METHOD FOR PREVENTING ACTIVATION OF SILICA IN ORE FLOTATION


ABSTRACT OF THE DISCLOSURE

A small amount of a water-soluble ferrocyanide or ferricyanide salt is added to a flotation pulp in order to prevent activation of quartz by iron sols when the pulp is floated in the presence of a fatty acid collector.

This invention relates to ore beneficiation, especially to the beneficiation of ores containing silica or quartz gangue.

When silica minerals, such as quartz, are present in aqueous ore pulps which also contain soluble iron salts, the silica tends to become activated by the iron compounds. When an aqueous ore pulp containing the activated silica is conditioned for flotation beneficiation with collector reagents, such as higher fatty acids, the silica will tend to report in the froth concentrate along with the desired metals. This will occur even when a conventional silica depressant, such as sodium silicate, is present. Washing of the ore pulp is helpful, especially when the iron is present as a ferrous salt, but it is usually not possible or practical to wash the ore to the extent that the silica is no longer activated. I have discovered that iron-activation is especially pronounced when conditions in the pulp result in hydrolysis of the iron salts, forming certain iron sols, especially ferric monohydrate sol.

As a result of hypothesizing as to the nature and mechanism of iron-activation of quartz, I have discovered a simple and highly effective method for depressing quartz in an aqueous ore pulp containing iron compounds which would normally activate the quartz, i.e., iron compounds that cause quartz to float when conditioned with collector reagents such as fatty acid reagents which normally do not collect silica.

Briefly stated, in accordance with the present invention, a water-soluble hexacyanoferrate, preferably potassium ferrocyanide, \( K_2(Fe(CN)_6) \), is used to depress silica in an aqueous ore pulp containing soluble iron compounds. A very small quantity of the soluble complex coordination compound is incorporated with agitation into an aqueous ore pulp containing the silica. The ore pulp, thus treated, is then conditioned for froth flotation with flotation reagents, such as high fatty acids, which are selective to a desired constituent of the ore. The silica, depressed as a result of the hexacyanoferrate treatment, reports in the flotation tailings, as desired.

It is believed that the depression of iron-activated silica is obtained by reversing the charge on the iron-containing sol adsorbed on the surface of the silica by means of the polyelectrolyte complex, with especially noteworthy results being realized with the tetravalent ferrocyanide ion.

The present invention is applicable to the treatment of metal oxide ores, such as iron, tin, manganese, titanium, and chromite ores, containing silica or quartz gangue and also containing soluble ferrous and/or ferric salts. The invention is especially applicable to the treatment of heavy metal oxide ore which is collected with the familiar anionic (higher fatty acid) collector reagents, such as tall oil acids, oleic acid, sulfo-oleic acid, lauric acid, etc.

The water-soluble hexacyanoferrates can be hexacyanoferrates (II) or hexacyanoferrates (III). These materials are also referred to as alkali and alkaline earth metal salts of ferrocyanic or ferricyanic acid. I prefer to use the ferrocyanide salts, which contain the quadrivalent anion \( Fe(CN)_6^{3-} \). Ferricyanide salts are similar in structure but contain the trivalent anion \( Fe(CN)_6^{4-} \). Of the water-soluble ferrocyanides, I prefer to employ potassium ferrocyanide \( K_2(Fe(CN)_6) \) because of its comparatively low cost and availability. Examples of other soluble ferrocyanides are ammonium ferrocyanide, sodium ferrocyanide and calcium ferrocyanide. The quantity of soluble hexacyanoferrate is usually within the range of 0.001 to 1 pound per ton of ore.

In putting the invention into practice, the ore is crushed and ground to flotation-size feed and pulped. In many cases it may be desirable to add water or dilute acid to remove partially soluble salts. The hexacyanoferrate reagent is dissolved in water and aqueous ferrocyanide solution is added with agitation to the ore pulp. This can be carried out at ambient temperature. The pulp is normally acid at this point of the process since soluble iron salts occur in ores of an acid nature. After the solution of hexacyanoferrate is mixed thoroughly with the ore pulp, normally activated silica will be depressed. The ore pulp can then be conditioned for froth flotation of the metal oxides from the silica and siliceous material. When finely divided ores or ores containing slimes are being beneficiated, a dispersant is employed. As examples of dispersants may be mentioned soluble alkali metal silicates, ammonium or alkali metal carbonates, and mixtures thereof. Alkali metal silicates also have a depressing effect on silica (when the silica is not iron-activated). Collector reagents or reagents for the desired metal oxide minerals are then added. The pulp is aerated and a froth withdrawn. The froth product is a concentrate of metal oxide minerals and the silica and siliceous minerals are concentrated in the tailings. The froth may be cleaned one or more times, and/or the middlings recirculated, as in conventional flotation procedures.

The following examples illustrate this invention in greater detail. It will be distinctly understood, however, that the invention is not limited to the flotation concentration of the specific oxidized metals illustrated since the benefits of the invention are realized in the treatment of a wide variety of ores containing iron-activated silica minerals.

