

Adsorption and Microflotation Studies with Pure Minerals
and an Arylhydroxamic Acid Collector

by

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Abstract

A study was conducted to understand the adsorption of *N*-hydrocinnamoyl-*N*-phenylhydroxylamine (HCNPHA) on the surfaces of various pure minerals: sphalerite, pyrite, galena, chalcopyrite and quartz. HCNPHA is a member of the *N*-arylhydroxamic acids that are good base metal mineral collectors. HCNPHA was selected because it was reported to give the most promising results as compared to other arylhydroxamic acids.

In this work, equilibrium studies were conducted at pH 9 and 10 using pure minerals, and some microflotation studies were also undertaken. All adsorption isotherms followed Langmuir model, however, Freundlich type was observed for quartz. As HCNPHA is a strong chelating agent, formation of monolayer by chemisorption appeared to be the most probable mechanism of adsorption on the base-metal sulphide minerals. Specific adsorption of HCNPHA on iron containing minerals namely, chalcopyrite and pyrite, was about three times that on galena and sphalerite, and specific adsorption on quartz was the lowest as it adsorbed only 5% in comparison to pyrite amongst the minerals studied. Comparing to pH 9, specific adsorption of HCNPHA on the minerals decreased at pH 10 and this might be due to hydroxylation of mineral sites because of higher hydroxide ion concentration. The complexation of HCNPHA with Fe^{3+} was used to develop a purple coloured complex that absorbs in the visible region with $\lambda_{\text{max}} = 500$ nm. A spectral colorimetric procedure based on this coloured complex was developed for the quantitative estimation of HCNPHA.

Microflotation studies were also conducted to understand the flotation response of various minerals to HCNPHA at different pH values. Sphalerite, galena and pyrite were floated at a pH range of 7 to 11. Optimum pH for sphalerite flotation was found to be 9. Sphalerite was floated

without the need for copper sulphate which is a very significant finding because xanthates are unable to float sphalerite without copper sulphate as they need insoluble copper xanthates to be formed on sphalerite surface. In the differential flotation of a lead-zinc ore, sphalerite is suppressed in the lead rougher stage using the depressants such as sodium cyanide, zinc sulphate and sodium metabisulphite (MBS). In order to study the behaviour of HCNPHA in the presence of these reagents, microflotation of sphalerite was studied by adding each of these reagents individually and in combination. These microflotation tests indicated that once sphalerite is suppressed, it needs reactivation by copper sulphate for HCNPHA to float sphalerite efficiently. However, the amount of copper sulphate needed was much less than that needed from the xanthate collector.

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I. Introduction

Research on testing a new collector (*N*-arylhydroxamic acid) for the flotation of sphalerite is reported in this thesis. The research involved adsorption studies and microflotation tests. Hence, outlines of adsorption, adsorption isotherms, flotation reagents and microflotation systems are given below:

1.1. Objectives

This research work aimed at evaluating the feasibility of using HCNPHA as a collector for flotation of lead-zinc ores without the activation of sphalerite with copper sulphate which is not feasible when using xanthates.

Adsorption of HCNPHA on various pure minerals such as sphalerite, galena, pyrite, chalcopyrite and quartz was studied in order to evaluate the specific adsorption of HCNPHA on various minerals that are present in typical zinc ores. Similarly, with respect to a Pb-Zn ore, microflotation of its typical constituents was conducted in order to assess the dosages and the optimum pH for the flotation of each mineral.

In the past studies (Natarajan and Nirdosh, 2006) in which sphalerite was floated without activation, the ore was either Cu-Zn ore or Pb-Zn ore. Hence, there was every possibility of inadvertent activation of sphalerite by Cu^{2+} ion (from chalcopyrite) or Pb^{2+} ion (from galena). Thus, the flotation of sphalerite by HCNPHA without surface activation is arguable. This present study was intended to verify the flotation of sphalerite by HCNPHA without activation. Moreover, in a Pb-Zn ore, sphalerite is suppressed in the Pb-rougher stage using sodium cyanide, zinc sulphate and sodium metabisulphite. In such a situation if sphalerite whether or not reactivation is an important aspect that requires attention. This was explored in the current

research by using microflotation tests.

1.2. Background

1.2.1. Adsorption

Adsorption is a phenomenon wherein a species in fluid phase is able to accumulate itself onto a solid phase in contact with the fluid. Adsorption is observed in many natural and is used in industrial processes like water purification. Materials such as activated charcoal utilize adsorption for water purification.

Adsorbate is the solute in the fluid that accumulates on the solid in contact with the fluid.

Adsorbent is the solid surface where the adsorption takes place. Adsorption mainly occurs when an adsorbate is able to selectively transfer itself from a liquid phase to the surface of insoluble rigid particles either suspended in a container or packed in a column. The atoms of the solid on the surface are not completely surrounded by other adsorbent atoms and hence are capable of attracting adsorbates and thus causing adsorption.

There are two types of adsorption, namely, physical adsorption or physisorption and chemical adsorption or chemisorption. Physisorption occurs when the adsorbate and adsorbent are bonded through van der Waals forces. Such bonds are weak as their bond energies tend to be lower than 10 kcal/mol (Sparks, 2003). The bonds in chemisorption are stronger as they involve ligand exchange, covalent bonding, ionic bonding and hydrogen bonding which tend to have bond energies of 20 kcal/mol or higher (Sparks, 2003). Inner-sphere complexation is important in chemisorption because the ion binds directly to the surface without the interference from the surrounding water molecules. On the other hand, if the ion binds to water molecules, the

electrostatic forces between water and ion result in the adsorption of the ion on the surface. This is referred to as outer-sphere complexation

Surface reactions are important as they dictate which ion would be able to adsorb itself on the surface. The two types of reactions that may take place are *protonation* and *deprotonation* reactions. *Protonation* reactions would tend to adsorb negative ligands and *deprotonation* reactions would favour positive ligands.

1.2.2. Adsorption Isotherms

Adsorption isotherms are obtained by plotting the sorbed amount of adsorbate against the amount of adsorbate left in solution. Adsorption isotherms can take four shapes: S, L, H and C curves (Giles et al., 1960). Typical S, L, H and C curves are shown in Fig. 1.

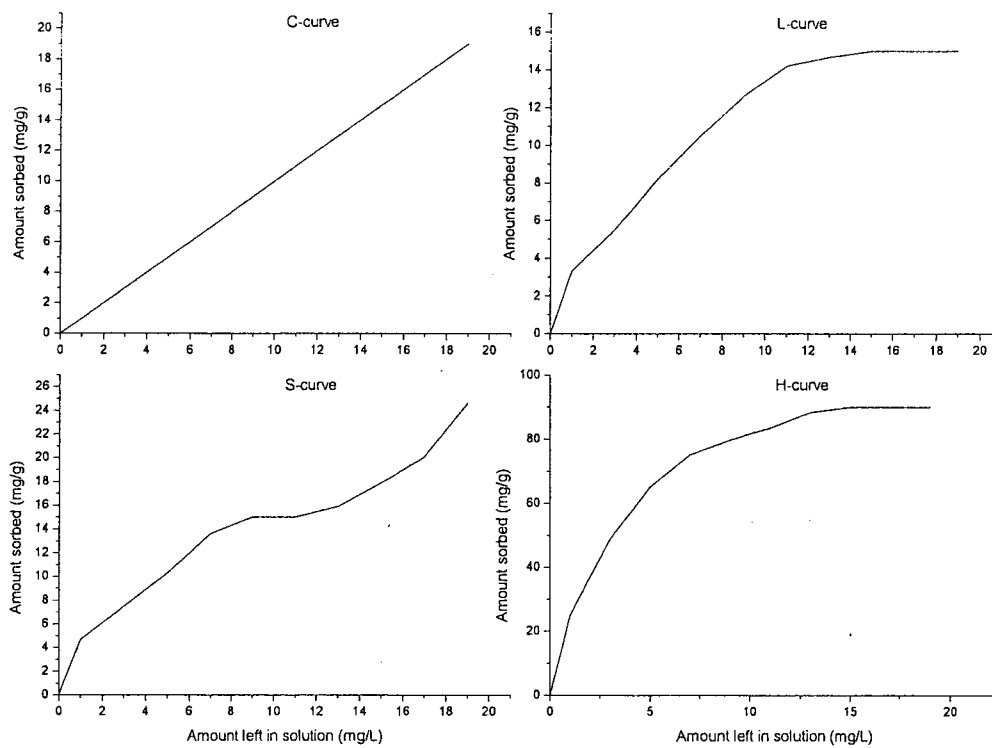


Fig. 1. C-, L-, S-, and H-curves commonly obtained for adsorption isotherm.

The initial slope of the L-curve and the later stages of S-and H-curves indicate that to adsorb a given amount of adsorbate, the solute concentration in solution must be increased by a considerable amount. Initial slope of the S-curve indicates that the more adsorbate is adsorbed on the surface, the easier it becomes for more adsorbate to find a suitable site. The reason behind this is an association between the molecules to help each other to hold on to the surface, i.e., co-operative adsorption. A linear relationship is used only for C-curves, as the sorbed amount is directly proportional to unadsorbed sorbate. Such a phenomenon is observed in systems like amino acids and peptides, in water, on silica dust. In comparison, L-type curves are the most recognizable types of isotherms as they are used in both Freundlich and Langmuir relationships. Various types of adsorption isotherms are briefly discussed below:

1.2.2.1. S-curve

S-curve refers to the adsorption isotherm that is obtained when adsorption of the adsorbate on the adsorbent increases with its concentration in the solution. S-curve is observed when the solute molecules are monofunctional, have moderate intermolecular attraction and meet strong competition for the adsorbent sites from other solvent molecules. Monofunctionality refers to the orientation that the adsorbate attains when it is adsorbed on the surface of a solid. As the concentration of adsorbate increases in the solution, the shift from a horizontal to vertical orientation is noticed. Such a change in orientation makes it easier for the adsorbent sites to accommodate extra adsorbate molecules and therefore, at increased concentrations, the tendency becomes greater for the adsorbate molecules to adsorb themselves on the surface.

1.2.2.2. *L-curve*

L-curve implies that as more surface sites become occupied, the harder it becomes for the adsorbate to adsorb itself. Such a finding would lead one to believe that the adsorbate molecules follow a horizontal orientation and not the vertical orientation that is observed in the S-curve. The reason for this is the fact that adsorbed molecules usually get adsorbed in the horizontal orientation and since there is no competition for the sites from the solute in solution, the orientation does not change to allow more adsorbate to be adsorbed on the mineral surface.

1.2.2.3. *H-curve*

H-curve is a type of L-curve but in this case, the adsorbate has such affinity for the adsorbent that it either completely adsorbs itself to the surface or it seizes to remain in the solution. Such occurrences lead to the typical shape of the H-curve which shows high values in the y-axis (adsorbed amounts) compared to the amount that is left in solution or the x-axis. Hence, the initial part of the isotherm is observed to be vertical with the adsorbed species to be in a polymeric format or in large units.

1.2.2.4. *C-curve*

C-curve is characterised by the constant partition of solute between the adsorbate and the adsorbent. The C-curve is obtained when the number of unoccupied sites for adsorption is constant, meaning that as more adsorbate is adsorbed, more sites should be created. A possible explanation for the site creation is that adsorbate could break the inter-substrate bonds more readily than the solvent itself provided the adsorbate has suitable molecular size to penetrate into the structure of the adsorbent (Giles et al., 1960). Adsorbate therefore has “unlimited” access to the sites for adsorption.

1.2.3. Langmuir and Freundlich models

Understanding adsorption process is key to successful flotation performance of the minerals as explained in *Section 1.2.5*. Adsorption isotherms are commonly fitted using Langmuir and Freundlich equations.

The most common form of Langmuir equation is:

$$q = \frac{kCb}{1 + kC} \quad (1)$$

where q = adsorbate adsorbed on solid (mg/g)

C = solute concentration in solution (mg/L)

k = Langmuir constant (L/mg)

b = maximum possible amount of adsorbate adsorbed (mg/g)

Langmuir equation assumes various conditions:

- a) the number of sites is fixed
- b) each site can only hold 1 molecule of adsorbent
- c) all the sites have to be equivalent
- d) The surface containing the adsorbing sites is a perfectly flat plane.

When the equation is linearized in order to confirm if the Langmuir type isotherm is followed, the following equation is attained:

$$\frac{C}{q} = \frac{1}{kb} + \frac{C}{b} \quad (2)$$

where C/q is plotted against C . The constant b is derived from the slope of the line and using b , k is derived from the intercept of the line.

When the sites are a rough plane, the Langmuir equation cannot be used and Freundlich equation is required for analysis. The Freundlich equation is:

$$q = K_d C^{1/n} \quad (3)$$

where q = adsorbate adsorbed on solid (mg/g)

C = solute concentration in solution (mg/L)

K_d = partition coefficient ($L^{1/n}/g$)

$1/n$ = constant (unique to the adsorbate and adsorbent at a given temperature)

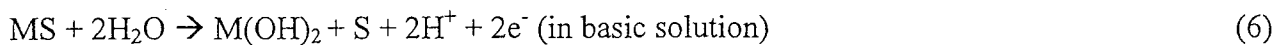
This equation better fits the rough surfaces however it cannot be used to predict the adsorption maximum. In order to confirm if the data points are indeed following the Freundlich type isotherm, the equation is linearized and the $\log q$ is plotted as the y-axis and $\log C$ is plotted as the x-axis.

$$\log q = \log K_d + \frac{1}{n} \log C \quad (4)$$

From this linear plot, K_d is derived from the y-intercept of the line. The slope of the line would give the value for $1/n$.

1.2.4. Surface reactions in flotation

Collector-less flotation is possible by maintaining proper anodic conditions. Anodic conditions will cause the base sulphide mineral to either dissolve or form oxidised metal species on the surface which would be entirely dependent on the pH of the solution (Wills, 1992). Initial oxidation of base sulphide mineral would lead to the formation of elemental sulphur, the presence of which on the surface of mineral could lead to hydrophobicity and hence allows the mineral to be floated without the aid of a collector. The formation of elemental sulphur in acidic or basic solutions is determined by the following reactions:



However, in industrial processes, the conditions for these reactions to occur are hard to control thus making it difficult to achieve high recovery and grade. In order to counter this disadvantage, collectors such as xanthates are required in flotation circuits. It is also important to understand that the oxidation of mineral surface is an important intermediate step towards the proper adsorption of a collector (Wills, 1992). These surface reactions also indicate that to ensure flotation, chemisorption is required on the mineral sites instead of physisorption due to the higher bond strength needed between a collector molecule and a mineral surface.

The accepted model of reaction between a mineral (base metal sulphide) surface and a collector is that under anodic conditions, the collector donates its electrons and then adsorbs itself on the mineral surface. These reactions are (Wandelt and Thurgate, 2003):





where X= collector and MS= base metal sulphide mineral

1.2.5. Mechanism for Adsorption by Chelating Agents

Adsorption on mineral surfaces by chelating agents was known to take place via three possible mechanisms:

- a) chemisorption
- b) surface reaction
- c) bulk precipitation

In chemisorption, the adsorption takes place only in a monolayer formation. Surface reaction is caused by the non-thermal reaction between a species that is present on the surface and a species that is desired to be adsorbed. Bulk precipitation is the phenomenon that occurs when the surface reactions allow for the multiple stacking of adsorbed species due to weak induced dipole forces. Both surface reaction and bulk precipitation allow for the formation of multilayers.

1.3. Flotation

Ores containing valuable minerals are present in nature surrounded by a matrix of rock, clay, and sand (gangue minerals) which are less valuable. Since these matrices have no commercial value, it is important to separate the minerals from the gangue before smelting or other metal recovery operations. The most common way for the beneficiation of low grade ores is flotation.

Flotation is preceded by comminution to liberate the minerals from their surrounding matrices. Particle size is dependent on two factors: cost and ability to float. If the ore is ground for a longer time to achieve maximum liberation, the cost for grinding would off scale the benefit of

liberating valuable minerals. In the contrary aspect, if the grinding is coarse, minerals have a potential of not being able to be carried by air bubbles. For flotation, the appropriate particle size (average equivalent diameter) usually varies from ≈ 100 to $200 \mu\text{m}$ (Osipow, 1962). The crushed ore is sent to a flotation cell where it is thoroughly mixed with water and various flotation aids. This step is referred to as *conditioning* and it is conducted at high pulp density in order to ensure that maximum adsorption of collector takes place on the surfaces of valuable minerals in order to render their surface hydrophobic. After a period of conditioning, air is introduced to the system which is responsible to keep the pulp agitated and to aid the formation of froth. Introduction of air causes the hydrophobic mineral particles to attach themselves on to the air bubbles and form a mineral-rich foam on top of the pulp and the gangue such as pyrite, pyrrhotite and sand are left behind. Gangue materials in flotation are referred to, but not limited to, unwanted sulphide minerals and various silica forms. The froth is then skimmed off as the concentrate is to be processed further.

A mineral particle would not attach itself to an air bubble unless it has been rendered hydrophobic. Most minerals possess a surface that is slightly hydrophilic and therefore it is important to have flotation reagents, known as collectors, to impart hydrophobicity to the mineral surface. When introduced to a pulp containing many different minerals, the collector would have a tendency to adsorb itself on all the available surfaces. Hence, other aids such as regulators are added to the mixture with the basic goal of modifying the action of the collector either by increasing or decreasing the hydrophobicity effect on the mineral surface. Such modifications help the collector to be more selective towards desired minerals. Regulators can be considered as: activators, depressants or pH modifiers (Wills, 1992). Vast majority of information has been taken from Wills, 1992.

1.3.1. Collectors

Base metal sulphide minerals are weakly polar due to their covalent bonding. In order to float them, their hydrophobicity has to be increased and to achieve that, surfactants are used. These surfactants are known as collectors. Collectors are organic compounds which contain a polar group and a non-polar chain. They selectively render the surface of a desired mineral hydrophobic by adsorption of ions on mineral surface allowing for mineral adhesion on the bubbles. Time allowed for such adsorption to take place is referred to as the *conditioning time*. Most collectors are classified as ionising collectors since they dissociate into ions when in contact with water and their classification is based upon the nature of the ions produced.

1.3.2. Activators

Reagents that alter the chemical nature of mineral surfaces in order to allow the collector to render it hydrophobic for flotation are known as activators. Activators are soluble salts which ionize in solution and their ions then react with the mineral surface. Copper sulphate is one of the most commonly used activators in sphalerite flotation. It is also used to reactivate the surface of minerals which have been suppressed with cyanide (Crozier, 1992). The activation that occurs is due to the formation of copper sulphide on top of mineral surface. For example, activation of sphalerite via copper sulphate would occur through the reaction:



Xanthate process for the flotation of sphalerite utilizes copper sulphate as an activator since zinc xanthate complexes are water soluble and would not float sphalerite readily. Copper sulphate allows for the above reaction to take place and resultant copper xanthate complexes, which are

water insoluble, would deposit on the sphalerite surface making it hydrophobic and therefore allows its flotation easily.

1.3.3. *Depressants*

Reagents that are used to increase the selectivity of a collector by rendering the surface of an undesired mineral hydrophilic are called depressants. Usually in mineral processing, depression may occur due to the slime coating which is not discriminating on which types of minerals it decides to settle on. Slime coating of mineral particles inhibits for collector adsorption and retards flotation (Parsonage, 1985). In order to increase the selectivity for depression of a mineral, various reagents are used. Cyanides for example are widely used in the form of sodium cyanide for the suppression of sphalerite. Sodium cyanide is also very capable in the depression of various iron minerals such as pyrite, pyrrhotite, marcasite and arsenopyrite along with galena (Crozier, 1992). When dissolved in water, sodium cyanide hydrolyzes into sodium hydroxide and hydrogen cyanide. The reaction is as below:



Cyanides, as mentioned above, are seen to depress all kinds of minerals and this may not be well suited for differential flotation of a desired mineral. Hence, a different reagent is usually added in order to ensure a more selective depression of sphalerite. The reagent of choice tends to be zinc sulphate (Crozier, 1992; Fuerstenau, 2007). Reaction that occurs when zinc sulphate is added to sodium cyanide is as below:



Resultant zinc cyanide is relatively insoluble and precipitates on the surface of sphalerite. This precipitation leads the surface to become more hydrophilic and prevents the adsorption of collector. In addition to this action, if pH of the pulp is in the alkaline range, the formation of zinc hydroxide will occur and it also would precipitate on the surface of sphalerite and therefore prevent collector adsorption.

