiglas cell (Changchun, China), at an impeller speed of 1800 rpm. First, either 2 g of single mineral powder with or without ultrasonic pretreatment, or 2 g of mineral mixture powder (1 g of galena and 1 g of pyrite) with the different method of ultrasonic pretreatment was placed into the Plexiglas cell filled with approximately 38 mL of deionized water. Then, the suspension was agitated for 3 min. After that,

a regulator CaO of 150 mg/L was added into the suspension. The suspension was agitated for 3 min. The pH value of the pulp is 10-11. Subsequently, the collector DDTC was added, and the suspension was agitated for 3 min. Afterward, a frother MIBC of 12.5 mg/L was added, and the suspension was agitated for another 1 min. The concentrates were collected for 5 min. After being filtered, dried, weighed, and chemical analysis. The recovery, and grade of galena concentrates from the flotation was obtained (Sui et al., 1995; Lu et al., 2020).

2.4. ICP-OES analyses

Inductive coupled plasma-optical emission spectrometry (ICP-OES; Perkin Elmer Optima 8300, USA) was used to determine dissolved ions concentration. To facilitate the separation of galena and pyrite from their mixture after ultrasonic pretreatment, and carry out XPS analysis on the single mineral subsequently, galena with particle size 38-74 μm and pyrite with a particle size of $<38 \mu\text{m}$ were used in ICP-OES analyses. Measurements were repeated three times, and the results show the average of concentrations from the triplicate assay. The processes of obtaining the supernatant of the single and the mixture sample are as follows:

1. Weighing 2 g of galena with 38-74 μm fraction and 2 g of pyrite with $<38 \mu\text{m}$ fraction respectively, placing in the different beaker filled with 100 mL of DI water, and each sample was carried out ultrasonic pretreatment according to the process of Method A (Fig. 2b). Centrifuging the two kinds of slurry at the rotation speed of 9000 r/min for 10 min respectively, the supernatants of two single minerals for ICP-OES measurement were obtained.
2. Weighing 1 g of galena with 38-74 μm fraction and 1 g of pyrite with $<38 \mu\text{m}$ fraction, placing together in a beaker filled with 100 mL of DI water, the mixed samples were pretreated by ultrasound according to the process of Method B (Fig. 2b). After the slurry was centrifuged at 9000 r/min for 10 min, the supernatant of the mixture was obtained for ICP-OES measurement.

2.5. XPS analyses

The XPS spectra of the ultrasonic pretreated samples were measured using a Thermo ESCALAB 250XI system (USA). For the single ultrasonic pretreated galena, it was washed three times with DI water, dried in a vacuum oven at 40°C until this sample became dry, and stored by filling nitrogen gas. For the ultrasonic pretreated mixture of galena and pyrite, firstly, the mixture was rapidly separated according to the particle size by using a 38-micron standard sieve. The single galena was obtained from over this sieve. This single galena was washed three times by using deionized water, dried in vacuum, and stored by filling nitrogen gas. Afterward, the prepared samples were used for XPS measurements. The C 1s peak was referenced to binding energy at 284.8 eV for calibration. Finally, the XPS spectra were analyzed by peak fitting software.

3. Results and discussion

3.1. Flotation results for the single mineral

The flotation recovery of the ultrasonic pretreated and raw galena samples as a function of DDTC dosage is shown in Fig. 3 at pH 10 - 11.

Fig.3 shows the effect of ultrasonic pretreatment on galena recovery using DDTC as a collector. With an increase in the dosage of DDTC, the recovery of galena increased. However, the flotation recovery of the non-pretreated galena was lower than that after using ultrasonic pretreatment. The recovery of the non-pretreated galena was 85.78% when the dosage of DDTC was 10 mg/L. The recovery rate of galena was slightly increased to 88.72% when the dosage of DDTC was continuously increased to 20 mg/L. After ultrasonic pretreatment, the recovery of galena was 91.50% when the dosage of DDTC was 10 mg/L. And the recovery of 92.74% was obtained when the dosage of DDTC increased to 20 mg/L. The reason may be that ultrasonic pretreatment can remove the oxide film from galena surface contacting with oxygen during sample preparation, thus improving the hydrophobicity of galena, and facilitating the adsorption of the reagents. That is probably the main reason for the increase of galena recovery after ultrasonic pretreatment. The research results are in good agreement with the literature reports (Videla et al., 2016; Cao et al., 2017).

