An innovative flotation technology for the lime-depressed pyrite recovery from copper sulphide ore via acid mine drainage (AMD) activation

Jiaqiao Yuan [1], Zhan Ding [1], Yunxiao Bi [1], Jie Li [1], Shuming Wen [1,2,3], Shaojun Bai [1,2,3]

[1] Faculty of Land Resource Engineering, Kunming University of Science and Technology, Kunming 650093, Yunnan, China

[2] State Key Laboratory of Complex Nonferrous Metal Resources Clean Utilization, Kunming University of Science and Technology, Kunming 650093, China

[3] Yunnan Key Laboratory of Green Separation and Enrichment of Strategic Mineral Resources, Kunming 650093, China

Corresponding author: baishaojun830829@126.com (Shaojun Bai)

Abstract: In this study, an innovative flotation technology consisted of Cu differential flotation with high alkali lime and pyrite recovery with acid mine drainage (AMD) activation was investigated for the cleaner beneficiation of the copper sulfide ore. Flotation test results showed that H_2SO_4-$CuSO_4$ and AMD could effectively activate the pyrite flotation with SBX collector. Moreover, the recovery of S concentrate is increased by 5.33% in the AMD system. Adsorption amount results of SBX collector indicated that the hydrophilic species (Ca^{2+}, $CaOH^+$ and FeOOH) were formed on the pyrite surfaces in the high alkali lime craft (pH=11.3) and degraded the interaction between SBX and pyrite surfaces. AMD can effectively clear off the hydrophilic calcium species and the copper ions originated from the AMD absorb onto the pyrite surfaces, facilitating the SBX collector adsorption. Composition analysis results of tailings water confirmed that the tailing water obtained by the AMD flotation system was more desirable to be recycled in the Cu differential flotation due to its higher pH value (8.7). The present study provides a novel approach for the treatment of AMD, and has the vital practical significance for the emission reduction of AMD and the increase of beneficiation profits.

Keywords: copper sulfide ore, acid mine drainage (AMD), lime-depressed-pyrite, activator, hydrophilic species

1. Introduction

The copper sulfide ore is an important copper source for the extraction and production of metal copper (Huang et al., 2012, Khoso et al., 2021). Generally, copper and sulfur in the copper sulfide ore are predominantly presented in the form of chalcopyrite ($CuFeS_2$) and pyrite (FeS_2) (Lü et al., 2018; Mu et al., 2016). During the beneficiation of copper sulfide ore, "Cu-S flotation separation" must be performed to produce a high-quality copper concentrate after the rejection of pyrite (Wang and Forssberg, 2002). At present, high alkali lime craft is widely applied for the Cu-S flotation separation, and the craft is usually performed on an extremely high pH>11 by adding large amounts of lime to depress the pyrite (Li et al., 2021; Li et al., 2012; Zanin et al., 2019). As a result, copper sulfide minerals are enriched in the copper concentrate, and the depressed-pyrite enters into the tailing. In the pursuit of profit maximization and cleaner production of copper sulfide ore, the recovery of depressed-pyrite is imperative. This has stemmed from the fact that the pyrite is one of the most important sulfur resources for the production of sulfuric acid. Besides, the recovery of pyrite can prevent the acid mine drainage (AMD) pollution originated from the oxidation of pyrite minerals once exposed to air and water (Altinkaya et al., 2018; Crundwell, 2021; Holmes and Crundwell, 2000; Mafra et al., 2020; Parbhakar-Fox and Lottermoser, 2015).

To enhance the flotation recovery of depressed-pyrite with xanthate collector, the activator is urgently needed. Assiduous efforts on the activator types and activation mechanisms of depressed-

pyrite from copper sulfide ore have been performed (Chandra and Gerson, 2009; Hu et al., 2000; Tang and Chen, 2020). Acids and copper ions are frequently applied to obtain an acidic solution for the activation of iron sulfides. The presence of acids can desorb the hydrophilic calcium and iron species from pyrite surfaces after the formation of soluble complexes or insoluble salts (Liu et al., 2018). Researches on pyrite activation with Cu^{2+} ions have shown a single fast step of copper adsorption onto the pyrite surface will occur (Boulton et al., 2003; Pecina et al., 2006; Weisener and Gerson, 2000; Wong et al., 2002). After acids and copper ions activation, dixanthogen and Cu-xanthates could be formed and were responsible for pyrite flotation (Deng et al., 2021; Leppinen, 1990; Shen et al., 2001). However, the main drawbacks of the above-mentioned methods are that plenty of acids and expensive toxic copper sulfate are added for the depressed-pyrite flotation, which will increase the mineral processing costs and pollute the surrounding environment. Thus, the development of cost-effective and environmentally friendly technologies to activate the lime-depressed-pyrite is of huge interest for cleaner beneficiation of copper sulfide ore.

Acid mine drainage (AMD) will be formed during the mining and transportation of copper sulfide ore after the oxidation dissolution of sulfide minerals (Johnson and Hallberg, 2005). It is well known that AMD's emissions will cause a lot of damage to ecosystems and human health (Igarashi et al., 2020; Jurjovec et al., 2002; Kaur et al., 2018; Nariyan et al., 2018). Therefore, growing interest is an AMD treatment in the past few decades. The treatment methods of neutralization, precipitation, oxygen wetland, ion exchange, and permeable reactive barrier are applied in real mining locations (Kaur et al., 2018; Masindi et al., 2015; Ňancucheo et al., 2018; Nariyan et al., 2018; Pat-Espadas et al., 2018; Tan et al., 2018). However, the available treatment methods are mainly focused on degrading the contents of H^+ ions, metal and sulfate ions of the AMD itself, and most of them are unsustainable because long-term monitoring and continuous supply of chemicals and energy for the affected ecosystems are inevitable. AMD contains acid and copper ions, which can be served as a natural activator for depressed pyrite flotation. The application of AMD in the beneficiation of pyrite can not only reduce the continuous supply of chemicals, but also provides easy access to the prevention of AMD pollution and environmental remediation.

Recently, we have studied the activation mechanism on the lime-depressed pyrite flotation by the addition of acid mine drainage (AMD) with the aims of displacing traditional activators and the innovative utilization of AMD (Bai et al., 2021). The pure mineral flotation test results demonstrated that the lime suppressed pyrite flotation recovery was increased by 64% at the volume ratio of AMD to the high alkali solution (HAS) of 3:1. Solubility tests and Visual MINTEQ model analysis revealed that AMD facilitated the calcium ion desorption from the surface of pyrite, leading to the precipitation formation of calcium sulfate. XPS and ToF-SIMS analysis further confirmed that the effect of AMD on the activation performance of pyrite was primarily due to the removal of hydrophilic calcium and iron species, as well as the increase in Cu active sites on the pyrite surface. In this paper, the lime-depressed pyrite flotation from Cu differential flotation tailings in both AMD and H_2SO_4-$CuSO_4$ activation systems were further investigated to evaluate the AMD activator efficiency for the beneficiation of copper sulfide ore on the laboratory scale. The important test parameters (sulfuric acid dosage, copper sulfate dosage, AMD dosage, and collector dosage) and the adsorption amounts of SBX collector were determined. Meanwhile, the physicochemical analysis of the tailing water of two activated flotation systems was also carried out to provide a theoretical basis for the utilization of the return water. The findings of the present study provided technical support for the cleaner beneficiation of similar copper sulfide ore.

