THE FLOTATION OF PYRITE USING XANTHATE COLLECTORS

by

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Submitted to the University of Cape Town in fulfilment of the requirements for the degree of Master of Science in Engineering

April 1986

ACKNOWLEDGEMENTS

I would like to thank

The Council for Mineral Technology (MINTEK) for having sponsored this project

Associated Professor O'Connor of the Department of Chemical Engineering for his supervision

Mr R. Dunne of MINTEK for his assistance and interest in the project

Dr J.P. Franzidis of the Department of Chemical Engineering for his assistance

Dr P. Harris of MINTEK for his assistance

The staff of the Chemical Engineering Department for their assistance and interest

The Mineral Proccesing group of the Chemical Engineering Department

Mrs Petro Human for her assistance in typing

ABSTRACT

The flotation properties of pyrite were found to be significantly influenced by variations in the pH. In acidic solutions the pyrite floatability is very high, and recoveries of 95% could be achieved using only a frother. A sharp decrease in floatability was observed in alkaline solutions, possibly due to the formation of hydrophilic ferric hydroxide. The addition of a xanthate collector improved the flotation properties of pyrite at all pHs. In acidic solutions the main effect observed was on the rate of pyrite recovery and on the grade of the concentrates. In alkaline solutions the addition of a xanthate collector improved the final recovery, the rate of flotation and the grades. Variations in the pH had no effect on the recovery of pyrite to which xanthate was added. There was, however, a continual decrease in the final grade of the concentrates with an increase in pH, due to the increase in the recovery of the gangue mineral.

Oxidation of pyrite in air showed a marked effect on the flotation properties of pyrite. In alkaline surroundings the recoveries were reduced by 30%. This effect was not observed during flotation in acidic solutions, since in situ leaching was taking place thus removing the oxidation products from the pyrite surface. The effects of oxidation were also altered by acid leaching the pyrite before flotation.

The use of different types of xanthate collectors did not show any effect on the floatability of pyrite, as the final recoveries were not affected. They had however a significant effect on the final grade of the concentrates. The longer the hydrocarbon chain of the collector, the better the grade. The use of a normal xanthate resulted in better grades than when its isomer used.

The variation of the concentration of the xanthate collector showed no effect on the floatability of pyrite as the recoveries were not affected. A significant increase in the final grade was observed with an increase in the collector concentration. This observation, that an increase in xanthate concentration and hydrocarbon chain length increased the grade of the concentrates, is attributed to the fact that both of these factors increase the hydrophobicity of the pyrite and thus enhance elutriation in the froth phase.

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INTRODUCTION

1.1 PRINCIPLES OF FLOTATION

The intense exploitation of rich ore bearing deposits which has taken place over the last century, caused an increased interest in the economic exploitation of vast but poor ore bearing deposits. Therefore, it became necessary to develop methods of concentrating the desired mineral. Flotation is a method of ore enrichment developed over the last years which serves this need and thus covers a wide and still growing field of application.

Froth flotation is a method of separating minerals based on differences in the physicochemical characteristics of mineral surfaces. These surfaces, after crushing, result in a greater or lesser affinity towards being wetted by water. Water molecules behave as dipoles and therefore tend to wet the polar mineral surface to an extent which is dependent on the degree of polarity and the previous history of the mineral. The less the water-avid behaviour, the more hydrophobic is the mineral. Therefore, if air comes into a contact with the mineral-water interface, rupture of the water film occurs, and the air bubbles become attached to the mineral surface (see Figure 1.1). Young's equation

$$\gamma_{sg} = \gamma_{lg} * \cos\theta + \gamma_{sl}$$

expresses the thermodynamic of the system, where γ_{sg}, γ_{lg}, γ_{sl} are the surface tensions between gas-solid , liquid-gas, and solid-liquid interfaces, and θ is the contact angle. The change in the free energy accompanying the replacement of a unit area of the solid-liquid interface by solid-gas interface, is given by the Dupre's equation, viz.

$$\Delta G = \gamma_{sg} - (\gamma_{sl} + \gamma_{lg})$$

The combination of Dupre's equation with Young's equation, yields the following expression for the free energy change, viz.(Fuerstenau and Raghavan, 1976)

$$\Delta G = \gamma_{lg} * (\cos\theta - 1)$$

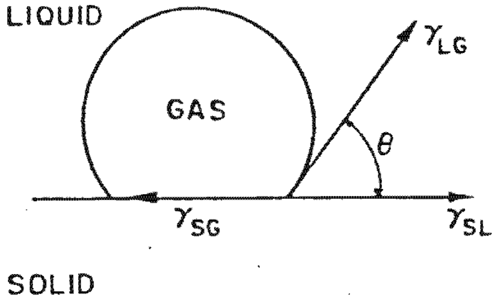


Figure 1.1 Schematic representation of the equilibrium contact between an air bubble and a solid immersed in a liquid. The contact angle θ is the angle between the liquid/gas and the liquid/ solid interfaces, measured through the liquid.

Thus, for any finite value of the contact angle there will be a free energy decrease upon attachment of a mineral particle to an air bubble. This equation also shows that the higher the contact angle, the stronger the attachment between air and mineral. Some mineral surfaces, if they are carefully cleaned, can be perfectly wetted, e.g. quartz, while others have an almost zero contact angle, e.g. graphite, talc and pyrophyllite.

When a solid is immersed in an aqueous solution, a region of electrical heterogeneity is produced at the solid-solution interface. An excess charge, apparently fixed at the solid surface, is counterbalanced by a diffuse region of equal but opposite charge on the aqueous side. This region, the surface charge and its counter-ions in the aqueous phase, is referred to as the electrical double layer. Figure 1.2 is a simplified model of the electrical double layer, showing the solid surface charge, and the diffuse layer of counter-ions extending out into the aqueous phase. The closest distance of approach of the ions δ, defines the location of the Stern plane. Figure 1.2 also shows a drop in potential across the double layer. (Fuerstenau and Raghavan, 1976)

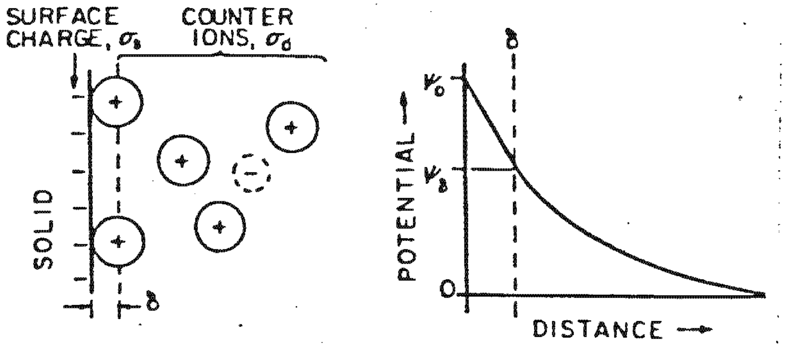


Figure 1.2 Schematic representation of the electrical double layer and the potential drop across the double layer at a solid/water interface.

Some of the ions of the solution, the nature of which is dependent on the particular system, show a strong inclination to be adsorbed onto the mineral surface and in the Stern plane. These ions, called potential determining ions, are of great importance as their presence can enhance or reduce the adsorption of flotation reagents. For sulphides for example, hydrogen and hydroxyl ions have long been considered to be potential determining ions, although the mechanism whereby pH governs the surface charge is still speculative. When pyrite is immersed in water, a change of the pH of the solution will markedly affect the magnitude and even the sign of the surface charge. This in turn will affect the flotation properties of the mineral.

Modification of the mineral surface with flotation reagents can intensify the hydrophobic or hydrophilic properties of the minerals so that they can be selectively separated. A close study of the surface characteristics of the minerals in aqueous solutions, by means of measuring the surface charge, and of the interaction with the counter-ions present in solution, can assist us in succesfully selecting the type of flotation reagents, which can be adsorbed onto the mineral surface increasing its hydrophobic or hydrophilic properties.

mineralized froth thus becomes so heavy that mineral patricles start dropping back into the pulp. (Wark and Sutherland, 1955). The increase in the collector concentration influences also the hydrophobicity of the particles viz. causes an increase in the value of contact angle. Dippenaar (1978) showed that particles with contact angles greater than 74° can cause thinning of the liquid films in the froth phase by attempting to establish equilibrium position. This results in the rupture of the films and destabilization of the froth. He also showed that the type, condition and size of the particles can have a dramatic effect on the stability of the froth, and in some systems, changes to the froth stability may be brought about more easily by modifying, for example, the particle hydrophobicity or the degree of flocculation rather than by changing the type of frother used (Harris, 1982; Dippenaar, 1978).

According to their molecular dissociative properties, collectors are classified into two major groups viz. ionizing and non-ionizing collectors.

1.2.1.1 Ionizing collectors.

Ionizing collectors are complex molecules which are asymmetric in structure and heteropolar. The non-polar hydrocarbon end is hydrophobic whereas the polar group is hydrophilic. Because of the electrostatic atttaction between the polar portions and the mineral surface sites, the collectors adsorb onto the particles with their nonpolar ends oriented towards the bulk of the solution, thereby inducing hydrophobicity to the particles. According to the charge of their polar ends they are distinguished as anionic or and cationic collectors. (Glembotskii, Klassen, and Plaskin, 1972)

Anionic collectors: These are the most widely used collectors, and are classified according to the structure of the polar group. The most important are:

a) Oxydryl collectors. These are organic acids or soaps, which are salts of alkali metals and organic acids. The surface active group is represented by the carboxyl $-C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow O^-}$ Oxydryl reagents such as oleic acid, sodium oleate, etc. have found wide application in flotation of minerals having a crystalline lattice with alkali earth metals as cations, and also in flotation of certain rare oxidized ferrous and non-ferrous metals (e.g. carbonates, oxides and sulfates). (Glembotskii et al, 1972)

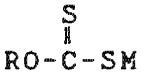
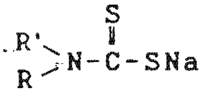
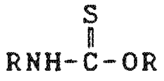
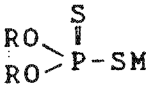
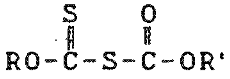
b) Sulphates and sulphonates They have the following general chemical structure

$$R-O-\overset{O}{\underset{O}{S}}-O^- \quad ; \qquad R-\overset{O}{\underset{O}{S}}-O^{--}$$

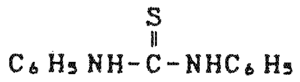
These reagents are extensively used as wetting agents, but have also found application as collectors for both sulphide and non-sulphide minerals. Their frothing properties in alkaline pulps limit their usefulness (Senmin handbook; Glembotskii et al, 1972).

c) Sulphydric collectors. These collectors are of the greatest practical importance. They are used widely for the flotation of sulphide minerals. Here, the polar group of the collector consists of a single bivalent sulphur atom bonded either to a carbon or to a phosphorous atom.

Derivatives are:

xanthates	 $RO-\overset{\overset{S}{\parallel}}{C}-SM$	(M=Na or K)
Dithiocarbamates	 $\genfrac{}{}{0pt}{}{R'}{R}{>}N-\overset{\overset{S}{\parallel}}{C}-SNa$	(R' =R or H)
Thionocarbamates	 $RNH-\overset{\overset{S}{\parallel}}{C}-OR$	
Dithiophosphates	 $\genfrac{}{}{0pt}{}{RO}{RO}{>}\overset{\overset{S}{\parallel}}{P}-SM$	(M=H, NH_4 or metal)
Xanthogen formates	 $RO-\overset{\overset{S}{\parallel}}{C}-S-\overset{\overset{O}{\parallel}}{C}-OR'$	

Thiocarbanilide



$$C_6H_5NH-\overset{\overset{\displaystyle S}{\|}}{C}-NHC_6H_5$$

Because of this similarity in structure, substantially all of the sulphide minerals can be floated with varying degree of success by any of the sulphydric collectors. The most widely applied collectors of this group are the xanthates and the dithiophosphates. This wide application is due to a combination of low cost and high collecting power (Senmin handbook).

d) **Organic sulphides.** Over the years, many sulphides have been evaluated as collectors for sulphide minerals, and all have collecting strength in varying degree. The most important collectors of this group are; the mercaptans which have the general formula RSH, and are selective collectors for the flotation of copper minerals; 2-mercaptobenzothiazole which is a good collector for oxidized and partially oxidized gold ores. Since it does not adsorb on sphalerite it can be used in differential flotation (Senmin handbook).

Cationic collectors: The most important members of this group of collectors are the alkylamines such as dodecylamine, and certain organic quaternary ammonium salts. Since these collectors are basic, they are used for flotation of acidic minerals such as silicates. Their collecting properties for minerals such as tungstates, molybdenates and chromates, have also been demonstrated.

1.2.1.2 Non-ionizing collectors

Non-ionizing collectors are non polar compounds which are practically insoluble in water. They render the mineral water-repellent by covering its surface with a thin film. (Glembotskii et al, 1972). A number of non-polar hydrocarbons and oils such as kerosene, naphtha, fuel oils and various resins are included in this class. These compounds are used either alone for readily or naturally floatable minerals such as graphite and coal, or together with conventional collectors to "extend" the hydrophobic effect of the collector (Lovell, 1982).

1.2.2 FROTHERS

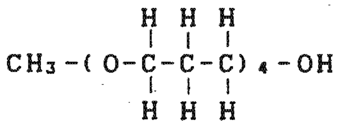
When mineral particle surfaces have been rendered water-repellent by a collector, stability of bubble attachment to these particles depends to a considerable extent on the efficiency of the frother. Pure liquids of nonpolar, polar or heteropolar structure, do not form a stable froth when agitated in the presence of air. The bubbles which are produced by agitation break down very quickly and rapidly coalesce, forming larger and even less stable bubbles. However, if a small amount of a heteropolar surface active substance (for example alcohol) is added to the water, a fairly stable froth will be formed as a result of agitation or the introduction of air in dispersed form. The mechanism of frothing is due to the heteropolar nature of the frother molecules or ions, just as collection is due to the heteropolar nature of collectors. The distinction is that, in case of a frother one portion of the molecule is still hydrophobic (the hydrocarbon chain) and orientates itself towards the gas phase while the other portion of the molecule is still hydrophilic, that is it shows an affinity for water rather than for solid surfaces, and orientates itself towards the water face.

The result of the adsorption of the frother molecules or ions in the water-air interface is the reduction of the surface tension of water. This results in the formation of smaller bubbles, keeps them dispersed for relatively long periods, and prevents them coalescing. Additionally, the bubble's mechanical strength increases, and adsorption layers produced in bubble skins, reduce the speed of bubble movement in the pulp. Thus, bubble contact with the mineral particle is prolonged, creating more favorable conditions for attachment (Glembotskii et al, 1972).

General requirements for a good flotation frother are: (Harris, 1982)

1. The stability of the froth formed must be such that a further degree of separation of the valuable mineral from the non-floatable (entrained) materials is obtained in the froth.
2. Once the froth containing the valuable mineral is removed, it must break readily for any further treatment.
3. It must form a froth of sufficient volume and stability to act as a medium of separation at low concentrations.
4. In the case of the neutral frother, it should have limited collecting tendencies.
5. It must possess a low sensitivity to changes in pH and dissolved salt concentrations.
6. It should be relatively cheap and abundant for large scale use.

The following are some of the frothers most commonly used today; alcohols such as methylisobutylcarbinol (MIBC), pine oil, cresylic acid, polyalkoxyl paraffin, triethoxybutane (TEB), and polypropyleneglycolethers. The frother used in this investigation was polypropylene glycol methyl ether (DOWFROTH 250), with the following stuctural formula (Klimpel and Hansen, 1981):



$$CH_3-(O-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}})_4-OH$$

1.2.3 REGULATORS

Regulators are reagents used for improving recovery and selectivity in flotation. Collectors only lower the wettability of different minerals, whereas regulators may favour or hinder it. In addition, they are used to decrease the ill-effects of many of the ions present in the flotation pulp. They are also used for freeing mineral surfaces from surface complexes which hinder selectivity.

The most important groups that are distinguished in literature are (Gaudin, 1932):

1. Depressants. These are reagents which adsorb on the surface of minerals suppressing in turn the adsorption of collectors, and thus reducing the floatability of the minerals.

2. Activators. These are reagents which form films on the surface of minerals which aid adsorption of collectors.

3. pH modifiers. These are substances which are used to control the hydrogen ion concentration in the pulp. In almost all cases a strict control of pH is essential if maximum efficiency is to be achieved in the flotation operation. Lime, because of its low cost is almost universally used to control pH in alkaline circuits. However, in the case of pyrite, it is known to adsorb calcium ions at high pH values which inhibit collector adsorption in the presence of lime. Therefore soda ash and caustic soda are the pH modifiers of choice. In acid pulps sulphuric acid is used to modify the pH in almost all cases.

4. Dispersants. These are the reagents used to "clean" mineral surfaces from slime coating which may inhibit collector adsorption.

It should be made clear though, that the action of regulating reagents is specific to the mineral present in the ore and the substances dissolved in the liquid phase of the pulp. The same reagent can act as a depressant for one mineral and as an activator or a pH regulator for another, or even have two functions at the same time. So an alternative classification by Klassen and Mokroussov (1963), is in electrolytes and non-electrolytes.

1.3 FLOTATION KINETICS

Flotation is a complex interactive engineering system where the study of kinetic effects involves the study of a variety of factors. These factors are generally mentioned as chemical factors, equipment factors, and operating factors (Klimpel, 1985). Chemical factors cover the choice of pH, type and dosage of flotation reagents. Equipment factors involve the cell design, agitation, air flow, cell bank configuration and cell bank control. Operation components involve the feed rate, mineralogy of the ore, particle size, pulp density and temperature. Some of these factors cause variations in the kinetic response of a particular flotation system, while others can significantly affect the physicochemical or potential nature of the system when they influence significantly the final recovery.

The solution to many problems associated with the design or control of flotation circuits is dependent upon the existence of a good mathematical model which can utilize laboratory batch flotation data to predict changes in the plant. In evaluating the effect of changing operating parameters, the recovery profile leading to equilibrium recovery is often more informative than the actual equilibrium recovery itself. Experience in practice with the classical one time point equilibrium recovery approach, has shown that there were poor correlations between plant and laboratory textwork. The addition of the time dimension of rate has proved invaluable in explaining and improving laboratory data to plant scale up. For example consider the flotation response of two different systems, illustrated in Figure 1.3. System 1 results in higher equilibrium recovery while system 2 indicates a higher rate. Depending on the residence time in the flotation plant, System 1 is beneficial if the residence time is higher than the time equal to t_k, while System 2 has better performance if residence time is smaller than t_k. Therefore a study on the response of both flotation parameters rate and equilibrium recovery is significant in order to consider if a change in a parameter's response will be beneficial in plant performances.

Klimpel, (1980), Klimpel et al (1982) and Huber-Panu et al (1976), developed a simple model to calculate equilibrium recoveries and flotation rates, based in the following equation:

$$r=R\ \{1-(1/kt)[1-\exp(-kt)]\}$$

where r is the cumulative recovery at time t, k is the first order rate constant of total mass removal from the cell, and R is the ultimate equilibrium recovery at long flotation times. This type of equation can be applied twice to any given set of time-recovery data, once for the time-recovery profile of the major component to be floated, and once for the time-recovery profile of the gangue component. This allows for a direct comparison of the behaviour of the two components and can be combined with the use of the more standard grade-recovery curve. This model has been used in the present work whenever equilibrium recoveries and flotation rates are recorded.

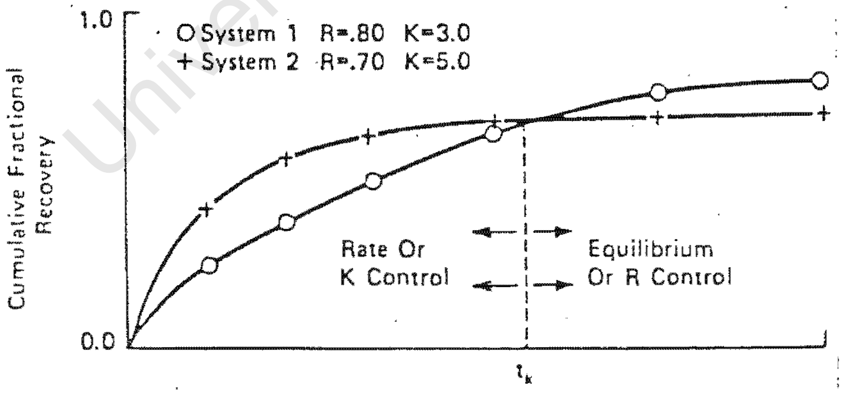


Figure 1.3 An illustration of two laboratory time- recovery profiles run under different conditions.

In fact in some systems a variation of a flotation parameter causes a significant deviation in the final recoveries. In these cases the use of Klimpel model to estimate and compare the rate of the recovery does not seem to be realistic. For this reason the recovery over the first 30 seconds can be used as an indication of initial rates.

1.4 LITERATURE SURVEY

The study of the surface characteristics of pyrite, such as the surface charge, variable reactivity, and the degree of oxidation is a useful way of understanding the processes which are taking place in flotation. A modified mineral surface can undergo reactions with surfactants used as flotation reagents and can then be selectively separated. Xanthates are the most common collectors in pyrite flotation, but the mechanism of their behaviour as collectors is not yet completely understood. In recent years researchers have shed some light on the mechanism of xanthate adsorption by using solid state infrared spectroscopy and ultra-violet adsorption studies. This has led to the now widely accepted hypothesis that xanthate ions can be oxidized in the presence of pyrite and the resulting dixanthogen is the species which is active in improving the floatability of the pyrite.

1.4.1 PYRITE

Pyrite has a cubic crystal structure in which the ferrous ions are at the corners, and the face centres are occupied by sulphur ions. The bonding is predominantly covalent.

No extensive work has been reported on the oxidation of pyrite in air; however, it has been reported that sulphides follow the following order of decreasing susceptibility to spontaneous oxidation (Wark and Sutherland, 1955; Glembostkii et al, 1972):

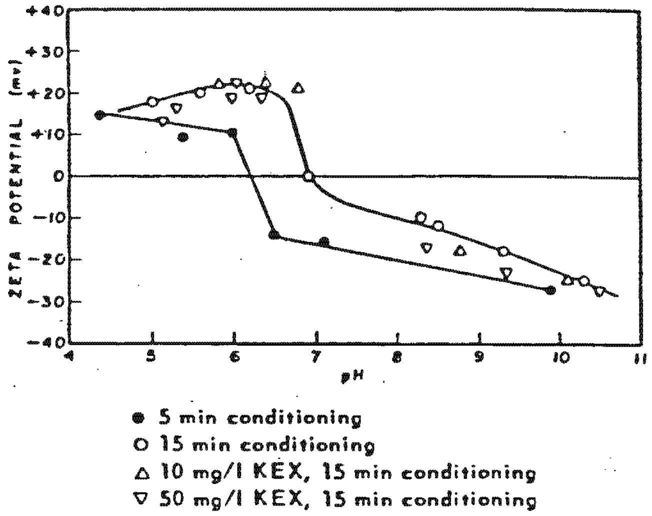
$$FeAsS > FeS_2 > CuFeS_2 > ZnS > PbS > Cu_2S$$

Thus, it seems that in comparison with other sulphides pyrite tends to oxidize quite readily in air, which may contribute to its electrokinetic and flotation behaviour being different from that of other sulphides. Majima, (1971), reports that ordinary pyrite is in an "electrochemically passive " state after exposure to air, and that the film formed on its surface may be absorbed oxygen or an oxygen-sulphur compound. Gaudin, (1956), reported that unoxidized pyrite is more easily floatable than oxidized pyrite. This is also confirmed by Glembotskii, Klassen and Plaksin (1972). They also report that elemental sulphur is possibly present on the surface of the freshly crushed pyrite according to the equation:

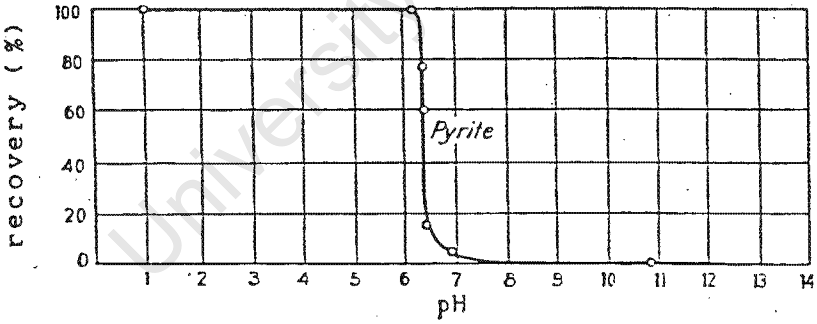
$$FeS_2 \rightarrow FeS + S$$

This sulphur on the surface may increase the water repellent properties of pyrite, which can then be completely floated by the mere use of a frother alone.

In aqueous solutions the products of the oxidation of pyrite, include Fe^{++}, H^{+} and $SO4^{=}$ in the acid to neutral pH range, and various polythionates and surface iron species in the alkaline range (Wark and Sutherland, 1955). At very low pH values elemental sulphur is stable in the pyrite system (Majima, 1971). More revealing information concerning the surface charge of pyrite is obtained from zeta potential measurements. Figure 1.4 shows that the pyrite surface is positively charged in an acid or acid to neutral solution, and negatively charged in an alkaline solution. Plaskin, (1960), reported that in fact pyrite surfaces consist of a mosaic of anodic and cathodic areas even on a single grain.



<u>**Figure 1.4**</u> Zeta potential of pyrite in presence of oxygen with and without KEX (Fuerstenau et al, 1968).



<u>**Figure 1.5**</u> Relation of recovery to hydrogen ion concentration. Reagents: terpineol, 0.20lb/t; PAX, 0.03 lb/t; NaOH or HCl to suit (Gaudin, 1932).

One of the most important features of pyrite flotation behaviour is the observation that at alkaline pHs it undergoes an extreme depression whereas in acid pHs it is easily floated (Figure 1.5) (Gaudin, 1932). This behaviour of pyrite is closely connected with its susceptibility to rapid oxidation (which is apparent even after 20 minutes in water or 30 minutes in air). When pyrite is oxidized in the presence of water, a film of ferric hydroxide forms on its surface, leading to an extremely high level of hydration. In addition, the collectors normally used in sulphide ore flotation are not easily attached to ferric hydroxide. Thus pyrite oxidation leads to a drastic reduction in floatability, up to the point of complete depression. Pyrite oxidation (up to the point of $Fe(OH)_3$ formation) is particularly active in an alkaline medium, due to the increased chemical activity of oxygen under these conditions. In addition, hydroxyl ions can detach the anions of collectors such as xanthates from the pyrite mineral surface. The process of xanthate ion detachment from the surface of pyrite is particularly rapid due to the high stability of $Fe(OH)_3$ which is formed. The solubility product of $Fe(OH)_3$ is $3.8*10^{-38}$ (Glembotskii et al, 1972).

The depressive effect of lime on pyrite flotation is of great importance in flotation in practice, as lime is extensively used as a pH regulator. It causes a reduction in the extent of attachment of the xanthate species and this phenomenon becomes more pronounced as the carbon chain length of the xanthate decreases. In an alkaline medium calcium ions form an insoluble or relatively insoluble compound with the products of sulfide oxidation (most likely calcium sulfate) and these are deposited on the pyrite surface thus increasing its hydration and intensifying the depressive effect of the hydroxyl ions (Glembotskii et al 1972).

One other property of pyrite and all other sulphide minerals that should be mentioned, is its variable composition. This is due in part to the nonstoichiometric nature of natural compounds and other mineral inclusions. The variability in chemical character is usually due to the depositional environment, and can create differences in the flotation behaviour of different samples of pyrite. Botelho de Sousa, (1984) and Haradat, (1984) studied the flotation behaviour of different pyrites and found significant differences in the floatability of pyrites from different origins. The preparation procedures carried out prior to flotation also have a signifficant effect on the surface of the pyrite and therefore on the flotation characteristics of the pyrite. The type of grinding, either wet or dry, seems to have a serious effect on the zeta potential and the ultimate flotation recovery of pyrite (Haradat, 1984).

1.4.2 XANTHATES

Xanthates are the reaction products of alcohols, carbon disulphide and sodium or potassium hydroxide according to the following equation (Senmin handbook):

$$ROH + CS_2 + K(Na)OH \rightarrow ROCS_2K(Na) + H_2O$$

Depending on the structure of the alkyl group and the type of the metal component, a variety of xanthate reagents are available on the market.

Properties of xanthates in aqueous solution

Xanthates in aqueous solution exhibit complex behaviour and all these properties have at one time or another been used in postulating why pyrite responds to flotation with xanthates as the collector. Of particular interest is the fact that the alkali metal xanthates are highly soluble, yield a variety of decomposition products at various pHs, and undergo facile oxidation.

Alkali metal and alkaline earth xanthates are soluble in water. Sodium ethyl xanthate for example, has a solubility of 8 mol/l (Fuerstenau, 1982). On the other hand, heavy metal xanthate salts possess only a limited solubility in aqueous solution. Kakovsky (1957), reported the value of $8.0*10^{-8}$ for FeX_2. He also found that the solubility products of the heavy metal xanthates decrease as the carbon chain length increases.

The stability of xanthates in aqueous solutions has been found to depend on the solution pH (Fuerstenau, 1982), the carbon chain length, the concentration of xanthate and impurities contained in the case of commercial xanthates (80% to 95% pure) (Harris, 1984; Wronski, 1959). Below pH=0.5, the rate of decomposition is extremely rapid and independent of pH. Between pH=0.5 and pH=8, the rate of decomposition decreases sharply with a rise in pH and, between pH values of 8 and 12, the rate of decomposition is at its slowest and virtually independent of pH. Throughout the pH range the rate of decomposition is found to be first order with respect to the concentration of the xanthate. Various researchers have reported relationships between pH and half life decomposition times and these results are shown in Figure 1.6 (Granvill, Finkelstein and Allison, 1972).

