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Effect of sodium sulfide waste water recycling on the separation of chalcopyrite and molybdenite

Di Wu, Huiqing Peng, Mohamed Abdalla

School of Resource and Environmental Engineering, Wuhan University of Technology, 122 Luoshi Road, Wuhan 430070, China

Corresponding author: wd1771@163.com (Di Wu)

Abstract: The effect of sodium sulfide waste water recycling on the separation of chalcopyrite and molybdenite was investigated in this work. The waste water, which was separated from the slurry after selective flotation, was recycled in the flotation system. This operation significantly improved the subsequent flotation of chalcopyrite and saved the reagent. The results showed that the depression efficiency of sodium sulfide gradually disappeared in the recycling tests due to the consumption. The consumption of sodium sulfide in the separation was not only caused by the adsorption on mineral surfaces but also resulted from the precipitation of metal ions which released from minerals. These effects decreased the solution reducibility and the adsorption of hydrosulfide ions, finally resulting in the less depression for chalcopyrite flotation. After adding a certain amount of sodium sulfide to the recycling, the depression of chalcopyrite performed well and the pulp potential maintained at a relatively lower level. Moreover, the pulp potential was an available parameter to control the flotation separation of chalcopyrite and molybdenite, which made the method easily applied to industry.

Keywords: *vanadium slag, low pressure leaching, liquid phase oxidation, kinetics*

1. Introduction

Huge amounts of waste water were produced in the plant during mining and beneficiation operations everyday (Sychkov and Bochkarev, 1976; Lambert et al., 2008). The indiscriminate discharge would cause a series of environmental problems, especially the waste water in the flotation process which contained large numbers of toxic reagents (Gonzalez et al., 2010; Liu et al., 2013; Gao et al., 2016). The waste water was generally reused in the beneficiation plant as backwater after purification including natural degradation, biodegradation and artificial degradation (Turner et al., 2003; Mullett, 2011). Sodium sulfide as a kind of flotation reagents had been used in plants for many years (Bulatovic, 2007). The low concentration sodium sulfide can activate the sulfide ore and metal oxide ore by forming sulfur-rich surface (Trahar, 1983). However, the high concentration can commonly depress sulfide ore by creating hydrophilic films and have the effect of reagents removal via competitive adsorption (Abeidu et al., 1978). It is announced that sodium sulfide is very extensive in the application of mineral processing. In the selective flotation of molybdenite and chalcopyrite, sodium sulfide was used as a depressor for chalcopyrite (Wada et al., 1962; Peng et al., 2017) and its dosage was enormous (Qiu, 2009), resulting in the production of big amounts of polluting waste water which couldn't be fully utilized and inevitably cause environmental problems.

The sodium sulfide waste water contained soluble H_2S, HS^-, S^{2-}, suspended soluble sulfide or acid soluble metal sulfide and non-ionized inorganic or organic sulfides (Zhao et al., 2013). After long-term placement, the waste water showed the color of black (sulfur oxide compound), and irritating odor mainly due to H_2S gas released from the water continuously. The treatment of waste water usually uses degradation. Finally, the sulfide will be changed to some nontoxic substance such as sulfate. Or, using some reagents to adsorbed or precipitate the sulfide ions (He et al., 2013). Those works are

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always done by the people engaging in the environmental engineering. Their treatments also cost a lot of money on the materials. However, for the field of mineral processing, this processed waste water is possible to be returned back into the flotation system. No harmful waste water discharges, no environmental pollution occurs.

In this work, the waste water from chalcopyrite-molybdenite separation contained a lot of sodium sulfide which wasn't fully used. The flotation tests, pulp potential measurements, inductively coupled plasma-optical emission spectrometer (ICP-OES) analyses and adsorption calculation was carried out in this study. Recycling tests were undertaken to evaluate the performance of the waste water, and verification flotation tests were presented to demonstrate the feasibility of the recycling. This work is worthy of attention in terms of technology, economy and environmental protection.

