THE STUDY OF 8-HYDROXYQUINOLINE AND SALICYLALDOXIME ACTION AT THE MALACHITE FLOTATION

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Abstract

In this paper we followed up the data correlation of analytical chemistry of complexation for Cu (II) with chelatants in aqueous solution and the collector power of these reagents in the flotation of the mineral malachite that contain this ion. We studied the salicylaldoxime and 8-hydroxyquinoline (oxyne) concentration influences on the recovery percentage of copper from the malachite-quartz and malachite-calcite mixtures and on the copper percentage in the concentrates obtained using the flotation minicell. The compounds formed during flotation with oxyne and salicylaldoxime at the surface of malachite were studied by I.R. spectroscopy.

Keywords: flotation, malachite, oxyne, salicylaldoxime, I.R. spectroscopy

1. Introduction

The reagents with chelatant action are used in analytical chemistry due to their selectivity of certain metal ions [1]. A molecule may be chelatant when it has at least two functional groups whose donor atoms form links with the
coordinated metal. In the formation and stability of the chelated cycles the following factors have an important role: the pH of the solution, the basic capacity of ligants, the size and number of chelated cycles, the resonance effect and the steric effect.

The reagents flotation selection is made considering that the fixation of flotation reagent on the minerals surface takes place, in a many cases, through chemical bonds when formed chelat compounds between superficial adsorption centre and the reagent atoms. The reagent, which has specifically to a metallic ion in solution, keeps in certain conditions its selectivity even in the case of adsorption over the surface of the mineral that contains this metallic ion [2-7]. These reagents are used for the ores that contains oxidates minerals when neither a good concentration with the usual collectors nor a selective separation of the sterile can be achieved.

Because malachite - Cu₂(OH)₂CO₃ - contains the Cu (II) ion, from the reagents with chelating action that form stable chelat compounds with the ion Cu (II) in solution, have been studied the following: 8-hydroxyquinoline (oxyne), eriochrome black T, acetylacetone, salicylaldoxime, antranilic acid, and α benzoinoxime.

To study the collecting action of these reagents with chelating action, we used flotation, which has been done, in the Hallimond cell [2]. The experiments were orientated towards the determination of the optimum conditions necessary for a good recovery, namely the concentration of the reagent and the pH domain

The best results in the Hallimond cell are obtained with oxyne (8-hydroxyquinoline) and salicylaldoxime and therefore these reagents were utilized for copper recovery from the synthetic mixtures malachite-quartz and malachite-calcite in a flotation minicell. These experiments follow to find the work conditions, which must be applied to the oxidized copper ores.

I.R. spectroscopic detemination have also been used for surveying the formation of certain species at the surface of minerals during adsortion of various reagents and there are many reports on this subject [8-14].The nature of the compounds formed over the malachite surface under the oxyne and salicylaldoxime action are studied by I.R. spectroscopy.

2. Experimental
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The minerals used malachite, calcite and quartz had the grading between 100-250 µm. One gram of mineral and also the collector solution, with known concentration and pH, are introduced in the Hallimond cell. The work conditions, kept constant were: the conditioning time (180 seconds), the flotation time (30 seconds), the debit of air (10 l/hour). The floated product is filtrated, dried in the drying stove at 80°C and weighed. The percent of recuperation, %R, for the studied minerals at different pH values and reagent concentrations was calculated.

In table 1 are presented for each reagent the amount of the substances weighed (m), the solvent used and the molar concentration (c) of the obtained solution.

Table 1. The solutions of the reagents prepared in 1 l marked balloon

<table>
<thead>
<tr>
<th>r.</th>
<th>Reagent</th>
<th>m, g</th>
<th>Solvent</th>
<th>c,mol/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Oxyne</td>
<td>0,145</td>
<td>acetone and water</td>
<td>10⁻³</td>
</tr>
<tr>
<td>2</td>
<td>Acetylacetone</td>
<td>0,500</td>
<td>water</td>
<td>5.10⁻³</td>
</tr>
<tr>
<td>3</td>
<td>Eriochrome black T</td>
<td>0,230</td>
<td>water</td>
<td>5.10⁻⁴</td>
</tr>
<tr>
<td>4</td>
<td>Salicylaldoxime</td>
<td>0,411</td>
<td>water</td>
<td>3.10⁻⁴</td>
</tr>
<tr>
<td>5</td>
<td>Antranilic acid</td>
<td>0,137</td>
<td>water</td>
<td>10⁻³</td>
</tr>
<tr>
<td>6</td>
<td>Benzoinoxyme</td>
<td>0,227</td>
<td>alcohol</td>
<td>10⁻³</td>
</tr>
</tbody>
</table>

