Chemistry and applications of chelating agents in flotation and flocculation

P. Somasundaran and D. R. Nagaraj

Synopsis

Chelating agents, because of their metal specificity or selectivity, can function as good flotaids and selective flocculants. In addition to the metal selectivity, chelating agents offer certain advantages over conventional mineral processing reagents even from the synthesis point of view. With the major donor atoms—S, N, O and, to some extent, P—numerous possibilities exist to tailor-make reagents for specific applications. For polymers the backbone offers further possibilities for the incorporation of the required properties.

In general, the choice of a chelating agent or a group is made on the basis of its function in well-known analytical metal separations. Such a choice is limited in that the number of well-known analytical separations is also limited. In the present work, a new and effective *donor atom* approach is discussed for the design of mineral-specific chelating groups. This generalized approach is focused on the chemical properties of the important donors both in the reagent and on the mineral. Data from many chemical sources have been summarized and applied to systems of relevance to mineral processing. Understanding of the chemical behaviour of donors is of paramount importance in predicting the properties of chelating groups.

Numerous investigations have been made of the application of chelating agents in mineral processing. The various fundamental aspects of the interactions between a mineral and a chelating group are, however, not clearly understood, although there is evidence to suggest that some form of a metal complex is formed at the surface.

The separation of minerals from one another by flotation and flocculation depends mainly on the selective adsorption of surfactants and polymers on them. Although many reagents have long been used in practice for the flotation of minerals, most are not as selective as is required for the efficient separation, in particular, of mineral fines and ultrafines. Reagents with chelating functional groups have received increased attention for this purpose in recent years, being known to exhibit excellent metal selectivity in analytical separations. Many chelating agents have been tried as collectors for various mineral systems and excellent separations have been obtained in certain cases. The mechanisms that involve their collecting action are, however, not adequately understood. In particular, the differences in their mode of action at the mineral surface versus that in the bulk are not fully recognized and, as a result, the development of collectors based on their use in analytical separations is not achieved easily. It is to be noted in this regard that chelating collectors are seldom metal-specific or mineral-specific and the properties of both the chelating agents and the mineral are important in determining their collecting action. The donor atoms on the chelating agents, as well as those associated with the mineral species, play a governing role in their interactions on the surface. In this paper the application of chelating agents in mineral processing systems is reviewed on the basis of the donor properties of the chelating groups and the metal species, and

recent approaches to understand chelation are discussed briefly. Emphasis is given to the criteria for selection of chelating agents as collectors for various minerals and the predictability of the behaviour of a chelating agent for a given mineral system.

Chelating agents

Chelating agents are compounds that form metal complexes characterized by ring structures illustrated in Fig. 1.[1,2,3] In type I the metal is coordinated to the four nitrogens of two molecules of ethylene diamine, giving rise to a charged double ringed complex with chloride neutralizing the two charges.[1] Other types of chelating complexes include type II, with an intra-molecular hydrogen bridge, and type III, involving polynuclear halogen bridges.
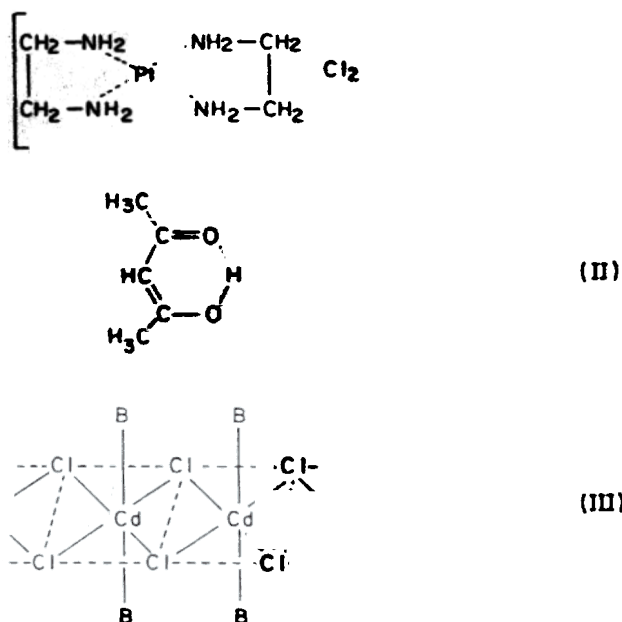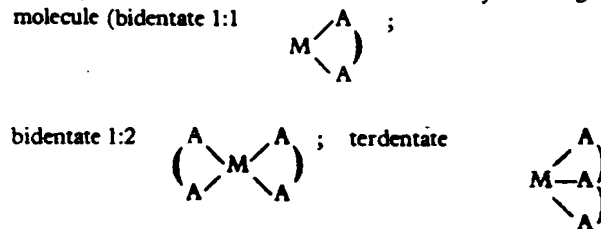

Fig. 1 General structures of chelating agents[1]

Chelating agents can be classified on the basis of donor atoms involved (O–O, N–O, N–N, S–O, S–S, S–N) or ring size (4-, 5- or 6-membered) or charge on the complex (anion, cation, neutral) or number of bonds to the metal for every chelating molecule (bidentate 1:1

bidentate 1:2 ; terdentate

Specificity of chelating agents depends on the interaction

ween donor atoms and surface species on the particle. A list of nor atoms and functional groups containing the four major ms (N, O, P and S) are given in Table 1. Halogen atoms, Cl, and I, participate in chelate ring formation in bridged

HO–CH–COOH
|
HO–CH–COOH

CH₂–COOH
|
CH₂–COOH

Table 1 Donor atoms and functional groups containing major donor atoms[3]

Major donor atoms	Functional groups	
	Acidic (lose a proton)	Basic (donate electron pair)
		–NH₂
O	–COOH	=O
	–OH (enol or phenol)	–OH (alcohols
	–P(O)(OH)₂	
S	–SH	–S–R

polynuclear complexes that are of minimal importance in mineral processing. As and Se form only a few useful complexes and, therefore, are seldom used.

Requirements for chelating agents

There are, essentially, two basic requirements that chelating agents must satisfy to form metal chelates: the molecules should have suitable functional groups and the functional groups must be situated to permit the formation of a ring with a metal as the closing member.

These two conditions are necessary, but not sufficient for the formation of a chelate ring. For example, under certain conditions and under sufficiently low pH values, a potential chelating molecule may attach itself to a metal atom through only one ligand atom:

HOOC.CH₂NH₂   Cl

Pt

Cl   NH₂CH₂COOH

or

HOOC.CH₂S–M
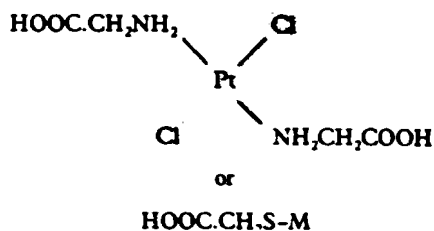
It has been generally observed that certain additional requirements must be satisfied by chelating agents for mineral processing applications: the chelates should, preferably, be neutral, if the chelating agent is to function as a collector, and the chelates should, preferably, be charged and very hydrophilic if the chelating agent is to function as a depressant. On a polymeric depressant or a flocculant this requirement is not stringent so long as the backbone has other hydrophilic groups (see below).

