Effect of particle size on the oxidation and flotation behavior of galena particles

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Abstract: The aim of this study was to determine the effect of particle size on the oxidation and flotation behavior of galena particles. Coarse (-0.074+0.038 mm), intermediate (-0.038+0.025 mm) and fine (-0.025 mm) galena particles were used in this study. Dissolution tests demonstrated that the amount of oxidation products increased with the decrease of particle sizes. The surface oxidization of galena was the greatest at pH 7.3, followed by pH 12 and 9, which were consist with the result of XPS. The micro-flotation results indicated that the effect of pH on the flotation recovery of galena enhanced with the reduction of particle sizes. The decreasing of particle sizes increases both the sorption rate of collector and the dissolution of galena, while the generation of hydrophilic product caused by dissolution is dominant, rendering the mineral hydrophilic. This study shows the differences in the surface oxidation and flotation behavior of different size fractions of galena particles. To promote the flotation recovery of the fine size fraction of galena particles, alleviating their oxidation is the key.

Keywords: galena; particle size; surface oxidation; flotation behavior

1. Introduction

Galena is one of the commonest sulfide minerals and it is usually associated with other sulfide minerals such as sphalerite and pyrite (Mernagh and Trudu, 1993). Galena has been shown to be the most easily ground mineral within the complex Pb–Zn–Cu ores (Cveticanin et al., 2012), which results in the overgrinding of galena during the conventional grinding process; thus, large amounts of fine galena particles may exist in the flotation pulp. As is known, the mineral flotation response decreases substantially when the mineral particles are present in the fine size range, because of the collapse of the probability of collision and adhesion of solid particles to air bubbles (Song et al., 2000). In addition, particle size has been found to be an important factor in geochemical processes, thus, much research has been conducted to study the effects of particle size on floatability (Trahar, 1976; Loewenberg and Davis, 1994; Polat and Chander, 2000; Cveticanin et al, 2015; Leistner, 2017). However, these studies have paid little contention to the oxidation of differently sized galena particles.

The surface oxidation of galena has been object of countless studies. Oxidation of the galena surface is of crucial importance in environmental and geochemical processes and extraction technologies (Alpers, 1994; Ndzbet et al., 1994). In addition, almost every new surface analytical method, including Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and Raman spectroscopy, has been applied to study the oxidation of the galena surface (Fornasiero et al. 1994; Nowak et al., 2000; Nowak and Laajalehto, 2000; Shapter et al., 2000; Chernyshova, 2013; Mikhlin et al., 2015). For base metal sulfide minerals, such as galena and pyrite, oxidation may accelerate mineral dissolution. Therefore, the solubility, or dissolution rate, of minerals is a critical property for predicting the fate of minerals and dissolved species in the environment. Further, it is generally accepted that fine particles enhanced solubility (Stober and Arnold, 1961; Peng and Grano,

2010). Some investigations have examined the effect of pH values on the dissolution of the galena surface (Hsieh and Huang, 1989; Fornasiero et al., 1994). Hsieh and Huang (1989) found that the dissolution of galena was drastically influenced by pH and that the amount of dissolved Pb^{2+} decreased rapidly with increasing pH (pH values ranged from 2.5 to 9). However, few studies have considered the dissolution of differently sized galena particles in a highly alkaline solution.

In industrial practice, many of the fine (-0.025mm) galena particles are lost in the mine tailings, which results in a waste of lead resources. This study describes the difficulty of recovering fine galena particles and provides an important finding for the utilization of galena resources, and the oxidation and flotation behavior of three different size fractions of galena particles, coarse (-0.074+0.038 mm), intermediate (-0.038+0.025 mm) and fine (-0.025 mm), are discussed.