2. Materials and methods

2.1. Materials and reagents

The feed sample was obtained from the Dapingzhang copper sulfide mine of Yunnan Province in China. X-ray diffraction (XRD) analysis was applied to determine the principal mineral components in the raw ore samples and the results were shown in Fig. 1. It is confirmed that chalcopyrite ($CuFeS_2$) and pyrite (FeS_2) are the predominate minerals in the sample. In addition, the significant amounts of gangue minerals are quartz. The chemical composition analysis results of ore samples are presented in

Table 1. The main recoverable valuable elements in the raw ore are Cu (0.38 %), S (8.92%), and Fe (12.87%), respectively. Besides, the gangues are mainly SiO_2 (61.19%). Thus, the ore belongs to the low-grade single copper sulfide ore, and the effective recovery of chalcopyrite and pyrite is the key to the flotation of this ore.
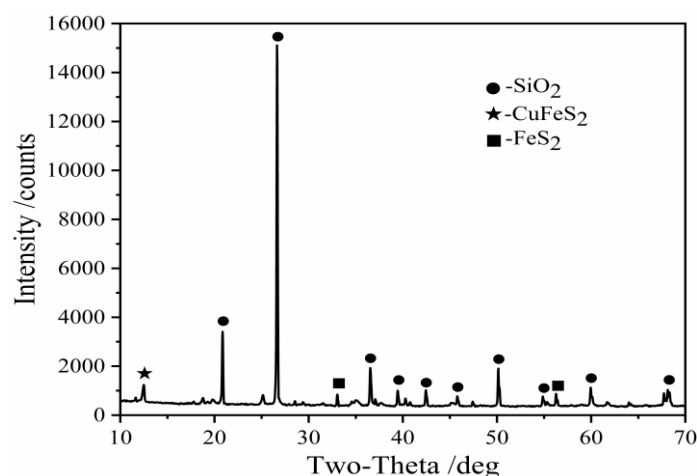

Fig. 1. X-ray diffraction pattern analysis of the raw material

Table 1. Chemical analysis results of the ore samples

Components	Cu	Fe	S	Pb	Zn	Au*	Ag*
Content /%	0.38	12.87	8.92	0.0064	0.26	0.2	<5.0
Components	SiO_2	MgO	Al_2O_3	CaO	Na_2O	K_2O	-
Content /%	61.19	3.68	7.64	0.60	0.13	0.95	-

* Unit is g/t

Acid mine drainage (AMD) obtained from the Dapingzhang copper sulfide ore was used in the flotation studies. The major chemical constituents of AMD analyzed are presented in Table 2. The concentrations of Cu^{2+} and SO_4^{2-} in the AMD are 22.8 mg/L and 5902 mg/L, respectively. The concentrations of Al^{3+} and Mg^{2+} reach 141 mg/L and 156 mg/L, which may play a negative role in the pyrite flotation. Notably, the concentration of Fe^{3+}/Fe^{2+} in present AMD is extremely lower comparing with the reported data that the iron ion concentration usually ranges from 200 to 1000 mg/L (Naidu et al., 2019). It is possible that the iron ions convert to hydroxyl iron precipitation during the storage. Zhang et al. indicated that the $Fe(OH)_{3(S)}$ was considered to the dominated species in the solution when the pH is over 2.3 (Zhang et al., 2014). Hence, major chemical properties (strong acidity and rich

Table 2. Results of chemical analysis of the acid mine drainage

Product	Ions	Ion concentration	Units
	Cu^{2+}	22.8	mg/L
	Pb^{2+}	<0.07	mg/L
	Zn^{2+}	30.7	mg/L
Acid mine	Fe^{3+}/Fe^{2+}	<0.03	mg/L
drainage	Al^{3+}	141	mg/L
(AMD)	Mg^{2+}	156	mg/L
	Ca^{2+}	5.12	mg/L
	SO_4^{2-}	5902	mg/L
	pH	3.88	-

in copper ions) in AMD render this natural acidic wastewater to a promising activator for the lime-depressed-pyrite in the copper sulfide ore. Additionally, chemical reagents used in this study included lime, sulfuric acid, copper sulfate, sodium butyl xanthate (SBX), potassium ethyl xanthate (PEX) and pine oil, which are purchased from domestic reagent companies.

2.2. Experimental procedures

2.2.1. Mineralogy study of raw ore

Mineralogy study of raw ore was conducted to determine the mainly metal mineral species (chalcopyrite, pyrite and sphalerite) and their disseminated characteristic. Firstly, the raw ore with a size of 0.02~0.40 mm was prepared to the sanding sheet, and then observed by optical microscope (QUANTA650F, America). The mineral classification and naming scheme were defined according to GB/T17413.1-1998 and GB/T17413.3-1998.

2.2.2. Laboratory scale flotation tests

The XFD flotation equipment (Jilin Exploring Machinery Plant, China) was adopted for the flotation experiments. Cu differential flotation with high alkali lime craft (pH=11.3), as depicted in Fig. 2, is applied for the beneficiation of the copper sulfide ore on the basis of on-spot craft. 5 kg/t lime was used as the pyrite depressant with stirring at 1700 rpm for 5 min. Potassium ethyl xanthate (PEX) (60 g/t, with 3 min of conditioning) and pine oil (30 g/t, with 1 min of conditioning) were sequentially added into the flotation cell for the chalcopyrite recovery. After 4 min of flotation, the Cu rougher concentrate was obtained.