Sodium metabisulfite (MBS) is used in combination with zinc sulphate in order to reduce the amount of sodium cyanide suppress sphalerite. Use of MBS ensures that the suppressed sphalerite does not get re-activated inadvertently by ions in a Pb-Zn ore or Cu^{2+} ions in a Cu-Zn ore.

1.3.4. pH modifiers

pH is a very important factor which aids in the selectivity of collector adsorption on the desired mineral surfaces. Delicate balance between collector dosage and pH of the slurry is needed to be achieved as they are responsible for deciding the selectivity in complex separations of minerals. pH modifiers used in the industry include lime, soda ash and sodium hydroxide for alkalinity purposes, and sulphuric acid for acidity purposes (Crozier, 1992). Since flotation process is a surface phenomenon, it is very important to research the effect of pH condition. Collectors work optimally at certain specific pH values which enable the best yield of flotation of valuable minerals and hence pH maintenance becomes very important.

1.4. Microflotation

Microflotation tests have been used for many years to evaluate potential collectors in respect to their flotation efficiency of a pure mineral. These tests require a small sample of a pure mineral, usually 0.5 to 5 g, and have been able to show high reproducibility due to good control of

variables. Many flotation cells have been developed for their feasibility in microflotation tests, however, modified Hallimond tube has been a forefront in terms of cell choice for microflotation. Frother is not used in Hallimond tube which is essential in industrial flotation and, therefore, microflotation does not simulate industrial processes accurately.

A brief outline of microflotation system is given since microflotation tests were conducted in the present research to evaluate the use of a new collector for flotation. Schematic diagram of a modified Hallimond tube is shown in Fig. 2.

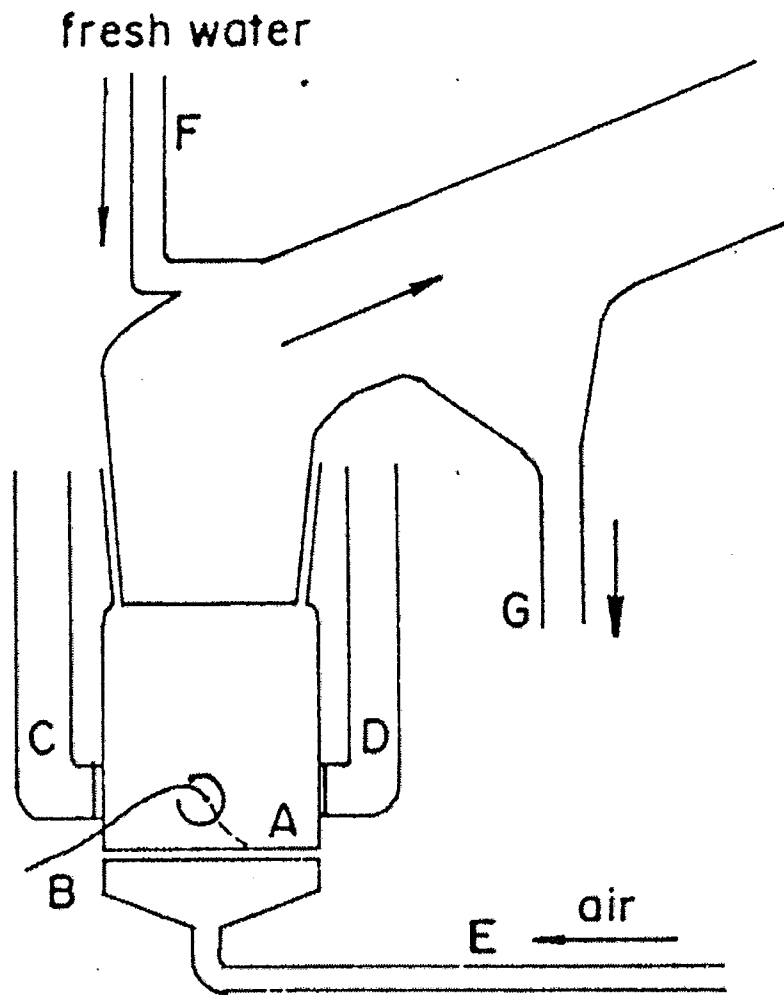


Fig. 2. A typical Hallimond tube used for microflotation.

- A- Upper section of the Hallimond tube
- B- Lower section of the Hallimond tube with a frit at the bottom of the well
- C- Sampling port for pH
- D- Other sampling port for pH
- E- Air inlet
- F- Water inlet
- G- Collection tube

The lower part of the Hallimond tube (B) consists of a glass well with a frit at the bottom of the well. The pores of the frit are uniform with a minimum size of 40 μm . Bent glass tube with a vertical stem forms the upper part of the Hallimond tube (A). The angle of the bending is at 30°. Air is allowed through the bottom of the well or through the top of the upper part of the Hallimond tube (E) depending on the modifications conducted. Water is filled through the top of the Hallimond tube (F). Hydraulic pressure and air pressure are maintained with adjustments in air flow rate and air provides the hydrophobic surface for minerals to attach themselves to. If needed, air could be replaced by nitrogen gas as a medium in order to prevent the oxidation of minerals. A Teflon-coated magnetic stirrer is placed in the bottom well in order to keep the mineral particles in suspension. It is essential that mineral suspension is properly attained before air flow is started. Conditioning of the minerals could be done either in the bottom of Hallimond tube or outside of the apparatus as some sizes of Hallimond tube are not large enough to allow for conditioning. Floated minerals are collected in an exit tube (G) where they could be withdrawn. Sampling ports (C, D) are used for checking the pH of the slurry during conditioning.

1.5. Current Practices for the differential flotation of a Pb-Zn ore

For the flotation of lead-zinc ores, xanthate process is the most commonly used by the industry. Xanthates were patented in the 1920s as collectors for the flotation of sulphide ores and research was continued into optimization of flotation conditions for the next 50 years (Wills, 1992). Xanthates are salts of xanthic acid and a typical structure is shown in Fig. 3. R in the figure refers to the hydrocarbon chain that is altered depending on the flotation application.

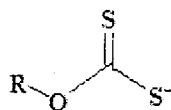


Fig. 3. Typical structure of a xanthate anion.

Mining industries have utilized xanthates for the beneficiation of low grade zinc ores for many years. Xanthates are preferred as collector of choice by many mills due to the high grade and mineral recovery of valuable minerals obtained with them. Large production and easy synthesis of xanthates have meant that the cost of xanthates have been relatively low in comparison with a lot of new collectors. This, coupled with their ability for floating many minerals, has resulted in xanthates being the prime collectors of choice for the industry for the flotation of base metal sulphide ores.

Xanthates work by adsorbing on the sulphide mineral surfaces due to chemical forces between them and polar groups of xanthates which form highly hydrophobic metal xanthates (Wills, 1992). Xanthates have been stated to work at a wide pH range of 8 to 13 (Wills, 1992). However, xanthates are not found to be efficient in terms of sphalerite flotation because the zinc xanthate formed on the surface is soluble and hence does not attach to air bubbles.

In order to alleviate this problem either: a) a long-chain xanthate that could form an insoluble xanthate has to be used or b) an activator could be used (Wills, 1992). Long-chain xanthates would be naturally hydrophobic due to the long hydrocarbon chain, however, the solubility would be severely diminished and therefore activators such as copper sulphate are preferred.

1.5.1. Sphalerite activation by copper sulphate

Copper sulphate is used as an activator in the flotation of sphalerite when xanthates are used. Copper sulphate activates the surface of sphalerite by the formation and deposition of copper sulphide on the sphalerite surface so xanthates could react with it to form the hydrophobic copper xanthate. The reaction describing the mechanism of copper sulphate on the mineral surface has been explained previously in *Section 1.3.2*. Through addition of copper sulphate, xanthate process ensures high separation of sphalerite from the gangue and hence provides high recovery and high grade of float.

In the case of lead-zinc or copper-zinc ore, the Pb^{2+} ion (Trahar et al., 1997; Rashchi et al., 2002) or the Cu^{2+} ion formed in solution due to the abrasion of the mineral surface can inadvertently activate sphalerite.

Even though copper sulphate usage ensures high grade and recovery, which are both financially attractive, its nature poses difficulties for industry when it comes to meeting environmental compliance. Copper sulphate is a toxic compound which is extensively used in flotation circuits in high dosages, and its elimination or a reduced need may provide an attractive financial incentive. Copper sulphate is also one of the most expensive reagents used in the flotation circuit.

The amount of copper sulphate required to activate sphalerite depends on the grade of the ore and it varies from 200 g/t to 1.2 kg/t. Canada produces about 0.15 million – 0.75 million tonnes of zinc concentrate per year (USGS, 2006). Assuming an average copper sulphate consumption of 1 kg/t ore for an average ore containing 10% zinc, the average cost of copper sulphate in a mineral processing facility is approximately \$0.5-2.5 million per month for processing based on

the current market prices of \$3.2/kg for copper sulphate (Natarajan and Nirdosh, 2006). Along with the staggering costs of copper sulphate to an industry, further costs are increased due to the toxicity of copper sulphate. A review on copper sulphate's MSDS by Old Bridge Chemicals indicated toxicity of the compound which eventually enters the environment through the tailing ponds (Old Bridge, 2007). Furthermore, copper sulphate is shown to be corrosive for stainless steel and iron which increases the operating costs of the plant.

In order to overcome the limitation of xanthates to float sphalerite, new collectors have been developed and tested in order to find their suitability in elimination or a major reduction in dosage of copper sulphate for lead-zinc ores (Natarajan and Nirdosh, 2006).

1.6. Use of -O-O- type chelating agents as collectors

Chelating agents are a class of metal complex-forming compounds. Chelates are metal complexes which are formed by a chelating agent which is usually described as a ring structure with the metal ion being at the center. The donor electrons are provided by chelating groups (ligand), which are present in the chelating agent and are characterized by having a lone pair of electrons which is free to interact with a positive charge.

Chelating agents are classified with the types of chelating atoms in their molecules. The donor atoms in a chelating agent are known to coordinate through two or more sites with a single metal ion and hence they are given the name, multidentate. The classifications based on the types of chelates are known as monodentates, bidentates, tridentates etc.

Initially, the use of chelating agents as collectors was based on trial and error experimentation. Attempts at understanding the chemistry of chelating agents on mineral surfaces have only been made in past 30-40 years but all that knowledge has been barely able to find its application in

mineral processing. There are several types of chelating agents that have been explored in their feasibility to be used as flotation collectors and these are with groups such as the -N-O-, -N-N-, -S-S-, -N-S-, -S-O- and -O-O- that are able to form stable metal complexes with the mineral. The best example of an -S-S- type collector is xanthate. However in this research, an *N*-aryhydroxamic acid that belongs to the -O-O- type collectors was explored.

Fuerstenau et al. (2007) discussed the use of chelating agents in flotation with emphasis on industries' hesitation onto changing their flotation reagents. Surface reactions highlighted the chemisorption as mode of adsorption regarding chelating agents. Chemisorption between hydroxamates and mineral surfaces indicated the existence of a strong bond between the metal and the chelating end of the collector molecule whilst the nonpolar ends of the collector molecule were hydrophobic and therefore, their suitability as the flotation agents was acknowledged (Fuerstenau, 2007). Furthermore, the author argued that the increased research into xanthates may have stalled the development of alternative collectors like -O-O- type chelating agents.

Fuerstenau (2007) compiled the use of various collectors in current industrial processes which are summarised in the Table 1 below.

Table 1. Comparison of xanthates and alternative collectors in terms of industrial use.

Collector	Extent of Industrial use
Alkyl- xanthates	Widely used for sulphide ores
Fatty acids	Widely used for many non-sulphide ores
Primary amines	Widely used for many non-sulphide ores
Alkyl sulfates ^a	Very limited use
Alkyl hydroxamic acids ^a	Mostly for speciality applications
Alkyl phosphonates ^a	Mostly for speciality applications
Dialkyl phosphonates ^a	Very limited use

^a –O-O- type chelators

As noted by Fuerstenau (2007), alternative collectors have been very much limited in their use due to the lack of optimization knowledge as compared to that available for xanthates that are known to produce high grades and recoveries for many sulphide minerals. However, in the past 25 years, several chelating agents have been tested as alternatives to xanthates for processing industrial minerals. These developments have not been analysed for their suitability for replacing xanthates and therefore further research on this subject was needed to be conducted.

Nagaraj (1987; 1988) has compiled many of the works regarding application of chelating agents as flotation agents. Chelating agents of the –O-O- type (such as cupferron and hydroxamic acids) were discussed amongst the various other types such as –N-N- or –N-O-. Cupferron was first reported as a collector in the flotation of cassiterite in an aqueous pulp containing acetic acid in 1927 with 90% of tin recovered with a grade of 25% from ore containing 2.5% cassiterite (Vivian, 1927). Cupferron and its modified forms were tried to float several other minerals

including pitchblende and was found to float uranium successfully (Muthuswami et al., 1983; 1985; Nirdosh et al., 1994).

Nirdosh and Natarajan (2002) were also able to successfully provide an alternative to the industry in the flotation of zinc. They were able to float sphalerite from a copper-rougher-tails of a sphalerite-chalcopyrite-pyrite ore with the use of *p*-heptylcupferron. The optimum pH of flotation was 9, and copper sulphate, used commonly for the activation of sphalerite surface, was not required as 93 wt% of zinc was recovered by *p*-heptylcupferron. Added benefit of using *p*-heptylcupferron was that no frother was required as the collector had stable frothing characteristics in itself.

The recovery was very substantial and competed with recoveries achieved by the industry however the collector was considered potentially hazardous to humans and, more over, pyrite was co-floated with sphalerite. Therefore, arylhydroxamic acids, which are organic acids with structural similarity with cupferrons, were considered as potential chelating agents for sphalerite flotation.

1.7. Chelation Chemistry of hydroxamic acids

Hydroxamic acids are compounds where the hydroxyl group (OH) of a carboxylic acid is substituted by hydroxylamine group (NHOH). General structure of hydroxamic acid is $R-C(=O)-NH(OH)$ (Agarwal, 1979). R refers to a hydrocarbon chain, CO as a carbonyl group and NH-OH as the hydroxylamine. In nature, hydroxamic acids have been deduced to be essential growth factors for some microbes and have been used in organic chemistry for many years (Dhungana, 2003; Yale, 1943). Hydroxamic acids are known to be very good metal chelators and because of this property, they have found applications in spectral colorimetric analysis and medicine, etc.,

where strong metal complexation is required. Medicinal uses include chelation therapy (Dhungana, 2003) and anti-tumour drugs, some of which are to be taken orally.

Agarwal (1979) and Chatterjee (1979) independently echoed the metal complexation properties of hydroxamic acids. Agarwal (1979) discussed the chemical and thermodynamic properties of hydroxamic acids in his paper. Hydroxamic acids are very capable of forming metal complexes which in turn could be used in the detection and estimation of metal ions with the use of hydroxamic acids. Stabilities of metal-hydroxamate complexes were discussed by Agarwal (1979). Many of the complexes formed by hydroxamic acids with metal ions such as Cu^{2+} , Fe^{3+} , V^{5+} have strong color, hence hydroxamic acids could be used as analytical reagents.

Chatterjee (1979) analysed various hydroxamic acids for their pK_a and stability constants of their metal complexes. Hydroxamic acids allow for chelation with a metal ion as the $=\text{O}$ and OH^- groups act like a bidentate and arylhydroxamic acids are compounds in which H on N is replaced. Molecular structure of metal-hydroxamate is shown in Fig. 4.

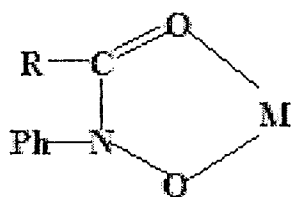


Fig. 4. Structure of a metal hydroxamate.

1.8. Alkylhydroxamates as mineral collectors

Hydroxamic acids belong to the –O-O- type chelating collectors. The stabilities of chelates formed with hydroxamates follow the order:

Alkaline earth metals (Be, Mg, Ca) < transitional metals (Ti, Tu, Nb, Zr) < rare earth minerals (zirconolite, bastnaesite) and Al < Fe, Cu metals

The differences in the stabilities of chelates allowed for better selectivity in flotation while using hydroxamic acids as collectors. Hydroxamic acids were used in various flotation applications in the Soviet Union during 1960s (referred to as IM-50) and in China during 1970s. A summary of using octyl hydroxamates as collectors is presented in Table 2 (Nagaraj, 1987).

Table 2. Studies on Hydroxamate collectors in the flotation of various minerals.

Mineral	Reagent	Investigation	pH optimum (recovery or adsorption)	Reference
Hematite	K –octyl hydroxamate	Flotation	9.0	Nagaraj (1987)
		Adsorption	8.5	Fuerstenau et al. (1975)
γ - MnO ₂		Flotation	9.0	Nagaraj (1987)
		Adsorption	9.0	
Rhodonite		Flotation	9.0	Nagaraj (1987)
Chrysocolla		Flotation	6.0	
Chrysocolla		Flotation	6.0	Fuerstenau and Pradip (1984)
Malachite		Flotation	9.5	Lenormand and Salman (1979)
Malachite		Adsorption	9.0	
Chrysocolla/malac hite/azuruite		C7 – C9 hydroxamate	Flotation	7.5- 8
Pyrochlore	IM- 50 (C7- C9)	Flotation	6.0	Nagaraj (1987)
Flourite	IM- 50	Flotation/Adsor ption	8.5	
Huebnerite			9.0	
Barite	K-octyl hydroxamate	Flotation	9.5	Pradip (1981)
		Adsorption	9.0	
Calcite		Flotation	9.5	
		Adsorption	9.5	
Quartz		Flotation	1.5	

Most of the research on hydroxamic acids has been dedicated on alkylhydroxamates as they have been able to float majority of oxide minerals and rare earth minerals successfully. It was widely suspected that the dissociation constant of hydroxamic acid would have a large bearing on the optimum flotation conditions for the mineral. This was formally researched and tested by Fuerstenau and Pradip (1984). The authors reported the use of K-octyl hydroxamates to float several minerals such as barite, bastnaesite, calcite and chrysocolla. For all minerals tested and reported, there was a correlation between the pK_a of the collector and optimum pH for flotation and adsorption, because they both were close to 9 which is near the pK_a of K-octyl hydroxamate (Fuerstenau and Pradip, 1984). The authors further supported the finding that with increased temperatures, the adsorption of hydroxamate was higher giving further evidence that the probable mechanism of adsorption was chemisorption (Fuerstenau and Pradip, 1984).

Nagaraj (1992) used alkylhydroxamates in combination with xanthates to process platinum group metals (PGM) from sulphide groups containing pyrite and pyrrhotite. Hughes (2002) used a combination of different hydroxamates for the flotation of minerals. The flow sheet for flotation would have required several changes to existing plants which would have further increased the costs of operations. The cost of these changes for using alkylhydroxamates were too high for industries to have seriously considered their uses unless used for speciality applications as indicated in Table 1 (Fuerstenau, 2007).

1.9. N-arylhydroxamic acids as mineral collectors

Marabini (1993) first used an arylhydroxamic acid, *N*-phenylbenzohydroxamic acid, in the flotation of rutile however, the use of *N*-arylhydroxamic acids for flotation has been investigated

significantly by Natarajan and Nirdosh (2001; 2002, 2003; 2006). There is a large scope for structural variation in arylhydroxamic acids.