2. Materials and methods

2.1. Minerals

The highly mineralized galena sample used in this study was obtained from the Yiliang Mine, Yunnan Province, China. After the manual removal of gangue minerals, the galena samples were prepared by dry hand-grinding in an agate mortar and pestle and by screening into three different particles size fractions, i.e., -0.074+0.038 mm, -0.038+0.025 mm and -0.025 mm. The specific surface area of these different size fractions measured by Multipoint BET method using nitrogen was 0.061, 0.12 and 0.812 m^2/g, respectively. A detailed description of the mineral samples can be found in Table 1.

All inorganic reagents used in this study were of analytical grade, and the ethyl xanthate was of industrial purity. Ultrapure water with a resistivity of 18.25 $M\Omega/cm^{-1}$ was used throughout the study.

Table 1. Chemical composition of the galena samples (%)

Pb	Zn	Fe	S	SiO_2
85	0.07	0.46	14.14	< 0.50

2.2. Dissolution tests

A 1.0 g sample of each of the differently sized galena particles was added to three 50 cm^3 reaction vessels with 20 cm^3 of ultrapure water. The temperature of the suspensions was kept constant at 25 °C by a thermostatically controlled water bath, and the pH of the suspensions was adjusted using HCl or NaOH solutions. A magnetic stirrer was used for stirring the suspensions at a speed of 800 rpm.

After conditioning for the given time intervals, the suspensions were centrifuged at 500 rpm for 10 min. The solids at the bottom of the centrifuge tubes were obtained and subjected to EDTA extraction or XPS measurement. Then, the Pb^{2+} concentrations of the aqueous solutions were analysed using an F type atomic absorption spectrophotometer (AAS).

2.3. EDTA extraction

EDTA extraction has been proven to be an important technique to study the dissolution and oxidation of base metal sulfides due to its selectivity in extracting metals from oxidation products instead of sulfides (Peng and Grano, 2010). The amounts of lead ions adsorbed onto the galena surfaces were measured by ethylene diamine-tetra acetic acid disodium salt (EDTA) extraction. A 3% solution of analytical grade EDTA was prepared and a sodium hydroxide solution was used to adjust the pH to 7.5. For each measurement, 100 cm^3 of the EDTA solution was placed in a vigorously stirred reaction vessel and continuously purged with nitrogen for 10 min to eliminate oxygen from the solution. Then, a solid sample was added to the EDTA solution and leached for 10 min under continuous N_2 purging. The slurry was then processed in a centrifuge at 3000 rpm, the concentration of lead ions in the supernatant was analysed using an F type atomic absorption spectrophotometer, and the solids were retained to obtain the dry weights and calculate the sorption of per unit of mass solid.

3.   Results and discussion

3.1. Mineral dissolution

The concentration of Pb^{2+} is an important indicator of the surface oxidation of galena. To investigate the oxidation of the three different size fractions of galena, the concentrations of Pb^{2+} both in solution and presented at the mineral surface were considered. Therefore, the total amount of dissolved lead ions should be the sum of the dispersed Pb^{2+} in aqueous solution and the lead present at the surface. These results are shown in Fig.2.
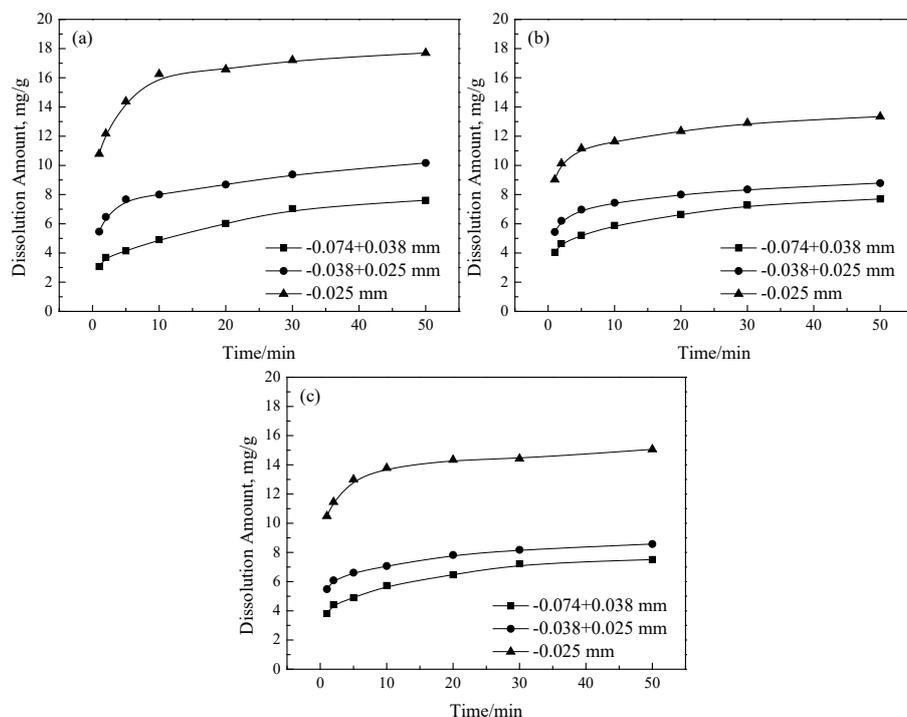
Fig. 2. The total amount of Pb^{2+}released from the galena surface at (a) pH = 7.3, (b) pH = 9 and (c) pH = 12