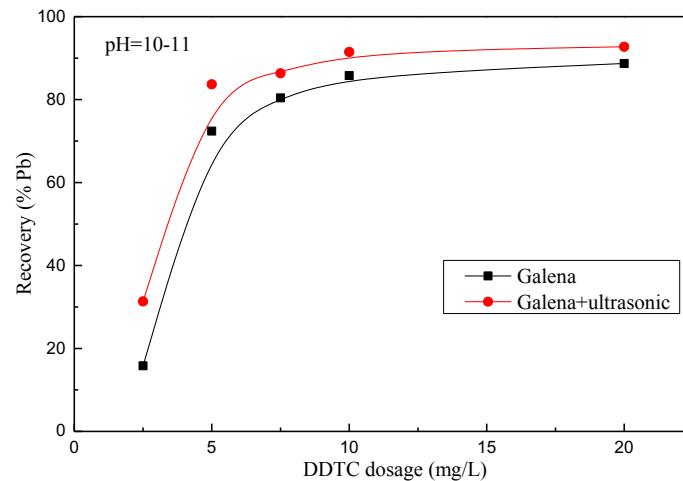


Fig. 3. Effect of ultrasonic pretreatment on the flotation recovery of the single galena

3.2. Effect of the single mineral and the mixture ultrasonic pretreated on the separation performance of galena

After the samples were processed by the ultrasonic pretreatment using Method A and Method B in Fig. 2(b), the flotation experiments were carried out follow the procedure in Fig. 2(c), and the results were shown in Fig. 4. With the increase of collector DDTC usage, the Pb recovery in flotation concentrate increased while the Pb grade decreased. However, although the two ultrasonic pretreatment methods in Fig. 2(b) both cleaned the mineral surface, the separation efficiency of the galena from Method A treatment was much higher than that of the galena from Method B treatment. After the sample was pretreated by Method A, a concentrate containing 74.22% Pb with a Pb recovery 91.21% was obtained when the dosage of DDTC was 10 mg/L. As the dosage of DDTC increased to 20 mg/L, the Pb grade and recovery of concentrates were 72.15% and 92.15%, respectively. There is little difference in the flotation performance of the galena without and with the presence of pyrite. It means when pyrite and galena were pretreated separately by ultrasound, the effect of pyrite on the flotation efficiency of galena is not obvious in the flotation process.

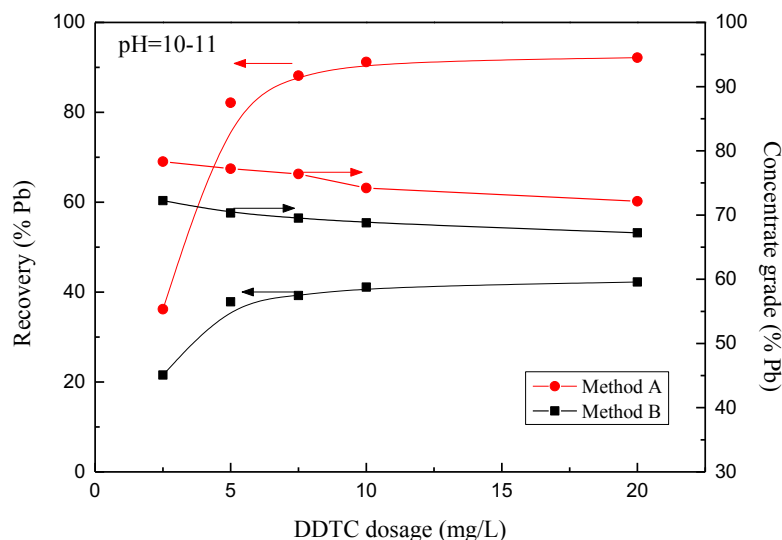


Fig. 4. Effect of the different ultrasonic pretreatment methods on the separation performance of galena from the mixture of galena and pyrite (Method A-the single galena and pyrite were pretreated by ultrasound firstly, and then they were mixed; Method B-galena and pyrite were mixed firstly, and then ultrasonic pretreatment was carried out)

