COPPER DEPRESSANTS: CORRELATION BETWEEN STRUCTURE AND ACTIVITY

D. R. Nagaraj, S. S. Wang and P. V. Avotins
American Cyanamid Company, Stamford, Connecticut, USA.

ABSTRACT

A systematic study was made of the structure vs. copper depressant activity of a large number of organic complexing agents and some commonly used inorganic depressants. An efficient technique was developed for the evaluation of depressants for copper using Cu-Mo plant concentrates. A correlation between practical solution redox potentials and depressants activity was obtained, which enables a useful classification of depressants. Such a correlation would be of importance in both the laboratory and the industry. Several requirements were identified for a reagent to be a satisfactory depressant. Some starch xanthates showed promise. The useful correlation obtained between structure vs. depressant activity and solution redox potentials is discussed in light of the present understanding of the electrochemical mechanism of sulfides flotation and depression.

INTRODUCTION

By-product molybdenite recovery from copper porphyry ores currently constitutes about 40% of the Western Hemisphere's molybdenum production.1 Four general approaches have been used for recovering molybdenite:2 flotation of copper minerals followed by that of MoS2 and vice-versa; separation of MoS2 from Cu-Mo bulk concentrates by either depressing the MoS2 or the copper minerals. The last approach, namely, MoS2 flotation/Cu depression, is now almost universally used.

A typical Cu-Mo separation scheme is given in Figure 1. Several excellent commercial processes have been developed based on this scheme. The important copper depressants, currently in use, are also listed in Figure 1.

MoS2 depression followed by copper flotation is practiced in only two plants (notably at the Kennecott Utah Division), using dextrin. Starches, saporin, various organic dyes and formaldehyde are some of the effective MoS2 depressants.2

Among the important, commercially used copper depressants, sodium hydrosulfide (or sodium sulfide) is by far the more extensively used reagent. In theory, Na2S/NaHS could be used for all Cu-Mo concentrates but, in practice, it is not used in all cases for reasons (ex. unfavorable economics, metallurgy and ore characteristics) that are unique to certain individual plants. Nokes reagent and Na4Fe(CN)6 are two important alternatives to Na2S/NaHS.2,13

Although Na2S/NaHS has been used in the industry for over several decades, the mechanism of its depressant action is not well understood. There has been, indeed, very little work done in this area apart from the early discussions by Gaudin3 and Sutherland and Wark.4 Other than the knowledge that HS- ions are responsible for the depression of sulfide minerals for xanthate flotation, it is not at all clear how
exactly HS⁻ ions function on xanthate-treated sulfide surfaces. For the most part, the depressant properties of NaN₅S/Na₂HS have largely been taken for granted. The frequently found erratic behavior when using this depressant has been either ignored or rationalized on the basis of oxidatic, changes in ore or mineral characteristics and changes in collector properties or operating conditions. In fact, this is true of the other depressants used. Only recently has there been an attempt to monitor the depressant action via solution redox potential (Eh) measurements, although there appears to be no understanding of the possible role of redox potentials in the mechanism of depression.

It is now well known that adsorption or desorption of thiol collectors on many sulfide minerals proceeds, at least to a large extent, via an electrochemical mechanism. On the basis of this, and the fact that HS⁻ is the most important potential determining ion, it is quite possible that the electrochemistry of the sulfide-solution system may significantly contribute to the depression process. In the absence of direct electrode potential measurements at sulfide surfaces (which at present have been achieved at best for idealized systems), solution redox potentials should provide the next best alternative.

A majority of the currently used copper depressants are inorganic compounds, although numerous organic depressants have been developed over the years. A few examples are sodium thioglycollate, β-mercaptoethanol, disodium acetodithiocarbonate, 2-thiourea, 2-thiobarbituric acid, thiocrotic acid, 2-thiophenoxantoin, pseudothiohydantoin, 2-mercapto-3-pyridinol, thioxyanuric acid, dithiooxamide, pseudothiocyanogen, cysteine, rhodanine N-acetic acid, 2-imino-4-oxo-5-thiosolidine acetic acid (all of ref. 9), thioglycerol, and xanthates of polysaccharides.

