Chelating Agents as Collectors in Flotation: Oximes—Copper Minerals Systems

D. R. Nagaraj and P. Somasundaran

Abstract—Based on our finding that commercial copper chelating solvent extractants such as LIX65NR and LIX67R are excellent collectors for copper minerals, a detailed study was made using several water-soluble chelating agents belonging to the class of aromatic hydrox oximes and having a gradual structural variation. A basic study of the system salicylaldoxime-tenorite was also carried out. Microflotation tests as a function of concentration of oxime, pH, addition of copper, etc., using acidic copper minerals such as chrysocolla and tenorite, and batch laboratory flotation tests using synthetic mixtures of quartz and acidic copper minerals were carried out.

The results have demonstrated that the hydrox oximes studied have comparable collector property, and in all cases the oxime was found to be partitioned between the mineral surface and the copper in the bulk aqueous phase in the form of a bulk copper chelate. The occurrence of the latter could be accounted for by formation in the bulk phase of a chelate between oxime and copper released from the mineral and/or by the detachment of the surface chelate. The role of surface and bulk chelates in flotation is discussed based on the results of partitioning of chelating agents into bulk and surface chelates in the salicylaldoxime-tenorite system. The effect of structural aspects such as isomerism and substitution in the molecule on the collector property of the oximes is also discussed. Substitution on oximic carbon by alkyl groups is found to promote collector activity. Only the anti-isomer has the ability to collect.

Introduction

Hydrox oxime chelating agents such as the LIX series of reagents are now widely used for commercial solvent extraction of copper from leach liquors. A new application for these solvent extractants—as froth aids for copper mineral flotation—was discussed in earlier papers (Nagaraj and Somasundaran, 1976 and 1977).

In this paper, results of the investigation of structure vs. collector property of water-soluble aromatic hydrox oximes for chrysocolla flotation (both microflotation and batch laboratory tests) are discussed.

The mechanism of collector action of hydrox oximes has been discussed, based on the study of the tenorite-salicylaldoxime system and in the light of findings that:

a) the chelating agent is partitioned between the mineral surface (to form a surface chelate) and the bulk aqueous phase (either as a chelate with dissolved copper or as a chelate detached from the surface),

b) the bulk chelate does not aid flotation of the mineral and

c) the solubility of the mineral largely controls the extent of partitioning of the chelating agent and, hence, flotation.

Experimental

Materials

Oximes: First, a survey of all the currently marketed hydrox oxime solvent extractants was made to find any structural variations between the reagents warranting a detailed investigation of structure vs. collector property. These reagents were used in the preliminary investigation after purifying the commercial samples by chemical and liquid chromatographic (Prep LC, Waters Associates) methods and purity checked by thin layer chromatography (TLC) and infrared spectra (IR). The results of chrysocolla flotation demonstrated that the commercial chelating extractants were not suitable for the structure-collector activity study because:

- The reagents are water-insoluble. Problems were encountered in obtaining representative emulsions of these oximes in water.
- The benzophenone oximes are not monoisomeric, mutual transformations between isomers being sensitive to a large number of variables.
- The Cu chelate of these oximes is not a well defined solid, unlike chelates formed by lower oximes such as salicylaldoxime. This becomes an important consideration in the separation of bulk and surface chelates.

For these reasons, a series of sparingly water-soluble oximes—shown in Table 1—was selected. Except for SALO and OHCHO, all the oximes were prepared from their respective reagent-grade ketones essentially by the methods of Blatt (1955)
Salicylaldoxime from LaChat Chemicals was recrystallized from petroleum ether containing benzene.

The standard methods of oxidation failed to give the oxide of o-hydroxy cyclohexanone (OHCHO). It was prepared essentially by the method of Nenz et al. (1964) by reacting cyclohexene and nitrosylhydrogen sulfate in cyclohexane below -5°C. Crude OHCHO was found by TLC to contain only the anti-isomer and was used as-is.

The water solubility at 25-26°C of the oximes was determined (Nagaraj, 1979). Solubility values in terms of molar concentration of the saturated solutions are also given in Table 1.

For the investigation of the mechanism of collector action of oximes, SALO was selected since it was water-soluble (solubility 2 × 10^{-1}M), monoisomeric, and is one of the better studied hydroxoximes with regard to its chelating and other chemical properties and the structure and stoichiometry of its Cu chelate, which is a well-defined crystalline solid.

Minerals: Chrysocolla used in earlier work was also used for the structure-collector property study, except that the size was -500 + 150 μm (48 + 100 mesh) in the present investigation. Tenorite was used for the basic study using SALO. Its preparation is described in detail elsewhere (Nagaraj, 1979). Briefly, natural cuprite (20%) from Kennecott was upgraded to about 92% CuO by heavy liquid separations using tetrabromoethane (S.G. 2.95) and thalious format malonate (S.G. 4.5) and, after thoroughly washing the mineral free of the above liquids, was heated in a furnace at 510°C for 100 hours to give -212 + 106 μm (-65 + 150 mesh) CuO analyzing 70.7% Cu, and 6.7% insolubles. No Cu2O was detected in the X-ray diffraction pattern and the infrared spectrum.

**Method**

**Structure vs. Collector Property: Microflotation Tests**—The setup used for reagentizing is shown in Fig. 1. Chrysocolla (0.7 g) was reagentized by agitating with aqueous collector solution containing 1% acetone (added to obtain smaller bubbles and a more uniform bubble size distribution) and at the required pH and ionic strength (I.S.); pH was continuously monitored by adding KOH or HNO3 from a Dosimat buret and recorded on a strip chart recorder. The reagentized mineral was floated in a Hallimond tube for one minute at 20 mL/min nitrogen.

**Batch Laboratory Cell Tests**—Mixtures of chrysocolla with quartz were prepared by wet-grinding in a laboratory porcelain ball mill at 60% solids by weight, and wet-screened to obtain -212 + 44 μm (-65 + 325 mesh) fraction assaying approximately 1.7% CuO. Some 250 g of this fraction was reagentized by agitating with aqueous collector solution containing 1% acetone (added to obtain smaller bubbles and a more uniform bubble size distribution) and at the required pH and ionic strength (I.S.); pH was continuously monitored by adding KOH or HNO3 from a Dosimat buret and recorded on a strip chart recorder. The reagentized mineral was floated in a Hallimond tube for one minute at 20 mL/min nitrogen.