Fig. 2 shows that for these three different size fractions of galena particles, the total amount of Pb^{2+} released from the galena surface increased with increasing dissolution time until reaching a plateau. As seen, the galena dissolution was strongly dependent on the particle size, and the amount of lead oxidation products produced during dissolution increased following the decreasing of particle sizes. For example, when the dissolution time was 30 minutes in Fig. 2(a), the fine galena particles produced approximately 2 times more lead (mg/g) than did the coarse and intermediate particles. This behavior should be attributed to the smaller size and higher reactive surface area per unit volume in galena nanocrystals (Liu et al., 2008).

These results also illustrated that pH value played an important role in the oxidation of galena. For coarse (-0.075+0.038 mm) galena particles, pH effect was so small that it was unnoticeable. However, for the intermediate (-0.038+0.025 mm) and the fine (-0.025 mm) galena particles, pH had a significant influence on the oxidation of the galena, especially for the fine galena particles. Under neutral and slightly alkaline (pH=9) conditions, the surface of the galena is covered by a monolayer of OH groups, which would make the surface hydrophilic (Lam-Thi et al, 1984; Ndebet et al., 1994; Chernyshova, 2003), thus, the main oxidation product on the galena surface may be PbOH (Fornasiero et al., 1994). For the fine and intermediate galena particles, from pH 7.3 to 9, there was a decrease in the dissolution of the galena surface, which was consistent with the results of previous studies (Hsieh and Huang, 1989; Fornasiero et al., 1994). However, some research findings on the oxidation of galena in alkaline solutions have shown that a compound covering may form on the galena surface (Goryachev et al, 2010; Goryachev and Nikolaev, 2012; Goryachev and Nikolaev, 2012), which indicates that more oxidation occurs on the galena surface in strongly alkaline solutions (pH>11), resulting in an increase of the

dissolution of the galena surface. Thereto, PbOH and thiosulfate-ions are the products formed by galena oxidation in strongly alkaline solutions (pH>11), according to the results of Goryachev (Goryachev et al, 2010).