We used for the experimental determinations a flotation minicell (Fig. 1). This minicell works in the hydrodynamic regime of the flotation cell with normal foam formation.

The mixtures floated contain 5 g malachite and 45 g quartz or calcite having the granularity in the range 100-250 µm. Calcite and quartz, which represents the sterile in the ores, are incorporated in the studied mixtures to check the selectivity of the reagents.

When salicylaldoxime is used as chelating reagent, the experimental took place in the following way: the mixtures of the studied minerals are introduced in a 0,3 l tub, then water is added to obtain 0,2 l cloudiness. After one minute of stirring, the reagent solution is introduced and the pH is maintained at 7 or 8 (depending on the nature of the mixture). Through this procedure, conditioning time (5 minutes and the rotor speed 1800 rotations/minute), flotation time (5 minute and the rotor speed 2400 rotations/minute) and the
flow of the air (14 l/hour) were kept constant. When isooctane is utilized, this is introduced 30 seconds before the finish of the conditioning.

For 8-hydroxyquinoline (oxyne) a different procedure is adopted, because its solution in gasoline forms an emulsion with water. The reagent’s solution and the water are introduced in the flotation minicell and stirred for 3 minutes (the rotor speed 2400 rotations/minute). Then the minerals mixture is introduced and the same stages as at salicylaldoxime procedure are followed.

In the experiments that the oil is used it is introduced together with the reagent.

The concentrates obtained by the flotation are filtered, dried in the drying stove and weighted. The copper content is polarographic determined.

The I.R. spectre have been realised using the technique of the potassium bromide pelleting for malachite, Cu (II) oxynate, Cu (II) salicylaldoximate and malachite after being treated with solution of oxyne or salicylaldoxime.

The natural malachite has been ground in the agate mortar till 2-10 m m; part of the sample obtained is used to draw the spectres I.R.; some part of the sample is treated with solution of oxyne or salicylaldoxime, followed by
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filtration, drying in air and the drawing of the I.R. spectre.

The Cu (II) oxynate was prepared by using 150 cm$^3$ aqueous solution of Cu(NO$_3$)$_2$·3H$_2$O 0.1 M which is treated with 100 cm$^3$ oxyne 0.3 M solution in acetic acid 10%; the precipitate formed was filtered, washed with 10% acetic acid, then with water; after that it was dessicated at 110°C for one ore.

The Cu(II) salicylaldoximate was prepared by using 150 cm$^3$ aqueous solution of Cu(NO$_3$)$_2$·3H$_2$O 0.1 M which is treated with 300 cm$^3$ alcoholic solution 1% salicylaldoxime; the precipitate formed was filtered, washed with water and it was dessicated at 110°C for one ore.

3. Results and discussion

3.1. Flotation in the Hallimond cell

If the precipitation takes place in solution, the Cu(II) oxynate presents the maximum stability for the pH between 7 and 10.

During the determinations in the Hallimond cell we have maintained constant the concentration of the oxyne, 10$^{-3}$ mol/l, in the presence of 0.1 g/l diesel oil and we have changed the pH from 3 to 12. Figure 2 shows the variation of the recovery percent depending on the pH for malachite, quartz and calcite. The maximum recovery (90%-95%) was obtained for malachite with the pH between 7 and 9. Calcite and quartz float little with oxyne. Malachite float well for the same domain of pH where the stability of the chelats formed in solution is maximum.