One of the major advantages of organic depressants over inorganic depressants is the potential versatility for design of the molecule to suit requirements such as stability, reducing power, coordinating ability, hydrophilicity, solubility and cost. In spite of the large number of depressants that have been developed, there has been no systematic work, to date, with regard to the relationship between the structure of organic depressants and the depressant activity. It is also not known whether the redox properties of the depressant have any role in the mechanism of depressant action.

The currently used inorganic depressants have certain drawbacks such as the excessive dosages that must often be used, the potential safety hazards in making and handling them, and the environmental problems with regard to disposal. Ideally, organic depressants may be so designed as to minimize, if not completely eliminate, these drawbacks.

The present study was initiated with the aim of systematically investigating the structure-activity relationships and the role of solution redox potentials on depressant activity for Cu depressants. A large number of organic and inorganic copper depressants was investigated on Cu-Mo plant concentrates from the Western U.S., using a 50 g. glass cell, as a function of pH and dosage of the depressant. Eh measurements were made for the flotation system and for the depressant solutions as a function of pH. Several tests were also
carried out to investigate the desorbability in the non-xanthate collector systems.

A correlation between solution redox potential and depressant activity and several interesting structure/activity features were observed.

**EXPERIMENTAL**

**Material:** A Cu-Mo bulk cleaner concentrate from the Western USA was used for the present study.

**Sample Preparation:** Two separate batches of concentrates were received.

The as-received concentrate slurry was suspended in a large Nalgene cylinder and samples containing 50 g. dry solids were tapped into 250 ml glass bottles and stored in a freezer at -18°C to prevent further oxidation/aging. The samples were characterized with respect to pH, Eh, size, frothability and floatability, mineralogical composition, and Cu, Mo and Fe assays.

Some relevant details of the two batches of concentrates are given below.

**Batch A conc.:** Natural pH - 7.6; size - 69% -325 mesh, 84% -200 mesh, 100% -48 mesh; Cu 25.5%, Mo 1.8%, Fe 22%.

**Batch B conc.:** pH 8.0; 83% -325 mesh, 96% -200 mesh, 100% -65 mesh; Cu 27.73%, Mo 0.43%.

Both concentrates contained mainly chalcopyrite.

**Flotation Tests**

**Scrubbing:** Since the samples had presumably undergone some aging/oxidation and since, being flotation concentrates, they had already been activated with appropriate collectors, it was decided to scrub the solids in order to at least partially remove aging products from the surfaces, thus reactivating the minerals and/or exposing fresh surfaces. A 5 min. scrubbing time was selected for all depressant evaluation on the basis of optimum flotation.

**Flotation Apparatus:** A semi-automated apparatus was assembled for the flotation tests. Nitrogen was used as the gas phase to avoid complications with air, such as oxidation of minerals, collectors and the depressants, and a strong influence on Eh. A 250 cc cylindrical sintered-glass fritted cell was used as the flotation cell. Nitrogen flow rate was maintained constant at 0.6 l/min. through a timed-solenoid valve, and the stirring speed at 1150 rpm which was also controlled by a timer. The pulp density in the cell was 17.5 wt. %.

**Redox Potentials:** The solution redox potentials of both the flotation systems and the depressant solutions were measured using a combination Pt electrode (Orion #96-78). The electrode was calibrated against the Ferrocyanide/Ferricyanide redox couple. The calibration
was checked every day (and frequently in between tests on the same day). All of the potentials reported here are with reference to the standard Ag/AgCl electrode.

**Standard Test Conditions**

**pH/Lime:** For tests at constant pH, a pH between 10.5 and 11.0 was maintained by the addition of appropriate amounts of lime (0.03–0.06 g) in the scrubbing stage.

**Frother:** The as-received concentrate slurry already had some residual frother and, as a result, only small amounts of additional frother were required. It was observed that an excess of frother caused complete flotation.

**Collectors:** Although the concentrates received had been activated with xanthate and diethiophosphate collectors, it was decided to ascertain complete floatability of sulfides by further additions of collectors during and after scrubbing. It was, indeed, found that additional collectors were necessary in order to give complete flotation (perhaps the as-received samples were oxidized/aged).

Figure 2 shows the standardized depressant testing scheme.

