Improved flotation of auriferous arsenopyrite by using a novel mixed collector in weakly alkaline pulp

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Abstract: The purpose of using a mixed collector is to increase both flotation efficiency and selectivity. The mixed collector of potassium isopentyldithiocarbonate and N-dodecyl mercaptan exhibits high efficiency for the flotation of auriferous arsenopyrite, and the 2:1 mixing mass ratio of potassium isopentyldithiocarbonate and N-dodecyl mercaptan is preferred. Batch flotation tests indicate that a concentrate with the grade of 47.58 g/Mg Au and the recovery of 86.45% Au is achieved by using the mixed potassium isopentyldithiocarbonate/N-dodecyl mercaptan in weakly alkaline pulp. The collector mixture potassium isopentyldithiocarbonate + N-dodecyl mercaptan has greater adsorption density on the arsenopyrite surface than other conventional mixed collectors. The mixed potassium isopentyldithiocarbonate/N-dodecyl mercaptan can adsorb onto the arsenopyrite surface by intense chemisorptions, and the Sulfur-Iron chemical complexation is considered as the main adsorption mode. This is the reason why mixed potassium isopentyldithiocarbonate and N-dodecyl mercaptan collector can improve the flotation efficiency of auriferous sulfides.

Keywords: gold mine, arsenopyrite, mixed collector, flotation

1. Introduction

Western Dachang Gold Mine in Qinghai province, China contains large gold reserves with Au grades as low as 2.2 g/t (Ding et al., 2013). The gold generally occurs in association with arsenopyrite (nearly 68%) and pyrite (nearly 22%). The mineral properties of the gold mine are those of a fine-grained erosion-altering gold mine. The gold's inlaid grain size is extremely fine, and 90% of gold grain size is less than 30 µm. The main gangue minerals in the ores are clay minerals (accounting for 37.2%), such as mica, kaolinite, chlorite, etc., which are readily sliming minerals. The nature of the ore is typical of refractory gold ore. In addition, arsenopyrite is one of the poorest floatable minerals among the sulfide minerals. In general, its floatability is lower than that of commonly found pyrite. When gold is mainly associated with arsenopyrite, the poor flotation response of this mineral results in lower gold recovery (Misra et al., 2003). Hence, improving gold flotation recovery and reducing production costs become increasingly important to profits when treating low-grade refractory gold ores containing auriferous arsenopyrite (Dunne, 2016; O’Connor and Dunne, 1994).

In the flotation process of auriferous sulfides, the main chemical effects are reagent type and pulp pH value (Nagaraj, 1997; Valdivieso et al., 2003). Due to the poor floatability of arsenopyrite and the high clay contents in the Western Dachang low grade gold ores, H2SO4/H2C2O4 and CuSO4 were used as modifier and activator, respectively, and sodium O-isobutyl dithiocarbonate (SID) and ammonium dibutylthiophosphate (ADD) were used as collectors in the flotation operation. A number of experiments have shown that the recovery of gold might decrease by 10-15% in the absence of H2SO4.
However, using large quantities of H2SO4 (5-10 kg/t) may contaminate the environment, accelerate equipment corrosion, hasten collector decomposition and increase production costs (Chaiprapat et al., 2015; Feng et al., 2019).

There have been numerous reports on flotation of auriferous sulfides using the mixture of the two different collectors for improving the recovery of gold (Dunne, 2016; Lu et al., 2016; Wang et al., 2020). Tert-dodecyl mercaptan (TM, C12H25SH) has been used as the collector for sulfide flotation (e.g. molybdenite, arsenopyrite, sphalerite, etc.), but its application is limited due to odor and complex procedures. N-dodecyl mercaptan (NM, C12H25S) is the isomer of TM, and therefore they have the same molecular formula and functional groups. NM is odorless and can be easily used in sulfide flotation (Zhu, 2011). Studies have shown that the longer-chain xanthates are more readily oxidized, generating dixanthogen at lower potentials. An increase in thiol chain length increases the maximum contact angle, thereby increasing the hydrophobicity of the surface species. Both of these attributes favor the use of longer-chain xanthates, such as potassium isopentylthiophosphate (PID), for the flotation of gold-bearing ores (Lu et al., 2016; Gardner and Woods, 1974; Misra et al., 2003; Valdivieso et al., 2003). Therefore, a mixture of the two different collectors of NM and PID is used to float auriferous arsenopyrite without adding any H2SO4 to the weakly alkaline pulp. The collection mechanism of this mixed collector on arsenopyrite was investigated by adsorption, Fourier transform infrared (FTIR) determinations and molecular dynamics (MD) simulation analysis.

