CHAPTER II

LITERATURE SURVEY
Chelating agents have received attention in the past four decades for their potential use as flotation collectors with high selectivity for minerals.

In the field of flotation, where selectivity is often a quality of paramount importance for the collector, various workers have attempted to apply their knowledge of specific organic analytical reagents to this purpose.

Vivian in 1927 concentrated cassiterite by using ammonium nitroso-phenyl hydroxylamine (cupferron), \( \text{C}_6\text{H}_5\text{NO} (= \text{NONH}_4) \). Holman in 1930 tested dimethyl-glyoxime for the flotation of nickel oxide minerals. Diphenylguanidine has been tried in flotation work by Taggart, Batheley, and Jaeger. Dewitt et al. have shown in a series of systematic experiments, that alpha-dioximes were generally selective collectors for nickel ores. Their data showed that salicylaldoxime is an effective reagent for the separation of chalcopyrite from other minerals, and heptaldoxime and octaldoxime as flotation reagents for the separation of sulphide, oxide and carbonate minerals of heavy metals from siliceous gangue material. Taurin, \( \text{NH}_2\text{(CH}_2)\text{SO}_3\text{H} \) has been proposed for the concentration of oxidized lead ores.
Diphenylthiocarbazone, a well known analytical reagent was suggested as a collector by Persson who has shown that diphenyl urea (carbanilid) has no collecting properties, while thiocarbanilic, produced through replacement of oxygen atom by a sulphur atom in the carbonyl group was an excellent collector. Gutzeit used o-oxyquinoline, phenyl dithio hydantoic acid, phenyl dithiocarbamide and similar chemicals in laboratory flotation tests.

Christman presented the derivatives of glycolic acids, such as phenylglycine (C₆H₅ NH CH₂COOH) as collectors for oxide ores, which form inner complexes with metallic ions. Mineralia A.G. in Fichtelberg, Germany, has been floating hematite (Fe₂O₃) on an industrial scale (3 tons per hour) by using a triphenyl methane dye, brilliant acid green together with tar oil as collector in an acid circuit. Luat and Dewitt in 1949 studied on flotation of chrysocolla with alkyl substituted malachite green as collector. They concluded that this dye can act as a collector for chrysocolla in synthetic silica-chrysocolla mixture and the octyl substituted malachite green is more effective than the lower substituted homologues.
In their investigation of alizarin dyes in soap flotation of cassiterite and fluorite Schuman and Prakash\(^{(12)}\) studied chelation in the process. In 1953 Hines\(^{(13)}\) patented a differential froth flotation process by using urea and its derivatives as collectors and in 1959 he reported the use of guanidine compounds and derivatives as collectors in flotation of sphalerite\(^{(14)}\). He concluded that diphenyl guanidine gives better recovery of the sphalerite and marmatite with higher grade concentrate than the grade obtained with potassium ethyl xanthate. From their conclusions diphenyl and dibutyl derivatives of both urea and guanidine are excellent flotation collectors.

In 1964 Daelleubach and Tiemann\(^{(15)}\) described the prevention of quartz by chelation of activating ions with the tetra-sodium salt of EDTA in oleic acid flotation of hematite. Gorlovskii\(^{(16)}\) et al. have conducted tests on the use of water soluble salts of hydroxamic acids from the methyl esters of synthetic carboxylic acids fraction C\(_7\)-C\(_9\) to be used as the collectors. They proposed a new complexing collector iM-50, in which the active part is the alkyl hydroxamic acid, which makes it possible to selectively float non-sulphide minerals, and technology was developed for niobium-containing ores with the reagent iM-50 used as collector.
Feterson et al. \(^{(17)}\) floated pure chrysocolla with chelating agents, ethylene diamine, hexamethylene-tetramine, dimethylglyoxime, benzoin-oxime and octyl-hydroxamate, which form insoluble complexes with copper at ambient temperature and complete flotation was obtained with potassium octyl hydroxamate as collector at pH 6.0. Flotation response was enhanced with increased temperature when low additions of hydroxamate involved.