2. Experimental methods

2.1 Minerals and reagents

Chalcopyrite (Cp) and molybdenite (Mot) pure minerals, obtained from Guangxi Province, China, were used as experimental samples in this study. The lumps of the chalcopyrite and molybdenite were separately crushed manually and hand-picked in order to obtain high-purity samples, then further crushed and pulverized in an agate mortar. Those samples were screened to -100+45μm for flotation tests. XRD results of chalcopyrite and molybdenite were presented in Fig. 1. The chemical analyses showed that the chalcopyrite contained 32.02% Cu, 29.13% Fe and 33.16% S, the molybdenite contained 58.88% Mo and 40.03% S. The purities of chalcopyrite and molybdenite were 92.06% and 98.13%, respectively. The Brunauer-Emmett-Teller (BET) specific surface area of these size fractions of chalcopyrite and molybdenite was 0.31 m^2/g and 0.57 m^2/g, respectively, determined by an Autosorb-iQ analyzer (Quantachrome, US).

Sodium butyl xanthate (SBX) and terpenic oil were used as a collector and frother, respectively. Specially, kerosene was the collector of the molybdenite in the separation. Collector and frother were both industrial grade. Other chemicals were of analytical grade. Sodium sulfide (Na_2S) was used as a depressor for chalcopyrite. The pH was adjusted by the addition of diluted hydrochloric acid (HCl) and sodium hydroxide (NaOH) solutions. De-ionized water was used throughout the experiments. All chemical solutions were prepared fresh every day.

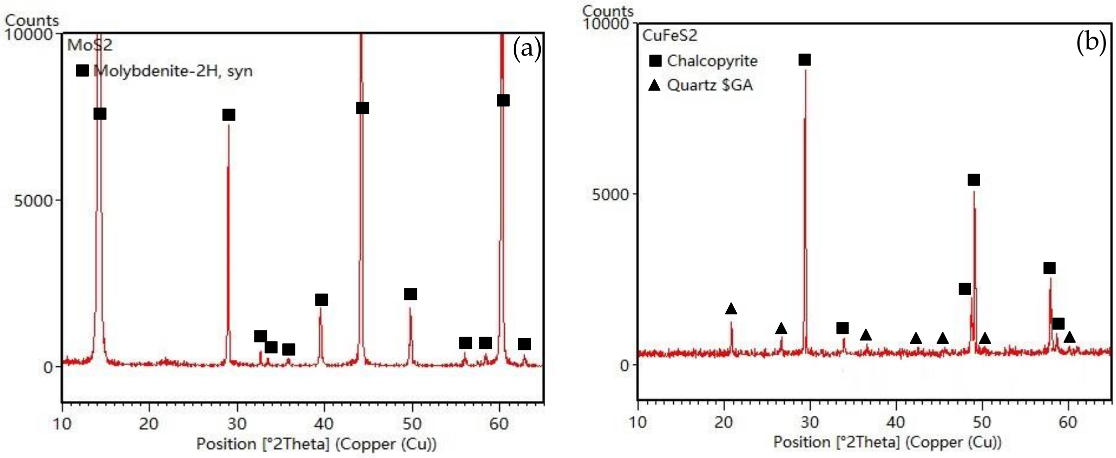

Fig. 1. XRD analyses of pure minerals, molybdenite (a) and chalcopyrite (b)

2.2 Flotation

To simulate the separation of molybdenum-bearing chalcopyrite flotation concentrate and eliminate the interference of other sulfide ore, mixed minerals were prepared by mixing high-purity chalcopyrite and molybdenite with a mass ratio of 1:1. The bulk flotation of the mixture was carried out by adding 100 g/Mg SBX and 40 g/Mg terpenic oil to get full recoveries of chalcopyrite and molybdenite (see Fig. 2). The bulk flotation concentrate was dried at a low temperature and negative pressure environment to prevent the surface oxidation. It was obvious that the chalcopyrite-molybdenite concentrate was covered with the flotation reagents and it had good floatability. Chemical analyses showed that the concentrate contained 30.19% Mo and 16.58% Cu. Ten grams of the dried concentrate were weighed and transferred into a 200 cm^3 microflotation cell and mixed with various concentrations of sodium sulfide solution to fix a pulp density at about 5%. After adjusting the pH to 10, kerosene (50 g/Mg) and terpenic oil (40 g/Mg) were added as collector and frother, respectively, into the separation. The flotation machine operated at 1200 rpm and a nitrogen flow rate of 0.6 dm^3 per minute. Each reagent condition time was 2 min, the flotation proceeded for 1, 2 and 3 min. After that, each product was weighed and analyzed to calculate the recoveries.