**Table 1—The Structures and Water-Solubility of Hydroxy Oximes**

<table>
<thead>
<tr>
<th>Structure</th>
<th>Water Solubility</th>
<th>Stock Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>SALO</td>
<td>2 × 10^{-1}</td>
<td>10^{-2}</td>
</tr>
<tr>
<td>OHAP</td>
<td>0.5 × 10^{-2}</td>
<td>10^{-3}</td>
</tr>
<tr>
<td>OHBOP</td>
<td>0.5 × 10^{-2}</td>
<td>10^{-3}</td>
</tr>
<tr>
<td>OHBA</td>
<td>0.5 × 10^{-2}</td>
<td>10^{-3}</td>
</tr>
<tr>
<td>2HBAP</td>
<td>1.5 × 10^{-4}</td>
<td>10^{-4}</td>
</tr>
<tr>
<td>2HBMAO</td>
<td>1.5 × 10^{-4}</td>
<td>10^{-4}</td>
</tr>
<tr>
<td>2HBA</td>
<td>1.5 × 10^{-4}</td>
<td>10^{-4}</td>
</tr>
<tr>
<td>2HBCA</td>
<td>1.5 × 10^{-4}</td>
<td>10^{-4}</td>
</tr>
<tr>
<td>2HBCA</td>
<td>1.5 × 10^{-4}</td>
<td>10^{-4}</td>
</tr>
<tr>
<td>2HBCA</td>
<td>1.5 × 10^{-4}</td>
<td>10^{-4}</td>
</tr>
<tr>
<td>2HBCA</td>
<td>1.5 × 10^{-4}</td>
<td>10^{-4}</td>
</tr>
</tbody>
</table>

Tenorite-salicylaldoxime System: Microflotation Tests—From the initial tests it was observed that the pH of the aqueous SALO solution decreased very sharply upon adding the mineral owing to chelate formation (by deprotonation) between SALO and copper species on the mineral surface as well as those released from the mineral into the bulk aqueous phase:

$$[\text{CuO}_{\text{min}}] + [\text{Cu-species}]_{\text{aq}} + x\text{SALO} \rightarrow [\text{Cu-SALO}]_{\text{min}} + [\text{Cu-SALO}]_{\text{bulk}} + x\text{H}^+$$

The pH decrease was most pronounced when the initial pH of the SALO solution was between 4.5-8.5.

The rapid and large pH decrease (followed by an increase) occurring in the CuO-SALO system necessitated rapid and continuous monitoring of pH during reagentizing. 0.8 g of CuO was reagentized with 94 mL of SALO solution (containing 1% acetone) at an I.S. of 2 × 10^{-3}M (KNO3) and constant pH, and floated for one minute.

Partitioning of SALO—The possibility of partitioning of oximes into surface and bulk chelates was discussed in earlier publications. In the present investigation these chelates have been separately determined quantitatively for the SALO-Tenorite system, using the scheme shown in Fig. 2, by extracting the chelates with chloroform, which, among all the solvents tested, had the highest solubility for chelates. Briefly, the tests involved the following steps:

a) The mineral was reagentized as described.

b) The supernatant with the bulk chelate dispersed in it was separated from the mineral bed by mixing, allowing the mineral to settle (the S.G. difference between mineral and chelate is more than three units) and decanting the supernatant.

c) Step (b) was repeated using fresh 2 × 10^{-3}M (KNO3) until all the bulk chelate was separated from the mineral bed.

d) The supernatant from steps (b) and (c) was filtered, bulk chelate was washed with water and extracted with chloroform (to eliminate any mineral slimes reporting as bulk chelate); the solvent was then evaporated and the bulk chelate weighed.

Fig. 1—The experimental setup for mineral reagentizing.
RINSE ELECTRODE

OHBePO

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Fig. 2 — The experimental scheme for quantitative determination of partitioning salicylaldoxime into bulk and surface chelates.

e) The chelate on mineral was extracted by vigorously mixing the mineral bed (after c) with chloroform and repeating this step with fresh chloroform. The solvent was evaporated and the surface chelate weighed.

Results

Chrysocolla-Oximes

Chrysocolla flotation as a function of concentration of the oximes is shown in Fig. 3 and Table 2. The effect of pH on chrysocolla flotation is shown in Fig. 4 for SALO, OHAP0, and OHBuPO. The results of batch laboratory flotation are summarized in Fig. 5 for SALO and OHAP0.

The following become evident from the results shown in Fig. 3 and Table 2.

a) Substitution of -CH3 (to give OHAP0) in place of -H in R1 (see) causes a large increase in the collector efficiency; concentration of OHAP0 is about half that of SALO for 60% flotation. The water-solubility of the oxime is lowered by almost two orders of magnitude upon -CH3 substitution.

b) Increasing the chain length of R1 by two more -CH2 groups (to give OHBuPO) further improves the collector efficiency, but not to the extent as in (a); the water-solubility of OHBuPO is only an order of magnitude less than that of OHAP0.

c) Substitution in the 5-position on the benzene ring, (R1 = CH3, R2 = CH3·2H5MeAPO and R1 = H, R2 = OCH3·2H5MBAO) drastically affects the collector efficiency; both 2H5MeAPO and 2H5MBAO are inferior to SALO.

d) A fused aromatic ring (napthalene), instead of the benzene, again lowers the collector efficiency, thus 2HNAO is inferior to SALO.

e) Substitution of a phenyl for R1 in (I) decreases both the collector efficiency and water-solubility; thus, OHBePO is inferior to even SALO.

f) OHCHO could be considered to belong to the class of acyloan oximes, although the oxime is distinct because of the cyclic alkane. OHCHO was found to be highly soluble in water. Its chelate with copper was soluble in slightly acidic solutions — no chelate probably formed below pH 4.0 — and precipitated in the basic pH range. OHCHO was a poor collector for chrysocolla even at high concentrations (Table 2).

For the oximes OHBePO, 2H5MeAPO, and 2H5MBAO, it was observed that bubbles during flotation were smaller than for the other oximes at similar concentrations.

Compared with SALO, the collector efficiency for OHBuPO and OHAP0 is higher at almost all the pH values, as can be seen from Fig. 4. Flotation of chrysocolla is maximum around pH 5.0 for these oximes and for 2HNAO. On the other hand, flotation with OHCHO increases with increase in pH from 3.0 to about 6.5 above which it remains constant.

Results of batch laboratory flotation tests presented in Fig. 5 confirm the improved collector efficiency of OHAP0 over SALO for chrysocolla flotation from its synthetic mixtures with quartz. The grade of chrysocolla concentrate using OHAP0 is better than that using SALO, which suggests that OHAP0 may be more specific than SALO.

Salicylaldoxime-Tenorite System

Microflotation Tests: Flotation behavior of tenorite as a function of initial concentration of SALO at pH 4.8 and I.S. of 2 x 10^-2 M (KNO3) and 10 minutes reagentizing is shown in Fig. 6. As can be seen from Fig. 6, flotation of tenorite is complete at about 5 x 10^-4 M SALO, and minimum at approximately 5 x 10^-5 M SALO. It must be noted that in all tests Cu-SALO chelate was found dispersed in the bulk phase, the amount increasing with concentration of SALO and reagentizing time.