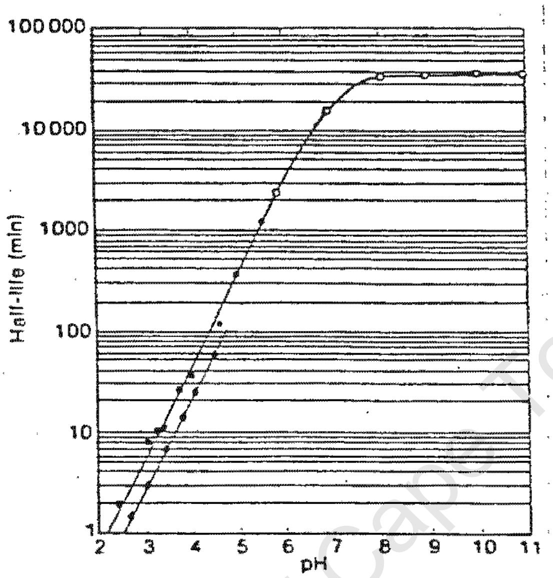


Figure 1.6 Variation of half life of decomposition of xanthate with pH: Allison and Finkelstein (25°C); Iwasaki and Cooke (23.5°C); Homylev (25°C); Finkelstein (25°C). Data from Granville et al, 1972).

The mechanism of the reaction in the acid region is well understood. The reaction involves hydrolysis of the xanthate ion to xanthic acid, which further decomposes into carbon disulphide and alcohol as follows:

$$EX^- + H^+ \rightarrow HEX_{(aq)} \rightarrow CS_2 + ROH$$

where HEX and ROH represent ethyl xanthic acid and alcohol respectively (Fuerstenau, 1982). The decomposition of the unstable xanthic acid is the rate controlling step. There is some disagreement over the value of the dissociation constant of ethyl xanthic acid. For example, values reported by various researchers are as follows; Majima (1961), $2.9*10^{-2}$, Iwasaki and Cooke (1959), $2.4*10^{-2}$, Cook and Nixon (1950), $7*10^{-3}$, and Fuerstenau (1980), $1*10^{-5}$. In the acid region there is essentially no chain length effect.

In the alkaline region the mechanism of reaction and the products formed are much less certain. Philipp and Fichte, (1960), proposed very complex reactions with final products CO_3^{2-}, S_2^- and CS_3^{2-}, the hydrolysis of the xanthate ion being the rate controlling reaction. Finkelstein, (1967), identified CS_2 and $ROCOS^-$. However it is important to note that in alkaline media xanthate ion decomposes very slowly, and can be considered stable during flotation operations. A carbon chain length effect on the decomposition of xanthates has been reported to occur in alkaline media. Wronski, (1959) and Harris (1984) both confirm the sequence of increasing stability to be :

methyl < ethyl < n-propyl < n-butyl < iso-propyl

The role of impurities has been a matter of controversy. Harris, (1984) found that the rate of decomposition of commercial xanthates is similar to those of high purity sample, in contrast to most previous researchers (Rao, 1971; Allison and Finkelstein, 1971) who found that impurities, particularly metal ions, catalyse the decomposition of xanthates. None of them however reported specifically on the nature of the impurities present.

Oxygen and heavy metal ions such as Fe^{3+} and Cu^{2+} can oxidize xanthate ion to the dimer dixanthogen (Fuerstenau, 1982). The reactions are:

$$2X^- + 1/2\ O_2 + H_2O \rightarrow X_2 + 2\ OH^- \qquad (1)$$

$$2X^- + Cu^{2+} \rightarrow CuX_{(s)} + 1/2\ (X_2) \qquad (2)$$

$$2X^- + 2\ Fe^{3+} \rightarrow 2\ Fe^{2+} + (X_2) \qquad (3)$$

Although xanthate oxidation by dissolved oxygen is thermodynamically favourable, it is slow kinetically. As a result, dixanthogen formation in this manner can be assumed not to occur to any appreciable extent in flotation systems. It should be mentioned however, that electrochemical oxidation of xanthate on a solid surface such as pyrite by oxygen, does occur. With Fe^{3+} and Cu^{2+}, however, the reaction is relatively fast kinetically. Xanthate is oxidized completely to dixanthogen at pH=2 with Fe^{3+}, but is not oxidized at pH≥6 over a 10 minutes reaction period. Ferric hydroxide which has a very low solubility product is the stable iron species in alkaline medium. With regard to dixanthogen, it is not stable at pHs greater than approximately 10.5. The xanthate ion is the stable species under these conditions (Fuerstenau, 1982). The rate at which dixanthogen reduces to xanthate ion is presented as a function of pH in Figure 1.7.

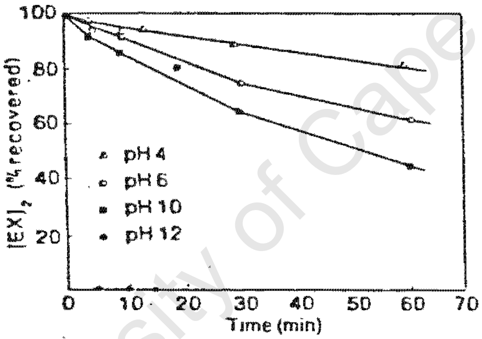


Figure 1.7 Decomposition of 2 mg of diethyl dixanthogen in 100 ml of solution (Kakovsky, 1957).

Proposed mechanisms of action of xanthate collectors on pyrite.

Early experiments indicated clearly that xanthate ions were extracted from solution by pyrite, and thus the mineral was rendered floatable. Unlike other systems such as lead and copper, evidence to date indicates that ferric xanthate is not formed. Thus the traditional theory that the pyrite xanthate species is formed in the system is negated. Gaudin de Bruyn and Mellgren (1956), using radiometric techniques found that dixanthogen is the species which is adsorbed on the pyrite surface. This was also suggested by Mamiya,

(1960) and confirmed independently by Fuerstenau et al (1968), and Majima and Takeda (1968). The similarity between the pyrite recovery curves obtained by potassium ethyl xanthate (Figure 1.8) and diethyl dixanthogen (Figure 1.9) led Fuerstenau, Kuhn and Elgillani (1968), to suggest that dixanthogen is the species which is primarily responsible for flotation. The question which arises is the mechanism where by the dixanthogen is formed.

Fuerstenau et al (1968), suggested that the oxidation of xanthate to dixanthogen is due to either Fe^{3+} or $Fe(OH)_3$ according to the following equations:

$$2\ Fe^{3+} + 2\ EX^- \rightarrow 2\ Fe^{2+} + (EX)_2 \qquad (1)$$

$$2\ Fe(OH)_3 + 6\ H^+ + 2\ EX^- \rightarrow 2\ Fe^{2+} + 6\ H_2O + (EX)_2 \qquad (2)$$

Klymonsky and Salman (1970), who did adsorption studies in deoxygenated and aerated systems, support the mechanism of reaction (2) as proposed by Fuerstenau et al (1968). According to Majima, (1971), ordinary pyrite after exposure to air is in a passive state, and the surface film formed may be adsorbed oxygen or an oxygen-sulphur compound. Assuming that adsorbed oxygen leads to passivity, the author proposed the following mechanism:

$$1/2\ O_{2(ad)} + 2\ X^-_{(aq)} + H_2O \rightarrow X_{2(ad)} + 2\ OH^-_{(aq)} \qquad (3)$$

In this case it is assumed that an equilibrium exists between the adsorbed species and bulk solution species. The production of hydroxyl ions as indicated by this equation is in agreement with the increase in pH which is noticed when xanthate is added to the system. In this case pyrite acts as a catalyst in allowing the one redox system, $O_{2(ad)}$ and $OH^-_{(aq)}$, to equilibrate with another system i.e. $X^-_{(aq)}$ and $X_{2(ad)}$. Usul and Tolum (1974), supported the above theory basing the conclusions on polarogram studies. According to these theories, pyrite flotation ceases at low pH values because of the formation and decomposition of xanthic acid;

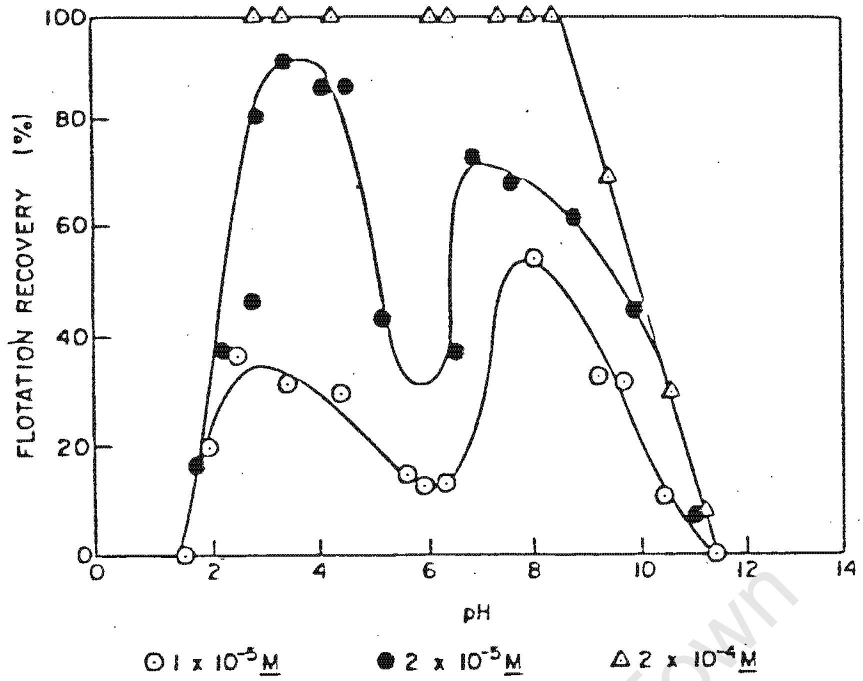


Figure 1.8 Recovery of pyrite as a function of flotation pH with various additions of KEX (Fuerstenau et al, 1968).

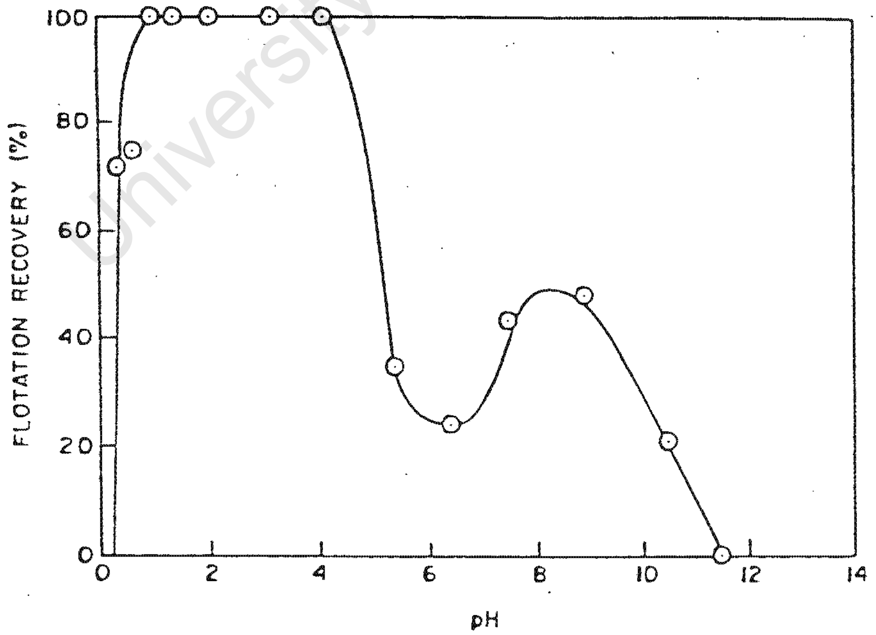


Figure 1.9 Recovery of pyrite as a function of pH with $1.3*10^{-5}$ M diethyl dixanthogen (Fuerstenau et al, 1968).

at high pH values (pH>11), flotation ceases because the amount of dixanthogen that can form is exceedingly small (Fuerstenau et al 1968). However, it is still not clear as to why poor recoveries are obtained at the pH approximately pH=6, as this cannot be due to the absence of dixanthogen (Figure 1.8).

Recent electrokinetic and adsorption studies, (Fuerstenau and Mishra, 1980), provide evidence of xanthate ion adsorption on pyrite, particularly in deoxygenated systems. Figure 1.10 indicates that xanthate ions appear to be chemisorbing on pyrite when oxygen is excluded. Figures 1.11 and 1.12 also show strong interaction between xanthate ions and pyrite at pH values below the isoelectric point; however this interaction is not characteristic of chemisorption, as indicated by the minimal effect on the mobility of pyrite at pH values near isoelectric point. At alkaline pH values xanthate ions again seem to be specifically interacting with the pyrite-aqueous interface. Such changes in the electrophoretic mobility of pyrite cannot be expected if dixanthogen is the only species present at the pyrite interface, since dixanthogen is a neutral molecule, and does not effect the electrophoretic mobility of pyrite (Figure 1.13). Fuerstenau and Mishra, (1980), attempted to explain this behaviour by the following reactions:

$$1/2\ O_{2(aq)} \rightarrow 1/2\ O_{2(ad)}$$

$$X^{-}_{(aq)} \rightarrow X^{-}_{(ads)}$$

$$2\ X^{-}_{(ads)} + 2\ H^{+} + 1/2\ O_{2(ads)} \rightarrow X_{2(ads)} + H_2O$$

Comparison of the flotation behaviour of pyrite (Fig. 1.8) with its electrokinetic behaviour (Figures 1.10, 1.11 and 1.12), shows clearly that the pH regions of increased flotation recovery, are the same as the regions in which xanthate affects the electrokinetic behaviour of pyrite. Reduced flotation of pyrite around the i.e.p. coincides with the minimal effect of xanthate on pyrite in this region.

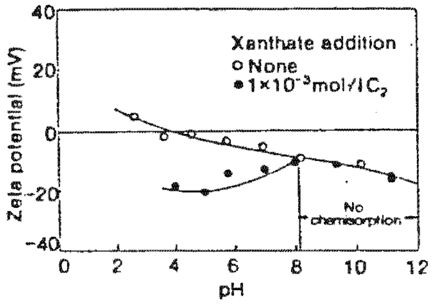


Figure 1.10 Zeta potential of pyrite in virtual oxygen-free conditions and in presence and absence of potassium ethyl xanthate (KEX) (Fuerstenau Natalie and Mishra).

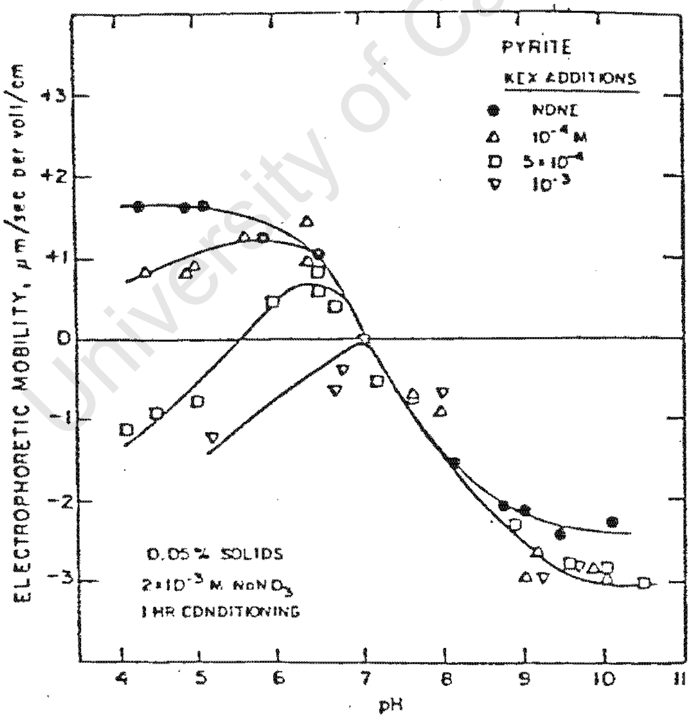


Figure 1.11 Electrophoretic mobility-pH plot of pyrite in presence of different concentrations of KEX and $2*10^{-3}$ M $NaNO_3$ (Fuerstenau and Mishra, 1980).

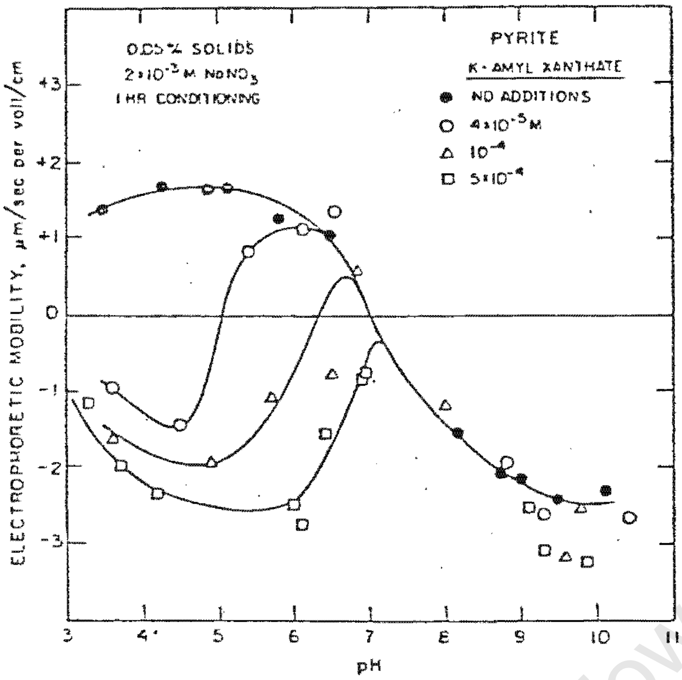


Figure 1.12 Electrophoretic mobility-pH plot of pyrite in presence of different concentrations of potassium amyl xanthate (KAX) and $2*10^{-3}$ M $NaNO_3$ (Fuerstenau and Mishra, 1980).

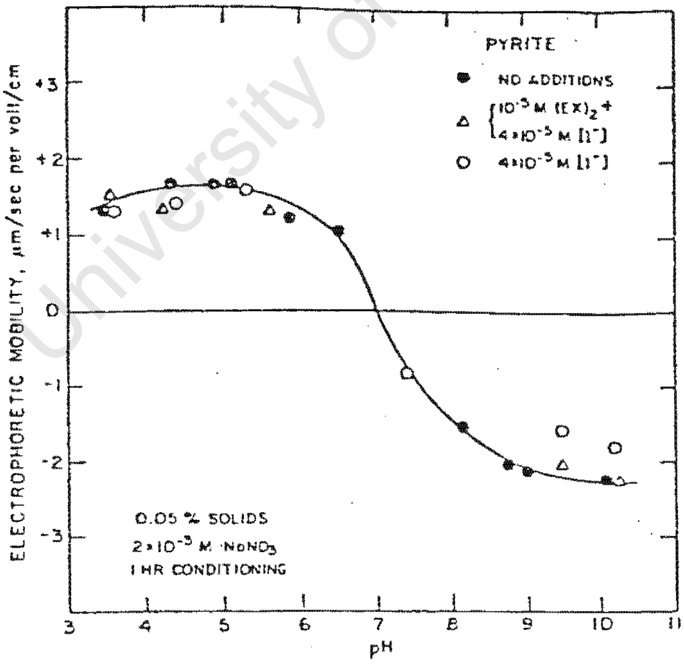


Figure 1.13 Electrophoretic mobility-pH behaviour of pyrite in presence of ethyl dixanthogen (EX_2) and iodide. Supporting electrolyte: $2*10^{-3}$ M $NaNO_3$ (Fuerstenau and Mishra, 1980).

This correlation between flotation and electrokinetic behaviour of pyrite, led the authors to suggest that the xanthate ion plays a significant role in pyrite flotation. Finkelstein and Harris (1975), have shown that there is evidence of the formation of soluble monothiocarbonate, (MTC), at pyrite surfaces. Pointing to the fact that very small amounts of ferric xanthate could be present at the surface, these authors proposed that MTC is formed from a minor adsorbed species, which is the surface analogue of the compound $FeOHX_2$. Thus

$$FeS_2 \xrightarrow{O_2,\, X^-} FeOHX_2 + S^0 \quad \text{(or sulphoxides)}$$

$$FeOHX_{2(s)} + OH^- \rightarrow FeSX_{(s)} + MTC + H_2O$$

The authors noted that the major adsorbed species (dixanthogen), will be formed by a parallel reaction, either between $FeOHX_{2(s)}$ and oxygen, or directly from pyrite, oxygen, and xanthate.

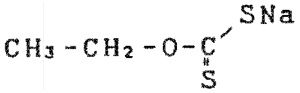
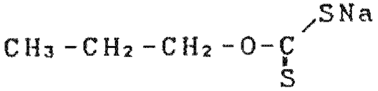
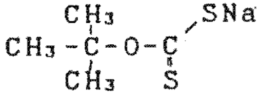
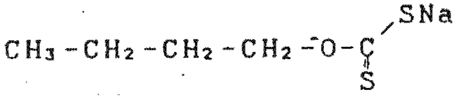
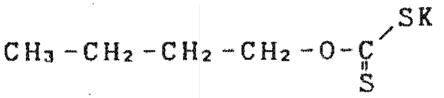
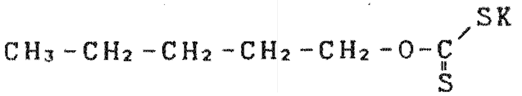
The xanthates homologous series.

The xanthate reagents consist of an homologous series, in which there are differences in the carbon chain length and structure, and in the type of the metal component. For example the homologous series that is to be examined in this study, is shown in Table 1.1. The influence of carbon chain length can be observed using types 1-2-3, which share a common sodium ion, and between types 5-6, which share a common potassium ion. The influence of structure can be observed using types 3-4, as these have the same empirical formula. The influence of the metal component can be observed using types 3-5.

The adsorption of xanthates of differing carbon chain length on pyrite.

Fuerstenau, Natalie and Mishra have studied the adsorption density on pyrite of various xanthates as a

Table 1.1 Homologous xanthate series

1. Sodium ethyl xanthate (SEX)	
2. Sodium normal propyl xanthate (SNPX)	
3. Sodium iso-butyl xanthate (SIBX)	
4. Sodium normal butyl xanthate (SNBX)	
5. Potassium normal butyl xanthate (PNBX)	
6. Potassium amyl xanthate (PAX)	

function of pH, in the virtual absence of oxygen. Figure 1.14 clearly indicates that the adsorption density increases with increasing carbon chain length. It is also seen that adsorption of short chain xanthates does not occur above pH=8, while adsorption of long chain xanthates occurs only above pH=7. An electrokinetic study on the effect of short chain length potassium ethyl xanthate (Fig. 1.11) and the long chain length potassium amyl xanthate (Fig. 1.12) on the electrophoretic mobility of pyrite, has shown that the longer chain xanthate has a stronger interaction with the pyrite surface.

Values of the contact angle of various xanthate collectors on pyrite have been reported by Glembotskii (1968). Table 1.2 shows that the contact angle is improved as the length of the carbon chain increases. Table 1.2 also shows that the xanthates with branched chains are more effective than those with straight chains. Glembotskii also reports that only in xanthates with up to 4-5 CH_2 links the hydrophobicity of minerals increases with an increase in the length of the carbon chain. In xanthates with longer hydrocarbon chains there is appreciably less increase. Wark and Sutherland, (1955), also reported that the collector concentration also affects the value of the contact angle. For example the angle for ethyl xanthate may lie anywhere between 0° and 60°, the last value is only obtained if sufficient collector is added.

Table 1.2 Contact angles on the surface of pyrite treated with different xanthate collectors.

Hydrocarbon structure of xanthate collector	contact angle, θ°, on pyrite
isobutyl	78
n-butyl	74
isopropyl	67
ethyl	60

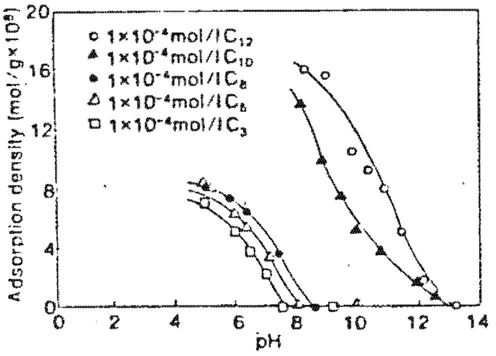


Figure 1.14 Adsorption density of various xanthates on pyrite as a function of pH in the virtual absence of oxygen (Fuerstenau, Natalie and Mishra).

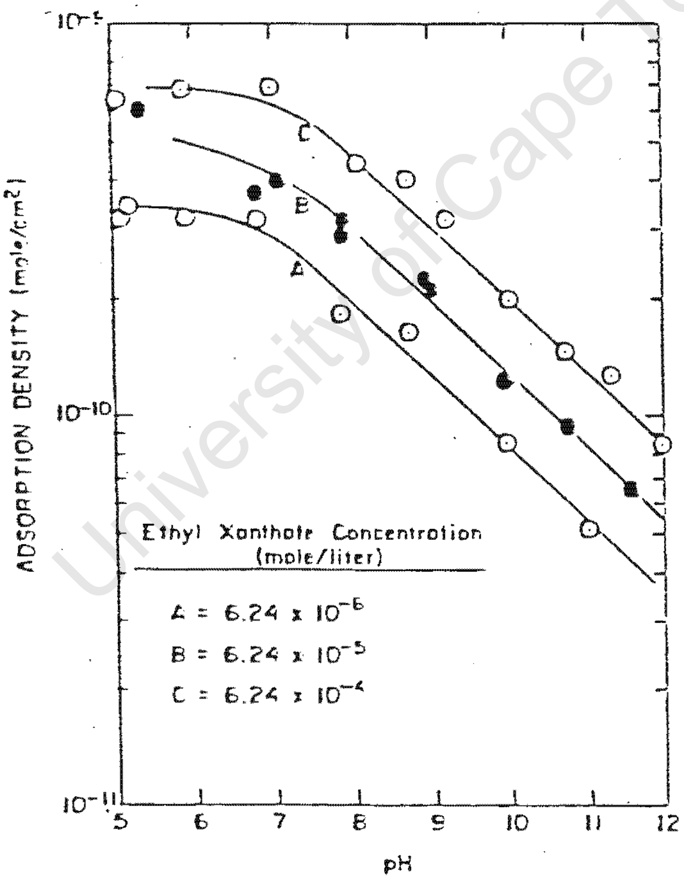


Figure 1.15 Effect of pH on adsorption of ethyl xanthate on pyrite with three concentrations of ethyl xanthate (Gaudin, de Bruyn and Mellgran, 1956).

Adsorption of xanthates of different concentration levels on pyrite.

The concentration of xanthate also affects the adsorption density (Ball and Rickard, 1976; Fuerstenau, 1982). Figure 1.15 shows the adsorption density of ethyl xanthate on pyrite, at three concentration levels, in a deoxygenated system (Gaudin et al, 1956). For a constant adsorption density, a ten fold increase in the hydroxyl ion concentration, required a similar increase in collector concentration. From an electrokinetic point of view, a stronger interaction between pyrite and xanthate can be seen in Figures 1.11 and 1.12 as the xanthate concentration increases.

Mellgren's work, (1954), with oxygen-free solutions showed that the adsorption density (T) of xanthate as a function of concentration of potassium ethyl xanthate (c), followed a relationship given by $T=A+c^n$, where A and n are constants, and $n=0.2-0.25$. This relationship held until the adsorption density became independent of concentration, and the coverage was close to a monolayer. Mellgren's general results were confirmed also by Swami (1973), who reported a value of $n=0.44$. Both investigators found that when oxygen was not excluded from the system, adsorption densities much greater than that corresponding to a monolayer were recorded.

The influence of xanthate on the flotation of pyrite.

Fuerstenau and Mishra (1980), examined the Hallimond tube flotation recoveries of pyrite, using different potassium ethyl xanthate additions as a function of pH. Figure 1.16 clearly shows that the variation of the pH influences the recovery of pyrite. Such sinusoidal shape flotation recovery curves appear to be typical of pyrite and this is also confirmed by Fuerstenau et al (1968). Figure 1.16 also indicates that the recovery of pyrite is influenced by the concentration of the collector. An increase in the concentration of xanthate results in higher pyrite recoveries, a fact which corresponds with the increased adsorption of collector as mentioned above. On the other hand, the concentration of the collector has no effect on the recovery of the pyrite at pHs at which virtually complete depression of pyrite has been observed. At these pHs it is the stability of the species which is mainly responsible for the flotation of the pyrite (Fuerstenau et al, 1968).

The effect of different xanthates on the froth quality has been investigated by Dudenkov et al, (1959). They found that the extent to which the air bubbles disperse in the solution increases as the xanthate concentration increases. Moreover xanthates with longer carbon chain lengths are conducive to a more favourable dispersion of the air. For example, during the aeration of a solution which contains 60 mg/t of potassium methyl xanthate, bubbles with a diameter of 1.2 mm are predominant, whereas when the potassium amyl xanthate of the same concentration is used, bubbles of 0.4mm of diameter are predominant. Figure 1.17 shows the relationship between the concentration of xanthate collector, and a time variable τ which is proportional to the total surface area of the bubbles in the cell. For a constant aeration rate, the value of τ increases, as the average diameter of the bubble decreases. Figure 1.17 shows that as the concentration of collector increases, the bubbles thus produced become smaller. It also shows that for the same collector concentration the longer the carbon chain length, the smaller the diameter of the bubbles.

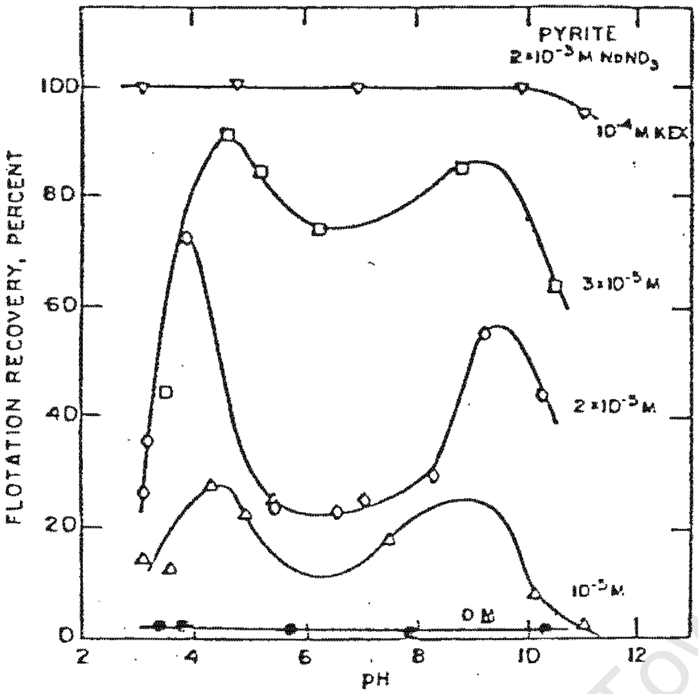


Figure 1.16 Hallimond tube flotation recovery of pyrite as a function of pH for various additions of KEX (conditions: 2% solids (-150 + 270 mesh), 15 min conditioning, 1 min flotation, 30 ml N_2/min, supporting electrolyte: 2×10^{-3} M $NaNO_3$ (Fuerstenau and Mishra, 1980).