For malachite with pH = 8 we have followed the variation %R depending on the concentration of the oxyne solution in the presence and in the absence of diesel oil (table2). The maximum recovery (95%) is obtained only in the presence of diesel oil and at the minimum concentration of 10$^{-3}$ mol/l oxyne.

The experiments without diesel oil show that there does not exist a possibility of malachite flotation only with oxyne for maximum recovery.
Fig. 2. The variation of the recovery percentage (%R) depending on the pH using the oxyne as flotation reagent.

Table 2. The variation %.R of malachite with the concentration of oxyne.

<table>
<thead>
<tr>
<th>concentration oxyne mol/l $\cdot 10^{-3}$</th>
<th>0.2</th>
<th>0.5</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>6</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>%R with 0.1 g/l diesel oil</td>
<td>12</td>
<td>70</td>
<td>95</td>
<td>94</td>
<td>95</td>
<td>94.5</td>
<td>95</td>
</tr>
<tr>
<td>%R without diesel oil</td>
<td>5</td>
<td>11</td>
<td>17</td>
<td>24</td>
<td>27</td>
<td>40</td>
<td>40</td>
</tr>
</tbody>
</table>

If the precipitation takes place in solution, the Cu(II) acetylacetonate presents the maximum stability for the pH between 8 and 10. The tested solution includes $5 \cdot 10^{-3}$ mol/l acetylacetone and 0.1 g/l isooctane. We have worked with a pH between 5.5 and 10 for malachite, quartz and calcite. It can be noticed that malachite floats little, maximum recovery of 38-40% at pH 6.5-7 being realized. The obtained result is in contradiction with the stability of the chelates Cu (II) with acetylacetone in solution.

The reagent, eriochrome blackT, forms stable compounds with Cu (II) in solution for pH between 4 and 10. For flotation we used solution $5 \cdot 10^{-4}$ in the presence of 0.1 g/l isooctane (for a suitable foam) for malachite, quartz and calcite. It is noticed that this solution does not floats malachite in contradiction with the pretty high stability of the Cu (II) chelat compounds in solution.
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The salicylaldoxime have chelating action for Cu(II) in solution, with which forms a chelatic compound. The flotation tested solution have the following composition: 3.10^{-3} mol/l salicylaldoxime and 0.1 g/l isoctane. We worked at pH between 3 and 10. Fig. 3 shows the variation of the recovery percent depending on the pH for malachite, quartz and calcite. The maximum recovery (92%) was obtained for malachite with the pH between 7 and 8. Calcite and quartz float little with salicylaldoxime.

![Fig. 3. The variation of the recovery percente (%R) depending on the pH using salicylaldoxime as flotation reagent](image)

For malachite with pH = 7 we have followed the variation %R depending on the concentration of the salicylaldoxime solution. The maximum recovery (92%) is obtained at the minimum concentration of 10^{-3} mol/l reagent.

In the analytical chemistry the antranilic acid is indicated as precipitation reagent for Cu(II) with which forms a chelatic compound. The tested solution contains 10^{-3} mol/l antranilic acid and 0.1 g/l light oil; we worked at pH between 3 and 11 for malachite, calcite and quartz. It was noticed that the maximum recuperation of 76% for malachite was obtained at pH between 5 and 8.

α benzoinoxime forms a chelatic compound with Cu(II); the structure is
presented in Table 1. We tested a solution of $10^{-3}$ mol/l benzoinoxime and 0.1 g/l isoctane at different values of pH for malachite, calcite and quartz. The maximum recuperation for malachite (80%) were obtained at pH=8.

### 3.2. Flotation minicell

Salicylaldoxime and 8-hydroxyquinoline (oxyne) gave the best results in the microflotation apparatus so they were utilized for the copper recovery from the synthetic mixtures malachite-quartz and calcopirite-calcite in a flotation minicell (Fig. 1).

Malachite contains 50% copper, percent that represent the maximum possible limit of % Cu in the concentrate.

In a series of experimental determinations salicylaldoxime was used as chelating action reagent for the copper recovery from the following mixtures: malachite-quartz with 140 g/t isoctane and malachite-calcite with 140 g/t isoctane.