**EXAMPLE I**

The following experiment was carried out to demonstrate the iron-activation of quartz and the depression of the quartz in the system by means of potassium ferrocyanide. In order to avoid complexities and uncontrollable variables inherent in the use of a natural ore pulp, a synthetic ore pulp was made up with substantially pure calcite and silica flour. The object of the test was to float the calcite from the silica flour with fatty acid collector reagents. Iron-activation was simulated by adding ferrous sulfate to the pulp and then adding hydrogen peroxide, thereby forming a ferric sol which activated the silica.

The calcite collector employed was a mixture of crude tall oil acids and mineral oil solution of an oil-soluble petroleum sulfonate. It was found that in the absence of ferrocyanide deactivation, 66.8% by weight of the silica flour was activated and floated. Because of the presence of silica in the froth, the CaCO3 grade of the froth product was only 18.3% when the silica was iron-activated. By treating the iron-activated pulp with a small amount of potassium ferrocyanide before conditioning the pulp for flotation with the calcite collector reagents, only 12.7% by weight of the silica floated. The CaCO3 grade of the resulting froth product was 54.1%. In other words, more
than five times as much silica was activated and floated when the pulp was not treated with a ferrocyanide. The details of the flotation tests are as follows.

In a typical flotation test, 128 milliliters of pulp were brought up to 400 mg/mL solids in distilled water. A 1% aqueous solution of FeSO₄·7H₂O was added to the water in amounts of 128 milliliters, the amount being calculated to provide 100 mg Fe⁺⁺ per liter of solution. The system was agitated for 5 minutes. The pH was 6.0. Three milliliters of 5% sulfuric acid solution was added, bringing the pH to 3.7. Following this, 10 milliliters of 3% hydrogen peroxide was added to promote hydroxide formation. The pH was 3.4. In the test made with potassium ferrocyanide reagent, 2.5 milliliters of a 1% aqueous solution of potassium ferrocyanide, K₃(Fe(CN)₆)·3H₂O was added after peroxide addition, bringing the pH to 3.3. The amount of potassium ferrocyanide used corresponded to 0.067 pound K₃(Fe(CN)₆)·3H₂O per ton of silica. In the control test, no ferrocyanide was added after the addition of peroxide and before conditioning the pulp for flotation of calcite. In conditioning the pulp for flotation of calcite, the pulp was alkalized by adjusting 4.3 milliliters of a 10% aqueous solution of sodium hydroxide and 112.5 grams of calcite was added and the pulp agitated for one minute. Forty-five milliliters of a 5% aqueous solution of ammonium sulfate was added and the pulp conditioned for 30 seconds. The pulp was treated with five pulses with an aqueous emulsion containing 20 milliliters of 2.5% aqueous ammonium hydroxide solution, and 137 drops (equivalent to 9.0 pounds per ton of silica) of a mixture of equal weight proportions of crude tall oil acids and “Calcium Petronate.” “Calcium Petronate” is the trade name of a 50% solution of neutral oil-soluble petroleum sulfonate in mineral oil.) The pH of the conditioned pulp was 8.6. The pulp was then conditioned for 12 minutes with 127 drops of hydrocarbon oil (“Eureka M”), equivalent to 8.0 pounds per ton of oil of calcite.

The pulp was subjected to froth flotation in a 1000 gram Air Flow flotation cell, the froth floated three times and the froth products combined. The results are summarized in Table I.

**Table I—Effect of Potassium Ferrocyanide on the Flotation of Calcite from Iron-Activated Silica**

<table>
<thead>
<tr>
<th>Test</th>
<th>K₃(Fe(CN)₆)·3H₂O</th>
<th>Li₂O/Ti SiO₂</th>
<th>Weight Percent CaO/silica</th>
<th>Weight Percent Sn on Froth Conc.</th>
<th>Weight Percent Sn on Froth Floated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>None</td>
<td>128.9</td>
<td>68.5</td>
<td>41.7</td>
<td>3.3</td>
</tr>
<tr>
<td>Ferrocyanide depression</td>
<td></td>
<td>0.007</td>
<td>54.6</td>
<td>12.8</td>
<td>1.0</td>
</tr>
</tbody>
</table>

**Example II**

This example demonstrates the application of the process of this invention to the rougher benefication of a very low grade (Bolivia) tin ore containing iron-activated silica. The main purpose of the rougher flotation was to produce a preconcentrate containing about 20% of the weight of the ground ore and the highest possible grade and recovery in terms of the tin values. The ore contained less than 0.5% Sn. In tests run with and without ferrocyanide, cassiterite (SnO₂) was floated with fatty acid reagents from gangue containing large amounts of calcium and silicate minerals. When the ferrocyanide reagent was used, less gangue reported with the cassiterite in the froth, as evidenced by the higher Sn grade and lower weight of the froth obtained with the ferrocyanide treated pulp.

The details are as follows.