However, the flotation efficiency of galena decreased significantly after the mixture of galena and pyrite was pretreated by ultrasound using Method B. A concentrate containing 68.78 % Pb with a Pb recovery 41.12% was obtained when the dosage of DDTC was 10 mg/L. As the dosage of DDTC increased to 20 mg/L, the Pb grade and recovery of the concentrates were 67.24 % and 42.24 %, respectively. Compared with the separation efficiency of galena from Method A treatment, the Pb recovery in the concentrate from Method B treatment reduced by more than half. Meanwhile, the Pb grade reduced by more than 5%. Note that the presence of pyrite reduces the hydrophobicity of galena during the ultrasonic pretreatment, thus reducing the flotation efficiency of galena.

3.3. Effect of the presence of pyrite with different particles size in ultrasonic pretreatment process on the separation performance of galena

In the actual flotation process, the galena often mixed with pyrite with different particle sizes (Awatey et al., 2013; Feng et al., 2019). The pyrite with different particle sizes has a different effect on the flotation efficiency of galena. Similarly, to study the effect of the presence of pyrite with different particle sizes in the ultrasonic pretreatment on the separation performance of galena, the pyrite with particle sizes of 74-150 μm , 38-74 μm and -38 μm were used. After the pyrite with the different particle sizes was mixed with the galena with 38-74 μm size respectively, the mixtures were subjected to the ultrasonic pretreatment according to the Method B process in Fig. 2 (b) and flotation tests according to the process in Fig. 2(c). The results are shown in Fig. 5.

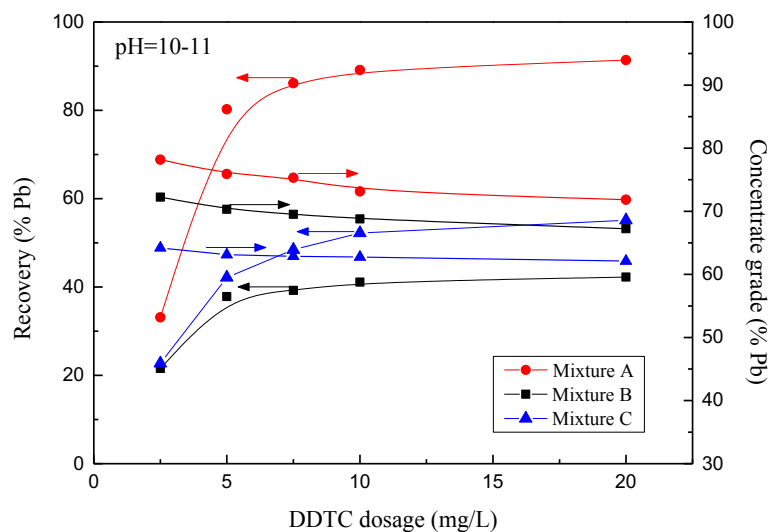


Fig. 5. Separation performance of galena as a function of the particle size of pyrite in ultrasonic pretreatment (Mixture A-galena particle size with 38-74 μm + pyrite particle size with 74-150 μm ; Mixture B-galena particle size with 38-74 μm + pyrite particle size with 38-74 μm ; Mixture C-galena particle size with 38-74 μm + pyrite particle size with -38 μm)

As can be seen from Fig. 5, in the ultrasonic pretreatment process, the effect of pyrite with different particle sizes on the flotation efficiency of galena was very significant. The pyrite particles with 74-150 μm size had the least influence on the flotation efficiency of galena, followed by the pyrite particles with -38 μm size, and the pyrite particles with 38-74 μm size had the greatest effect. Meanwhile, with the decrease of pyrite particle size, the Pb grade in the concentrate showed a downward trend. The main reason is that when a mixture of galena and pyrite is pretreated by ultrasound, the surface area ratio between galena and pyrite changes with the change of pyrite particle size, resulting in the difference in electrochemical reaction efficiency. Rao et al. (1989) found that the surface area ratio of anode mineral and cathode mineral would affect their electrochemical reaction speed, and he pointed out that the electrochemical reaction process can change by adjusting the surface area ratio of anode and cathode minerals. Therefore, when the surface area of pyrite and galena is close to 1:1, the speed of electrochemical reaction is the fastest, and the surface oxidation of galena is also the most serious, which