For the recovery of pyrite from the tailings of Cu differential flotation, the flow-sheets consisted of one roughing-one scavenging-three cleanings were conducted. AMD and H_2SO_4-$CuSO_4$ were used as
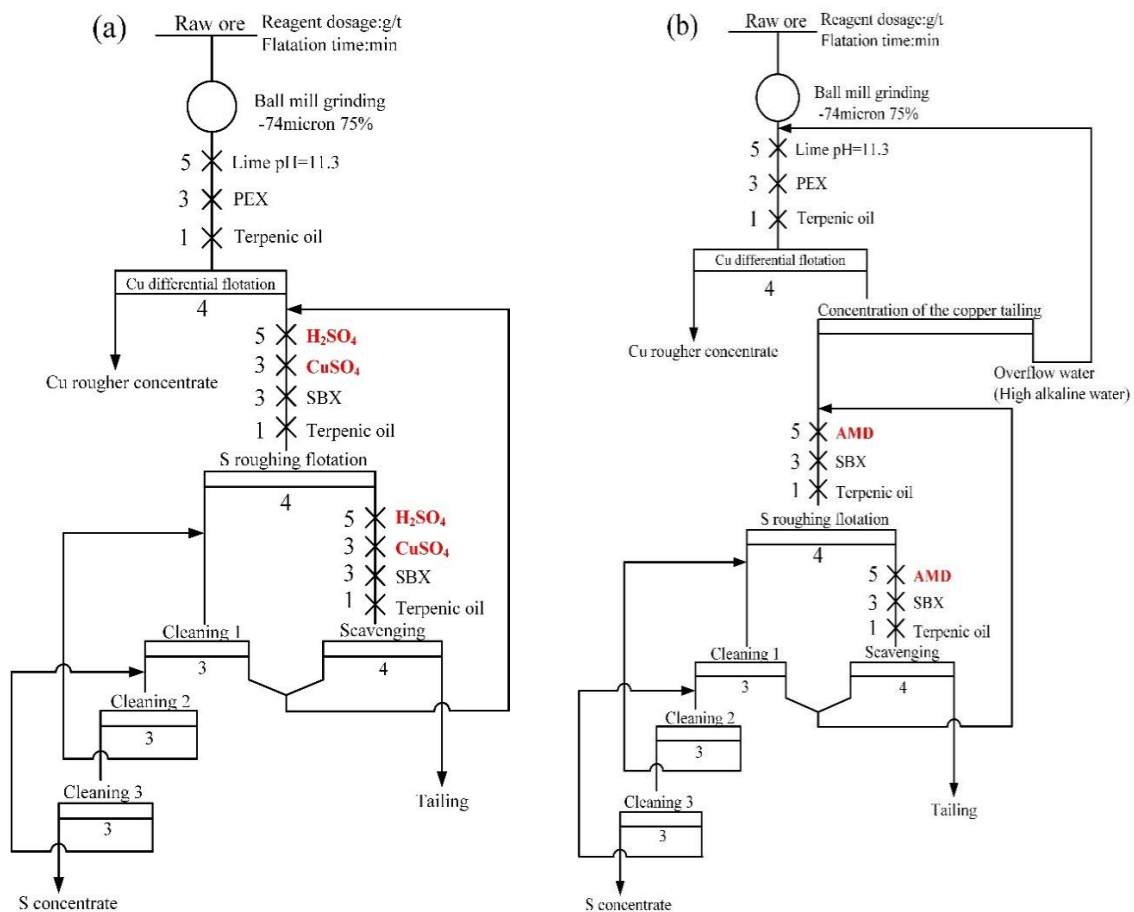

Fig. 2. Closed-circuit flotation flow-sheets and reagent regime for pyrite with (a) sulfuric acid and copper sulfate as activators and (b) AMD as activator

the activators during the roughing and scavenging process. The AMD activation effects on the pyrite flotation were investigated with emphasis. The sulfur rougher concentrate was transferred into the XFD−0.5L flotation cell for cleanings. The conditioning time was 2 min and the collecting time was 3 min for each cleaning processing. The middle materials from scavenging and each cleaning stage were in turn returned to the appropriate location. Finally, all the froth products were filtered, dried, and weighed. When the mass balance calculation achieves balance, the recoveries of Cu and S were calculated to evaluate the flotation efficiency.

2.2.3. Adsorption amount of collector measurements

Collector adsorption measurements on the Cu differential flotation tailings were performed on UV-vis spectrophotometer (UV765, Shanghai). Firstly, different dosages of AMD ($0\sim1.9$ m³/t) were added to the Cu differential flotation tailings, and adjusted for 30 minutes at a SBX concentration (33.3 mg/L, and equal to 100 g/t) with a stirring of 1700 rpm to ensure equilibrium in the adsorption process. After the adsorption process is completed, it is assumed that the depleted dose of reagent has been fully adsorbed to the mineral surface. Then, part of the pulp was extracted and conducted the solid-liquid separation in the centrifuge (TL-4.7W, SCI, China) for 30 min. Finally, the supernatants were taken to measure the residual SBX dose. The adsorption amount of SBX (Γ) on the sample is calculated by the following formula:

$$\Gamma = \frac{(33.3 - c_t)}{m} v \tag{1}$$

where Γ is the adsorption amount of SBX (mg/g); c_t is the residual concentration of SBX in the supernatant (mg/L); v is supernatant fluid volume (L) and m is sample weight (mg).

2.2.4. Physico-chemical analysis of tailing water in different flotation systems

Physico-chemical analysis of tailing water in both AMD and H_2SO_4-$CuSO_4$ flotation system were conducted to determine the water qualities. The samples of tailings slurry were freely settled for 4 h, and the liquid supernatants were collected for the analysis of suspended solids and total hardness. Meanwhile, the pH of liquid supernatants was measured by pH Meter (pH-25, Rex Electric Chemical). Additionally, part of liquid supernatants was performed the solid-liquid separation in the centrifuge (TL-4.7W, SCI, China) for 10 min with stirring at 1500, and the concentrations of the interest ions (Fe^{3+}/Fe^{2+}, Cu^{2+}, and SO_4^{2-}) were measured by ICP and IC analysis (ICPS-1000II, Shimadzu, Japan).

3.   Results and discussion

3.1.   Mineralogy study results of raw ore

The main metallic minerals in the raw ore were observed under an optical microscope. The result showed that the metallic minerals were mainly in the form of chalcopyrite, pyrite, sphalerite and limonite. The dissociation degree of the metallic mineral was about 90%, and their total contents were approximately 2.0%. Specially, the pyrite and chalcopyrite contents occupied about 1.3% and 0.2%, respectively, and disseminated grain size ranged 0.02~0.40 mm. Additionally, the intergrowths were mainly interlinked with chalcopyrite (Ch), sphalerite (Sp) and gangue (Ga), as depicted in Fig. 3. Table 3 showed the disseminated grain size results of pyrite and chalcopyrite in the raw ore. It can be concluded that the embedding granularities of pyrite and chalcopyrite were relatively coarse, and the accumulating content of +0.046 mm grain size was more than 90%. Thus, the dissociation degree of the metallic mineral can be desirably obtained after a coarse grinding, which will provide an easy access to the recovery of pyrite and chalcopyrite.

