

Development of Flotation Reagents with Chelating Functional Groups

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ABSTRACT

Recently in search for new methodology for flotation separation of complex ores, studies have been directed to develop reagents with chelating functional groups. Some of the chelating reagents have been successfully utilised as flotoids. This paper presents the design, selectivity and development of chelating type flotation reagents. The chemistry and applications of chelating type reagents as flotation collector have been discussed. Some salient results based on author's own work showing the efficacy of chelating type reagents for flotation of complex Indian ores are presented. The general mechanism of chelating reagent-mineral interaction is highlighted.

Key Words : Flotation reagents, Chelating agents, Complex ores, Design and selectivity, Indian ores,

INTRODUCTION

Froth flotation is one of the most important processes in the field of mineral processing, which has contributed significantly to the vast expansion of raw materials industry. The process utilizes a group of chemical reagents known as collector, frother, depressant and dispersant. Flotation collectors are the surfactants, which are used to impart hydrophobicity by their selective adsorption on the mineral surface. This in turn facilitates the attachment of air bubbles to mineral particles for flotation. The success of flotation process largely depends on the proper control of the solid-liquid-gas interfaces and the judicious choice of the reagents combination. With the fast depletion of rich and easy to process ores, the exploitation of lean grade, complex and finely disseminated ore deposits is essential. There is an urgent need to develop new reagents for separating the valuable mineral from the associated gangue minerals having similar surface properties at relatively fine size ranges. In this context reagents with chelating functional groups which strongly adsorb on the mineral surface, offer lot of promise. A number of successful attempts have been made for developing tailor made chelating type flotation collectors for the specific application^[1-10]. In this paper an attempt has been made to present an

overview on chemistry and applications of chelating type flotation collectors in treating ores which are difficult to process using the conventional reagents due to the complexities in surface properties of minerals. Typical results showing the efficiency of chelating type reagents for the flotation of Indian ores are presented.

CHELATING AGENTS

Chelating agents are a special class of compounds which are having atleast two donor atoms to form complex (characterized by a ring structure) with a metal ion. The donor atoms are normally oxygen, sulphur and nitrogen. The co-ordinating species providing these donor atoms is known as 'ligand' while the resulting complex is called 'chelate'. In order to form complex with metal, the chelating agents should have suitable functional groups. The situation of the functional group should allow the formation of a ring structure with a metal as the closing member.

The important donor atoms and the functional groups are shown in Table 1^[6].

Table 1 : Important donor atoms and chelating functional groups ^[6]

Major donor atoms	Functional Groups	
	Acidic (lose a proton)	Basic (donate electron pair)
N		$\begin{array}{c} \text{H} \\ \\ -\text{N} \\ \\ \text{H} \end{array}$ $> \text{N}-\text{H}$ $> \text{N}-$
O	$\begin{array}{c} \text{O} \\ // \\ -\text{C} \\ \backslash \\ \text{O}-\text{H} \end{array}$ $-\text{OH}$ (enol or phenol) $\begin{array}{c} \text{O} \\ \\ -\text{P} \\ \backslash \\ \text{OH} \end{array}$	$-\text{OH}$ (alcohols)
S	$-\text{SH}$	$-\text{S}-\text{R}$