Requirements for depressants: ionic chelates, e.g. [Co(DMG)₂(H₂O₂]⁻, and hydrophilizing groups on molecule
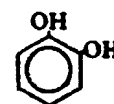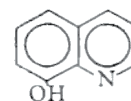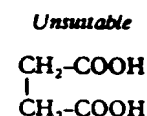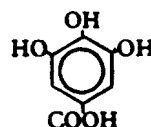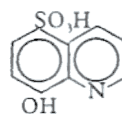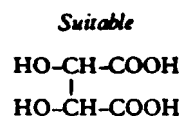
Neutral complexes are usually insoluble in water and, therefore, promote hydrophobicity. For insolubility in water, however, it is not sufficient that the chelate be a neutral complex. A classic example is that of chelates of dimethylglyoximes (DMG) (see Fig. 2). The 1:2 complex of nickel with DMG is insoluble in water. The copper complex is, on the other hand, relatively water-soluble. This results from the subtle differences in the shapes of the two molecules and consequent differences in the mode of packing of the two molecules in their respective crystals (Fig. 2). The nickel compound is planar and the molecules are stacked in the crystal, so the Ni atoms are co-linear and have a weak bond between them. In the copper compound, however, the chelate rings are not co-planar but make a small angle of 28° with one another and there is no metal–metal bonding.[1] The tetragonal pyramidal copper chelate molecules are paired in the crystal in such a way that each copper atom has an O atom from its adjacent molecule as one of its five immediate neighbours. In the Ni complex the –OH and the –O⁻ are strongly internally hydrogen bonded and, hence, less readily solvated. The copper complex actually has a higher stability constant than the Ni complex but, since no internal hydrogen bonding is possible, the complex is easily solvated.
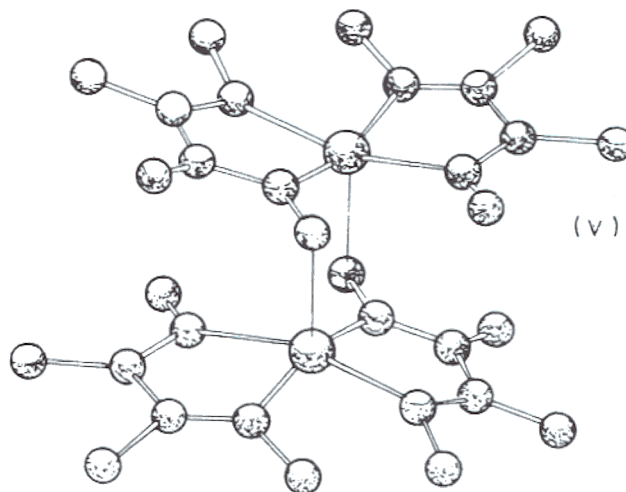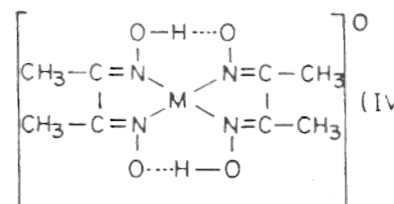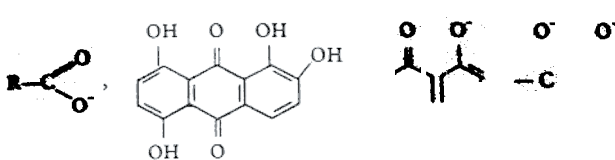

Fig. 2 Geometric structures of DMG chelates of Ni and Cu[1]

210

Specificity and selectivity

Most of the chelating groups form complexes with almost all of the transition and many non-transition metals and, therefore, specificity is not as absolute as is required for their selective adsorption on minerals. In practice selectivity is achieved by making use of differences in stability constants and chelate formation under various solution conditions. As was indicated earlier, contribution from the donors as they are located in the mineral lattice has to be considered in obtaining the selectivity. Also, the solubility of the mineral, in addition to that of the metal chelate, has a pronounced influence on the selectivity and the collection power of the chelating agent.

Stability of complexes

Major factors that determine the stability constant are, in order of decreasing importance, pK_a of the ligand molecule, substituents, nature of donor atoms, central metal atom, and ring size, number of rings.

The first four factors are very important in that they determine the nature and strength of bonds. pK_a of the chelating agent has a direct influence on the chelate formation since it represents the tendency of the donor atoms to donate electrons to metal atoms (or accept from metals, in certain cases) and thus form a chelate. Substitution on the chelating molecule has two important effects:[1] it alters the pK_a and/or it introduces steric factors for the formation of a chelate.

The influence of the nature of donor atom and the central metal atom should be considered together because of the inter-relationship between their behaviour (see later).

Properties of acceptors

Acceptors can be divided conveniently into two main groups based on the unidentate ligands: (a) those which form most stable complexes with N, O and F, and (b) those which form most stable complexes with P, S, and Cl (Table 2).

The stability constants of metal complexes that belong to the two groups follow the general orders N>>P>As>Sb; O>S; F>Cl>Br>I; and for similar ligands N>O>F; differences in the series P>S>Cl are found to be less pronounced.[4] It is seen that a vast majority of elements belong to group (a), i.e. they preferentially complex with O- and N-containing ligands.

A given metal, furthermore, may belong to group (a) or (b), depending on its oxidation state: for example, Cu(I) belongs to group (b), wheras Cu(II) belongs to the overlap region of (a) and (b).

A major shortcoming of the above grouping is that it is based on *unidentate* ligands; the situation is complicated when chelates (or bidentates) are involved. Consideration must be given in this case to chelating agents in which the donor atoms are the same (examples are ethylene diamine, oxalate or thiooxalate) and chelating agents in which the donor atoms are different (examples are o-aminothiophenol and o-aminophenol). For nickel, thiooxalate ion is believed to form a more stable nickel chelate than the oxalate ion. For zinc, stability constants of the o-aminophenol and o-aminothiophenol complexes show that the substitution of S for O does have a marked influence on stability.

A more useful grouping is that based on the electronic configuration of the metals. Thus metals can be classified into three groups—those which contain (a) inert-gas type configuration, (b) partially filled d or f orbitals and (c) ions of metals with filled d orbitals (Ag$^+$, Zn^{2+}, etc).

Metals of group (a) react preferentially with O-containing ligands, such as carboxylate ions and the anions of quinalizarin, and the β-diketones.

Table 2 Classification of acceptors based on unidentate ligands

H																	
Li	Be											B	C	N	O	F	
Na	Mg											Al	Si	P	S	Cl	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	
Fr	Ra	Ac	Ku	Ha													

☐ CLASS A   Form stable complexes with N,O,F

▨ BORDER REGION

▦ Class B: Form stable complexes with P,S,Cl

OH O OH
OH

O O⁻ O⁻ O⁻

Transition-metal ions form more stable complexes with ligands that contain polarizable portions, such as amino groups and heterocyclic nitrogen atoms.

Metals in group (c) also prefer highly polarizable ligands, especially if the latter have suitable vacant orbitals into which some of the d electrons from metals can be 'back-bonded'. Examples of such ligands are those which contain S as the donor which is highly polarizable and has vacant $3d$ orbitals. Thus, thioanalide forms insoluble complexes with Cu, Ag, Cd, Hg(II), Tl, Sn(II), Pb, As, Sb, Bi, Pt and Pd.

