ABSTRACT OF THE DISCLOSURE

Molybdenum is recovered from a metallic sulfide ore containing molybdenum, copper and iron, along with siliceous gangue minerals by conditioning a water suspension of such ore with an S-substituted isothiouronium salt, introducing a frothing agent and air to float the molybdenum and copper together away from the iron and siliceous gangue minerals, and depressing the copper to separate the molybdenum as product.

This invention relates to the flotation of bulk concentrates of molybdenum and copper sulfide minerals and separation thereof, and more particularly to the flotation of molybdenum and copper minerals from metallic sulfide ores containing molybdenum, copper and iron minerals and to the subsequent separation of molybdenum minerals from the copper-bearing ores.

An object of the present invention is to provide, in a froth flotation process for the treatment of metallic sulfide ores containing molybdenum, copper and iron minerals, collectors which alone or in synergistic use with common collectors, have better rejection of iron and less affinity for siliceous materials whereby higher recoveries of molybdenum and copper are obtained. Another object is to provide new and improved collectors or combinations of collectors for the recovery of molybdenum and also copper minerals. A further object is to provide a novel process for the separation of molybdenum and copper concentrates in a flotation system. Other specific objects and advantages will appear as the specification proceeds.

In one embodiment of the invention, S-substituted isothiouronium salts are preferably prepared by reacting an alcoholic solution of thiourea with a fatty halide or with an aromatic halide and are represented by the following formula:

\[ \text{RSC(NH}_3)_2\text{[X]} \]

where R is an aliphatic (straight chain or branched chain), cycloaliphatic, or aromatic hydrocarbon group having 2 or more but not more than 24 carbon atoms and preferably not more than 8 carbon atoms, or mixtures thereof, and where X is a halide such as Cl, Br, I, etc. Best results have been obtained when the hydrocarbon group has from 4 to 10 carbon atoms. Other methods of preparation of the collectors may be employed.

The isothiouronium halide compounds thus derived are employed to condition the metallic sulfide pulp together with a frother, if desired, such as methyl amyl alcohol or a polypropylene glycol ether, and following the conditioning, flotation is conducted in the usual manner to effect a bulk concentration and recovery of the molybdenum and copper minerals. As a specific example, a sulfide ore containing copper and molybdenum sulfides is ground to a finely-divided state, and a water pulp of the finely-divided ore is mixed or conditioned with about 0.03 lb. of the collector and about 0.03 lb. of a frother per ton of dry ore. Following conditioning, flotation is conducted for several minutes. An additional amount of collector and frother may then be added and flotation continued for another period. In this illustrative example, the bulk molybdenum and copper concentrates are floated from the iron sulfides and siliceous gangue minerals.

The bulk concentrates obtained as described are then subjected to a process to separate the copper and moly-...
In combination with the common reagents, such as isopropyl ethyl thionocarbonate or sodium isoamyl xanthate, etc., we prefer to employ isothiouronium chloride collector in combination with such common collector in the proportions of 1:1 to 5:1. Best results have been obtained when the proportion of 4:1 is employed. It will be understood that such proportions may be varied widely depending upon the character of the ore being treated.

In the second stage in which the concentrates are separated, we have discovered that among depressants which may be employed, sodium ferrocyanide is unusually effective as a depressant and when used with the collectors permits greater filterability of the molybdenum and also the copper concentrates, compared with the use of such depressants as Nokes reagents, which are dispersants. The filtration is accomplished in less time and with less use of separating equipment. In the second stage in which the depressant is added, it is common to add a small amount of collector at the same time that the depressant is added. By the use of ferrocyanide, it is found that less collector need be added, while at the same time greater filterability of the molybdenum concentrates, etc., is obtained.

The invention may be further illustrated by the following examples and discussion, which are illustrative of preferred embodiments of the invention, but the invention is not limited thereby.

**Example I**

Following the procedure described above, a copper-molybdenum sulfide ore containing iron sulfide was treated using the collector agents described in the following Table I at a pH level between 11 and 11.5, and with the results thereof shown.