2. Experimental

2.1. Samples and reagents

Natural specimens of arsenopyrite samples were all obtained from Western Dachang Gold Mine, Qinghai province, China. According to X-ray diffraction (XRD) and chemical analysis (Zhang et al., 2020), the purity of auriferous arsenopyrite was 92.3% (42.47% As, 18.11% S, 31.69% Fe, 101 g/t Au). The samples were dry ground and screened to −74+38 µm and −10 µm for microflotation tests and mechanism determinations, respectively.

The real ores for batch flotation tests were also obtained from Western Dachang Gold Mine. Chemical analysis indicates that the main composition of the ore is as follows: 2.2 g/t Au, 4.1 g/t Ag, 0.52% As, 1.65% S, 4.13% Fe, 63.79% SiO2, 14.12% Al2O3, 2.88% K2O, 1.91% MgO, 1.71% Na2O and 1.69% C. As determined through chemical analysis and microscopy studies, the ores are primarily composed of 2.8% arsenopyrite, 1.0% pyrite, 36.4% quartz, 24.5% mica, 10.2% feldspar, 7.3% kaolinite, 5.6% dolomite, 5.4% chlorite and 4.9% calcite. The grain size of arsenopyrite particles is between 1 µm and 1000 µm. The degree of liberation of arsenopyrite is below 90 µm. Samples were milled to particle sizes of −74 µm (88.7 wt%).

In the experiments, N-dodecyl mercaptan (NM, CH3(CH2)11CH2SH, MW 202.4), potassium isopentylthiophosphate (PID, C5H11KOS2, MW 202.38), sodium O-isobutyl dithiocarbonate (SID, C5H10NaOS2, MW 172.24) and ammonium dibutyldithiophosphate (ADD, (C6H12O2)2P5S2NH4, MW 259.4) were used as collectors. The chemical structure of each collector is shown in Fig. 8. Sodium carbonate (Na2CO3)/sulfuric acid (H2SO4) and copper sulfate (CuSO4) were used as modifier and activator, respectively, and methyl isobutyl carbinitol (MIBC) was used as frother. All reagents used in microflotation tests and mechanism determinations were of analytical grade. Deionized double distilled water was used for microflotation, zeta-potential and infrared spectroscopy experiments. The reagents used in batch flotation tests were of industrial grade. Tap water was used in both grinding and batch flotation tests. Pulp pH was recorded by the PHS-3 meter. All experiments were conducted at room temperature.

2.2. Flotation experiments

The microflotation experiment was carried out in an XFG-type slot-type flotation machine (XFG-40 mL type). During the process, 2.0 g of arsenopyrite powder was placed in a Plexiglass cell, which was then filled with 30 mL of distilled water. HCl or NaOH was added to adjust the pH. After adding the desired amount of collector, the suspension was stirred for 4 min. Then, flotation was carried out for 5 min. The froth products and tailings were weighed separately after filtration and drying, and the recovery was
calculated based on the weight of the product (Feng et al., 2019). The impeller speed of the flotation machine was 1,600 r/min. Three microflotation experiments were performed and the average results were reported.

The bench-scale flotation tests for the real ore were performed in an XFD-63 flotation cell (with self-aeration), with 3,000 mL for rougher-scavenger flotation and 1,000 mL for cleaner flotation, respectively. The impeller speed was 1,590 rpm. The froth product was collected with an automatic froth scraper device. In the flotation stage, the desired amount of reagent was added in sequence to the flotation cell with 3 min intervals, and the flotation time was 7 min. The final products of concentrates and tailings were filtered, dried, weighed and analyzed for Au, respectively. The flowsheet of bench-scale locked cycle tests is shown in Fig. 1. The experimental system used the 2:1 collector mixture of PID + NM, and the comparative system used the 2:1 collector mixture of SID + ADD (the total dosage of every mixed collector in the locked cycle tests was 411 g/t). To assure the accuracy of bench-scale flotation tests, the calculated grade of feed was compared with the head assay. If the calculated Au grade of feed was not in the range of 2.2±0.02%, then the concentrates and tailings were re-assayed, and even the flotation tests were repeated.