O   SH
‖ |
NH — C — CH₂

Thioanalide
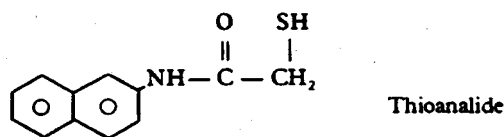
A reagent, such as dithizone, which contains N and S donors therefore reacts with a large part of the transition metal and filled d orbital series. To achieve the degree of selectivity that is desirable in practical applications it is usually necessary to arrive at the appropriate combinations of donors.

Donor–acceptor relationships

A useful classification of acceptors as well as donors is that based on Pearson's concept of *hard* and *soft acids* and *bases* (Table 3).[5,6,7] The acids (or electrophiles) are mostly (metal) cations. This group also includes such electrophiles as CO_2, O, Cl and N and metals in the zero oxidation state. The bases (or nucleophiles) are non-metal anions, neutral atoms and molecules. It should be noted that the donors O and N are hard bases and donor S and P are soft bases.

Table 3   Characteristics of hard and soft acids and bases

Hard (acid or base)	Soft (acid or base)
Small size	Large size
Orbitals involved far apart in energy	Orbitals close in energy
Ionic bonding coulombic attraction	Covalent bonding
High charge ions	High charge ions
Non-polarizable	Polarizable
	Bases have low proton affinity
Hard likes hard	Soft likes soft
High electronegativity	Low electronegativity

The bonding characteristics of these groups are given in Table 3. In general, hard bases preferentially react with hard acids, and similarly for soft bases. The former interaction is characterized by ionic bonding since the orbitals involved are far apart in energy, thereby promoting coulombic attraction. On the other hand, the interaction between soft bases and soft acids is characterized by covalent bonding since the orbitals involved are close in energy.

It is questionable whether this sort of classification will be valid for mineral species, although there is some evidence in the literature that the metal cations that prefer to react with O donors also tend to preferentially adsorb O-containing

collectors on their mineral surfaces.[7] Similarly, S donors react preferentially with sulphide minerals. It has been pointed out that a bond between metal ions and soft bases makes the metal ions soft acids and vice versa.[8] This is especially important to borderline cations. From this viewpoint sulphidization of oxidized minerals should lead to an increase in the capacity of their reactive centres to react with sulphhydryl collectors.[7] Thus, the important contribution of donors on the mineral surfaces to interactions between minerals and chelating agents must be noted. Oxide minerals (which have O donors) of soft-acid metal ions would preferentially adsorb O⁻ and N-containing collectors, whereas their corresponding sulphides would preferentially adsorb S-containing collectors.

Properties of donor atoms

The donors O and N belong to the first row of elements in the periodic table and follow the octet rule[1-4,6,9,10,11] with valencies 2 and 3. The donors P and S belong to the second row, and these also follow the octet rule with valencies 3 and 2; however, P and S can exhibit higher valence states also since they have easily accessible vacant $3d$ orbitals. It is the electrons at or near the surface of atoms and ions that are the most important in determining their chemical and physical properties. This is especially true of donors P and S and transition metal ions. The latter have incompletely filled d orbitals, which have quite large fractions of their total volumes near the outsides of the ions, so they are easily accessible for bond formation. Additionally, the d orbitals are much more easily polarized, promoting a much more favourable orbital overlapping.

The important properties of the four donors O, N, S and P are summarized in Table 4.

O and N have $2p$ electrons and no accessible vacant d orbitals. S and P have $3p$ electrons in their outermost shells, but they have, in addition, easily accessible vacant $3d$ orbitals. The electronegativities decrease in the order

O	N	S	P
(3.5)	(3.07)	(2.44)	(2.06)

Consequently, O invariably forms ionic bonds with a majority of elements in the periodic table. Thus, chelating agents with O–O donors often form chelates with a large number of metals and are, therefore, less selective. The selectivity in general should increase from O to P.

The normal valencies are 2, 3, 2 and 3 for O, N, S and P, respectively. O has two unpaired electrons or two electron pairs to donate, but it seldom donates both pairs; only one pair is active. It can form a maximum of four bonds, but seldom attains all four (three bonds are common). O forms multiple bonds. N has five valence electrons, but only four orbitals and, therefore, a maximum of four bonds can be formed. It has one lone pair of electrons to donate when three electron-pair bonds are formed. Like its neighbours C and O, N also readily forms multiple bonds. In this respect N differs from P, S, As, Sb and Bi. S has two valence electrons and its normal valency is 2. But it has four orbitals and easily accessible d orbitals. Consequently, S can form two to six bonds. Similarly, P forms three to six bonds, although its normal valency is 3 and it has five valence electrons. All four donors have one active lone pair of electrons. Although O and N show strong $p\pi$–$p\pi$ bonding (because of the p outer orbitals and no d orbitals), S and P show very little or no tendency for $p\pi$–$p\pi$. On the other hand, only S and P show strong $d\pi$–$d\pi$ bonding. In addition, S and P show $d\pi$–$p\pi$ bonding (or back-bonding) since they can accommodate electrons from metals in their vacant d orbitals. This ability for back-bonding for P and S, indeed, is an important distinction that puts these donors in a special class. The polarizability of the lone-pair electrons on these donors follows an almost reverse

Table 4 Major properties of donor atoms O, N, S and P

	O	N	S	P
CONFIGURATION	$1s^2 2s^2 2p^4$	$1s^2 2s^2 2p^3$	$[Ne] 3s^2 3p^4 3D^0$	$[Ne] 3s^2 3p^3 3D^0$
ELECTRONEGATIVITY	3.5	3.07	2.44	2.06
VALENCE ELECTRONS	2	5	2	5
NORMAL VALENCY	2	3	2	3
# OF ORBITALS	4	4	4 + D	4 + D
# OF BONDS (VALENCY EXPANSION)	3	4	2-6	
LONE PAIRS	2	1	1	1
Pπ-Pπ	STRONG	STRONG	POOR	NONE
Dπ-Pπ (BACK-BONDING)	NONE	NONE	STRONG	STRONG
POLARIZABILITY	NIL	GOOD	STRONG	GOOD
H-BONDS	STRONG	STRONG	VERY WEAK	NONE
BONDS	MORE IONIC	LESS IONIC	COVALENT	COVALENT
STERIC ACCESSIBILITY	LOW	LOW	HIGH	HIGH

order of the electronegativities. Thus, for polarizability

$$O < N \ll S \sim P$$

O and N have the distinction of having the ability to form very strong H bonds, whereas S and P show little or no such tendency. Since P and S have d orbitals, and large size, these donors are much more sterically accessible for bond formation than O or N.

S is unique in its ability for catenation (forming bonds with itself); its common occurrence is in the form of an eight-membered ring. S is also known to form higher polymers. This unique feature of S is very important in all its interactions.

O and S can enter into chelation either through the ether or thioether form R-O-R, R-S-R, or the R-OH, R-SH. The -SH group is much more acidic than -OH and is highly polarizable, but not an effective acceptor. The R-S-R group forms pyramidal bonds and is an effective $d\pi$ acceptor. The R-SH shows a strong tendency for unidentate bonds, and the R-S-R shows a strong tendency to form chelate rings. The C=S is more ionizable and has a greater volume than C=O. S is a better donor than O with regard to sharing or donating the lone pair of electrons. Similarly, N is also a better donor than O.