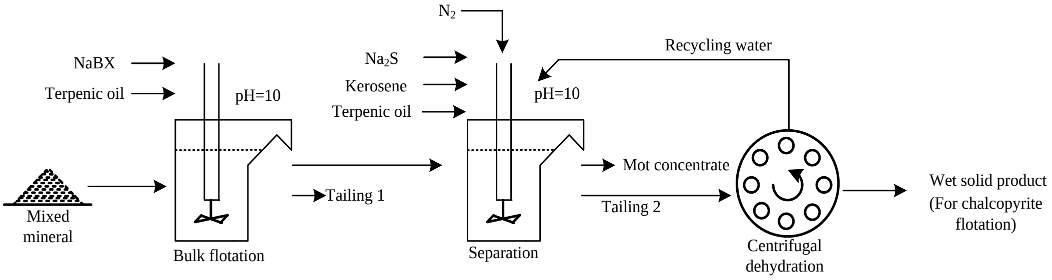

Fig. 2. The flotation flowsheet of the mixture separation

2.3 Recycling tests

The recycling water which contained sodium sulfide was obtained from chalcopyrite-molybdenite separation. The slurry after separation was centrifuged (5000 r/min for 3 min) to waste water and wet solid product. The waste water was returned back to the separation system. Whilst, the wet solid was considered as the feeding of chalcopyrite flotation. Due to the removal of depressor, the chalcopyrite flotation was greatly improved.

As the waste water contained big amounts of sodium sulfide, it would destroy the ecological environment if it discharged directly. The waste water recycling in the flotation is a sensible idea to save the reagent and treat the environment problem. To better understand the effects, the recycling water in the flotation circuit was recycled for 6 times. During the circuit, none of the fresh water was added to the separation system to ensure the pH and the sulfide concentration was only caused by the adsorption. The metal contents of copper and molybdenum in the froth and tailing were calculated based on chemical analysis.

2.4 Measurements

During the recycling tests, Eh and pH of the recycling water were measured with a platinum / calomel electrode system and a pH composite electrode in an electrochemical equipment (PHS-3C, Rex, China), respectively. The results were calibration with the standard solution and the Eh was reported on a hydrogen scale by adding 0.2415 V. Before each measurement, cleaning electrodes with diluted hydrochloric acid and deionized water was significant necessary.

An inductively coupled plasma-optical emission spectrometer (Perkin Elmer, Model Optima 4300 DV, USA) was used to quantify the elements in the recycling water. Those liquid samples were then introduced into the plasma formed in the quartz torch by an alumina injector (1.2mm internal diameter (ID)).

3. Results and discussion

3.1 Flotation tests

The flotation results of chalcopyrite-molybdenite concentrate as functions of different dosages of sodium sulfide were presented in Fig. 3. Particularly, the flotation time here was total 3 min which could fully recover valuable minerals. In this Fig., chalcopyrite flotation recovery was significantly decreased with sodium sulfide added in the concentration range of 0.01-0.025 mol/dm^3. However, the molybdenite recoveries were relatively stable and they only slightly reduced as sodium sulfide added.

After the sodium sulfide concentration arrived at 0.03 mol/dm^3, the chalcopyrite recovery reached to a minimum at about 10%. This didn't mean chalcopyrite was not effectively and completely depressed, the 10% recovery of chalcopyrite might be caused by the entrainment. The flotation results indicated that the optimal condition of molybdenite and chalcopyrite separation was at sodium sulfide concentration of 0.03 mol/dm^3.