<table>
<thead>
<tr>
<th>Test #</th>
<th>Collector</th>
<th>Concentrate Cu</th>
<th>Percent Cu</th>
<th>Percent Mo</th>
<th>Tails Cu</th>
<th>Percent Cu</th>
<th>Percent Mo</th>
<th>Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>485-009</td>
<td>Z-200</td>
<td>1.12</td>
<td>1.16</td>
<td>4.16</td>
<td>0.071</td>
<td>0.060</td>
<td>0.044</td>
<td>94.4</td>
</tr>
<tr>
<td>485-098</td>
<td>Z-11</td>
<td>10.82</td>
<td>3.00</td>
<td>0.100</td>
<td>0.096</td>
<td>0.086</td>
<td>0.091</td>
<td>97.1</td>
</tr>
<tr>
<td>490-068</td>
<td>Z-200</td>
<td>15.78</td>
<td>3.46</td>
<td>0.008</td>
<td>0.008</td>
<td>0.008</td>
<td>0.008</td>
<td>97.1</td>
</tr>
<tr>
<td>490-168</td>
<td>Z-200</td>
<td>19.36</td>
<td>4.49</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>97.1</td>
</tr>
<tr>
<td>500-256</td>
<td>Z-200</td>
<td>18.43</td>
<td>3.99</td>
<td>0.093</td>
<td>0.093</td>
<td>0.093</td>
<td>0.093</td>
<td>97.1</td>
</tr>
<tr>
<td>500-257</td>
<td>Z-200</td>
<td>20.07</td>
<td>4.39</td>
<td>0.006</td>
<td>0.006</td>
<td>0.006</td>
<td>0.006</td>
<td>97.1</td>
</tr>
<tr>
<td>500-257</td>
<td>Ethyl Isothiocyanate</td>
<td>21.37</td>
<td>4.39</td>
<td>0.006</td>
<td>0.006</td>
<td>0.006</td>
<td>0.006</td>
<td>97.1</td>
</tr>
</tbody>
</table>

In the above Table I, Z-200 is a designation for isopropyl thionocarbonate, and Z-11 is a designation for sodium isoamyl xanthate. This combination of these collectors is considered standard for the type of ore tested.

From Table I, it can be seen that good recovery of copper and molybdenum minerals is produced by the use of the collectors of the invention. It is also illustrated that the number of carbon atoms and the arrangement of these carbon atoms in the hydrocarbon group has influence on the so-called "collecting power" of the collector on a particular ore.

**Example II**

A South American ore (2.85% Cu and 0.7% Mo—considered a high grade ore) was crushed and ground for 12 minutes in a laboratory rod mill to a mesh of grind containing 20.3% by weight of plus 65 mesh size particles and 30.0% by weight of minus 200 mesh size particles.

Grind was at 50% solids and the amount of collector added to the mill varied with the collectors tested. The bulk flotation pH level varied between 11.3 and 11.7. The ground pulps were diluted to about 20% solids in a 1,000 gram stainless steel Denver flotation cell of (1800 r.p.m.), conditioned for 30 seconds (60 seconds if the collector was added to the flotation cell) with Dowfroth 250 and floated 5 minutes. An additional flotation step, preceded by a collector addition and conditioning in the cell, was made for 3 minutes. The two rougher concentrates were combined and thickened. The thickened bulk concentrate was then reground in a ball mill for 5 minutes at approximately 45-50% solids. A minimum pH level of 11.9 was used in a cleaner flotation step. The regrind pulps were diluted to about 20% solids in a 250 gram stainless steel Denver flotation cell (1200 r.p.m.) conditioned 15 seconds (1 minute, if additional collector was added to the cell) and floated 3 minutes, constituting the first cleaner flotation step. A second cleaner flotation product was collected for 2 minutes after another 15 seconds conditioning period. The two cleaner products were combined and assayed for metal content. Test results are set out in Table II.

**Example III**

A low grade Cu-Mo ore from a mining company in the Southwestern United States was crushed to minus 10 mesh and ground with lime in a laboratory rod mill. The ground feed to flotation contained 5.1% by weight of plus 65 mesh particles and 49.4% by weight of minus 200 mesh particles.