It can be readily seen from the foregoing discussion that each donor has some unique properties. The acceptors also fall into certain well-recognized patterns. A judicial combination of donors for any given acceptor, taking into account the properties of both acceptors and donors (on mineral as well as the chelating agent), should provide the required selectivity in minerals processing applications.

The Molecular Orbital treatment is a powerful tool in understanding the donor-acceptor interactions. In this approach[1,9,10,12,13] the individual atoms with their nuclei are all placed in position and all the electrons concerned in bond formation are allotted to the various molecular orbitals. This treatment, however, has scarcely been used in understanding the mechanism of adsorption on minerals.

Substituent effects

The electron-donating or withdrawing tendencies of organic groups will influence the electron densities on donor atoms and the pK_a of the molecule.[9,11,14-17] The inductive effect results from electronegativity differences. Much stronger changes in electron density and delocalization of electrons arise from the resonance or mesomeric effects. With alkyl amines, for example, the alkyl group exerts an inductive effect on the nitrogen, making its unshared electron pair more available for bonding and thereby increasing the basicity.

$$R \rightarrow N\!:\,+H^+ \rightleftharpoons R \rightarrow N \quad H^+$$

(with H substituents shown above and below N on each side)
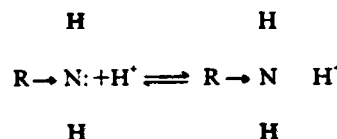
In carboxylic acids the inductive effect of an alkyl group decreases the acidity; for formic acid the dissociation constant $K_a = 17.7 \times 10^{-5}$, whereas for acetic acid $K_a = 1.75 \times 10^{-5}$—almost one-tenth of the value for formic acid.
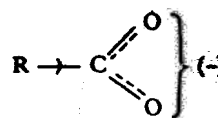
[K_a decreases]

If, on the other hand, the R group exerts an opposite inductive effect owing to certain substituents on R such as Cl or NO_2, the acid strength of the carboxylic acid increases.
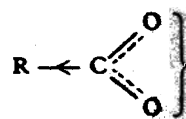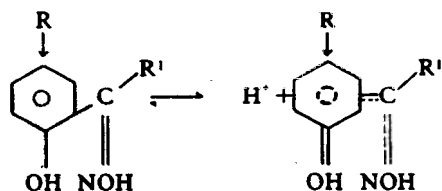

[K_a increases]

The electronic effects are much stronger in aromatic compounds. A benzene ring could exert both electron-donating and electron-withdrawing effects. In benzoic acid the aromatic ring exerts an electron-withdrawing effect and, hence, it has a much higher K_a than that of acetic acid. An alkyl group in the para position on the ring exerts an electron-releasing effect. Groups such as —OH or —OCH_3 are electron-releasing owing to resonance, in spite of the electronegative oxygen and the

electron-withdrawing inductive effects that the groups can be shown to possess.

The effect of electron-active substituents on an aromatic ring is well exemplified by aromatic hydroxy oximes. For an electron-releasing R group, such as —CH₃ or —OCH₃, the acid strength decreases, and the pK_a increases, the release of electrons destabilizing the phenolate ion (the electron density on N may also increase):

Substituents $R = Cl$, NO_2 etc., have opposite effects. The increase in electron density on donors can (a) enhance basicity and (b) therefore enhance σ bond stability, but (c) it may also decrease π acceptor ability of ligand and (d) therefore decrease donor π-bond stability.

Effects (c) and (d) could be pronounced for donors such as S since the donor-π bond (or dative bond) is formed between the metal and the organic reagent (in addition to the coordinative or s-bond) as a result of transfer of electrons from d orbitals of metal into vacant d orbitals of the donor. The formation of a dative bond, which reinforces the σ bond, is more probable for metals in their lower oxidation state since these would have more electrons than those in the higher oxidation state. Another important requirement is that the donor atom should have easily accessible vacant d orbitals (S). O and N, which do not have these d orbitals, do not form a dative bond. The nitrogen in oximes, however, forms a donor-π bond and, therefore, oximes are an exception. This explains the order of the ligand field stabilization effects observed for the chelates betweeen substituted salicylaldoximes (SALO) and Cu, Ni and Co (Table 5).

Table 5 pK_a of SALO and ligand field stabilizations[18]

pK_a ±0.05	CH₃.SALO	SALO	Cl.SALO	NO₂.SALO
	11.06	10.70	10.25	8.72
	7.5	8.4	10.1	
	0.6	1.5	2.6	3.8
	0.8	1.1	2.4	3.5

The ligand field stabilization (LFS) increases for each metal as the pK_a decreases, i.e. as the electron density on the donor atoms decreases. This increase in LFS is attributed to the effect of substituents on the π-acceptor capability of the ligands.[18]

The thionocarbonates (Z-200 type) are not only excellent sulphide collectors but also offer an interesting case for study. The molecule contains the three important donors O, N and S. O and N are hard bases and S is a soft base.
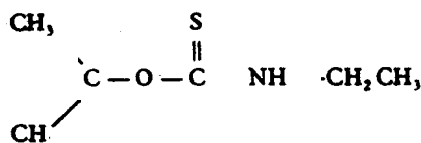
O and N exert an electron-withdrawing inductive effect.
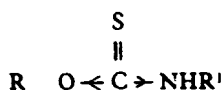
Simultaneously the groups RO and R'NH could exert an electron-donating effect since the C^*—S^- is more stable than —C=S. This tautomerism, together with the inductive effect, would delocalize electrons over the entire active group

$$\begin{array}{c} S \\ \| \\ -O-C-NH. \end{array}$$ Thus,
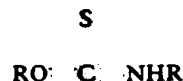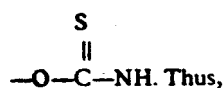
The electron-density order may follow S>O>N and, considering the sizes and polarizability of the donors, the steric accessibility would follow the order S>N,O. S may also show a tendency to bond with S on the sulphide surface. Thus, S is a very active donor in the thionocarbamate molecule.[7]

Substituents introduced into the molecule influence the electron distribution and, therefore, produce some interesting effects. Russian investigators[7,13] have done some extensive study on substituted thionocarbamates—especially phenyl substituents. The N-benzoyl thionocarbamate has been studied the most:
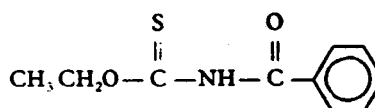
The aromatic ring accentuates the electronic effects compared with an alkyl analogue
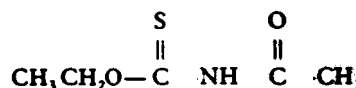

In addition, the O of the C=O exerts some electron-withdrawing effect, being strongly electronegative. The delocalization of electrons is more pronounced. There is a decrease in electron density on S and the pK_a.
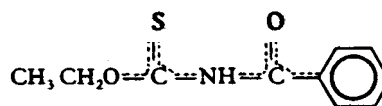
The substitution of a phenyl group instead of a benzoyl group may lead to a different electronic effect, since the phenyl group can either be electron-donating or electron-withdrawing.
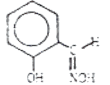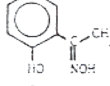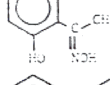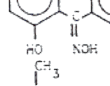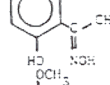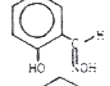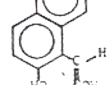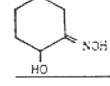
For thiol collectors (dithiophosphates, xanthates, and dithiocarbamates) the electron densities on the active S donors depend on the inductive effects in the molecules.