**Depressants:** The following compounds were tested as depressants.

Reagent grade or pure (> 95%) - Sod. hydrosulfide (NaHS), sod. thioglycollate (NaTG), β-mercapto ethanol (ME), sod. thiophosphate (NaTP), sod. thiolactate (NaTL), thiglycerol, 2-thio-diethanol, sod. dithiodipropionate, guanyl thiourea, 2-thiouracil, guanidine nitrate, guanidine acetate, sod. cyanide, dicyandiamide, sod. ferrocyanide, thiocetic acid, pyridine dicarboxylic acid, 2-mercapto-thiazoline, 5-mercapto-1,2,3-triazole, S-(thiobenzoyl thioglycollic acid), sod. sulfite, sod. thiosulfate, hydrogen peroxide, and proprietary depressants 3 and 4.

Compounds prepared in the lab - Sod. dithiocarbamate, disod. trithiocarbonate, cellulose xanthate (% 10% xanthation), starch xanthate (10% and 100% xanthation, different MW), Nokes reagent, dicyanodimercapto ethene, glycercyl xanthate, glycol xanthate, glycrol dithiophosphate, copper cyanide, carbowax analogs of thionocarbamates, and proprietary depressants 1 and 2.

**Results and Analysis**

Effect of Dosage of Depressants: The general effect of dosage of depressants on depressant activity will be illustrated with only the results for the three well known depressants, NaHS, NaTG and ME*.

It must be noted that similar trends were observed for these three depressants. The effect of dosage of NaHS, NaTG and ME on Cu flotation is shown in Figure 3a (for Batch A conc.) and Figure 4a (for Batch B conc.), and that on Mo flotation is shown in Figure 3b (Batch A) and

*These abbreviations stand for sodium hydrosulfide, sodium thioglycollate and mercapto ethanol. Since these compounds are referred to very frequently in the text, the abbreviations are used throughout.
Figure 4b (Batch B). All the three depressants show similar behavior for both Cu and Mo flotation. For Batch A conc., NaHS and NaTG are extremely effective Cu depressants above about 1 kg/T. ME is as effective at 1.5 kg/T. These dosages are consistent with those used in the plant (10 lb./T of 30% NaHS). Above 1 kg/T the depressant has little further effect under the conditions tested, viz. single stage addition of depressant and single stage flotation. For Batch B conc., NaHS and ME are both very effective depressants, but NaTG is slightly inferior. This kind of a slight difference for different batches of conc. can be expected, especially in view of the large differences between the concentrates.

At dosages below 1 kg/T, NaHS had an activation effect on Cu flotation. This result is consistent with the general observation that small amounts of NaHS can act as an activator for tarnished sulfides via a sulfidization (or oxide removal) mechanism.

In general, ME gave higher Mo recoveries than the other depressants for both batches of conc. It is interesting to note that Mo recoveries decrease with an increase in the dosage of depressants. This result, contrary to the general belief that the Cu depressants have no effect on Mo, is not surprising for -SH containing compounds since such compounds do adsorb on MoS2 depending upon the conditions; mercaptans are good collectors for MoS2. It must be noted here that Mo recoveries in general were somewhat erratic, especially compared with Cu recoveries. This is not unusual, and is observed invariably in Cu-Mo operations, both in Cu-Mo bulk flotation circuit and in the Mo circuit.2,13

The effect of dosage of a depressant can be summarized in a single number such as selectivity index (SI)*. This is illustrated in Figure 5a. Despite the general deceptive nature of SI in summing up metallurgical separations, it was found useful in the two-product separations of the present study (an SI of 3 is considered satisfactory). The SI for PD3 increased almost linearly with the dosage. The scatter in SI values reflects the scatter in Mo rec. values. This almost linear increase should be followed by a plateau and/or a slight decrease since Cu rec. remains unaffected above a certain dosage and Mo rec. gradually, but continuously, decreases.

Effect of pH: Copper flotation was unaffected for NaHS, NaTG and ME as a function of pH (Figure 6a, Batch A). Mo flotation, however, decreased with pH for NaHS and ME, while for NaTG it was either constant or increased slightly. It is severally reported that Mo recoveries decrease with increase in pH, but this sensitivity to pH is minimal in the presence of a MoS2 booster such as hydrocarbon oil.2 In the present study, a hydrocarbon oil was indeed used to improve Mo recovery and, as a result, a pronounced decrease in Mo recovery with increase in pH could, perhaps, be attributed to the depressant.**

\[
SI = \frac{\left(\frac{\% \text{ Mo rec.}}{100 - \% \text{ Cu rec.}}\right) \times (100 - \% \text{ Cu rec.})}{\% \text{ Mo rec.}}
\]

An SI of 3 or higher (corresponding to 70% Mo rec. and 20% Cu rec. in the concentrate) is considered satisfactory.