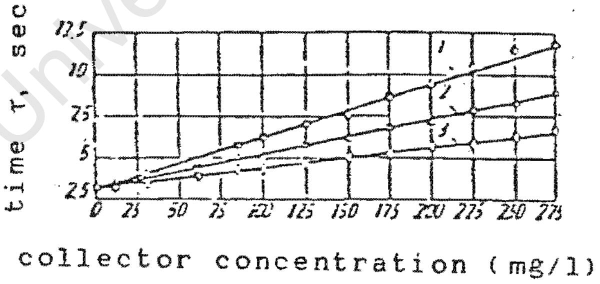


Figure 1.17 Relationship between the time τ and the concentration of various xanthates in distilled water:
1-potassium butyl xanthate;
2-potassium ethyl xanthate;
3-potassium ß-etoxyethyl xanthate

1.4.3 QUARTZ

Quartz belongs to the silicate group of minerals. In the case of quartz all four oxygen atoms which are bonded with silicon are shared with other tetrahedra forming an infinite three dimensional structure. It is for this reason that quartz does not possess good cleavage planes. Fracture of the Si-O bonds results in the formation of a polar surface (Aplan and Fuerstenau, 1962; Lidstrom, 1967).

When quartz is crushed under water, the broken bonds at the surface react with water molecules to form a surface silicic acid. The ionization of this surface silicic acid gives rise to the charge on the surface of quartz as follows:

$$-Si-OH \rightarrow -Si-O^- + H^+$$

Thus, H^+ and OH^- are the potential determining ions for quartz, since the pH of the solution controls the extent of surface ionization. The zero-point charge of quartz has been reported to be at pH=2 to pH=3.7, the different values are corresponding to two different ways of treating prior to measurement of the ZPC. Eitel, (1936), points out that quartz always carries a negative charge, whethere it is in an alkaline, acid or neutral media. Therefore, quartz is by nature an extremely hydrophilic mineral. If its surface carefully cleaned to remove possible traces of grease, a drop of water will easily flow over the surface, and the contact angle will be almost zero.

It has been established that mineralogically pure quartz cannot be floated with anionic collectors; on the other hand, cationic collectors readily float quartz. Heavy metal ions as Fe^{2+}, Fe^{3+}, Cu^{2+}, Ca^{2+}, Ba^{2+}, etc., can be adsorbed on quartz surface and the quartz is then able to be floated with anionic collectors (Gaudin, 1932; Glembotskii, Klassen and Plaskin, 1972). When an anionic collector attaches itself to quartz, this surface compound is metamorphosed in such a way, that the activator metal ion uses some of its valency to combine with the quartz, and the remainder to attach to the collector anion; it is therefore the connecting link between the collector anion and the quartz lattice (Glembotskii, 1972). The heavy metal ions which activate quartz, iron, copper, and calcium are of particular importance in practice. The activating effect of bivalent and trivalent iron ions in quartz flotation, is shown in Fig. 1.18. It has been established that quartz can be activated by iron, as a result of crushing in a metal mill, even when the iron concentration is extremely low, corresponding to a solubility product of the ferrous hydroxide which is formed under these conditions.

Calcium ions are present in the system, either in the water which is being used, or in the lime which is used to modify the pH of the pulp. Adsorption experiments by Clark and Cook, (1968), showed a limited adsorption of hydrated calcium ions on quartz, between the pH=4 and pH=11 (Figure 1.19). However, the sharp increase of calcium adsorption at pH=12 might be caused by the increase of $CaOH^+$ in solution (Figure 1.20). This is confirmed by Fuerstenau and Palmer, (1976), who reported that 90% recovery of quartz is obtained in the presence of calcium ions only at pH≥12. Figure 1.21 also indicates that the quartz flotation increases at the pH values where the hydroxy complex of the heavy metal ions is formed. Fig. 1.21 also shows that the charge and the size of the hydroxy complex also influences the pH where quartz flotation occurs.

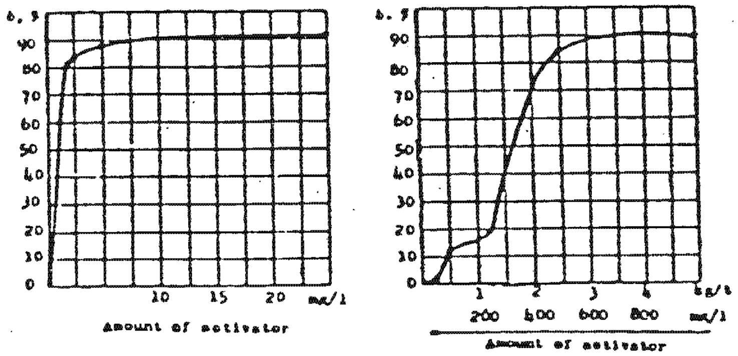


Figure 1.18 Quartz flotation results depending on activator concentration (Glembotskii et al, 1972).
a-ferrous sulphate; b-ferric chloride

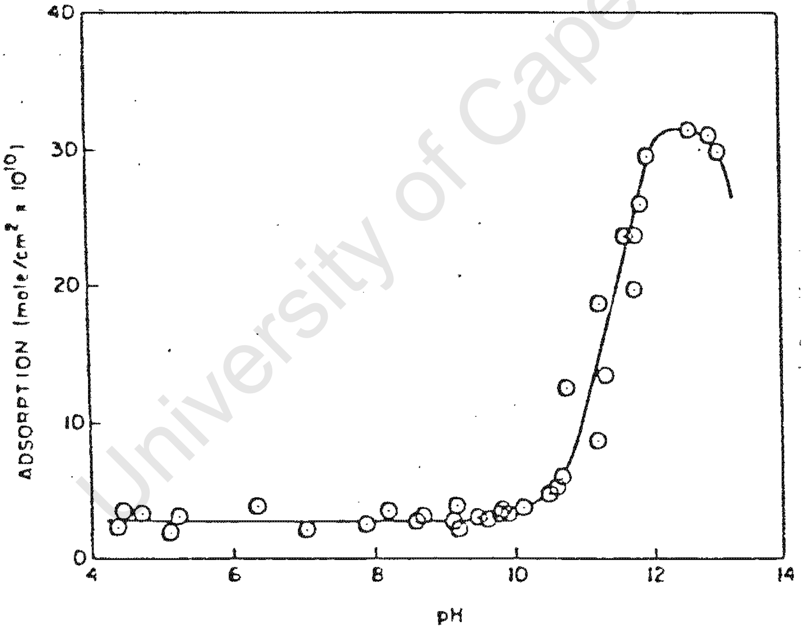


Figure 1.19 Adsorption of calcium species on quartz as a function of pH from solutions 100 ppm in Ca^{++} (Clark and Cooke, 1968).

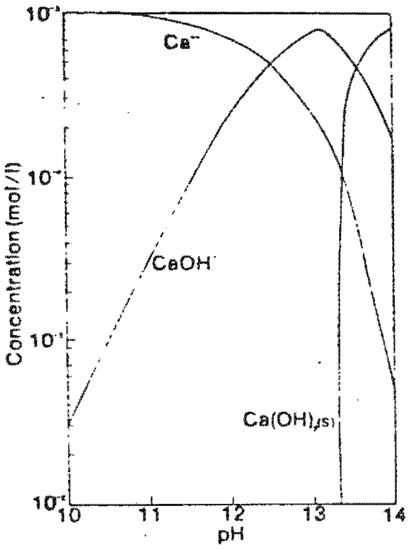


Figure 1.20 Logarithmic concentration diagram for $1*10^{-3}$ M Ca^{++}. Equilibrium data (Fuerstenau and Palmer, 1976).

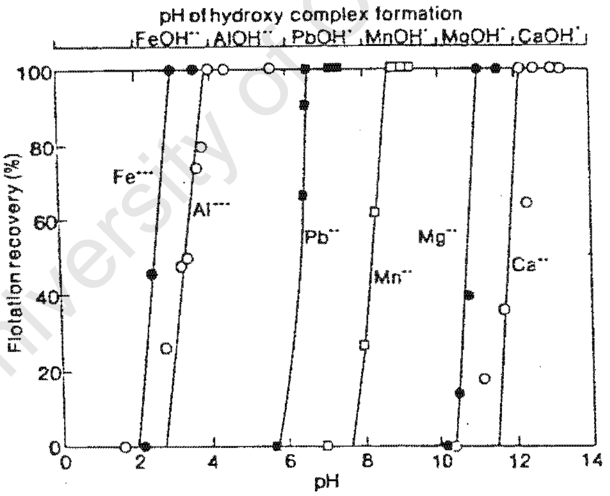


Figure 1.21 Minimum flotation edges of quartz as a function of pH; $1*10^{-4}$ M sulfonate, $1*10^{-4}$ M metal ion.

1.5 THE FLOTATION OF PYRITE IN SOUTH AFRICA

The Witwatersrand reefs contain gold, uranium and pyrite in the following average concentrations: 0.001 per cent, 0.02 per cent, and 1.7 per cent respectively. The close minerological association of gold, uranium and pyrite makes it difficult to consider the extraction of these three constituents separately (Lloyd, 1981).

Gold is probably the most floatable of all the constituents of the reef, but the close association between as much as 30 % of the gold and the radioactive minerals (both uraninite and kerogen), and between as much as 20 % of the gold and the various sulphide minerals (mainly pyrite) present in the reef, means that in general high recoveries of gold are associated with the simultaneous recovery of both uranium and sulphides. The low percentage of gold in the reef, and the lack of experience, make the extraction of gold by direct flotation difficult. Instead, cyanidation is applied for its extraction (Lloyd, 1981).

The uranium in the reef is present at about 0.02 % on average , but there have been problems in the development of a flotation technique that will give an adequate uranium concentrate because:

i) much of the uranium is present as uraninite which is inherently difficult to float;

ii) the uraninite tends to be very finely ground during milling, which makes its selective flotation even more difficult;

iii) a small but significant fraction of the uranium is carried by siliceous minerals such as zircon, lencoxene, titanite, monasite, and various phyllosilicates all of which are difficult to float selectively;

iv) kerogen is floated very readily, but tends to be rather coarse because its low density permits it to escape from milling circuits before being milled.

There has been considerable experience in the production of a relatively high-grade pyrite concentrate, containing all other associated sulphides (see Table 1.3), as well as comparatively small amounts of gold and uranium. The gold is usually present in economic quantities in these concentrates, which therefore require cyanidation. The uranium is mainly present as kerogen in the concentrates, and is accordingly not present in economic quantities (Lloyd, 1981).

The purpose for which pyrite is usually concentrated by flotation is for the production of sulphuric acid by the roasting of the concentrate and catalytic oxidation of the resultant sulphur dioxide. In this way sulphuric acid which is essential for the acid leach extraction of uranium, and for pyrite flotation circuits, would be in sufficient supply. Accordingly, it is necessary to prepare a fairly high grade concentrate, that is relatively free of siliceous materials. The need for the high grade arises partly from the fact that the roasting reaction is autocatalytic, and partly because any gangue minerals in the concentrate tend to be fine flaky phyllosilicates which would make the concentrate difficult to thicken, dewater, and roast, and also because the costs of transportation of the gangue minerals in some cases exceeds the cost of their removal.

It has been found that most flotation reagents have a deleterious effect on the cyanidation of gold (Lloyd, 1981; Mrkusic et al, 1970). Accordingly, the flotation of pyrite is usually conducted after cyanidation. The fact that pyrite is normally floated after gold recovery, leads to the most interesting aspect of pyrite flotation. Cyanide is inherently a depressant for pyrite, and traces of cyanide present in the gold plant residues are quite sufficient to have a significant effect. Similarly, the lime used to ensure alkaline conditions during cyanidation, can have a deleterious effect on flotation. This effect is believed to be not only one of pH, but also to be due to "calcium activation of quartz". Therefore, it appears that high

Table 1.3 Composition units (Lloyd, 1981)

Constituent	Atomic %Fe	Atomic %S	Atomic ratio Fe_xS	Atomic ratio FeS_x	Mole fraction of FeS	Sulphur %(by mass)	Mineral
Fe_9S_8	52.94	47.06	1.125	0.889	1.059	33.79	Pentlanditic FeS
$FeS_{0.975}$	50.63	49.37	1.026	0.975	1.013	35.89	Mackinawite
FeS	50.00	50.00	1.000	1.000	1.000	36.47	Troilite
$Fe_{11}S_{12}$	47.83	52.17	0.917	1.091	0.957	38.51	Intermediate pyrrhotite
$Fe_{10}S_{11}$	47.62	52.38	0.909	1.100	0.952	38,71	
Fe_9S_{10}	47.37	52.63	0.900	1.111	0.947	38.94	
Fe_7S_8	46.67	53.33	0.875	1.143	0.933	39.62	monoclinic pyrrhotite
Fe_9S_{11}	45.00	55.00	0.818	1.222	0.900	41.23	smythite
Fe_3S_4	42.86	57.14	0.750	1.333	0.857	43.36	greigite
Fe_2S_3	40.00	60.00	0.667	1.500	0.800	46.27	Gamma FeS
FeS_2	33.33	66.67	0.500	2.000	0.667	53.45	Pyrite marcasite

<u>Table 1.4</u> Collectors and pH conditions on typical flotation plants on the Witwatersrand (Lloyd, 1981).

Mine	Feed to flotation	Collector	Rougher pH
Merriespruit	Au residue	xanthate	5.5
Virginia	U residue	xanthate	4.9 to 5.7
G.G.M.A.	Au residue	xanthate	5.4 to 5.8
Loraine	Fresh coarsh ore	xanthate	10 to 11
Zandpan	Fresh coarse ore	xanthate	10.8
Hartebeestfontein	Fresh coarse ore	xanthate	9.9
Virginia	U residue	mercaptobenzothiazole	4.8 to 4.9
Free State Geduld	Various residues	mercaptobenzothiazole	4
President Brand	Various residues	mercaptobenzothiazole	4
Buffelsfontein	U residue	mercaptobenzothiazole	5.5
Rand Leases	Reclaimed dam	mercaptobenzothiazole	4.6
G.G.M.A.	Reclaimed dam	mercaptobenzothiazole	3.8 to 4.4
Libanon	Fresh coarse ore	amines	10 to 11
Venterspost	Fresh coarse ore	amines	10 to 11

recoveries of pyrite gold and uranium can be achieved only if a rougher concentrate prior to cyanidation, of perhaps 20 % by mass of the feed is produced. It seems that reverse leaching (leaching before cyanidation) of the concentrate, followed by a cleaning flotation step to recover the pyrite, would permit significantly higher overall recoveries, than the routes being employed at present (Lloyd, 1981; Bushell, 1970).

A variety of collectors has been used, mainly xanthates at the pH range 4.9 to 11. However, sodium mercaptobenzothiazole has found fairly wide usage in the treatment of reclaimed slimes-dam material or uranium plant residues, at somewhat lower pH values. Table 1.4 summarizes typical collector and pH conditions for various feeds. A wide range of frothers has been used such as triethoxybutane (TEB), polypropyl glycol ethers (DOWFROTHS), pine oil, etc. Copper sulphate is often added as a sulphide activator when xanthates are used, particularly at high pH values. It has been suggested that the copper also forms complexes with the cyanide ions and thus reduces the depressing effect of cyanide, but the evidence in favour of this mechanism is slight (Lloyd, 1981; Westwood, 1970). Dextrin has found favour as a depressant for pyrophyllite and other phyllosilicates, and certainly appears to assist in producing a clean concentrate when the feed is finely ground or has a high shale content. Another parameter that determines the quantity of siliceous material floated, is the amount of the water in the concentrate; the flotation cell acts as a classifier, and water in the concentrate tends to entrain fine particles into the concentrate without selectivity.

The increase in the price of gold and the strategic importance of uranium, has made the retreatment of low grade residues possible. Ergo plant on the East Rand as well as the Joint Metallurgical Scheme at OFS, are treating millions tons of residual material per month. A typical set of average operations statistics of residue treating flotation plant from the low grade curcuit of JMS are given below;

<u>Throughput</u> (t/m)		1 530 000
Grade in feed	Au (g/t)	0.53
	U_3O_8 (Kg/t)	0.081
	S (%)	0.88
<u>Reagents</u>		
collector	SENKOL 50*	102g/t
frother	TEB (triethoxybutane)	25g/t
depressent	Acrol J2P	53g/t
modifier	$CuSO_4$	50g/t
pH		3.8
<u>concentrate</u> (t/m)		38000
Grade	Au(g/t)	9.8
	U_3O_8(Kg/t)	**
	S (%)	31.0
Recovery	Au (%)	46.1
	S (%)	84.0
	U_3O_8 (%)	**

The process illustrated at Figure 1.22, is a flowsheet at Zandpan flotation plant. This flowsheet can be regarded as a classical type since it embodies most of the features incorporated in other processes. In essence, a bulk sulphide float is conducted in a series of rougher, cleaner and recleaner cells, with an additional treatment of the tailings of the rougher cells in scavengers cells. The product is then fed to the acid leach plant for uranium extraction and finally to gold extraction

*sodium mercaptobenzothiazole based collector
** Not disclosed in terms of the Atomic Energy Act No.90 of 1967. (Anglo American Corporation of SA Ltd.)

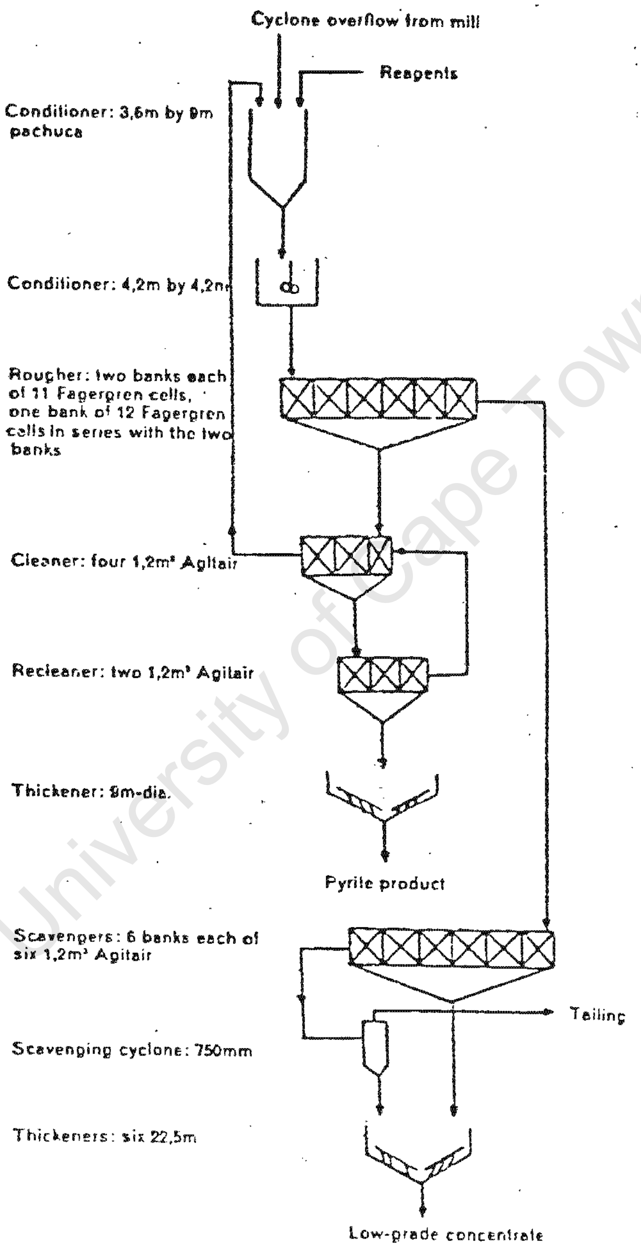


Figure 1.22 Flowsheet employed at Zandpan

CHAPTER 2

OBJECTIVES OF RESEARCH

As shown in Chapter 1 the pyrite-xanthate system behaves in a complex manner. Pyrite is able to float easily in acidic pH ranges, but the final choice of pH depends on influence it has on other minerals present in the system such as silicates and phyllosilicates which are minerologically associated with pyrite. In addition other parameters such as the procedures followed both before and after the pyrite flotation, temperature, the various ions present and the concentrations in solution, particle size and other parameters, should also be taken into account such as they are often able to influence significantly the flotation efficiency.

The research described in this work was aimed at investigating the flotation behaviour of pyrite using xanthate reagents as collectors. An attempt has been made to investigate the following questions;

i) What is the effect of different types of xanthate collectors on the pyrite flotation behaviour?

ii) How does the variation of pH influence the system?

iii) How does the concentration of xanthate collectors influence the pyrite flotation behaviour?

iv) What is the effect of type and concentration of xanthate as well as pH on the behaviour of quartz, which is often one of the main gangue constituents of pyrite ore deposits?

Six different xanthate collectors were chosen, (Table 1.1). The influence of the carbon chain length can be observed using types 1, 2 and 3, which share a common sodium ion, and between types 5 and 6, which share a common potassium ion. The influence of the structure can be acertained from using types 3 and 4, such these have the same empirical formula. The influence of the metal component can be observed using types 3 and 5.

Initially the effect of pH was investigated in the range of pH=4 to pH=12. For these experiments the collector SIBX was chosen. Then, the effects of other xanthate collectors were examined at a constant pH value, keeping the molecular concentration of the collector constant. Four different collector concentrations were studied keeping the pH value constant throughout. The behaviour of leached pyrite was studied using PAX as collector, while the effect of oxidized pyrite on the flotation behaviour was studied using SIBX collector.

Finally adsorption tests were carried out using both oxidized and acid leached pyrite, in order to investigate the extent and the rate of adsorption of the different collectors.

The above mentioned experimental program was also carried out using pure quartz, in order to study the influence of pH and type of xanthate collector on quartz, without the interference of pyrite.

CHAPTER 3

EXPERIMENTAL METHODS

3.1 FLOTATION TESTS

3.1.1 Preparation of ore

A synthetic mixture of pyrite and quartz was used instead of an actual ore sample in the flotation experiments. Pyrite from Durban Roodepoort Deep (Transvaal) of S.G.=4.7 was used, with a size distribution of 96%<38μ. The analysis for sulphur and iron was carried out at MINTEK. Two samples were analysed 8 times and the average values are presented in Table 3.1

Table 3.1 Sulphur and iron analysis of Durban Roodepoort Deep pyrite.

	S %	Fe %
D.R.D pyrite	47.5	41.5
D.R.D pyrite	48.8	42.8
pure pyrite	53.33	46.67

The minerological analysis of the D.R.D. pyrite used is given in Table 3.2. This was also carried out at MINTEK.

Table 3.2 Mineral species identified by point counting in DRD pyrite sample (500 point counts).

Mineral	Percentage
Compact pyrite	59.0
Porous pyrite	35.2
Concretionary pyrite	3.6
Pyrite with iron-copper sulphide inclusions*	2.0
Pyrite with associated galena	0.2

* Usually chalcopyrite, but other iron-copper sulphides also occur.

The D.R.D. pyrite was concentrated by gravity separation and then dry milled to the above mentioned size distibution. The pyrite was then stored in 100 g vacuum sealed plastic packets. To prevent oxidation after opening a packet, the pyrite was kept in a dessicator and nitrogen was flushed through for 5 minutes. Nevertheless, it was proved that storing the pyrite in vacuum sealed packets is not sufficient to prevent further oxidation over long periods. It was therefore decided to clean the pyrite surface of oxidation products by acid leaching. A constant method was followed prior to each flotation run. 17 g of oxidized pyrite was placed in a beaker with 300 ml of HCl solution, (50 % v/v), and agitated for one hour using a magnetic stirrer. The pyrite was then filtered and washed with excess water until no acid could be traced when measuring the pH of the solution. After acid leaching the mass of pyrite reduced by approximately 12 %. This mass reduction is mainly an indication of the mass of oxidation products removed from the pyrite surface. It was also observed that there was an increase in the natural pH of the pulp from pH=4.5 for non-oxidized pyrite, to pH=7.5 for the acid leached pyrite, while the pH of highly oxidized pyrite was pH=2.9.

Quartz from Delmas of S.G.=2.7, with the size distribution of 70 %<75μ was used as the gangue mineral. Particle size analysis using wet sieving and a malvern laser beam particle size analyzer, gave the data presented in Table 3.3.

<u>Table 3.3</u> Particle size analysis of Delmas quartz.

Malvern analyzer		Wet sieving	
size fraction (μm)	distribution (%)	size fraction (μm)	distribution (%)
+5.8 -23.7	21.2	-38	37.3
+23.7 -39.0	12.3	+38 -45	8.4
+39.0 -50.2	6.5	+45 -75	20.0
+50.2 -64.6	9.4	+75 -106	13.8
+64.6 -84.3	10.9	+106 -180	16.0
+84.3 -112.8	11.6	+180	1.4
+112.8-261.6	21.3		

For the pyrite-quartz flotation experiments the ore mixture consisted of 15 g of pyrite and 985 g of quartz. For the pure quartz flotation runs 1000 g of quartz was used.

3.1.2 Water for flotation tests.

Cape Town tap water was used for the flotation and adsorption experiments. The pH of the water was measured daily, and varied between pH=7.8 and pH=9.1. A typical analysis of the water is presented in Table 3.4 (Tyler, 1984).

Table 3.4 Typical analysis of the Cape Town tap water (Tyler, 1984).

cations	Concentration (ppm)	anions	Concentration (ppm)
Na^+	11	Cl^-	21
Mg^{++}	1.5	SO_4^{--}	1.6
Ca^{++}	18 (15 to 21)		
K+	0.4		
Fe^{++}	0.047		

pH=9
conductivity : 15 ms/m
total hardness : 52 ppm
TDS : 98 ppm

3.1.3 Flotation reagents

Collector

All the xanthate collectors were triply purified as the crude commercial xanthates contain about 39% impurities. The impurities were removed by dissolving the xanthate in acetone. Then the solution was filtered to remove the impurities, and the xanthate was precipitated by adding benzene. To avoid unnecessary losses of reagents during the precipitation, the temperature of the solution was reduced using an ice bath. The recovered pure xanthate was dried in a vacuum at room temperature. The analysis of the purified xanthates was done at MINTEK spectrophotometrically, and they were found +90% pure.

The various xanthate collectors were added in equivalent molecular concentrations, using an initial solution concentration of $4.2*10^{-2}$ moles/l. $4.2*10^{-4}$ moles were added per run. This concentration is equivalent with 60 g/t SEX, 65,5 g/t SNPX, 71.7 g/t SIBX, 71.7 g/t SNBX, 78.2 g/t PNBX, and 84.2 g/t PAX.

Frother

Polypropelyne glycol ether, (DOWFROTH 250) of S.G.= 0.973, was used at the dosage of 30 g/t.

Modifiers

In all experiments calcium hydroxide and sulphuric acid were used to modify the pH. In the flotation tests where pure quartz ore was used, sodium hydroxide was added in some cases and this will be indicated when appropriate.

3.1.4 Constant parameters

The following flotation parameters were kept constant during the flotation runs:

Pulp density : 1.2
Percentage of solids : 25.5 %
Impeller speed : 1300 r.p.m.
Aeration rate : 7.5 l/min
Froth height : 3 cm

No attempt was made to control the temperature which was found to vary between 21°C and 28°C. The temperature was measured at the end of each run. Previous studies however showed that over this range no serious effect of temperature was observed (Botelho De Sousa, 1983).

3.1.5 Flotation tests and flotation procedure.

All flotation runs were carried out in a 3 litre Leeds cell. It was found though that the solenoid valve used to control the pulp height was not sensitive enough, and this was replaced by the constant head device illustrated in Figure 3.1. This consists of a reservoir with overflow. The height of this reservoir was adjusted to the required level in the flotation cell. Therefore the level of the water in the reservoir was such that water was just beginning to overflow. While no water is removed from the cell, the water in the reservoir would continue to overflow. As soon as flotation begins and water is removed from the cell, the pulp level begins to drop and water then flows from the reservoir in order to re-establish the required pulp level. The sensitivity of this level control device was found to depend on the diameter of the line between the reservoir and the cell. If the line was too narrow, water was removed from the cell at a faster rate than it could be replenished resulting in a lowering of the pulp level. With this simple device the pulp level was found to vary by no more than 2 or 3 mm.

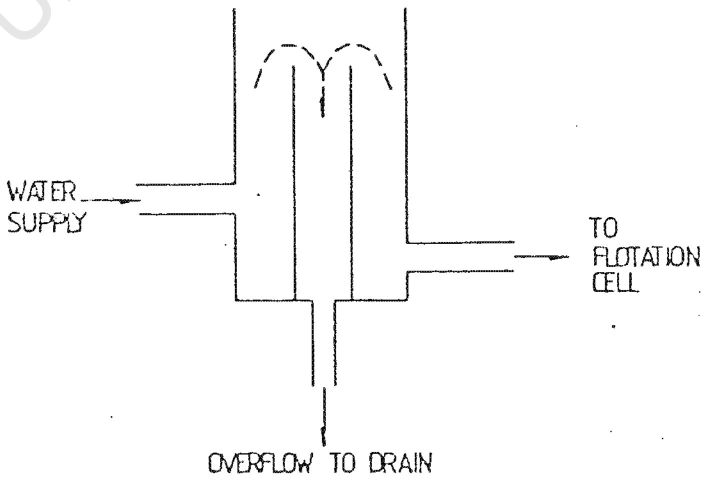


Figure 3.1 Device to maintain a constant pulp level.

For each flotation run 1000 g of ore and 3 litres of tap water were placed in the cell. The pulp was conditioned at the desirable pH level for 30 minutes. This time period was found adequate to obtain a fairly stable pH. Calcium hydroxide and sulphuric acid were used to modify the pH as required. The collector, when added, was conditioned for 4 minutes. Finally frother was added and conditioned for 1 minute.

A scraping technique as opposed to a sweat plate was used to remove the froth. The froth collecting time intervals were in every case 15, 15, 30, 60, 120, 180, 180 seconds. The total froth collecting time was 10 minutes. In the case of the flotation runs with almost zero froth height, the froth was allowed to overflow for the above mentioned time intervals.

The concentrates were weighed, filtered by means of a Buchner funnel, and dried at 90°C. The dried samples were weighed again and thus the mass of water removed at each time interval could be recorded. The tailings were emptied from the cell, filtered in a pressure filter, and dried at 90° C. After drying, both concentrates and tailings were prepared for sulphur analysis. For this, the concentrates and tailings were pulverized using pestle and mortar in order to become homogenous mixtures. A representative sample of tailings was obtained using a riffler, and they were sent to MINTEK for analysis.