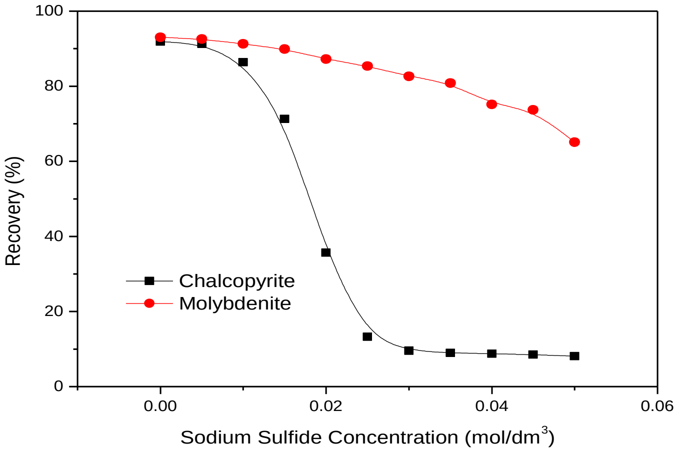

Fig. 3. Flotation results of chalcopyrite-molybdenite concentrate as function of different dosages of sodium sulfide at pH=10

3.2 Recycling tests

After the chalcopyrite and molybdenite separation, the liquid in the flotation cell was separated out and returned to the next separation. During the process, none of sodium sulfide was added into the pulp, but the pHs were adjusted to 10 before the recycling. Flotation results of the molybdenite concentrate in the 6 recycling tests were presented in Fig. 4. Each recycling test had 3 points referred to the 3 products in different flotation time which were 1, 2 and 3 min from left to right, respectively. The results showed that the depression effects of sodium sulfide performed well in recycling 1 and 2, both gave lower chalcopyrite recoveries (<10%), showing good quality of molybdenite concentrates. With the recycling times of the sodium sulfide waste water continuously increasing, the concentrate quality was significantly dropped, especially when the flotation time was extended. The results indicated that the sodium sulfide waste water gradually lost its depression during the recycling tests.

According to the optimal dosage of sodium sulfide used in Fig. 3, it was found that sodium sulfide might be consumed in the recycling tests. The lower sulfide ions left in the pulp, the less depression occurred. The hydrolysis equilibrium of sulfide ions in the water was well studied from the literature (Rao and Gorin, 2002). Sodium sulfide solution hydrolyzes three kind of sulfur-containing components, S^{2-}, HS^- and H_2S. The hydrolysis equations and constants were presented as follows:

$$H_2S \rightarrow HS^- + H^+ \qquad K_1 = 10^{-7.02}, \tag{1}$$

$$HS^- \rightarrow S^{2-} + H^+ \qquad K_2 = 10^{-13.9}. \tag{2}$$

The percentages of the three components were calculated and presented in Fig. 5. As shown in the Fig., when the pH was adjusted at 10, the percentages of HS^-, S^{2-} and H_2S were 99.88%, 0.01% and 0.11%. Therefore, the main function ion must be HS^- which depressed chalcopyrite flotation. This finding has been detailedly described in the previous studies (Peng et al., 2017), that is, HS^- removed the collectors and formed hydrophilic films on mineral surfaces via competitive adsorption.

Actually, the flotation in the beneficiation plant could not avoid air and used water. Oxygen and metal ions would speed up the consumption of S^-, promoting hydrolysis equation (1) moving to the left. However, this experiment was operated under the nitrogen atmosphere with deionized water, the oxidation of sulfide ions was significantly reduced. And, the harmful ions in the liquid were mostly released from the mineral surfaces. It assumed that the consumption of the sulfide ions in the liquid was only caused by the adsorption and precipitation (metal sulfide).

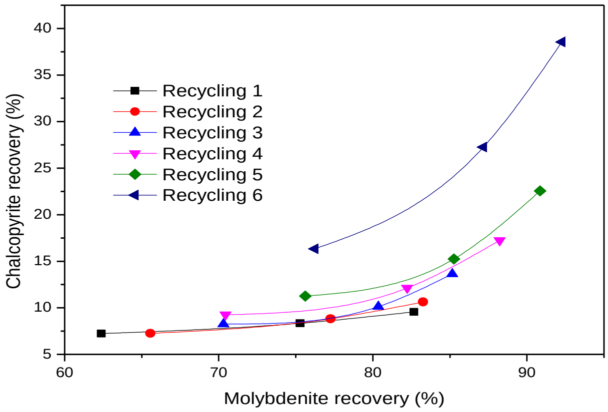

Fig. 4. Flotation results of molybdenite concentrates in the six recycling tests
(the three points of each curve from left to right refer to 1, 2 and 3 min flotation)