In 1967 Fuerstenau et al. \(^{(18)}\) floated pure goethite and natural iron ores selectively by using potassium octyl hydroxamate as collector and in 1970 Fuerstenau et al. \(^{(19)}\) carried out experiments on hematite with octyl-hydroxamate and oleate as collectors to determine the mechanism of collector adsorption and also to establish the role of conditioning time and temperature in this system, and concluded that the presence of hydroxy complexes of iron are apparently necessary for chemisorption of collector to occur, and it appears as if extended conditioning times and elevated temperature promote greater dissolution of the mineral and hence greater concentrations of hydroxy complexes. They could not obtain satisfactory concentrate with fatty acid under the same conditions as with hydroxamate.
Rinelli et al.\(^{(20)}\) worked to develop specific collectors for the most troublesome selective floatations, with combinations of insoluble chelate forming compounds and fuel oil; a new way to flotation. They described that the chelate compound is the specific conditioning agent, while the fuel oil imparts to the system the collecting power. They studied hematite, niccolite, cobaltite and pyrochlore using for each of them the most suitable one, viz.: Cupferron, diethylglyoxime, \(\alpha\)-nitroso-\(\beta\)-naphtol, \(\alpha\)-hydroxyquinoline respectively, and demonstrated that under proper conditions the response of each mineral to flotation is quite complete, whereas no flotation occurs without the chelate compound.

In 1975 Marabini\(^{(21)}\) studied the action of salicylaldehyde, a new collector for cassiterite flotation, was related to the formation of an inner complex salt with the Sn\(^{4+}\) ion, and confirmed the technical feasibility of the process with an oil frother. Rinelli et al.\(^{(22)}\) studied the flotation of cassiterite with salicylaldehyde as collector. Their infrared and nuclear magnetic resonance studies clearly show that salicylaldehyde can form a chelate compound in bulk and at the surface of the mineral. In 1978 Marabini\(^{(23)}\) studied the adsorption of salicylaldehyde on cassiterite to investigate the way of adsorption and the main properties that differentiate this reagent from common collectors.
Nagraj et al. (24) studied the use of a class of chelating agents having active nitrogen and oxygen chelating atoms, and which can form insoluble chelates with copper, as reagents for the recovery of copper from the copper-bearing materials by froth flotation and like techniques. The same authors (25) studied the chelating agents that can form insoluble hydrophobic chelates on the surface of the minerals and concluded that they could be potential collectors for selective flotation of minerals. In their study it was observed that LIX series of reagents, which are highly selective commercial copper chelating solvent extractants, function as collectors for the oxidized copper minerals. Flotation of cuprite and chrysocolla has been carried out with LIX 65N and LIX 65N (26).

Nagraj and Somasundaran (27) studied the collecting properties of several water-soluble chelating agents belonging to the class of aromatic hydroximes and having a gradual structural variation and a basic study on salicylaldoxime-tenorite system. Their results have demonstrated that all of the hydroximes studied, had comparable collector properties and in all cases the oxime was found to be partitioned between the mineral surface and the copper in the bulk aqueous phase in the form of bulk copper chelate. They concluded that
the substitution of CH$_3$ for increasing the chain length, increases the collector efficiency which is decreased by the substitution of benzene rings.

Lenormand et al.(28) studied the flotation of malachite with potassium octylhydroxamate as a collector, and concluded that maximum floatability was obtained between pH 6 and 10 region. Their infra-red and adsorption measurements indicated that in that pH range octylhydroxamate chemisorbs on malachite surface and suggested chemisorption mechanism.

Oxine as collector in mineral flotation

Oxine, (8-hydroxyquinoline) a well known organic analytical reagent, which forms insoluble chelate compounds with metal ions, is a good collector in the flotation of various minerals. There were some reports on this compound as a collector in mineral flotation.