3.2 ADSORPTION TESTS

Adsorption studies have proved to be a valuable way to understand some of the processes taking place in flotation systems. The study of the rate of adsorption of the flotation reagents on different mineral surfaces, is a key for selective flotation processes where this is the rate controlling step, while the study of the extent of adsorption gives information about the efficiency of a reagent to adsorb on a specific mineral at different conditions. In this research adsorption tests were carried out mainly to study the extent of adsorption of the different xanthate reagents on the pyrite and quartz surfaces. The question related to the pyrite flotation properties was why the oxidized pyrite has such poor floatability compared to the acid leached pyrite. The adsorption experimental work was hence aimed at detecting the extent of adsorption of the different xanthate collectors on oxidized and acid leached pyrite. In addition, adsorption runs were done using quartz in order to see if the xanthate collector adsorbed on quartz surfaces, and to what extent this occured.

The conditions under which the adsorption tests were as similar as possible to those in the flotation cell. The adsorption of the xanthate ions on the pyrite surface is highly influenced by the pH and all runs were carried out at pH=9, as for the flotation tests with different xanthates. The adsorption tests on quartz were carried out at pH=9 and pH=12, the latter level being that at which the highest quartz recovery was obtained.

The absorption of a liquid varies with the wavelength at which it is measured, the characteristic wavelength being that at which the adsorbance is the highest. The characteristic wavelength for all xanthate reagents was found to be 300 nm.

3.2.1 Description of the apparatus

The apparatus consisted essentially of a U-shape vessel of circular cross-section, with an approximate capacity of one litre. The reactor was covered with a five port glass lid. The central port housed a stainless steel stirrer driven by an electric motor at the speed of 650 r.p.m.. The other ports were used to measure the pH, to adjust the sintered disc (of 4µ porosity), through which the solution was pumped out for U.V. measurements, and to add pH modifying reagents and the collector.

The reactor was immersed in a water bath for temperature control; the temperature was kept constant at 25°C at all runs. A pump was used to suck the solution from the reactor. An automatic sampler was connected in the circuit, so that a sample could be taken every 5 seconds. The flow rate of the pump was adjusted to 30 cm^3/min so that adequate solution was collected for the absorption measurements. Figure 3.2 shows a schematic diagram of the apparatus used.

3.2.2 Preparation of ore.

In the case of the oxidized pyrite and the quartz no special preparation procedure was followed. For the oxidized pyrite runs, 4.4 g were used. For the acid leached pyrite experiments a particular preparation procedure was followed. Initially it was estimated, by measuring various samples, that 5 g pyrite cake, obtained from acid leaching and subsequent filtration, was equivalent with 4.4 g of dry pyrite. Two runs were carried out under identical conditions using PAX collector and showed good reproducibility.

In the case of quartz, a larger amount of ore viz. 50 g, was used to provide a larger surface area for collector adsorption.

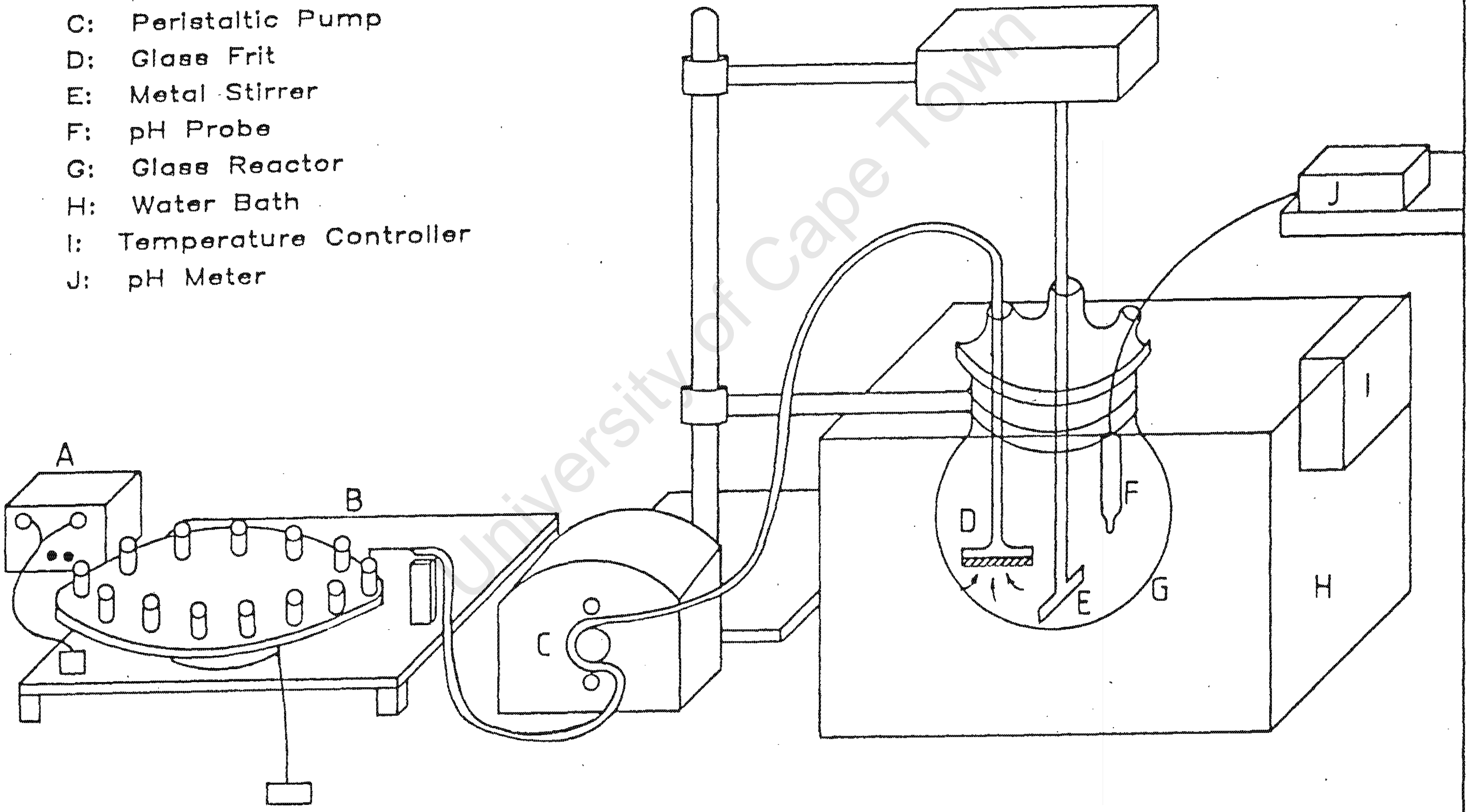
3.2.3 Experimental procedure.

The procedure which was followed was identical for all adsorption runs. The ore was added to the reactor with one litre of tap water. In the case of acid leached pyrite, the ore cake with a fraction of the water to be added in the

Figure 3.2 EQUIPMENT USED IN ADSORPTION STUDIES

KEY

A: Timer
B: Automatic Sampler
C: Peristaltic Pump
D: Glass Frit
E: Metal Stirrer
F: pH Probe
G: Glass Reactor
H: Water Bath
I: Temperature Controller
J: pH Meter



reactor, was placed in the ultra-sonic bath for 3 minutes to ensure adequate particle segregation and then added to the reactor with the rest of the water. The pulp was then conditioned for 30 minutes at the desired pH value using $Ca(OH)_2$. At time zero 10 ml of collector solution ($1.11*10^{-2}$ moles/l) was added to the reactor. The pump had been switched on 20 seconds earlier in order to obtain samples of the solution prior to collector addition. Samples were collected every 5 seconds for 3 minutes. Samples were also collected every minute for 7 minutes. The U.V. spectrometer was referenced with tap water at 300 nm wavelength. The maximum collector adsorption in the reactor could not be measured directly from the reactor, as adsorption had started taking place while the collector was added. So it was estimated measuring the adsorption of a standard solution of $1.11*10^{-4}$ moles/l.

3.3 SULPHUR ANALYSIS

3.3.1 Method

The combustion method, a technique used successfully for the determination of sulphur in metals, inorganic materials and some organic materials, was used to analyse the sulphur content of the feed and the flotation concentrates. In theory, combustion sulphur analysis is quite simple. The sample is burned in oxygen at high temperatures and the sulphur combustion products are carried to a titrator by the oxygen stream. These combustion products are generally SO_2 and SO_3 with the SO_2/SO_3 equilibrium dependent on the combustion temperature. The SO_3 tends to condense in the delivery system, so it is often partially or totally lost. When this occurs, low and erratic results are obtained. Since the iodate titration method determines only SO_2, any variations resulting from SO_3 condensation are eliminated. One hundred percent conversion of sulphur to SO_2 would be the ideal situation although in actual practice it is seldom, if ever, realized. A correction factor, estimated by analysing several standard samples, is then used to determine the total sulphur content of the sample (LECO).

3.3.2 Apparatus

Induction furnace

The high frequency furnace of the Leco sulphur determinator, which is capable of combustion temperatures of up to 1650°C, was used to burn the sample. Temperature conditions are set by means of a Variac so that a current of 60 mA is set on the grid and a current of +200 mA is set on the plate.

The oxygen used for combustion and for carrying the combustion products to the titrator was first passed through a magnesium perchlorate purifying train at a constant flow rate of 0.5 l/min.

Manual titrator

The manual titration is based on the iodate method as follows: Sulphur is combusted to SO_2 (approximately 90%) and to SO_3 (approximately 10%). The concentration of KIO_3 titrator is simply factored to compensate for that portion of sulphur combusted to SO_2. The fraction of sulphur released as SO_3 is considered by calibration. The calibration factor is determined by analysing several known standards. Experience has shown the fraction to be constant for the same type of materials over long periods of time so that sulphur determinations obtained by this method are accurate and consistent.

The chemical reagents used are the follows:

50 ml HCl 2% v/v
15 ml KI-starch indicator
1.1125 g/l KIO_3 - titrant

The reaction which is taking place is:

$$KIO_3 + KI + 6\ HCl \rightarrow 3I_2 + 6KCl + 3H_2O$$

The iodine and the starch form a complex which is blue in colour. The SO_2 reduces the iodine to iodate destroying the blue starch iodine complex according to the following equation:

$$SO_2 + I_2 + 2H_2O \rightarrow H_2SO_4 + 2HI$$

In the manual titration in order to avoid initial losses of SO_2, a few drops of titre are added to the initial solution of HCl and KI-starch indicator. When the SO_2 bleaches the blue colour to faint blue, more KIO_3 is added. The endpoint is indicated when the solution achieves a permanent faint blue colour.

Knowing the mass of the sample as well as the volume of KIO_3 solution used to titrate that mass, the percentage of sulphur is determined. For the concentration of the KIO_3 solution used, this relationship is given by the following equation: (Appendix A)

$$\%S(\text{released as } SO_2) = \frac{\text{volume of } KIO_3 \text{ used}}{\text{mass of sample} * 20.04}$$

This amount of sulphur is related to the total sulphur by the equation,

$$\text{Total } \%S = \%S \text{ released as } SO_2 * \text{Correction factor}$$

This correction factor was obtained by comparing the actual sulphur content of a set of standard samples to the values determined by the combustion method. Four analyses were done for each sample and the results obtained are shown in the Table 3.5. Knowing the actual sulphur percentage of the standard samples, the calibration factors were obtained (Table 3.6). The calibration factors which were used in this work to estimate the sulphur content of the feed and the concentrates, are given in Table 3.7.

Details of the design of the manual titrator and the method of analysis on which the above is based are contained in Appendix B.

Table 3.5 Assays obtained for the pyrite standards used for the calibration of the Leco sulphur analyser.

Sample No	%S released as SO_2				$\bar{m}$	ΔS
16/81	1.13	1.12	1.13	1.10	1.12	0.014
17/81	3.7	3.6	3.7	3.7	3.68	0.05
18/81	7.1	7.4	7.3	7.3	7.28	0.126
19/81	13.4	13.5	13.0	13.2	13.28	0.222
20/81	31.0	31.3	31.3	31.6	31.30	0.245
D.R.D	46.1	47.1	46.6	47.2	46.74	0.509

where $\bar{m}$ is the mean value obtained for the sulphur assays done to each of the standards, and ΔS is the corresponding standard deviation.

Table 3.6 Calibration factor obtained for each of the pyrite standards.

Sample No	actual S%	estimated S% from Table 3.5	calibration factor
16/81	1.15	1.12	1.027
17/81	3.7	3.68	1.007
18/81	7.3	7.28	1.003
19/81	13.9	13.28	1.047
20/81	33.3	31.30	1.064
D.R.D	50.2	46.74	1.073

Table 3.7 Calibration factors used at the determination of the sulphur content.

sulphur range	calibration factor
$x < 2\%$ S	1.027
2% S $< x < 10\%$ S	1.005
10% S $< x < 25\%$ S	1.047
25% S $< x < 40\%$ S	1.064
40% S $< x$	1.073

CHAPTER 4

RESULTS

4.1 FLOTATION TESTS

4.1.1 Reproducibility tests

A reproducible technique was established during the flotation experiments in order minimize operating errors. This involved a daily check on water pH and temperature, accurate pH control, addition of reagents, as well as a regular calibration of the air rotameter and the impeller speed. However, as shown in section 4.1.2.2, the gradual oxidation of pyrite proved to be one of the major parameters which influenced the reproducibility of the system over a long period of time.

In order to eliminate operator errors during the froth removal procedure, a constant technique was used. The rate of the froth removal for the first, second and third concentrates was one scrape per 3 seconds. The rest of the concentrates were collected by scraping every 5 seconds, allowing 5 seconds at the begining of the froth removal to remove the froth collecting tray and to clean the flotation cell lip. The high speed of the froth removal was decided upon after it had been observed that during flotation at high pH values a very fast moving froth was produced. Therefore, a rapid scraping technique was required to control the removal of the froth and this was kept constant at all flotation tests.

Four reproducibility tests were carried out at pH=9 using 84.2g/t PAX collector. The results of these experiments are presented in Tables 4.1 to 4.6 and are shown diagramatically in Figures 4.1 to 4.4. The method of calculating the flotation parameters is explained in Appendix C. However, it should mentioned that when the flotation parameters were varied, particularly the pH, the system behaved in a different but reproducible manner. Hence, duplicated experiments were carried out during most of the flotation work, especially when the effect of pH was investigated.

Table 4.1 Flotation reproducibility experiments using pyrite-quartz mixtures and 84.2 g/t PAX collector at pH=9. Cumulative mass of the concentrate with increasing flotation time.

time(sec)	test 1	test 2	test 3	test 4	$\bar{m}$	std. dev.
15	15.3	15.8	15.0	15.5	15.4	0.41
30	20.7	21.8	20.5	21.3	21.1	0.59
60	24.8	25.9	24.2	25.1	25.0	0.71
120	26.3	27.5	26.0	27.1	26.7	0.69
240	26.7	27.9	26.4	27.6	27.2	0.71
420	26.9	28.2	26.6	27.8	27.4	0.75

Table 4.2 Flotation reproducibility experiments using pyrite-quartz mixtures and 84.2 g/t PAX collector at pH=9. Cumulative grade, (%S), of the concentrate with increasing flotation time.

time (sec)	test 1	test 2	test 3	test 4	$\bar{m}$	std. dev.
15	29.7	29.3	29.9	29.5	29.6	0.26
30	27.7	27.2	28.0	27.5	27.6	0.34
60	26.8	26.2	27.1	26.5	26.7	0.39
120	26.6	26.1	26.2	26.5	26.5	0.33
240	26.4	25.8	26.8	26.3	26.3	0.41
420	26.3	25.7	26.6	26.2	26.2	0.37

Table 4.3 Flotation reproducibility experiments using pyrite-quartz mixtures and 84.2 g/t PAX collector at pH=9. Cumulative pyrite recovery, (%), with increasing flotation time.

time (sec)	test 1	test 2	test 3	test 4	$\bar{m}$	std. dev.
15	59.1	58.2	57.7	58.8	58.5	0.62
30	74.8	74.3	73.8	75.3	74.6	0.65
60	86.8	85.3	84.4	85.6	85.5	0.99
120	91.2	89.9	90.0	92.4	90.9	1.18
240	92.0	90.6	90.9	93.5	91.8	1.31
420	92.2	90.8	91.1	93.7	92.0	1.31

Table 4.4 Flotation reproducibility experiments using pyrite-quartz mixtures and 84.2 g/t PAX collector at pH=9. Cumulative gangue recovery, (%), with increasing flotation time.

time (sec)	test 1	test 2	test 3	test 4	$\bar{m}$	std. dev.
15	0.69	0.73	0.67	0.71	0.70	0.026
30	1.02	1.09	0.99	1.05	1.04	0.043
60	1.26	1.34	1.22	1.29	1.28	0.051
120	1.34	1.43	1.32	1.39	1.37	0.050
240	1.38	1.47	1.34	1.43	1.41	0.057
420	1.39	1.49	1.36	1.44	1.42	0.057

Table 4.5 Flotation reproducibility experiments using pyrite-quartz mixtures and 84.2 g/t PAX collector at pH=9. Cumulative mass of water removed with increasing flotation time.

time (sec)	test 1	test 2	test 3	test 4	$\bar{m}$	std. dev.
15	81	90	77	85	83	5
30	123	140	119	130	128	9
60	162	182	155	172	168	11
120	173	194	170	185	181	11
240	176	197	172	189	184	11
420	177	198	174	190	185	11

Table 4.6 Flotation reproducibility experiments using pyrite-quartz mixtures and 84.2g/t PAX collector at pH=9. Klimpel values for pyrite and gangue.

	test 1	test 2	test 3	test 4	$\bar{m}$	st. dev.
pyrite rec. ψ, (%)	95.0	93.5	93.7	96.1	94.6	1.2
pyrite rate $k*10^3 sec^{-1}$	161.9	163.0	158.2	154.4	159.4	3.9
ΣE^2	6.6	5.5	3.5	3.1		
gangue rec. ψ, (%)	1.44	1.54	1.50	1.50	1.50	0.04
gangue rate $k*10^3$ sec^{-1}	106.2	104.5	103.8	102.9	104.4	1.4
ΣE^2	0.4	0.4	0.3	0.3		

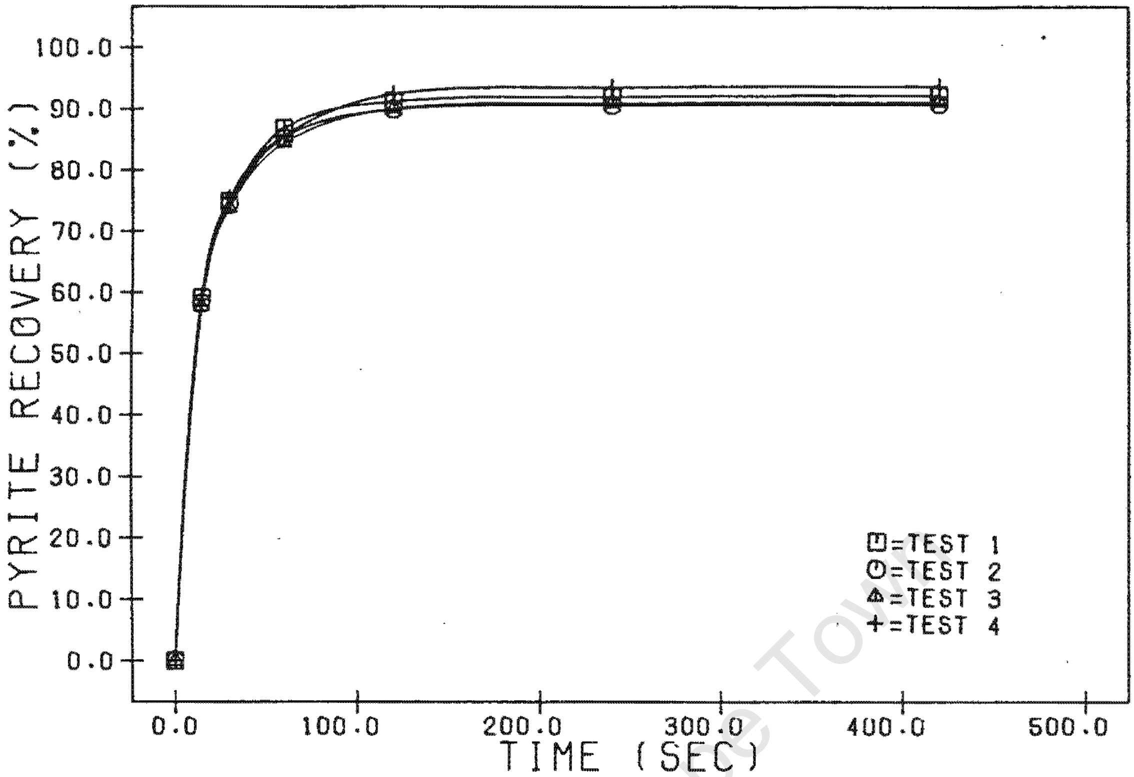


FIG 4.1 REPRODUCIBILITY FLOTATION EXPERIMENTS USING PYRITE-QUARTZ MIXTURES AND 84.2 G/T PAX COLLECTOR AT PH=9. CUMULATIVE PYRITE RECOVERY WITH INCREASING FLOTATION TIME.

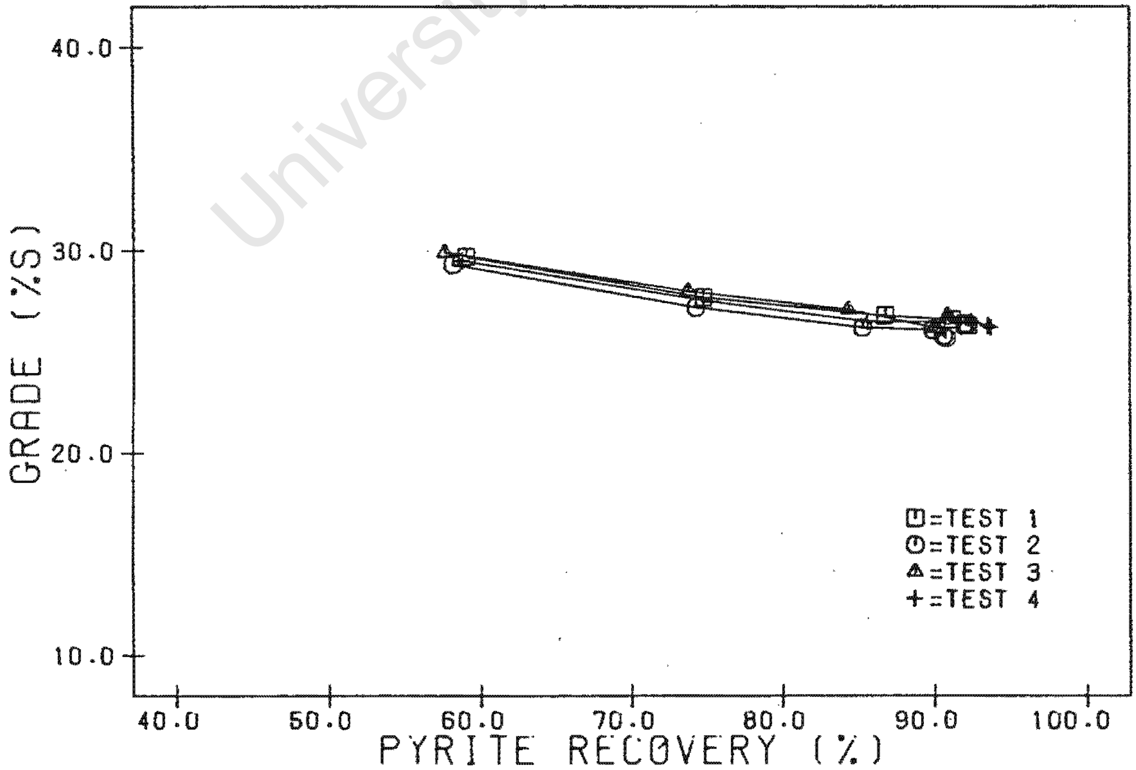


FIG 4.2 REPRODUCIBILITY FLOTATION EXPERIMENTS USING PYRITE-QUARTZ MIXTURES AND 84.2 G/T PAX COLLECTOR AT PH=9. GRADE-PYRITE RECOVERY CURVES.

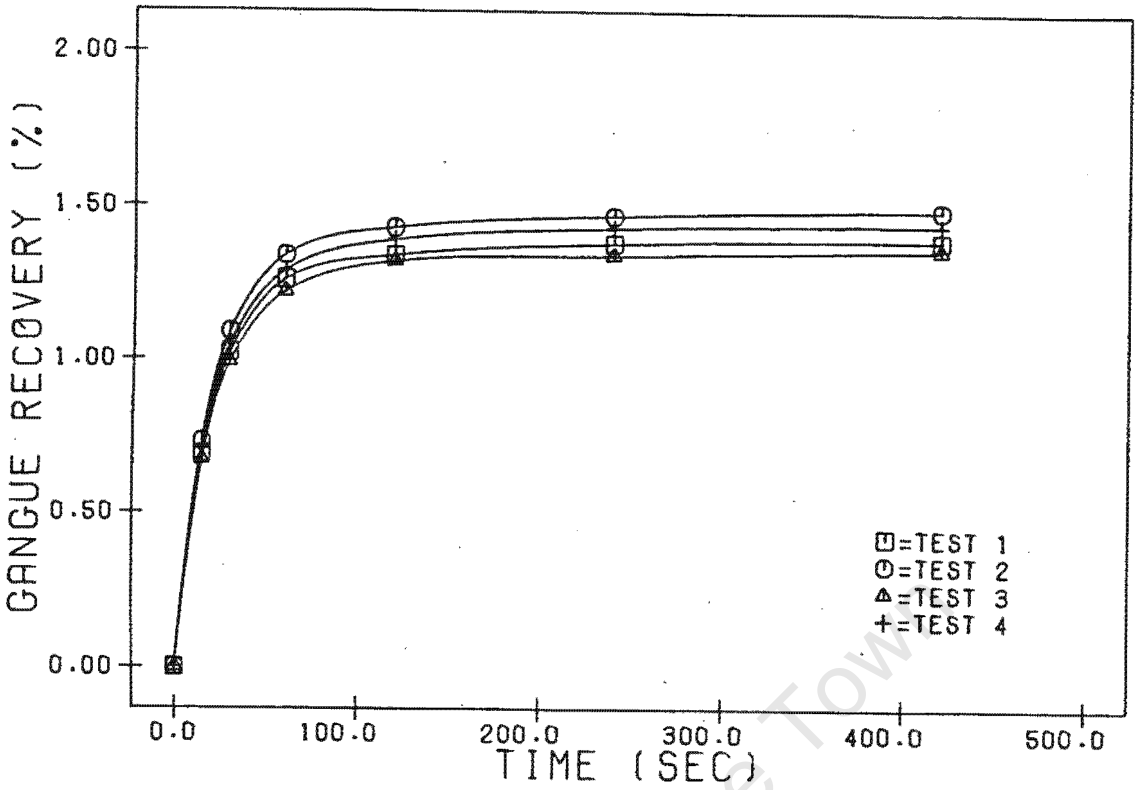


FIG 4.3 REPRODUCIBILITY FLOTATION EXPERIMENTS USING PYRITE-QUARTZ MIXTURES AND 84.2G/T PAX COLLECTOR AT PH=9. CUMULATIVE GANGUE RECOVERY WITH INCREASING FLOTATION TIME.

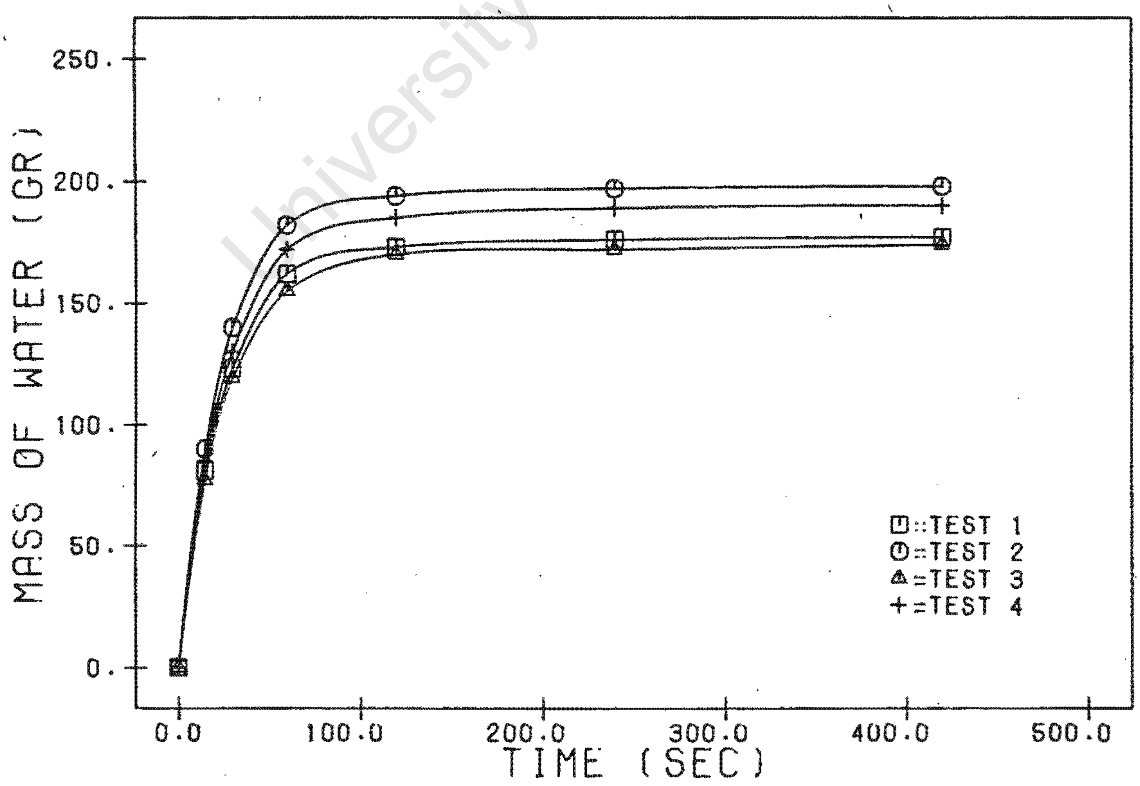


FIG 4.4 REPRODUCIBILITY FLOTATION EXPERIMENTS USING PYRITE-QUARTZ MIXTURES AND 84.2G/T PAX COLLECTOR AT PH=9. MASS OF WATER REMOVED WITH INCREASING FLOTATION TIME.