3.2. XPS study

Galena oxidation and dissolution have been studied previously (Fornasiero et al., 1994; Peng and Grano, 2010). Some authors stated that metal sulfides, like metal oxides, undergo the surface hydration (or surface hydrolysis) in an aqueous solution (Forsling and Sun, 1997). In this study, XPS was used to determine the lead from sulfide and oxidation products. Coarse, intermediate and fine galena particles were analyzed by XPS after dissolution. Fig. 3 presents the O 1s spectra of three different size galena fractions after dissolution at pH 7.3, 9 and 12.
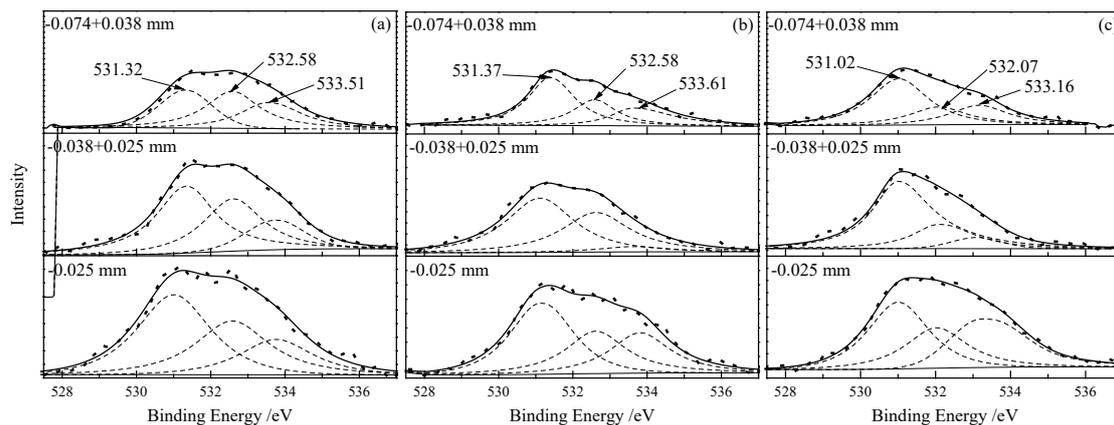
Fig. 3. The curve-fitted O 1s spectra of galena after dissolution at (a) pH = 7.3, (b) pH = 9 and (c) pH = 12

Table 2. XPS surface species and their atomic concentrations on galena particles after dissolution

pH	Species	Concentration (%)		
		Coarse	Intermediate	Fine
7.3	S_{2p}	33.43	31.43	20.24
	Pb_{4f} at 137.4 eV	19.92	14.06	5.42
	Pb_{4f} at 138.6 eV	2.48	5.87	10.77
	O_{1s}	44.17	48.64	63.57
9	S_{2p}	36.64	32.16	29.33
	Pb_{4f} at 137.4 eV	20.04	16.42	10.66
	Pb_{4f} at 138.6 eV	2.3	3.75	5.59
	O_{1s}	41.02	47.67	54.42
12	S_{2p}	34.18	30.76	25.43
	Pb_{4f} at 137.4 eV	19.6	15.44	7.98
	Pb_{4f} at 138.6 eV	2.45	5.22	8.88
	O_{1s}	43.77	48.58	57.71

Note: "Coarse" means particles -0.075+0.038 mm; "Intermediate" means particles -0.038+0.025 mm; "Fine" means particles -0.025 mm.

On the galena surface, the peak of the O 1s spectra at binding energy of 531.0-531.5, 532.0 and 532.6 are identified as the PbOH, PbS_2O_3 and $Pb(OH)_2$ respectively (Fornasiero et al., 1994; Nowak et al., 2000), and both physically adsorbed water and oxygen-containing organic contamination give the O 1s emission at higher BE (above 533 eV). Therefore, the result from Fig. 3 indicated that these three different size fractions of galena shared the same oxidation producs under the same condition, while the amount of oxidation products increased with the decreasing of particle sizes. Besides, the lead oxidation species on the galena surface were PbOH and $Pb(OH)_2$ for low pH conditioning values (pH=7.3 and 9), while for high conditioning pH values (pH=12), PbOH and thiosulfate-ions were formed in products of galena oxidation. The results were consistent with previous studies (Hsieh and Huang, 1989; Fornasiero et al., 1994; Goryachev et al, 2010).