On the basis of the experimental results at different salicylaldoxime concentrations (presented in Table 3), the Cu % in the concentrates obtained by flotation and the recovery percent of copper (% R) in the mixtures studied are calculated.

**Table 3. The concentrates obtained by salicylaldoxime flotation and their copper content**

<table>
<thead>
<tr>
<th>Salicylaldoxime g/t</th>
<th>malachite-quartz</th>
<th>malachite-calcite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>concentrate, g</td>
<td>Cu, g</td>
</tr>
<tr>
<td>70</td>
<td>5,3970</td>
<td>0,755</td>
</tr>
<tr>
<td>140</td>
<td>8,1730</td>
<td>2,125</td>
</tr>
<tr>
<td>280</td>
<td>4,8910</td>
<td>2,250</td>
</tr>
<tr>
<td>420</td>
<td>5,3488</td>
<td>2,300</td>
</tr>
<tr>
<td>560</td>
<td>4,8910</td>
<td>2,250</td>
</tr>
<tr>
<td>700</td>
<td>5,2272</td>
<td>2,300</td>
</tr>
<tr>
<td>1000</td>
<td>5,0000</td>
<td>2,300</td>
</tr>
</tbody>
</table>

Figures 4 and 5 show the variation of the % Cu and % R depending on the
salicylaldoxime concentration for the two mixtures. For malachite-quartz mixture, we noticed that we have obtained a maximum recovery 92% and a great % Cu in the malachite concentrate (46%) when we used minimum 280 g/t reagent and 140 g/t iso-octane, namely using the ratio reagent/iso-octane 2:1. The great content of Cu in the concentrate (46%) compared with the maximum content (50%) demonstrates a good selectivity of the reagent.

For malachite-calcite mixture, the maximum recovery (90%) and the maximum % Cu in the flotate (40%) is achieved with 420 g/t salicylaldoxime. The content of only 40% copper in the concentrate compared with the maximum value (50%) demonstrates that the reagent is less selective because a certain quantity of calcite passes in the concentrate.

In another series of experiments, 8-hydroxyquinoline (oxyne) was utilised as chelating action reagent for copper recovery from malachite-quartz mixture with 250 g/t light oil and without light oil. The experimental results are presented in Table 4 and the diagrams are shown in figures 6 and 7.

![Graph](image)

**Fig. 4. Variation of recovery percent of copper (%R) in malachite-quartz and malachite-calcite mixtures depending on salicylaldoxime concentration**

At 1500 g/t oxyne in the presence of 250 g/t light oil, a great recovery is achieved (90%) at a copper percent in the concentrate of 46.1% ; the reagent selectivity being good.

Without light oil, the recovery don’t exceed 84% and also the copper content in the concentrate is smaller that 42%.
Fig. 5. Variation of copper percent (%Cu) in malachite concentrate depending on salicylaldoxime concentration for malachite-quartz and malachite-calcite mixtures

Table 4. The concentrates obtained by oxyne flotation and their copper content

<table>
<thead>
<tr>
<th>Oxyne g/t</th>
<th>Concentrate malachite</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>with 250g/t oil</td>
<td>without oil</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>concentrat, g</td>
<td>Cupru, g</td>
<td>concentrat, g</td>
<td>Cupru, g</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>3,023</td>
<td>0,650</td>
<td>2,317</td>
<td>0,475</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>4,258</td>
<td>1,362</td>
<td>2,750</td>
<td>0,962</td>
<td></td>
</tr>
<tr>
<td>1500</td>
<td>4,880</td>
<td>2,250</td>
<td>5,263</td>
<td>2,000</td>
<td></td>
</tr>
<tr>
<td>2000</td>
<td>5,000</td>
<td>2,300</td>
<td>5,185</td>
<td>2,100</td>
<td></td>
</tr>
<tr>
<td>2500</td>
<td>5,110</td>
<td>2,325</td>
<td>4,970</td>
<td>2,087</td>
<td></td>
</tr>
</tbody>
</table>

3.3. The I.R. spectres for malachite – oxyne system

Fig. 8 combines the IR spectra for malachite (curve a), copper oxynate (curve b) and malachite after treatment with acetone solution of oxyne (curve c). By comparing the spectra we can notice the presence of bands characteristic to the Cu (II) oxynate from 1580; 1505; 1470; 1390; 1330; 1240 and 528 cm⁻¹ in the spectrum of malachite treated with oxyne. Therefore on
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the surface of smithsonite treated with the solution of reagent with chelatant action is formed Cu (II) oxynate.