leads to a sharp decrease of surface hydrophobicity as well as the recovery of galena. It shows that the flotation recovery of galena is much easier to be affected by the pyrite when the particle size of pyrite is similar to the galena. Besides, hydrophobic agglomeration and mechanical entrainment between pyrite and galena become more significant when the pyrite particle size decreases in the flotation process. Therefore, the smaller the particle size of pyrite, the more significant the effect on the Pb grade in the concentrate.

3.4. Mineral dissolution analyses

It is well known that dissolution ions have played an extremely important role in mineral flotation from literature (Hughes et al., 1972; Bicak et al., 2018). The electrochemical reactions between galena and pyrite will lead to the dissolution of ionic components on the mineral surface. Fig. 6 describes the effect of ultrasonic pretreatment of the single mineral and the mixed minerals on the surface dissolution, such as lead ion, iron ion and sulfur ion on the surface of galena and pyrite, respectively.

After the ultrasonic pretreatment of galena alone, the dissolution amount of the lead ion and sulfur ion in the supernatant obtained were 0.3 mg/L and 0.1 mg/L, respectively. After ultrasonic pretreatment of pyrite alone, the dissolution amount of the lead ion and sulfur ion in the supernatant were 0.2 mg/L and 0.7 mg/L, respectively. After ultrasonic pretreatment of the mixture of galena and pyrite, the dissolution amount of the lead ion, iron ion and sulfur ion in the supernatant was 2.1 mg/L, 0.01 mg/L, and 0.6 mg/L, respectively. Compared with ultrasonic pretreatment of galena alone, the concentration of lead ions in the supernatant from the ultrasonic pretreated mixture was seven times higher than that from treatment of galena alone. At the same time, the dissolution concentration of iron ions decreased from 0.2 to 0.01 mg/L. The results show that in the ultrasonic pretreatment process of the mixture of galena and pyrite, the electrochemical reaction between galena and pyrite intensifies. As the anode, galena surface dissolution is accelerated, and the concentration of the lead ions increases in the solution. As the cathode, the pyrite surface dissolution is slowdown, thus the concentration of iron ions decreases in the solution (Nowak et al., 2000).

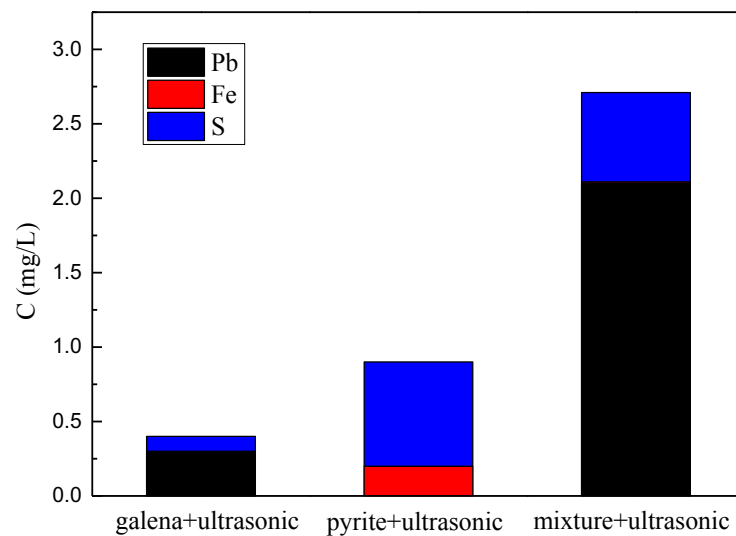


Fig. 6. Dissolution amount of elements of galena and pyrite as a function of the different ultrasonic pretreatment methods

3.5. XPS analyses

To further reveal the effect of the different ultrasonic pretreatment methods on the element contents of the minerals surfaces, XPS analyses were carried out. Fig. 7 presents the relative contents of several main elements on galena and pyrite surfaces from the different ultrasonic pretreatment methods.