The effect of pH on tenorite flotation at 7.5 x 10^-4 M SALO, I.S. = 2 x 10^-2 M and 10 minutes reagentizing is shown in Fig. 7. Flotation of tenorite attains a maximum at pH 2.5 and 9.0, and a minimum at pH 3.5.

<table>
<thead>
<tr>
<th>Oxime</th>
<th>Initial Concentration, M</th>
<th>Reagentizing Time, Min.</th>
<th>pH</th>
<th>% Floated</th>
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<td>OHCHO</td>
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<td>4.8</td>
<td>15.0</td>
<td>15.5</td>
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<td></td>
<td>5 x 10^-5</td>
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<td>20.0</td>
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<td>10^-4</td>
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<td></td>
<td>10^-3</td>
<td>4.8</td>
<td>9.5</td>
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<td></td>
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<td>4.8</td>
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<td></td>
<td>10^-1</td>
<td>4.8</td>
<td>8.0</td>
<td></td>
</tr>
<tr>
<td>OHBePO</td>
<td>10^-5</td>
<td>4.8</td>
<td>14.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2 x 10^-4</td>
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<tr>
<td></td>
<td>5 x 10^-5</td>
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<td>33.8</td>
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<td>5 x 10^-5</td>
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<td>36.5</td>
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<td></td>
<td>10^-4</td>
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<td>8.4</td>
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<tr>
<td></td>
<td>10^-3</td>
<td>4.8</td>
<td>19.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10^-2</td>
<td>4.8</td>
<td>18.5</td>
<td></td>
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<tr>
<td></td>
<td>10^-1</td>
<td>4.8</td>
<td>57.4</td>
<td></td>
</tr>
</tbody>
</table>

By improved technique of solubilizing OHBePO.
<table>
<thead>
<tr>
<th>Concentration</th>
<th>Time, Min.</th>
<th>pH</th>
<th>% Floated</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5 x 10^-4</td>
<td>10</td>
<td>4.8</td>
<td>29.7</td>
</tr>
<tr>
<td>1 x 10^-4</td>
<td>10</td>
<td>4.8</td>
<td>35.7</td>
</tr>
<tr>
<td>7.5 x 10^-5</td>
<td>10</td>
<td>4.8</td>
<td>32.5</td>
</tr>
<tr>
<td>5 x 10^-5</td>
<td>10</td>
<td>4.8</td>
<td>20.7</td>
</tr>
<tr>
<td>2.25 x 10^-5</td>
<td>10</td>
<td>4.8</td>
<td>13.7</td>
</tr>
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</table>
Partitioning of SALO: The total and individual amounts of bulk and surface chelates determined as a function of concentration of SALO and pH, under the same conditions as those used for microflotation tests, are shown in Figs. 8 and 9, respectively. The amounts of bulk and surface chelates at $5 \times 10^{-3}$ M SALO (Fig. 8) are only apparent values since the bulk chelate formed was very coarse and settled as fast as the mineral, making its complete separation from the mineral almost impossible. The points at $5 \times 10^{-3}$ M are, therefore, joined by dashed lines. The actual amount of bulk chelate should be higher, and that of surface chelate correspondingly lower, than the apparent value shown in Fig. 8. These apparent values were corrected for using the same surface to bulk chelate ratio as obtained for $2 \times 10^{-3}$ M SALO, and the corrected values are also plotted (asterisks) in Fig. 8. It is to be noted that the flotation behavior (Fig. 6) is correlated very well by the results in Fig. 8, particularly for surface chelate.

The following become evident from the results in Fig. 9:

a) the amounts of surface chelate correlate very well with the flotation behavior (Fig. 7),
b) the total amount of chelate formed in the system reaches a maximum at pH 3.5 and decreases sharply below pH 2.5 and above 9.5, and
c) the curve for total chelate closely follows that for bulk chelate.
Discussion

Chrysocolla-oximes Systems

In formula (I) when \( R_2 = H \) and \( R_1 = -H, -CH_3 \) or \(-CH_2CH_2CH_3\) the apparent effect is the increase in the collector efficiency in the order

\[ -H < -CH_3 < -CH_2CH_2CH_3 \]

This increase in collector efficiency with increase in chain length is in general agreement with results of Fuerstenau, Healy, and Somasundaran (1964) for quartz flotation using amine collectors of increasing hydrocarbon chain length. As can be expected, introducing the first \(-CH_2\) in SALO results in a much larger change in polarity of the molecule compared with further addition of two \(-CH_2\) groups. This is reflected not only in the water-solubility of the oximes—SALO, OHAPO and OH-BuPO—but also in the collector efficiency. Furthermore, the electron donating tendency of \(-CH_2\) group may also favor chelation reaction.

Substitution of a phenyl group on \( R_1 \) \((R_2 = H)\) will make the molecule much less polar than SALO as reflected in the water-solubility. On the basis of this, OHBPO can be predicted to have a higher collector efficiency than SALO. The actual finding was, however, contrary to the prediction, and this can be due to the possible steric hindrance to chelation offered by the second benzene ring and the slower kinetics of adsorption of OHBPO. Recent adsorption tests (Nagaraj, 1979) have indicated that adsorption of OHBPO on chrysocolla is significantly higher than that of SALO at the same oxime concentration, thereby suggesting that steric hindrance or slow chelation kinetics may not be responsible for the lower collector efficiency of OHBPO compared to that of SALO. Bubble size reduction observed during flotation is, therefore, a major factor.

Substitution in \( R_2 \) (see formula I) by \(-CH_3 \) \((R_1 = CH_3 \) or \( H, \) respectively) not only decreased the water-solubility of the parent oximes, but also decreased the collector efficiency. The decrease in water-solubility is to be expected from the decrease in polarity of the molecule as a result of substitution. The decrease in collector efficiency could be attributed to the decrease in acid-strength \((\log \mathbf{P}^H \text{, the proton-ligand stability constant, Irving \& Rossotti})\) of the molecule owing to the increase in electron density on the phenolic oxygen caused by the nucleophilic substituents (Patel and Patel, 1970). This can, however, increase the metal-ligand stability as is generally observed (Martell and Calvin, 1952). The effect of electron-releasing groups on the ring is, therefore, generally favorable for chelation. Again, the reduction in bubble size appears to be the major factor responsible for the lower collector efficiency. This appears to hold for the low collector efficiency observed in the case of OHNHO, although the solution concentrations studied were severely limited by its low solubility.

As could be expected from the high solubility of OHCHO and
chelate. This indicates that the surface chelate is responsible for flotation, provided the bulk chelate does not contribute to flotation. Results of previous investigation showed that bulk Cu - LIX65N chelate had no ability to collect, and the LIX65N associated with bulk chelate was essentially unavailable for flotation. These results were also confirmed for SALO-CuO system (Nagaraj, 1979).