4.1.2 Pyrite-quartz ore mixture

4.1.2.1 Effect of the variation of pH

The literature reports that the flotation properties of pyrite and xanthate collectors are influenced by the pH (see sections 1.4.1. and 1.4.2). Therefore, the pyrite-quartz synthetic mixture was examined at pH values covering the acid, neutral and alkaline region, in the range of pH=4 to pH=12. Initially, the natural floatability of non-oxidized pyrite, viz. pyrite used shortly after storage, was examined. Repeatability flotation experiments were carried out with frother addition only. In these experiments the temperature varied between 21°C and 25°C.

The detailed results of these tests are tabulated in Appendix D (Tables D.1 to D.5). From these data the ultimate recovery, Ψ, and the rate constant, k, were calculated using the Klimpel model and the values are presented in Table 4.7 where also the actual values are recorded. The grade and mass of water removal are also included in this table.

The results from these experiments are also presented diagramatically in Figures 4.5 to 4.8. As discussed in section 1.3 the recovery of pyrite after 30 seconds, (R_{30sec}), is used here as a measure of the rate of flotation rather than the Klimpel rate constant. Figure 4.10 shows the gangue recovery-pH curve, and Figure 4.11 the cumulative mass of water removed at the different pHs. The method of calculating the flotation parameters is explained in Appendix C.

Non-oxidized pyrite-quartz synthetic mixtures were examined in the same pH range in presence of xanthate collector. For this, SIBX collector was added at a dosage of 71.7g/t. The temperature of the pulp, measured at the end of the experiment, varied between 20°C and 22°C. The temperature of the pH=12 run was 27°C.

Flotation parameters / pH	pyrite rec.(%)		pyrite rate		E^2 for pyrite	gangue rec(%)		gangue rate		E^2 for gangue	grade(%S)	mass of water (gr)
	actual	ψ	R_{30sec}	$K/10^{-3}\ sec^{-1}$		actual	ψ	R_{30sec}	$K/10^{-3}\ sec^{-1}$			
4	91.2	93.3	43.4	45.5	11.2	1.75	1.85	0.55	22.8	0.90	22.3	296
	91.2	93.5	43.4	45.6	10.2	1.51	1.61	0.48	24.0	0.18	24.2	265
5	87.3	89.6	39.8	40.0	8.3	1.51	1.60	0.52	26.7	0.29	23.6	277
	86.1	88.4	39.8	44.2	9.6	1.57	1.62	0.60	32.5	0.50	22.9	293
6	82.7	85.4	39.7	46.3	1.3	2.21	2.30	0.98	41.0	0.61	18.2	372
	83.3	85.4	39.1	45.6	5.1	2.26	2.34	0.92	37.0	0.54	18.0	412
7	50.0	52.3	20.4	37.2	1.8	2.20	2.29	1.24	61.3	3.50	12.7	327
	51.9	54.3	21.3	37.1	4.3	2.23	2.32	1.24	58.8	2.65	12.9	352
8	28.0	29.5	11.7	40.0	4.8	2.51	2.65	1.47	66.5	9.10	7.1	356
	37.0	38.6	15.4	39.3	2.3	1.95	2.05	1.16	66.9	3.1	11.0	298
9	22.7	23.6	10.2	44.5	1.8	2.20	2.30	1.36	70.0	5.0	6.6	322
	25.5	27.5	11.2	40.1	1.8	2.57	2.76	1.59	67.3	7.7	6.4	375
10	17.2	18.3	7.8	42.1	0.3	2.61	2.78	1.65	72.4	5.2	4.5	389
	16.7	17.9	7.7	43.2	1.5	2.73	2.95	1.71	67.4	12.4	4.1	395
11	20.7	21.8	9.0	41.4	1.2	3.32	3.51	1.95	64.9	11.6	4.2	457
	26.3	27.8	10.5	35.4	0.9	3.54	3.74	2.03	62.9	15.4	4.9	490
12	19.9	21.0	8.3	37.1	0.6	4.77	5.04	2.35	47.9	7.6	2.9	478
	16.7	17.5	7.3	41.2	1.4	4.31	4.57	2.20	50.8	13.0	2.7	440

Table 4.7
Flotation parameters for pyrite and gangue at different pH values, during flotation of pyrite-quartz mixtures in the absence of collector.

Flotation parameter / pH	pyrite rec (%)		pyrite rate		E^2 for pyrite	gangue rec.		gangue rate		E^2 for gangue	grade(%S)	mass of water (gr)
	actual	ψ	R_{30sec}	$Kx10^3$ sec^{-1}		actual	ψ	R_{30sec}	$Kx10^3$ sec^{-1}			
4	97.1	97.1	67.0	108.8	14.9	0.62	0.65	0.27	40.9	0.05	36.5	89
	95.5	96.3	66.0	109.7	14.6	0.61	0.64	0.26	42.0	0.13	36.4	88
5	90.9	90.6	52.3	70.0	37.8	1.19	1.22	0.50	38.0	0.19	27.4	169
	94.0	94.0	56.0	70.0	38.9	0.96	1.00	0.42	40.0	0.06	30.5	148
6	84.7	84.5	44.7	59.5	37.9	1.53	1.58	0.74	47.8	0.41	23.1	213
	82.5	81.6	49.0	77.3	42.1	1.30	1.33	0.65	51.9	0.13	24.9	192
7	80.3	79.2	49.0	81.0	16.6	1.50	1.55	0.84	59.8	1.8	22.6	201
	84.6	83.7	51.0	77.9	22.3	1.75	1.78	0.97	60.7	1.5	21.4	229
8	74.5	75.1	48.5	84.4	6.4	2.16	2.26	1.37	71.2	8.1	17.2	259
	81.4	82.1	47.5	71.3	4.3	2.48	2.61	1.41	60.8	10.5	16.6	295
9	77.0	79.4	42.8	62.8	5.7	3.69	3.95	1.87	51.9	33.2	11.9	344
	73.0	75.6	45.8	79.2	5.3	3.56	3.81	2.03	61.3	25.0	11.8	336
10	74.6	76.2	45.7	78.1	5.2	4.45	4.67	2.58	64.4	31.0	10.0	368
	75.6	78.1	45.3	71.8	13.0	4.04	4.31	2.31	61.5	43.0	10.9	348
11	78.5	81.4	46.7	70.9	10.5	6.00	6.46	3.11	55.3	99.9	8.1	495
	82.7	85.6	48.1	65.7	6.0	6.59	7.06	3.38	53.5	102.0	7.9	553
12	80.9	84.3	38.5	47.2	3.0	6.62	7.04	3.22	49.1	34.0	7.7	544
	68.6	71.7	34.9	50.9	3.7	6.39	6.80	3.27	51.9	38.0	6.9	547

Table 4.8
Flotation parameters for pyrite and gangue at different pH values during flotation of pyrite-quartz using 71.7 g/t SIBX collector

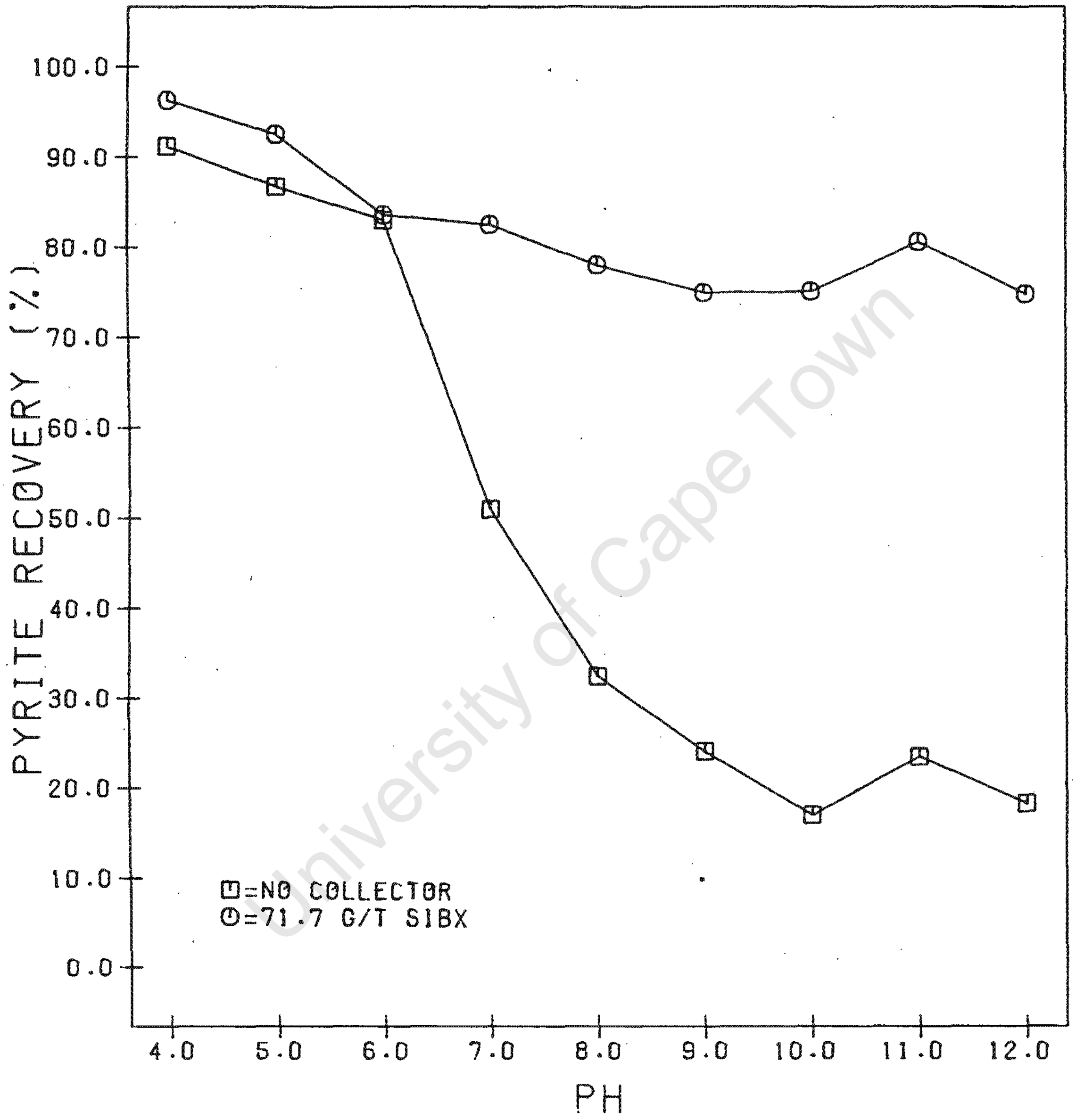


FIG 4.5 VARIATION OF FINAL RECOVERY OF PYRITE WITH PH DURING FLOTATION OF PYRITE-QUARTZ MIXURES USING NO COLLECTOR AND 71.7G/T SIBX.

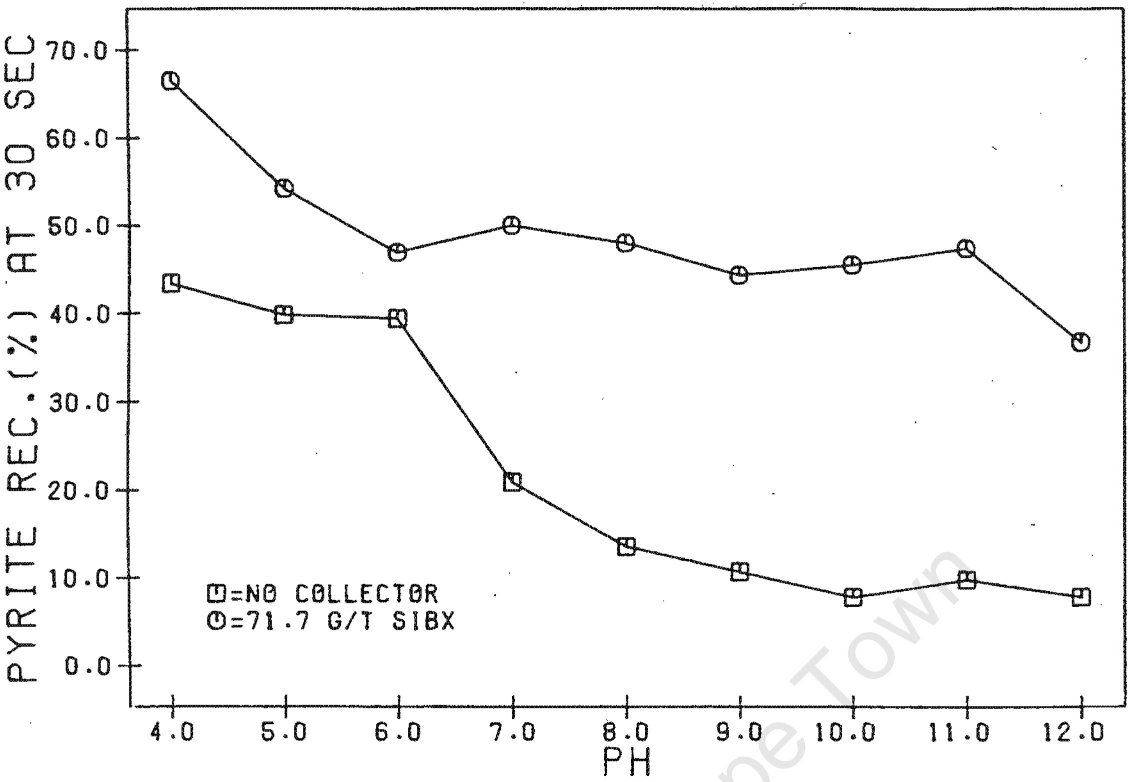


FIG 4.6 VARIATION OF INITIAL RATE OF PYRITE RECOVERY WITH PH, DURING FLOTATION OF PYRITE-QUARTZ MIXTURES USING NO COLLECTOR AND 71.7 G/T SIBX.

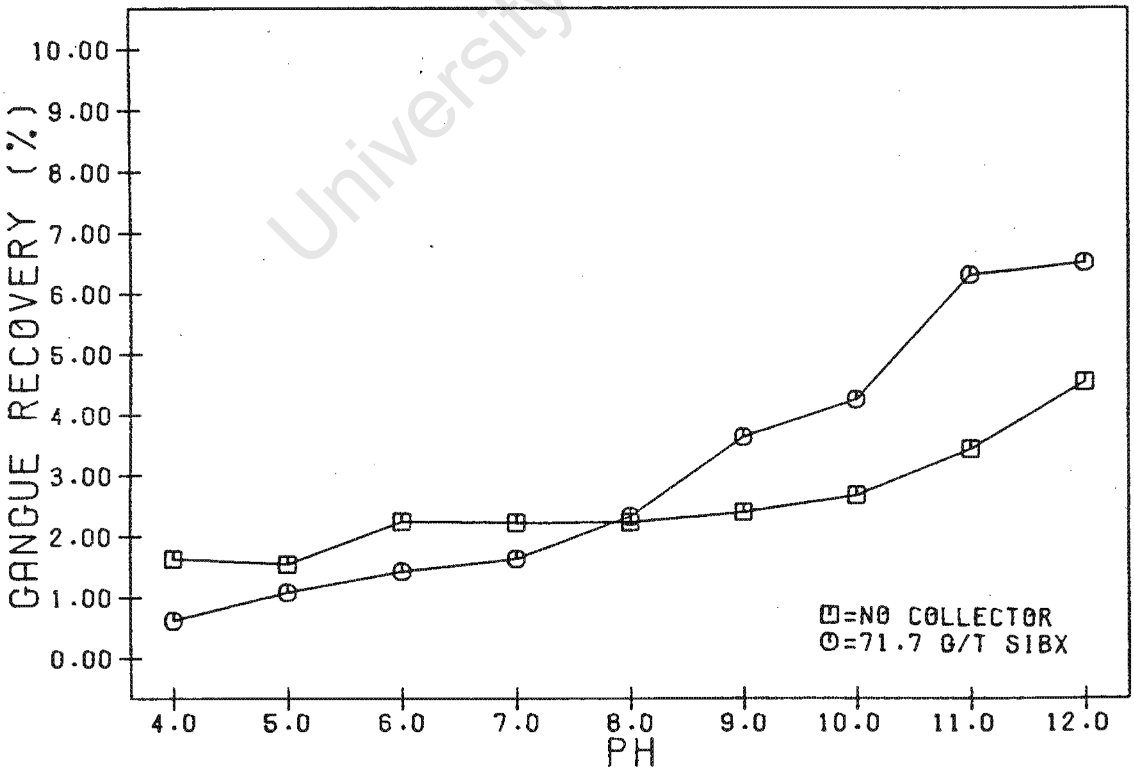


FIG 4.7 VARIATION OF FINAL GANGUE RECOVERY WITH PH DURING FLOTATION OF PYRITE-QUARTZ MIXTURES USING NO COLLECTOR AND 71.7 G/T SIBX.

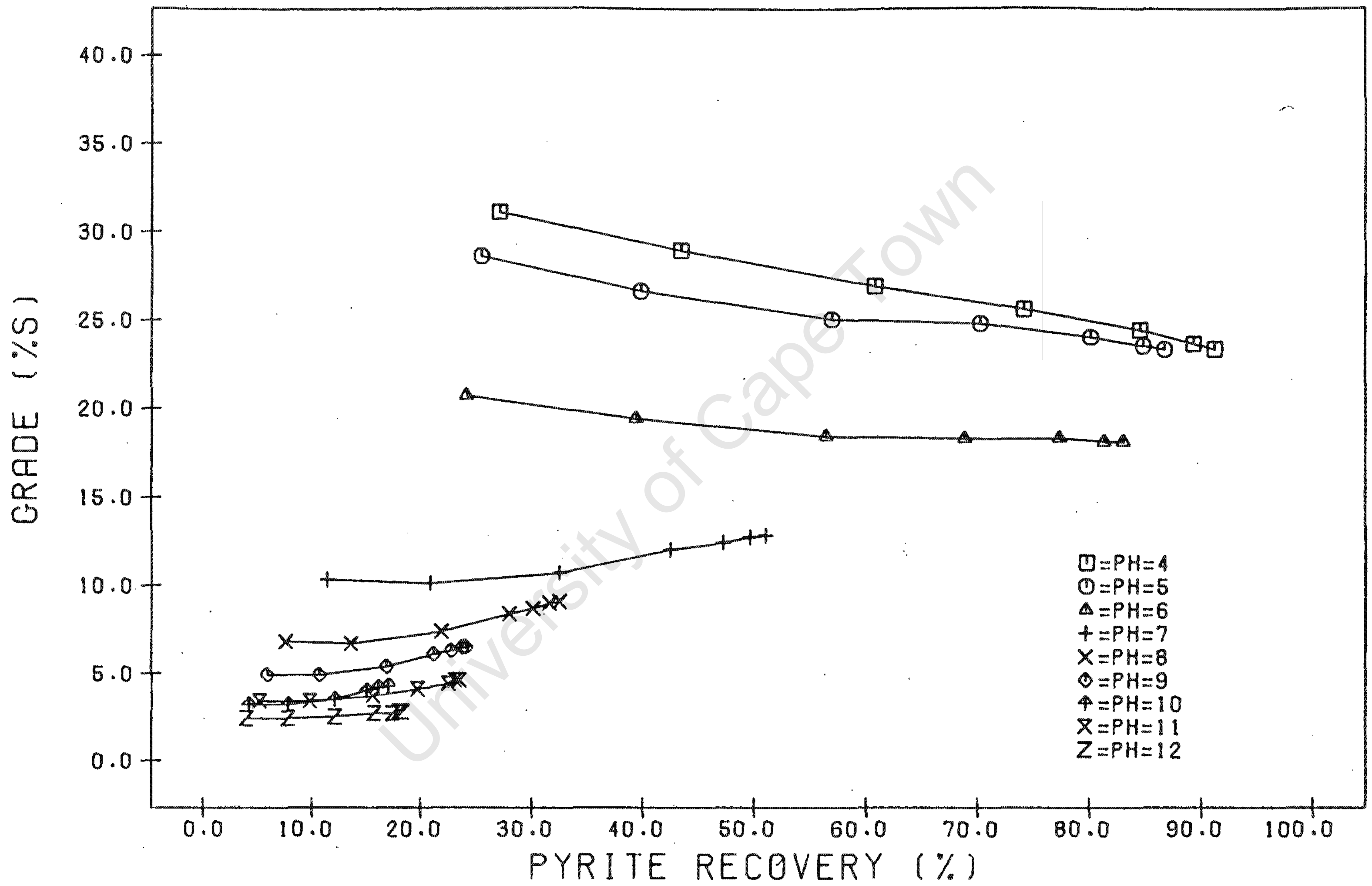


FIG 4.8 GRADE-RECOVERY CURVES FOR FLOTATION OF PYRITE-QUARTZ MIXTURE IN ABSENCE OF COLLECTOR.

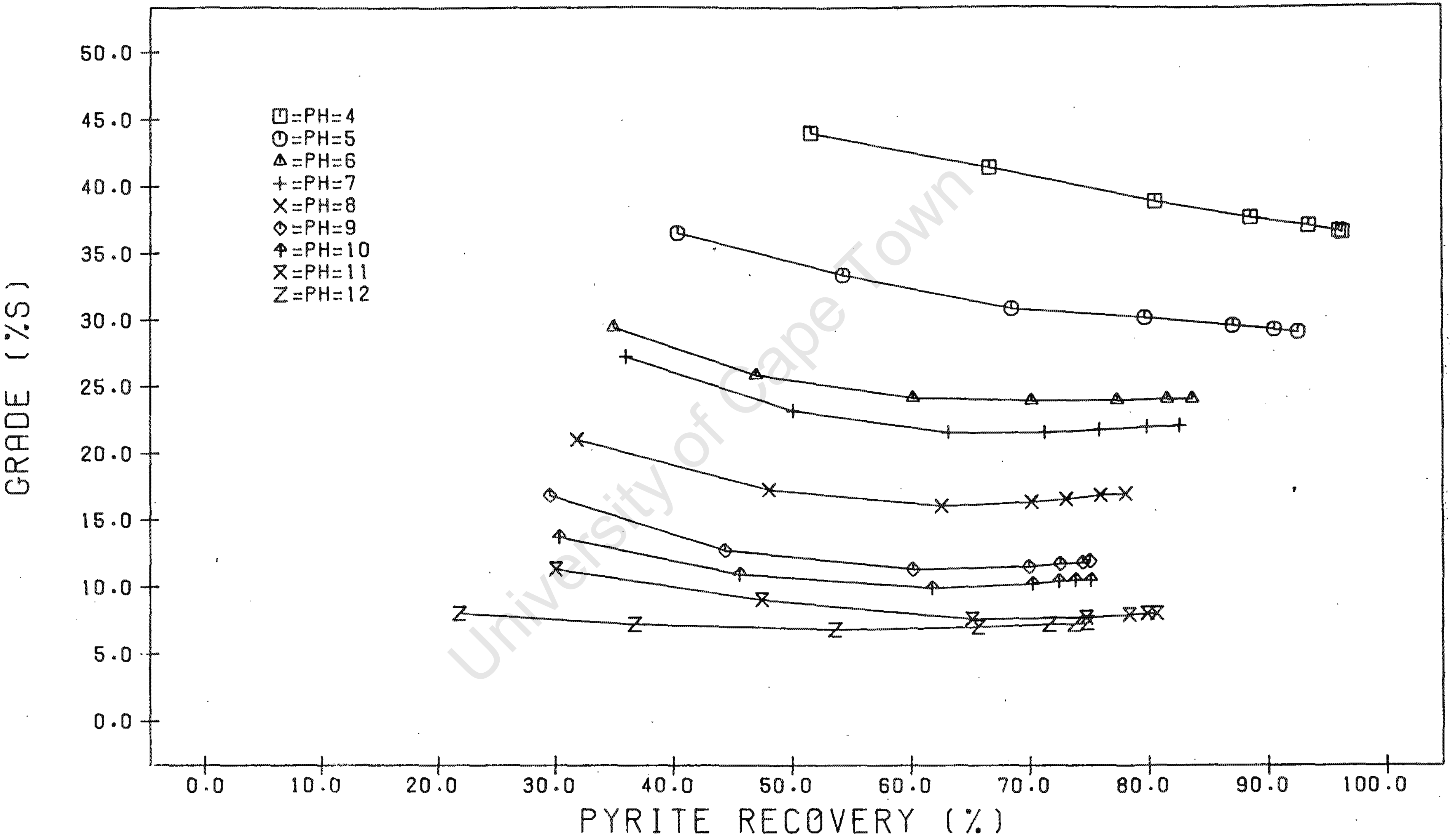


FIG 4.9 GRADE-RECOVERY CURVES FOR FLOTATION OF PYRITE-QUARTZ MIXTURES, USING 71.7 G/T SIBX.

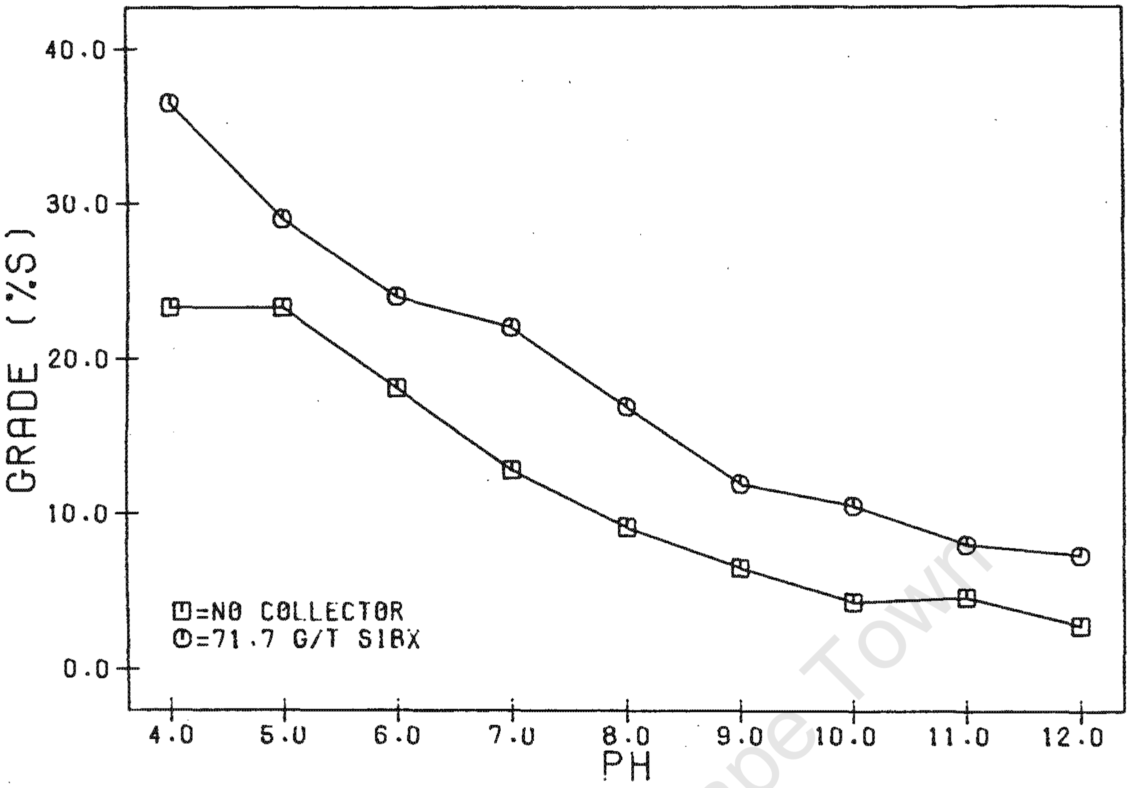


FIG 4.10 VARIATION OF THE FINAL GRADE OF THE CONCENTRATES WITH PH, DURING FLOTATION OF PYRITE-QUARTZ MIXTURES USING NO COLLECTOR AND 71.7 G/T SIBX.

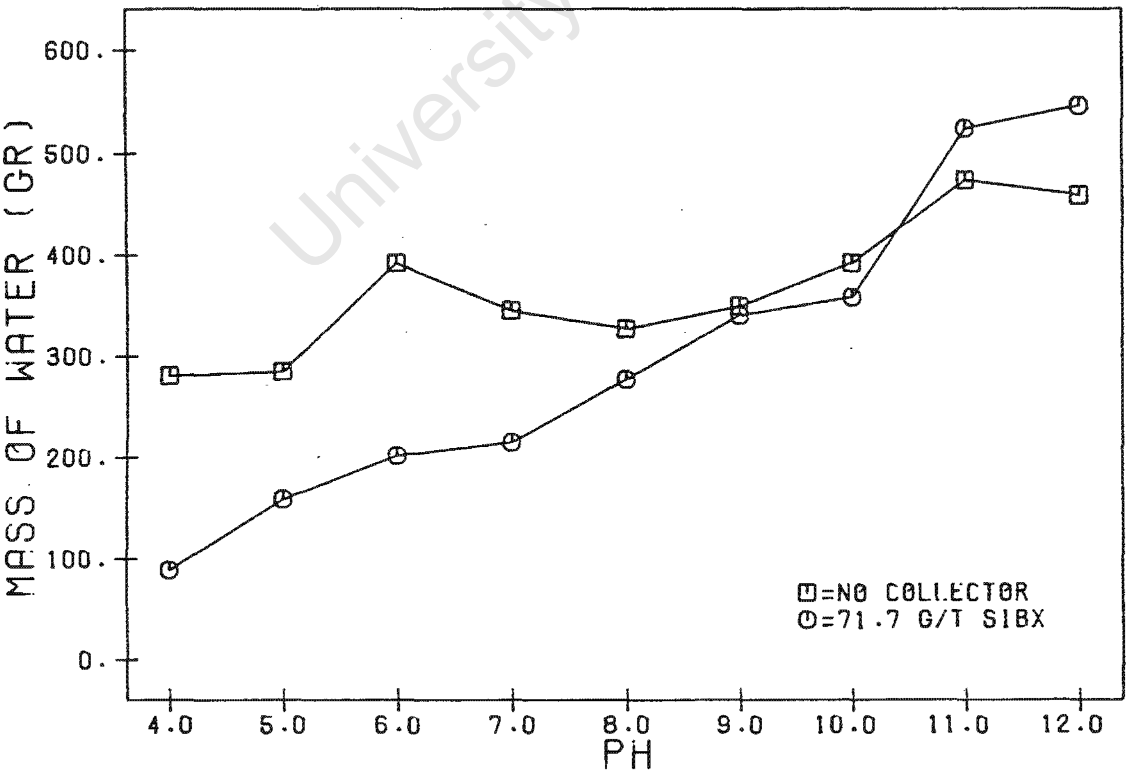


FIG 4.11 VARIATION OF CUMULATIVE MASS OF WATER REMOVED WITH PH, DURING FLOTATION OF PYRITE QUARTZ MIXTURES USING NO COLLECTOR AND 71.7 G/T SIBX.