Compared with the single galena ultrasonic pretreated, after the mixture of galena and pyrite was pretreated by ultrasound, the relative element contents of Pb and S on the galena surface decreased from 19.64% to 14.19% and from 21.00% to 16.20%, respectively. Meanwhile, the relative element

contents of O increased from 16.00% to 25.16%. But at the same time, there was a little change of the relative element contents on the surface of pyrite from the different ultrasonic pretreatment processes. As can be seen from Fig. 7, when galena and pyrite were mixed for ultrasonic pretreatment, the oxidation degree of the galena surface was much higher than that after ultrasonic pretreatment alone.

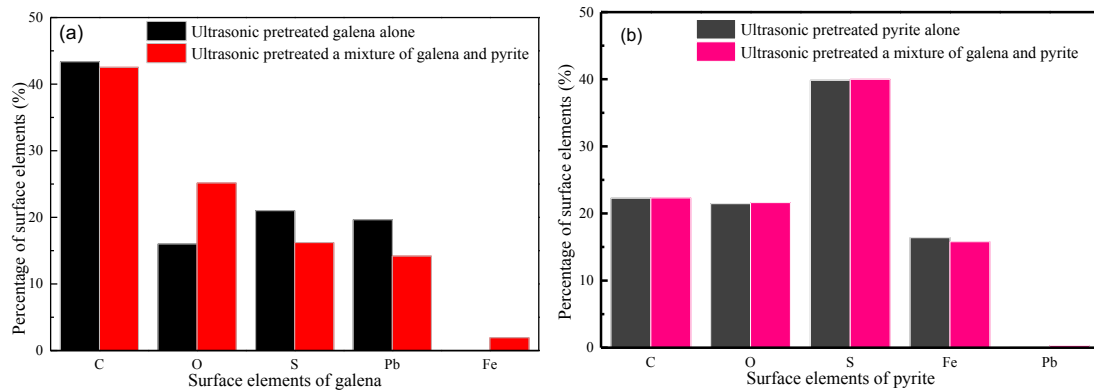


Fig. 7. The relative content of the surface elements on the galena and pyrite as a function of the different ultrasonic pretreated methods (a - galena; b - pyrite)

To reveal the effect of the different ultrasonic pretreatment methods on binding energy spectra of the galena surface's Pb4p, S2s, and O1s singles, the spectra of peak fitting separation and the corresponding data were presented in Fig. 8-10. As shown in Fig. 8, compared with the single galena ultrasonic pretreated, when the mixture of galena and pyrite was pretreated by ultrasound, two new peaks caused by PbSO_4 were observed at 139.2 eV and 144.1 eV (Fig. 8b), and the other two new peaks caused by Pb(OH)_2 were observed at 138.0 eV and 142.9 eV (Fig. 8c), respectively. Meanwhile, when the mixture was pretreated by ultrasound, it can be noted that the peak intensity caused by PbS was weaker than that of the galena ultrasonic pretreated alone. It indicates that galena and pyrite undergo an electrochemical reaction to generate PbSO_4 and Pb(OH)_2 during the ultrasonic pretreatment process of the mixture.