After grinding, the pulp was transferred to a Denver laboratory flotation machine, diluted to proper pulp density and the pH adjusted to that required, if necessary.
Collectors and frothers were added to the cell and the pulp conditioned 2 minutes. After a 2-minute float, a second increment of reagents was added and the pulp reconditioned and refloated. The separate froths were dried, weighed, and assayed.

Three stages, to the same total consumption as in the tests using the diethylphosphate collector.

Table IV illustrates an advantage in the use of aryl or alkyl isothiouronium chloride compounds for the recovery of molybdenum and copper minerals.

<table>
<thead>
<tr>
<th>Collector</th>
<th>#/T</th>
<th>Rougher Concentrate</th>
<th>Rougher Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium diethyl dithiophosphate</td>
<td>0.025</td>
<td>0.088</td>
<td>12.9</td>
</tr>
<tr>
<td>n-Amyl isothiouronium chloride</td>
<td>0.025</td>
<td>0.112</td>
<td>12.3</td>
</tr>
<tr>
<td>Benzyl isothiouronium chloride</td>
<td>0.025</td>
<td>0.098</td>
<td>11.5</td>
</tr>
<tr>
<td>2-ethylhexyl isothiouronium chloride</td>
<td>0.025</td>
<td>0.074</td>
<td>8.0</td>
</tr>
</tbody>
</table>

Table III illustrates an advantage in the use of alkyl-isothiouronium chloride reagents alone or in combination with other promoters such as potassium amyl xanthate to provide improved recovery of molybdenum and copper.

Example V

Bulk cleaner concentrates of copper and molybdenum were obtained as described in Example II, dewatered, and were subjected to a flotation process for the separation of molybdenum minerals from copper minerals using various depressing agents for copper minerals in accordance with the following procedure.

The thickened copper-molybdenum bulk cleaner concentrate was subjected to the particular depressant system being tested by conditioning in a stainless steel beaker with an air-driven mixer. The conditioned pulps were then diluted in a 250 gram stainless steel Denver flotation cell (1200 r.p.m.), pH adjusted to 7.0–7.3 (except when the sodium sulfide depressant system was used, in which case the pH level was near 12.0), conditioned for 2 minutes and floated for 4 minutes.

The rougher Mo concentrate thus obtained was then subjected to a second addition of the depressant system being tested. The conditioned pulp was then diluted to flotation density in a 250 gram stainless steel Denver flotation cell (1000 r.p.m.), pH adjusted to 7.0–7.3, conditions for 1 minute and floated for 3 minutes.

Test results are shown in Table V.
Table V illustrates the advantage of using alkylisothiouronium chloride reagents, alone or in combination with other reagents for recovery of copper and particularly molybdenum, utilizing Nokes LR 744 depressant for separation of molybdenum and copper minerals from bulk concentrates.

Table V also illustrates the effectiveness of alkylisothiouronium compounds, alone or in combination with other reagents, utilizing depressants such as sodium ferricyanide, sodium sulfide, or potassium permanganate. It can be seen that the alkylisothiouronium reagents, when used with the sodium ferricyanide, show much improved recovery of molybdenum over recoveries obtained when Nokes LR 744 reagent was used, while at the same time greater filterability of the molybdenum concentrates and also of the copper concentrates was obtained, the filtering operation being accomplished in much less time compared for instance to the results obtained with Nokes LR 744 reagent which is by nature a dispersing agent.

While in the foregoing specification we have set forth specific procedure in considerable detail for the purpose of illustrating embodiments of the invention, it will be understood that such details of procedure may be varied widely by those skilled in the art without departing from the spirit of our invention.

We claim:

1. A process for the separation of metallic ores containing molybdenum, copper and iron minerals, the steps of conditioning a water suspension of such ores in finely-divided condition with a collector comprising an S-substituted thiourea salt having the structure

\[
\text{[RSC(NH}_2 \text{)_2} \text{)]^+X^-}
\]

where R is an aliphatic, cycloaliphatic or aromatic hydrocarbon having 2 to 24 carbon atoms and where X is a halide, introducing a frothing agent and air to float the molybdenum and copper concentrates away from said iron, and subsequently depressing the copper to recover the molybdenum concentrate.