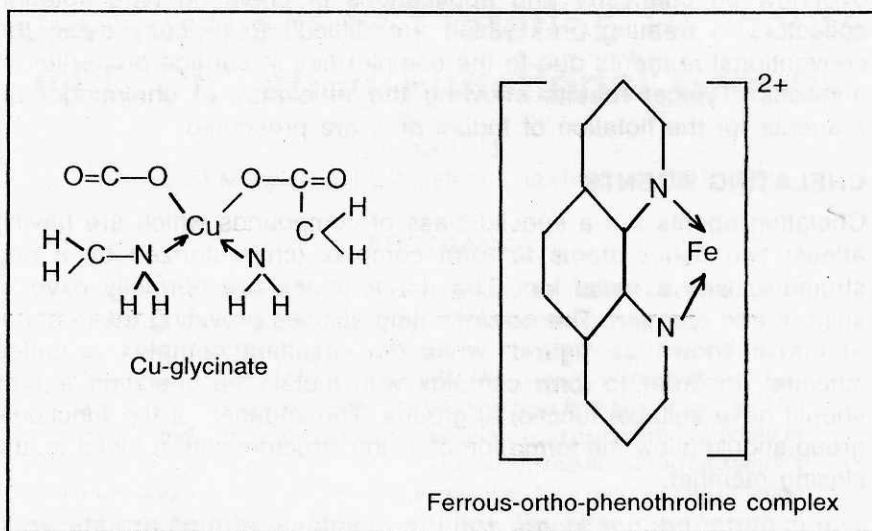


Fig. 1 : Some examples of chelates

The chelating agents can be classified in several ways, but a convenient classification is the one based on donor atoms eg. O-O, N-N, S-S, N-O type etc. Fig. 1 shows some examples of chelates.

DESIGN AND SELECTIVITY OF FLOTATION REAGENTS WITH CHELATING FUNCTIONAL GROUPS

To function as a flotation collector the chelating functional group must be a part of a sufficiently long hydrocarbon chain so as to impart hydrophobicity to the mineral on adsorption. The resulting chelate should preferably be neutral complex, because neutral complexes are usually insoluble in water and therefore promote hydrophobicity. Although this is not a sufficient condition. Another important requirement for the chelating type collector is that the chelate formed, preferably at the mineral/water interface, must be bound to the mineral sufficiently strongly to resist scaling off.^[11]

Again for a depressant the chelates should preferably be charged and very hydrophilic in nature. However, in case of polymeric depressant with sufficient number of hydrophilic groups on the backbone, this requirement is not stringent^[12-14].

Thus in a broad sense the design of chelating type collector mainly involves :

- Selection of the functional group, and
- Design of the molecular structure for the specific separation to be achieved.

The selection of appropriate functional group is one of the most important factors in designing a selective reagent. So far the selection of functional groups has been either based on trial-and error method or the knowledge available from analytical chemistry literature. But these approaches have their own limitations.

There are different types of chelating functional groups and almost all of them form complexes with almost all of the transition and many non-transition metals. Thus for mineral processing applications absolute selectivity does not exist, it is varying degree of selectivity which is of interest. Selectivity of the chelating reagent towards a metal atom is closely related to the stability of metal complexes, which is expressed in terms of stability constant 'K'. The factors like nature of donor atoms, central metal atom, the pKa of the ligand, substituents, size and number of the rings influence the 'K' and hence the selectivity of the reagent^[12-14].

Marabini et al^[15] have developed a method for the selection of chelating type flotoids based on theoretical calculation of stability constants. According to them a given ligand (L) will function as a selective flotation collector for a mineral having cation M1 against another that contains M2 provided the stability constant satisfies the following :

$$pK'_{M1L} \geq 6, \text{ and}$$

$$pK'_{M1L} - pK'_{M2L} \geq 5$$

The first criterion characterises the absolute chelating power towards the cation M1 while the second one defines the difference in the relative chelating power of a ligand vis-a-vis two cations M1 and M2. This has been validated for several mineral-reagent systems. But this method suffers from the limitation that it can not explain the differences in the response of two minerals containing the same cation to a particular ligand. Attempts are being made to use molecular orbital approach and the concept of crystal structure specificity for developing flotation collectors^[4,12,16-17].

In the Molecular Orbital Theory (MOT), the molecular orbitals (MOs) of a complex are considered to be determined from the overlap of original atomic orbitals which gives rise to a two new MOs-bonding and antibonding. Wang^[17] has carried out calculation on the determination

of MOT parameters for commonly used flotation reagents using the concept of linear combination of atomic orbitals (LACO) and the Hückel theory. MOT is considered quite promising for studying the interaction between minerals and the chelating agents and hence in the development of suitable flotation reagents. But considerable work is needed to use this as a routine practical tool for development of flotation reagents.

CHELATING TYPE REAGENTS IN FLOTATION OF ORES AND MINERALS

In the recent past extensive studies have been carried out by various researchers to develop chelating type floatants and now some of these are being marketed for commercial use. The various steps involved in the development of flotation reagent upto the commercialisation are schematically shown in Fig. 2^[16].