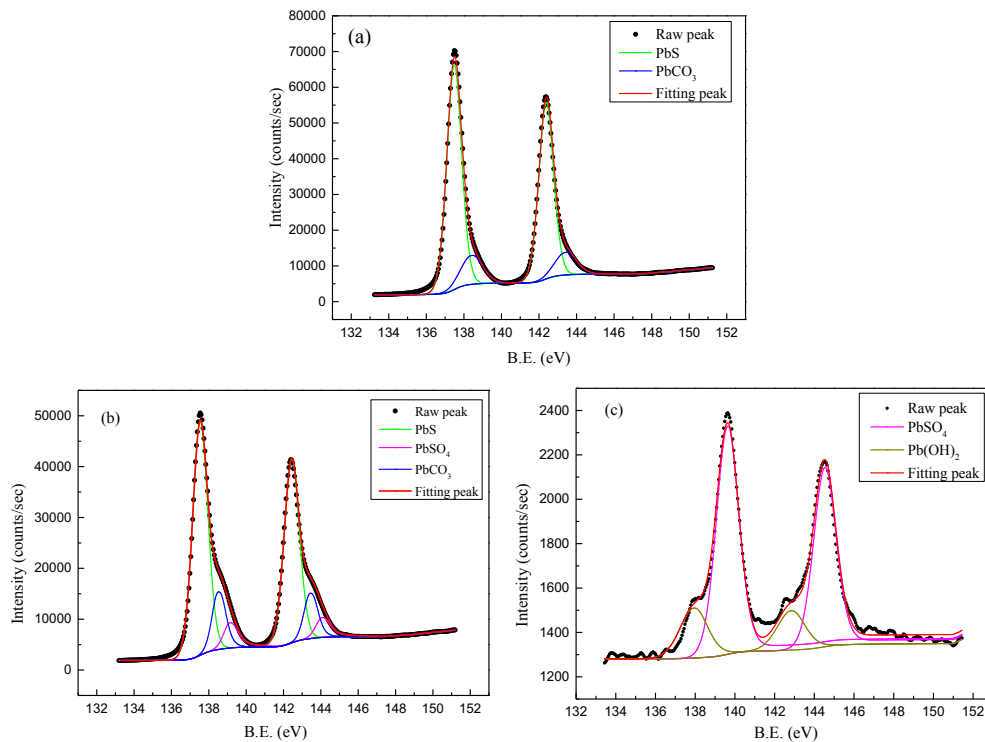


Fig. 8. X-ray photoelectron spectroscopy(XPS) fitting peaks for galena Pb 4p (a-ultrasonic pretreated galena alone; b, c-ultrasonic pretreated mixture of galena and pyrite)

As shown in Fig. 9, compared with the binding energy spectra of the galena surface's S2s singles, the new peak caused by PbSO₄ was observed at 232.5 eV (Fig. 9b) when that the mixture of galena and pyrite was pretreated by ultrasound. It shows that S²⁻ on the surface of galena was oxidized to SO₄²⁻ when the mixture of galena and pyrite was subjected to the ultrasonic pretreatment. The SO₄²⁻ and Pb²⁺ form PbSO₄ which may be absorbed on the surface of galena, and leads to a sharp decrease in hydrophobicity causing a decreased flotation recovery of galena. The peak caused by FeS₂ was attributed to the pollution of pyrite to galena during the ultrasound pretreatment process. Compared with the binding energy spectra of the galena surface's O1s singles, the new peak caused by PbSO₄ was observed at 531.4 eV, and the other new peak caused by Pb(OH)₂ was observed at 532.6 eV when the mixture of galena and pyrite was pretreated by ultrasound, as shown in Fig. 10. The binding energy spectra of the galena surface's O1s singles once again proved the conversion of PbS to PbSO₄ and Pb(OH)₂ during the ultrasonic pretreatment process (Nowak et al., 2010).

Besides, as shown in Fig. 11, the peaks caused by PbCO₃ appeared after the ultrasonic pretreatment. It is well established that dissolved gas and water vapor in the cavitation bubble undergo thermal decomposition, resulting in the formation of OH and H. Hydroxyl radicals react with CO₂ dissolved in water to generate CO₃²⁻, which reacts with Pb²⁺ to generate PbCO₃. The specific chemical reaction equations are as followed,