**Changes in frothing conditions could also affect Mo rec., but no perceptible changes were observed during the experiments.
The effect of pH on the depressant activity of PD1, PD2, and PD3 is plotted in Figure 6b (Batch B conc.). For PD1, Cu recoveries are unaffected by pH, which behavior is similar to NaHS, NaTG and ME. pH has a strong influence on Cu flotation for PD2 and PD3; the depressant activity increases with increase in pH.

The Mo recoveries are either unaffected or show a slightly decreasing trend as a function of pH for PD1 and PD3. For PD2 also, except at lowest pH, Mo recoveries do show a slight decreasing trend.

Since the Mo recoveries are only slightly affected, with a decrease in Cu flotation (Figures 6a and b), the SI should increase; in fact, the curve SI vs. pH should be the inverse of Cu vs. pH curve, which can be seen in Figure 5b.

Comparison of Depressants and Eh vs. Depressant Activity: The depressant activity of a large number of compounds is given in Table 1 along with the corresponding redox potentials. These results are plotted in Figure 7 (Eh vs. % Cu floated) and Figure 8 (Eh vs. Cu grade in the conc.). It must be emphasized here that the numbers in circles on Figures 7 and 8 correspond with the depressants listed in Table 1 and that the correlation is between all the depressants under identical conditions. It is indeed possible to classify the compounds into several groups on the basis of this correlation (as indicated in Figures 7 and 8). In Figure 7, compounds 14 and 15, which are xanthated starches, are grouped as depressants-non-reducing because they effectively depress copper under non-reducing conditions (relative to the natural Eh of the Cu-Mo conc. viz. 0 to -50 mV vs. SCE).

Guanyl thiourea (#21, Table 1 and Figure 7) is a good example of a reducing agent that is not a depressant. Depressants 17-29 (except 21) are non-reducing and non-depressants (relative to the depressants 1-14).

These different groups are adequately delineated in Figure 9.

DISCUSSION

An increase in dosage of a majority of depressants increased the Cu depressant activity, but at the expense of other performance and, in particular, slightly lower Mo recoveries. Consequently, the SI, which initially increased with increasing dosage, reached a plateau (or even a small decrease) depending on how low the Mo recovery was at constant Cu flotation. In the pH range 8-11, the depressant activity for several depressants either remained constant or increased slightly. The SI followed a similar trend. Since several structurally different compounds showed a depressant activity similar to NaHS, it is possible that the depression mechanism is at least to a large extent similar for these compounds.

The exact mechanism of the depressant action is still not understood, perhaps owing to the experimental difficulties in actually determining the various sulfur species present on the mineral surfaces or in solution after treatment with the depressant. In fact, such a determination has not been made even for thiol collector adsorption on sulfides. The literature abounds with speculations for collector
adsorption, and the depressant action of Na₂S or even NaCN has not been systematically investigated.

It is quite evident from flotation practice that Na₂S/NaHS acts as a depressant for most sulfide minerals. It has been observed that even quartz that is activated with Cu or Fe can be effectively depressed with Na₂S. There is widespread agreement that HS⁻ is the species responsible for depression. Being a potential determining ion, it specifically adsorbs on sulfides even at low concentrations (HS⁻ is considered more mineral-surface-active than xanthate ion), giving the surface a highly negative charge.³,¹⁴

\( \text{NaHS/Na}_2\text{S additions can lead to three distinct possibilities:} \)

(a) Sulfidization of tarnished or heavily oxidized sulfide surfaces – this usually results in an activation of the sulfides and only small amounts of sulfide ions are necessary. In the present study, such an activation was indeed observed at low dosages of NaHS.

(b) Act as a reducing agent, thereby controlling the level of oxygen and of oxidation or act as an effective thiophilic agent neutralizing the collector properties of elemental sulfur that is often a product of oxidation of sulfides.⁵ In the role as a depressant, NaHS/Na₂S is certainly providing a powerful reducing medium, and, in addition, it is possibly functioning as a thiophilic agent for the products of xanthate adsorption.