Some of the chelating type flotation reagents which have been successfully used for the beneficiation of natural ores include :

- Alkyl hydroxamate for tungsten ore, rare earth ores, mixed sulphide-oxide copper ores, iron ores etc.;
- Alkyl derivatives of mercapto benzothiazole and amino phenol for oxidised lead-zinc ore;
- Dodecyl mercaptans, alkyl dithiocarbamates and dithio phosphates for sulphide ores;
- Styrene phosphonic acid for tin and tungsten ores, etc.

The applications of various chelating type reagents used as collector and depressant for the flotation of low grade ores and minerals are summarised in Table 2 and 3 respectively. Figs. 3 and 4 present some salient results showing the efficacy of alkyl hydroxamate and N-alkyl phosphonic acid as collectors for the flotation of mixed sulphide-oxide copper ore from Malankhand and wolframite from Degana, India respectively^[13,14,18].

MECHANISM OF MINERAL - REAGENT INTERACTION

Like conventional reagents the adsorption phenomena occurring at the solid-liquid interface is primarily responsible for the performance of chelating type surfactants as flotation collector. IR and NMR studies carried out for several mineral-chelating reagent systems have confirmed the formation of chelate bond with the metal ion on the surface ^[1,19-20].

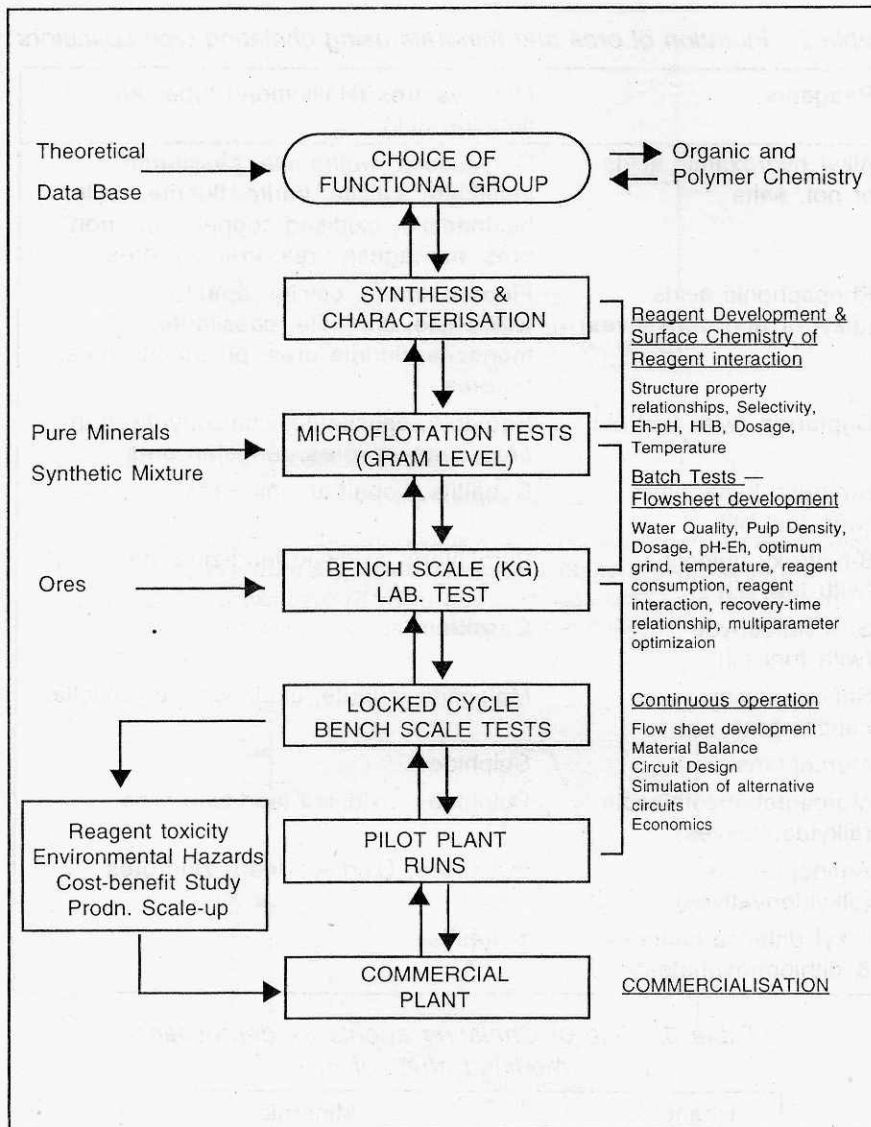


Fig. 2 : Schematic diagram showing the various steps involved in the development of a flotation reagent^[16].