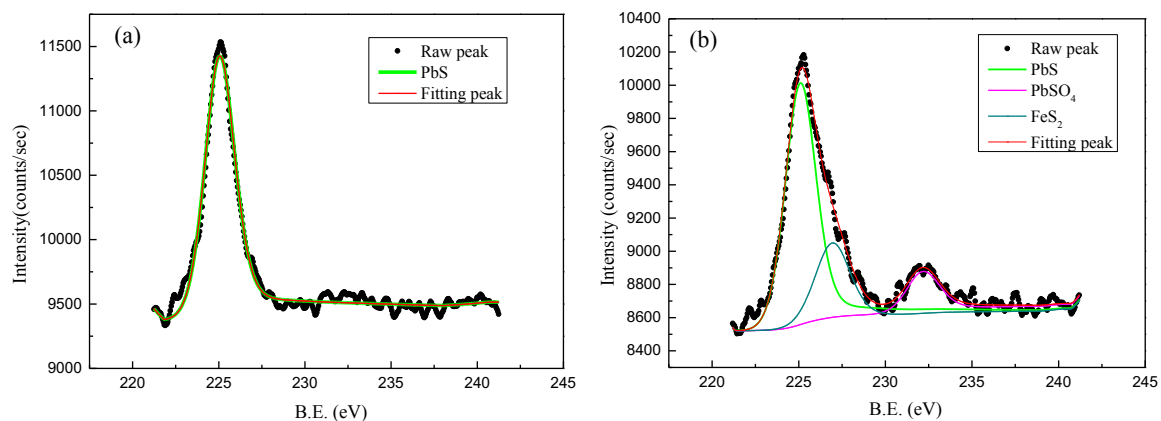


Fig. 9. X-ray photoelectron spectroscopy (XPS) fitting peaks for galena S 2s (a-ultrasonic pretreated galena alone; b-ultrasonic pretreated mixture of galena and pyrite)

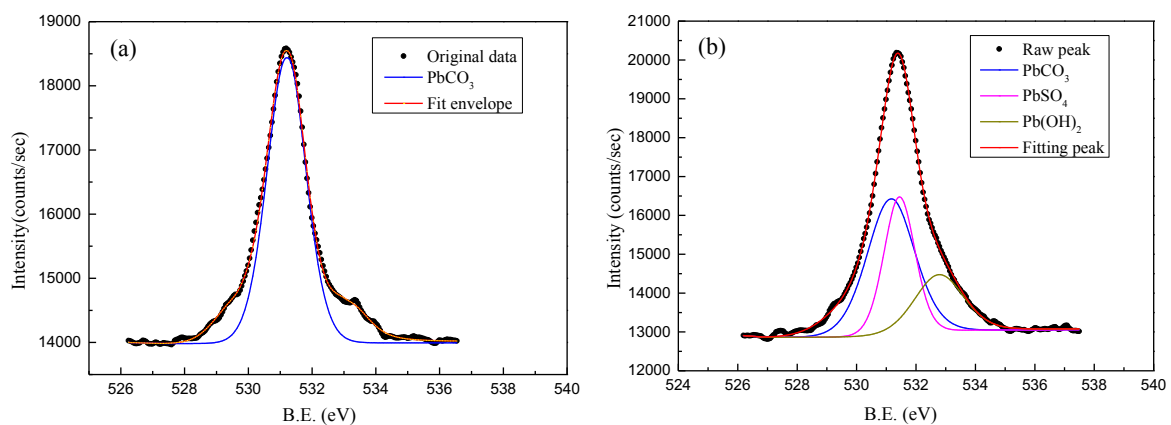


Fig. 10. X-ray photoelectron spectroscopy (XPS) fitting peaks for galena O 1s (a-ultrasonic pretreated galena alone; b-ultrasonic pretreated mixture of galena and pyrite)

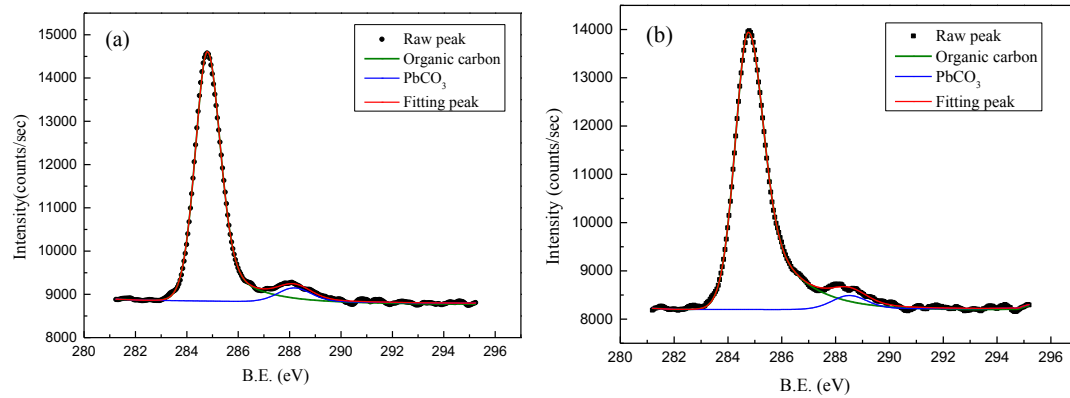


Fig. 11. X-ray photoelectron spectroscopy (XPS) fitting peaks for galena C 1s (a-ultrasonic pretreated galena alone; b-ultrasonic pretreated mixture of galena and pyrite)