2. The process of claim 1 in which sodium ferricyanide is introduced to depress the copper concentrate.

3. The process of claim 1, in which the hydrocarbon has from 4 to 10 carbon atoms.

4. The process of claim 3 in which the halide is chloride.

5. The process of claim 1 in which the salt is n-butylinothiouronium chloride.

6. The process of claim 1 in which the salt is 2-ethylhexyl isothiouronium chloride.

7. The process of claim 1 in which the salt is 2-ethylhexyl isothiouronium chloride.

8. In a process for the separation of metallic sulfdie ores containing molybdenum, copper and iron minerals, the steps of conditioning a water suspension of such ores in finely-divided condition with a collector comprising an S-substituted thiourea salt having the structure

\[
\text{[RSC(NH}_2 \text{)_2} \text{)]^+X^-}
\]

where R is an aliphatic, cycloaliphatic or aromatic hydrocarbon having 2 to 24 carbon atoms, and where X is a halide, introducing a frothing agent and air to float the molybdenum and copper concentrates away from said iron, and subsequently depressing the copper to recover the molybdenum concentrate.

9. In a process for the separation of metallic sulfide ores containing molybdenum, copper and iron minerals, the steps of conditioning a water suspension of such ores in finely-divided condition with a collector comprising an S-substituted thiourea salt having the structure

\[
\text{[RSC(NH}_2 \text{)_2} \text{)]^+X^-}
\]

where R is an aliphatic, cycloaliphatic or aromatic hydrocarbon having 2 to 24 carbon atoms, and where X is a halide, introducing a frothing agent and air to float the molybdenum and copper concentrates away from said iron, and subsequently depressing the copper to recover the molybdenum concentrate.

10. In a process for the separation of metallic sulfdie ores containing molybdenum, copper and iron minerals, the steps of conditioning a water suspension of such ores in finely-divided condition with a collector comprising an S-substituted thiourea salt having the structure

\[
\text{[RSC(NH}_2 \text{)_2} \text{)]^+X^-}
\]

where R is an aliphatic, cycloaliphatic or aromatic hydrocarbon having 2 to 24 carbon atoms, and where X is a halide, introducing a frothing agent and air to float the molybdenum and copper concentrates away from said iron, and subsequently depressing the copper to recover the molybdenum concentrate.

11. In a process for the separation of metallic sulfdie ores containing molybdenum, copper and iron minerals, the steps of conditioning a water suspension of such ores in finely-divided condition with n-butylinothiouronium chloride and isopropyl ethyl thionocarbonate, introducing a frothing agent and air to float the molybdenum and copper concentrates away from said iron, and subsequently depressing the copper to recover the molybdenum concentrate.

12. In a process for the separation of metallic sulfdie ores containing molybdenum, copper and iron minerals, the steps of conditioning a water suspension of such ores
in finely-divided condition with n-butyl isothiouronium chloride and isopropyl ethyl thionocarbamate, adding a frothing agent and air to float molybdenum and copper concentrates from iron sulfide and depressing the copper concentrate from the molybdenum concentrate by the addition of sodium ferrocyanide.

13. In a process for the separation of metallic sulfide ores containing molybdenum, copper and iron minerals, the steps of conditioning a water suspension of such ores in finely-divided condition with n-butyl isothiouronium chloride and a collector selected from the group consisting of isopropyl ethyl thionocarbamate and sodium isopropyl xanthate, introducing a frothing agent and air to float the molybdenum and copper concentrates away from said iron, and subsequently depressing the copper to recover the molybdenum concentrate.

14. In a process for the separation of metallic sulfide ores, the steps of conditioning a water suspension of such ores in finely-divided condition with n-butyl isothiouronium chloride and a collector selected from the group consisting of isopropyl ethyl thionocarbamate and sodium isopropyl xanthate, introducing a frothing agent and air to float the molybdenum and copper concentrates away from said iron, and subsequently depressing the copper to recover the molybdenum concentrate.

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