Table 2 : Flotation of ores and minerals using chelating type collectors

Reagents	Minerals/ores (Hallimond tube/Lab. flotation cell)
Alkyl hydroxamic acids or pot. salts	Chrysocolla, wolframite, cassiterite, malachite, calcite, barite, fluorite, rutile, bastnaesite; oxidised copper ores, iron ores, manganese ores, uranium ores
Phosphonic acids (alkyl or aryl derivatives)	Fluorite, barite, calcite, apatite, wolframite, chromite, cassiterite, monazite; fluorite ores, phosphate ores, tin ores
Cupferron (with fuel oil)	Hematite, cassiterite, chalcopryrite, iron ores, uranium ores, tungsten ores
α -nitroso- β -naphthol (with fuel oil)	Cobaltite, cobalt-arsenic ores
8-hydroxy quinoline (with fuel oil)	Pyrochlore; oxidised lead-zinc ores
Salicylaldehyde (with fuel oil)	Cassiterite
Salicyladoxime copper ores	Malachite, cuprite, chalcocite, chrysocolla,
Mercaptans	Sulphides
Mercaptobenzothiazole (alkyl derivatives)	Sulphides, oxidised lead-zinc ores
Aminophenols (alkyl derivatives)	Sulphides, Oxidised lead- zinc ores
Alkyl dithiocarbamates & dithiophosphates	Sulphides

Table 3 : Use of Chelating agents as depressants (modified after ref. 6)

Reagents	Minerals
Tartric acid	Fluorite
Gallic acid	Fluorite
Alizarin red	Siliceous gangue
Starch xanthates	Sulphides
Thioglycerol	Sulphides
Sodium thioglycollate	Copper sulphide

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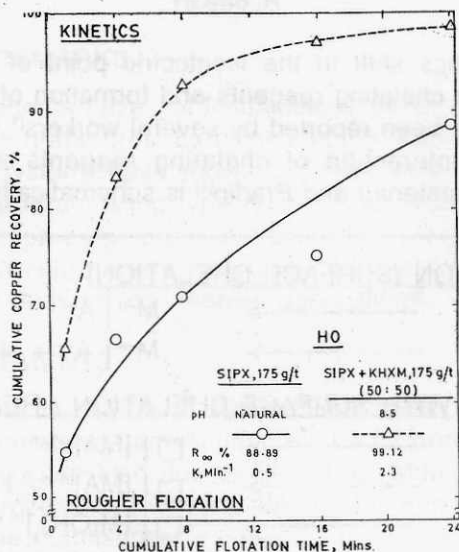


Fig. 3 : Improvement of flotation kinetics and recovery from oxidised copper sulphide ore from Malanjkhand using a reagent combination of pot. octyl hydroxamate (KHXM) and sod. isopropyl xanthate (SIPX) against zanthate alone as the collector

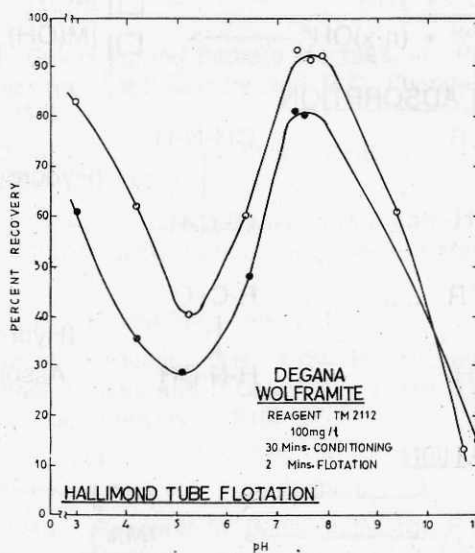


Fig. 4 : Flotation of Degana wolframite using N-dodecyl-bismethylene phosphonic acid collector