Fig. 6. Variation of % Cu in malachite concentrate depending on oxyne concentration for malachite-quartz mixture

Fig. 7. Variation of copper recovery percent (%R) in malachite-quartz mixture depending on the oxyne concentration

3.3. The I.R. spectres for malachite – oxyne system

Fig. 8 combines the IR spectra for malachite (curve a), copper oxynate
(curve b) and malachite after treatment with acetone solution of oxyne (curve c). By comparing the spectra we can notice the presence of bands characteristic to the Cu (II) oxynate from 1580; 1505; 1470; 1390; 1330; 1240 and 528 cm\(^{-1}\) in the spectrum of malachite treated with oxyne. Therefore on the surface of smithsonite treated with the solution of reagent with chelatant action is formed Cu (II) oxynate.

**Fig. 8. I.R. spectra indicating the adsorption of oxyne onto malachite**
- a) malachite; b) copper oxynate;
- c) malachite after treatment with solution of oxyne
3.4. The I.R. spectres for malachite-salicylaldoxime system

In Fig. 9 are reunited the spectres I.R. copper salicylaldoximate, curve (a) and malachite after the treatment with salicylaldoxime solution curve (b), respectively. By comparing the spectres we can notice the presence of bands characteristic to the Cu (II) salicylaldoximate from 1600; 1550; 1475; 1340; 1310; 1030 cm\(^{-1}\) in the spectre of malachite treated with salicylaldoxime. Therefore on the surface of malachite treated with the solution of reagent with chelatant action is formed the Cu (II) salicylaldoximate.

Fig. 9. I.R. spectra indicating the adsorption of salicylaldoxime onto malachite: a)copper salicylaldoximate; b)malachite after treatment with solution of salicylaldoxime
4. Conclusions

In the Hallimond cell 8-hydroxyquinoline floats well malachite and the maximum recoveries takes place in a pH domain where the stability of the chelat complexes formed in solution is also maximum. The collector system must contain both oxyne and diesel oil, because oxyne forms along with the cation Cu (II) on the surface of the mineral insoluble metallic chelats to which diesel oil adheres by physical adsobtion, ensuring the hydrophobization of the mineral. Salicylaldoxime, \(\beta\)-benzoinoxime in the presence of isoctane and antranilic acid in the presence of light oil, float well malachite. Acetylacetone and eriochrome black T floats little malachite in the presence of isoctane, in contradicition with the pretty high stability of the Cu (II) chelat compounds in solution. Calcite and quartz floats very little with the mentioned reagents.

Salicylaldoxime and 8-hydroxyquinoline (oxyne) were utilized for the copper recovery from the synthetic mixtures malachite-quartz and malachite-calcite in a flotation minicell. A good copper recovery (92%) and a great copper percent (46%) in the mixture malachite-quartz, demonstrates a good selectivity of the reagents. For the mixture malachite-calcite, a maximum copper recovery (90%) is realised, but the smaller copper percent in the concentrate (38-40%) show that in this case the reagent is less selective.

With the chelating action reagents utilised, the salicylaldoxime and the oxyne, the realised a good copper content (%Cu) and the recoveries (%R) for malachite, which is an oxydated mineral of copper.

The I.R. spectres analysed in the present work give evidence of the formation of Cu(II)oxinate and Cu(II)salicylaldoximate on the surface of malachite during the flotation process in which 8-droxyquinoline and salicylaldoxime is used as a collector. This evidence is supported by the numerous bands belonging to Cu (II) oxynate and salicylaldoximate in the I.R. spectrum of malachite treated with the reagents with chelatant action.

References

The study of 8-hydroxyquinoline and salicylaldoxime action at the malachite flotation