3.2.   Flotation tests of pyrite in sulfuric acid and copper sulfate systems

3.2.1. Effects of sulfuric acid dosage on the pyrite flotation

For the recovery of pyrite from the tailings of Cu differential flotation with high alkali lime craft, sulfuric acid is used as activator. Effects of H_2SO_4 dosage on the flotation of pyrite during the sulfur rougher stage are shown in Fig. 4. The specific flotation conditions are as follows: the particle size
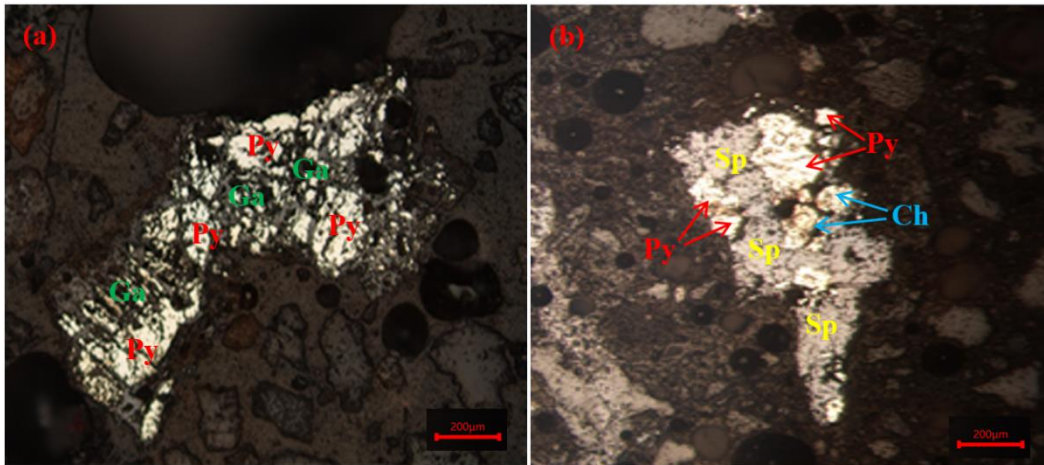
Fig. 3. The disseminated characteristics of interest minerals (a) Intergrowth of pyrite (Py)-gangue (Ga) and (b) Intergrowth pyrite (Py)-chalcopyrite (Ch)-sphalerite (Sp)
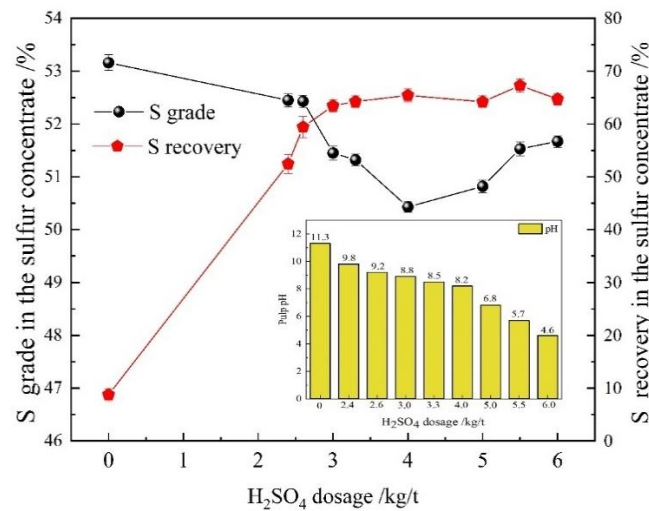

Fig. 4. Effects of H_2SO_4 dosage on the flotation of pyrite during sulfur rougher stage

Table 3. Disseminated grain size results of pyrite and chalcopyrite in the raw ore

Minerals	Particle size range /mm	Content distribution /%	Accumulating content /%
Pyrite	-0.368～+0.184	27.60	27.60
	-0.184～+0.092	27.60	55.20
	-0.092～+0.046	35.50	90.70
	-0.046～+0.023	5.90	96.60
	-0.023	3.40	100.00
Chalcopyrite	-0.368～+0.184	28.20	28.20
	-0.184～+0.092	29.60	57.80
	-0.092～+0.046	35.30	93.10
	-0.046～+0.023	5.60	98.70
	-0.023	1.30	100.00

distribution is below 74 μm accounting for 75%, and the SBX collector dosage is 100 g/t. As depicted in Fig. 4, the H_2SO_4 dosage plays an important role in the pyrite flotation. The S concentrate recovery increases remarkably from 8.75% to 64.21% when the H_2SO_4 dosage increases from 0 to 5.0 kg/t. With a further increase in H_2SO_4 dosages to 6.0 kg/t, the change in S recovery (64.71%) is negligible. The

results confirm that H_2SO_4 can effectively activate the flotation of pyrite once depressed by lime. It is possible that H^+ ions can effectively remove the hydrophilic calcium and iron species (Ca^{2+}, $CaOH^+$ and FeOOH) on the lime-depressed-pyrite surfaces via acid base neutralization reaction. Meanwhile, the SO_4^{2-} ions stemming from H_2SO_4 will promote the Ca^{2+} and $CaOH^+$ to generate calcium sulfate species, which further reinforce the desorption of hydrophilic calcium once wrapped on the pyrite surface. Additionally, the S grade in the sulfur concentrate has a little change (50.43%~53.19%) during the whole experiments. As can be seen from the inside illustration, the pH value of the pulp decreases from 11.3 to 4.6 when the H_2SO_4 dosage increases from 0 to 6 kg/t. Obviously, a weak acid or neutral pulp caused by H_2SO_4 is in favor for the lime-depressed pyrite flotation. However, the chief drawback lies in that large dose of H_2SO_4 will be consumed for the pyrite activation. Taking the reagent cost and the flotation index into account, the recommended dosage of H_2SO_4 is 5 kg/t, corresponding to the pH of 6.8.

3.2.2. Effects of copper sulfate dosage on the pyrite flotation

Copper sulfate was adopted as the activator for lime-depressed pyrite during the sulfur roughing stage. The effects of $CuSO_4$ dosage on the pyrite flotation are investigated (condition: the SBX dosage is 100 g/t), and the results are indicated in Fig. 5. From Fig. 5, it can be concluded that the addition of an appropriate $CuSO_4$ dosage can significantly increase the S recovery. Moreover, the addition of $CuSO_4$ is helpful to the increase of S grade in the concentrate overall. When the $CuSO_4$ dosage is 100 g/t, the S grade in the concentrate is 51.21%, and the S recovery reaches 79.33%, which is about 10 percent points higher than the S recovery (69.71%) in the absence of $CuSO_4$. A further increase in the $CuSO_4$ dosage, the S recovery decreases sharply. It is possible that plenty of copper ions will consume the collector. Thus, an appropriate $CuSO_4$ dosage can effectively activate the lime-depressed pyrite flotation, and its recommended dosage is 100 g/t.
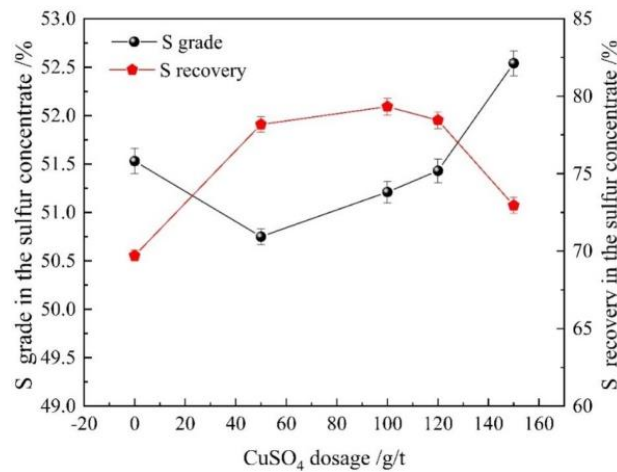

