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 has seldom been 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 oxime 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 (Barbary et al, 1977; Drzymala and Laskowski, 1981; Fuerstenau 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 attributed to the alkyl hydroxamates (Fuerstenau and Pradip, 1984) in the former Soviet Union at least until a few years ago. Current usage of this is not known. Limited application can also 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 fall 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 chalcopyrite, 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 mullerite and other nickel minerals with DMG and other dioximes. It should be noted here that DMG forms water-soluble copper chelate. Usuki et al (1971) showed that a hydrocarbon oil was necessary to obtain acceptable flotation of nicoelite with DMG. Teoh et al (1982) used several homologous dioximes for the flotation of nickel bearing minerals. Optimum flotation was obtained with 2,3-nonanedione dioxime. Peterson et al (1965) also suggested the use of alpha-benzoxyamine 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 Wakamatsu (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.

Barbary 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 LI/X 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

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### Table 1
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><img src="image1" alt="Structure" /></td>
<td>SALO (Salicylaldoxime)</td>
<td>137.1</td>
<td>$2.0 \times 10^{-1}$</td>
</tr>
<tr>
<td><img src="image2" alt="Structure" /></td>
<td>OHAPo (O-Hydroxy Acetophenone Oxime)</td>
<td>151.2</td>
<td>$4.5 \times 10^{-3}$</td>
</tr>
<tr>
<td><img src="image3" alt="Structure" /></td>
<td>OHBuPO (O-Hydroxy Butyrophene Oxime)</td>
<td>179.2</td>
<td>$5.0 \times 10^{-4}$</td>
</tr>
<tr>
<td><img src="image4" alt="Structure" /></td>
<td>OHBePO (O-Hydroxy Benzophenone Oxime)</td>
<td>213.2</td>
<td>$1.5 \times 10^{-4}$</td>
</tr>
<tr>
<td><img src="image5" alt="Structure" /></td>
<td>2H5MeAPO (2-Hydroxy 5-Methyl Acetophenone Oxime)</td>
<td>166.2</td>
<td>$3.0 \times 10^{-4}$</td>
</tr>
<tr>
<td><img src="image6" alt="Structure" /></td>
<td>2H5MBAO (2-Hydroxy 5-Methoxy Benzaldehyde)</td>
<td>168.2</td>
<td>$5.0 \times 10^{-3}$</td>
</tr>
<tr>
<td><img src="image7" alt="Structure" /></td>
<td>OHNAO (2-Hydroxy 1-Naphthaldoxime)</td>
<td>189.2</td>
<td>$1.0 \times 10^{-4}$</td>
</tr>
<tr>
<td><img src="image8" alt="Structure" /></td>
<td>OHCHO (O-Hydroxy Cyclohexanone Oxime)</td>
<td>129.0</td>
<td>$-1.0$</td>
</tr>
<tr>
<td><img src="image9" alt="Structure" /></td>
<td>OMeAPO (O-Methoxy Acetophenone Oxime)</td>
<td>165.0</td>
<td></td>
</tr>
<tr>
<td><img src="image10" alt="Structure" /></td>
<td>OHAPOMeO (O-Hydroxy Acetophenone O-methyl Oxime)</td>
<td>165.0</td>
<td></td>
</tr>
</tbody>
</table>

**Generalized Structure**

![Generalized Structure](image11)

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 of not only understanding fundamental mechanistic aspects, but also for the commercial viability of action of hydroxyoximes. Aliaga and Somasundaran (1987) found an interesting correlation between the UV spectra of several structurally-related oximes, their copper chelates and their collector properties.

Kierszniicki et al (1981) studied the effect of alkyl chain length in 5-alkyl SALO in the flotation of sphalerite, smithsonite and dolomite and suggested that a propyl group gave optimum results.
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, deslimed 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. SALO 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 OHAPMeO were purified by recrystallisation. OHAPMeO 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 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 CO₂ flow 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 - SALO, 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 R1 (see generalised structure, Table 1) while keeping R2 = H results in an increase in the flotation efficiency in the order -H < -CH3 < -C3H7. Adding the first carbon in R1 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 R1 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 in SALO (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 R1 (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 LIX65 (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 flotation of chrysocolla around pH 5 can be explained on the basis of CuOH⁺ species on the surface (Palmer et al., 1975), another 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). pKₐ 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, Fuerstenau, Healy, and Somasundaran (1964) documented this for quartz flotation with homologous amines. As can be expected, introducing the first -CH₂ in SALO causes a much larger change in solubility 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 pKₐ of the oxime in going from SALO to OHBePO, which can be expected.
The very low water solubility restricted the maximum concentration studied to ~10^{-4} M.

The drastic reduction in the collector efficiency associated with methyl substitution for phenolic hydrogen (i.e. 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 (SAO), 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 oxime 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 SAO 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 SAO lowered the collector efficiency drastically. Substitution of a phenyl group on the oxime carbon in SAO 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 SAO destroyed the collector property as expected. Methylation of the oxime group, on the other hand, merely 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.

**Fig 5 - Flotation of chrysocolla as a function of concentration of oximes: SALO; OHBePO; OHNAO; OMeAPO; OHAPOMeO; OHCHO.**
ACKNOWLEDGEMENT

The authors acknowledge the financial support provided by the National Science Foundation and the Engelhard Corporation for carrying out this work.

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