In highly acidic solutions, chelation of Cu by SALO is not complete, and even the chelate that is formed is highly soluble (Biefeld and Howe, 1959). As the pH is increased, say, from 1.0, Cu-SALO chelate starts precipitating and at pH ~2.6 the precipitation is complete. The pH of quantitative precipitation is dependent on the nature and composition of the aqueous phase. In the present system, the total amount of Cu-SALO chelate increased with pH, reaching a maximum value at pH ~3.5. Between pH 1.5 and 3.5, therefore, lies the precipitation edge for the chelate. A similar situation exists in the basic pH region: a second precipitation edge exists between pH ~9.0 and up to, possibly, 10.5 (see total Cu-SALO chelate, Fig. 9). Along the precipitation edge, the kinetics of chelate precipitation are expected to be slow unless a nucleating center such as the mineral surface exists to favor chelate formation (precipitation). This can explain the increasing amount of chelate on mineral surface with increase in pH from 1.5, even though the mineral has very high solubility in this pH range (Nagaraj, 1979). Simultaneously, the amount of bulk chelate increases, since conditions become more favorable in the bulk phase for precipitation of chelate as the pH is increased. Above the pH of quantitative precipitation, bulk chelation predominates (because of the high concentration of copper species released from mineral) over surface chelation, which reaches a maximum followed by a decrease. Bulk chelation should also reach a maximum (and surface chelation a minimum) since the solubility of the mineral continuously decreases with increase in pH (Nagaraj, 1979). The maximum in flotation (pH ~2.5) corresponds to the maximum in the amount of surface chelate, and the minimum (pH 3.5) corresponds to both a minimum in amount of surface chelate and maximum in bulk chelate.

Salicylaldoxime-Tenorite System

The results of the earlier investigations of the systems LIX65N-CuO and LIX65N-chrysocolla gave a qualitative indication that LIX65N was partitioned: partly on the mineral surface - aiding flotation - and partly in the form of copper chelate dispersed in the bulk. This has been confirmed for the SALO-CuO system in the present study and, in addition, the surface and bulk chelates have been separated and quantitatively determined.

The results of Figs. 6 and 8 are plotted together in Fig. 10, and similarly those of Figs. 7 and 9 are plotted in Fig. 11, in order to clearly show the correlation and to better understand the role of partitioning of SALO.

It is clear from Figs. 10 and 11 that flotation follows the same trend as the extent of SALO abstracted in the form of surface chelate. It exhibits poor collector efficiency. The lower solubility of the copper chelate in the basic pH range suggests the possibility of an increase in flotation of chrysocolla by OHCHO with increase in pH, and this, in fact, was observed (Fig. 4). It would be interesting to test the effect of substituents on the collector property of this class of oximes, as there is no information in the literature. For example, introduction of one or two CH₂ groups on the ring might sufficiently decrease the polarity as well as the solubility of both the oxime and its copper chelate in order for the oxime to be an efficient collector.

It is to be noted that except OHBePO, all the oximes were monoisomeric; only the anti-isomer was present. Oximes such as OHBePO with an additional phenyl group have both the anti- and syn-isomers with comparable stability, and the mutual transformation being sensitive to temperature, pH, etc. For the oxime to function as a collector, it must be in the anti form. Syn isomer does not function as a collector. This finding was discussed earlier for LIX65N (Nagaraj and Somasundaran, 1977).
chelates has been quantitatively determined in order to elucidate the role of these chelates in flotation of tenorite and the mechanism of adsorption of salicylaldoxime on tenorite. Results indicated that flotation correlates very well with the extent of SALO abstracted in the form of a chelate on the mineral surface. Solubility of the mineral has a large influence on the extent of bulk chelation. The bulk chelate has no role to play in contributing to flotation since it has no ability to collect; moreover, it depletes the reagent, which otherwise would be available for adsorption on the mineral. The extent of SALO abstracted as surface chelate depends upon the solubility of both the mineral and the chelate itself, and upon the nature of surface copper species.

Acknowledgements

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References


Detachment of surface chelate is also an important possibility to be considered in evaluating the partitioning of SALO. However, in the present system, results have indicated that detachment of surface chelate does not have a significant influence on the partitioning compared with that of solubility of the mineral and the chelate.

The concentration of copper species released from the mineral decreases sharply with increase in pH up to about 5.0, and decreases slowly above pH 5.0. As a consequence, the rate and extent of bulk chelation also decrease above pH 5.0. Furthermore, surface chelation is influenced by the nature of the surface copper species (depending upon pH) and the ease with which these species form a chelate with SALO. As seen from Fig. 11, the amount of surface chelate increases with increase in pH from 4.0 and reaches a maximum at pH~9.0. Flotation results are again correlated by the amount of surface chelate in this pH range. The continuous decrease in bulk chelate above pH 5.0 follows the continuous decrease of solubility with pH.

Summary and Conclusion

The effect of the structure of hydroxyoxime chelating agents on their collector property and some results of the basic study of the salicylaldoxime-tenorite system are discussed in this paper. Microflotation of chrysocolla with a number of water-soluble aromatic (and one cycloalkane) hydroxyoximes indicated that:

a) Increasing chain length on R1 (R2 = H, see formula I) increases the collector efficiency.
b) Substitution in R2 (R1 = CH3 or H) or substitution of a phenyl in R1 (R2 = H) decreases the collector efficiency to levels inferior even to the parent oxime (R1 = R2 = H).
c) A fused ring instead of the benzene ring does not improve the collector efficiency.
d) Both ortho-hydroxy cyclohexanone oxime and its copper chelate have a high water solubility compared with other oximes and, as expected, this oxime is a poor collector.

Partitioning of salicylaldoxime into bulk and surface copper
An Overview of Methods for Monitoring Diesel Pollutants in Underground Mines

David H. Carlson and John H. Johnson

Abstract—The paper presents background information, a description of mine characteristics that affect air monitoring techniques, and a review of portable measurement techniques and instruments for gas and particulate matter sampling. A general review of the laboratory and field research being conducted at Michigan Technological University in the area of diesel emissions is presented. The facilities involved with this research are also described. These are the experimental mine, the diesel dilution tunnel test cell, the mine air monitoring lab (MAML), portable instruments, and the production mines used.

The application of diesel powered equipment to underground mines is generally believed to be advantageous due to elimination of electric shock, fire hazards, methane ignition, and physical safety hazards associated with electric cables, and reduced costs resulting from greater mobility (Ogden, 1978). However, mine operators and mine employee organizations are concerned about the potential hazards from exhaust emissions and the potential for increased ventilation costs to reduce emission concentrations to levels not harmful to the health of exposed personnel. These concerns form the basis for the research work described in this paper. The ultimate goal is to optimize methodology for air quality control for the miner’s health. A recent paper by Johnson, Reinbold, and Carlson, 1981 discusses the engineering control of diesel pollutants in underground mines.