DTP   Xanthate   DTC
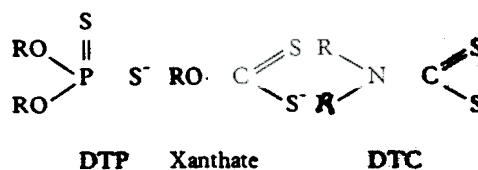
In DTP the two RO groups exert an electron-withdrawing inductive effect because of the higher electronegativity of the O atoms. This will delocalize the electron and stabilize the anion. Furthermore, P is more electropositive than C in xanthate. The electron density on S in DTP would be decreased and, consequently, DTP is a stronger acid, weaker collector and more selective than xanthate. These electronic effects are less pronounced in xanthate since there is one less RO group and C is less electropositive than P. In DTC N is less electronegative than

O and has a higher tendency to donate electrons. As a result the DTC would be a stronger collector, weaker acid and less selective than DTP (DTC<X<DTP).

Table 6   Structure and water solubility of various hydroxy oximes[19]

Name	Mol. Wt.	Water Solu- bility M	Stock Solution M
SALO (Salicylaldoxime)	137.1	2×10^{-1}	10^{-2}
OHAPO (O-Hydroxy Acetophenone Oxime)	151.2	4.5×10^{-3}	2×10^{-3}
OHBuPO (O-Hydroxy Butyro- phenone Oxime)	179.2	5.0×10^{-4}	3×10^{-4} & 5×10^{-4}
OHBePO (O-Hydroxy Benzo- phenone Oxime)	213.2	1.5×10^{-4}	1.5×10^{-4} & 2×10^{-4} (1.2% acetone)
2H5MeAPO (2-Hydroxy-5- Methyl Acetophenone Oxime)	166.2	3×10^{-4}	3×10^{-4}
2H5MBAO (2-Hydroxy-5- Methoxy Benzaldoxime)	165.2	5×10^{-3}	5×10^{-3}
2HNAO (2-Hydroxy-1- Naphthaldoxime)	189.2	1×10^{-4}	1.25×10^{-4}
OHCHO (O-Hydroxy Cyclo- hexanone Oxime)	129.0	~1.0	5×10^{-1}

A recent detailed study with several water-soluble chelating agents (Table 6) of the class of aromatic hydroxy oximes showed several interesting effects of substitution. Flotation results obtained with these chemicals, which can be represented by the general formula

$$\text{R}_2 \quad \text{R}^1$$
$$\begin{array}{c} \text{OH} \quad \text{C} \\ \quad \text{NOH} \end{array}$$
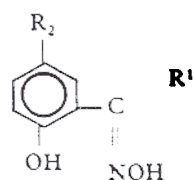
are given in Fig. 3. If R_2=H and R_1=—H, —CH$_3$ or —CH$_2$CH$_2$ CH$_3$, the effect on the collector efficiency was observed to increase in the order —H<<—CH$_3$<—CH$_2$CH$_2$CH$_3$.

The introduction of the first —CH$_2$ in SALO results in a much larger change in polarity of the molecule in comparison with further addition of two —CH$_2$ groups. This is reflected also in the water-solubility of the oximes–SALO, OHAPO and OH–BuPO. Furthermore, the electron-donating tendency of —CH$_2$ group may also favour 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 this basis OHBePO can be predicted to have a higher collector efficiency than SALO. The actual finding was, however, contrary to the prediction, suggested as being due to the possible steric hindrance to chelation offered by the second

△ SALICYLALDOXIME
□ O-HYDROXY ACETOPHENONE OXIME
○ O-HYDROXY BUTYROPHENONE OXIME
⬭ 2-HYDROXY-5-METHOXY-BENZALDOXIME
◐ 2-HYDROXY-5-METHYL-ACETOPHENONE OXIME
⬛ 2-HYDROXY-1-NAPHTHALDOXIME
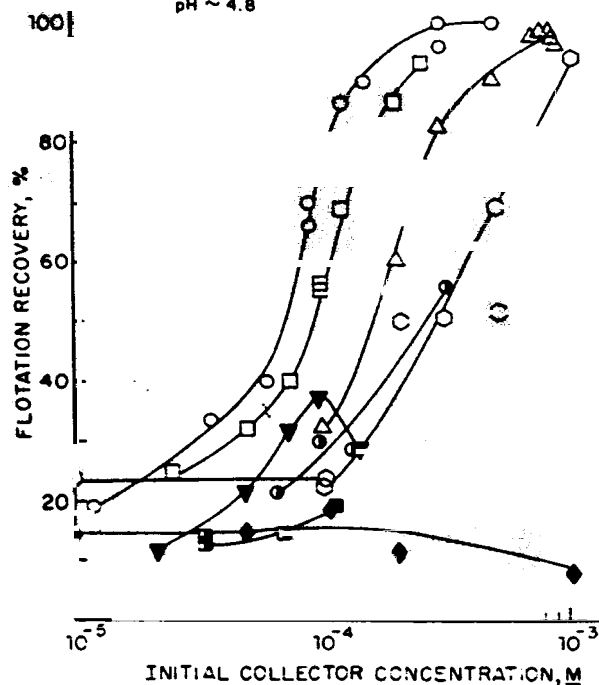◆ O-HYDROXY CYCLOHEXANONE OXIME
▼ O-HYDROXY BENZOPHENONE OXIME
       pH ~ 4.8

Fig. 3   Flotation of chrysocolla with salicylaldoxime and various substituted oximes[19]

benzene ring and the slower kinetics of adsorption of OHBePO. Adsorption tests, however, snowed the adsorption of OHBePO on chrysocolla to be 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 OHBePO than that of SALO. Bubble size reduction observed during flotation may be the major factor in this case.

Substitution in R$_2$ 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 of the molecule owing to the increase in electron density on the phenolic oxygen caused by the nucleophilic substituents.[20] This can, however, increase the metal–ligand stability, as is generally observed.[3] The effect of electron-releasing groups on the ring is, therefore, generally favourable for chelation. Again, the reduction in bubble size appears to be the major factor in regard to the lower collector efficiency. This appears to hold for the low collector efficiency observed in the case of OHNAO, although the solution concentrations studied were severely limited by its low solubility.

Surface chelation

It is now generally believed that the adsorption of xanthate on galena proceeds by the formation of a chelate compound PbX on the surface of galena — as opposed to PbX$_2$ in the bulk.[21] Thus, the first layer on galena is believed to be PbX (with a high

215

tenacity) over which layers of PbX_2 build up by 'sheer physical attachment'.[22]

Taggart and co-workers[23] proposed that surface compounds differ greatly in their properties from normally expected bulk compounds. This is because the lattice ions or atoms on the surface have only a part of their coordination sphere to contribute to the formation of a surface compound. In addition, steric effects assume a particularly significant role for reactions on surface of mineral as opposed to those in the bulk. It is therefore conceivable that the first-layer compound on mineral may be different from the compound formed by a reaction in the bulk. If it proves that the bulk compound is energetically more favourable (even after taking into account the fact that adsorption of collector is, in general, energetically favourable), either the collector molecules or the surface compound comprising the collector molecules and lattice ion or atom will be scaled-off or detached. Of course, contribution to this detachment could also come from physical factors.