Natarajan and Nirdosh (2001) synthesized and tested several *N*-arylhydroxamic acids as collectors for the flotation of a Cu-Zn ore and they were able to float copper efficiently. Furthermore, the authors concluded that substitution in the *N*-phenyl ring increased the efficiency whilst increase in the alkyl-chain beyond C-6 in the acyl group decreased the efficiency of the collector. *N*-butanoylphenylhydroxylamine was found to give the best results as recoveries of 93 wt% of Cu were achieved from a feed of 32 wt% Cu. Authors reported that collector dosage in order to achieve the reported recoveries was 70 g/t of ore. Flotation of pyrite was seen to be lowest at a pH of 11. These findings helped to establish the use of arylhydroxamic acids in the flotation of sulphide ores as majority of flotation done by hydroxamic acids were done on oxide ores as indicated previously. *N*-arylhydroxamic acids were considered to be more hydrophobic due to the phenyl group as in comparison with alkylhydroxamic acids which utilized the long chain to achieve the same hydrophobicity. However, with increased hydrophobicity, the solubility of the collector was compromised. Therefore, the most suitable collector for the flotation of sphalerite would need to be very hydrophobic whilst having good solubility. This prompted the authors to come up with a model that the flotation capabilities of *N*-arylhydroxamic acids depend on the substituents present in the structure. Similar models have been used by Marabini (1988; 1989) in the use of a chelating agent as a collector in the flotation of oxidised Pb-Zn ore.

These developments helped in narrowing the focus onto the class of *N*-arylhydroxamic acid collectors that may be efficient in the flotation of sphalerite. Natarajan and Nirdosh (2006) synthesized and tested several *N*-arylhydroxamic acids in the flotation of sphalerite from a lead-

zinc ore. *N*-arylhydroxamic acids were classified in four types- *N*-aryl-*C*-alkyl, *N*-aryl-*C*-aryl, *N*-aryl-*C*-aralkyl, and dihydroxamic acids where the researchers discovered that their flotation for sphalerite increased in order dihydroxamic acids < *N*-aryl-*C*-aryl < *N*-aryl-*C*-alkyl < *N*-aryl-*C*-aralkyl. The collector which stood out in terms of flotation of sphalerite was *N*-hydrocinnamoyl-*N*-phenylhydroxylamine or HCNPHA as it was able to recover 80% of sphalerite at pH 9. It has to be understood that sphalerite was floated without activation with copper sulphate and therefore these recoveries were actions of the collector itself. The dosage used for HCNPHA was 67 g/t. However, one major problem was that the grade of the float achieved with HCNPHA was 32% which was very low and this was due to the concomitant flotation of pyrite with sphalerite. These results were important as they left many potential approaches that could be taken in order to increase the recovery and grade of sphalerite from a Pb-Zn ore. It was deduced that flotation of pyrite was a result of HCNPHA's affinity for iron containing minerals, however, adsorption characteristics of HCNPHA onto different mineral surfaces were needed to be understood. Furthermore, the activation of sphalerite surface without the use of copper sulphate was debatable as there might have been a presence of Pb^{2+} ions in the slurry which might have inadvertently activated the surface of sphalerite. In order to fully comprehend the capability of HCNPHA for the flotation of sphalerite and understand the differential flotation characteristics for minerals such as sphalerite, pyrite and galena, adsorption studies using pure minerals and microflotation of pure minerals using HCNPHA were explored and the results of these studies are reported in this thesis.

2. Materials and Methods

2.1. Materials

2.1.1. Adsorbate/Collector: HCNPHA

HCNPHA synthesized at Lakehead University was used in this research. Stock solutions of HCNPHA were prepared by dissolving appropriate amounts in de-ionized water at pH 9 and 10 adjusted with sodium hydroxide.

2.1.2. Adsorbent: Minerals

Pure minerals, namely, chalcopyrite (CuFeS_2), galena (PbS), pyrite (FeS_2), quartz (SiO_2) and sphalerite (ZnS) were bought from Ward's Natural Science. Big pieces of each mineral sample were crushed with hammer and the smaller pieces, handpicked under light microscope, were grinded using a mechanical mortar and pestle with an agate medium. Mineral particles of size $< 75 \mu\text{m}$ were used for adsorption studies. Purities of the grinded mineral samples were obtained from the d -spacing of the powder X-ray diffraction.

Before conducting the adsorption tests, 1 g of each of the five minerals was agitated overnight with 35 mL of distilled and de-ionized water to verify whether any compounds formed due to surface oxidation of the minerals during storage leached out into water. The solution was filtered and analysed by Inductively Coupled Argon Plasma Atomic Emission Spectrometer (ICAP). No detectable amounts of any metal ions were found in filtrates. However, pyrite was an exception to this observation. The filtrate obtained after agitating water overnight with pyrite was detected to have nearly 20 ppm iron. This might be due to the dissolution of any oxidation product formed on the surface of pyrite. Presence of free Fe^{3+} ions in solution would interfere with the

adsorption as part of HCNPHA would be consumed through complexation. Hence, pyrite was washed with 0.1 N hydrochloric acid several times and then washed thoroughly with water before use. The wash-water after cleaning the pyrite surface was mixed with *N*-benzoyl-*N*-phenylhydroxylamine (NBPHA) which forms a purple coloured complex with Fe^{3+} . The purple coloured NBPHA- Fe^{3+} was used to detect any Fe^{3+} ion in the wash-water. Washing with dilute hydrochloric acid (0.1 N HCl) and water was repeated until the wash-water did not give any color on adding NBPHA. Freshly cleaned pyrite, through thorough washing, was used for all equilibrium adsorption studies.

For microflotation, samples of pure minerals (sphalerite, galena, pyrite) were grinded, and prepared, as mentioned above. The particles were then sieved to remove fines and therefore, the solids with particle size between 75 μm and 20 μm were taken for microflotation tests.

2.1.3. Chemicals

All chemicals used in the study were of Analytical grade. A list of chemicals used and their composition are given below:

NaOH: 1.0 M and 0.1 M in water

FeCl_3 : 1000 ppm in water

Ethanol: 85%

HCl: 0.1 M in water

NaCN: 0.1% solution in water

ZnSO_4 : 0.1% solution in water

MBS: 0.1% solution in water

MIBC: 0.1% solution in water

H_2SO_4 : 0.1 M in water

2.2. Methods

2.2.1. Procedure for Adsorption Tests

Adsorption tests were conducted at pH 9 and 10 to be consistent with the pH values used in the flotation studies conducted by Natarajan and Nirdosh (2006). Solutions of different HCNPHA concentrations were prepared with de-ionized water. Aliquots of 30 mL of each of the HCNPHA solutions were added individually to 50 mL conical flasks that contained weighed amount of an adsorbent (galena, chalcopyrite, quartz, sphalerite or pyrite). A blank test was run with the same mass of the adsorbent and 50 mL of de-ionized water, and the supernatant from the blank was used in the reference cell of the UV spectrometer during colorimetric analysis. All the flasks were stoppered and shaken at room temperature for 4 h at 200 rpm on Barnstead Labline Max Q 2000 E Class table top shaker. The solutions were allowed to stand overnight for settling and also to ensure equilibrium had been established (please see *Section 3.4.* for equilibration time). From each of the HCNPHA stock solutions, 10 mL aliquots were pipetted into conical flasks (50 mL capacity) which were stoppered and left undisturbed on the bench at room temperature for the same duration for which the adsorption tests were conducted on the shaker. This was followed to take into account any thermal or photochemical decomposition of HCNPHA that might have taken place during experimentation. It was also confirmed that 500 ppm HCNPHA solution at pH 9 did not decompose to detectable levels by recording the UV spectrum at various time intervals up to 72 h. Each equilibrated solution was filtered through a 0.45 μm Millipore filter paper and then analyzed following the spectralcolorimetric procedure described in *Section 3.2.* Concentrations of the feed solution and the filtrate (equilibrated solution) after adsorption were obtained from the absorbance of the coloured iron(III) complex at 500 nm. Thus, depletion in concentration of HCNPHA was determined by the difference between the initial and the

residual equilibrium concentrations of the solutions. This gave the amount of HCNPHA adsorbed on the adsorbent. The measurements were taken at room temperature.

2.2.2. Microflotation

2.2.2.1. Hallimond tube

A custom-designed Hallimond tube was used for microflotation tests. Unlike the modified Hallimond tubes which can be used to float about 0.5 g of a mineral (shown in *Section 1.6. Hallimond tube*), the Hallimond tube used in the current research could handle much higher amount of solids (up to 10 g). The dimensions of the Hallimond tube used are sketched in Fig. 5. Air from laboratory supply was used with a needle valve and a digital mass flow meter to control the air flow. In all microflotation tests air flow of 0.30 L/min was used in order to achieve uniform bubble formation whilst neutralizing hydraulic pressure.

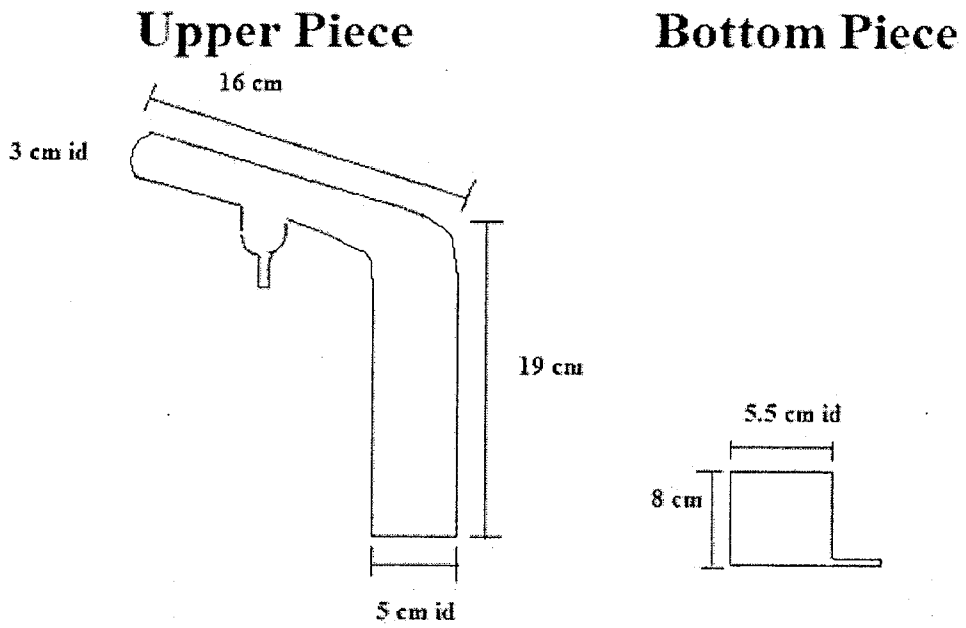


Fig. 5. Custom designed Hallimond tube used for current research.

2.2.2.2. Microflotation tests

Microflotation tests were conducted with the Hallimond tube described above. Approximately 5g of a mineral was weighed accurately into the bottom part of the Hallimond tube, and 50 mL aliquot of stock solution of HCNPHA was added. The solution was conditioned for a specified period of time. The period of time (10 to 60 min) was determined based upon the nature of the variable/effect studied. The mineral was conditioned with HCNPHA in Hallimond tube itself by stirring the slurry with a magnetic stirrer. Unless otherwise indicated, no frother was used. pH was maintained during the entire period of conditioning using 0.1 M NaOH or 0.1 M H₂SO₄. At the end of the conditioning time, the upper piece (overflow tube) was fixed and water at the same pH as the slurry was added to the overflow level of the Hallimond tube. Air was used to float the mineral particles for a given period of time (depending on the nature of the test) at the flow rate of 0.30 L/min. The concentrate was filtered, dried and weighed to calculate the percent recovery.

2.3. Instruments

2.3.1. Ultraviolet (UV) Spectrometer

Cary 5E UV-Vis-NIR spectrophotometer was used for measuring absorbance of solutions after equilibration and also, to record the UV visible spectra of HCNPHA-Fe³⁺ complex. The use of HCNPHA-Fe³⁺ complex formation is explained in *Section 3.2*. The UV spectrometer has an built-in program for quantitative estimation using calibration solutions.

2.3.2. Powder X-Ray Diffractometer

Purity of minerals used in the study was ascertained from the *d*-spacings of X-ray diffraction. Powder X-ray diffractions were carried out in a copper tube medium in a Phillips 3710 diffractometer. Bruker Eva software was used in order to identify the d-lines using the sets 1-50 provided by the International Center for Diffraction Data (ICDD).

2.3.3. Equilibration Shaker

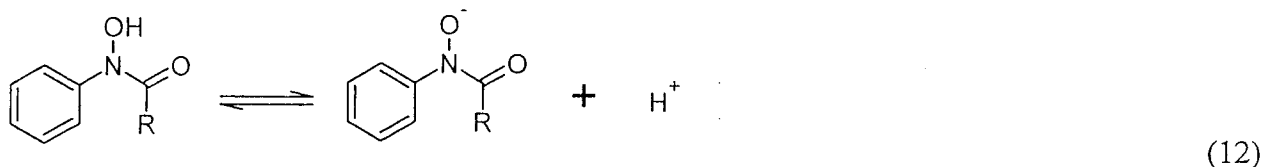
For adsorption studies, the solutions were equilibrated using the Barnstead Labline Max Q 2000 E-Class equilibrium shaker. The shaker was operated at a speed of 200 rpm for all equilibrium studies.

3. Results and Discussion

UV spectral studies on *N*-arylhydroxamic acids were reported by various authors (Tandon, 1967; Yale, 1943). Hence, it appeared that direct estimation of HCNPHA from its UV spectra could be possible. Muthuswami et al. (1985) had been able to estimate the amount of cupferron, which is another -O-O- type collector, by directly using its λ_{\max} discovered in its UV region at 284 nm.

3.1. Spectral photometric procedure: direct estimation of HCNPHA

N-hydrocinnamoyl-*N*-phenylhydroxylamine (HCNPHA) is a weak acid which dissociates into its conjugate base and hydrogen ion and such dissociation equilibrium for an *N*-aryl hydroxamic acid is shown below:



The relative concentration of the undisassociated acid (hydroxamic acid) and the conjugate ion (hydroxamate) depends on the pH of the medium. The hydroxamic acid and the hydroxamate have maximum absorbance (λ_{\max}) at different wavelengths. Hydroxamate ion tends to absorb at a lower energy (higher wavelength) due to the free electron pair which occurs in the absence of H^+ from the hydroxamic acid. This phenomenon is referred to as the red-shift. The red-shift indicated the absorbance at a lower energy level which indicates the formation of the hydroxamate ion. The relevant theory on the behaviour of acids states that the complete dissociation of an acid to its conjugate base occurs at its pK_a value. In order to verify this fact, UV spectra were recorded by dissolving a known amount of HCNPHA in a solution for a pH range of 3.6 to 13. Hence, as observed in Fig. 6, the effect of pH maybe evident because a shift

of λ_{\max} was observed after pH 9. The change as observed was the shift in the dissociation equilibrium towards the hydroxamate ion. Earlier research by Chatterjee (1978) reported that pK_a values of hydroxamic acids ranged from 7.05 for *o*-nitrobenzohydroxamic acid to 11.33 for *N*-phenyl-*n*-butyrohydroxamic acid. Similar observations were reported by Agarwal (1978). λ_{\max} would change due to the nature of substituent present of *N*-arylhydroxamic acids.

The pH corresponding to the change for HCNPHA as seen in Fig. 6 was around 9 and this is near the pK_a of several *N*-arylhydroxamic acids.

Abs, as indicated by y-axis in Figs. 6 to 8, refers to absorbance which is the negative log ratio of intensity of light exiting the sample against the intensity of light entering the sample.

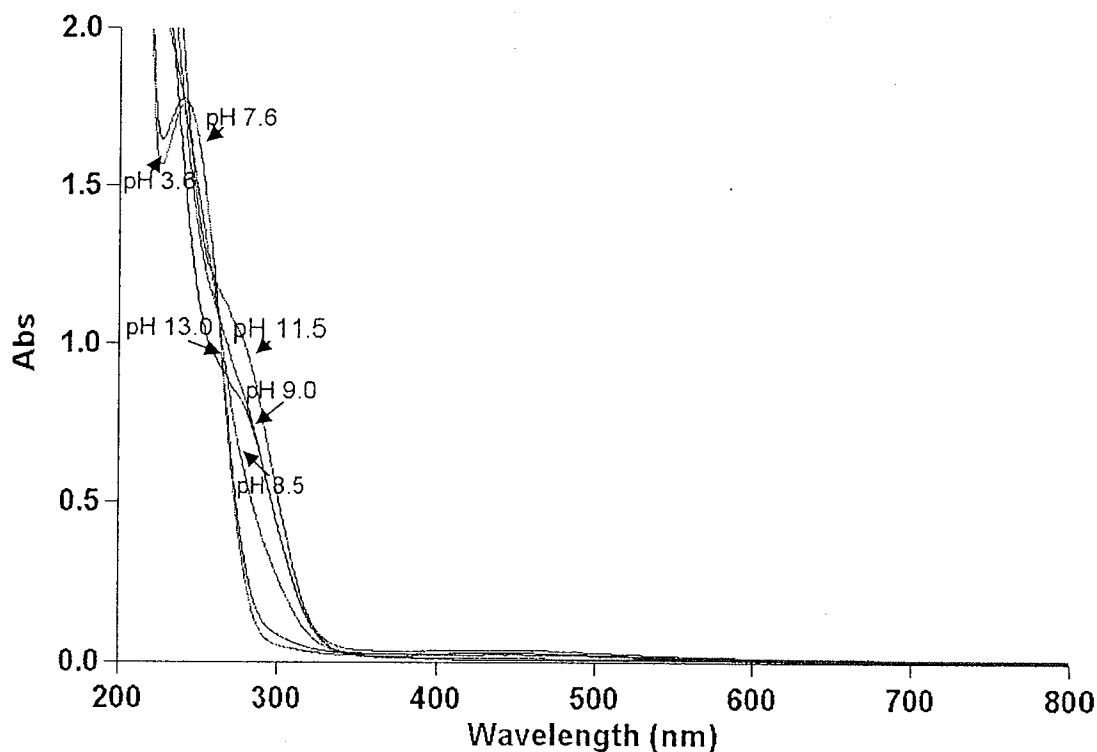


Fig. 6. Effect of pH on UV absorption for HCNPHA.

In order to confirm such behaviour of *N*-arylhydroxamic acids, similar studies (UV spectral) were conducted on NBPHA for a pH range of 6.5 to 14. UV scans for NBPHA are shown in Fig. 7. UV spectra of NBPHA agreed with the findings of HCNPHA as complete transition occurred at pH value close to 8.5 which is close to the pK_a of NBPHA. λ_{max} shifted from 260 nm to 297 nm indicating the hydroxamic acid and the hydroxamate species (Fig. 7).