Nonetheless, according to the study of electrochemistry of the sulfide ore flotation, the flotation performance is controlled by the pulp potential (Herrera-Urbina et al., 1999). The potentials of the recycling water in the six recycling tests were given in Fig. 6. The Fig. showed that the potentials were increased more and more quickly as the recycling times went on. Combined with the flotation results in Fig. 4, the potential under -270mV could effectively decrease the copper recovery in molybdenite concentrates, consistent with previous studies (Chander, 2003). Therefore, the addition of sodium sulfide in the slurry to reach its potential under the threshold value could solve the problem that the recycling water lost its inhibitory effect in the returned processing. The consumptions of the function depression ions (HS^-) in the recycling waste water were evaluated as follows.

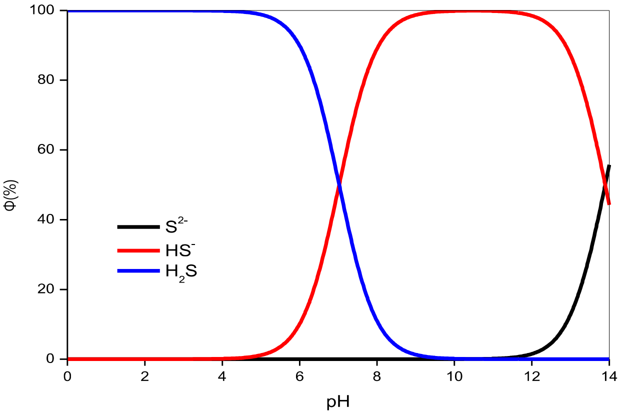

Fig. 5. The phase diagram of sulfide ions in various pH

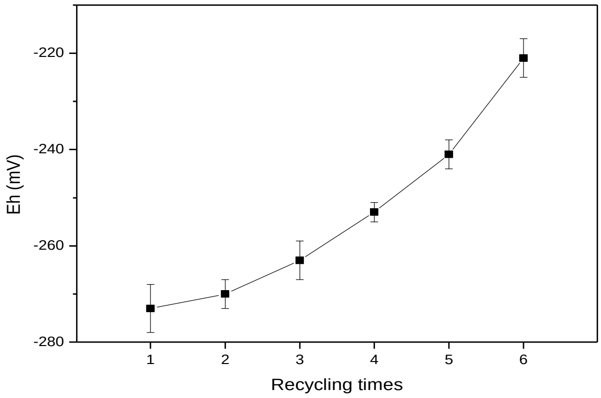

Fig. 6. Potentials of the recycling water in the six recycling tests at pH=10

3.3 ICP-OES analysis

The ICP-OES was specially used for the solution of trace element measuring method. In this research, the experiments were designed to use this method to find out the relationship between recycling times and element concentration in the solution, further to reveal the value of the sodium sulfide waste water recycling and the control of its properties. The concentrations of 18 kinds of elements were determined for liquid samples in the 6 recycling tests (see Table 1). In this table, the mineral leaching was obtained from the minerals leached in the deionized water for 5 min; sodium sulfide solution was 0.03 mol/dm^3 prepared with deionized water.

As shown in the data of mineral leaching, the mixed mineral dissolved its surface element into the water, it mainly included Ca, S, Na, Mg, Si, K, Fe, Cu, Mo, Sr and Al (concentrations > 0.2 mg/dm^3), and a small amount of B, Ba, Mn, Ni, Pb, V and Zn (concentrations < 0.2 mg/dm^3) still existed. It indicated that the mixed mineral had some impurities which most likely to be silicate containing Ca, Mg, Na, K, Al and Sr.