Development of suitable measurement techniques must logically precede adoption of optimum methodology for control. The measurement of mine air quality has been primarily based upon various collection devices and detector tubes that give a single number representing the entire period over which the measurement was made.

The advent of continuous battery operated portable instruments and recording devices offers the important advantages of providing detailed data to evaluate control technology. The underground mine poses special problems for many presently available instruments, and measurement techniques are unsuitable.

Michigan Technological University (MTU), under contracts supported by the Mine Safety and Health Administration (MSHA) and by the US Bureau of Mines, has put together a comprehensive research program in mine air monitoring. The objective is the development of optimum methodology for control of air quality. The work has been directed toward development of systems for monitoring mine ambient air. Studies have been carried out in three production mines and the MTU experimental mine. The three production mines are the White Pine mine (copper), St. Joe Minerals, Brushy Creek mine (lead), and the Colorado Westmoreland Orchard Valley mine (coal).

Ranges of concentrations of various pollutants in diesel exhaust (Marshall and Fleming, 1971) are listed in the upper part of Table 1. Total amounts emitted are listed in the lower part of the same table. Each of the diesel exhaust pollutants has an effect on an exposed individual related to the degree of exposure.

Detailed discussions of the amounts and characteristics of diesel exhaust pollutants and health effects and standards applying to personal exposure limits are discussed in the references. A new health effects index that takes into consideration combined harmful effects of CO, NO, respirable combustible particulate, SO2, and NO2, and sets a limit based on a mathematical formula, is also discussed in Mogan (1978). This paper is based on a more detailed paper presented at the 1979 AIME Annual Meeting. An overview of monitoring technology and the health effects index are presented in Johnson (1980), including the use of CO2 concentrations for pollutant control.

Mine Characteristics That Affect Air Monitoring

The unusual nature of underground mining requires special considerations in designing monitoring systems. Some features peculiar to underground mines are not common in other enclosed spaces where monitoring must be performed:

- Large spaces with few people occupying them.
- Most people work at a specific location for only part of a shift. This location will be unmonitored during the remainder of the shift, and distances as great as 0.4 km between personnel in a single section at the face are common.
- Most work in underground mines is performed with mobile equipment. In conventional mining, driving tunnels usually involves a sequential cycle of drilling, blasting, loading, and hauling ore to conveyor feeders, and bolting for roof support. Usually one or two people operate a single piece of equipment. Mined out areas become inactive, and only certain tunnels are maintained through the old workings to the new workings. Ventilation air and supplies are often brought considerable distances from main shafts or portals through old workings to those being mined on the perimeter.
- Underground lighting is usually limited to lunch areas and conveyor feed points. Electrical power suitable for operation of electronic instruments is often unavailable. Power used for lighting may have voltage variations that can damage instruments or cause erroneous readings.

Table 1 - Ranges of Pollutant Concentrations and Total Amounts Emitted by Diesel Engines at Rated Power and Speed (Marshall and Fleming, 1971)

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Range of Concentration</th>
<th>Range of Amounts Emitted at Rated Power and Speed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pollutant</td>
<td>Concentration</td>
<td>Amounts Emitted</td>
</tr>
<tr>
<td></td>
<td>ppm</td>
<td>(lb HHP-h)</td>
</tr>
<tr>
<td>Hydrocarbons (as CH2)</td>
<td>1-5 ppm</td>
<td>50-150 lb HHP-h</td>
</tr>
<tr>
<td>Aldehydes</td>
<td>2-10 ppm</td>
<td>25-50 lb HHP-h</td>
</tr>
<tr>
<td>Unburned hydrocarbons</td>
<td>0.1-5 ppm</td>
<td>5-25 lb HHP-h</td>
</tr>
<tr>
<td>Smoke</td>
<td>0.5-5 ppm</td>
<td>25-125 lb HHP-h</td>
</tr>
<tr>
<td>NOx</td>
<td>0.3-3.0 ppm</td>
<td>15-75 lb HHP-h</td>
</tr>
<tr>
<td>CO</td>
<td>2.5-14.0 ppm</td>
<td>125-700 lb HHP-h</td>
</tr>
<tr>
<td>CO2</td>
<td>300-14,000 ppm</td>
<td>1,400-7,000 lb HHP-h</td>
</tr>
<tr>
<td>Nitrogen oxides</td>
<td>0.1-20 ppm</td>
<td>1-10 lb HHP-h</td>
</tr>
<tr>
<td>Paraffins</td>
<td>10-200 ppm</td>
<td>50-1000 lb HHP-h</td>
</tr>
<tr>
<td>Aldehydes</td>
<td>0.1-0.6 ppm</td>
<td>0.5-3.0 lb HHP-h</td>
</tr>
<tr>
<td>Hydrocarbons (as CH4)</td>
<td>0.2-3.0 ppm</td>
<td>1-15 lb HHP-h</td>
</tr>
<tr>
<td>Aldehydes (as CHO)</td>
<td>0.1-0.5 ppm</td>
<td>0.5-2.5 lb HHP-h</td>
</tr>
</tbody>
</table>

*This was not presented by Marshall, but was calculated from the smoke opacity using the relationship presented by Vuk et al. (SAE Trans., 1978) for a 102 mm path length.
**Measured as NO by NDIR instruments.

ABSTRACT
Organic complexing agents have received special attention over the past few decades in the search for reagents for improved flotation separation of minerals, especially non-sulphides. The majority of such reagents that have been proposed over the past few decades have remained largely a laboratory curiosity, except perhaps alkyl hydroxamates, because their selection is seldom based on commercial viability. In this regard, the choice of complexing agents such as oximes may be more realistic because of their widespread use in solvent extraction of copper. Our earlier studies have confirmed that they are also effective as collectors for copper oxide minerals, including chrysocolla which is the most difficult copper mineral to beneficiate.

The flotation behaviour of chrysocolla for several structurally-related hydroxyoximes were studied as a function of pH and oxime concentration and the role of structural features examined. The structural changes studied included substitutions in both chelating and non-chelating parts of the molecule. The results indicated that, contrary to expectations, many of the structural changes in the basic molecule, salicylaldoxime, do not have a positive effect on collector efficiency. The reduction in collector efficiency is rationalised on the basis of possible steric factors affecting complexation and packing of the collector species on the mineral surface as well as effects due to changes in electron density brought about by substituents. Introduction of alkyl substituents on the oximic carbon of salicylaldoxime yielded the highest collector efficiency.