It is not known whether there is a direct relationship between surface and bulk compounds. In many studies a 1:1 surface

chelate has been tacitly assumed with little experimental evidence to support the assumption. Often elaborate structures for surface chelates have been proposed[24,25] (two examples are shown in Fig. 4).

The importance of distinguishing between surface and bulk chelates and quantitatively determining them in the same system under flotation conditions was clearly shown by Nagaraj and Somasundaran.[19,26,27] Surface chelate was favoured under certain conditions and these conditions coincided with those in which flotation of tenorite was obtained with SALO (Fig. 5). The bulk chelate formed under a wide range of conditions and this chelate was ineffective in causing flotation when dispersed in the bulk aqueous phase. This chelate, however, could aid flotation when it is still attached to the first layer on the mineral, as for thiol collectors on sulphides. Chander and Fuerstenau[28] discussed the roles of surface reaction and bulk reaction in the system chalcocite–DTP. Ananathapadmanabhan and Somasundaran,[29] based on detailed calculations of relevant mineral–collector equilibria, have clearly shown that much of the flotation results in the literature can be explained on the basis of surface reactions or precipitation (as opposed to bulk reaction or precipitation).

The influence of bulk chelation as opposed to surface chelation has not been taken into consideration in the past for most systems, even when the bulk chelation is very pronounced. For minerals that have finite solubility (or speciation) in water, bulk chelation (or precipitation) is inevitable if the kinetics of metal chelation (or other complex formation) are reasonably rapid. Any collector associated with this chelate can be considered essentially wasted in flotation systems.

Selective flocculation

The use of chelating agents for selective flocculation and dispersion has been clearly illustrated by several
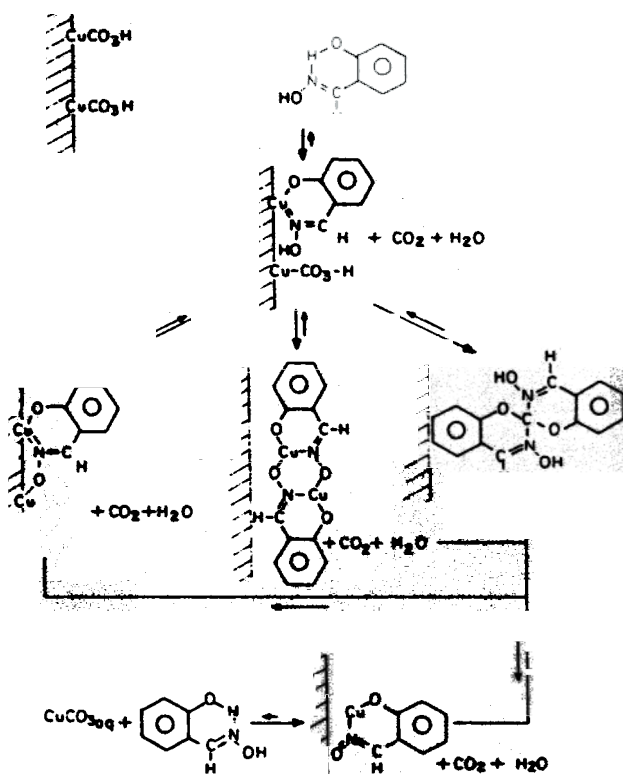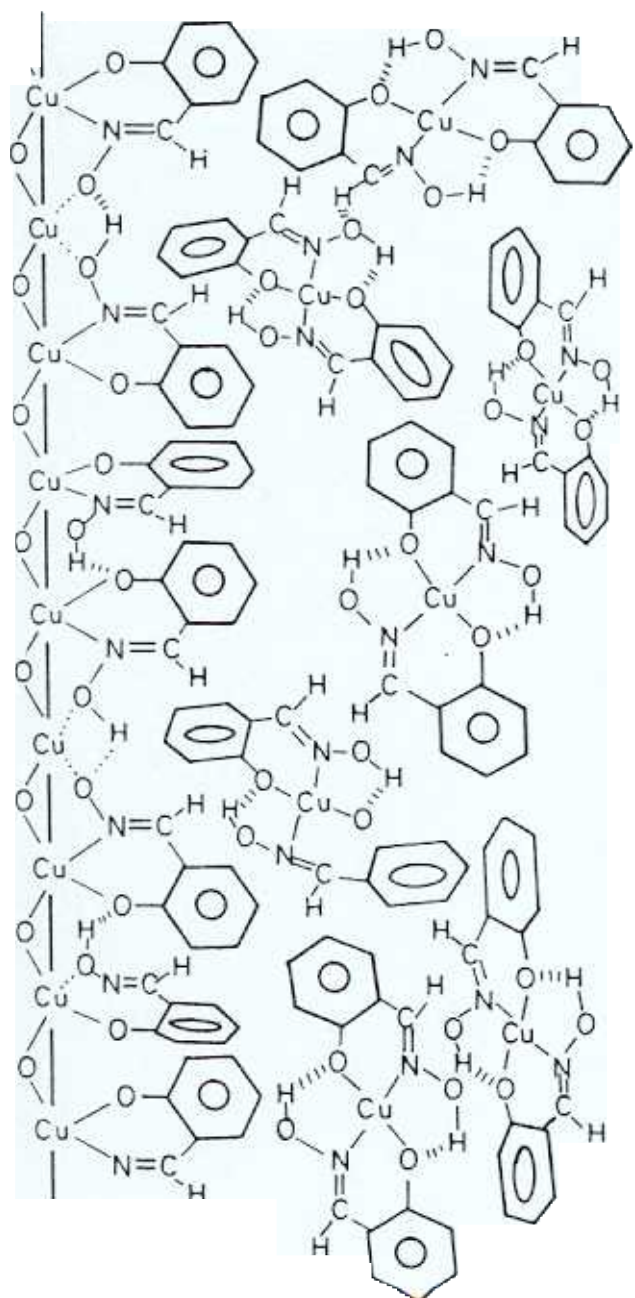
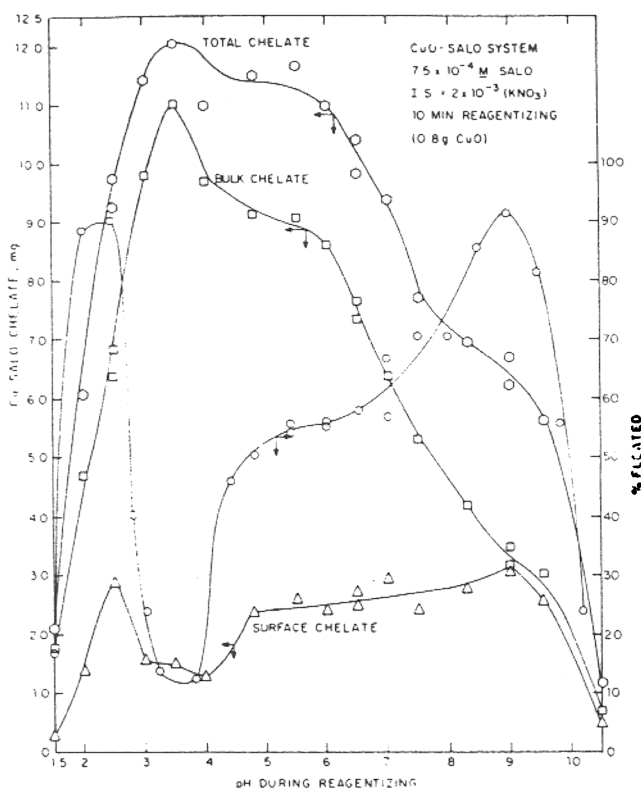Fig. 4 Schematic illustrations ((a)(left)[25] and (b) (above)[24]) of surface chelations