All flotation runs were duplicated and the detailed results are tabulated in Appendix D (Tables D.6 to D.10). Table 4.8 presents the flotation parameters for the pyrite and for the gangue mineral. The results are also presented diagramatically in Figures 4.5 to 4.7. Figure 4.9 shows the grade-recovery curves. Figure 4.10 shows the gangue recovery at different pH values while Figure 4.11 shows the cumulative mass of water removed at the different pHs.

4.1.2.2 The effect of oxidation on pyrite floatability

One year after the experiments mentioned in section 4.1.1.1 were done, it was decided to repeate a few flotation runs in order to check the reproducibility of the system. These runs revealed a marked deviation in the flotation behaviour of pyrite. Attempts were made to see if the reason for this behaviour were probable changes of the flotation reagents used, or the deformation of the impeller which may have resulted from excessive wear. Neither of these factors were pertinent. The different flotation behaviour was found to be a result of pyrite oxidation.

Figures 4.12 and 4.13 present the final recovery, and the initial rate of the recovery of pyrite, using both oxidized and non-oxidized pyrite. Table 4.9 also presents the final grade of the concentrates at various pHs, in both the oxidized and non-oxidized form. The detailed results from these experiments are presented in Appendix D (Tables D.11 to D.15).

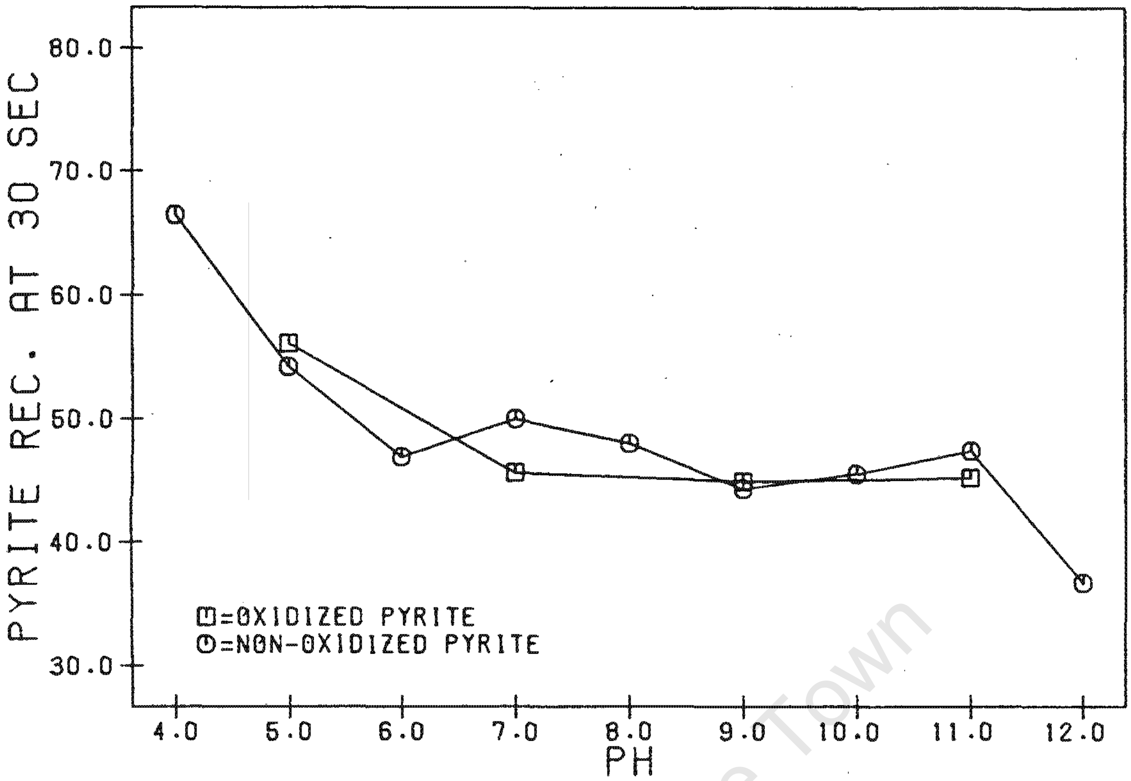


FIG 4.13 VARIATION OF THE INITIAL RATE OF RECOVERY OF OXIDIZED AND NON-OXIDIZED PYRITE WITH PH DURING FLOTATION OF PYRITE-QUARTZ MIXTURES USING 71.7 G/T SIBX.

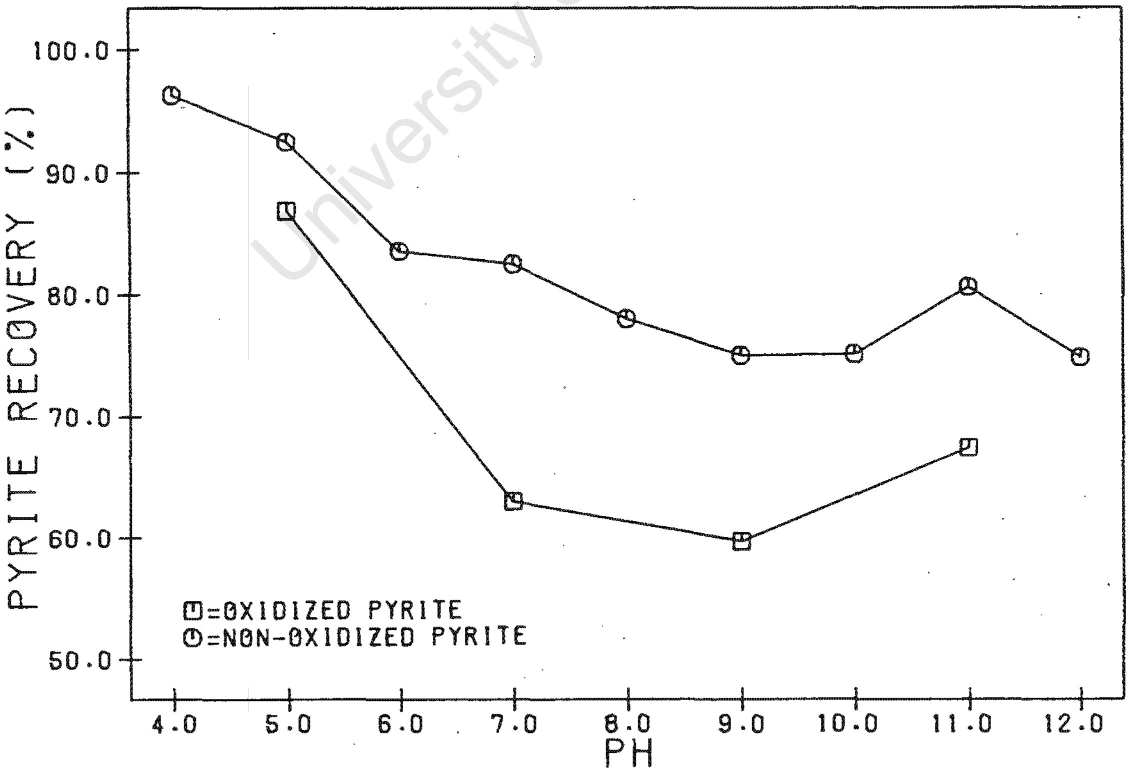


FIG 4.12 VARIATION OF FINAL RECOVERY OF OXIDIZED AND NON-OXIDIZED PYRITE WITH PH, DURING FLOTATION OF PYRITE-QUARTZ MIXTURES USING 71.7 G/T SIBX.

Table 4.9 Flotation experiments with pyrite-quartz synthetic mixture at different pH values, using 71.7g/t SIBX collector. Grade (%S) for oxidized and non-oxidized pyrite at different pH values.

	Grade (%S)							
state of pyrite	pH=5		pH=7		pH=9		pH=11	
non-oxid.	27.4	30.5	22.6	21.4	11.9	11.8	7.8	8.1
oxidized	27.3	-	30.5	29.4	19.7	16.7	6.9	6.7

It was then decided to acid leach the pyrite before the flotation experiments. This method is described in section 3.1.1. These experiments were done at pH=9 using SIBX collector. The flotation parameters for the pyrite and quartz are presented in Tables 4.10 and 4.11. Table 4.12 shows the flotation results for oxidized (long term oxidized pyrite), non-oxidized (partly oxidized pyrite used within two months of storage) and acid-leached pyrite for comparative purposes.

The oxidation also affects the natural floatability of pyrite. Table 4.13 presents the flotation data obtained by non-oxidized and acid-leached pyrite using frother addition only (natural floatability). Detailed results are presented in Appendix D (Tables D.23 to D.27).

Table 4.10 Flotation experiments with acid leached pyrite-quartz synthetic mixture at pH=9, using 71.7g/t SIBX collector. Flotation parameters for pyrite.

	Flotation parameters					
	pyrite rec.(%)		pyrite rate			grade
No of run	ψ	actual	$k*10^3 sec^{-1}$	R_{30sec}	ΣE^2	(%S)
run 1	91.2	88.8	143.1	69.2	3.9	17.7
run 2	93.7	91.2	140.4	70.7	4.3	19.5

Table 4.11 Flotation experiments with acid leached pyrite-quartz synthetic mixture at pH=9 using 71.7g/t SIBX collector. Flotation parameters for gangue.

	Flotation parameters				
No of run	gangue rec.(%) ψ	actual	gangue rate $k*10^3$ sec^{-1}	R_{30sec}	mass of water (g)
run 1	2.84	2.71	102.2	2.01	278
run 2	2.41	2.32	108.1	1.73	247

Table 4.12 Flotation experiments with pyrite-quartz synthetic mixture at pH=9 using 71.7g/t SIBX collector. Flotation parameters for oxidized pyrite, non-oxidized pyrite and acid-leached pyrite.

Flotation parameters	Oxidized pyrite	Non-oxidized pyrite	Acid-leached pyrite
pyrite rec. (%)	59.7	75.0	90.0
pyrite ψ	59.0	77.5	92.5
pyrite rate $k*10^3$ sec^{-1}	144.9	71.0	141.8
R_{30sec}	44.9	44.3	70.0
quartz rec.(%)	1.62	3.63	2.52
quartz ψ	1.62	3.88	2.63
quartz rate $k*10^3$, sec^{-1}	104.5	56.6	105.2
$R_{30\ sec}$	1.18	1.95	1.87
mass of water, (g)	213	340	262
grade, (%S)	18.2	11.9	18.6

Table 4.13 Flotation experiments with pyrite-quartz synthetic mixture at pH=9 using no collector. Flotation parameters for non-oxidized and acid leached pyrite.

Flotation parameters	non-oxidized pyrite	acid leached pyrite
pyrite rec.(%)	24.1	44.8
pyrite ψ (%)	25.6	46.0
pyrite rate $k*10^3$, sec^{-1}	42.3	48.9
$R_{30\ sec}$	10.7	21.9
quartz rec.(%)	2.39	3.08
gangue ψ (%)	2.53	3.14
quartz rate $k*10^3$, sec^{-1}	68.7	82.8
$R_{30\ sec}$	1.48	2.01
grade, (%S)	6.5	9.3
mass of water (g)	348	415

4.1.2.3 Effect of the type of xanthate collector

The effect of the various types of xanthate collectors on the pyrite floatability was examined using the pyrite-quartz synthetic mixture. The pyrite was acid leached before the flotation runs. These experiments were carried out at pH=9. In order to investigate the influence of the chemical structure of the xanthate collectors, the same molecular dosages were used in each flotation experiment viz. $1.4*10^{-4}$ mol/l. This collector molecular concentration is equivalent with 60g/t SEX, 65.8g/t SNPX, 71.7g/t SIBX and SNBX, 78.2g/t PNBX and 84.2g/t PAX (Section 3.1.3). The runs with SEX, SIBX and PAX collectors were duplicated for reproducibility purposes. The temperature at which these experiments were carried out was 24°C.

The results from these experiments are presented in Table 4.14. Figures 4.14 to 4.19 present diagramatically the flotation parameters for pyrite and quartz, varying the type of collector. Detailed results from these experiments are presented in Appendix D (Tables D.11 to D.15).

4.1.2.4 Flotation experiments with zero froth height.

In section 4.1.1.3 it was found that the variation of the type of xanthate collector had a minimal effect on the recovery and rate constant of pyrite. It seems however, that it affects significantly the quartz behaviour. Figure 4.18 shows that as the carbon chain length of the collector becomes shorter, more quartz is recovered. In order to find out if this phenomenon is affected by the froth or by the pulp phase mechanisms, two experiments were done with 0.5 cm (practically zero) froth height. In these experiments the froth was allowed to overflow during the prescribed time intervals. The weaker collector, SEX, and the stronger, PAX, were chosen for this investigation. The pH for these experiments was also 9, and the temperature 22°C. The results from these experiments are presented in Table 4.15, while Tables D.21 and D.22 in Appendix D present the detailed data.

Table 4.15 Flotation of pyrite-quartz synthetic mixture at 0.5 cm and 3 cm froth height. Flotation parameters for acid leached pyrite using 60g/t SEX collector and 84.2g/t PAX collector at pH=9.

Flotation parameter	SEX		PAX	
	0.5 cm	3 cm	0.5 cm	3 cm
pyrite rec.(%)	90.4	92.2	95.1	92.0
grade, (%S)	6.8	11.4	12.8	26.0
gangue rec. (%)	9.43	5.09	4.56	1.44
mass of water, (g)	1010	502	512	188

Flotation parameter type of collector	pyrite rec. (%) actual	ψ	pyrite rate R_{30sec}	$Kx10^3$ sec^{-1}	E^2 for pyrite	gangue recov. actual	ψ	gangue rate R_{30sec}	$Kx10^3$ sec^{-1}	E^2x10^2 for gangue	grade(%S)	mass at water (gr)
SEX	91.8	93.0	69.1	138.5	7.9	5.08	5.28	3.49	90.1	16.5	11.4	497
	92.6	94.0	68.3	127.2	5.5	5.10	5.31	3.48	87.2	20.2	11.5	506
SNPX	87.9	89.2	68.2	148.3	2.8	2.13	2.16	1.58	113.5	0.7	20.4	253
SIBX*	90.0	93.4	70.0	142.7	4.6	2.52	2.84	1.87	104.9	3.1	17.8	272
SNBX	92.3	94.2	72.3	151.9	6.6	1.83	1.87	1.35	108.3	0.8	23.0	223
PNBX	86.9	89.1	71.6	180.5	5.0	1.57	1.62	1.23	134.0	0.4	24.3	187
PAX	92.2	95.0	74.8	161.9	6.6	1.39	1.44	1.02	106.2	0.4	26.3	177
	90.8	93.5	74.3	163.0	5.5	1.49	1.54	1.09	104.5	0.4	25.7	198

Table 4.14

Flotation parameters for pyrite and gangue, varying the type of xanthate collector during flotation of acid leached pyrite-quartz mixtures at pH=9 using 1.4×10^{-4} mol/l collector concentration.

* average values. For detailed data, see Tables 4.10 and 4.11

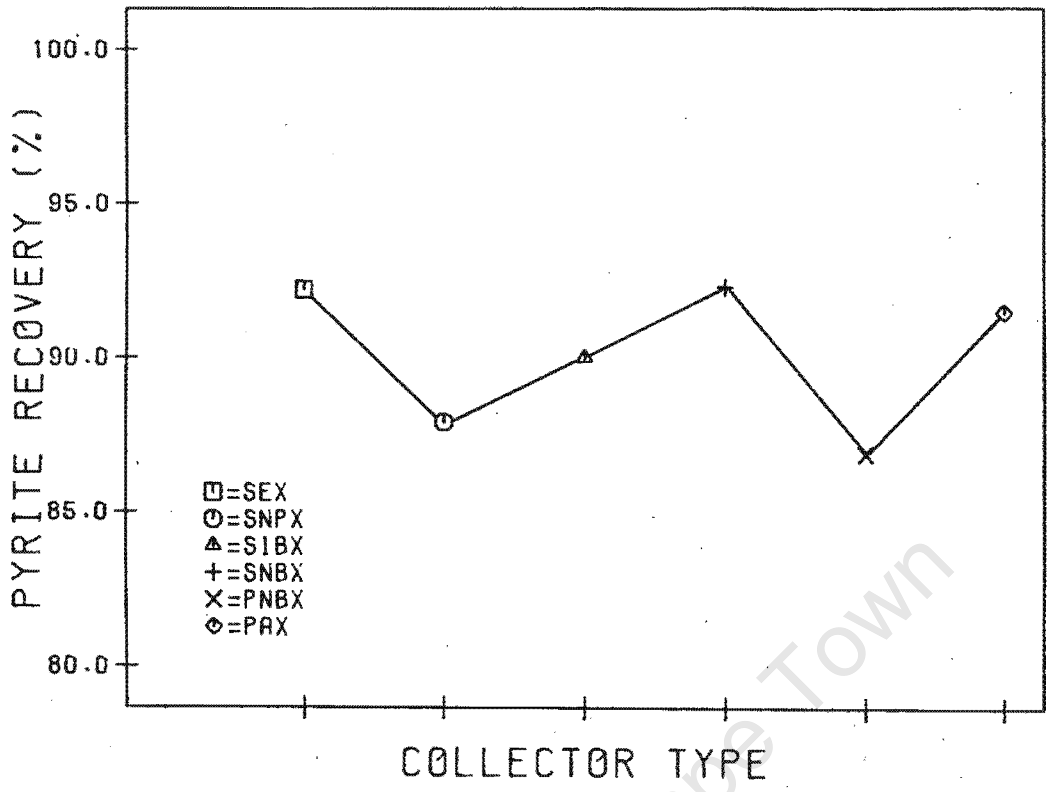


FIG 4.14 FLOTATION OF PYRITE-QUARTZ MIXTURES AT PH=9 USING DIFFERENT XANTHATE COLLECTORS AT THE SAME MOLECULAR CONCENTRATION. FINAL PYRITE RECOVERY FOR DIFFERENT COLLECTORS.

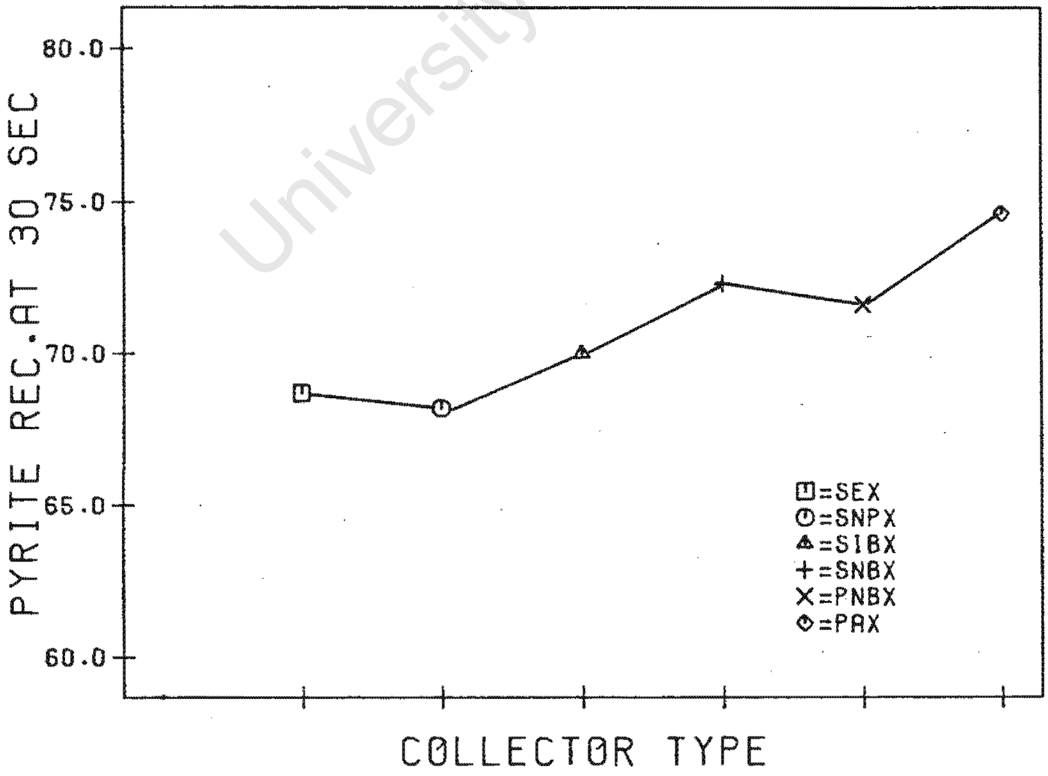


FIG 4.15 FLOTATION OF PYRITE-QUARTZ MIXTURES AT PH=9 USING DIFFERENT XANTHATE COLLECTORS AT THE SAME MOLECULAR CONCENTRATION. INITIAL RATE OF PYRITE RECOVERY FOR DIFFERENT COLLECTORS.

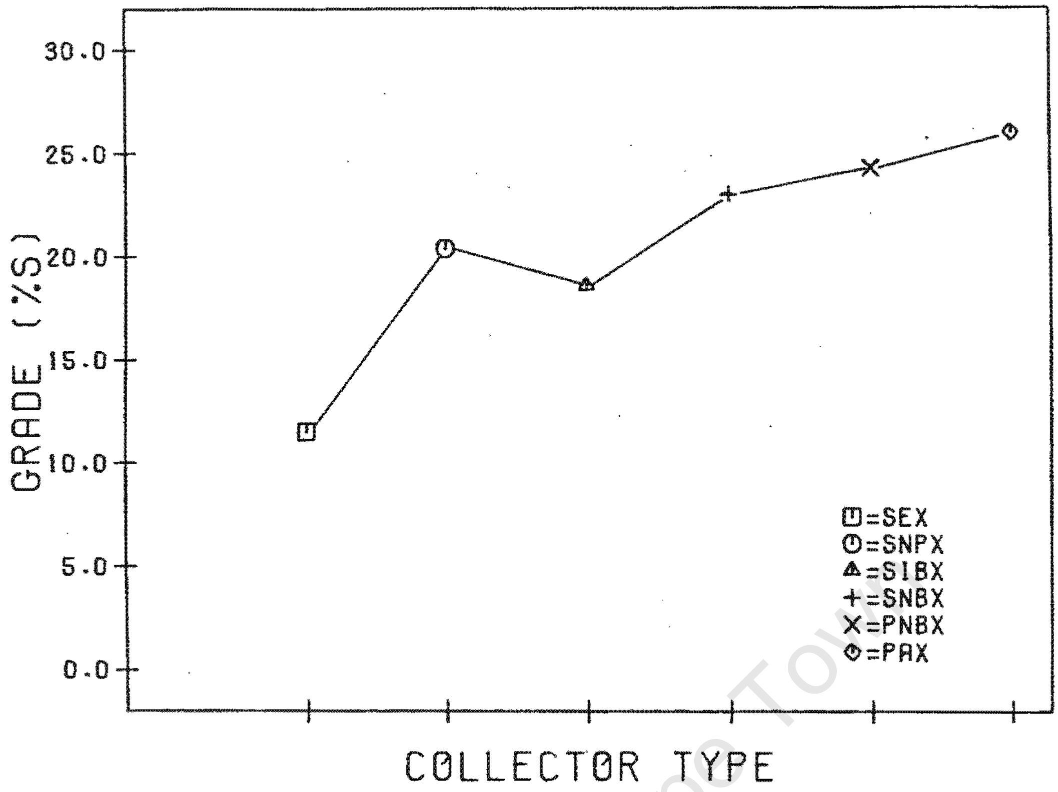


FIG 4.16 FLOTATION OF PYRITE-QUARTZ MIXTURES AT PH=9 USING DIFFERENT XANTHATE COLLECTORS AT THE SAME MOLECULAR CONCENTRATION. GRADE OF THE CONCENTRATES FOR DIFFERENT COLLECTORS.

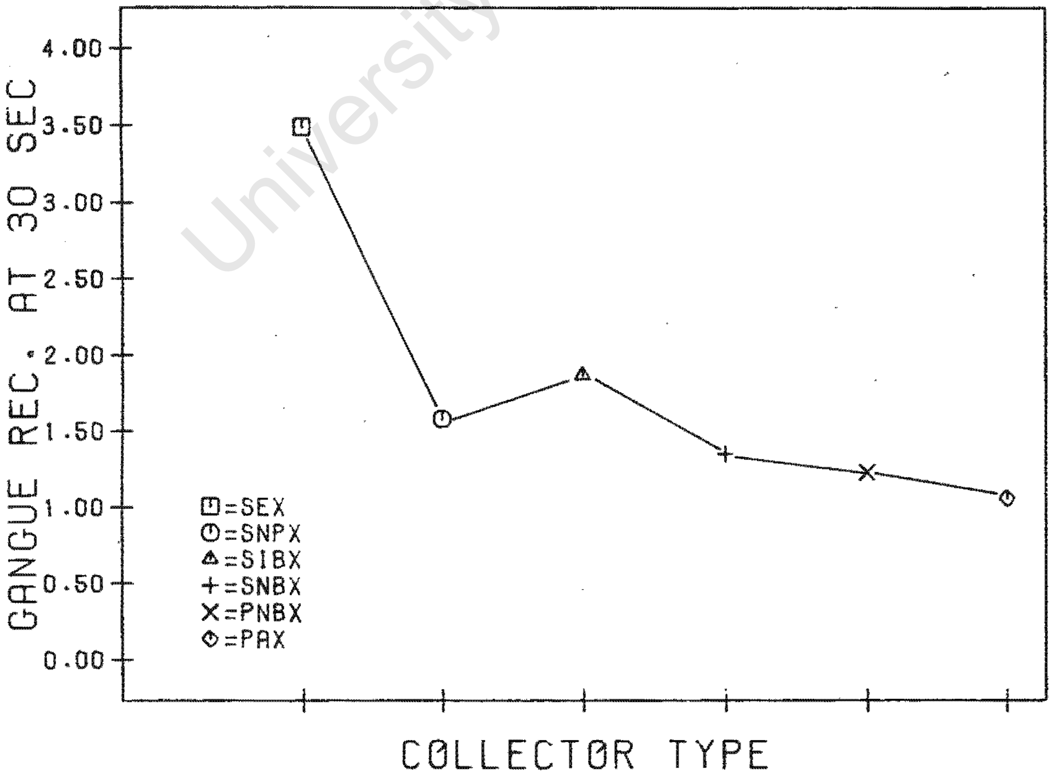


FIG 4.17 FLOTATION OF PYRITE-QUARTZ MIXTURES AT PH=9 USING DIFFERENT XANTHATE COLLECTORS AT THE SAME MOLECULAR CONCENTRATION. INITIAL RATE OF GANGUE RECOVERY FOR DIFFERENT COLLECTORS.

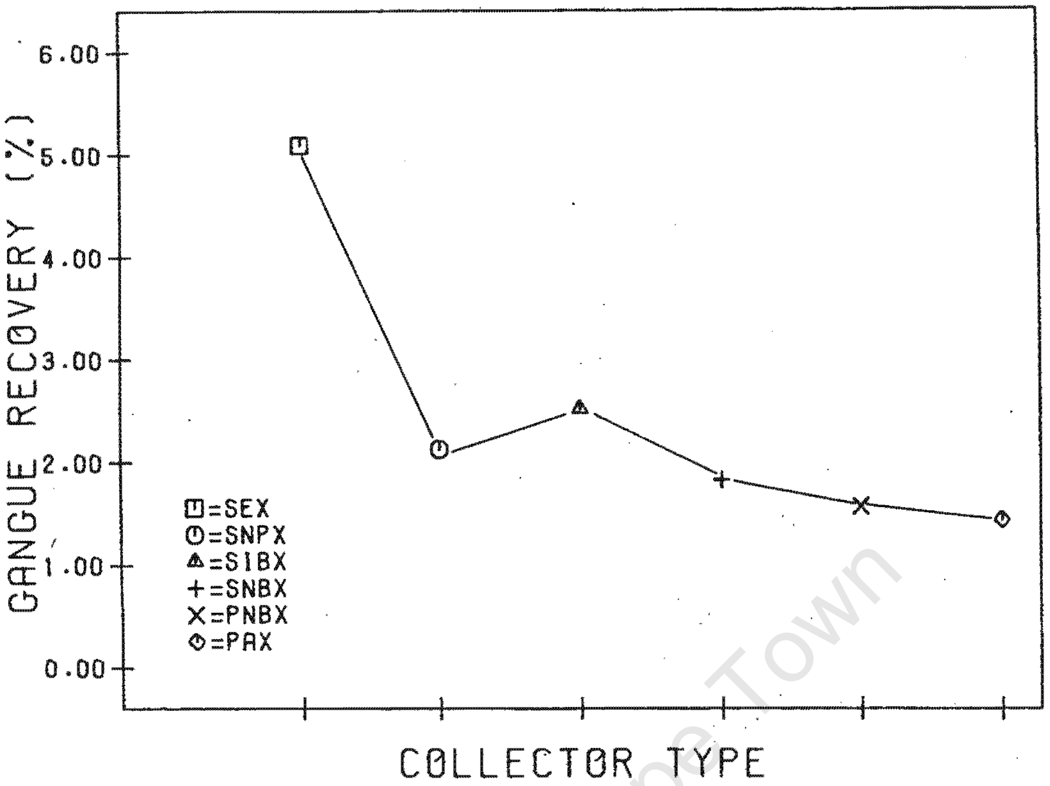


FIG 4.18 FLOTATION OF PYRITE-QUARTZ MIXTURES AT PH=9 USING DIFFERENT XANTHATE COLLECTORS AT THE SAME MOLECULAR CONCENTRATION. FINAL GANGUE RECOVERY FOR DIFFERENT COLLECTORS.