3.6. The model of electrochemical reactions between galena and pyrite in ultrasonic pretreatment process

Based on the results discussed above, a possible model of electrochemical reactions between galena and pyrite in the ultrasonic pretreatment process was proposed and illustrated in Fig. 12. Note that ultrasonic pretreatment releases a large but localized burst of energy, accompanied by high pressures (up to 50MPa), and temperatures (up to 5000 K) (Aldrich et al., 1999; Shu et al., 2019). The ultrasonic wave not only improves the intensification of electrochemical reaction between galena and pyrite but also promotes the conversion from S^0 to SO_4^{2-} , as shown in reactions 11-13, which are difficult to perform at normal temperature and pressure. Thus, a large number of lead oxides, such as $PbSO_4$ and $Pb(OH)_2$, were generated on the galena surface, which leads to a decrease of galena's hydrophobicity. It is an important reason why ultrasonic pretreatment technology is difficult to be applied in the flotation processes of the poly-metallic sulfide minerals.

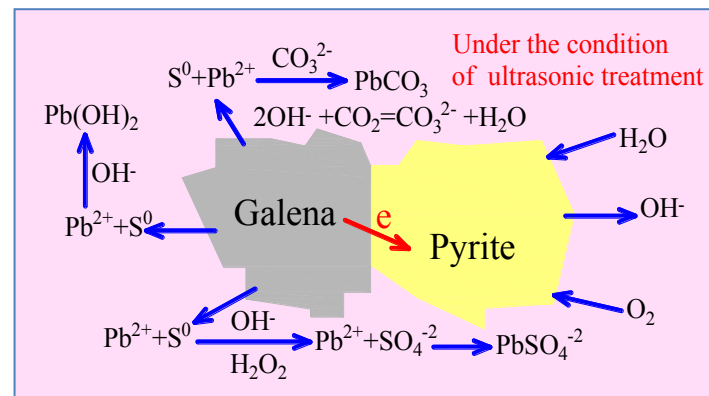
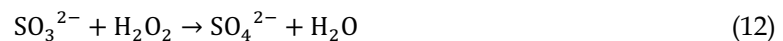
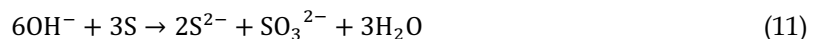


Fig. 12. Model of chemical reactions between galena and pyrite in ultrasonic pretreatment process



4. Conclusions

This study examined the galena with or without pyrite ultrasonic pretreated on the separation efficiency of galena, via performing comprehensive flotation tests, along with ICP-OES, and XPS analyses. The main conclusions are as follows:

(1) After the single galena pretreated by ultrasound, the recovery of galena increased. However, after the mixture of galena and pyrite pretreated by ultrasound, the recovery of galena decreased.

(2) In the ultrasonic pretreatment process, the effect of pyrite with different particle sizes on the flotation efficiency of galena is quite different. When the particle sizes of pyrite and galena are close to 1:1, the speed of electrochemical reaction is the fastest, which leads to a sharp decrease in surface hydrophobicity of galena.

(3) Ultrasonic pretreatment not only improves the intensification of electrochemical reaction between galena and pyrite but also promotes the conversion from S^0 to SO_4^{2-} , which is difficult to realize at normal temperature and pressure. A large number of lead oxides generated, such as $PbSO_4$ and $Pb(OH)_2$, which lead to a sharp decrease in hydrophobicity of galena.

Further studies are required to investigate the effects of ultrasonic's power, frequency, intensity, and time on the flotation efficiencies of galena after the mixture pretreated by ultrasound. Besides, the effect of ultrasonic pretreatment on the flotation efficiencies of other poly-metallic sulfides will also be studied.

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