216

Fig. 5 Correlation of bulk and surface chelation of salicylaldoxime with tenorite and its species with flotation in tenorite-salicylaldoxime system[19]

Table 7 Examples of chelating agents as collectors

Reagents	Minerals
O-O type	
Cupferron	Cassiterite, uraninite, hematite
Salicylaldehyde	Cassiterite
α-Nitroso β-naphthol	Cobaltite
Acetylacetone	Malachite, chrysocolla
Alkylhydroxamic acid (IM50)	Chrysocolla, hematite and minerals containing Ti, Y, La, Nb, Sn and W
Phosphonic acids	Cassiterite
N-O type	
β-Hydroxy oximes	Cu oxide minerals
α-Hydroxy oximes	Cu oxide minerals
8-Hydroxyquinoline	Cerussite, pyrochlore, chrysocolla
N-N type	
Diphenylguanidine	Cu minerals
Dimethylglyoxime	Ni minerals
Benzotriazole	Cu minerals
S-S type	
Xanthates	
Dithiophosphates	All sulphide minerals
Dithiocarbamates	
N-S type	
Mercaptobenzothiazole	Sulphide and tarnished sulphides
Dithizone	Sulphides
S-O type	
N-benzoyl O-alkyl thionocarbamate	Sulphides

investigators.[ ] [ ] In some of these works chelating groups were incorporated into a polymeric-type molecule, which acted as selective flocculants. For example, Sresty and Somasundaran[32,37] observed hydroxypropyl cellulose xanthate containing an active thiol group to produce good flocculation of chalcopyrite with little effect on quartz (Fig. 6).
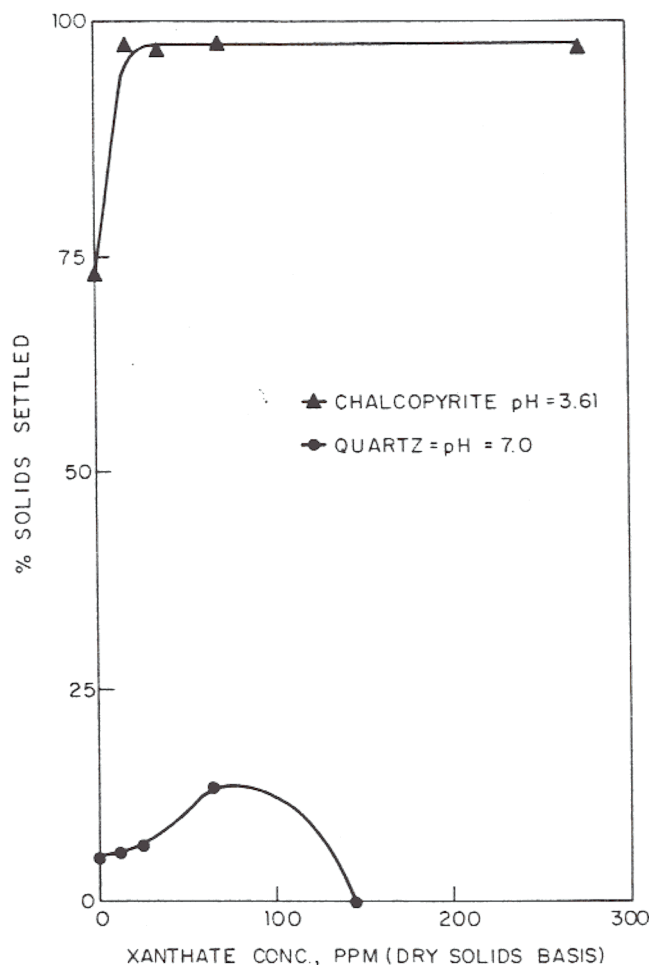

Fig. 6 Flocculation of chalcopyrite and quartz fines in terms of per cent solids settled in 45 s as a function of hydroxypropylcellulose xanthate (reagentizing time, 30 s)[37]

Tests with synthetic mixtures of these minerals showed both grade and recovery of chalcopyrite in the sediment portion to improve with increase in the concentration of the above polymer, but at very high dosages entrapment of the quartz by the bulky chalcopyrite flocs caused a decrease in the grade. This problem can, however, be overcome easily by cleaning the product by redispersion followed by settling.

Applications of chelating agents

Even though the relative proportion of chelating-type reagents among the industrial non-thio collectors is not significant, the actual number of chelating agents that have been tested successfully as collectors, depressants and flocculants for various mineral systems, at least on a laboratory scale, is large (Tables 7, 8 and 9). It is evident that the actual use of these types of reagents in the processing of minerals is likely to undergo a significant rise in the coming decades.

217

Table 8 Examples of chelating agents as depressants

Reagent	Mineral
Tartaric acid	
Gallic acid	
Alizarin red S	
Starch xanthates	
Cellulose xanthates	

Table 9 Polymers containing chelating groups

Reagents	Application
Starch xanthates	
Cellulose xanthates	Selective flocculation and depression of sulphides
Poly (4- and 5-acrylamido salyclic acids)	Cation-exchange polymer for Fe^{3+}, Cu^{2+}, Cr^{3+} and UO_2^{2+}
Resin containing hydroxy oximes group	,, ,, ,,
Polyhydroxamic acids	,, ,, ,,

Concluding remarks

It is clear that although chelating agents can be used effectively for the flotation of ores, they do not possess absolute specificity towards mineral species and it is only the judicious choice of the chelating agents and conditions for selective separation that will make their use possible for the beneficiation of many problematic ores. In this regard a full understanding of the basic mechanisms involved in their chemical interaction with mineral species in the bulk and on the surface becomes essential, even though those in the interfacial region might be understood accurately only by use of new experimental approaches that will permit direct probing of this region.

The role of surface chelation versus bulk chelation has to be taken into account in the development of any mechanism for it to be of significant use in flotation.

Also, more importantly, the role of surface chemical alterations due to either change in oxidation state of surface species or precipitation of various dissolved mineral species will have to be considered for application of the above information in actual mineral processing systems.