Fig. 5. Effects of $CuSO_4$ dosage on the pyrite flotation during sulfur rougher stage

3.3. Flotation tests of pyrite in AMD system

3.3.1. Effects of AMD dosage on the flotation of pyrite

In order to displace the traditional activator for pyrite flotation (H_2SO_4 and $CuSO_4$) and realize the comprehensive utilization of AMD, we investigated the effect of AMD on the pyrite flotation from the tailing of Cu differential flotation. The specific flotation conditions and flow-sheet are the same as the 3.2.1 section, and the results are presented in Fig. 6. As shown in Fig. 6, AMD exerts a positive role in the pyrite recovery. The S recovery is only 8.75% in the absence of AMD, indicating that the pyrite has suffered severe inhibition by lime. The S recovery reaches the maximum value (80.09%) when an AMD dosage of 1.8 m^3/t is added, which increases about 70 percent points compared with the S recovery without the addition of AMD. The result confirms that the AMD has a strong activation effect on the flotation of lime-depressed pyrite. It is possible that the AMD can effectively remove the hydrophilic species (Ca^{2+}, $CaOH^+$ and FeOOH) once wrapped on the pyrite surface after the acid-base

neutralization reaction. Meanwhile, the adsorption of Cu^{2+} ions stemming from the AMD can increase the Cu-active sites on the pyrite surfaces, which is beneficial to adsorption of collector onto mineral surfaces. Whereas, the S recovery decreases to some extent and it is about 77.26% when the AMD dosage is 1.9 m^3/t. We infer that excessive H^+ and Cu^{2+} ions presented in the pulp may hinder the interaction between collector and pyrite surfaces. Thus, AMD dosage is determined to be 1.8 m^3/t. It is noteworthy that the variation of the grade of the S concentrate is inconspicuous during the whole AMD dose range, indicating that the inclusions of gangue minerals are negligible during the AMD-activated pyrite flotation process. Additionally, the inside illustration shows that the pH value of the pulp decreases from 11.3 to 8.2 when the AMD dosage increases from 0 to 1.9 m^3/t. Obviously, the remarkable decrease in the pulp pH caused by AMD will create describable condition for the lime-depressed pyrite flotation. Given these results, the addition of a suitable content of AMD facilitates the flotation of lime-depressed pyrite, and it can be viewed as a promising natural activator instead of traditional chemical reagents (such as H_2SO_4 and $CuSO_4$). It is worth mentioned that the utilization efficiency of AMD reaches 96.94% when the AMD dosage of 1.8 m^3/t was used. This activity can not only economize the great mass of fresh water, but also provides an innovative path to a cleaner beneficiation of copper sulfide ore, and has the vital practical significance for the emission reduction of AMD and the increase of beneficiation profits.
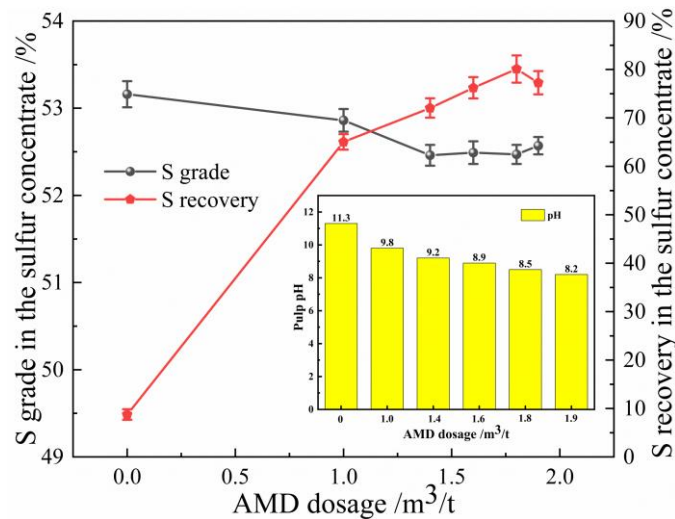

Fig. 6. Effects of AMD dosage on the flotation of pyrite during sulfur rougher stage

3.3.2. Effects of sodium butyl xanthate (SBX) dosage on the pyrite flotation

The influences of SBX dosage on the S recovery and grade in the concentrates are shown in Fig. 7 (Conditions: the AMD dosage is 1.8 m^3/t and the rougher pulp pH is 8.5). The results show that the S recovery increases rapidly from 56.45% to 79.22% when the SBX dosage increases from 40 to 100 g/t. A further increase in SBX dosage to 120 g/t, the change in S recovery (79.64%) is negligible. Whereas, the S grade shows the downtrend trend with the increase of SBX dosage. Thus, the recommended SBX dosage is 100 g/t in the AMD system, and the S grade and recovery are 52.46% and 79.22%, respectively. The S grade is enhanced by 1.25% comparing with the corresponding flotation index (51.21% grade and 79.33% recovery) in sulfuric acid (5 kg/t) and copper sulfate (100 g/t) systems with the same dosage of SBX (100 g/t). It can be concluded that the AMD plays more superior activation effects on the flotation of lime-depressed pyrite, which provides strong support for the application of AMD and the replacing of the H_2SO_4 and $CuSO_4$ during the mineral processing of copper sulfide ore.

3.4. Adsorption amount of SBX collector on the Cu differential flotation tailings

In order to study the adsorption amount of SBX collector Cu differential flotation tailings and the implications for the lime-depressed pyrite flotation, adsorption tests are carried out in the AMD system and the corresponding results are shown in Fig. 8. As can be seen, the addition of AMD
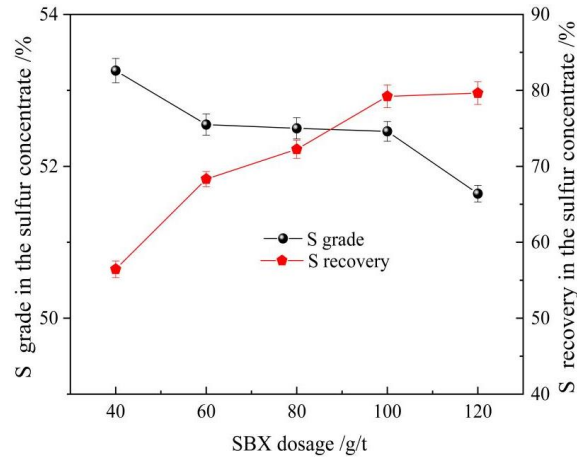
Fig. 7. Effects of SBX dosage on the flotation of pyrite during sulfur rougher stage