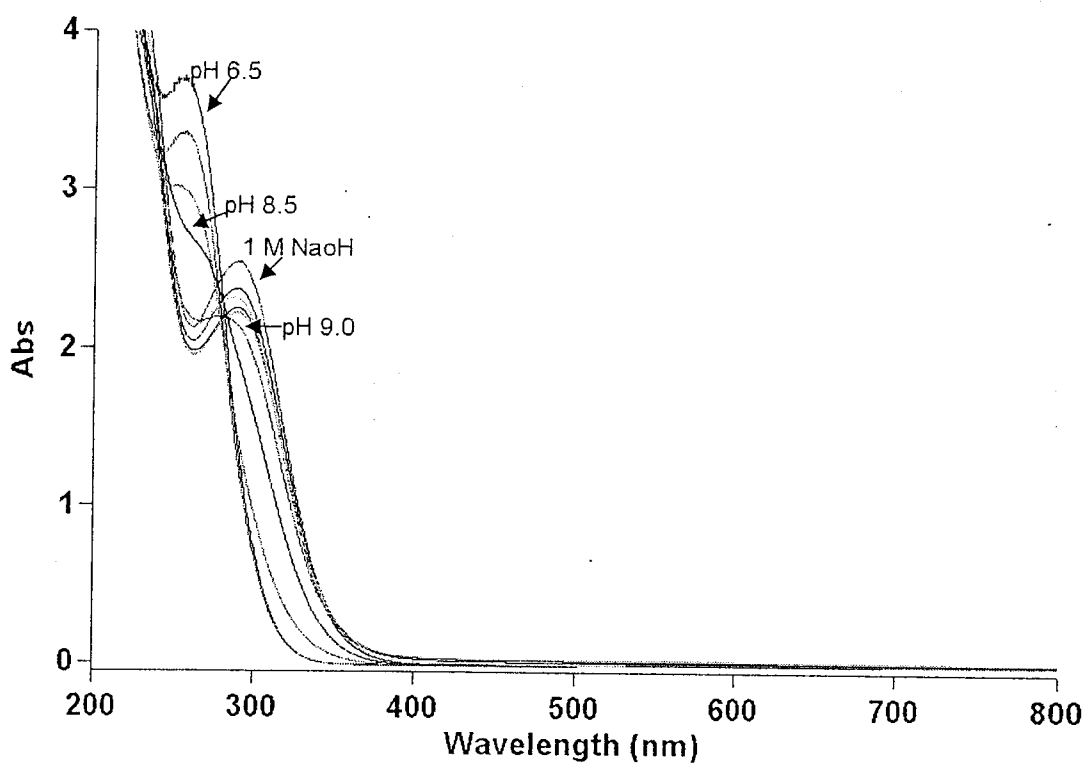


Fig. 7. Effect of pH on UV absorption of NBPHA.

However, the limitations imposed by HCNPHA due to its shift of λ_{max} at different pH values effectively ruled out the use of direct estimation previously employed by Muthuswami et al. (1985).

3.2. *Quantitative estimation of HCNPHA Using Ferric-ion complexation*

The ability of hydroxamic acids to complex with various transitional metal ions had been reported by several researchers (Agarwal, 1979; Chatterjee, 1978). This is the reason for the reported use of NBPHA as an organoanalytical reagent in the determination of various metal ions like iron, copper, aluminum, tin, titanium, vanadium and tantalum (Armour and Ryan, 1957). Armour and Ryan stated that NBPHA was a better complexing agent than cupferron as it is noted to be more stable to heat and light and could be dried at 110°C. As NBPHA and HCNPHA have the same chelating group and only differ in the *N*-acyl group, quantitative estimation of HCNPHA via its complex with Fe^{3+} ion appeared to be a possible method. Hydroxamic acids tend to form very stable complexes with Fe^{3+} which get stronger at increasing pH values in the presence of alcohol (Armour and Ryan, 1957).

In the present study, 5 mL of ethanol (85%) was added to 10 mL of HCNPHA before adding FeCl_3 solution. Ethanol was added in order to ensure that HCNPHA remains in solution while adding 10 mL of 1000 ppm FeCl_3 . FeCl_3 solution was prepared in an acidic medium (pH 2.0). As FeCl_3 solution was in acidic medium, without the presence of alcohol, HCNPHA would have precipitated due to pH change while mixing solutions of HCNPHA and FeCl_3 . The HCNPHA- Fe^{3+} complex had a strong red color and hence an absorption band occurred in the visible region (λ_{max} at 500 nm) as shown in Fig. 8 below. The absorption band that occurred at a wavelength of 329 nm represented the excess FeCl_3 present in the solution.

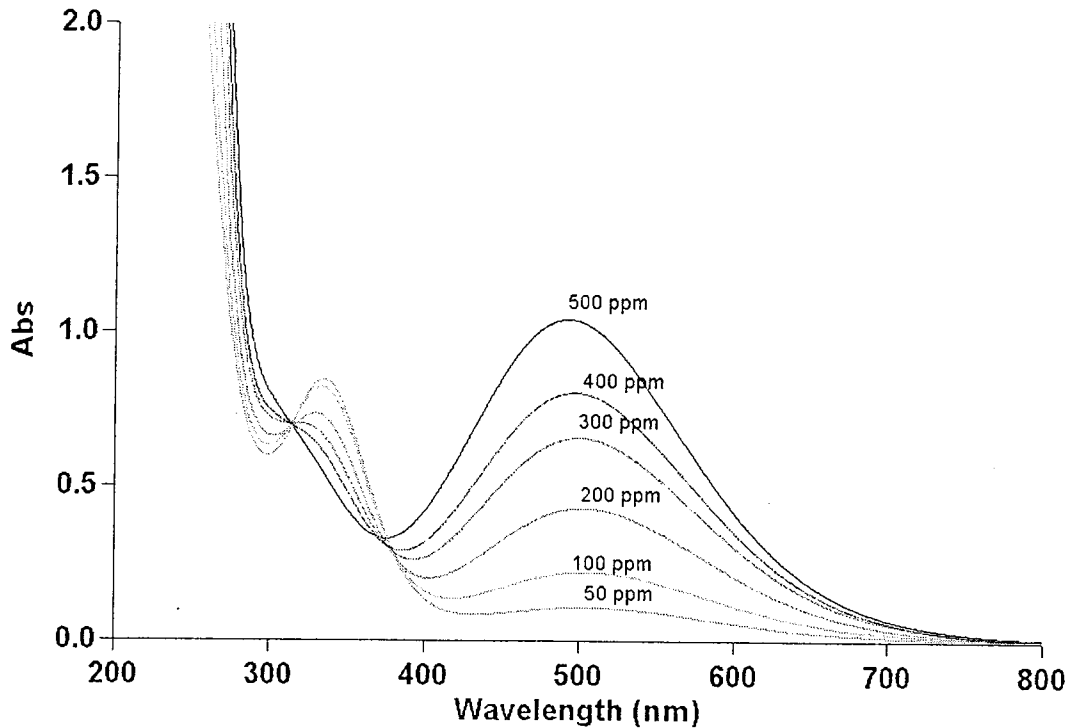


Fig. 8. UV spectra of HCNPHA-Fe(III) complex at various concentrations of HCNPHA.

Absorbance at 500 nm of the coloured complex was used for the quantitative estimation of HCNPHA. Calibration curves were drawn on several repeated tests of known HCNPHA concentration and the linear graph obtained had a R^2 value greater than 0.99. This was used further to estimate the concentrations of some standard solutions of HCNPHA and the precision was ± 5 ppm. The range for calibration was from 10 ppm to 500 ppm. It could be stated that the reproducibility of results via iron complexation would be a suitable method of HCNPHA estimation.

3.3. Preparation of Pure minerals for Adsorption

It was important to understand the purity and behaviour of minerals that were to be studied. As the minerals were to be agitated in water, their solubilities in water are to be known. Minerals were sparingly soluble in water (Perry, 2008).

Table 3. Chemical composition and solubilities of various minerals in water (Perry, 2008).

Mineral	Chemical Composition	Solubility (mg/L)
Sphalerite	ZnS	0.065
Galena	PbS	0.086
Chalcopyrite	CuFeS	0.033
Pyrite	FeS ₂	0.490
Quartz	SiO ₂	Insoluble

Furthermore, the purity of minerals was ascertained by Powder X-ray Diffraction from their unique d -spacing. For any crystal, planes exist in a number of different orientations and the spacing between them is referred to as d -spacing. The obtained d -spacing of different mineral samples was compared against sets 1-50 provided by International Center for Diffraction Data (ICDD) with the use of Eva software. The d -spacings, 2θ angles and identified minerals for different mineral samples used in this study are listed in Appendices D and E.

The minerals were found to be more than 90% pure and the percentage purity of the minerals used in the study were: sphalerite: 92% (with 8% quartz); galena: >99%; pyrite: 95% (with 2% quartz and, 3% bornite); chalcopyrite: 98% (with 2% pyrite).

Pyrite was washed with dilute hydrochloric acid (0.1 N) and water prior to equilibration and adsorption studies to remove the free ferric ions as outlined in *Section 2.1.2*.

Pretreatment of pyrite may have caused it to require a longer time to attain equilibrium compared to other minerals which were not prewashed before the experiments.

3.4. Equilibration time for Adsorption

In adsorption studies, it is important to find the time required for achieving equilibrium. Feed concentration of HCNPHA was constant for a set of tests for a mineral and the pH of HCNPHA solution was 9.

The tests were conducted by addition of same mass of mineral in different aliquots of HCNPHA (of the same concentration) and equilibration. At various time intervals (10, 20, 30, 60, 120 and 240 min), one of these mixtures was removed from the shaker and filtered. Then, the amount of HCNPHA left in solution was determined colorimetrically. The amount of HCNPHA adsorbed on the mineral was then determined and plotted against the various time intervals by subtracting the amount of HCNPHA left in solution from the feed. The data thus obtained were plotted against various time intervals.

Plotting specific adsorptions of HCNPHA in mg/g against time intervals as shown in Fig. 9 indicates the minimum required time for equilibrium to be established for different minerals. It was found that for sphalerite, galena, chalcopyrite and quartz, minimum equilibration time was close to 20 min. However, pyrite showed an exception to this general trend as it required close to 60 min to attain equilibrium. This may be due to the pyrite surface being altered due to the washing by water and dilute hydrochloric acid as it could have increased the adsorption time for HCNPHA on pyrite surface.

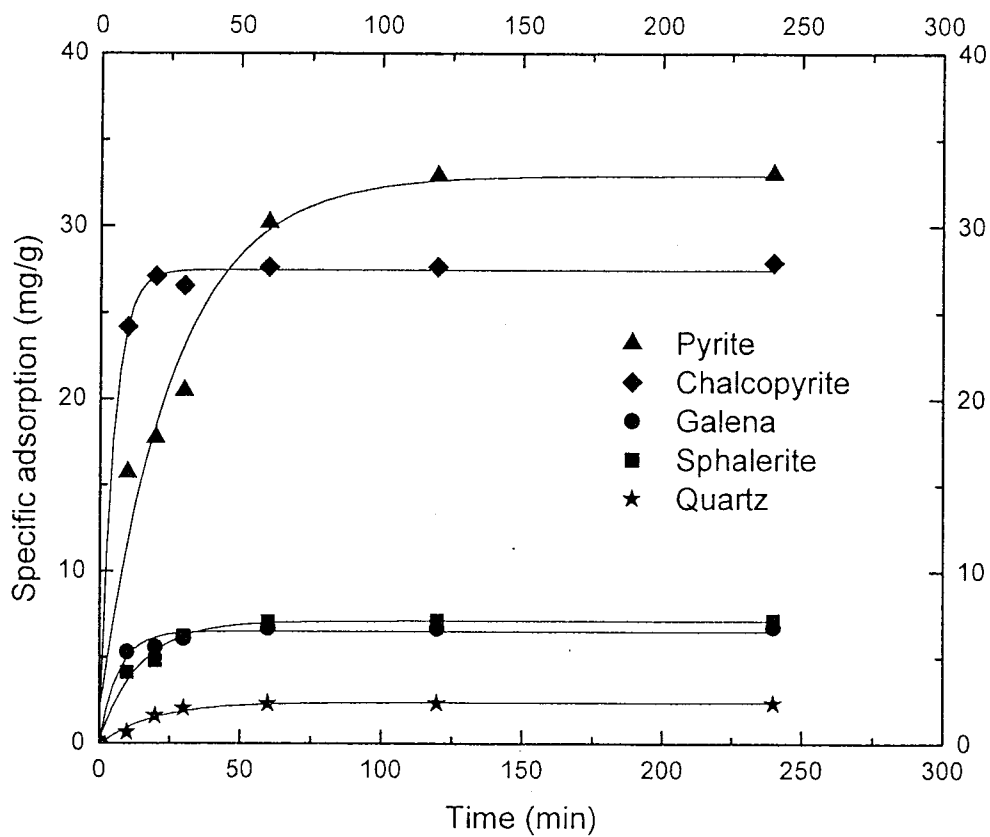


Fig. 9. Equilibration time for different minerals.

In order to ensure that solutions achieved equilibrium, they were agitated on a shaker at ambient room temperature for 4 hours and left overnight to settle.

3.5. HCNPHA adsorption on minerals

Specific adsorption of HCNPHA on different minerals is given in mg of HCNPHA (adsorbate) adsorbed per g of mineral (adsorbent). Adsorption isotherms obtained for pH 9 are given in Fig. 10. It may be noted that adsorption studies were conducted at room temperature.

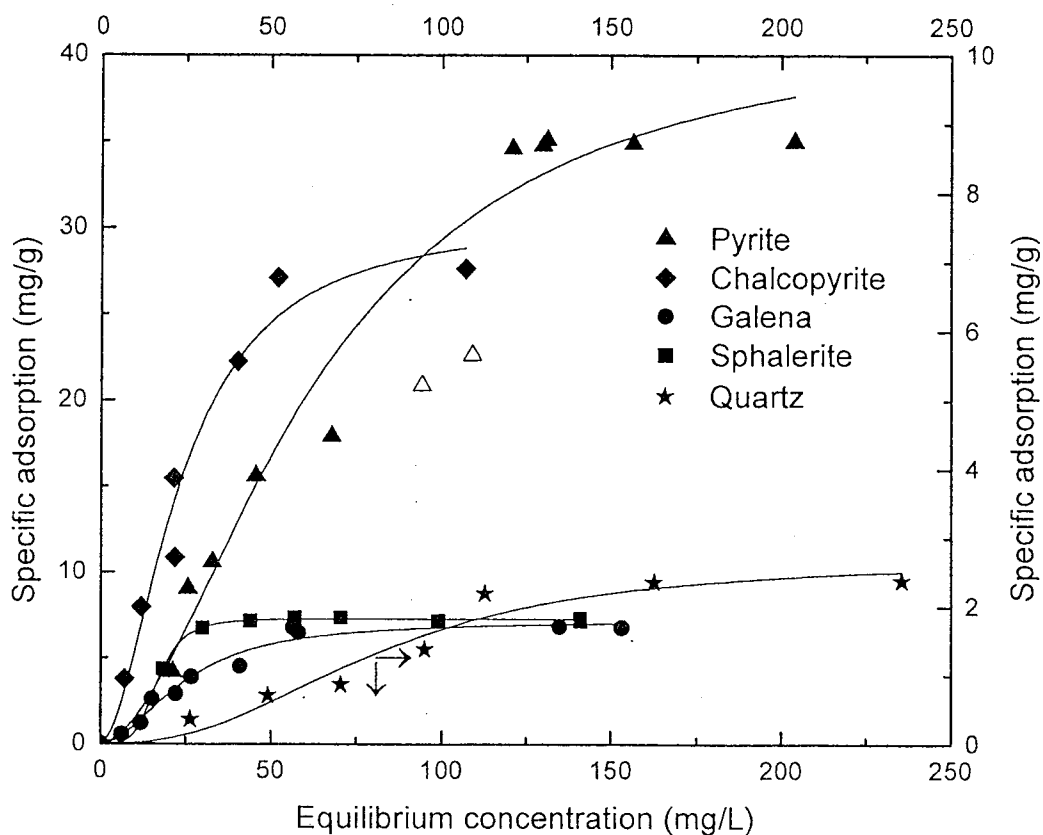


Fig. 10. Adsorption isotherms at pH 9 (for pyrite the two data points (Δ) were not included in curve fitting[§]).

[§]Excluded as pH 10 isotherm confirmed Langmuir type adsorption of HCNPHA on pyrite hence those data points appear to be due to experimental error.

The adsorption isotherms for different minerals except for quartz (Fig. 10) followed Langmuir model with a correlation coefficient or R^2 value ≥ 0.9 . Adsorption isotherm for quartz followed the Freundlich model. Specific adsorption of HCNPHA on different minerals decreased in the order of pyrite > chalcopyrite > sphalerite = galena > quartz. R^2 values and specific adsorption on various minerals are shown in Table 6. R^2 values and the data fitting were obtained by using a trial version of Origin Pro 8.0.

Table 4. Maximum specific adsorption, adsorption type and correlation coefficient values for various minerals at HCNPHA feed pH of 9.

Mineral	Maximum specific adsorption (mg/g)	Adsorption type	R^2
<i>Sphalerite</i>	7.27	Langmuir	0.990
<i>Galena</i>	7.21	Langmuir	0.953
<i>Pyrite</i>	42.16	Langmuir	0.960
<i>Chalcopyrite</i>	30.60	Langmuir	0.939
<i>Quartz</i>	2.69	Freundlich	0.899

As seen in Table 4, specific adsorption values for pyrite and chalcopyrite are nearly 6 and 4 times larger than that of sphalerite respectively. Both pyrite and chalcopyrite are iron based sulphide minerals. The high affinity that hydroxamic acids have for iron could be the reason for their high specific adsorptions. This also offers an explanation for the concomitant flotation of pyrite in the flotation of sphalerite by HCNPHA (Natarajan and Nirdosh, 2006).

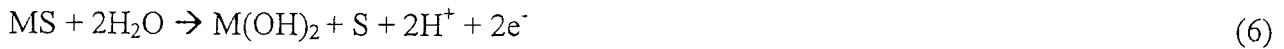
3.5.1. Mechanism of adsorption

Urbina (1985) studied flotation of chrysocolla using octylhydroxamate as collector.

Octylhydroxamate is also an –O-O- type collector which chelates to the mineral surface and helps it to float. Adsorption on mineral surfaces by chelating agents was known to take place via three possible mechanisms: chemisorption, surface reaction or bulk precipitation as outlined in *Section 1.3*.

As discussed earlier, the pK_a values for most hydroxamic acids are close to pH 9 and hence if the pH is around its pK_a , they are almost completely ionized into their hydroxamate forms which in turn act as strong chelating agents on metal ions. Hence, at pH 9 or 10, they can adsorb on mineral surfaces as hydroxamates by any of the three mechanisms. Chemisorption seems to be the most probable mechanism for adsorption of HCNPHA onto the surfaces of galena, sphalerite, chalcopyrite and pyrite (fresh surface after washing) because dissolution of metal ions from mineral surfaces was significantly low at pH 9 and 10. Furthermore, literature indicates that L-type curves are due to the formation of monolayers which are formed through chemisorption (Giles et al., 1960). Surface reaction and bulk precipitation, which lead to formation of multilayers, seem to be least probable as maximum adsorption density would not have been reached as noted in Table 4. Maximum adsorption density is only reached when all of the mineral sites are occupied leading to saturation and the remaining adsorbate is left in the solution. Multilayers accommodate more than one layer of adsorbate and not all adsorbate ions are in contact with the mineral sites. As hydroxamate ions are known to be very strong ligands and form stable complexes with transition metal ions, surface chelation on the cations of the minerals would lead to monolayer formation. It is understood that the adsorption of a collector in

a basic condition requires the hydroxylation of the mineral surface (Wills, 1992). The reaction that takes place under basic conditions as shown previously in *Section 1.2.4* is:



Therefore, the intermediate step that controls the overall mineral-hydroxamate interaction is the hydroxylation of the mineral cation followed by the chelation of mineral by a hydroxamate.

Metal cations are not present in quartz and therefore, only weak interactions between HCNPHA and quartz might have led to the adsorption of HCNPHA on the mineral surface. Weak interactions such as van der Waals forces would not lead to the close packed configuration of hydroxamate groups on the surface of quartz and, therefore, the mechanism for adsorption of HCNPHA on quartz appears to be different from that of the other metal sulphide minerals. This is confirmed as HCNPHA does not show any affinity for quartz as indicated by the low adsorption densities which may be due to weak interaction forces such as van der Waals.

It was noticed that in the cases of pyrite and chalcopyrite, no appreciable amount of HCNPHA was left in solution at low feed concentrations which would highlight the very strong interaction between HCNPHA and iron. All the equilibrium isotherm data points for pyrite and chalcopyrite were therefore obtained by using a reduced amount of mineral in the tests. Based on this, it may be suggested that the isotherms for iron containing minerals may belong to the H-type rather than L-type (Giles et al., 1960). It has been indicated that H-curve is similar to the L-curve, however, the adsorbate has high affinity for the adsorbent, which ensured that the adsorbate would completely adsorb itself to the surface or do not remain in solution. Similar observations were noted when HCNPHA was adsorbed on to iron bearing minerals. The high affinity of HCNPHA

for iron containing minerals is indicated by pyrite having the highest specific adsorption followed closely by chalcopyrite amongst the minerals studied.