INTRODUCTION
Over the past six decades or so, since the advent of soluble surfactants as collectors in flotation, there has been a relentless search for new chemistries for improved separation of minerals, both sulphides and non-sulphides. Whether it is for flotation or depression, organic-complexing agents or chelating agents* have received special attention (Barbery et al., 1977; Drzymala and Laskowski, 1981; Fuernestau and Pradip, 1984; Gutzeit, 1946; Holman, 1930; Marabini et al., 1971, 1974, 1973, 1976; Nagaraj, 1987; Somasundaran and Nagaraj, 1984; Taggart, 1930). This is largely driven by the success of these reagents in analytical separations. While in principle it is logical to expect metal specificity observed in analytical separations to translate into mineral specificity, in practice this is far from a straightforward transfer. Nevertheless, an assumption is made in the majority of studies that complexing agents adsorb on minerals by forming metal complexes on mineral surfaces under conditions most favorable for metal complexation in solution as observed in analytical separations, and that such metal complexes are responsible for imparting hydrophobicity to the solid. While a variety of complexing agents are already in large scale use in sulphides flotation, this is not the case in oxides flotation. Fatty acids and amines still dominate the industry though numerous complexing agents have been proposed. Perhaps the only significant commercial utility in the non-sulphides area can be found for certain phosphonic acids (Nagaraj, 1987). The prohibitively high cost and high dosages required of many of the proposed complexing agents are certainly major factors. The underlying factor, however, may be the choice of a complexing agent. Complexing agents have been chosen invariably on the basis of success in analytical separation rather than on the basis of commercial viability. Thus many of the proposed structures fail into the category of 'exotic' chemistry and remain largely a laboratory curiosity. In this regard the choice of complexing agents such as oximes may be more realistic.

The commercial viability of oximes has been well established because of their widespread use in solvent extraction of copper.

One of the early references to the proposed use of oximes is that of Vivian in 1927. Dimethylglyoxime (DMG) was proposed for floating nickel oxide ores. Delitsina et al. (1954, 1956) recommended the use of DMG for the flotation of chalcocite, bornite, malachite, pyrite and electrolytic copper and nickel. They concluded that the increase of hydrophobisation of the mineral was greater with DMG than with xanthate, which is an intriguing result, especially for sulphide minerals. Their findings contradict those of Peterson et al. (1965) who found lack of flotation of chrysocolla with DMG and of Drzymala and Laskowski (1981) who found lack of flotation of synthetic millerite and other nickel minerals with DMG and other dioxicim's. It should be noted here that DMG forms water-soluble copper chelate. Usioni et al. (1971) showed that a hydrocarbon oil was necessary to obtain acceptable flotation of naccolite with DMG. Teoh et al. (1982) used several homologous dioxicimes for the flotation of nickel bearing minerals. Optimum flotation was obtained with 2,3-nonanedione dioxicime. Peterson et al. (1965) also suggested the use of alpha-benzoin oxime for chrysocolla flotation.

De Witt and Batchelder (1939) investigated the collector function of salicylaldoxime (SALO), its meta- and para-isomers, and its monomethyl ether, for chalcocite, covellite, azurite, malachite and cuprite. Only SALO was found to function as a collector. The meta- and para-isomers could not function as collectors since their structure does not permit chelate formation. It was also proposed that if the phenolic hydroxyl is replaced by a methoxy group, the resulting monomethyl ether of SALO would not be a collector. Mukai and Wakaizumi (1976) also used SALO as a promoter of xanthate adsorption for the flotation of chrysocolla. Adsorption of xanthate increased with the addition of SALO, while a complete coating of SALO on chrysocolla adversely affected xanthate adsorption. No effort was made to investigate the collector action of SALO alone. It is not clear what the mechanism of this coadsorption is and why a xanthate is required in addition to SALO.

Barbery et al. (1977) and Cecile et al. (1981) investigated the collector function of oximes for malachite and chrysocolla. They studied adsorption of SALO on malachite with supporting information derived from IR analysis. Multilayers of copper chelate were observed on the mineral surface.

Nagaraj and Somasundaran have conducted many systematic studies on the adsorption of oximes on copper oxide minerals and their flotation (1979a, 1979b, 1981). The collector property of commercially used solvent extractants of the LIX type were evaluated for the flotation of chrysocolla and cuprite. These investigators also conducted a fundamental study of the system tenorite-SALO in order to elucidate the mechanism of collector.

The terms 'complexing' and 'chelating' will be used interchangeably in this paper since all of the discussion applies equally to both, and since 'chelation' is but a special case of 'complexation'.

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* The terms 'complexing' and 'chelating' will be used interchangeably in this paper since all of the discussion applies equally to both, and since 'chelation' is but a special case of 'complexation'.
The structures and water solubility of hydroxyoximes.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Name</th>
<th>Mol. Wt.</th>
<th>Water Solubility, M</th>
</tr>
</thead>
<tbody>
<tr>
<td>SALO</td>
<td>(Salicylaldoxime)</td>
<td>137.1</td>
<td>$2.0 \times 10^{-1}$</td>
</tr>
<tr>
<td>OHAPo</td>
<td>(o-Hydroxy Acetophenone Oxime)</td>
<td>151.2</td>
<td>$4.5 \times 10^{-3}$</td>
</tr>
<tr>
<td>OHBuPO</td>
<td>(o-Hydroxy Butyrophenone Oxime)</td>
<td>179.2</td>
<td>$5.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>OHBePO</td>
<td>(o-Hydroxy Benzo phenone Oxime)</td>
<td>213.2</td>
<td>$5.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>2H5MeAPO</td>
<td>(2-Hydroxy 5-Methyl Acetophenone Oxime)</td>
<td>166.2</td>
<td>$3.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>2H5MBAO</td>
<td>(2-Hydroxy 5-Methoxy Benzalzoxide)</td>
<td>168.2</td>
<td>$5.0 \times 10^{-3}$</td>
</tr>
<tr>
<td>OHNAo</td>
<td>(2-Hydroxy 1-Naphthaldoxime)</td>
<td>189.2</td>
<td>$1.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>OHCHO</td>
<td>(o-Hydroxy Cyclohexanone Oxime)</td>
<td>129.0</td>
<td>$-1.0$</td>
</tr>
<tr>
<td>OMeAPO</td>
<td>(o-Methoxy Acetophenone Oxime)</td>
<td>165.0</td>
<td></td>
</tr>
<tr>
<td>OHAPOMeO</td>
<td>(o-Hydroxy Acetophenone O-methyl Oxime)</td>
<td>165.0</td>
<td></td>
</tr>
</tbody>
</table>

Generalized Structure

The structure of a complexing agent and, therefore, its properties, can be changed by incorporating substituents in either the chelating part or the non-chelating part of the molecule. The effect of such changes on the collector efficiency of a number of structurally-related hydroxyoximes for chrysocolla as a function of pH and reagent concentration is discussed in this paper. Information on structure-activity relationships is important from the point of view not only understanding fundamental mechanistic aspects, but also for the commercial viability of...
oximes in flotation. Chrysocolla would be a logical choice among the oxide-type copper minerals because it is one of the most difficult to float. Its flotation aspects were reviewed recently (Laskowski et al., 1985).