In order to straightforward present the effects of the particle sizes and pH values on the degree of oxidation on galena surface, the types of surface species and their concentrations on the galena particles at pH 7.3, 9 and 12 are reported in Table 2. The XPS Pb 4f spectrum is composed of a doublet. The lower binding energy peak is situated at 137.4 eV, which is attributed to lead sulfide, and the shoulder at 138.6 eV is attributed to PbOH or lead sulfate (Laajalehto et al., 1997; Peng and Grano, 2010).

The ratio of the lead concentration from the oxidation products to the total lead concentration on the galena surface is an indicator of galena dissolution. At pH 7.3, the ratios of these three different sizes of galena particles were 11.07%, 29.45% and 66.52%, respectively. However, the same ratios of the galena particles were 10.30%, 18.59% and 34.4% at pH 9. Their ratios were 11.11%, 25.27% and 52.67% under the highest alkali, respectively. Apparently, galena dissolution is strongly dependent on particle size. With a decreasing particle size, the galena dissolution rate increased dramatically, consistent with the results of the mineral oxidation tests.

3.3. Flotation tests

Flotation tests were carried out to investigate the influence of the particle size on the flotation behavior of galena with ethyl xanthate as the collector. The flotation recovery of the three different size fractions of galena particles as a function of pH are shown in Fig. 4.
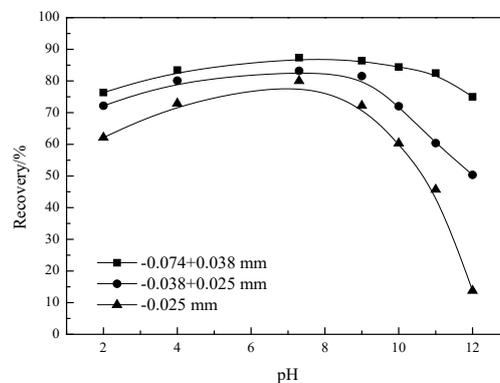
Fig. 4. Flotation behavior of the three different size fractions of galena

Fig. 4 shows the effect of pH on the flotation recovery of these three different size fractions of galena particles. As noted, the floatability of these three different size fractions was different, coarse (-0.074+0.038 mm) galena particles had the best floatability, followed by the intermediate (-0.038+0.025 mm) particles, and the fine (-0.025 mm) galena particles had the worst floatability.

It also illustrates that pH had significant influence on the flotation recovery of galena particles. The flotation behavior of these three different size fractions as function of pH is similar, although there is a large difference in the flotation amount. The flotation recovery of galena increased with increasing pH until it reached a maximum at the pH of approximately 7, and it then decreased in alkaline conditions. Under alkaline conditions, the competing sorption of hydroxyl and xanthate ions on the galena surface was the key factor influencing the flotation recovery of the fine size fraction of galena particles. Generally, the smaller the galena particles were, the more strongly they were influenced by pH of the pulp.