3.5.2 *Effect of pH*

Adsorption isotherms at pH 10 are shown in Fig. 11 and they indicate similarity to those obtained at pH 9 for each mineral. Isotherms corresponding to adsorption on sphalerite, galena, chalcopyrite and pyrite follow the Langmuir type plots similar to the adsorption isotherms at pH 9. Isotherm corresponding to quartz for pH 10 shows Freundlich type plot agreeing with its adsorption isotherm at pH 9. Specific adsorptions of HCNPHA on different minerals at pH 10 are lower than in comparison with those obtained at pH 9. This occurs due to the increased hydroxylation of cations present on the mineral surfaces due to a ten-fold increase in the OH^- concentration caused by a unit increase in pH.

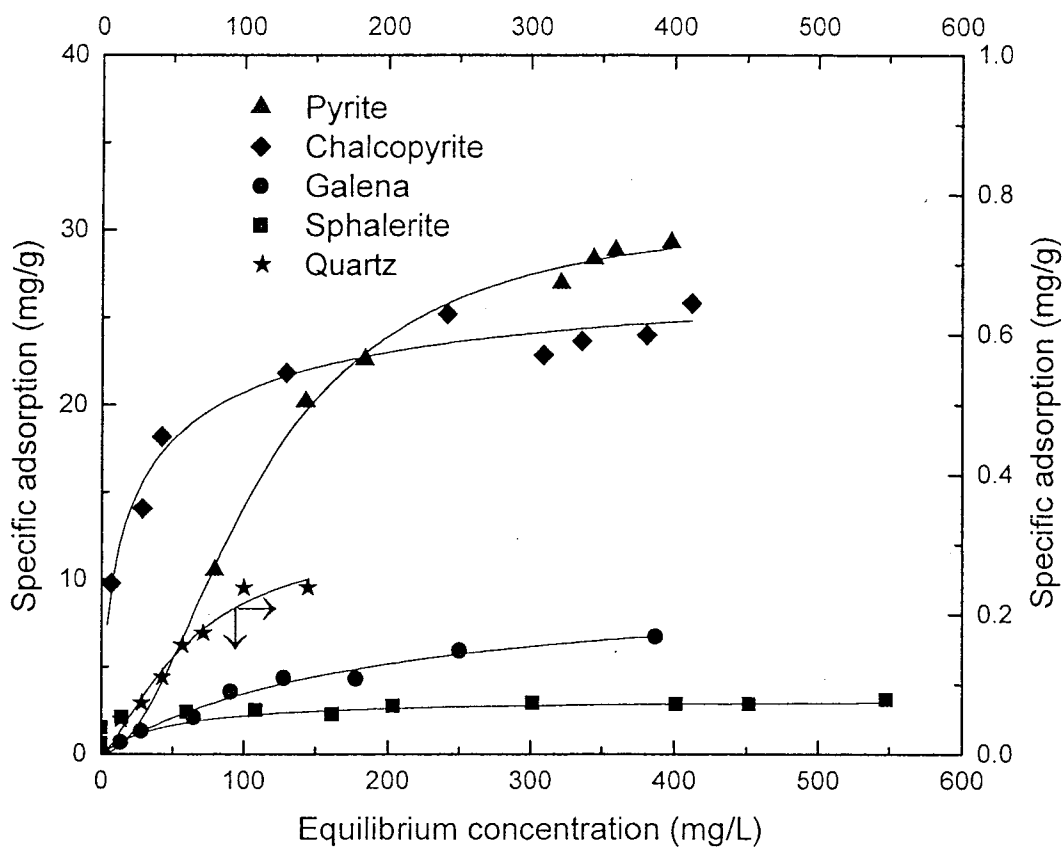


Fig. 11. Adsorption isotherms at pH 10.

Adsorption isotherms at pH 10 (Fig. 11) were similar to those obtained at pH 9 (Fig. 10) for each of the corresponding minerals. Specific adsorption of the minerals as observed in terms of strength concurred with that observed at pH 9. Isotherms corresponding to adsorption on sphalerite, galena, chalcopyrite and pyrite followed the Langmuir type plots while that for quartz followed the Freundlich type plot. Specific adsorptions were lower at pH 10 owing to the hydroxylation of cations of the minerals at ten-fold higher OH^- concentration. Increased hydroxylation of mineral sites would lead to more sites being already occupied on the mineral

surface and hence a reduction in the specific adsorption of HCNPHA. R^2 values and specific adsorption on various minerals are shown in Table 5. R^2 values and the data fitting were obtained by using a trial version of Origin Pro 8.0.

Table 5. Maximum specific adsorption, equation type and correlation coefficient values for various minerals at HCNPHA feed pH of 10.

Mineral	Maximum specific adsorption (mg/g)	Langmuir/ Freundlich	R^2
<i>Sphalerite</i>	3.16	Langmuir	0.993
<i>Galena</i>	6.74	Langmuir	0.968
<i>Pyrite</i>	31.17	Langmuir	0.991
<i>Chalcopyrite</i>	28.73	Langmuir	0.946
<i>Quartz</i>	0.32	Freundlich	0.953

3.5.3. Comparison of specific adsorptions on different minerals

Adsorption of chelating agents have been studied on various minerals by different authors (Urbina, 1985; Raghavan et al., 1975; Fuerstenau, 1975; Lenormand and Salman, 1979; Pradip and Fuerstenau, 1983; Muthuswami et al., 1985). The specific adsorptions of HCNPHA obtained in this study were compared to those in literature. Comparisons of chelating agents as collectors with various minerals are shown in Table 6.

In Table 6, Cupferron is also included because it is also an –O–O– type collector and has structural similarities to *N*-arylhydroxamic acids (Prabhakar et al., 1982; Muthuswami et al., 1985).

Table 6. Comparison of specific adsorption/adsorption density of octylhydroxamates and cupferron on minerals with the results of the present study.

Adsorbent	Adsorbate	pH	Conc. (mmol/L)	$\mu\text{mol/g}$	Reference
Hematite (0.5 m ² /g)	Octylhydroxamate	7.5	1.0	5	Raghavan et al. (1975); Fuerstenau (1975)
Malachite (<3 μm)	Octylhydroxamate	6.6	0.11	113	Lenormand and Salman (1979)
Chrysocolla (<75 μm)	Octylhydroxamate	9.0	0.17 1.13	415.0 685.0	Urbina (1985)
Calcite (2.15 m ² /g)	Octylhydroxamate	9.0	0.6*	1.7 ($\mu\text{mol/m}^2$)	Pradip and Fuerstenau (1983)
Barite (2.4 m ² /g)	Octylhydroxamate	9.0	1.0*	1.3 ($\mu\text{mol/m}^2$)	Pradip and Fuerstenau (1983)
Chalcopyrite (< 37 μm)	Cupferron	7.0	1.0	1.8	Prabhakar et al. (1982)
Pyrite (< 37 μm)	Cupferron	7	1.1 10	50 225	Muthuswami et al. (1985)
Quartz (< 37 μm)	Cupferron	7	1.0 10	0.13 1.3	Muthuswami et al. (1985)
Sphalerite (<75 μm)	HCNPHA	9 10	0.24 0.25	30.5 10.0	Present Work
Galena (<75 μm)	HCNPHA	9 10	0.24 0.27	26.9 8.8	
Pyrite (<75 μm)	HCNPHA	9 10	0.54 1.45	145.4 119.5	
Chalcopyrite (<75 μm)	HCNPHA	9 10	0.22 0.22	112.3 90.4	
Quartz (<75 μm)	HCNPHA	9 10	0.20 0.24	2.9 0.7	

*Feed concentration

Specific adsorption, reported in literature, of octylhydroxamate on copper minerals such as malachite at pH 6.6 and chrysocolla at pH 9 show similarity to the specific adsorption of HCNPHA on chalcopyrite observed in the present study. Quartz did not display much affinity for HCNPHA as the specific adsorption of HCNPHA was poor on its surface and literature confirms the finding as cupferron also showed little adsorption at pH 7 on quartz surface (Muthuswami et al., 1985). Further evidence of hydroxamic acids being weakly able to adsorb on quartz surface is shown by octylhydroxamate adsorption on calcite and barite at pH 9 (Pradip and Fuerstenau, 1983).

The low affinity of HCNPHA for quartz is of significant importance in flotation because usually silica is the major gangue mineral in any ore. Commercial feasibility of a collector being used in flotation depends highly on how selective the collector is and since HCNPHA does not adsorb on quartz, HCNPHA could be seen as a viable alternative to xanthate.

Specific adsorptions obtained in this study are comparable to those reported in literature.

Hydroxamates such as octylhydroxamate and HCNPHA showed that a low concentration of adsorbate in solution was sufficient to achieve specific adsorption that was almost equal to that of cupferron at higher concentration. This could be explained based on the molecular sizes of octylhydroxamate and HCNPHA which are far greater than the size of the cupferron molecule. Larger structure of hydroxamates disallows for adsorption of additional hydroxamates on adjacent mineral cation sites. These sites are blocked for any adsorption due to the bigger hydrocarbon part of adsorbate molecules. Cupferron being smaller in size comparatively would leave most of the adjacent sites available for additional adsorption. Literature confirmed that the smaller size of cupferron resulted in its large consumption in the flotation of a uranium ore (Muthuswami et al., 1983; 1985). Schematic representation of the relative sizes of the three

adsorbates is given in Fig. 12 and this provides validation for the above mentioned reason for the effect of size on specific adsorption of collectors on mineral surface is shown in Fig. 12.

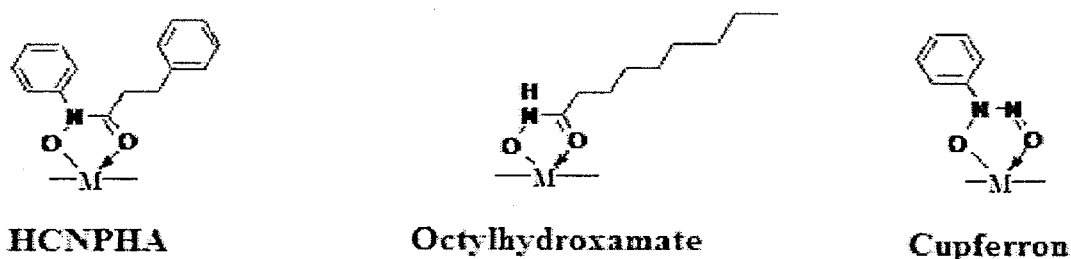


Fig. 12. Schematic representation of chemisorption on a sulphide mineral site (M) by chelating collectors.

3.6. Microflotation tests

Several tests were carried out using the custom-designed Hallimond tube in order to study the flotation response of different minerals towards HCNPHA. *Flotation response is reported as the wt % of pure mineral floated under specific experiments conditions and is used to study the effect of any variable such as air flow, conditioning time, and collector concentration.*

Effect of pH and collector concentration was studied on typical constituents of a Pb-Zn ore (sphalerite, galena and pyrite). The objectives of carrying out microflotation tests were to find answer to: a) does HCNPHA float sphalerite without activation and b) does sphalerite suppressed in the differential flotation of lead from a lead-zinc ore needs reactivation?

3.6.1. Collection time

Flotation responses were studied for all five minerals, namely, sphalerite, galena, pyrite, chalcopyrite and quartz at various collection times of 1, 3, 5, 8, 12 and 20 min. The minerals were conditioned at pH 9 with HCNPHA solution such that 1.5 mg HCNPHA per gram of

mineral was available. Flotation responses are given in Table 7. The same data are plotted as a graph in Fig. 13 for easy visual comparison.

Table 7. Flotation response for different minerals with varying collection time.

Collection time (min)	Flotation Response (%)				
	Sphalerite	Galena	Chalcopyrite	Pyrite	Quartz
Blank*	38.6	39.7	36.5	34.6	32.3
1	17.2	37.7	16.9	19.5	12.7
3	30.6	46.1	24.0	36.8	20.5
5	44.9	50.6	38.4	42.4	32.8
8	60.6	57.2	41.2	40.8	33.3
12	58.9	58.1	42.5	38.6	33.7
20	61.2 ^a	59.1 ^a	42.0 ^b	39.7 ^b	33.7

*Blank was conducted for a collection time for 8 min without any addition of HCNPHA

^{a, b} values followed by similar alphabets are statistically similar where the difference was less than the error of estimation.

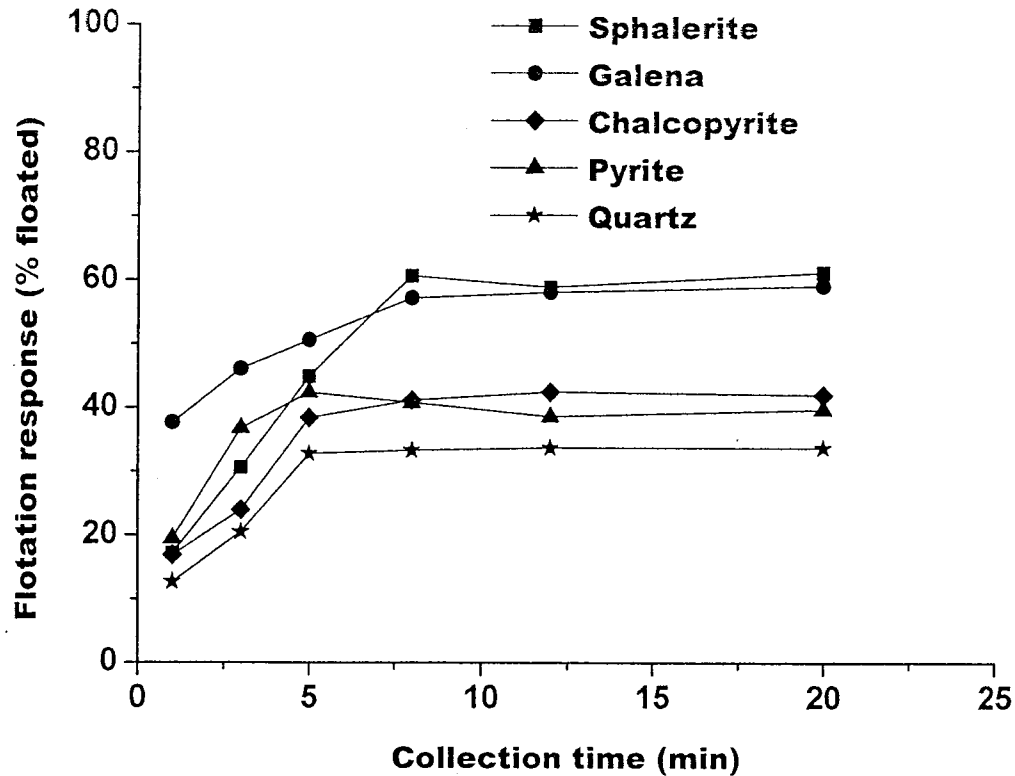


Fig. 13. Collection time for different minerals.

As confirmed by Fig. 13 and Table 7, the flotation response reached maximum at 8 min for all minerals. Hence, it was decided to collect the float concentrates for 10 min in each of the micro-flotation tests carried out.

3.6.2. Effect of pH

In the tests on effect of pH, the conditioning time for each pure mineral was decided from the corresponding adsorption study so that equilibration was ensured. Thus, the following conditioning times were used: sphalerite- 20 min, galena- 20 min and pyrite- 60 min.

3.6.2.1. Effect of pH on sphalerite flotation

The effect of pH on the flotation of sphalerite was studied at 3 different dosages of HCNPHA namely: 6 mg/g, 3 mg/g and 1.5 mg/g (this refers to mg of HCNPHA per gram of pure mineral). The results of tests are presented in Fig. 14.

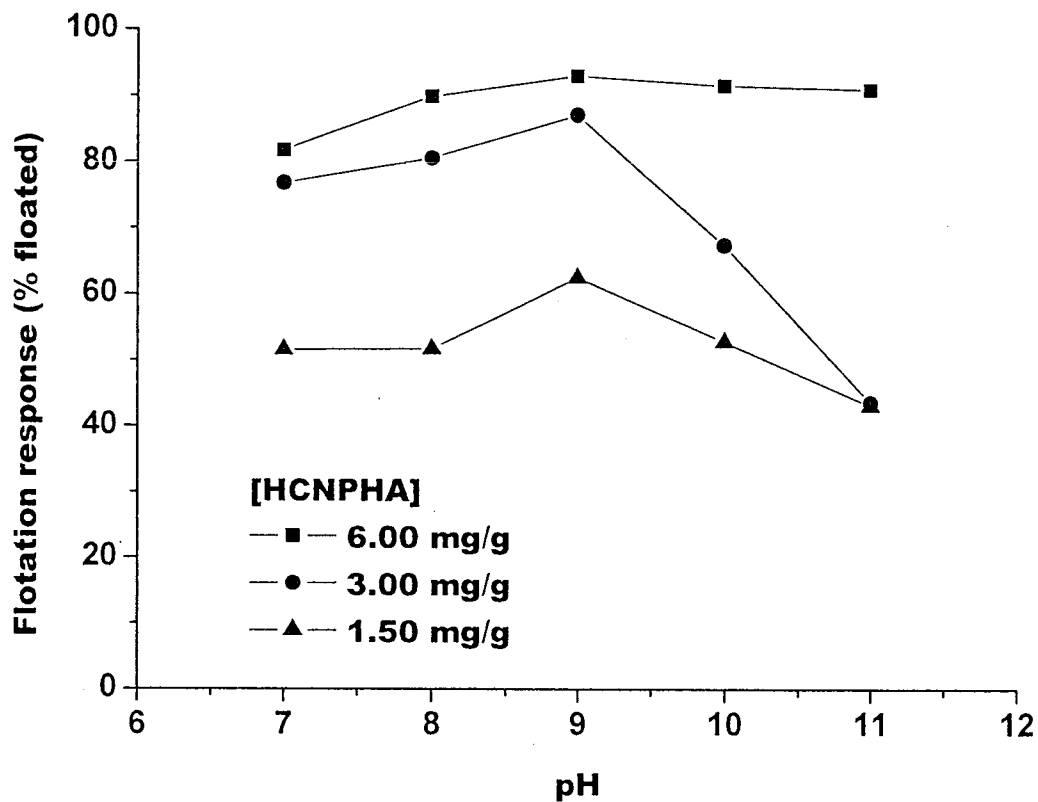


Fig. 14. Effect of pH and HCNPHA concentration on sphalerite flotation.

The results as plotted in Fig. 14 indicate that the maximum flotation occurs at pH 9. This is in conformity with the earlier report in batch flotation by Natarajan and Nirdosh (2006). When the concentration of HCNPHA in feed is *high*, the effect of OH^- is not predominant because more

collector species (dissociated or undissociated) are available for chelation. At pH lower than 9, HCNPHA does not fully ionize to form hydroxamate and remains unavailable for adsorption on the surface of sphalerite and effectively renders it hydrophobic. However at pH values greater than 9, the amount of OH⁻ ions present in the slurry increases substantially. Increased presence of OH⁻ ions competes with hydroxamates for the sphalerite surface and successful attachment of OH⁻ ions to the free metal surface demotes the flotation of the mineral. This is the reason why the effect of pH was more pronounced when the concentration of the hydroxamate ion was lower at reduced dosage of HCNPHA.

It also agrees with the finding made by many authors that the pH at which maximum adsorption takes place would also be the pH at which optimum flotation is obtained (Fuerstenau et al., 1970; 1973; Fuerstenau and Nagaraj, 1983; Lenormand and Salman, 1975; Bogdanov et al., 1973; Pradip, 1981; Urbina, 1985).

Since no copper sulphate was added in the tests, these microflotation results confirm that HCNPHA was able to float sphalerite without activation. This is a very significant observation because elimination of copper sulphate would be financially beneficial for the industry and would lead to less toxic tailings.