EXPERIMENTAL

Mineral
Chrysocolla, CuSiO₃, obtained as high-grade lumps from Black Hills Minerals, was crushed, hand-sorted, and crushed again to -14 mesh. The -14 + 100 mesh fraction was passed through a dry magnetic separator, ground in an agate mortar to -48 mesh. The -48 + 100 mesh fraction was passed through a magnetic separator again, destilled and dried. It analysed 24 per cent Cu. X-ray diffraction indicated minor amounts of quartz impurity.

Oximes

The oximes used are shown in Table 1. SAPO obtained from La Chat Chemicals was purified by recrystallisation from petroleum ether-benzene mixture. 2-hydroxy-1-cyclohexanone oxime was prepared by the method described by Nenz et al. (1964). All other oximes were prepared from their respective ketones or aldehydes by the methods described by Blatt (1955) and Kohler and Bruce (1931). All the oximes except OHAPOMeO were purified by recrystallisation. OHAPOMeO was obtained as a liquid and it was purified by ether extraction. The structures and purities were confirmed by IR and TLC techniques. Water solubility of the oximes was measured by determining the amount dissolved after shaking the oxime in 10 ml of triply distilled water for three days at 25 - 26°C. The values are given in Table 1. These solubilities are expected to be close to the equilibrium values.

Stock solutions of oximes in triply distilled water were prepared by adding one per cent acetone to ensure adequate solubility. This amount of acetone was also beneficial in flotation tests because it produced small, uniformly sized bubbles; a separate frother was, therefore, not necessary.

Flotation

95 ml of the oxime solution at the desired concentration was stirred in a 150 ml cylinder. After pH adjustment to the desired value, 0.7 g of the mineral was added and conditioned for the required period with continuous control and recording of the pH. pH was adjusted with KOH and HNO₃ to within ± 0.05 unit. After conditioning, the mineral was floated in a modified Hallimond tube for one minute with 20 cc/min nitrogen.

RESULTS

Flotation data for chrysocolla at pH 4.8 as a function of concentration of the three homologous oximes - SAPO, OHAP, and OHBuPO - are shown in Figure 1. pH 4.8 was selected for these tests because preliminary work with LIX type of reagents had indicated that flotation was optimum around pH 4.8. The
maximum amount of oxime that could be used in flotation was limited by its solubility.

It is evident from the results given in Figure 1 that an increase in the chain length of \( R_1 \) (see generalised structure, Table 1) while keeping \( R_2 = \text{H} \) results in an increase in the flotation efficiency in the order \(-\text{H} < -\text{CH}_3 < -\text{C}_3\text{H}_7\). Adding the first carbon in \( R_1 \) resulted in the largest increase. Thus the concentration of OHAPO required to obtain about 60 per cent flotation is about half that of SALO and the water solubility is lowered by almost two orders of magnitude. Increase in the chain length of \( R_1 \) by two more carbons (to give OHBuPO) further improved the collector efficiency, but not to the extent observed by introducing the first carbon. The water solubility of OHBuPO was only an order of magnitude less than that of OHAPO.

Flotation data for the three homologous oximes are given in Figure 2 as a function of pH. Less-than-optimum concentrations were chosen deliberately in order to observe the features of flotation behaviour vs pH and to discern differences between oximes. These data, in general, support the results discussed above. The collector efficiencies of OHBuPO and OHAPO were higher than that of SALO at all pH values, though the concentrations used with the former two oximes was lower than that used with SALO. Flotation of chrysocolla was maximum at pH 5.0. The effect of substitution on the benzene ring on the flotation of chrysocolla as a function of concentration of oximes at pH 4.8 is shown in Figure 3. Flotation data for SALO and OHAPO (from Figure 1) are replotted here for comparison. It can be seen that methoxy substitution in the 5-position of OHAPO (ie 2H5MBAO, see Table 1) as well as methyl substitution in the 5-position of OHAPO (ie 2H5MeAPO) decreased the collector efficiency (more so with 2H5MeAPO), though both 2H5MBAO and 2H5MeAPO had lower water solubility compared with their parent molecules.

Flotation of chrysocolla with 2H5MBAO and 2H5MeAPO are given in Figure 4 as a function of pH. Flotation behavior with 2H5MBAO is very similar to that with SALO, while that with 2H5MeAPO is quite different and unusual compared with that of OHAPO. Two flotation maxima are observed for 2H5MeAPO, one at pH 4 and the other at pH 8.

Flotation obtained with the remaining oximes - OHBePO, OHNAO, OMeAPO, OHAPOMeO, and OHCHO at pH 4.8 are shown in Figure 5 as a function of concentration and in Figure 6 as a function of pH. Flotation data with SALO (from Figure 1) are also plotted in Figures 5 and 6 for comparison. Most of the oximes tested in this group were characterised by very low collector efficiency at pH 4.8 compared with that obtained with SALO. Thus substitution of a phenyl group for \( R_1 \) (ie OHBePO, Table 1) decreased collector efficiency at pH 4.8. The pH for optimum flotation with this oxime, however, was at pH 6, not at 4.8. A fused aromatic ring (naphthalene) instead of the benzene ring in SALO resulted in a very large lowering of collector efficiency at pH 4.8 (though it was optimum at approximately this pH). Thus OHNAO was inferior to all the other closely related oximes. Similarly, methylation of the phenolic OH in SALO almost completely destroyed the collector property. On the other hand, methylation of the oximic OH of SALO (ie
OHAPOMeO) only reduced the collector efficiency without destroying it completely. pH for optimum flotation with this oxime was at approximately 8.

The case of OHCHO is a special one because it belongs to the class of alpha-acyloin oximes, though the oxime is distinct because of the cyclic alkane. OHCHO was found to have an appreciable solubility in water (the highest of the oximes tested). Its copper chelate was soluble in mildly acidic pH range and precipitated in the basic pH range. In accord with this OHCHO exhibited extremely low collector efficiency even at very high concentrations.

**DISCUSSION**

The flotation behavior for chrysocolla with the majority of the oximes studied was the same: optimum flotation occurred at approximately pH 5. For LIX65N (2-hydroxy-5-nonyl benzophenone oxime) two maxima in flotation occur, one at pH 5 and the other at pH 10. Chrysocolla flotation with octyl hydroxamate has a maximum at pH 6 (Peterson et al., 1965). Although the optimum in flotation of chrysocolla around pH 5 can be explained on the basis of CuOH⁺ species on the surface (Palmer et al., 1975), an alternative explanation would involve the partitioning of the oxime between the mineral surface and the bulk aqueous phase in relation to mineral solubility, as in the case of tenorite-SALO system (Nagaraj and Somasundaran, 1979).

pK₄ of the oxime would also make a significant contribution to the location of the flotation optimum.