As shown in the data of sodium sulfide solution, Na and S concentrations were 1353 mg/dm^3 and 951 mg/dm^3, respectively, agreed with the concentration 0.03 mol/dm^3 that previously prepared. The $Na_2S \cdot 9H_2O$ of AR grade also had some impurities, such as Mg, Sr, Ca, K, Al and Si. Mineral leaching and Na_2S solution were individual and they showed the standard ions concentrations in the solution. After comparing with the recycling water, the various trends of the element concentrations could be calculated. Obviously, Na concentration from Na_2S was reduced slightly after recycling. Whereas, the S concentration which decreased a lot from 951 mg/dm^3 to 603 mg/dm^3 gave a difference by 348 mg/dm^3 during the six recycling tests. It showed that the S in the recycling water decreased more and more quickly with the recycling times increasing, indicating that more sodium sulfide was consumed when its concentration was at high levels. Moreover, the other elements, Ba, Cu, Fe, Mg, Mn, Ni, Sr, Zn, Ca and Al, showed the same performance that their concentrations were significantly dropped after the sodium sulfide added.

However, those elements released from the mineral surface increased as the recycling times increasing. Due to the decreases of solution pH and S^{2-} in each recycling, metal ions were more and more difficult to be precipitated. Hence, the metal ions showed an increasing trend. The most important changes of ions were Ca^{2+} and Mg^{2+} which decreased from 33.0 mg/dm^3 to 3.6 mg/dm^3 and 8.4 mg/dm^3 to 2.6 mg/dm^3, respectively, in recycling 1. The precipitations must be hydroxide and sulfide, which helped to decrease the solution pH and consume the S^{2-} ions, respectively. The main possible reactions were listed as below, and each solubility product constant K_{sp} could be found from the literature (University, 2016).

$$Me^{2+} + 2OH^- \rightarrow Me(OH)_2 \downarrow \qquad C_{\lim}(Me^{2+}) = \frac{K_{sp}}{C(OH^-)^2} \tag{3}$$

$$Me^{2+} + S^{2-} \rightarrow MeS \downarrow \qquad C_{\lim}(Me^{2+}) = \frac{K_{sp}}{C(S^{2-})}. \tag{4}$$

According to the ion reactions in the slurry, most metal ions could turn into precipitations, especially the heavy metal ions (Reinders and Linda, 2016). Those precipitations were detected in the solution with the naked eyes. Since the precipitations were very fine and hard to settlement, the pulp showed turbid after long time placement. Generally, the metal sulfide precipitations showed the black and metal hydroxide precipitation presented the white, spreading in the solution as floccule. It was interesting that Ca, Ba and Sr ions could not react with S^{2-} but still decreased, it was maybe because of the existence of $S_xO_y^{n-}$ oxidized in the operation. Nonetheless, the operation in the experiment was oxygen exclusion and finished very quickly in each step, oxidation must be only a little compared to the big amount of sulfide ions. Quantification of $S_xO_y^{n-}$ is very difficult, not only because of the great varieties, but also the trace. The further calculation would optionally ignore the influence of $S_xO_y^{n-}$. Precipitation sequence is generated by the K_{sp} and the ion concentrations. The concentration of S^{2-} and OH^- ions were 3×10^{-2} mol/dm^3 and 10^{-4} mol/dm^3, respectively. The limited concentration of metal ions in the slurry was calculated to estimate the order of each reaction and the existence of those precipitations. Herein, the C_{lim} results of hydroxide precipitation and sulfide precipitation were presented in Table 2 and 3, respectively. It revealed that Cu^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} must form sulfide precipitation instead of hydroxide precipitate, due to the smaller C_{lim} values. Despite some metal ions could precipitate with S^{2-}, the S^{2-} ions consumed by precipitation were only a little (see Table 1, the total amount of Cu, Fe, Mn, Ni, Pb and Zn in the mineral leaching was 1.14 mg/dm^3) which could be ignored in the calculation, most of S in the form of HS^- were adsorbed on mineral surfaces. Fig. 7 presented the adsorption capacities and densities of HS^- on mineral surfaces in each recycling times. The calculation method was listed as follows:

$$m = (C_n - C_{n+1}) \cdot V \tag{5}$$

$$D = \frac{m}{S} \tag{6}$$

where *m* is the adsorption capacity of HS^- (mg), C_n is the S concentration in the solution of recycling times (n, mg/dm^3), *V* is the volume of the recycling water, (L, 0.2 dm^3), *D* is the adsorption density of HS^- on mineral surfaces, (mg/m^2) and *S* is the area of the mineral surfaces, (m^2, 4.4 m^2).