Acknowledgement

References

1. Dwyer F. P. and Mellor D. P. eds. *Chelating agents and metal chelates* (New York: Academic Press, 1964), 530 p.
2. Chaberek S. and Martell A. E. *Organic sequestering agents* (New York: Wiley, 1959).
3. Martell A. E. and Calvin M. *Chemistry of the metal chelate compounds* (Englewood Cliffs, N.J.: Prentice Hall, 1952).
4. Perrin D. D. *Organic complexing reagents* (New York: Wiley, 1964).
5. Pearson R. A. *J. Am. chem. Soc.*, 85, 1963, 3533; *J. Am. chem. Soc.*, 89, 1967, 103; *J. chem. Educ.*, 45, 1968, 581; 643.
6. Kettle S. F. A. *Co-ordination compounds* (New York: Appleton-Century-Crofts, 1969), 220 p.
7. Glembotskii A. V. Theoretical principles of forecasting and modifying collector properties. *Tsvet. Metally, Mosk.*, 50, no. 9 1977, 61-4. (Russian text); *Tsvet. Metally, N.Y.*, 18, no. 9 1977, 68-72.
8. Fleming I. *Frontier orbitals and organic chemical reactions* (London: Wiley, 1976), 258 p.
9. Cotton F. A. and Wilkinson G. *Advanced inorganic chemistry* (London: Interscience, 1966).
10. Orgel L. E. *An introduction to transition metal chemistry* (London: Wiley, 1966).

11. Zolotov Y. A. *Extraction of chelate compounds* (Ann Arbor: Humphrey Science, 1970).
12. Wang T. T. *J. Central-South Inst. Min. Metall.*, 4, no. 12 1980, 7-14. (Chinese text)
13. Bogdanov O. S. *et al.* Reagents chemisorption on minerals as a process of formation of surface compounds with a coordination bond. In *Proceedings of the 12th international mineral processing congress, 1977* (São Paulo, Brazil: D.N.P.M., M.M.E., 1982), vol. 2, 280-303.
14. Morrison R. T. and Boyd R. N. *Organic chemistry* (Boston: Allyn and Bacon, 1972).
15. March J. *Advanced organic chemistry: reactions, mechanisms and structure* (New York: McGraw-Hill, 1968).
16. Millar I. T. and Springall H. D. *Sidgwick's organic chemistry of nitrogen, 3rd edn* (Oxford: Clarenden Press, 1966).
17. Burger K. *Organic reagents in metal analysis* (New York: Pergamon, 1973).
18. Burger K. and Egyed I. J. Some theoretical and practical problems in the use of organic reagents in chemical analysis, V. *J. inorg. nucl. Chem.*, 27, 1965, 2361-70.
19. Nagaraj D. R. and Somasundaran P. Chelating agents as collectors in flotation: oximes–copper minerals sytems. *Min. Engng, N.Y.*, 33, Sept. 1981, 1351-7.
20. Patel R. P. and Patel R. D. Proton ligand stability constants of some ortho-hydroxy phenones and their oximes. *J. inorg. nucl. Chem.*, 32, 1970, 2591-600.
21. Granville A. Finkelstein N. P. and Allison S. A. Review of reactions in the flotation system galena–xanthate–oxygen. *Trans. Instn Min. Metall. (Sect. C: Mineral Process. Extr. Metall.)*, 81, 1972, C1-30.
22. Rao S. R. *Xanthates and related compounds* (New York: Marcel Dekker, 1971).
23. Taggart A. F. Taylor T. C. and Ince C. R. Experiments with flotation reagents. *Trans. Am. Inst. Min. Engrs*, 87, 1930, 285-368.
24. Cecile J. L. Utilisation de réactifs en flotation. Doctoral thesis, Université Orleans, France, 1978.
25. Nagaraj D. R. Chelating agents as flotaids: hydroximes–copper mineral systems. Doctoral dissertation, Columbia University, 1979.
26. Nagaraj D. R. and Somasundaran P. Chelating agents as flotaids: LIX®-copper minerals systems. *Recent Developments in Separation Science*, 5, 1979, 81-93.
27. Nagaraj D. R. and Somasundaran P. Commercial chelating extractants as collectors: flotation of copper minerals using "LIX" reagents. *Trans. Am. Inst. Min. Engrs*, 266, 1979, 1892-7.
28. Chander S. and Fuerstenau D. W. On the floatability of sulfide minerals with thiol collectors: the chalcocite/diethyldithiophosphate system. In *Proceedings 11th international mineral processing congress, Cagliari, 1975* (Cagliari: Istituto di Arte Mineraria, 1975), 583-604.
29. Ananthapadmanabhan K. P. and Somasundaran P. Chemical equilibira in hydrolyzable surfactant solutions and their role in flotation. Paper presented to 112th AIME annual meeting, Atlanta, March 1983.
30. Kitchener J. A. Principles of action of polymeric flocculants. *Br. Polymer J.*, 4, 1972, 217-29.
31. Somasundaran P. Selective flocculation of fines. In *The physical chemistry of mineral–reagent interactions in sulfide flotation: proceedings of symposium, April 6-7 1978* Richardson P. E. Hyde G. R. and Ojalvo M. S. comps. *Inform. Circ. U.S. Bur. Mines* 8818, 1980, 150-67.
32. Sresty G. C. Raja A. and Somasundaran P. Selective flocculation of mineral slimes using polymers. *Recent Developments in Separation Science*, 4, 1978, 93-105.
33. Somasundaran P. Principles of flocculation, dispersion and selective flocculation. In *Fine particles processing* Somasundaran P. ed. (New York: AIME, 1980), vol. 2, 947-76.
34. Attia Y. A. and Fuerstenau D. W. Principles of separation of ore minerals by selective flocculation. In *Recent Developments in Separation Science*, 4, 1978, 51-69.
35. Attia Y. A. I. and Kitchener J. A. Development of complexing polymers for selective flocculation of copper minerals. Reference 28, 1233-48.
36. Baudet G. *et al.* Synthèse et caractérisation de flocculants sélectifs à base de dérivés xanthés de la cellulose et de l'amylose. *Industrie minér.-minéralurgie* 1-78, 1978, 19-35.
37. Sresty G. C. and Somasundaran P. Selective flocculation of synthetic mineral mixtures using modified polymers. *Int. J. Mineral Process.*, 6, 1980, 303-20.
38. Clauss C. R. A. Appleton E. A. and Vink J. J. Selective flocculation of cassiterite in mixtures with quartz using a modified polyacrylamide flocculant. *Int. J. Mineral Process.*, 3, 1976, 27-34.
39. Attia Y. A. Synthesis of PAMG chelating polymers for the selective flocculation of copper minerals. *Int. J. Mineral Process.*, 4, 1977, 191-208.
40. Rinelli G. and Marabini A. M. A new reagent system for the selective flocculation of rutile. In *Thirteenth international mineral processing congress, Warsaw, 1979* Laskowski J. ed. (Amsterdam, etc.: Elsevier, 1981), vol. 1, 316-45.

218

41. Rinelli G. and Marabini A. M. Dispersing properties of tanning agents and possibilities of their use in flotation of fine minerals. Reference 33, 1012-33.

42. Drzymala J. and Laskowski J. Chelating compounds as flotation reagents. *Physico-chemical Problems of Mineral Processing*, 13, 1981, 39-64.

43. Barbery G. and Cecile J. C. Complexing reagents in flotation and selective flocculation: a review of possibilities and problems. Paper presented to CIM annual meeting, Winnipeg, 1983.