2.3. Adsorption analysis

The amount of adsorption was measured using a TU-1810-UV (Shimadzu enterprise management (China) Co., Ltd). During the process, 2.0 g of arsenopyrite powder and 40 mL of distilled water were transferred into an Erlenmeyer flask. After reagent addition to the solution, the Erlenmeyer flask was stirred on a magnetic mixer for 30 min, allowing the adsorption process to reach equilibrium. The solution was centrifuged and filtered, and the supernatant was collected for UV spectroscopy analysis. Different collectors were prepared to measure absorbance to draw the standard curve. Maximum adsorption peaks of xanthate, mercaptan and dithiophosphate were 301 nm, 308 nm and 267 nm respectively. The equation of mineral surface adsorption is expressed as follows (Jiao et al., 2016):

$$\Gamma = \frac{(C_0-C)V}{1000M}$$

(1)

where $\Gamma$ is adsorption capacity of mineral, mol/g; $C_0$ and $C$ are initial and residual concentration of collector in suspension, mol/L; $V$ is volume of suspension, mL; $M$ is the weight of mineral, g. All adsorption experiments were performed three times, and the average values were reported in the following sections.

2.4. FTIR tests

The following procedure was used for FTIR spectra tests. The untreated pure arsenopyrite sample spectrum was used as a reference. During the process, 2.0 g of arsenopyrite powder was added into 30 mL aqueous solution with or without the desired amount of reagents, followed by ultrasonication for 5 min. Next, the solutions were magnetically stirred for 40 min and allowed to settle for another 40 min. After filtering, a vacuum drying method was used to obtain the solids. Fourier transform infrared (FTIR) spectra of solids were recorded using a Nicolet FTIR-740 spectrometer at 25 ± 1 °C. The spectra of the solids were taken with KBr pellets (Xu et al., 2014).

2.5. Molecular dynamics (MD) simulation

The MD simulation was performed by using Material Studio 6.0 package. During the simulation process, the Cambridge Serial Total Energy Package (CSTEP) module was adopted for geometry optimization of arsenopyrite (010) crystal structure. The (010) surface is the common cleavage plane of arsenopyrite (Dyar et al., 2008; Gao et al., 2014; Li et al., 2018; Wang et al., 1982). Optimization of each collector molecule structure was performed in the DMol3 module. The simulation process was carried out in the experiential and parameterized universal force field of the Forcite module (Sun et al., 2015).

3. Results

3.1. Microflotation test results

First, effects of pulp pH and collector dosage on the flotation behavior of arsenopyrite using the collec-
Fig. 1. Flowsheet and corresponding conditions of bench-scale locked cycle tests

tors PID, NM, SID and ADD were evaluated by microflotation tests, respectively (shown in Fig. 2 and Fig. 3). In comparison to the use of the SID/ADD collector, arsenopyrite exhibited better floatability with PID/NM, indicating that PID and NM were better collectors for arsenopyrite than were SID and ADD. High recovery of arsenopyrite could be obtained at approximately pH 3.0 and pH 8.0. Considering the disadvantages of acid flotation, the pH value of 8.0 was chosen to acquire the following measurements. Better results could be achieved when the collector dosage was higher than 50 mg/L. When the concentrations of PID and NM were 50 mg/L, the recoveries of arsenopyrite were 81.5% and 78.3%, respectively.

Fig. 2. Effect of pulp pH on flotation behavior of arsenopyrite using PID, NM, SID and ADD as collector
The flotation behaviors of arsenopyrite using the mixed collectors of PID + NM and SID + ADD were investigated by microflotation tests (shown in Fig. 4 and Fig. 5). When the two collectors were mixed for flotation of arsenopyrite, higher recovery could be obtained than in the cases of single collectors. In comparison with the use of the mixed collector of SID + ADD, marked differences in the recovery of arsenopyrite implied that the flotation performance was improved using the collector mixture PID + NM. The mixed collector with a mass ratio of 2:1 (PID:NM = 2:1/SID:ADD = 2:1) achieved the best flotation performance. Arsenopyrite had a favorable recovery of 87% using the collector mixture PID + NM. With the increase of mixed collector dosage, the flotation recovery of arsenopyrite increased gradually. When 60 mg/L mixed PID/NM and mixed SID/ADD were added, the recoveries of arsenopyrite were 90.7% and 82.3%, respectively. Upon further increasing the concentration of mixed collector, the recovery of arsenopyrite remained almost unchanged.
3.2. Adsorption studies

The amount of adsorbed collector on the mineral surface affected the mineral flotation efficiency. A series of adsorption studies were completed to probe the adsorption behavior of the mixed collector (PID:NM = 2:1, SID:ADD = 2:1) on the arsenopyrite surface (shown in Fig. 6). Compared with adding the mixed collector of SID + ADD, the collector mixture PID + NM had a greater adsorption amount on the arsenopyrite surface under the condition of the same collector concentration within the entire pH range. High adsorption density values could be obtained at approximately pH 3.0 and pH 8.0, and the amounts of adsorbed mixed collector on the arsenopyrite surface were 1.1 mg/g and 0.92 mg/g, respectively, which explain the flotation results (Figs. 2-5).