Table 1. Element concentration at different conditions

Elements	Spectrum (nm)	Mineral leaching (mg/dm^3)	Na_2S solution (mg/dm^3)	Recycling water (mg/dm^3)					
				R1	R2	R3	R4	R5	R6
B	249.677	0.0474	---	0.0591	0.0621	0.0668	0.0721	0.0763	0.0859
Ba	455.403	0.0319	---	0.0005	0.0012	0.0056	0.0086	0.1420	0.0196
Cu	324.754	0.4041	---	0.1143	0.1256	0.1523	0.1842	0.2415	0.3041
Fe	259.940	0.5176	---	0.1219	0.1334	0.1534	0.1723	0.2156	0.2625
Mg	279.553	8.4345	0.0286	2.5621	2.7563	3.1256	3.2531	3.4621	3.6542
Mn	257.610	0.1319	---	0.0011	0.0012	0.0015	0.0021	0.0023	0.0022
Ni	231.604	0.0412	---	0.0101	0.0146	0.0241	0.0368	0.0513	0.0651
Pb	220.353	0.0149	---	---	---	---	---	---	---
Sr	407.771	0.2268	0.0064	0.0778	0.0784	0.0781	0.0805	0.0812	0.0881
V	310.230	0.0385	---	0.0375	0.0379	0.0364	0.0358	0.0355	0.0342
Zn	206.200	0.0473	---	0.0095	0.0134	0.0158	0.0246	0.0318	0.0407
Ca	317.933	32.9768	0.0186	3.6101	3.9256	4.5632	5.3856	6.7785	8.1563
K	766.491	2.5835	0.3025	2.2037	2.2913	2.4438	2.5318	2.6416	2.7856
Na	589.592	11.5865	1352.6452	1348.2643	1345.5426	1341.2653	1337.5986	1335.1568	1334.7584
Si	251.611	4.2904	0.1056	3.7271	3.7345	3.7225	3.6932	3.6623	3.6253
S	180.731	22.8906	951.2386	876.7589	806.495	743.2546	688.4156	642.1523	602.8456
Mo	277.540	0.3811	---	0.4024	04168	0.4325	0.4749	0.4935	0.5255
Al	396.152	0.2019	0.0082	0.0342	0.0423	0.0562	0.0821	0.0951	0.1121

---below detection limit. Element concentrations < 0.001 mg/dm^3 during mineral leaching are not presented

Table 2. Possible hydroxide precipitation reaction

Metal ion	K_{sp}	C_{lim} (mol/dm^3)
Cu^{2+}	2.2×10^{-20}	2.2×10^{-12}
Fe^{2+}	8×10^{-16}	8×10^{-8}
Mg^{2+}	1.8×10^{-11}	1.8×10^{-3}
Mn^{2+}	1.9×10^{-13}	1.9×10^{-5}
Ni^{2+}	2×10^{-15}	2×10^{-7}
Pb^{2+}	1.2×10^{-15}	1.2×10^{-7}
Zn^{2+}	1.2×10^{-17}	1.2×10^{-9}
Al^{3+}	1.3×10^{-33}	1.3×10^{-21}

It was found that the adsorption capacities and densities of hydrosulfide ions on mineral surfaces were dropped more and more quickly with the recycling times increasing. Combined with the flotation results in Fig. 4, the adsorption densities of HS^- (> 3 mg/m^2) could achieve good depression effects.