(c) Destroy or displace the collector coating on the sulfides – although no direct evidence to this effect has been reported in the literature, it is a distinct possibility that is responsible for efficient depression.

Experiments in the present study have clearly indicated that cuprous xanthate (the stable complex of Cu) is unstable in the presence of excess NaHS; a black precipitate of cuprous sulfide was obtained instantaneously when a dilute solution of NaHS was added to a fine suspension of cuprous xanthate in water. The log \( K_{sp} \) of cuprous sulfide is ≈ -47.6 to -49.4 while that of cuprous xanthate is ≈ -26.⁷ The role of NaHS could also be in destroying the hydrophobic character by forming thio anions or sulfanes or other hydrophilic thio compounds.⁵ The redox potential may also play an important role in the destruction/desorption of the thiol collector from the surface since it is well known that thiol collector adsorption proceeds via an electrochemical mechanism. Richardson et al.¹⁵ have shown that electro-adsorption and desorption of ETX can be potentiostatically controlled on packed beds of sulfide minerals such as chalcopyrite, galena and chalcopyrite. Chalcopyrite flotation was found to be dependent on electrochemical potential. Accordingly, it may be argued that redox potential may have an important role in the depression of sulfides. Although a majority of the compounds found in the present study to be effective depressants do contain an active -SH group, there are some that do not contain this group, but which were found to be Cu depressants. For ex. PD₂ and starch xanthates.

From this study it would appear that for inorganic compounds to function as effective depressants, they should be strongly reducing agents and
should preferably contain an active \(-\text{SH}\); for example, \(\text{NaHS}\) and Nokes reagent. An organic molecule is less predictive, however, it may benefit from containing a complexing group (preferably \(-\text{SH}\)) and polar groups that impart sufficient hydrophilicity (ex. \(-\text{OH}\), \(-\text{COOH}\) and \(\text{P}^{5\text{O}}\)).

In addition, it may be beneficial if the molecule be also reducing. Starch xanthates which are not powerful reducing agents and which do not contain an active \(-\text{SH}\) group, depress copper by a different mechanism. From a chemical standpoint, the depressant action of starch xanthates is interesting since both the collector and the depressant contain the same active group, viz. a xanthate. Competition between the two for active sites on the mineral site is, therefore, inevitable. Polymeric properties such as MW, \% xanthation, etc. may suggest whether starch xanthate adsorption is possible or not.

On the basis of the results, the compounds investigated in the present study have been grouped as depressants, non-depressants and non-selective depressants in Table 1 and Figure 9. Compounds belonging to the last group depress both Cu and Mo; for ex. disodium trithiocarbonate. It was indeed confirmed in an earlier collector study that dialkyl trithiocarbonates are efficient collectors for both Cu and Mo. It must be noted that \(\text{NaCN}\) and \(\text{Na}_3\text{Fe(CN)}_6\), which are commonly used depressants, were found to be non-depressants under the conditions tested. \(\text{NaCN}\) is seldom used as the major depressant for Cu-Mo separations (it may be used in the cleaners following depression with \(\text{NaHS}\) or others).\(^2\),\(^13\) \(\text{Na}_3\text{Fe(CN)}_6\), which is widely used, is effective under somewhat different conditions of pH, redox potential, etc.\(^2\),\(^13\) In many cases, the use of \(\text{Na}_3\text{Fe(CN)}_6\) is preceded by a treatment such as steaming, oxidation or acid conditioning. The ferricyanide/ferrocyanide couple is very oxidizing compared with \(\text{NaHS}\).