3.6.2.2. *Effect of pH on galena flotation*

Specific adsorption density of galena was only slightly less than that of sphalerite and hence it was hypothesized that flotation response of galena would be a reflection of the results found for sphalerite. Results as plotted in Fig. 15 of flotation response of galena at dosages of 3 mg/g, 1.5 mg/g and 0.75 mg/g HCNPHA do support the hypothesis.

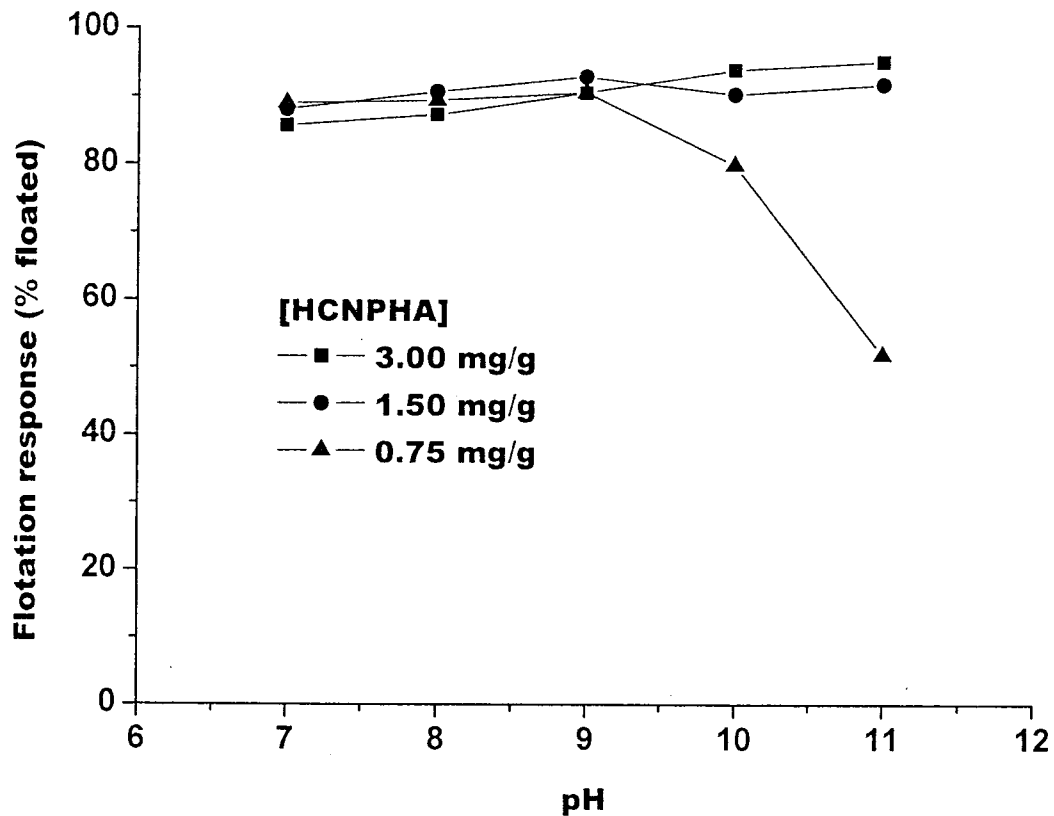


Fig. 15. Effect of pH and HCNPHA concentration on galena flotation.

However to achieve nearly 100% flotation, as indicated by dosages, galena did not require as much HCNPHA as required by sphalerite. This observation was surprising as it was generally assumed that specific adsorption governs the amount by which a mineral can be floated as noted in the collection time microflotation tests. However, when given sufficient time for conditioning, flotation response of galena increased substantially. This finding could be explained by the fact

that galena has a higher density than sphalerite and, therefore, if the same weight of both minerals is taken, sphalerite would have more unit cells than galena and hence more sites would be available for adsorption which would allow for high flotation response of galena at low concentration dosages of HCNPHA.

The effect of pH is not seen at dosages of 1.5 and 3 mg/g of HCNPHA. Flotation response was substantially affected when the HCNPHA dosage was 0.75 mg/g with indications that pH 9 was the most optimum pH for the flotation of galena. Competition for galena sites between collector and OH^- was increased substantially when HCNPHA dosage was 0.75 mg/g and therefore, at higher pH values, lower flotation response was found.

These results may also suggest that, much more reduced dosage of HCNPHA would be sufficient to float galena in the Pb-rougher stage at neutral pH value.

3.6.2.3. *Effect of pH on pyrite flotation*

Pyrite is usually suppressed by increasing the pH of the slurry while using xanthates as collectors. When HCNPHA was used as a collector with pure pyrite, it showed a different behaviour than xanthate. Specific adsorption of HCNPHA on pyrite has been stated to be 5 times more than that of sphalerite and hence, it was essential in understanding how pyrite would behave in terms of flotation response with changing pH values. Dosages used in this set of experiments were 3, 6 and 12 mg HCNPHA/g pyrite and the results given in Fig. 16 show that for all three HCNPHA concentrations values, the flotation response of pyrite increases with unit increment of conditioning pH.

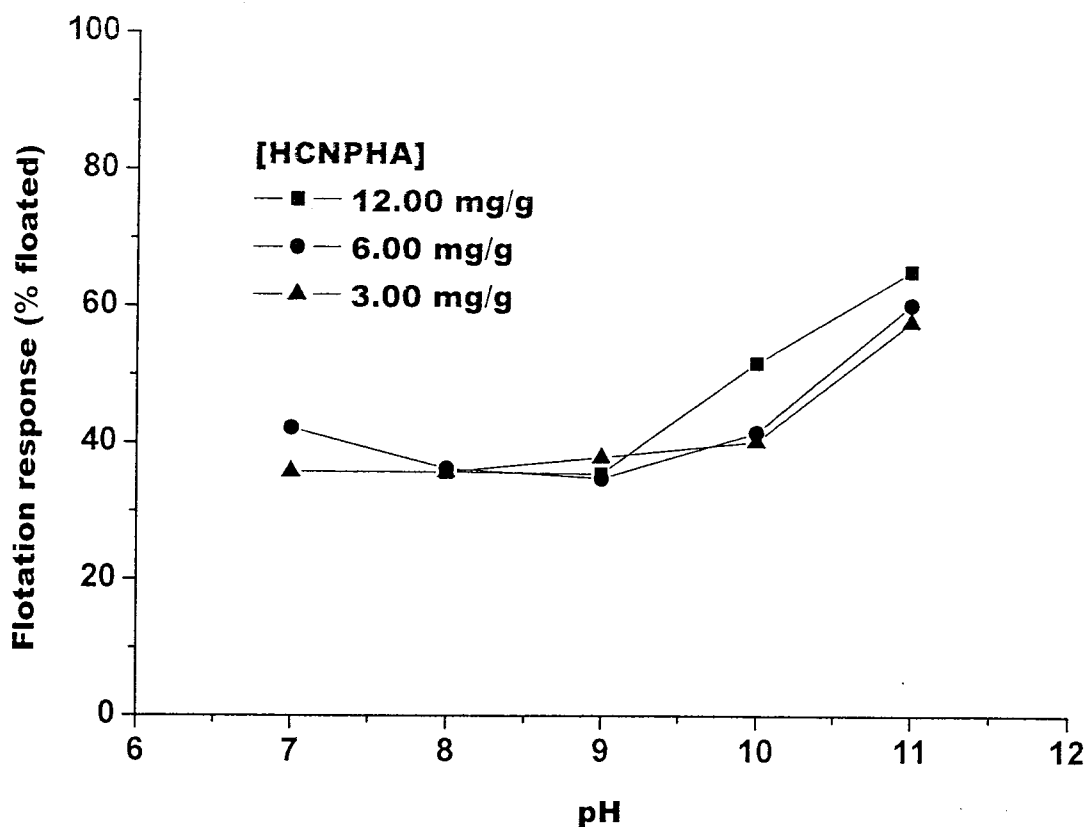


Fig. 16. Effect of pH and HCNPHA concentration on pyrite flotation.

Pyrite flotation is usually suppressed at pH values (> 9) due to the hydroxylation of the surface however in the present study, the flotation response of pyrite increased at higher pH values (> 9) This contradicts the usual flotation behaviour of pyrite and this unusual phenomenon observed in the current study needs more detailed research. In these tests, pyrite was not pretreated as it was done in the adsorption study and this was to follow the usual procedure for batch flotation. The presence of free ferric ions that might have been liberated in solution appeared to be the cause for the unusual increase in the flotation response of pyrite at higher pH (> 9).

3.6.3. Comparison of flotation response of sphalerite, galena and pyrite

The dosage that was common in the tests on effect of pH was 3 mg of HCNPHA/g of the mineral used for microflotation. Hence the data corresponding to the dosage of 3 mg/g were used to compare the flotation response of galena, sphalerite and pyrite.

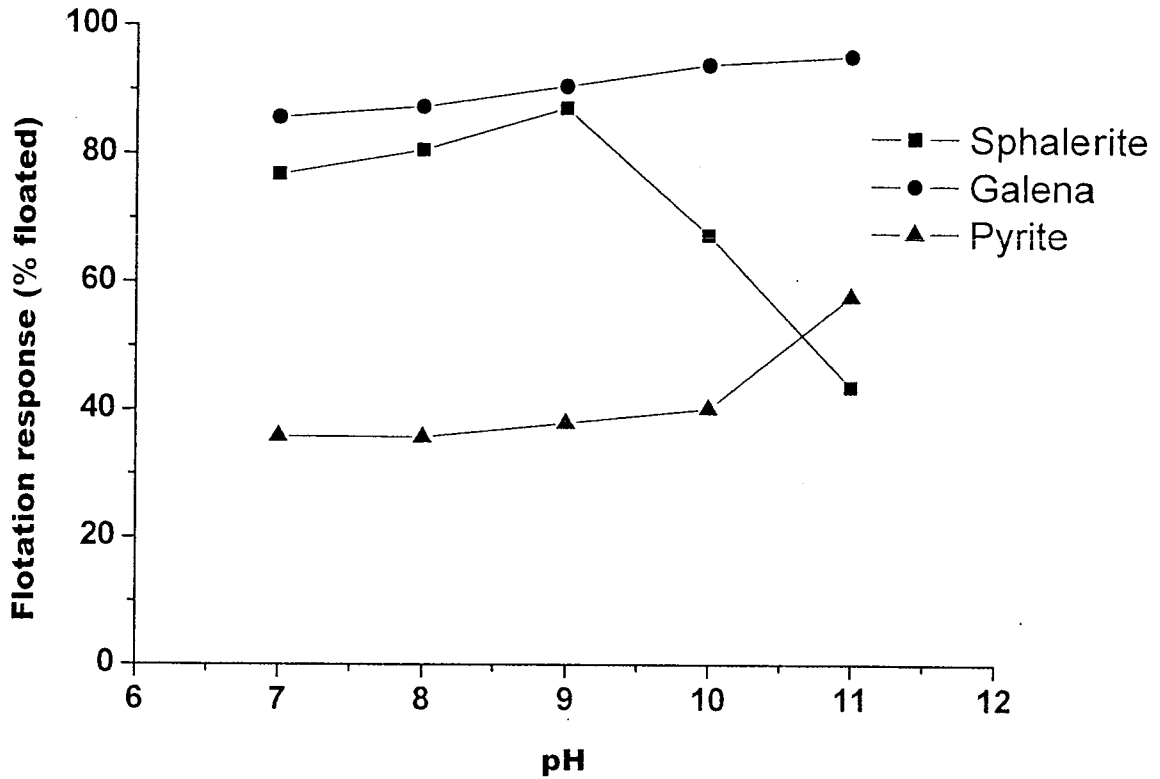


Fig. 17. Effect of pH at the dosage of 3 mg HCNPHA/g for sphalerite, galena and pyrite.

The results given in Fig. 17 show a very high flotation response for sphalerite and galena in comparison with pyrite. It is only at pH 11 that the flotation response of sphalerite is lower than that of pyrite. At a dosage of 3 mg HCNPHA/g mineral, it was noticed that pH 9 seems to be the most desirable for the flotation of sphalerite; galena was largely unaffected by the pH at this

dosage (though a slight increase was seen with pH); pyrite showed negligible flotation increase up to pH 10 and showed a slight increase at pH 11 (the value as it does not vary much from its blank shown in Table 7). From these results, it may be concluded that flotation of pyrite was not favoured when pH of the system was 9. Hence in order to float sphalerite selectively, pH 9 would be considered the most optimum pH. Such a comparison also showed the efficiency of HCNPHA as a reagent in the scavenger circuits because a very small dosage of HCNPHA would be efficient in floating galena and sphalerite.

3.6.4. Flotation of suppressed sphalerite

Microflotation of sphalerite using HCNPHA indicated flotation of sphalerite without any activation (*Section 3.6.2.1 Effect of pH on sphalerite*). In the differential flotation of galena with xanthate, usually depressants such as zinc sulphate, sodium metabisulphite and sodium cyanide are used in conjunction to suppress sphalerite during the Pb-rougher stage. Surface reactions due to these reagents which lead to the depression of sphalerite are discussed in *Section 1.5.3*

Depressants. Copper sulphate is used to reactivate the sphalerite suppressed during the Pb-rougher stage and it is facilitated due to the formation of insoluble copper xanthate. In the case of using HCNPHA, it is necessary to find out whether sphalerite needs reactivation for an efficient flotation after the Pb-rougher stage. Hence, the microflotation of sphalerite with and without the suppressants was studied.

For this set of tests, dosages of 3 mg and 6 mg of HCNPHA/g sphalerite were used with each individual suppressant reagent separately as well as in combination with each other. The flotation response was compared with the flotation response achieved with HCNPHA of the same dosage used on the un-suppressed sphalerite surface. Conditioning pH for HCNPHA was 9 as it was the

optimum pH for flotation of sphalerite. The results for these experiments are shown below in Tables 8 and 9.

The dosages of the suppressants were based upon the current mill practice by *Teck Resources* for its Pb-Zn ore. These dosages are given as: NaCN- 65 g/t, ZnSO₄- 130 g/t and MBS- 100 g/t. Dosage of CuSO₄ used was 200 g/t as reported in literature (Hamilton, 2009). The sphalerite content of the Pb-Zn ore is 22%. Thus, assuming this percentage, the dosages applied for the microflotation tests on pure sphalerite were: NaCN- 1.4 mg/g, ZnSO₄- 2.8 mg/g, MBS- 2.3 mg/g and CuSO₄- 4.5 mg/g. A further test was conducted with addition of 1 mg MIBC previous to the addition of HCNPHA.

These tests were conducted by conditioning sphalerite with any one of these reagents followed by flotation with HCNPHA (Test # 2, 3 and 4). In Test # 5, they were used together at the same time. Copper sulphate was added for reactivation after all the suppressants were used together in combination (Test # 6). Results of these tests are given in Table 8.

Table 8. Flotation response with the use of modifiers at HCNPHA dosage of 3 mg/g sphalerite.

Tests	Modifier(s) added	% sphalerite floated
1	None	87.3 ^a
2	130 g/t ZnSO ₄	68.9
3	100 g/t MBS	86.2 ^a
4	65 g/t NaCN	85.9 ^a
5	130 g/t ZnSO ₄ + 100 g/t MBS + 65 g/t NaCN	59.8
6	130 g/t ZnSO ₄ + 100 g/t MBS + 65 g/t NaCN + 200 g/t CuSO ₄	82.3 ^b
7	200 g/t CuSO ₄	82.8 ^b
8	1 mg MIBC	90.1 ^a

^{a, b} values followed by similar alphabets are statistically similar

Standard deviation of repeat tests- Test 5: 2.07%; Test 6 : 1.31%; Test 7: 0.82%

As these tests were repeated, the standard deviations of these tests were calculated using Microsoft Excel and are reported.

Test # 1 indicated the flotation of sphalerite with the HCNPHA dosage of 3 mg/g.

Test # 2 indicated some suppression of sphalerite by zinc sulphate thus HCNPHA was not able to float > 80% sphalerite. This is in agreement with literature as Wills (1992) stated that zinc sulphate is capable in the suppression of sphalerite by itself.

Tests # 3 and 4 indicated that when sodium metabisulphite and sodium cyanide were added individually, there was no suppression of sphalerite as HCNPHA was capable of floating > 80% sphalerite.

Test # 5 indicated that when all of the suppressants were added in combination (as is done in the Pb-Zn flotation) HCNPHA was not able to float sphalerite efficiently. Thus, sphalerite once suppressed, is not floatable even by HCNPHA which otherwise would float. Literature further agrees with this finding (Wills, 1992).

Test # 6 clearly indicated that sphalerite surface must be reactivated by using copper sulphate in order to increase the flotation response of sphalerite to > 80%. The dosage of copper sulphate used was adequate to float sphalerite efficiently (Hamilton, 2009).

Test # 7 shows that addition of copper sulphate on an unsuppressed surface of sphalerite would not increase the flotation response.

Test # 8 indicated that methylisobutyl carbinol increased the flotation response of sphalerite and this is due to the frothing action of the reagent as highlighted by Wills (1992).

Table 9. Flotation response with the use of modifiers at HCNPHA dosage of 6 mg/g sphalerite

Tests	Modifier(s) added	% sphalerite floated
9	None	93.0 ^a
10	130 g/t ZnSO ₄	89.9 ^a
11	100 g/t MBS	93.2 ^a
12	65 g/t NaCN	91.9 ^a
13	130 g/t ZnSO ₄ + 100 g/t MBS + 65 g/t NaCN	79.4 ^b
14	130 g/t ZnSO ₄ + 100 g/t MBS + 65 g/t NaCN + 200 g/t CuSO ₄	90.2 ^{a,c}

^a values followed by similar alphabets are statistically similar

Standard deviation of repeat tests- Test 13: 0.27%; Test 14: 0.07%

The results of HCNPHA dosage of 6 mg/g of sphalerite agreed with the findings made at 3 mg/g dosage. When the suppressants were used in combination (Test # 13), the flotation response reduced significantly to < 80% sphalerite from > 90% sphalerite when no suppressant was used (Test # 9). Similarly, copper sulphate is seen to reactivate the surface of sphalerite for flotation (Test # 14) as the flotation response returns to > 90% sphalerite confirming the need for copper sulphate when all suppressants are added in combination. The copper sulphate dosage used for reactivation was sufficient for flotation.

4. Conclusions

4.1. *Estimation of N-hydrocinnamoyl-N-phenylhydroxylamine (HCNPHA):* A

spectrocolorometric procedure was developed for quantitative estimation HCNPHA. This involved the formation of HCNPHA-Fe³⁺ complex that absorbed in the visible region with a $\lambda_{\text{max}} = 500$ nm. Wavelength at which maximum absorption was observed was found to be at 500 nm for the HCNPHA-Fe³⁺ complex. The method was found to be efficient in the quantitative estimation of HCNPHA.

4.2. *Adsorption Equilibration time:* Equilibration time studies indicated that all minerals may have attained equilibrium with the solution in 20 min except for pyrite which took 60 min. This might be due to change in the surface characteristics of pyrite by the pre-treatment using dilute hydrochloric acid and water.

4.3. *Mechanism of Adsorption:* The most probable mechanism of adsorption appeared to be chemisorption. The pH values of the study (pH 9 and 10) are close to the pK_a of HCNPHA. Langmuir model provided the best fitting for all base metal sulphide minerals and Freundlich model applied for quartz.

4.4. *Effect of pH on adsorption:* Specific adsorption of HCNPHA on the minerals studied was found to be higher for pH 9 than that at pH 10. At pH 10, the amount of OH⁻ ions in solution is 10 times larger than that at pH 9, which might have increased the hydroxylation of surface sites and provided competition to HCNPHA.

4.5. Differential Adsorption of HCNPHA on different minerals: Amongst the minerals studied, the iron containing minerals (pyrite and chalcopyrite) were found to have higher specific adsorption. This may be due to the affinity of HCNPHA towards iron. HCNPHA was found to have an affinity for pyrite hence increasing the need for a pyrite suppressant during the flotation of sphalerite. In comparison with all of the base metal sulphide minerals, quartz showed to have a very weak adsorption at both pH values. This indicated that silica suppressant might not be required when HCNPHA is used as a collector. The following order is observed for HCNPHA's affinity for minerals.