![Fig. 6. Relationship between adsorption amount of mixed collector (PID:NM = 2:1, SID:ADD = 2:1) on arsenopyrite surface and pulp pH](image)

3.3. FTIR analysis

To determine the type of adsorption of mixed collector (PID:NM = 2:1, SID:ADD = 2:1) on the arsenopyrite surface, the FTIR spectra were acquired: the results are shown in Fig. 7. The FTIR spectrum of arsenopyrite was essentially consistent with the standard spectrum of pyrite, and the characteristic absorption bands were 1633 cm\(^{-1}\) and 1125 cm\(^{-1}\) (Khummalai and Boonamnuayvitaya, 2005; Lu et al., 2019). After the collector mixture SID + ADD treatment, new bands appeared at 3463 cm\(^{-1}\) and 1321 cm\(^{-1}\), corresponding to -OH (SID and ADD) and C=S (SID)/P=S (ADD) stretching vibrations, respectively. After treatment with the collector mixture PID + NM, new bands appeared at 3463 cm\(^{-1}\), 2901 cm\(^{-1}\), 1403 cm\(^{-1}\), and 1321 cm\(^{-1}\), corresponding to -OH (PID), -CH\(_3\) (PID and NM), -CH\(_2\) (PID and NM), C-O-C (PID), and C=S (PID)/-SH (NM) stretching vibrations, respectively (Jiao, 2013). In addition, the bands of the original arsenopyrite shifted negatively. Analysis of the FTIR spectra indicated that the collector mixture PID + NM may have adsorbed onto the arsenopyrite surface in the form of intense chemisorption. Most of all, compared with the FTIR spectrum of arsenopyrite treated by the collector mixture SID + ADD, the corresponding band intensities treated by collector mixture PID + NM were strengthened, indicating that the collector mixture PID + NM could strongly adsorb on the arsenopyrite surface. This result is consistent with the microflotation and adsorption results.

3.4. MD simulation

To further investigate the adsorption mechanisms of different mixed collectors (PID + NM, SID + ADD) on the arsenopyrite surface, MD simulation was conducted using Material Studio 6.0 package. The adsorption models of mixed PID/NM and mixed SID/ADD on arsenopyrite (101) surface are displayed in Fig. 8 (a, b). These models indicate that the adsorption of sulphydryl collector on sulfide surface was based on the interaction between the sulfur atoms and the metal ions and that the -S functional groups reacted with Fe atoms on the arsenopyrite surface (Chanturiya et al., 2003; Chen et al., 2010; Sun et al., 2015). The average distances (equilibrated distance) between S and Fe were 2.162 Å (mixed PID/NM + arsenopyrite, Fig. 8 a) and 2.972 Å (mixed SID/ADD + arsenopyrite, Fig. 8 b), respectively, further revealing that easier adsorption of mixed PID/NM caused a stronger collection effect on arsenopyrite.
Fig. 7. FTIR spectra of arsenopyrite before and after treatment with 60 mg/L mixed collector (PID:NM = 2:1, SID:ADD = 2:1) at pH 8.0

Fig. 8. Adsorption models of mixed PID/NM (a) and mixed SID/ADD (b) on the arsenopyrite (101) surface. The color representations are as follows: white- hydrogen (H) atoms, gray- carbon (C) atoms, red- oxygen (O) atoms, yellow- sulfur (S) atoms, dark pink- arsenic (As) atoms, cyan- iron (Fe) atoms, and hot pink- phosphorus (P) atoms

than mixed SID/ADD. This is in accordance with the results in Figs. 2-7. The MD simulation results also illustrated that when mixed PIL/NM was added into the system, the -S functional groups could interact with Fe atoms to form S-Fe bonds on the arsenopyrite surface through chemical complexation. Meanwhile, -CH₃/-CH₂ hydrophobic groups were exposed outside, leading to the flotation of arsenopyrite.