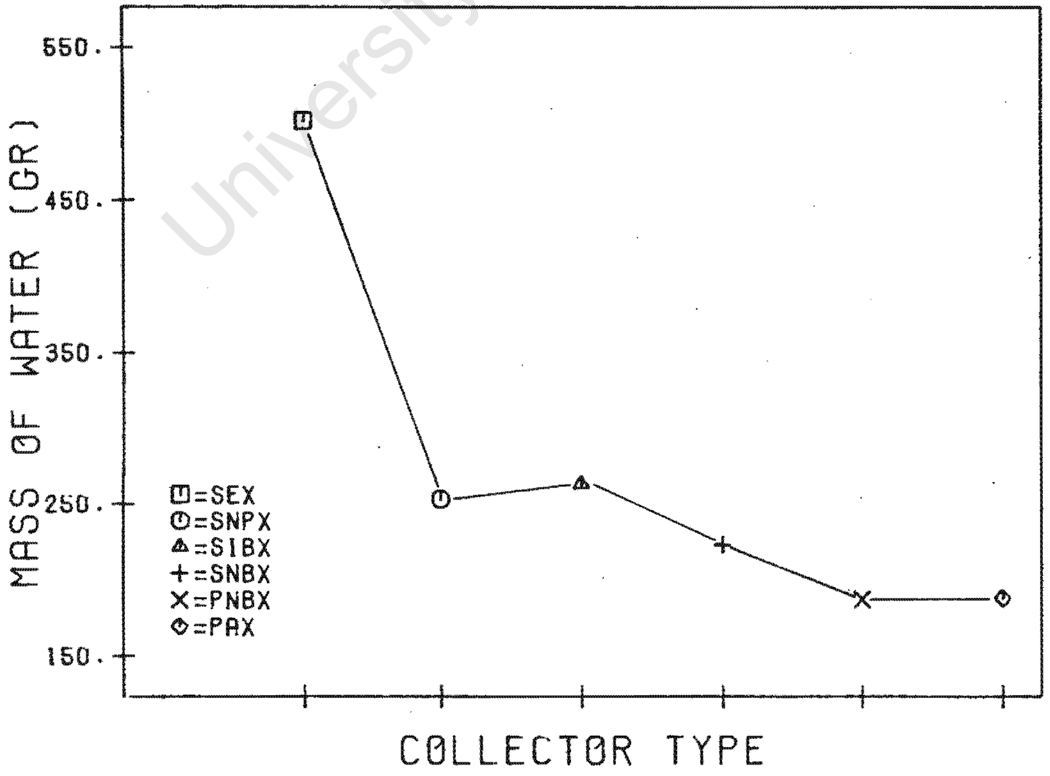


FIG 4.19 FLOTATION OF PYRITE-QUARTZ MIXTURES AT PH=9 USING DIFFERENT XANTHATE COLLECTORS AT THE SAME MOLECULAR CONCENTRATION. MASS OF WATER REMOVED FOR DIFFERENT COLLECTORS.

4.1.2.5 Effect of the concentration of the xanthate collector.

The pyrite flotation response was then examined varying the concentration of the xanthate collector. For this, the collector PAX was examined at four concentration levels, 30g/t, 40g/t, 60g/t, and 84.2g/t. These experiments were carried out at pH=9, and the pyrite was acid leached prior to flotation. The temperature varied between 22°C and 24°C.

The results from these experiments are summarized in Table 4.16. Figures 4.20 to 4.26 present diagramatically the flotation parameters for pyrite and quartz, varying the collector concentration. Table 4.17 shows the rates of the quartz and water removal at the corresponding time intervals. Detailed results from these experiments are also presented in Appendix D (Tables D.16 to D.20).

The effect of the xanthate collector concentration was also examined on oxidized pyrite. For this SIBX collector was used at the dosage of 36g/t, 71.7g/t, 108g/t and 144g/t. The pH at these runs was also pH=9 and the temperature varied between 20°C and 23°C. Table 4.18 summarizes the results from these experiments. Detailed results from these experiments are also presented in Appendix D (Tables D.21 to D.25).

Table 4.16 Flotation of pyrite-quartz synthetic mixture at pH=9. Flotation parameters for acid leached pyrite, varying the concentration of PAX collector.

	collector concentration				
flotation parameters	30g/t	40g/t	60g/t	84.2g/t	
pyrite rec.(%)	87.7	91.2	89.5	92.2	90.8
pyrite ψ,(%)	89.4	93.3	91.9	95.0	93.5
pyrite rate $k*10^3$, sec^{-1}	154.4	157.5	145.5	161.9	163.0
$R_{30\ sec}$	68.6	72.3	70.4	74.8	74.3
ΣE^2	5.5	4.4	2.9	6.6	5.5
grade, (%S)	12.7	16.4	20.6	26.3	25.7
gangue rec.(%)	3.97	2.92	2.17	1.39	1.49
gangue ψ (%)	4.16	3.03	2.26	1.44	1.54
gangue rate $k*10^3$, sec-1	107.8	114.5	105.6	106.2	104.5
$R_{30\ sec}$	2.99	2.23	1.61	1.02	1.09
ΣE^2*10^2	7.7	2.3	1.2	0.4	0.4
mass of water (g)	375	313	250	177	198

Time(sec)	30 g/t PAX		40 g/t PAX		60 g/t PAX		84.2 g/t PAX	
	rate of quartz (g/sec)	rate of water (g/sec)	rate of quartz (g/sec)	rate of water (g/sec)	rate of quartz (g/sec)	rate of water (g/sec)	rate of quartz (g/sec)	rate of water (g/sec)
15	1.28	10.2	0.98	8.9	0.70	7.2	0.45	5.4
							0.48	6.0
15	0.68	6.0	0.48	5.0	0.36	4.1	0.21	2.8
							0.24	3.3
30	0.24	3.0	0.15	2.2	0.12	1.8	0.04	1.3
							0.04	1.4

Table 4.17

Rate of quartz and water removal (g/sec) at the first three concentrates during the pyrite-quartz mixture flotation experiments, varying the concentration of the collector PAX.

Table 4.18 Flotation of pyrite-quartz synthetic mixture at pH=9. Flotation parameters for oxidized pyrite, varying the concentration of SIBX collector.

	concentration of collector SIBX				
flotation parameters	36g/t	71.6g/t		108g/t	144g/t
pyrite rec. (%)	57.8	59.9	59.5	59.9	61.5
pyrite ψ (%)	57.7	59.0	58.7	58.7	59.7
pyrite rate $k*10^3$, sec^{-1}	135.5	144.4	145.3	150	131.6
$R_{30\ sec}$	43.3	44.8	45.0	45.3	44.3
grade, (%S)	13.5	19.7	16.7	18.6	21.6
gangue rec. (%)	2.37	1.42	1.81	1.56	1.26
gangue ψ, (%)	2.42	1.42	1.83	1.56	1.24
gangue rate $k*10^3$ sec^{-1}	106.1	100.5	108.4	111.4	101.1
$R_{30\ sec}$	1.78	1.00	1.36	1.16	0.89
mass of water (g)	294	205	221	208	193

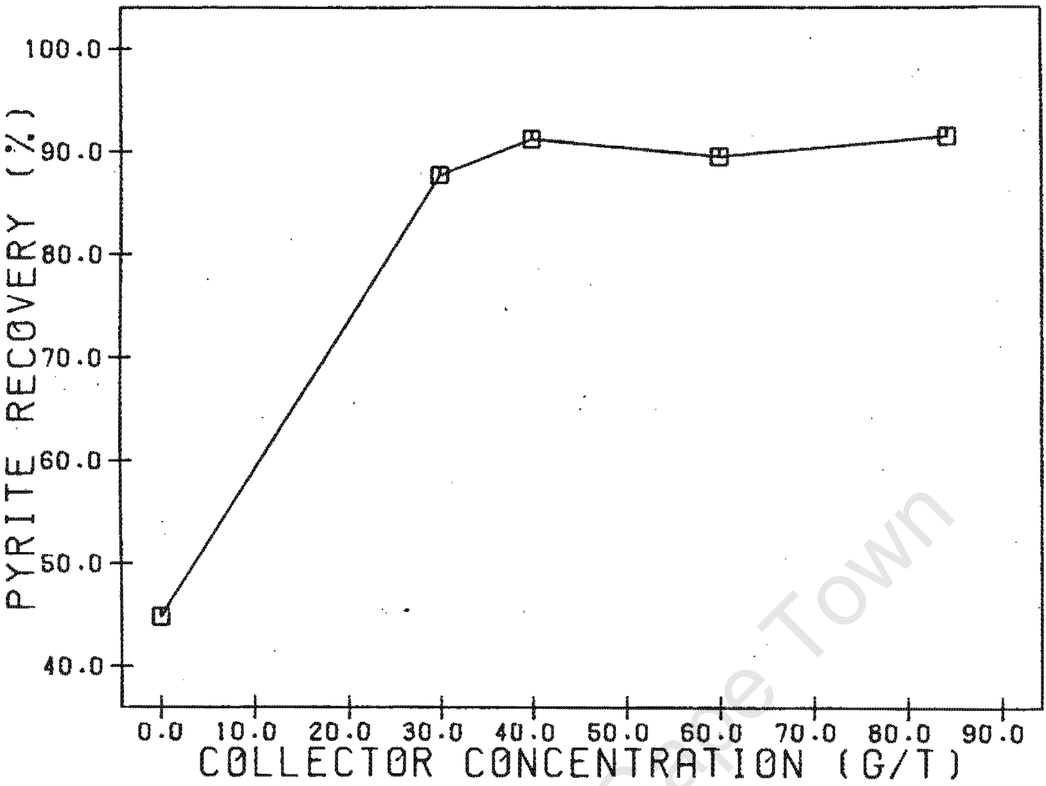


FIG 4.20 FLOTATION OF PYRITE-QUARTZ MIXTURES AT PH=9. VARIATION OF FINAL PYRITE RECOVERY WITH COLLECTOR PAX CONCENTRATION.

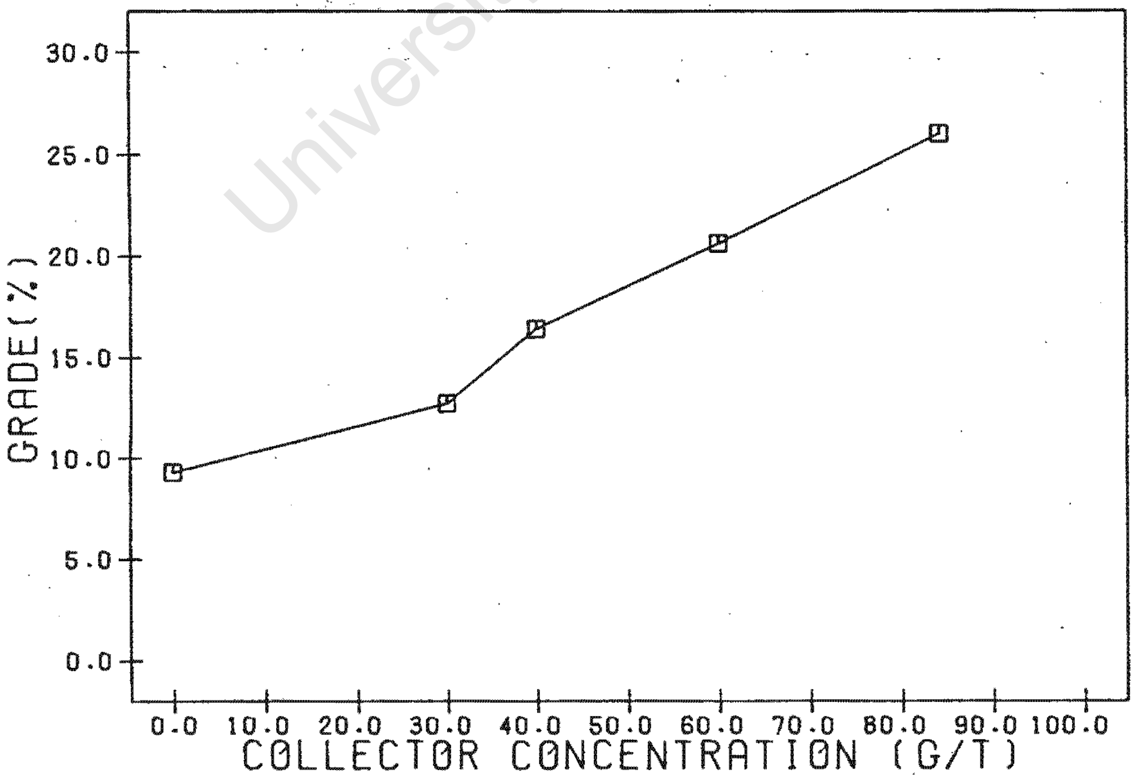


FIG 4.21 FLOTATION OF PYRITE-QUARTZ MIXTURES AT PH=9. VARIATION OF THE FINAL GRADE OF THE CONCENTRATE WITH COLLECTOR PAX CONCENTRATION.

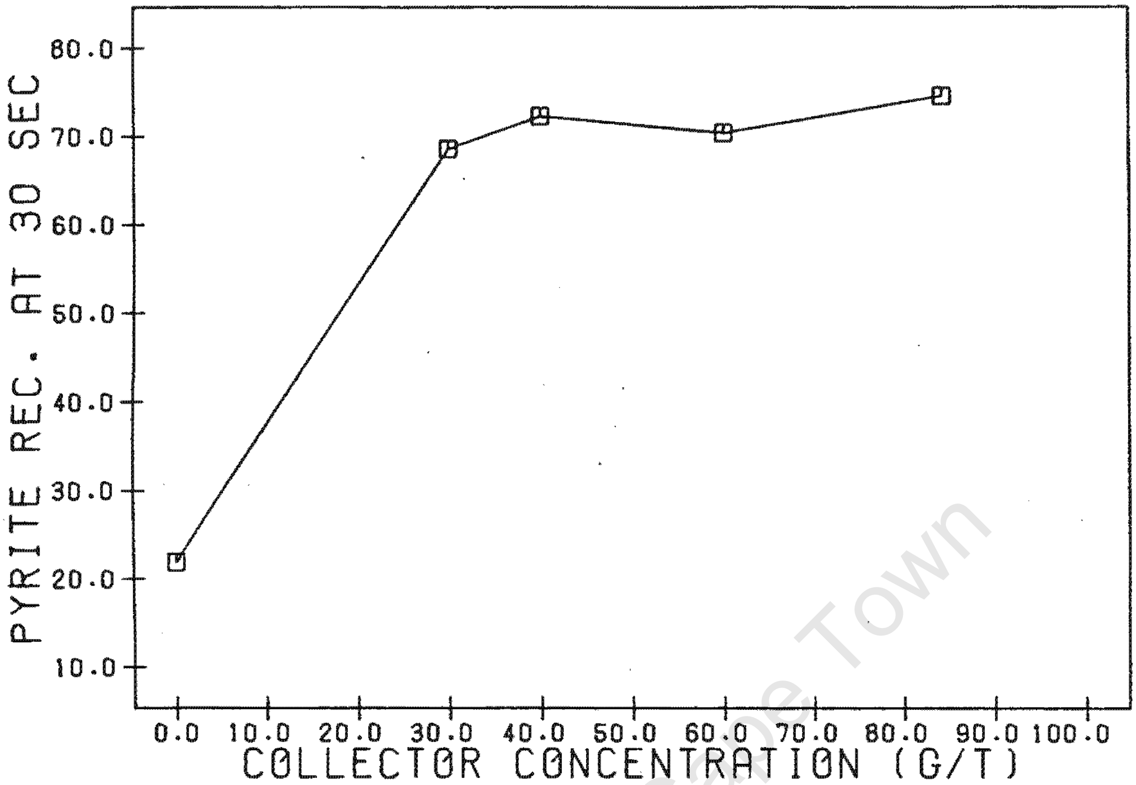


FIG 4.22 VARIATION OF INITIAL RATE OF PYRITE RECOVERY WITH COLLECTOR PAX CONCENTRATION, DURING FLOTATION OF PYRITE-QUARTZ MIXTURES AT PH=9.

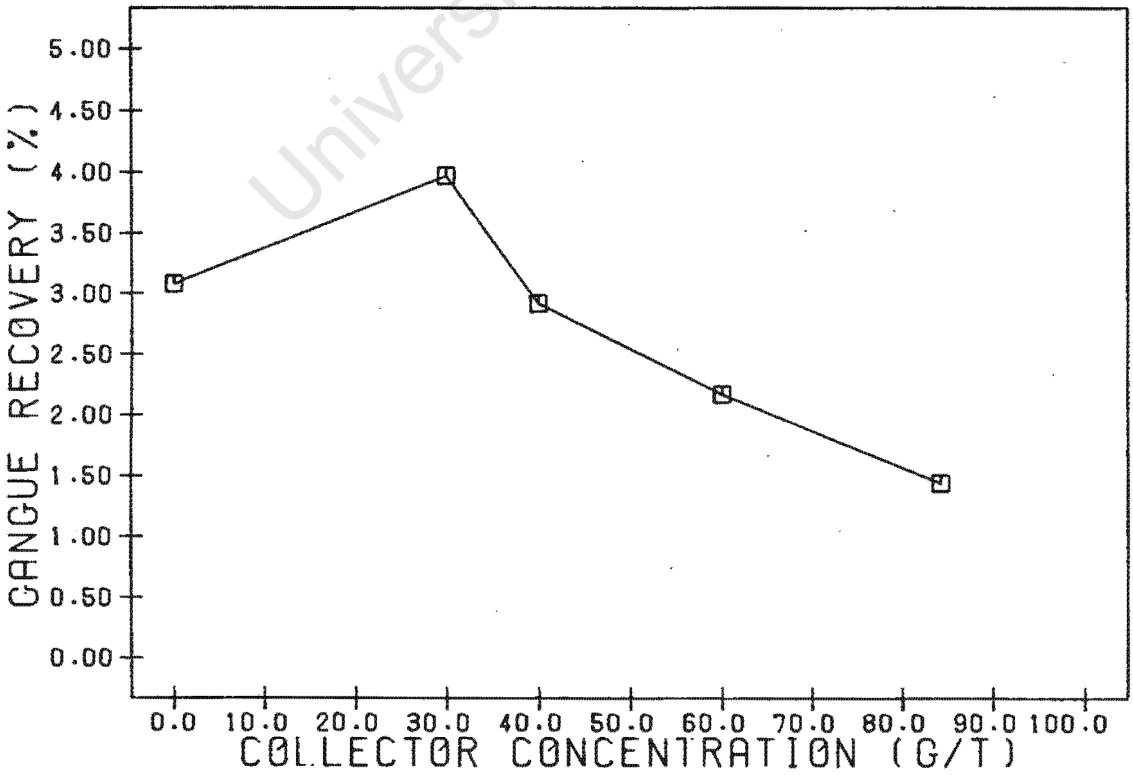


FIG 4.23 VARIATION OF THE FINAL RECOVERY OF GANGUE WITH COLLECTOR PAX CONCENTRATION DURING FLOTATION OF PYRITE-QUARTZ MIXTURES AT PH=9.

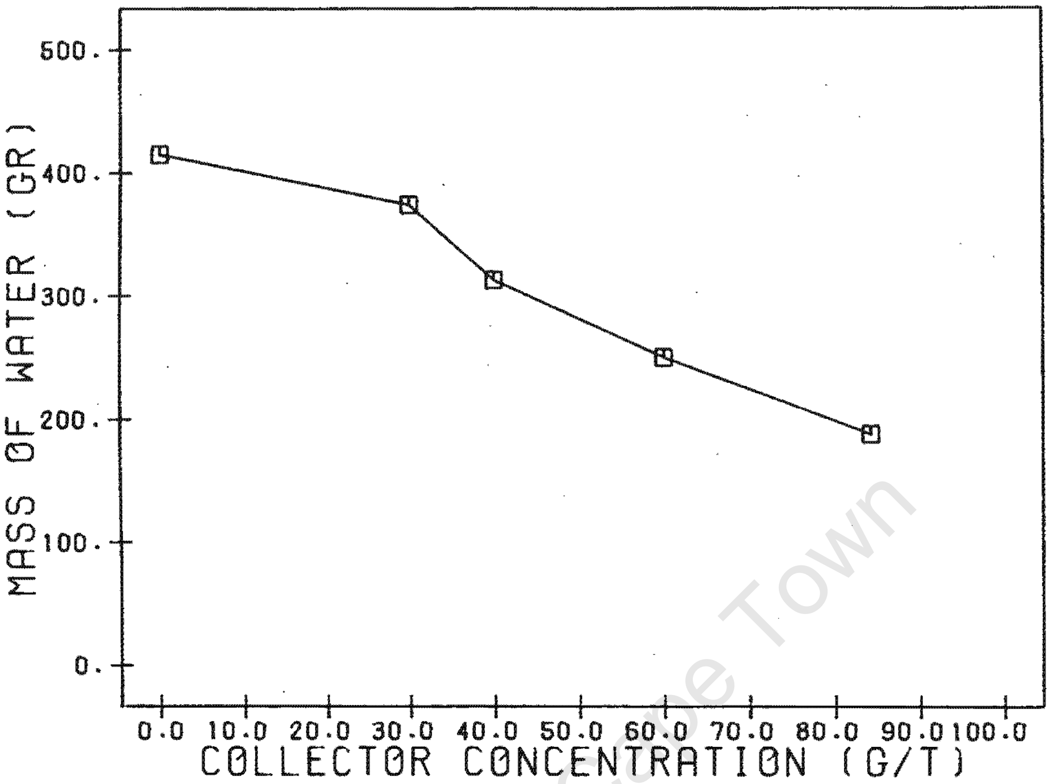


FIG 4.24 FLOTATION OF PYRITE-QUARTZ MIXTURES AT PH=9. VARIATION OF THE MASS OF WATER REMOVED WITH COLLECTOR PAX CONCENTRATION.

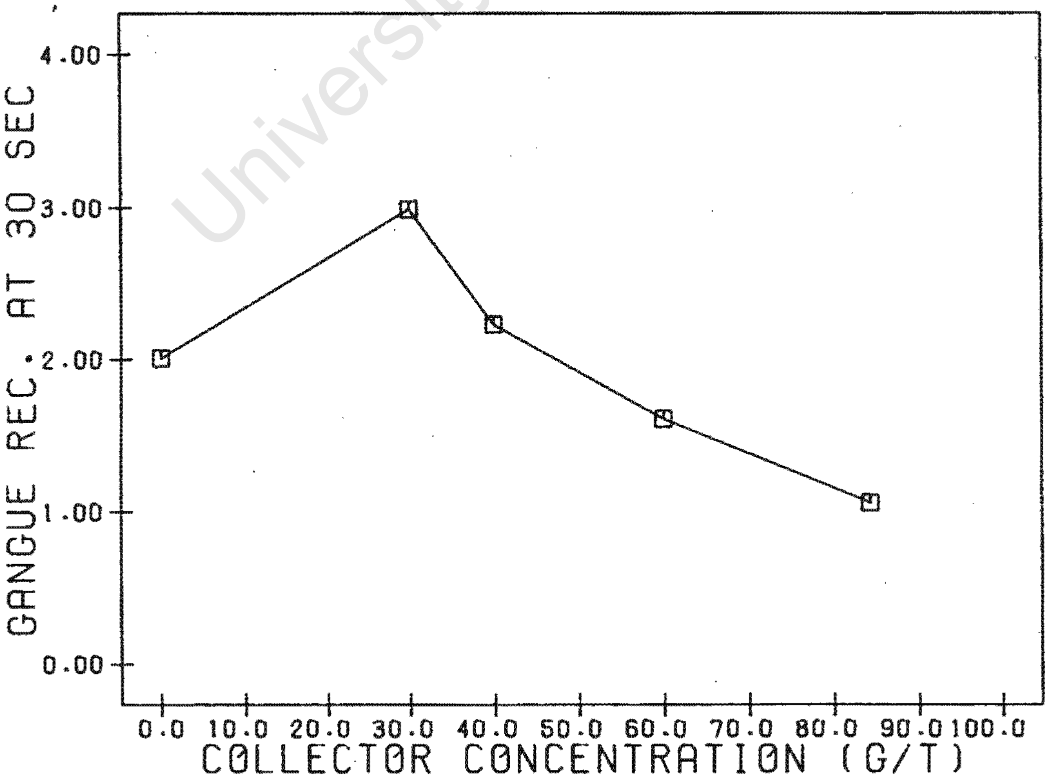


FIG 4.25 FLOTATION OF PYRITE-QUARTZ MIXTURES AT PH=9. VARIATION OF THE INITIAL RATE OF GANGUE RECOVERY WITH COLLECTOR PAX CONCENTRATION.

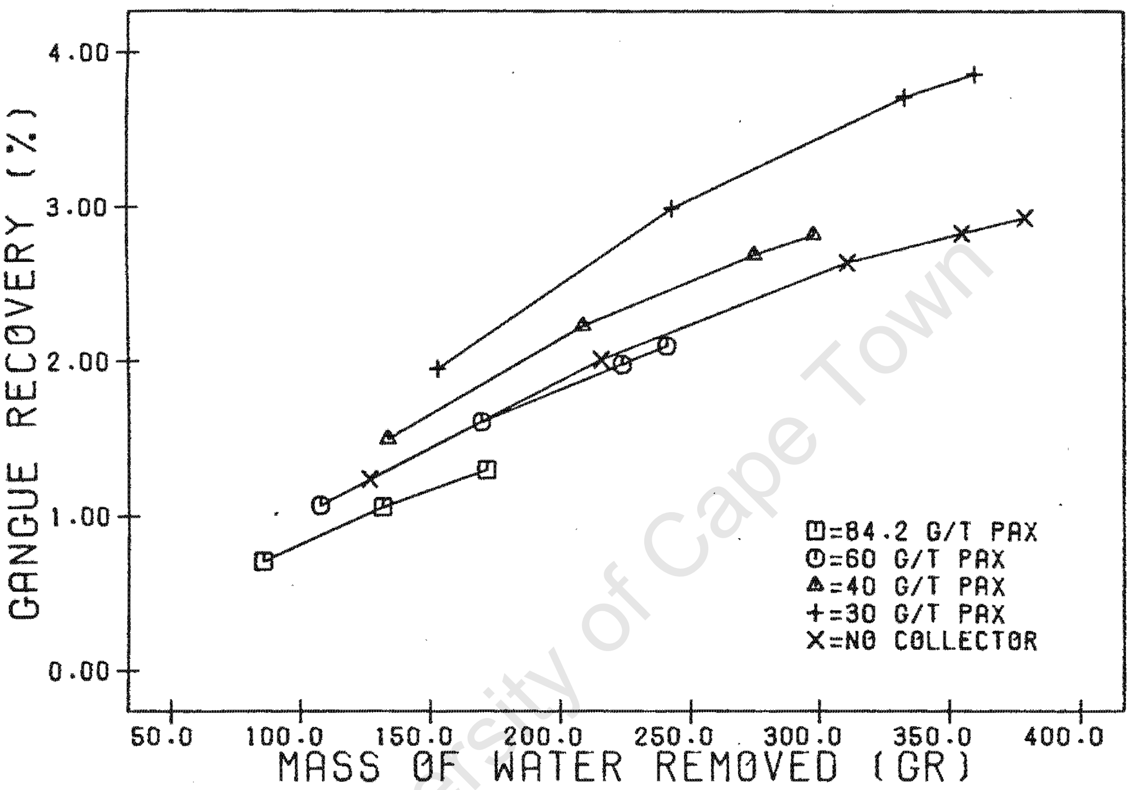


FIG 4.26 GANGUE RECOVERY-WATER REMOVAL CURVES DURING FLOTATION OF PYRITE-QUARTZ MIXTURES AT PH=9, USING COLLECTOR PAX AT DIFFERENT ADDITION RATES.

4.1.3 Pure quartz flotation experiments.

4.1.3.1 Effect of the variation of the pH.

One characteristic property of the flotation of pyrite which was found in section 3.1.1.1, is that, irrespective of the presence or absence of collector, the grade of the concentrates decreases as the pH increases. This phenomenon is caused by the continuous increase of the mass of quartz with an increase in pH value. The presence of a xanthate collector made the phenomenon more pronounced. In order to investigate the influence of the pH variation on the flotation properties of quartz without the interference of pyrite, flotation experiments were carried out using pure quartz ore. Initially the natural floatability of quartz was examined at nine pH values, from pH=4 to pH=12, without collector addition. The results of these runs are tabulated in Appentix E (Tables E.1 and E.2). From these the Klimpel model equilibrium recovery, ψ, and rate constant, k, were calculated and are presented in Table 4.19 where the actual recovery is also recorded.

Figure 4.27 shows the recovery-pH curve while Figure 4.28 shows the mass of water-pH curve. These runs were duplicated, and the temperature varied between 22°C and 26°C.

The flotation response of quartz was also examined in the same pH range in presence of a xanthate collector. For this, collector SIBX was added at the dosage of 71.7g/t. The temperature during these experiments varied between 23°C and 27°C.

Table 4.19 Flotation of pure quartz ore in absence of collector. Flotation parameters at different pH values.

pH	quartz rec.(%)		quartz rate $k*10^3$, sec^{-1}	ΣE^2*10^2	mass of water, (g)
	ψ	actual			
pH=4	0.60	0.62	62.8	0.28	106
	0.61	0.62	57.7	0.22	112
pH=5	0.63	0.64	82.6	0.21	97
	0.49	0.50	68.4	0.31	75
pH=6	1.09	1.13	87.0	2.1	153
	0.87	0.86	83.8	0.52	113
pH=7	0.99	1.01	101.1	0.71	143
	1.03	1.01	93.9	0.70	134
pH=8	0.84	0.82	97.8	0.63	120
	0.61	0.60	112.8	0.25	93
pH=9	0.51	0.48	111.8	0.08	79
	0.62	0.61	108.0	0.35	94
pH=10	0.93	0.89	123.0	0.9	137
	1.19	1.15	106.0	1.6	167
pH=11	2.78	2.65	78.0	8.0	351
	2.95	2.81	71.9	10.0	373
pH=12	5.34	5.08	61.6	20.0	448
	5.12	4.87	58.7	16.0	479

These runs were also duplicated, and detailed results are presented in Appendix E (Tables E.3 and E.4). The final recovery and the Klimpel model equilibrium recovery are presented in Table 4.20. The actual recovery values are also presented diagramatically in Figure 4.27. Figure 4.28 is a plot of the mass of the water versus pH. Table 4.21 shows the particle size analysis of the feed and of the concentrates of the tests done at pH=7, pH=10 and pH=11 in presence of collector.