The increase in collector efficiency observed with increase in chain length (i.e. SALO < OHAPO < OHBuPO, Figures 1 and 2) in the homologous series is in general agreement with observations made in other systems. For example, Fuersanau, Healy and Somasundaran (1964) documented this for quartz flotation with homologous amines. As can be expected, introducing the first -CH₃ in SALO causes a much larger change in polarity of the molecule compared with further addition of two CH₂ groups. This is reflected in the water solubility of the oximes - SALO >> OHAPO > OHBuPO - and also in the collector efficiency. Furthermore, the increase in collector efficiency of the higher homologues may be related to the electron-releasing (inductive) effect of CH₃, relative to -H, which would increase the electron density on the nitrogen. Water solubility of homologous compounds should provide an approximate indication of the hydrophobicity that they would impart to the mineral surface assuming that their mode of adsorption is similar. This has been observed in the case of fatty acids and amines.

Substitution of a phenyl group in R₁ (OHBePO, see Table 1) decreased the water solubility appreciably, which is to be expected from the less polar benzene ring. On the basis of lower solubility of OHBePO relative to SALO one might have predicted a higher collector efficiency than with SALO. The results, however, were quite contrary to this at pH 4.8 (Figure 5). An important reason for this is the shift of the pH of optimum flotation for OHBePO from pH 5 with SALO to ~6 with OHBePO. This shift is possibly related to a change in pK₄ of the oxime in going from SALO to OHBePO, which can be expected.
because the benzene ring can alter the electron density on the oxime group significantly. Significant differences between orientations of adsorbed SALO and OHBePO can also be expected based on their structures, which then translate into differences in hydrophobicity. Water contact angles, for example, on surfaces comprising -CH$_2$ or -CH$_3$ are higher than those comprising aromatic groups (Wu, 1982). Also in the case of OHBePO, there is a possibility that close packing of surface aromatic groups is hindered. This would further contribute to the lowering of contact angles.

The lower collector efficiency of oximes with substitution in the 5-position on the ring, viz 2H5MBAO and 2H5MeAPO, relative to SALO is rather surprising (Figures 3 and 4) in view of the fact that they both form stable, insoluble copper chelates with copper ions. The lower water solubility would suggest that they would be less polar. Separate adsorption measurements (not shown here) indicated that both substituted compounds adsorbed as effectively as SALO. In the case of 2H5MeAPO, the pH of optimum flotation is shifted (in fact there are two maxima, see Figure 4, at pH 4 and 8). This may explain the low flotation at pH 4.8. The reason for the two flotation maxima is unknown and it cannot be rationalised readily because all other oximes showed one flotation maximum. In the case of 2H5MBAO, pH of optimum flotation was approximately the same as that obtained with SALO, though the methoxy group on the ring can be expected to alter the pK$_a$ because of the electron releasing tendency. The only explanation that can be offered at this point for the lower collector efficiency of 2H5MBAO is that the methoxy group has reduced the hydrophobicity slightly because of the orientation effects.

The low collector efficiency of OHNAO (naphthalene group, see Table 1), as in the case of OHBePO, may also be related to low hydrophobicity imparted to the surface after adsorption and hindered packing on the surface because of the naphthalene rings. The very low water solubility restricted the maximum concentration studied to $\sim 10^{-4}$ M.

The drastic reduction in the collector efficiency associated with methyl substitution for phenolic hydrogen (ie OMeAPO, Figures 5 and 6) is expected because this molecule is unable to form a chelate with copper. This result is in agreement with that observed by De Witt and Batchelder (1939) for o-methyl benzaldoxime and supports the hypothesis that chelate formation is a prerequisite for flotation. In this context, the absence of collector property observed by Nagaraj and Somasundaran (1979) for the syn-isomer of LIX65N is noteworthy; the syn-isomer is also incapable of chelate formation. It can be argued, however, that OMeAPO could still adsorb on chrysocolla by forming a complex (though not a chelate) with copper via the oximic nitrogen and function as a collector because simple aldoximes (such as R-NOH) are known to complex with copper (Chakravarty, 1974). This does not appear to be the case from the flotation data obtained here, probably because the methyl substitution on phenolic OH may impose steric hindrance to such a complex formation with oximic nitrogen on the mineral surface.

Methylation of the oxime group (as in OHAPOMeO, Table 1)
is not expected to prevent chelate formation with copper and, therefore, its collector property should be similar to that of OHAPo, but the results obtained here are quite contrary to this expectation (see Figures 5 and 6). OHAPoMeO exhibited only weak collector property even at high concentrations. This can be rationalised at this stage only on the basis of possible steric hindrance to complex formation on the mineral surface. This is not unreasonable because steric factors are much more important for surface chelation than for chelation in bulk aqueous solutions.

The very poor collector efficiency of OHCHO (see Figures 5 and 6) is also rather surprising since after adsorption this compound should expose the cyclohexane group which should be sufficiently hydrophobic. OHCHO was not only very soluble in water (the highest among the oximes studied), but it formed soluble copper chelates in mildly acid and neutral pH range. The results given in Figure 6 suggest its collector activity to increase with increase in pH, but a very high concentration may be required to achieve high flotation of chrysocolla.

**SUMMARY**

Flotation behaviour of chrysocolla as a function of pH and concentration of several, sparingly soluble, structurally-related hydroxyoximes is discussed. Substitution in both the chelating and non-chelating parts of the basic hydroxyoxime molecule, the salicylaldoxime (SALO), was considered.

Flotation of chrysocolla was optimum at pH~5 with most of the oximes. The major flotation effects observed in this study are readily explained by examining the changes in structural features of the oximes. Contrary to what might be expected, many structural changes, however, made a negative contribution to the collector efficiency. Correlation existed between reduction in water solubility of the oxime and increase in its collector efficiency only for the homologous oximes.

Substitution of alkyl group on the oximic carbon of salicylaldoxime had the largest positive contribution to the collector efficiency which followed the order, o-hydroxy butyrophenone oxime > o-hydroxy acetophenone oxime > salicylaldoxime. Substitution of methoxy or methyl in the 5-position on the benzene ring in SALO and o-hydroxy acetophenone oxime, respectively, decreased the collector efficiency. This finding is contrary to expectations based on water solubility and chelation of copper in solutions, and can be rationalised at this stage on the basis of steric hindrance to complexation and packing on chrysocolla. The methoxy group, in addition, may lead to a reduction in hydrophobicity because of its more polar character. A fused aromatic ring (naphthalene for example) instead of the benzene ring in SALO lowered the collector efficiency drastically. Substitution of a phenyl group on the oximic carbon in SALO lowered the collector efficiency at pH 4.8, but it also shifted the pH of optimum flotation to 12. Also, methylation of phenolic group in SALO lowered the collector efficiency. This is attributed to the negative contribution from steric factors affecting complexation and packing on mineral surface. A hydroxyoxime group on a cyclohexane ring offered no advantage. In fact this oxime had extremely poor collector efficiency even at very high concentrations. This is attributed to the very high solubility of the copper chelate.
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