provides an easy access to the adsorption of SBX collector on the Cu differential flotation tailings. The adsorption amount of SBX collector (Γ) is only about 5.21×10^{-6} mg/g (as depicted in the inside illustration) in the absence of AMD. This phenomenon is attributed to the fact that the hydrophilic species (Ca^{2+}, $CaOH^+$ and $FeOOH$) are formed on the pyrite surfaces in the high alkali lime craft (pH=11.3) and degrade the interaction between SBX and pyrite surfaces. The adsorption amount of SBX increases from 8.41×10^{-3} mg/g to 7.9×10^{-2} mg/g when the dosage of AMD increases from 1.0 m³/t to 1.9 m³/t. It can be inferred that the addition of AMD can significantly improve the adsorption of collector SBX on the pyrite surfaces. As described earlier, AMD can effectively clear off the hydrophilic calcium species via the neutralization reaction. Moreover, the copper ions originated from the AMD can absorb onto the pyrite surfaces, increasing the Cu-active sites. Hence, this dual function will reinforce the activity of lime-depressed pyrite, and facilitate the SBX collector adsorption. The adsorption test results are well consistent with the flotation results. It is worth noting that the S recovery decreases to some extent when the AMD dosage is 1.9 m³/t although the adsorption amount of SBX gets to the maximum. As discussed earlier, excessive Cu^{2+} ions stemming from AMD presented may consume the SBX collector, all of which fail to contribute to the hydrophobicity of the pyrite.
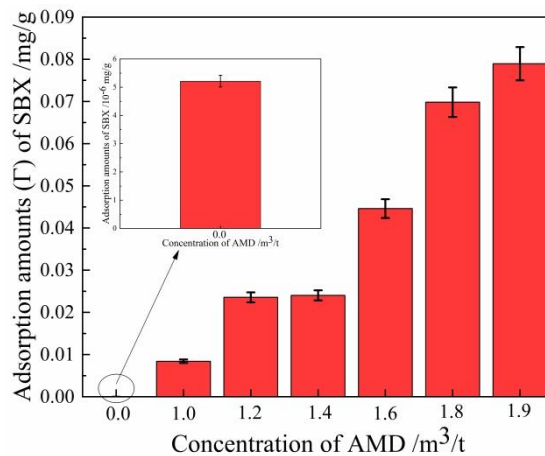

Fig. 8. Adsorption amount of SBX collector on the Cu differential flotation tailings

3.5. Closed-circuit flotation tests of copper sulfide ore

The closed-circuit flotation tests of copper sulfide ore, as depicted in Fig. 2 are carried out according to the recommend conditions acquired in the open-circuit flotation tests, and the test results are shown in Table 4. As presented in Table 4, the recoveries of S and Fe in the sulfur concentrate are 79.82% and 48.69% with grades of 51.16% and 42.54%, respectively in the H_2SO_4-$CuSO_4$ system. When the AMD is used as an activator, the recoveries of S and Fe in the sulfur concentrate are 82.95% and 50.34% with

grades of 51.08% and 43.55%, respectively. Compared with the former sulfur flotation index, the recovery rate of sulfur concentrate in the AMD system is increased by 5.33%. Moreover, the total contents of S and Fe in the concentrate reach 94.63%, belonging to a high-quality sulfur concentrate and meeting the needs of sulfuric acid production desirably. Thus, the results provide strong evidence that AMD can replace H_2SO_4 and $CuSO_4$ as an activator for pyrite flotation depressed by lime, and can more efficiently recover the pyrite. This method provides a novel approach for the treatment of AMD, and forms an innovative flotation technology consisted of Cu differential flotation with high alkali lime and pyrite recovery with AMD activation. Obviously, the application of AMD in copper sulfide flotation will bring considerable economic and environmental benefits. Firstly, the treatment cost of AMD and the fresh water can be saved. Secondly, the AMD negative impacts on the receiving environment can be solved. Thirdly, the efficient recovery of pyrite and the substitution of H_2SO_4 and $CuSO_4$ further increase economic benefits to the flotation plant.

The sulfur concentrates obtained by closed-circuit tests have been further analyzed by XRD pattern, to investigate the mineral composition of the products. The results are shown in Fig. 9. From Fig. 9, it can be concluded that the sulfur concentrates mainly contain pyrite minerals, while the contents of gangue minerals are extremely low and failed to be detected. Thus, the sulfur concentrates belong to quality raw materials for the sulfuric acid production. Additionally, the results indicate that the pyrite once depressed by lime can be selectively floated by the SBX collector in the two activation systems. Notably, the characteristic peak intensities of the pyrite obtained by AMD activation (Fig. 9(b)) are stronger than the intensities of the pyrite obtained by H_2SO_4-$CuSO_4$ activation (Fig. 9(a)), indicating that AMD displayed more superior activation than H_2SO_4-$CuSO_4$ for the pyrite flotation. The XRD results are well consistent with the results of closed-circuit flotation tests of copper sulfide ores.

Table 4. Results of closed-circuit flotation tests of copper sulfide ores

| Conditions	Products	Yields (%)	Grades (%)		Recoveries (%)	
			S	Fe	S	Fe
H_2SO_4-$CuSO_4$ system	Cu rougher concentrate	6.09	20.23	26.09	13.41	12.68
	S concentrate	14.34	51.16	42.54	79.82	48.69
	Tailing	79.57	0.86	6.12	6.77	38.63
	Feed	100.00	9.19	12.53	100.00	100.00
AMD system	Cu rougher concentrate	5.75	18.47	25.66	11.81	11.68
	S concentrate	14.60	51.08	43.55	82.95	50.34
	Tailing	79.65	0.36	6.02	5.24	37.98
	Feed	100.00	8.99	12.63	100.00	100.00
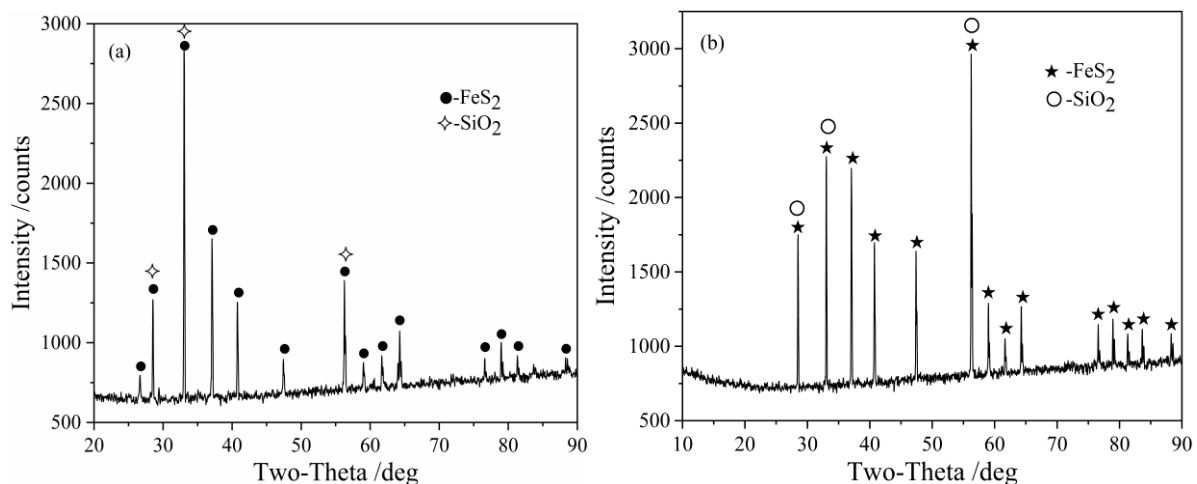
Fig. 9. XRD pattern of S concentrate obtained (a) by H_2SO_4-$CuSO_4$ activation and (b) by AMD activation