In 1942 Erlenmeyer,(29) et al conducted flotation experiments on synthetic two component mixtures, ZnCO$_3$-SiO$_2$ by using 8-hydroxyquinoline as collector, and a drop of terpineol. They found that no separation was obtained without oxine, but in its presence most of the zinc ions found in the foam, which is in agreement with the known fact that zinc ion forms an insoluble chelate with 8-hydroxyquinoline. In similar way PbCO$_3$-SiO$_2$ also
was separated only in weakly acidic medium. They have separated BaCO₃-ZnCO₃ mixture based on the fact that barium ions do not form insoluble chelate compound with oxine. The same workers extended their study to float Smithsonite (ZnCO₃), cerussite (PbCO₃) and with copper oxide, showed that either 8-hydroxyquinoline or 4-hydroxybenzothiazole can collect such compounds in foam. Their flotation experiments with dolomite and MgNH₄PO₄ showed that 8-hydroxyquinoline collects the mineral in foam while 4-hydroxybenzothiazole does not, because the latter does not form an insoluble compound with magnesium. Similar results were obtained with rutile, wolframite and quartz.

Erlenmeyer et al. studied the flotation behaviour of iron oxide hydrates towards 8-hydroxyquinoline as collector. Different samples were studied with regard to time and temperature of drying.

Steiger and Bayamgil studied the flotation of sulphides such as zincblende, galena, antimonite, pyrite and arsenopyrite with 8-hydroxyquinoline as collector, with the addition of Na₂CO₃, NaOH, water glass, HCl and with an artificial gangue of quartz and calcite, and the separation could be made in each case, the degree of completeness depending on the electrolytes added.

The flotation experiments of Erlenmeyer et al.
with different samples of magnesite, dolomite and brucite versus \( \beta \)-hydroxyquinoline as a collector are used that separation is more complete as the water content of the mineral decreases, calcite and argonite (presumably anhydrous) gave approximately equal separation. Theilheimer and Erlen Meyer \(^\text{(74)}\) studies revealed that the distribution of hydrated \( \text{Fe}_2\text{O}_3 \) between the foam and sediment in the presence of oxine as collector was strongly influenced by addition of metallic salts. Erlen Meyer etal \(^\text{(35)}\) performed the flotation experiments with ferric oxide, ferric oxide hydrate, chromic oxide, chromic oxide hydrate, hematite and chromite with \( \beta \)-Hydroxyquinoline as a collector, and studied the effect of added salts of Cu, Mg, Zn, Fe, Ni, Mn, Ca, Co and Cr. But no definite reasons for this behaviour were evident. The possibility of metal ferrite formation on the surface was suggested, and this is followed by the formation of the mixed complex as \( 0 = \text{Fe-O-M-Oxine} \).

Bunge etal \(^\text{(36)}\) reported on the concentration by flotation process of Smithsonite \((\text{ZnCO}_3)\) ores from the Alice and Rex mines in Missouri with various conditioning reagents, such as natural and synthetic tannins, sulfonates, \( \beta \)-Hydroxyquinoline, malic acid, tartaric acid, and citric acid. Niobium minerals such as columbrite, pyrochlore and perovskite are separated from
finely ground ore, suspended as a pulp in water, by adding about 0.2 - 0.4 % of 8-Hydroxyquinoline by weight of ore, and aerating the pulp with agitation to produce a froth in which the minerals were collected. Last and Harrardson floated niobium ores effectively and economically by the addition of small amount of 0.05 - 0.5%, of 8-Hydroxyquinoline by weight of the ore and smaller amount of burner oils. They stated that before flotation with oxine it is advisable to upgrade the raw ore by flotation with fatty acid, calcite and apatite, then by flotation with sulfonated petroleum oils and a xanthate to remove sulphides and mica. In 1960 the same workers recovered the 8-Hydroxyquinoline from the products of mineral flotation by conversion to the insoluble quinolate of a heavy metal such as Cu, Ni, Co, Cr or Sb followed by the removal of the metal ion by electrolysis or precipitation as the sulphide to yield 8-hydroxyquinoline solution for the further use in mineral flotation.