Pyrite > Chalcopyrite > Sphalerite = Galena > Quartz

4.6. Determination of flotation collection time: Microflotation tests showed that the float is to be collected for 10 min.

4.7. Effect of pH on flotation response: A solution of pH 9 was found to to be the best pH for the flotation of both sphalerite and galena for all of the dosages of HCNPHA used, where as pyrite gave good performance at pH values of 10 and 11.

4.8. Activation by copper sulphate on flotation response: HCNPHA does not require copper sulphate to activate the surface of sphalerite. However, in the case of differential flotation of lead in the Pb-rougher stage, where sphalerite is suppressed by a combination of zinc sulphate, sodium metabisulphite and sodium cyanide, copper sulphate is required for the reactivation and the efficient flotation of sphalerite.

5. Recommendations

The primary objectives of this thesis were accomplished. However there are further areas that may be explored to fully assess the capabilities of HCNPHA in mineral flotation.

- Microflotation tests involving of synthetic mixture of minerals for a typical Pb-Zn ore using HCNPHA. The results from this testing could further shed light on the behaviour of HCNPHA when different mineral surfaces are in competition.
- Behaviour of pyrite, with or without pretreatment washing, needs to be further researched in order to fully understand the effect that HCNPHA has on its flotation. Pyrite displayed an unusual behaviour attributed to pretreatment washing in 0.1 N HCl hence, more studies need to be conducted Due to the time constraints in the present study, no suitable explanation was given into the pyrite flotation as results were contrary to the literature present on the topic.
- The flotation conditioning and collection times used in the current study were much higher than that used in the current industrial procedures. Further tests maybe conducted to explore how the flotation response of various minerals might be affected when current industrial protocols are used in laboratory tests.

References

- Agrawal, Y.K.: Hydroxamic acids and their metal complexes. *Russ. Chem. Rev.* **48**, 948-963 (1979)
- Armour, C.A., and D.E. Ryan.: *N*-acyl substituted phenylhydroxamines: The effect of radical change on analytical behavior. *Can. J. Chem.* **35**, 1454-1460 (1957)
- Chatterjee, B.: Donor properties of hydroxamic acids. *Coord. Chem. Rev.* **26**, 281-303 (1978)
- Crozier, R.D.: Flotation- Theory, Reagents and Ore testing. Pergamon Press. Oxford. (1992) p 343
- Dhungana, S.: Iron chelation properties of an extracellular siderophore exochelin MN. *J. Am. Chem. Soc.* **125**, 7654-7663 (2003)
- Fuerstenau, D.W., T.W. Healy and P. Somasundaran.: The role of hydrocarbon chain of alkyl collectors in flotation, *Trans. SME-AIME.* **229**, 321-325 (1964)
- Fuerstenau, D.W. and S. Raghavan.: In P. Somasundaran and R.B. Grieves (Eds) *Advances in Interfacial Phenomena of Particulate/ Solution/ Gas Systems: Applications in Flotation Research.* AIChE Symp. Ser. **71** (150), 59-66 (1975)
- Fuerstenau, D.W. and Pradip.: Mineral flotation with hydroxamate collectors. In: M.J. Jones and R. Oblatt (Eds) *Reagents in the Minerals Industry. IMM Proceedings*, Inst. Min. Metall. London, UK. 161-168 (1984)
- Fuerstenau M.C., G. J. Jameson and R.H. Yoon.: Froth Flotation: A Century of Innovation. SME. (2007) p 891
- Giles, C.H., MacEwan, T.H., Nakhwa, S.N., and D. Smith.: Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface area of solids. *J. Chem. Soc.* 3973-3993 (1960)
- Hamilton, D., R. Natarajan and I. Nirdosh.: Sphalerite flotation using an arylhydroxamic acid collector: Improving grade while using a reduced amount of copper sulfate for Activation. *Ind. Eng. Chem. Research.* **48**, 5584-5589 (2009)
- Hughes, T.C.: Hydroxamate composition and method for froth flotation. European Patent Application EP1419012. <<http://www.freepatentsonline.com/EP1419012.html>> (2002)
- Lenormand, J., T. Salman and R.H. Yoon.: Hydroxamate flotation of malachite. *Can. Metall. Q.* **18**, 125-129 (1979)
- Marabini A., M. Barbarao and V. Alesse.: New synthetic collectors for selective flotation of zinc and lead oxidized minerals of zinc and lead oxidized minerals. In: E. Forssberg (Ed)

Proceedings of the XVI International Mineral Processing, Develop. Miner. Process. **10**, 1197–1208 (1988)

- Marabini A., J. Cases and M. Barbaro.: Chelating reagent as collector and their adsorption mechanisms. In: K.V.S. Sastry and M.C. Fuerstenau (Eds) *Challenges in Mineral Processing*. SME. Littleton. CO. USA. 35–50 (1989)
- Muthuswami, S.V., Vijayan, S., Woods, D.R., and S. Banerjee: Flotation of uranium from uranium ores in Canada: Part I- Flotation results with Eliot Lake uranium ores using chelating agents as collectors. *Can. J. Chem. Eng.* **61**, 7280-744 (1983)
- Muthuswami, S.V., Vijayan, S., D.R. Woods: Flotation of uranium from uranium ores in Canada: Part II- Cupferron adsorption on uranium oxide, quartz, illite and a uranium ore from Elliot Lake. *Can. J. Chem. Eng.* **63**, 650-661 (1985)
- Nagaraj, D.R.: The Chemistry and Application of Chelating or Complexing Agents in Minerals Separations. In: P. Somasundaran and B.M. Moudgil (Eds) *Reagents in mineral technology (Surfactant Science Series, Volume 27)*. Marcel Dekker. New York. (1987)
- Nagaraj, D.R.: The chemistry and applications of chelating or complexing agents in minerals separation. *Surfact. Sci. Ser. (Reagents Miner. Tech.)* **20**, 257–334 (1988)
- Nagaraj, D.R.: Process for improved precious metals recovery from ores with the use of alkylhydroxamate collectors. United States Patent 5126038.
<<http://www.freepatentsonline.com/5126038.html>> (1992)
- Natarajan, R. Synthesis of cupferron-derivatives as mineral collectors for ore-beneficiation. Ph.D. Thesis, Bharathidasan University, India (1995)
- Natarajan, I. Nirdosh and S.V. Muthuswami.: Flotation of a copper–zinc ore using *p*-nonylcupferron as collector. *Dev. Chem. Eng. Miner. Process.* **5**, 183–193 (1997)
- Natarajan, R. and I. Nirdosh.: *N*-arylhydroxamic acids as mineral collectors for ore-beneficiation. *Can. J. Chem. Eng.* **79**, 941–945 (2001)
- Natarajan, R. and I. Nirdosh.: Application of topochemical, topostructural, physicochemical and geometrical parameters to model the flotation efficiencies of *N*-arylhydroxamic acids. *Int. J. Miner. Process.* **71**, 113-129 (2003)
- Natarajan, R. and I. Nirdosh.: New collectors for sphalerite flotation. *Int. J. Miner. Process.* **79**, 141-148 (2006)
- Nirdosh, I. and R. Natarajan.: *p*-Heptylcupferron as collector for flotation of zinc from a Canadian copper-rougher-tails. *Metallforschung.* **56**, 366–371 (2002)
- Nirdosh, I., R. Natarajan, S.V. Muthuswami and R. Jeyaraman.: Effect of substituent on the performance of cupferron as a collector for uranium. *Dev. Chem. Eng. Miner.* **4**, 202 (1994)

- Old Bridge Chemicals., Copper Sulfate MSDS. Old Bridge, NJ.
<http://www.oldbridgechem.com/_docs/MSDS_Basic_Copper_Sulfate_Rev2.pdf> (2007)
- Osipow, Lloyd I.: Surface Chemistry- Theory and Industrial Applications. Reinhold Publishing Corporation. New York. (1962) p 473
- Parsonage, P.G.: Effects of slime and colloidal particles on the flotation of galena. *Dev. Miner. Process.* **6**, 111–139 (1985)
- Perry, R.H. and D.W. Green. *Perry's Chemical Engineers' Handbook* (8th Edition).. McGraw-Hill. (2008) pp 2-8- 2-27
- Prabhakar, S and P.R. Khangaonkar.: Flotation and adsorption studies of chalcopyrite with cupferron. *Intl. J. Miner. Process.* **9**, 87-95 (1982)
- Pradip.: The surface properties and flotation of rare earth minerals, PhD. Thesis, University of California, Berkeley. (1981)
- Pradip and D.W. Fuerstenau.: The adsorption of hydroxamate on semi-soluble minerals. Part I: Adsorption on barite, Calcite and Bastnaesite. *Colloids Surf.* **8**, 103-119 (1983)
- Pradip.: Applications of chelating agents in mineral processing. *Miner. Metall. Process.* **5**, 80–89 (1988)
- Raghavan, S., and D.W. Fuerstenau.: The adsorption of aqueous octylhydroxamate on ferric oxide. *J. Colloid Interface Sci.* **50**, 319-330 (1975)
- Rashchi, F., C. Sui and J.A. Finch.: Sphalerite activation and surface Pb ion concentration, *Int. J. Miner. Process.* **67**, 43-58 (2002)
- Sparks, D. L.: *Environmental Soil Chemistry*. 2nd Edition, Academic Press, New York. (2003) p 267
- Somasundran, P. and K.P. Anandthupadmanabhan. Role of Dissolved Mineral Species_in Calcite- Apatite Flotation. *Colloids Surf.* **20**, 145 (1985)
- Somasundaran, P., D.R. Nagaraj and O.E. Kuzugudenli.: Chelating agents for selective flotation of minerals. In: *Proceedings of the XVIII International Mineral Processing Congress*, 577–585 (1993)
- Trahar, W.J., G. D. Senior, G. W. Heyes and M. D. Creed.: The activation of sphalerite by lead -- a flotation perspective. *Int. J. Miner. Process.* **49**, 121-148 (1997)
- Urbina, R.H.: Surface properties and flotation behavior of chrysocolla in the presence of potassium octyl hydroxamate, Ph.D. Thesis, University of California, Berkeley (1985)

United States Geological Survey (USGS).: Zinc: World Mine Production (zinc content of concentrate) by Country. 2006 Minerals Yearbook: Zinc. Table 15. Washington D.C. <<http://minerals.usgs.gov/minerals/pubs/commodity/zinc/myb1-2006-zinc.pdf>> (2006)

Vivian, A.C.: Flotation of tin ores. *Miner. Mag.* **36**, 348–351 (1927)

Wandelt, K. and S. Thurgate.: *Solid- Liquid Interfaces Macroscopic Phenomena- Microscopic Understanding*. Springer. New York. (2003) p 444

Ward's Natural Science Establishment, Inc., St Catharines, Ontario, Canada.

Wills, B.A.: *Mineral Processing Technology*. 5th Edition. Pergamon Press. Oxford. (1992) pp 491-694

Yale, H.L.: The Hydroxamic Acids. *Chem. Rev.* **33**, 209-256 (1943)

Appendix A- Mineral analysis

Table 10. Solution pH and conductivity of various pure minerals when agitated with de-ionized water.

Equilibration time: 4 hrs

	pH	Conductivity ($\mu\text{S}/\text{cm}$)
<i>De-ionized water</i>	6.53	7.3
Sphalerite	7.06	10.1
Chalcopyrite	5.85	218.4
Galena	6.20	181.5
Pyrrhotite	5.57	269.0
Pyrite	2.78	408.0
Quartz	7.17	10.2

Table 11. Concentration of free metal ions present in de-ionized water after agitated with various pure minerals.

Equilibration time: 4 hrs

	ZnS	PbS	CuFeS	Fe _(1-x) S _(x=0 to 0.2)	FeS	SiO ₂
Zn ²⁺	0.641	0.0548	1.56	0.0208	1.28	0.0054
Fe ³⁺	0.0032	0.0020	0.0068	0.0513	22.8	0
Cu ²⁺	0.0024	0.0019	0.0121	0.0012	0.403	0.0034
Pb ²⁺	0.0056	0.0069	0	0.0049	0.0125	0.0123

Appendix B- Data for Adsorption

Table 12. Specific adsorptions of various pure minerals at given time intervals for equilibration time analysis.

HCNPHA feed solution pH: 9.0 ± 0.1

Time (min)	Sphalerite specific adsorption (mg/g)	Galena specific adsorption (mg/g)	Pyrite specific adsorption (mg/g)	Chalcopyrite specific adsorption (mg/g)	Quartz specific adsorption (mg/g)
0	0	0	0	0	0
10	6.20	5.31	15.73	24.17	0.63
20	7.20	5.59	17.74	27.09	1.60
30	9.35	6.09	20.47	26.55	2.03
60	10.62	6.70	30.20	27.61	2.31
120	10.70	6.68	31.60	27.64	2.33
240	10.74	6.77	31.71	27.89	2.33

Table 13. Equilibrium concentration in solution and the corresponding specific adsorption of HCNPHA on sphalerite.

HCNPHA feed solution pH: 9.0 ± 0.1

Equilibration time: 4 hrs

Equilibrium Concentration (mg/L)	Specific Adsorption (mg/g)
0	0
18.4	4.35
29.8	6.75
44.1	7.16
57.2	7.36
70.6	7.36
99.1	7.16
141.0	7.32
141.0	7.16

Table 14. Equilibrium concentration in solution and the corresponding specific adsorption of HCNPHA on galena.

HCNPHA feed solution pH: 9.0 ± 0.1

Equilibration time: 4 hrs

Equilibrium Concentration (mg/L)	Specific Adsorption (mg/g)
6.2	0.54
11.9	1.19
15.1	2.62
22.1	2.89
26.7	3.92
41	4.53
58.3	6.49
56.6	6.78
134.9	6.85
153.3	6.76

Table 15. Equilibrium concentration in solution and the corresponding specific adsorption of HCNPHA on pyrite.

HCNPHA feed solution pH: 9.0 ± 0.1

Equilibration time: 4 hrs

Equilibrium Concentration (mg/L)	Specific Adsorption (mg/g)
21.2	4.20
25.7	9.04
32.8	10.59
45.6	15.60
68.0	17.91
120.9	34.59
130.0	34.77
131.1	35.08
156.6	34.87
203.9	34.97

Table 16. Equilibrium concentration in solution and the corresponding specific adsorption of HCNPHA on chalcopyrite.

HCNPHA feed solution pH: 9.0 ± 0.1

Equilibration time: 4 hrs

Equilibrium Concentration (mg/L)	Specific Adsorption (mg/g)
7.1	3.79
12.0	7.98
21.8	10.86
21.4	15.46
40.2	22.26
52.1	27.10
107.1	27.64

Table 17. Equilibrium concentration in solution and the corresponding specific adsorption of HCNPHA on quartz.

HCNPHA feed solution pH: 9.0 ± 0.1

Equilibration time: 4 hrs

Equilibrium Concentration (mg/L)	Specific Adsorption (mg/g)
26.4	0.36
49.2	0.70
70.6	0.86
95.0	1.38
112.8	2.19
162.7	2.35
235.7	2.38

Table 18. Equilibrium concentration in solution and the corresponding specific adsorption of HCNPHA on sphalerite.

HCNPHA feed solution pH: 10.0 ± 0.1

Equilibration time: 4 hrs

Equilibrium Concentration (mg/L)	Specific Adsorption (mg/g)
0	0
0	1.54
0	0.61
14.4	2.11
59.6	2.42
108.3	2.53
161.4	2.29
203.3	2.77
301.5	2.96
401.1	2.88
451.9	2.88
547.7	3.16

Table 19. Equilibrium concentration in solution and the corresponding specific adsorption of HCNPHA on galena.

HCNPHA feed solution pH: 10.0 ± 0.1

Equilibration time: 4 hrs

Equilibrium Concentration (mg/L)	Specific Adsorption (mg/g)
0	0
13.7	0.68
27.9	1.32
64.4	2.12
90.5	3.58
128.4	4.38
177.8	4.31
250.4	5.95
387.1	6.74

Table 20. Equilibrium concentration in solution and the corresponding specific adsorption of HCNPHA on pyrite.

HCNPHA feed solution pH: 10.0 ± 0.1

Equilibration time: 4 hrs

Equilibrium Concentration (mg/L)	Specific Adsorption (mg/g)
0	0
79.5	10.55
143.3	20.18
183.8	22.60
321.4	26.96
344.2	28.35
359.3	28.83
397.7	29.30

Table 21. Equilibrium concentration in solution and the corresponding specific adsorption of HCNPHA on chalcopyrite.

HCNPHA feed solution pH: 10.0 ± 0.1

Equilibration time: 4 hrs

Equilibrium Concentration (mg/L)	Specific Adsorption (mg/g)
0	0
7	9.80
28.8	14.06
42	18.18
130.1	21.82
241.6	25.18
308.9	22.84
335.9	23.65
380.9	24.00
411.7	25.79

Table 22. Equilibrium concentration in solution and the corresponding specific adsorption of HCNPHA on quartz.

HCNPHA feed solution pH: 10.0 ± 0.1

Equilibration time: 4 hrs

Equilibrium Concentration (mg/L)	Specific Adsorption (mg/g)
0	0
14	0.049
28.5	0.073
42.8	0.11
56.9	0.16
71.5	0.17
100.2	0.24
145.3	0.24

Appendix C- Microflotation data

Table 23. Flotation response at various time intervals at pH 9.

[HCNPHA]: 50 mL of 150 ppm added; pH: 9.0 ± 0.1

Air flow: 0.30 L/min;

HCNPHA conditioning time: 10 min

Collection time (min)	Flotation Response (%)				
	Sphalerite	Galena	Chalcopyrite	Pyrite	Quartz
1	17.2	37.7	16.9	19.5	12.7
3	30.6	46.1	24.0	36.8	20.5
5	44.9	50.6	38.4	42.4	32.8
8	60.6	57.2	41.2	40.8	33.3
12	58.9	58.1	42.5	38.6	33.7
20	61.2	59.1	42.0	39.7	33.7

Table 24. Effect of pH and concentration of HCNPHA on sphalerite flotation response.

HCNPHA: 50 mL of 150 ppm, 300 ppm, and 600 ppm; Air flow: 0.30 L/min

HCNPHA conditioning time: 20 min;

Mineral collection time: 10 min

pH	Flotation Response (%)		
	600 ppm	300 ppm	150 ppm
11	90.9	43.6	43.1
10	91.5	67.4	52.8
9	93	87.1	62.5
8	89.9	80.6	51.7
7	81.8	76.8	51.6

Table 25. Effect of pH and concentration of HCNPHA on galena flotation response.

HCNPHA: 50 mL of 75 ppm, 150 ppm, and 300 ppm; Air flow: 0.30 L/min

HCNPHA conditioning time: 20 min;

Mineral collection time: 10 min

pH	Flotation Response (%)		
	300 ppm	150 ppm	75 ppm
11	95.2	91.8	51.9
10	93.9	90.3	79.9
9	90.5	92.9	90.6
8	87.3	90.7	89.4
7	85.7	88.1	89.0

Table 26. Effect of pH and concentration of HCNPHA on pyrite flotation response.

HCNPHA: 50 mL of 300 ppm, 600 ppm, and 1200 ppm; Air flow: 0.30 L/min

HCNPHA conditioning time: 60 min;

Mineral collection time: 10 min

pH	Flotation Response (%)		
	1200 ppm	600 ppm	300 ppm
11	65.1	60.2	57.7
10	51.7	41.5	40.2
9	35.4	34.8	37.9
8	35.7	36.2	35.7
7	-	42.2	35.8

Table 27. Comparison of flotation response of sphalerite, galena and pyrite for 3 mg/g collector dosage.

HCNPHA: 50 mL of 300 ppm;

Air flow: 0.30 L/min

Conditioning time: 20 min for sphalerite and galena, 60 min for pyrite

Mineral collection time: 10 min

pH	Mineral recovery (%)		
	Sphalerite	Galena	Pyrite
11	43.6	95.2	57.7
10	67.4	93.9	40.2
9	87.1	90.5	37.9
8	80.6	87.3	35.7
7	76.8	85.7	35.8

Table 28. Effect of modifiers on flotation response of sphalerite at 3 mg/g collector dosage.