The characteristics shift in the isoelectric point of minerals due to chemisorption of chelating reagents and formation of metal chelate at the interface has been reported by several workers^[1, 20-21]. The general mechanism of interaction of chelating reagents with minerals as proposed by Fuerstenau and Pradip^[1] is schematically shown in Fig. 5

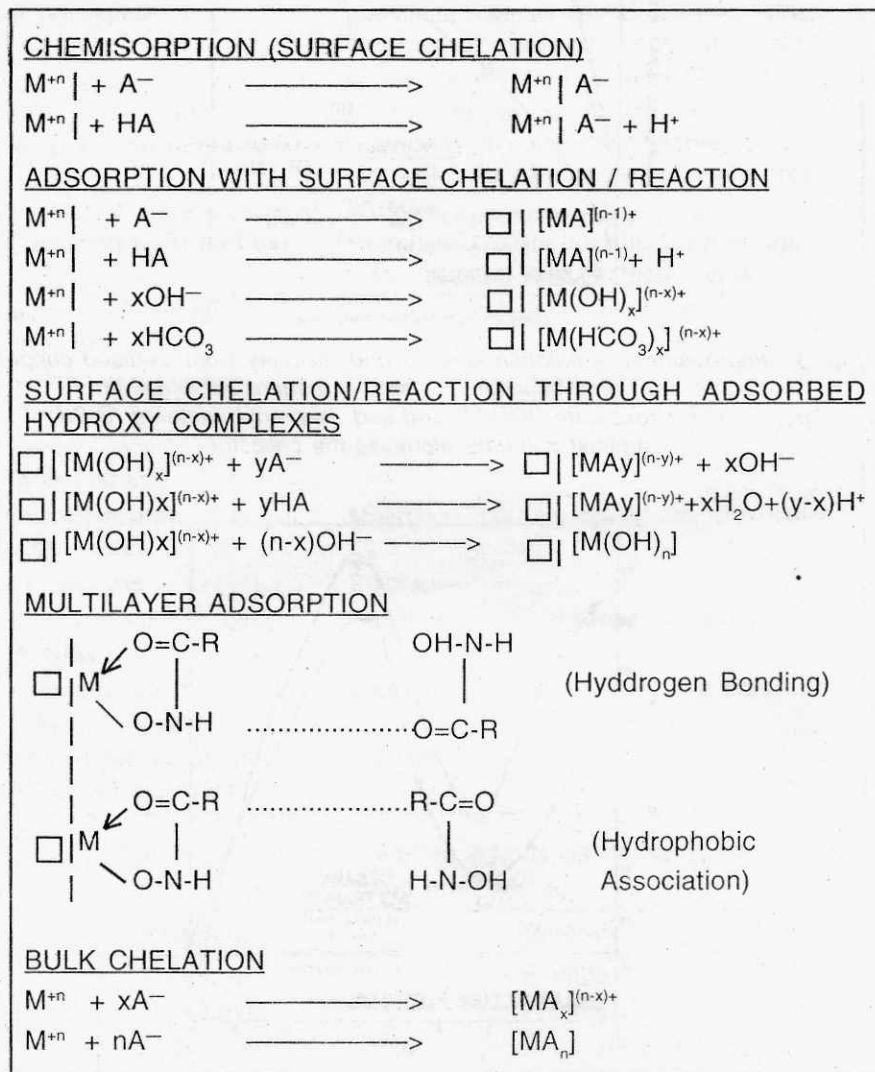


Fig 5 : Schematic representation of the mechanism of interaction of chelating reagents with mineral surfaces^[1].

CONCLUDING REMARKS

Conventional reagents have got limitations in treating the increasingly complex and lean grade ores. Extensive studies carried out on various mineral-reagent systems have shown that there exists the possibility to develop tailor made chelating type reagents as flotation collectors for such difficult to process ores. A rationale scientific approach is necessary to develop more selective, efficient and economical chelating type flotoids for commercial applications.

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