Rinelli and Marabini reported the possibility to float zinc and lead oxide-sulphide ores with a collector system containing a chelating agent and fuel oil. They carried out the flotation tests on pure Smithsonite in a Hallimond tube cell with zircon, anthranilic acid, quinaldic acid, pyridine and 8-Hydroxyquinoline, which are capable of forming stable
chelates with zinc, and found that 8-hydroxyquinoline was selective among all the reagents required. Further experiments were then carried out in a laboratory cell. The results obtained showed that under suitable conditions both the minerals (Zn and Pb) can be floated with high selectivity.

K. Shigeru and U. Takeide \(^{(41-45)}\) studied the flotation of copper silicate mineral by activation with organic copper-avid reagents, such as alicylandoxine, 8-hydroxyquinoline and benzoin-\(\alpha\)-oxime, and subsequent flotation by using potassium acyl xanthate as the collector. Baldauf \(^{(44)}\) studied the flotation and depressant characteristics for organic chelating agents used in separation of fluorite, barite, calcite, siderite, quartz, pyrite, corundum, magnesite, and cassiterite.

**Cupferron as a collector in mineral flotation**

Cupferron, ammonium salt of \(n\)-nitroso-\(n\)-phenylhydroxylamine, a well known organic analytical reagent, was also used as collector in the flotation, by Vivian \(^{(1)}\) in 1927 in cassiterite flotation. There were some reports in U.S.S.R. on cupferron as collector in mineral flotation, cupferron combined with liquid soap and kerosine was used for the separation of sphene, titanomagnetite and ilmenite from aegirite in the flotation of feldspar-aegirite-nepheline tailings obtained in apatite flotation \(^{(45)}\)
Bogdanov et al. (46) studied the floatability of the apatite-nepheline ore of the Khabin deposit, with a series of organic compounds, forming insoluble complexes with titanium, as collectors, positive results were obtained with cupferron as a collector in weakly acidic medium. Cupferron in the presence of foam-forming agent, floated sphene, titanomagnetite and ilmenite. Flotation took place slowly and coarse particles remained in tails, kerosene and sulphate soap were added to increase the collecting action of cupferron, flotation took place best of all in the presence of oxalic acid at pH 6. The use of cupferron permitted the extraction of about 78% titanium from the collective concentrate.

Fvanovskii (47) studied the flotation of synthetic quartz-cassiterite by using cupferron and alizarin. Maximum extraction was obtained when cupferron and alizarin were used jointly, the pH was critical, an increase in acidity or alkalinity affects the concentrate. Marabini and Rinelli (48) reported the use of cupferron as collector in the presence of fuel oil in the flotation of pitchblende. The results obtained with pitchblende alone or with the synthetic mixtures, pitchblende-quartz and pitchblende-hematite, demonstrated that pitchblende can be selectively floated under suitable conditions.
Discussion and Conclusion:

It is apparent that the emphasis in all earlier investigations prior to 1970 was primarily on the study of flotation response with reference to parameters like pH, concentration etc. Studies of basic nature aimed at the extent of adsorption, nature of adsorbed species, effect of structural variations in a given class of collectors etc., have been very few (23, 27, 28) and such efforts have been taken up apparently in the last 10 to 15 years only.

It is also noted that the major part of the past work is concerned with non-sulphides, barring few exceptions (40). No past work on sulphides attempting to use chalates like cupferron, Oxine etc. appears to have been reported.

The purpose of the present study is to examine the flotation process in chalcopyrite - Oxine and chalcopyrite cupferron systems, since such studies have not been done in the past and have good prospects of successful flotation systems. Since chelating agents can be expected to combine selectively with different metal ions irrespective of the form of the compound in which they present, such systems may be of better potential use in the separation of sulphides by flotation. Since the problem of treatment of multisulphide ores is important with reference to several ore bodies, a basic study of sulphide minerals with chelating collectors is desirable.
REFERENCES

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(10) L.J. Christiansen: U.S. Pat. 11952907 (1/11/1928) to American Cyanamid Co.