In a typical flotation test, 500 grams of the ore from Bolivia was crushed until it was fine enough to pass through a 20-mesh screen. A sample containing five hundred grams (dry basis) of the crushed ore was screened through a 65-mesh screen and the plus 65-mesh material rod milled for three minutes at 60% solids. Soft water was used in the rod mill. The pH during grinding was the natural pH of the ore, i.e., about 5.5 to 4.0. All of the minus 65-mesh ore was combined and the soluble salts were removed by placing the minus 65-mesh ore in a 4 liter beaker, allowing the solids to settle, decanting the liquid, adding soft water to the solids until the beaker was substantially full and decanting the liquid. The ore still contained soluble ferric salt, as shown by qualitative analysis. Ten milliliters of a 1% aqueous solution of K₃(Fe(CN)₆)·3H₂O was added to the washed minus 65-mesh ore at 30% solids and the pulp was agitated for 5 minutes. The pH was 4.4. The amount of ferrocyanide added corresponded to 0.4 pound K₃(Fe(CN)₆)·3H₂O per ton of ore. The ore was then conditioned for froth flotation of the cassiterite as follows. Forty milliliters of a 5% aqueous solution of sodium carbonate was added and conditioned for one minute. To this was added 40 milliliters of a 5% aqueous solution of “Calgon for iron” and sodium sulfate (about 38% solids and having a percent Na₂O: percent SiO₂ weight basis of 1:3.22). The pulp was then conditioned for 5 minutes. One hundred and twenty-five drops of a mixture containing equal parts by weight of crude tall oil acids and calcium petronate was added and conditioned for 30 minutes. The pH was 8.4. Addition of 0.6 milliliter of 5% aqueous solution of sulfuric acid reduced the pH of 8.2. The conditioned pulp was subjected to froth flotation in a 500 gram Air Flow flotation machine, removing a single float.

The procedure was repeated without addition of potassium ferrocyanide. The results are summarized in Table II. The Sn values reported in this table were obtained by spectrochemical analysis. The concentration efficiency index used in this table is a value that is a measure of both selectivity and recovery. This value is obtained by the following calculation:

\[ \text{Concentration Efficiency Index (CEI)} = \frac{\text{Percent Sn (Froth Product) – Percent Sn (Head)}}{(2.38 \times \text{Percent Sn Head})} \times 0.95 \]

2.38 is the maximum percent Sn that could be obtained in a froth product representing 20% of the total weight of the ore and containing 95% of the tin. The maximum concentration efficiency index would be 100.

**Table II—Effect of Addition of Potassium Ferrocyanide on Flotation of Cassiterite from Iron-Activated Siliceous Oanque**

<table>
<thead>
<tr>
<th>Froth Product</th>
<th>R₃(Fe(CN)₆)·3H₂O</th>
<th>Li₂O/Ti Ore</th>
<th>Percent Sn</th>
<th>Percent Sn Dist.</th>
<th>Percent Sn Discharge</th>
<th>Percent Sn Head</th>
<th>Concentration Efficiency Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>20.35</td>
<td>1.41</td>
<td>86.1</td>
<td>0.065</td>
<td>0.48</td>
<td>44.8</td>
<td></td>
</tr>
<tr>
<td>0.4</td>
<td>21.65</td>
<td>1.70</td>
<td>83.8</td>
<td>0.060</td>
<td>0.44</td>
<td>35.3</td>
<td></td>
</tr>
</tbody>
</table>

**Claim 1**

In the flotation benefication of an acidic ore pulp in the presence of a fatty acid collector reagent, said pulp containing silica, and also containing ferric monohydrate sol resulting from the hydrolysis of an iron compound in said pulp, a method for depressing said silica so as to prevent activation and flotation of said silica as a result of the presence of said sol which comprises incorporating an additive consisting essentially of a small amount of a water-soluble hexacyanoferrate salt into said
ore pulp before subjecting said ore pulp to flotation in the presence of fatty acid collector reagent.

2. The method of claim 1 wherein said soluble hexacyanoferrate salt is a ferrocyanide salt.

3. The method of claim 2 wherein said ferrocyanide salt is potassium ferrocyanide.

4. A method for beneficiating an aqueous acidic ore pulp containing silica and ferric monohydrate sol resulting from the hydrolysis of soluble iron salt, which sol tends to activate said silica and cause it to float in the presence of a fatty acid collector reagent, said method comprising incorporating into said aqueous ore pulp an additive consisting essentially of a small amount of potassium ferrocyanide, thereafter conditioning the pulp for selective flotation of said heavy metal oxide mineral with a fatty acid collector reagent and subjecting the pulp to froth flotation, producing a froth product which is a concentrate of said heavy metal oxide mineral and a tailing which is a concentrate of quartz.

5. The method of claim 4 in which said ferrocyanide salt is potassium ferrocyanide.

6. A process for the froth flotation of a heavy metal oxide mineral from an aqueous acidic ore pulp containing quartz gangue and ferric monohydrate sol resulting from the hydrolysis of a soluble iron compound which comprises incorporating into said ore pulp an additive consisting essentially of a small amount of potassium ferrocyanide, thereafter conditioning the pulp for selective flotation of said heavy metal oxide mineral with a fatty acid collector reagent and subjecting the pulp to froth flotation, producing a froth product which is a concentrate of said heavy metal oxide mineral and a tailing which is a concentrate of quartz.

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