Table 3. Possible sulfide precipitation reaction

Metal ion	K_{sp}	C_{lim} (mol/dm^3)
Cu^{2+}	6×10^{-36}	2×10^{-34}
Fe^{2+}	6×10^{-18}	2×10^{-16}
Mn^{2+}	2×10^{-10}	$6.7\times10^{--9}$
Ni^{2+}	1×10^{-24}	3.3×10^{-23}
Pb^{2+}	8×10^{-28}	2.7×10^{-26}
Zn^{2+}	2×10^{-22}	6.7×10^{-21}

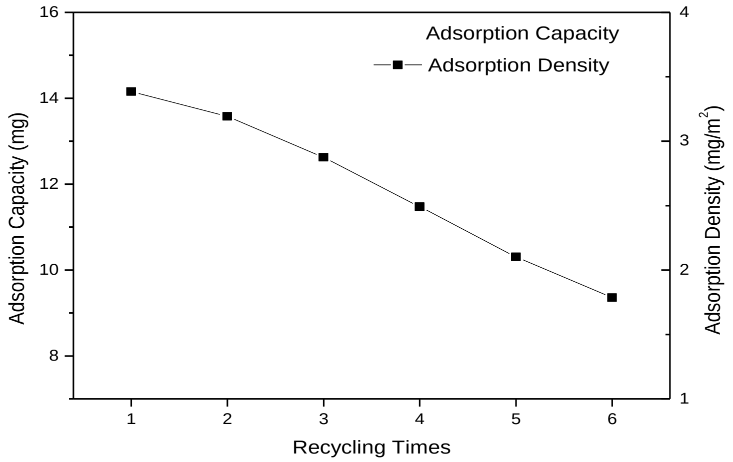

Fig. 7. The adsorption capacities and densities of HS^- on mineral surfaces in each recycling times

3.4 Verification flotation tests

Sodium sulfide solution (0 cm^3, 1 cm^3, 2 cm^3, 3 cm^3 and 4 cm^3) at the concentration of 0.5 mol/dm^3 were added into the sixth recycling water about 200 cm^3. The sodium sulfide replenishment, increased the concentration of S^{2-}, copper and molybdenum recoveries of the molybdenite concentrates, and pulp potentials were calculated, measured and presented in Table 4. Since the high concentration sodium sulfide solution addition could increase the pulp pH, diluted HCl solution should be added to adjust the pH to 10. As shown in this table, the flotation results and the solution Eh was improved after the sodium sulfide gradually added. The total S concentration larger than 800 mg/dm^3 could achieve a pulp potential less than -270 mV, finally obtained good quality of molybdenite concentrates, consistent with the previous studies. However, after addition quantitative amounts of sodium sulfide which equaled with the consumed amounts in the recycling tests, the depression effect seemed to have decreased a little according to the previous results. It was maybe due to the increased collectors, soluble salts and sulfur oxides in the recycling water. Although the solution ions were changeable, the potentials had only one parameter which was easy to control in this work. Therefore, the recycling tests were feasible by adjusting the potentials without considering the consumption of sulfide ions. This recycling method could be easily applied in the beneficiation plants.

4. Conclusions

It was found that the centrifugal dehydration could be used to collect the waste water from the pulp and recycle it in the separation flotation system. This operation made full use of the reagents in the waste water instead of discharging, indirectly protecting the environment. The study focused on the sodium sulfide waste water produced in the molybdenite-chalcopyrite flotation. To evaluate the depression performance of the sodium sulfide waste water, six times recycling tests were undertaken. It was found that HS^- was the function ion controlling molybdenite and chalcopyrite flotation via adsorption. The HS^- was gradually consumed during several times recycling, leading to the weak depression. After adding quantitative amounts of sodium sulfide in the recycling water to meet a relatively lower potential (below -270 mV), the depression could be recovered. The pulp potential control method could provide a possibility to apply the operation to the industry.

Table 4. Sodium sulfide replenished experiments for recovering the depression in the sixth recycling tests

Na_2S replenishment (mol)	Increased S concentration (mg/dm^3)	Total S concentration (mg/dm^3)	Recovery (%)		Potentials (mV)
			Mo	Cu	
0	0	602.85	92.27	38.57	-231
5×10^{-4}	79.60	682.45	88.23	18.26	-250
1×10^{-3}	158.41	761.26	85.88	13.16	-265
1.5×10^{-3}	236.45	839.3	83.26	10.13	-270
2×10^{-3}	313.73	916.58	82.67	9.56	-273

Acknowledgments

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