HCNPHA: 50 mL of 300 ppm;

Air flow: 0.30 L/min

Modifier(s) conditioning time: 5 min;

pH HCNPHA: 9.0 ± 0.1

HCNPHA conditioning time: 20 min;

Mineral collection time: 10 min

<i>Modifier(s)</i>	<i>% floated</i>
None	87.3
ZnSO ₄	68.9
MBS	86.2
NaCN	85.9
ZnSO ₄ + MBS + NaCN	59.8
ZnSO ₄ + MBS + NaCN + CuSO ₄	82.3
CuSO ₄	82.8
1mg MIBC	90.1
ZnSO ₄ + MBS + NaCN	56.8
ZnSO ₄ + MBS + NaCN + CuSO ₄	80.5
CuSO ₄	81.6

Table 29. Effect of co-reagents on flotation response of sphalerite at 6 mg/g collector dosage.

HCNPHA: 50 mL of 600 ppm;

Air flow: 0.30 L/min

Modifier(s) conditioning time: 5 min;

pH HCNPHA: 9.0 ± 0.1

HCNPHA conditioning time: 20 min;

Mineral collection time: 10 min

<i>Modifier(s)</i>	<i>% floated</i>
None	93.0
ZnSO ₄	89.9
MBS	93.2
NaCN	91.9
ZnSO ₄ + MBS + NaCN	79.4
ZnSO ₄ + MBS + NaCN + CuSO ₄	90.2
ZnSO ₄ + MBS + NaCN	79.0
ZnSO ₄ + MBS + NaCN + CuSO ₄	90.1

Appendix D- *d*-spacing of pure minerals

Table 30. Composition and *d*-spacing for sphalerite.

Constituents	SS-NNNN	Formula	2θ (°)	<i>d</i> -spacing	% Composition
Sphalerite	05-0566 (I)	ZnS	28.518	3.12739	90.8
			33.010	2.77141	
			47.438	1.91497	
			56.303	1.63266	
			58.981	1.56475	
			69.375	1.35354	
			76.651	1.24217	
			78.990	1.21114	
			88.378	1.10512	
Quartz	46-1045 (C)	SiO ₂	20.693	4.28904	9.2
			26.635	3.34408	

Table 31. Composition and *d*-spacing for galena.

Constituents	SS-NNNN	Formula	2 θ (°)	<i>d</i> -spacing	% Composition
Lead Sulfide	78-1056 (C)	PbS	25.927	3.43371	100
			30.084	2.96805	
			43.057	2.09911	
			50.994	1.78946	
			53.426	1.71361	
			62.516	1.48451	
			68.854	1.36251	
			70.979	1.32684	
			74.670	1.26882	
			78.985	1.21120	
			84.830	1.14204	

Table 32. Composition and *d*-spacing for pyrite.

Constituents	SS-NNNN	Formula	2θ (°)	<i>d</i> -spacing	% Composition
Pyrite	71-2219 (C)	FeS ₂	28.523	3.12686	94.6
			33.048	2.70836	
			37.123	2.41990	
			38.096	2.36029	
			47.416	1.91579	
			50.493	1.80604	
			56.312	1.63242	
			59.034	1.56348	
			61.706	1.50203	
			64.284	1.44788	
			76.573	1.24323	
			78.937	1.21182	
			81.293	1.18255	
			83.609	1.15558	
88.245	1.0644				
Bornite	02-1304 (C)	Cu ₅ FeS ₄	18.337	4.83449	3.3
Quartz, low	05-0490 (C)	SiO ₂	36.597	2.45343	2.1
			54.919	1.67049	

Table 33. Composition and *d*-spacing for chalcopyrite.

Constituents	SS-NNNN	Formula	2θ (°)	<i>d</i> -spacing	% Composition
Chalcopyrite	83-0984 (C)	CuFeS ₂	29.340	3.04162	81.2
			33.832	2.64737	
			48.950	1.85929	
			57.875	1.59201	
			58.600	1.57402	
			60.883	1.52035	
			71.267	1.32218	
			79.465	1.20510	
			81.430	1.18090	
Iron Sulfide	23-1123 (I)	FeS	28.513	3.12799	18.8
			33.040	2.70899	
			47.441	1.91484	
			56.314	1.63237	
			69.408	1.35297	
			76.710	1.24136	
			78.840	1.21307	
			88.416	1.10474	

Appendix E- Powder X-ray data

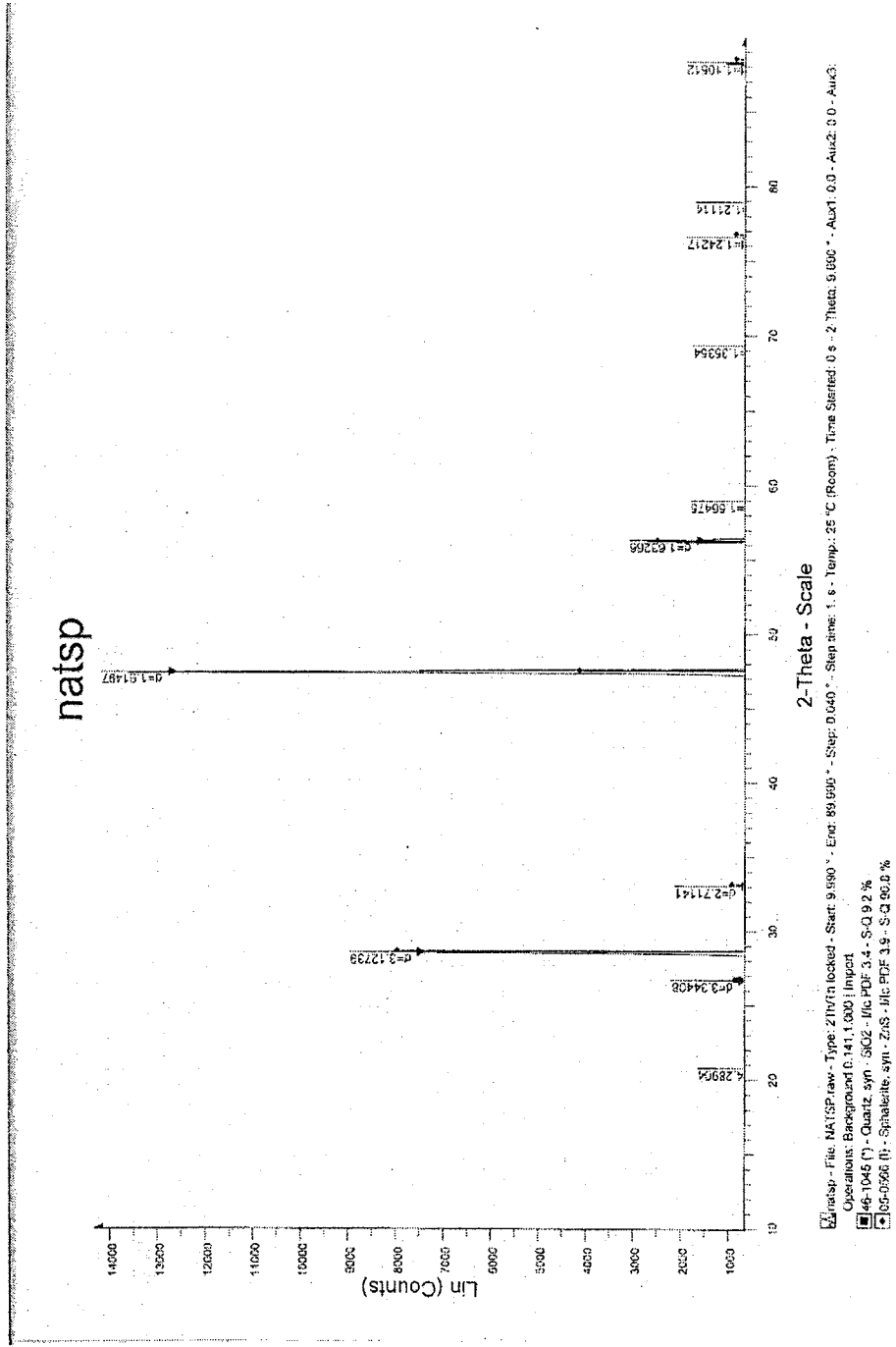


Fig. 18. Powder X-ray diffraction data for sphalerite

Fig. 18. Powder X-ray diffraction data for sphalerite.

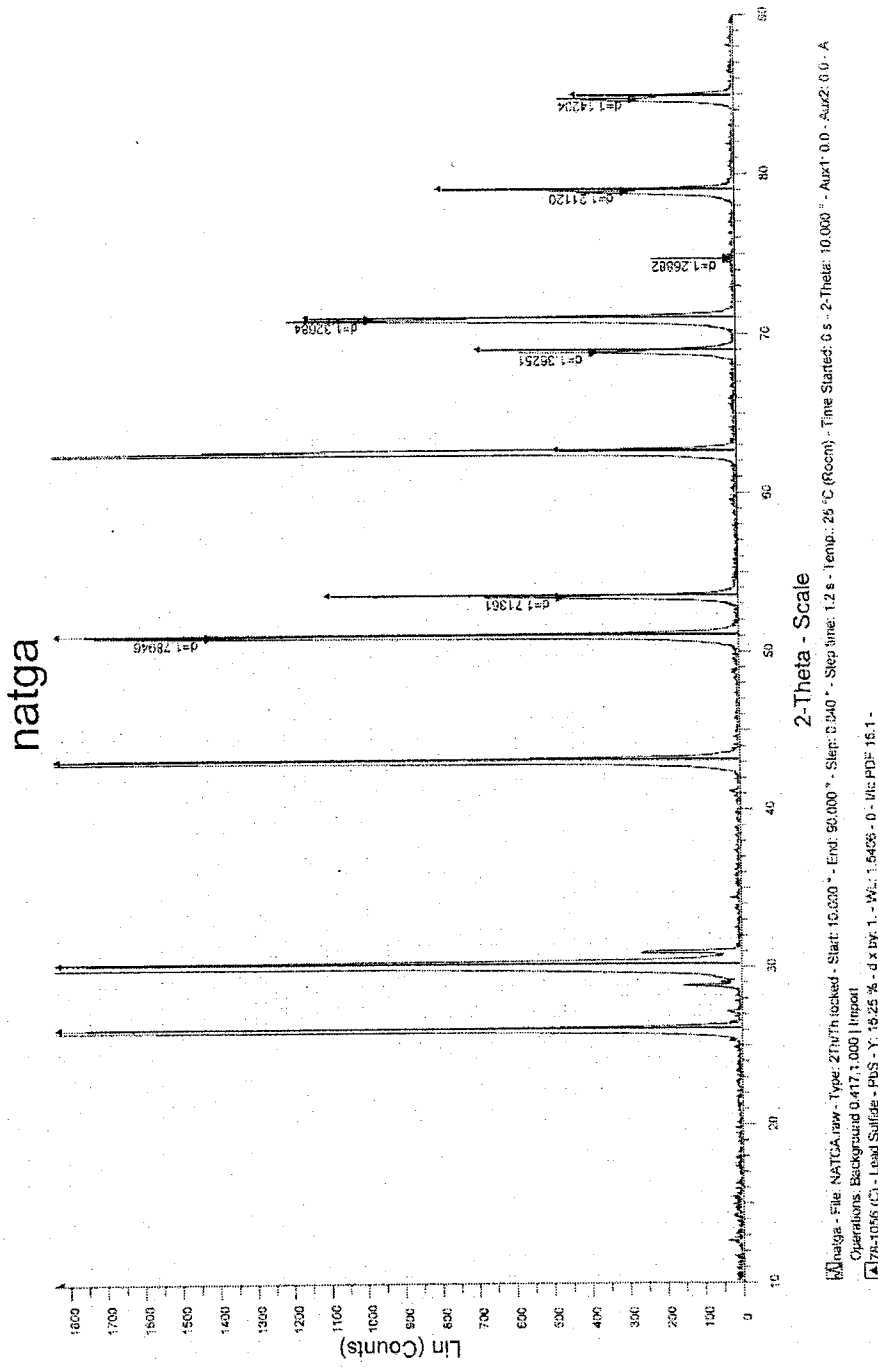


Fig. 19. Powder X-ray diffraction data for galena.

Fig. 19. Powder X-ray diffraction data for galena.

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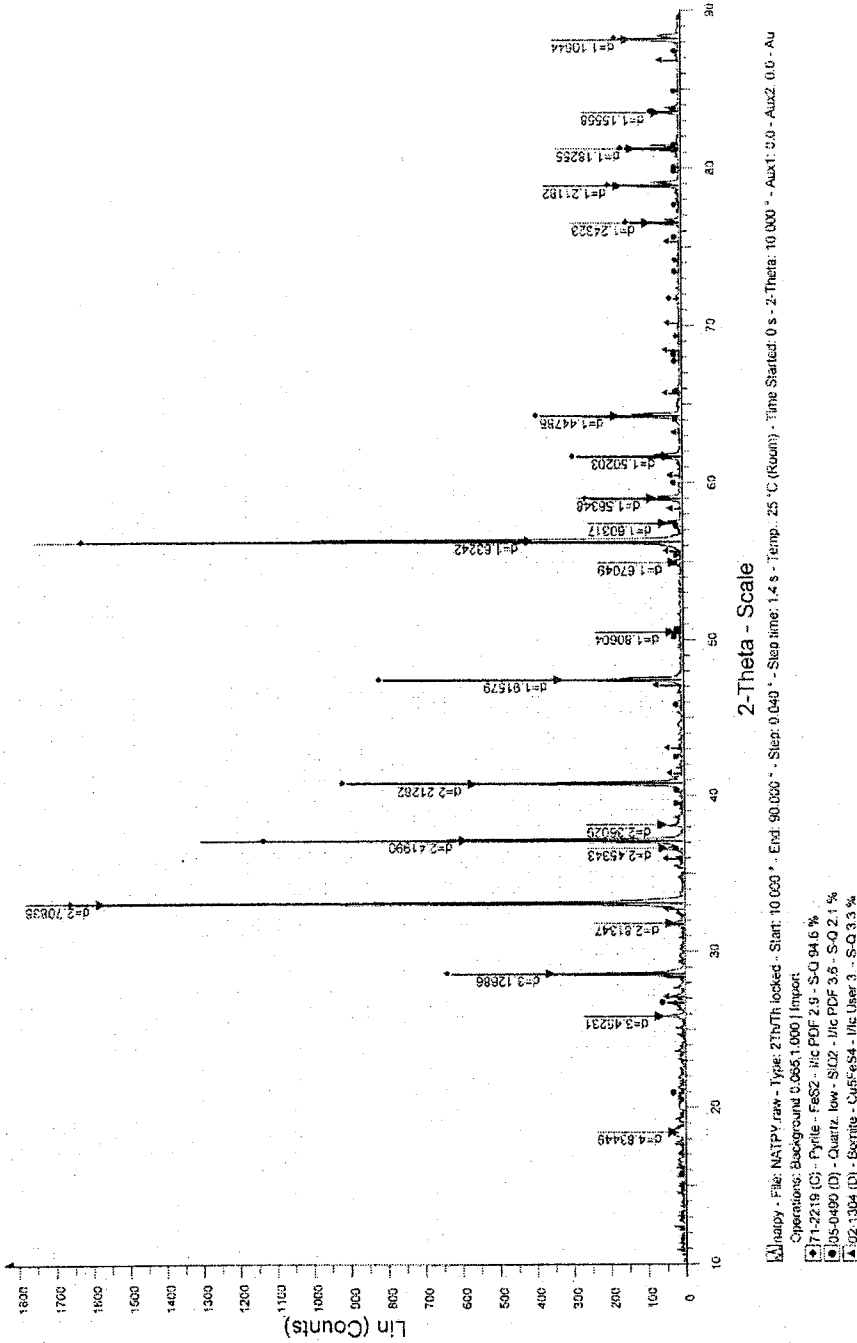


Fig. 20. Powder X-ray diffraction data for pyrite.

Fig. 20. Powder X-ray diffraction data for pyrite.

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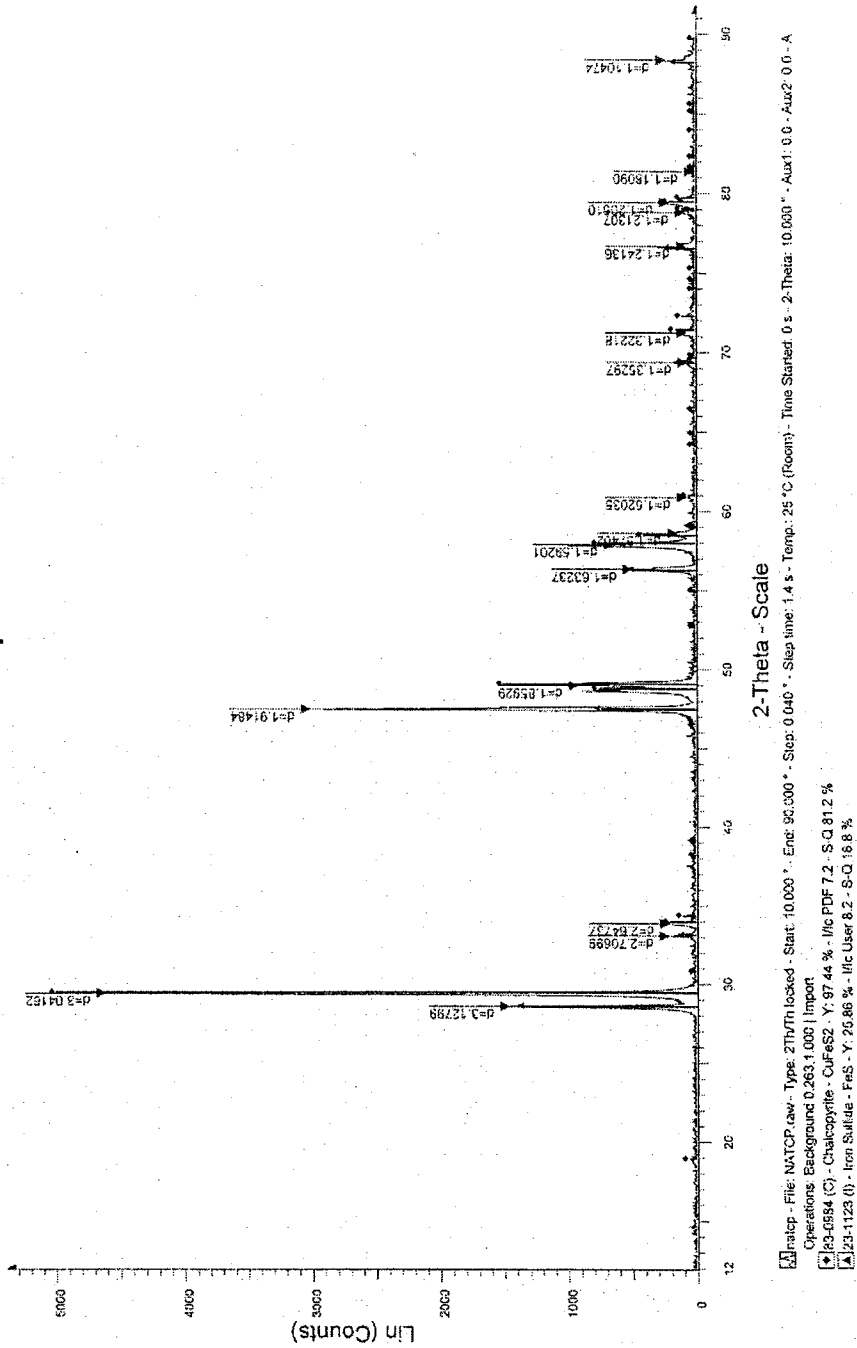


Fig. 21. Powder X-ray diffraction data for chalcopyrite.

Fig. 21. Powder X-ray diffraction data for chalcopyrite.