3.6. Analysis of tailings water composition under different flotation systems

Table 5 shows the results of the chemical analysis of tailings water in different flotation systems. As can be viewed from Table 5, the concentrations of suspended solids and total hardness in the two tailings water samples can meet the indicators of return water quality of mineral processing, and the corresponding concentrations are required to be below 300 mg/L and 450 mg/L, respectively. Meanwhile, Fe ions content in the sulfuric acid and copper sulfate systems is higher than that in the AMD system. It is possible that the alkaline media promote the oxidation of Fe^{2+} ions and Fe^{3+} ions will be formed, which can easily react with OH^- ions in the slurry to form $Fe(OH)_3$ precipitate, resulting in a decrease in Fe content in the tailings slurry(Jiang et al., 1998). Cu ions contents in both systems are extremely low, which mainly due to the adsorption of Cu ions onto minerals surfaces. Additionally, the pH value of the tailings water sample in the AMD system is 8.7, which is more desirable to be recycled in the Cu differential flotation with high alkali lime craft, compared with the tailings water sample in the H_2SO_4-$CuSO_4$ system (pH=6.9). It is worth noting that the SO_4^{2-} concentrations in both systems reach 2622.29 and 2974.14 mg/L, which are very unfavorable to the flotation of chalcopyrite with the return water used because the adsorption of SO_4^{2-} may increase the hydrophilicity of minerals. Indeed, many efforts should be paid to the application of tailings water in the flotation of copper sulfide ores in the future.

Table 5. Results of chemical analysis of tailings water in different flotation systems

Samples	Items	Concentrations	Units
H_2SO_4-$CuSO_4$ system	Suspended solids (SS)	126.78	mg/L
	Total hardness (Measured in calcium carbonate)	215.42	mg/L
	Cu^{2+}	<0.02	mg/L
	Fe^{3+}/Fe^{2+}	1.02	mg/L
	SO_4^{2-}	2622.29	mg/L
	pH	6.9	-
AMD system	Suspended solids (SS)	136.12	mg/L
	Total hardness (Measured in calcium carbonate)	283.54	mg/L
	Cu^{2+}	<0.02	mg/L
	Fe^{3+}/Fe^{2+}	1.02	mg/L
	SO_4^{2-}	2974.14	mg/L
	pH	8.7	-

4.   Conclusions

Flotation test results of pyrite from the tailings of Cu differential flotation with high alkali lime showed that H_2SO_4-$CuSO_4$ and AMD can effectively activate the pyrite flotation with SBX collector. The recommended conditions are as follows: the H_2SO_4 dosage is 5 kg/t and the $CuSO_4$ dosage is 100 g/t, while the AMD dosage of is 1.8 m^3/t. Adsorption amount results of SBX collector indicated that the hydrophilic species (Ca^{2+}, $CaOH^+$ and FeOOH) are formed on the pyrite surfaces in the high alkali lime craft (pH=11.3) and degrade the interaction between SBX and pyrite surfaces. AMD can effectively clear off the hydrophilic calcium species and the copper ions originated from the AMD can absorb onto the pyrite surfaces, facilitating the SBX collector adsorption. The closed-circuit flotation results showed the recovery of sulfur concentrate increases by 5.33% in the AMD system. Moreover, the total contents of S and Fe in the concentrate reach 94.63%, belonging to a high-quality sulfur concentrate and meeting the needs of sulfuric acid production desirably. Composition analysis results of tailings water confirmed that the tailing water obtained by the AMD flotation system was more desirable to be recycled in the Cu differential flotation due to its higher pH value (8.7). However, the SO_4^{2-} concentrations in both systems reached 2622.29 and 2974.14 mg/L, and would be unfavorable to the flotation of chalcopyrite with the return water using. The present study provides a novel approach

for the treatment of AMD, and the AMD can be viewed as a promising natural activator instead of traditional chemical reagents (such as H_2SO_4 and $CuSO_4$). It has the vital practical significance for the emission reduction of AMD and the increase of beneficiation profits.

Acknowledgments

References

ALTINKAYA, P., LIIPO, J., KOLEHMAINEN, E., HAAPALAINEN, M., LEIKOLA, M., LUNDSTRöM, M. 2018. *Leaching of Trace Amounts of Metals from Flotation Tailings in Cupric Chloride Solutions*. Mining, Metallurgy & Exploration, 36(2), 335-342

BAI, S., BI, Y., LI, J., YU, P., DING, Z., LV, C., WEN, S. 2021. *Innovative utilization of acid mine drainage (AMD): A promising activator for pyrite flotation once depressed in a high alkali solution (HAS)–Gearing towards a cleaner production concept of copper sulfide ore*. Minerals Engineering, 170, 106997

BOULTON, A., FORNASIERO, D., RALSTON, J. 2003. *Characterisation of sphalerite and pyrite flotation samples by XPS and ToF-SIMS*. International Journal of Mineral Processing, 70(1-4), 205-219

CHANDRA, A.P., GERSON, A.R. 2009. *A review of the fundamental studies of the copper activation mechanisms for selective flotation of the sulfide minerals, sphalerite and pyrite*. Advances in Colloid and Interface Science, 145(1-2), 97-110.

CRUNDWELL, F.K. 2021. *The impact of light on understanding the mechanism of dissolution and leaching of sphalerite (ZnS), pyrite (FeS2) and chalcopyrite (CuFeS2)*. Minerals Engineering, 161, 106728.

DENG, Z., CHENG, W., TANG, Y., TONG, X., LIU, Z. 2021. *Adsorption mechanism of copper xanthate on pyrite surfaces*. Physicochemical Problems of Mineral Processing, 57(3), 46-60.

HOLMES, P.R., CRUNDWELL, F.K. 2000. *The kinetics of the oxidation of pyrite by ferric ions and dissolved oxygen An electrochemical study*. Geochimica et Cosmochimica Acta, 64(2), 263-274.

HU, Y.H., ZHANG, S.L., QIU, G.Z., MILLER, J.D. 2000. *Surface chemistry of activation of lime-depressed pyrite in flotation*. Transactions of Nonferrous Metals Society of China, 10(6), 798-803.

HUANG, H., HU, Y., SUN, W. 2012. *Activation flotation and mechanism of lime-depressed pyrite with oxalic acid*. International Journal of Mining Science and Technology, 22(1), 63-67.