3.4. Sorption tests

The influence of particle size on sorption rate of ethyl xanthate was investigated at pH 7.3, 9 and 12, as illustrated in Fig. 5. It is obvious in Fig. 5 that the sorption rate of fine size fraction was much higher than coarse and intermediate size fractions under the same conditions.
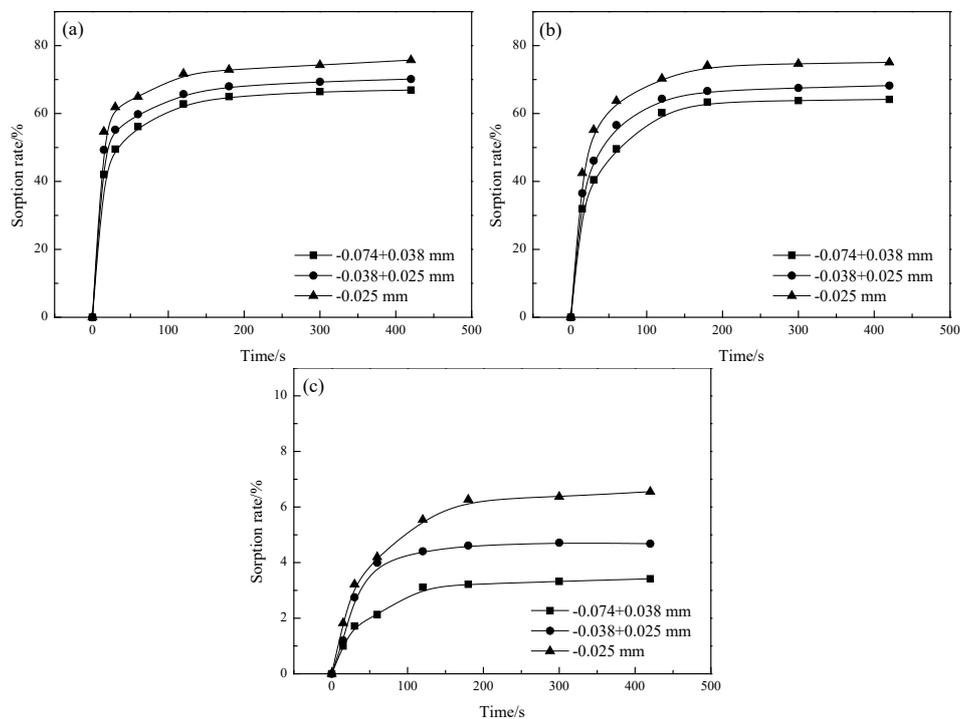
Fig. 5. Sorption of ethyl xanthate on the three different size fractions of galena at (a) pH = 7.3, (b) pH = 9 and (c) pH = 12

To better understand the influence of particle sizes on the sorption rate of ethyl xanthate, the specific surface area of should be taken into account, because the rate of sorption is proportional to the specific surface area. The specific surface area of these three different size fractions of galena was 0.061, 0.12 and 0.812 m²/g, respectively. Hence, the sorption rate of fine size fraction should be at least by 13 times higher than the sorption rate of coarse size fraction. However, the sorption rate, in case of the fine size fraction was by only approximately 10% higher than in the case of coarse size fraction. Considering the results of dissolution and XPS analysis, the amount of oxidation products formed on the surface of galena increased with the decrease of the particle sizes, and PbOH seemed to be the dominant lead species on the surface. The metal ions hydrolyzed to form hydro-complexes or precipitated hydroxides, which adsorbed on the mineral surface, may have counteracted the adsorption of collector and rendered the mineral surface hydrophilic (Zhang et al., 1997). In addition, some researchers have found that oxygen species formed in galena oxidation in aqueous solution are very strongly bound to the surface and cannot be replaced completely by the flotation collector (potassium ethyl xanthate) even if extremely high concentrations of the collector are used (Laajalehto et al., 1993). Therefore, the decreasing particle sizes increase both the sorption rate of collector and the dissolution of galena, while the generation of hydrophilic product caused by dissolution is dominant, rendering the mineral hydrophilic.

4. Conclusions

During dissolution, the amount of oxidation products increased with the decrease of particle sizes. In addition, the pH values played an important role in the oxidation of galena, especially for the fine galena particles. For the fine galena particles, the oxidation was the strongest at pH 7.3, followed by pH 12 and 9. The results of XPS analysis were consistent with the dissolution results. XPS test also illustrated that for low pH conditioning values (pH=7.3 and 9), the lead oxidation species on the galena surface were

PbOH and Pb(OH)$_2$, while PbOH and thiosulfate-ions were formed in products of galena oxidation for high conditioning pH values (pH=12).

The flotation behavior and sorption rate of galena were strongly dependent on the particle size and pH values. During flotation tests, the effect of pH on the flotation recovery of galena increased with the decrease of particle sizes. The decreasing of particle sizes increases both the sorption rate of collector and the dissolution of galena, while the generation of hydrophilic product caused by dissolution is dominant, rendering the mineral hydrophilic.

Acknowledgments

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