3.5. Batch flotation test results

Based on the results of microflotation tests, adsorption measurements, FTIR analysis, MD simulation and the subsequent flotation condition tests, locked cycle testing was carried out at batch scale using PID + NM (mass ratio of 2:1) as a mixed collector in weakly alkaline pulp (S₁, pH 8.0). The comparative test (S₂, pH 8.0) was conducted using the collector mixture SID + ADD (mass ratio of 2:1). The other comparative test (S₃, pH 3.0) was conducted using H₂SO₄ with collector mixture SID + ADD (mass ratio of 2:1, the reagent system of Western Dachang Gold Mine). The closed flotation circuit included one roughing, three scavenging, and two cleaning steps (shown in Fig. 1). The best flotation result achieved
is displayed in Table 1. A concentrate grade of 47.58 g/Mg Au with recovery of 86.45% was achieved using mixed PID/NM at pH 8.0. A concentrate grade of 31.42 g/Mg Au with recovery of 77.56% was achieved using mixed SID/ADD at pH 8.0. A concentrate grade of 42.17 g/Mg Au with recovery of 84.38% was achieved using mixed SID/ADD at pH 3.0. Compared with S2 and S3, the S1 procedure remarkably increased the grade and recovery of gold. For this low-grade refractory gold ore, collector mixture PID + NM exhibited excellent collection for auriferous sulfides, confirmed by the high grade and recovery of gold concentrate achieved using PID + NM without adding any H2SO4 into the weakly alkaline pulp. The 2:1 collector mixture PID + NM exhibits great potential for industrial application in Western Dachang Gold Mine flotation.

Table 1. Values of closed flotation circuit (S1, S2, S3)

<table>
<thead>
<tr>
<th>System</th>
<th>Products</th>
<th>Ratio (w/%)</th>
<th>Au grade (g/Mg)</th>
<th>Au recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1, Na2CO3 + PID+ NM (pH 8.0)</td>
<td>Au concentrate</td>
<td>3.99</td>
<td>47.58</td>
<td>86.45</td>
</tr>
<tr>
<td></td>
<td>Tailing</td>
<td>96.01</td>
<td>0.31</td>
<td>13.55</td>
</tr>
<tr>
<td></td>
<td>Feed</td>
<td>100.00</td>
<td>2.20</td>
<td>100.00</td>
</tr>
<tr>
<td>S2, Na2CO3 + SID+ ADD (pH 8.0)</td>
<td>Au concentrate</td>
<td>5.41</td>
<td>31.42</td>
<td>77.56</td>
</tr>
<tr>
<td></td>
<td>Tailing</td>
<td>94.59</td>
<td>0.52</td>
<td>22.44</td>
</tr>
<tr>
<td></td>
<td>Feed</td>
<td>100.00</td>
<td>2.19</td>
<td>100.00</td>
</tr>
<tr>
<td>S3, H2SO4 + SID+ ADD (pH 3.0)</td>
<td>Au concentrate</td>
<td>4.55</td>
<td>42.17</td>
<td>84.38</td>
</tr>
<tr>
<td></td>
<td>Tailing</td>
<td>95.45</td>
<td>0.36</td>
<td>15.62</td>
</tr>
<tr>
<td></td>
<td>Feed</td>
<td>100.00</td>
<td>2.21</td>
<td>100.00</td>
</tr>
</tbody>
</table>

4. Conclusions

The mixed potassium isopentylidithiocarbonate (PID) and N-dodecyl mercaptan (NM) collector demonstrated high selectivity for the flotation of auriferous arsenopyrite with a PID/NM mass ratio of 2:1 at pH 8.0. In comparison with the use of the mixed sodium O-isobutyl dithiocarbonate (SID) and ammonium dIBUTYLDITHIOPHOSPHATE (ADD) collector, the flotation performance of arsenopyrite was greatly improved by using the collector mixture of PID + NM, and high grade (47.58 g/Mg) and recovery (86.45%) of gold concentrate were obtained without using H2SO4 at pH 8.0. Adsorption studies revealed that the mixed PID/NM had greater adsorption density on the arsenopyrite surface than that of mixed SID/ADD. FTIR and MD simulation analyses indicated that the mixed PID/NM could adsorb onto the arsenopyrite surface by chemisorption, and the stretching vibration bands had greater intensity than those of mixed SID/ADD. The S-Fe chemical complexation dominated the interaction between mixed PID/NM and arsenopyrite. Meanwhile, -CH3/-CH2 hydrophobic groups were exposed outside, which lead to flotation of auriferous arsenopyrite. This was the reason why the higher flotation indexes could be obtained by using the mixed PID + NM in the weakly alkaline pulp. The 2:1 collector mixture PID + NM exhibits great potential for industrial flotation application in Western Dachang Gold Mine.

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