Sodium thioglycollate and mercaptoethanol are effective depressants. They contain an active \(-\text{SH}\), which may participate in adsorption, and a hydrophilizing group, \(-\text{COO}^-\) for \(\text{NaTG}\) and \(-\text{OH}\) for \(\text{ME}\). Additionally, it should be noted that these molecules have only two C-atoms. In order to be a depressant, an organic compound must either be a short-chain molecule or, if long-chained, must contain sufficient hydrophilic groups.\(^16\) In other words, the HLB should be such that the overall molecule is very hydrophilic. \(\text{NaTG}\) and \(\text{ME}\) could be potential chelating agents because they contain active \(\text{SH}\) and an oxygen donor in \(\alpha-\beta\) positions; if this is so, these molecules would not be effective depressants since the chelates formed would be insufficiently hydrophilic.\(^16\) It is, therefore, conceivable that only \(-\text{SH}\) is participating in adsorption. Thioglycerol is similar to \(\text{ME}\). Nokes reagent is similar to \(\text{NaHS}\) except that the \(-\text{SH}\) group is possibly attached to the phosphorus. The active species in Nokes reagent are believed to be sodium thiophosphate and \(\text{Na}_2\text{S}\) that is produced during the reaction between \(\text{P}_2\text{S}_5\) and \(\text{NaOH}\).\(^13\)

Sodium thiolactate and sodium thiopropionate were found to be slightly inferior to \(\text{NaTG}\), perhaps owing to the additional C atom that they possess.

Thiouarcil and 5-mercapto-1,2,3-triazole have similar active groups; the \(\text{SH}\) attached to the ring is the active group, while the rest of the molecule provides the hydrophilicity.
Guanidine nitrate, guanidine acetate and dicyandiamide (Table 1) contain no sulfur, especially -SH or C=S, both of which are active towards sulfide minerals. Furthermore, they are not strongly reducing agents. Guanyle thiourea has a potential complexing group (either $S\equiv N\equiv H$ or $N\equiv H\equiv S$) but is not sufficiently hydrophilic. For sulfide minerals, which possess some degree of natural hydrophobicity, it is essential that the depressant molecule be sufficiently hydrophilic.

2-Thiodiethanol and disodium dithio propionate have sufficient hydrophobic groups, but no complexing group (-C=S-C- is weakly complexing). 2-Mercapto-thiazoline has an excellent complexing group (-SH), but the molecule, on the whole, is not hydrophilic because of the ring sulfur. Pyridine dicarboxylic acid has sufficient hydrophilic groups (-COOH), but is weakly complexing towards sulfides (N, O donors are inferior for sulfides compared with N, S donors).

Glycerol dithiophosphate, glycerol xanthate and glycol xanthate molecules are sufficiently hydrophilic, but the active group xanthate or dithiophosphate is the same as the collector active group. Energetically, the sulfide minerals should show no preference to the short-chain hydrophilic xanthate molecules, unless other factors such as increased MW, entropy, etc. are brought in.

Sodium sulfide and sodium thiosulfate are neither strongly complexing nor strongly reducing; hence poor depressant activity.

SUMMARY AND CONCLUSIONS

A systematic investigation of the structure-activity relationships for Cu depressants has been made using bulk Cu-Mo concentrates. A large number of inorganic and synthetic organic depressants have been evaluated as a function of dosage and pH. Small-scale laboratory flotation tests and redox potential measurements of both the flotation systems and depressant solutions have been carried out. The following conclusions are evident from this study.

1. Sodium thioglycollate and mercaptoethanol are as effective as NaHS, which is an excellent Cu-depressant. Mercaptoethanol shows slightly improved Mo recoveries. The depressant activity of these compounds is unchanged above a dosage of about 1-1.5 kg/T and in the pH range 8-11.5. Mo recoveries decrease with increase in dosage and pH.

2. The presence of -SH, polar groups and redox properties seem to contribute to depressant activity; however, the relationship is very complex and accurate prediction of depressant activity is far from straightforward.

3. In addition to destabilizing thiol collector coating, the HS$^-$ ions, which are believed to be responsible for the depression of Cu, may also destroy the collector coating by forming the thermodynamically (and perhaps kinetically too) more favorable Cu$_2$S.
ACKNOWLEDGEMENTS

The authors wish to acknowledge the excellent contributions of Mair Churchill and Ed Dowling in the experimental part of this summer project. Discussions with David Dauplaise in the initial stages of the project are also acknowledged. The authors also wish to thank the Cyanamid Management for granting permission to publish this work.

REFERENCES

11. idem., U.S. 3,788,467.

OBSERVATION: THE TABLES AND FIGURES SENT BY THE AUTHORS DID NOT CONFORM WITH THE GIVEN FORMAT AND THUS WERE NOT INCLUDED