IGARASHI, T., HERRERA, P.S., UCHIYAMA, H., MIYAMAE, H., IYATOMI, N., HASHIMOTO, K., TABELIN, C.B. 2020. *The two-step neutralization ferrite-formation process for sustainable acid mine drainage treatment: Removal of copper, zinc and arsenic, and the influence of coexisting ions on ferritization*. Science of the Total Environment, 715, 136877.

JIANG, C.L., WANG, X.H., PAREKH, B.K., LEONARD, J.W. 1998. *The surface and solution chemistry of pyrite flotation with xanthate in the presence of iron ions*. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 136(1-2), 51-62.

JIE, Z., WEIQING, W., JING, L., YANG, H., QIMING, F., HONG, Z. 2014. *Fe(III) as an activator for the flotation of spodumene, albite, and quartz minerals*. Minerals Engineering, 61, 16-22.

JOHNSON, D.B., HALLBERG, K.B. 2005. *Acid mine drainage remediation options: a review*. Science of the Total Environment, 338(1-2), 3-14.

JURJOVEC, J., PTACEK, C.J., BLOWES, D.W. 2002. *Acid neutralization mechanisms and metal release in mine tailing a laboratory column experiment*. Geochimica et Cosmochimica Acta, 66(9), 1511-1523.

KAUR, G., COUPERTHWAITE, S.J., HATTON-JONES, B.W., MILLAR, G.J. 2018. *Alternative neutralisation materials for acid mine drainage treatment*. Journal of Water Process Engineering, 22, 46-58.

KHOSO, S.A., GAO, Z., SUN, W. 2021. *Recovery of high-grade copper concentrate from sulfur-rich porphyry ore using tricarboxystarch micromolecule as pyrite depressant*. Minerals Engineering, 168, 106916.

LEPPINEN, J.O. 1990. *FTIR and flotation investigation of the adsorption of ethyl xanthate on activated and non-activated sulfide minerals*. International Journal of Mineral Processing, 30(3-4), 245-263.

LI, M., LIAN, D., ZHAO, F., TONG, X., WU, C., GAO, X. 2021. *Structure-activity of chelating depressants for chalcopyrite/pyrite separation: DFT study and flotation experiment*. Physicochemical Problems of Mineral Processing, 57(6), 102-112.

LI, Y., CHEN, J., KANG, D., GUO, J. 2012. *Depression of pyrite in alkaline medium and its subsequent activation by copper*. Minerals Engineering, 26, 64-69.

LIU, J., LI, E.-L., JIANG, K., LI, Y.-J., HAN, Y.-X. 2018. *Effect of acidic activators on the flotation of oxidized pyrrhotite*. Minerals Engineering, 120, 75-79.

Lü, C., WANG, Y., QIAN, P., LIU, Y., FU, G., DING, J., YE, S., CHEN, Y. 2018. *Separation of chalcopyrite and pyrite from a copper tailing by ammonium humate*. Chinese Journal of Chemical Engineering, 26(9), 1814-1821.

MAFRA, C., BOUZAHZAH, H., STAMENOV, L., GAYDARDZHIEV, S. 2020. *Insights on the effect of pyrite liberation degree upon the acid mine drainage potential of sulfide flotation tailings*. Applied Geochemistry, 123, 104774.

MASINDI, V., GITARI, M.W., TUTU, H., DEBEER, M. 2015. *Efficiency of ball milled South African bentonite clay for remediation of acid mine drainage*. Journal of Water Process Engineering, 8, 227-240.

MU, Y., PENG, Y., LAUTEN, R.A. 2016. *The depression of copper-activated pyrite in flotation by biopolymers with different compositions*. Minerals Engineering, 96-97, 113-122.

NAIDU, G., RYU, S., THIRUVENKATACHARI, R., CHOI, Y., JEONG, S., VIGNESWARAN, S. 2019. *A critical review on remediation, reuse, and resource recovery from acid mine drainage*. Environmental Pollution, 247, 1110-1124.

ŇANCUCHEO, I., HEDRICH, S., JOHNSON, D.B. 2018. *New microbiological strategies that enable the selective recovery and recycling of metals from acid mine drainage and mine process waters*. Mineralogical Magazine, 76(7), 2683-2692.

NARIYAN, E., WOLKERSDORFER, C., SILLANPAA, M. 2018. *Sulfate removal from acid mine water from the deepest active European mine by precipitation and various electrocoagulation configurations*. Journal of Environmental Management, 227, 162-171.

PARBHAKAR-FOX, A., LOTTERMOSER, B.G. 2015. *A critical review of acid rock drainage prediction methods and practices*. Minerals Engineering, 82, 107-124.

PAT-ESPADAS, A., LOREDO PORTALES, R., AMABILIS-SOSA, L., GóMEZ, G., VIDAL, G. 2018. *Review of Constructed Wetlands for Acid Mine Drainage Treatment*. Water, 10(11), 1685.

PECINA, E.T., URIBE, A., NAVA, F., FINCH, J.A. 2006. *The role of copper and lead in the activation of pyrite in xanthate and non-xanthate systems*. Minerals Engineering, 19(2), 172-179.

SHEN, W.Z., FORNASIERO, D., RALSTON, J. 2001. *Flotation of sphalerite and pyrite in the presence of sodium sulfite*. International Journal of Mineral Processing, 63(1), 17-28.

TAN, L.C., PAPIRIO, S., LUONGO, V., NANCHARAIAH, Y.V., CENNAMO, P., ESPOSITO, G., VAN HULLEBUSCH, E.D., LENS, P.N.L. 2018. *Comparative performance of anaerobic attached biofilm and granular sludge reactors for the treatment of model mine drainage wastewater containing selenate, sulfate and nickel*. Chemical Engineering Journal, 345, 545-555.

TANG, X., CHEN, Y. 2020. *Using oxalic acid to eliminate the slime coatings of serpentine in pyrite flotation*. Minerals Engineering, 149, 106228.

WANG, X.H., FORSSBERG, K.S. 2002. *Mechanisms of pyrite flotation with xanthates*. International Journal of Mineral Processing, 33(1-4), 275-290.

WEISENER, C., GERSON, A. 2000. *An investigation of the Cu (II) adsorption mechanism on pyrite by ARXPS and SIMS*. Minerals Engineering, 13(13), 1329-1340.

WONG, G., LASCELLES, D., AFINCH, J. 2002. *Quantifying accidental activation. Part II. Cu activation of pyrite*. Minerals Engineering, 15(8), 573-576.

ZANIN, M., LAMBERT, H., DU PLESSIS, C.A. 2019. *Lime use and functionality in sulphide mineral flotation: A review*. Minerals Engineering, 143, 105922.

ZHANG, J., WANG, W.Q., LIU, J., HUANG, Y., FENG, Q.M., ZHAO, H. 2014. *Fe(III) as an activator for the flotation of spodumene, albite, and quartz minerals*. Minerals Engineering, 61, 16-22.