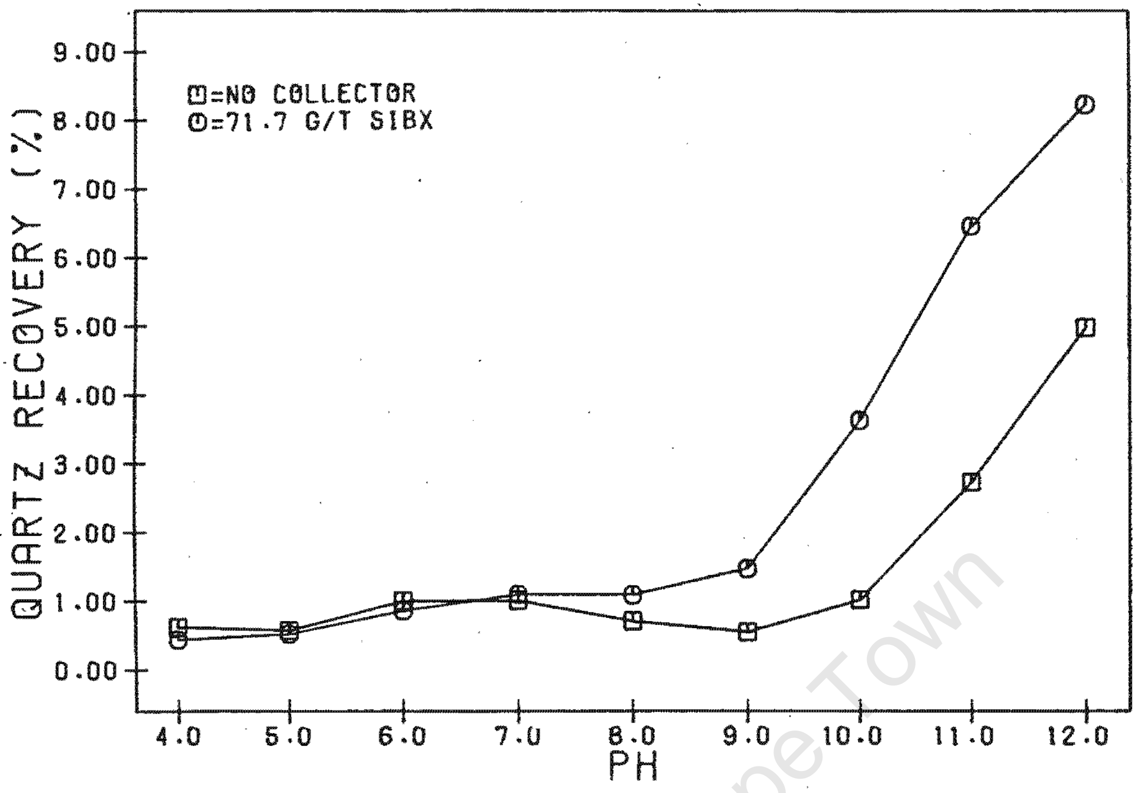


FIG 4.27 VARIATION OF FINAL RECOVERY OF QUARTZ WITH PH, DURING FLOTATION OF PURE QUARTZ USING NO COLLECTOR AND 71.7 G/T SIBX.

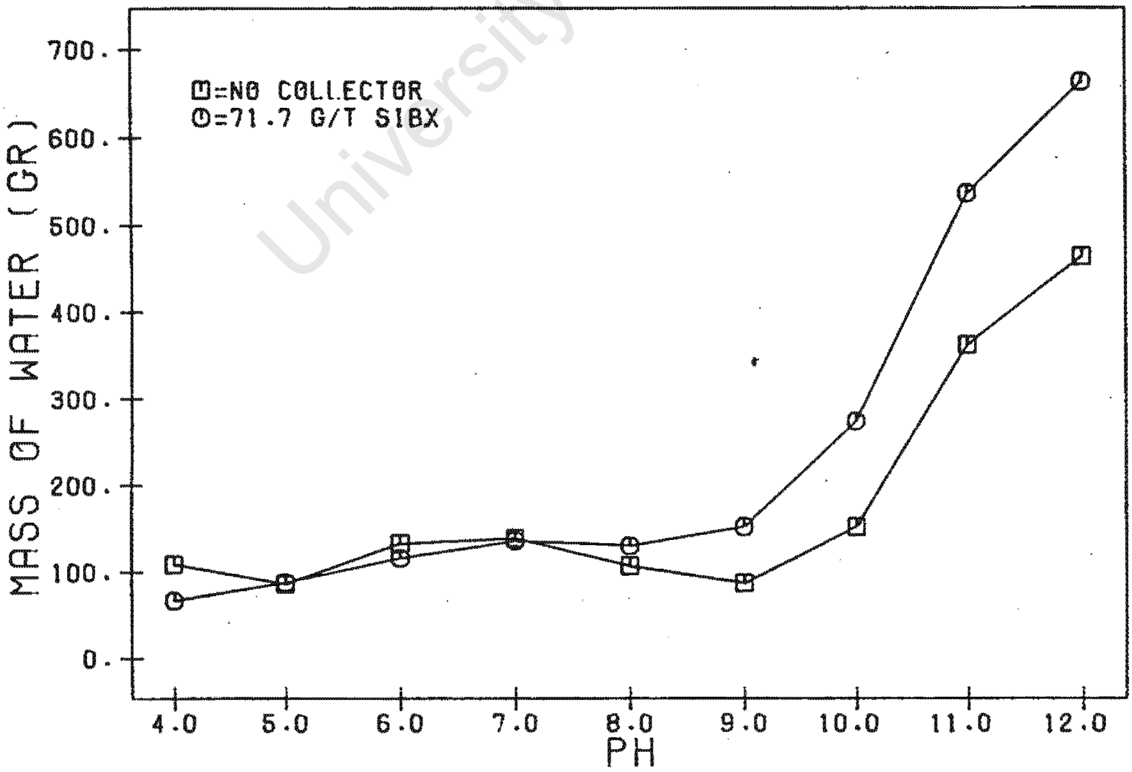


FIG 4.28 VARIATION OF CUMULATIVE MASS OF WATER REMOVED WITH PH, DURING FLOTATION OF PURE QUARTZ USING NO COLLECTOR AND 71.7G/T SIBX.

Table 4.20 Flotation of pure quartz ore using 71.7 g/t SIBX collector. Flotation parameters varying the pH value.

pH	quartz rec. (%) ψ	actual	quartz rate $k*10^3$ sec^{-1}	ΣE^2*10^2	mass of water (g)
pH=4	0.42	0.42	55.0	0.06	58
	0.45	0.45	62.4	0.05	75
pH=5	0.56	0.55	97.7	0.18	88
	0.49	0.49	101.6	0.10	87
pH=6	0.79	0.78	81.7	0.20	102
	0.95	0.93	95.1	1.10	130
pH=7	1.18	1.16	85.4	1.29	142
	1.05	1.04	88.0	0.60	130
pH=8	1.11	1.07	97.6	2.25	132
	1.13	1.10	88.5	1.56	127
pH=9	1.56	1.49	96.0	4.40	154
	1.49	1.44	100.4	4.10	149
pH=10	3.81	3.63	88.8	26.0	274
	3.86	3.63	73.3	43.0	273
pH=11	7.06	6.58	59.2	148.0	538
	6.74	6.33	63.0	107.0	535
pH=12	9.10	8.56	52.8	96.0	674
	8.42	7.91	50.0	97.0	652

Table 4.21 Particle size analysis of quartz feed and concentrates at pH=7, pH=10 and pH=11.

	particle size, µm (% of the mass)					
sample	-38	+38-45	+45-75	+75-106	+106-180	+180
feed	37.3	8.4	20	13.8	16	1.4
pH=7	88.6	0.5	3.6	1.6	1.6	0.1
pH=10	61.8	3.2	12.3	3.8	2.2	-
pH=11	73.6	5.9	11.5	4.0	1.9	0.1

4.1.3.2 Effect of the pH regulator.

The experimental work with pure quartz ore showed that irrespective of the presence of pyrite, the quartz seems to float better at higher pH values, viz. at pH>10, and the xanthate collector enhances its recovery. In this experimental work an attempt was also made to investigate if the calcium ions which were added to modify the pH, are in any way responsible for increasing the quartz recovery. For this, pure quartz experiments were carried out using NaOH as a pH regulator as sodium ions are not reported to activate quartz (Glembotskii, Plaksin and Klassen, 1972). The investigation was done in the range pH=8 to pH=12, as the natural pH of the pulp is 7.2. Initially no collector was added to the pulp to check the natural floatability of quartz. Subsequently the influence of the collector was investigated by adding 71.7g/t SIBX collector. The temperature of these runs varied between 24°C and 27°C.

The results of these runs are presented in Appendix E (Tables E.5 to E.8). Figures 4.29, 4.30, 4.31 and 4.32 show the quartz recovery and mass of water removal curves versus pH. For comparison purposes the corresponding curves obtained with $Ca(OH)_2$ were also plotted.

4.1.3.3 Effect of the type of xanthate collector.

In the experiments with pyrite-quartz mixtures and different xanthate collectors (see section 4.1.1.3), it was shown that decreasing the carbon chain length of the xanthate collector caused the grade of the concentrates to decrease as a result of the increased quartz recovery. The question arose as to how the quartz behaved in absence of pyrite. Experiments were therefore carried out using pure quartz ore and varying the type of the xanthate collector. The type and the concentration of the collector were as

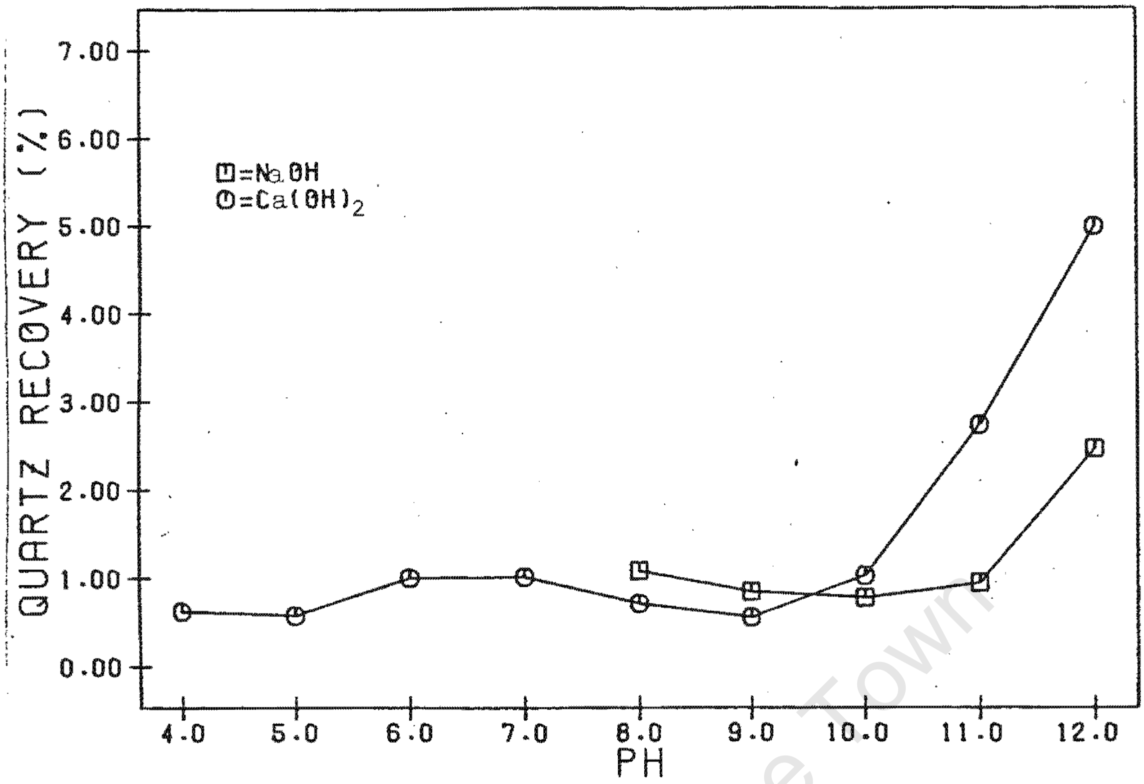


FIG 4.29 VARIATION OF FINAL RECOVERY OF QUARTZ WITH PH DURING FLOTATION OF PURE QUARTZ USING $Ca(OH)_2$ AND NaOH FOR PH MODIFICATION IN ABSENCE OF COLLECTOR

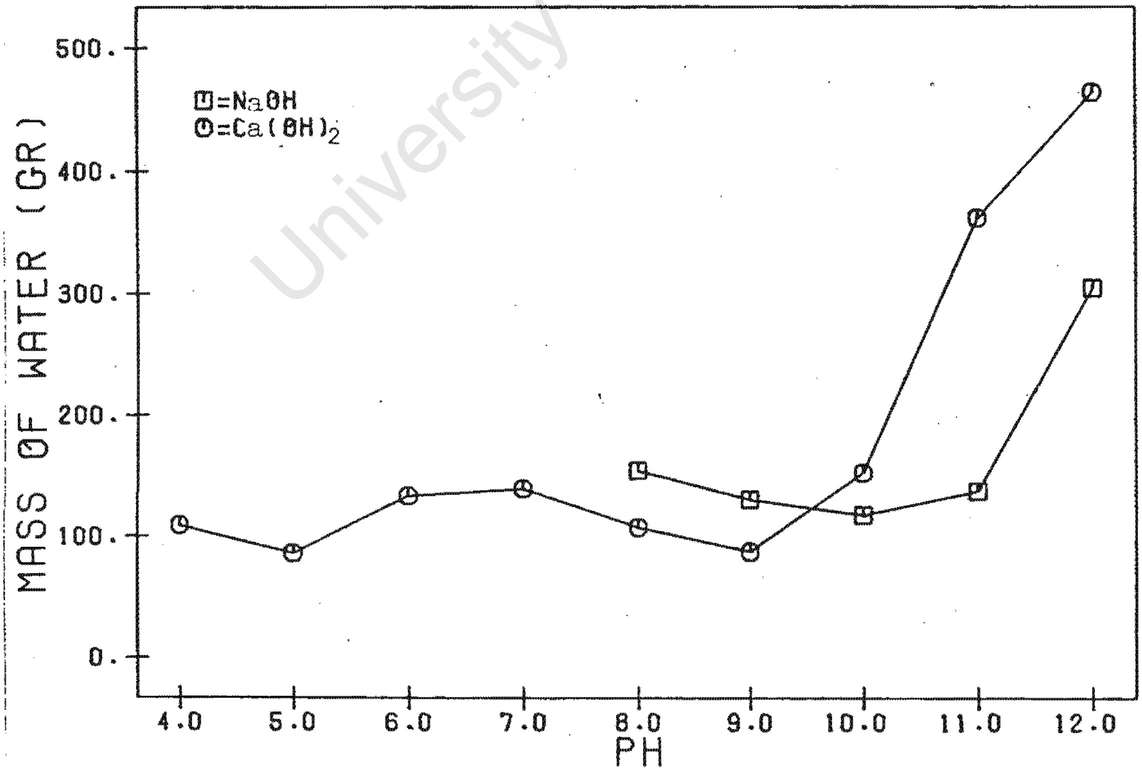


FIG 4.30 VARIATION OF CUMULATIVE MASS OF WATER REMOVED WITH PH, DURING FLOTATION OF PURE QUARTZ USING $Ca(OH)_2$ AND NaOH FOR PH MODIFICATION IN ABSENCE OF COLLECTOR.

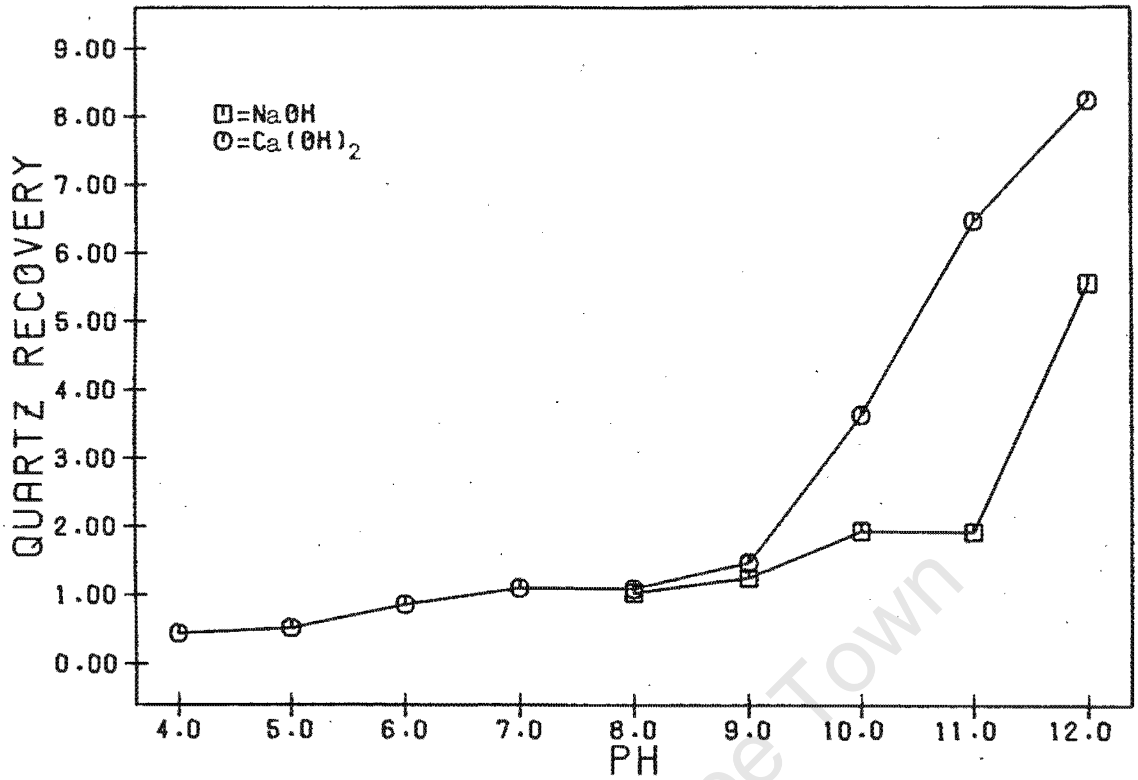


FIG 4.31 VARIATION OF FINAL RECOVERY OF QUARTZ WITH PH DURING FLOTATION OF PURE QUARTZ, USING NaOH AND $Ca(OH)_2$ FOR PH MODIFICATION AND 71.7 G/T SIBX.

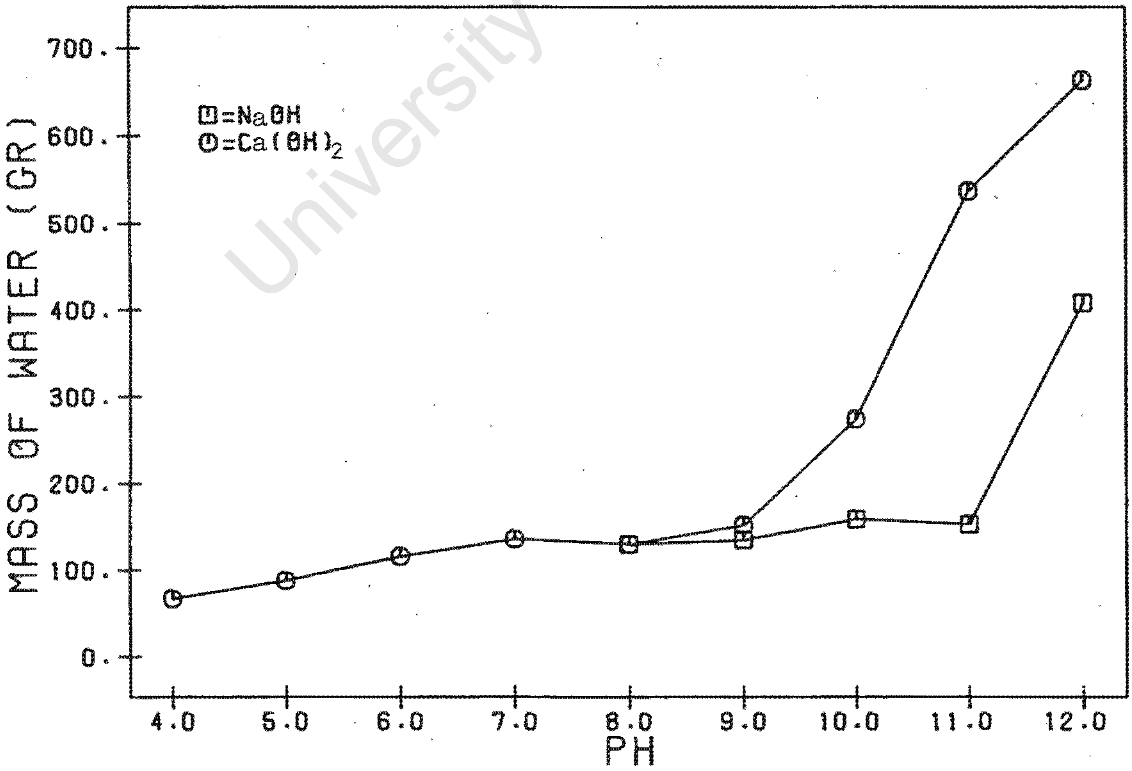


FIG 4.32 VARIATION OF CUMULATIVE MASS OF WATER REMOVED WITH PH DURING FLOTATION OF PURE QUARTZ USING NaOH AND $Ca(OH)_2$ FOR PH MODIFICATION AND 71.7 G.T SIBX.

mentioned in section 4.1.1.3. The runs were carried out at pH=9, and the temperature was 22°C.

The results from these experiments are summarized in Table 4.22. Figures 4.33 and 4.34 present diagramatically the variation in flotation parameters of quartz for different lengths of the carbon chain of the collector. Detailed data from these experiments is presented in Appentix E (Tables E.9 and E.10).

Table 4.22 Flotation parameters for quartz varying the type of the xanthate collector added in equivalent addition rates during flotation of pure quartz ore at pH=9.

type of collector	quartz rec.(%) ψ	quartz rec.(%) actual	quartz rate $k*10^3 sec^{-1}$	$\Sigma E^2/10^{-2}$	mass of water, g
SEX	2.46	2.41	115.9	3.0	267
SNPX	2.61	2.55	120.2	3.7	261
SIBX	3.99	3.87	110.7	12.6	351
SNBX	2.50	2.44	123.2	3.7	247
PNBX	2.27	2.21	117.2	4.0	236
PAX	6.32	6.06	90.4	50.5	473

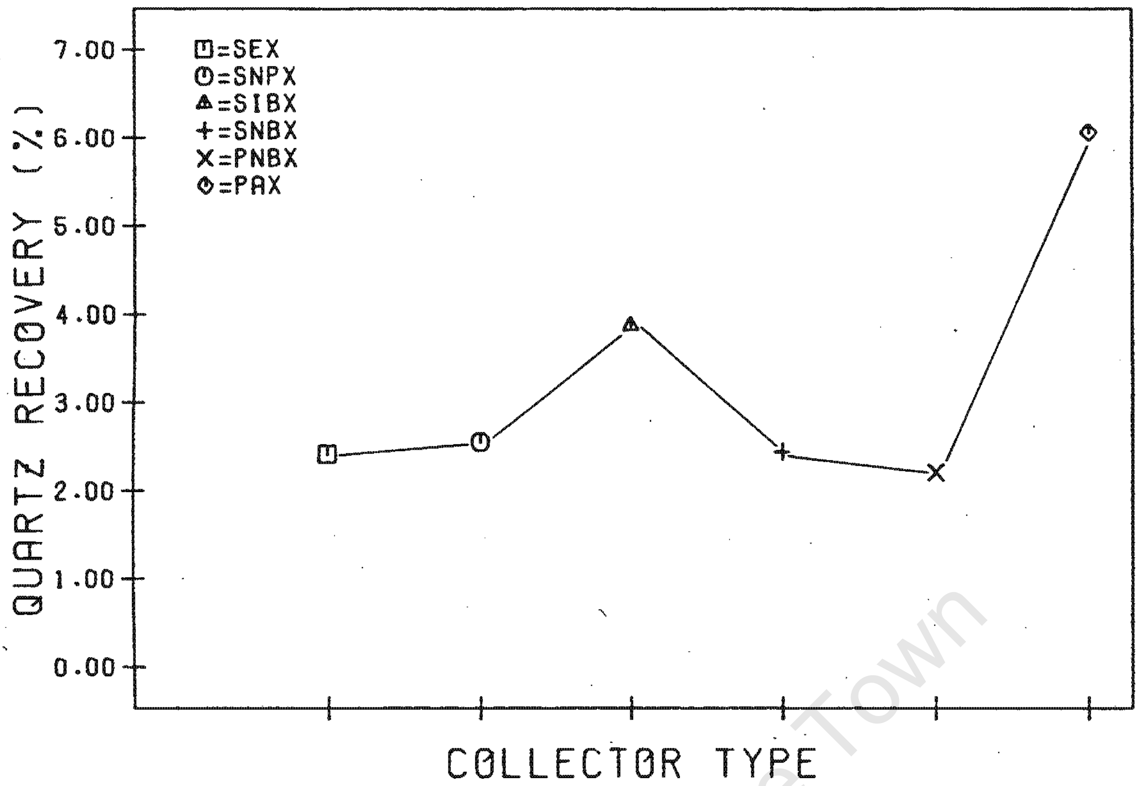


FIG 4.33 FLOTATION OF PURE QUARTZ AT PH=9 USING DIFFERENT XANTHATE COLLECTORS AT THE SAME MOLECULAR CONCENTRATION. QUARTZ RECOVERY AT DIFFERENT COLLECTORS.

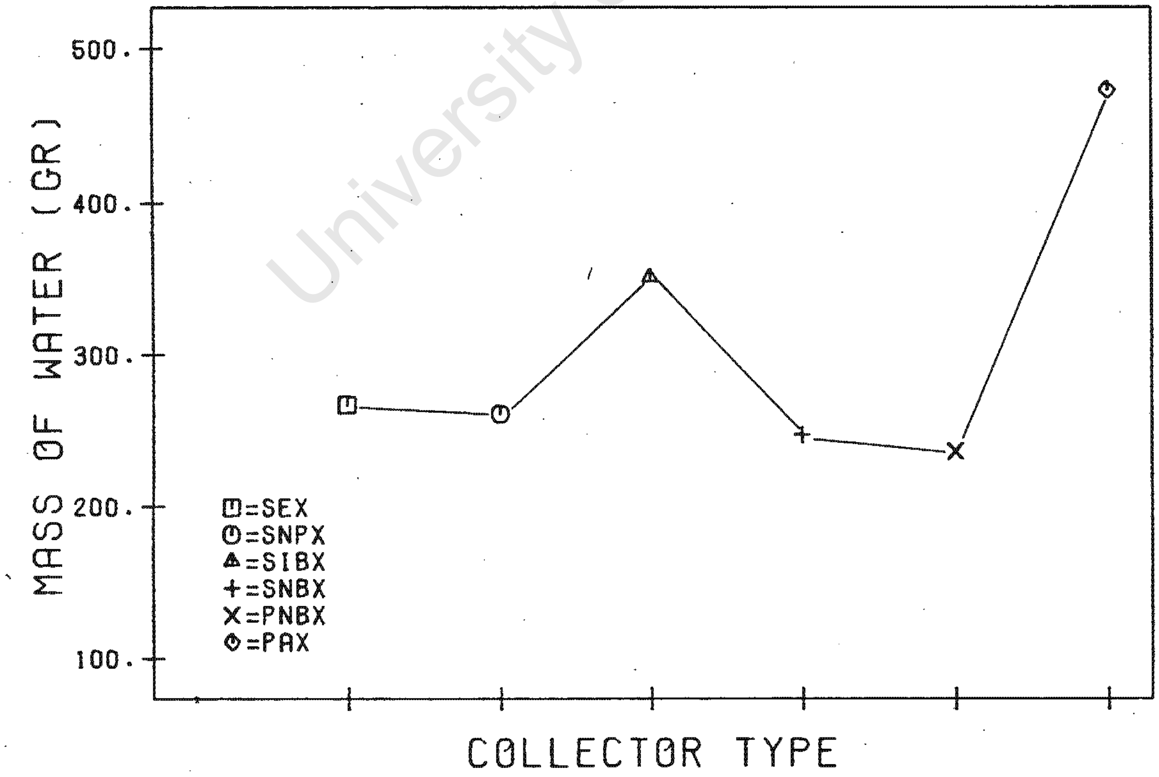


FIG 4.34 FLOTATION OF PURE QUARTZ USING DIFFERENT XANTHATE COLLECTORS AT THE SAME MOLECULAR CONCENTRATION. MASS OF WATER REMOVED AT THE DIFFERENT COLLECTORS.

4.2 ADSORPTION TESTS

4.2.1 Adsorption tests on pyrite

A number of adsorption tests were carried out in order to investigate possible differences on the rate and the extent of adsorption of difference xanthate collectors on pyrite (Section 3.2). The adsorption of six different xanthate collectors were first studied on oxidized pyrite. These runs were carried out at pH=9, and the temperature was controlled to 25°C. Two runs were done using SEX collector for reproducibility purposes. All collectors were added in equivalent molecular concentrations of $1.11*10^{-4}$ moles/l. This concentration corresponds to the collector concentration in the flotation cell, assuming that most of the collector is adsorbed by the pyrite particles.

Table 4.23 presents the percent of the collector molecules being adsorbed in one minute time period, indicating differences in the rate of adsorption. Table 4.23 also shows the percentage of the collector molecules being adsorbed in 4 minutes which is the time period available for collector adsorption in the flotation tests, viz. conditioning time. Figure 4.35 presents diagramatically the change in the adsorption of the different xanthate collectors with the time.

Adsorption tests were also carried out using acid leached pyrite. The conditions were similar to the ones mentioned above for the oxidized pyrite adsorption tests. Two reproducibility runs were done using PAX collector. Table 4.24 presents the percent of the collector molecules being adsorbed in one and four minutes respectively. Figure 4.36 illustrates the percent of the collector being adsorbed with time.

Table 4.23 Adsorption tests with oxidized pyrite using different xanthate collectors (concentration of 1.11*10-4 moles/l. Percentage of the collector adsorbed in 1 minute and 4 minutes time period.

	collector molecules adsorbed (%)	
type of collector	1 minute	4 minutes
SEX	22 22	- 54
SNPX	21	77
SIBX	26	81
SNBX	25	77
PNBX	23	74
PAX	29	88

Table 4.24 Adsorption tests with acid-leached pyrite using different types of xanthate collectors (concentration of $1.11*10^{-4}$ moles/l). Percentage of the collector adsorbed in 1 minute and 4 minutes.

	collector molecules adsorbed	
type of collector	1 minute	4 minute
SEX	40	76
SNPX	52	95
SIBX	60	98
SNBX	73	99
PNBX	62	98
PAX	73 74	99 99

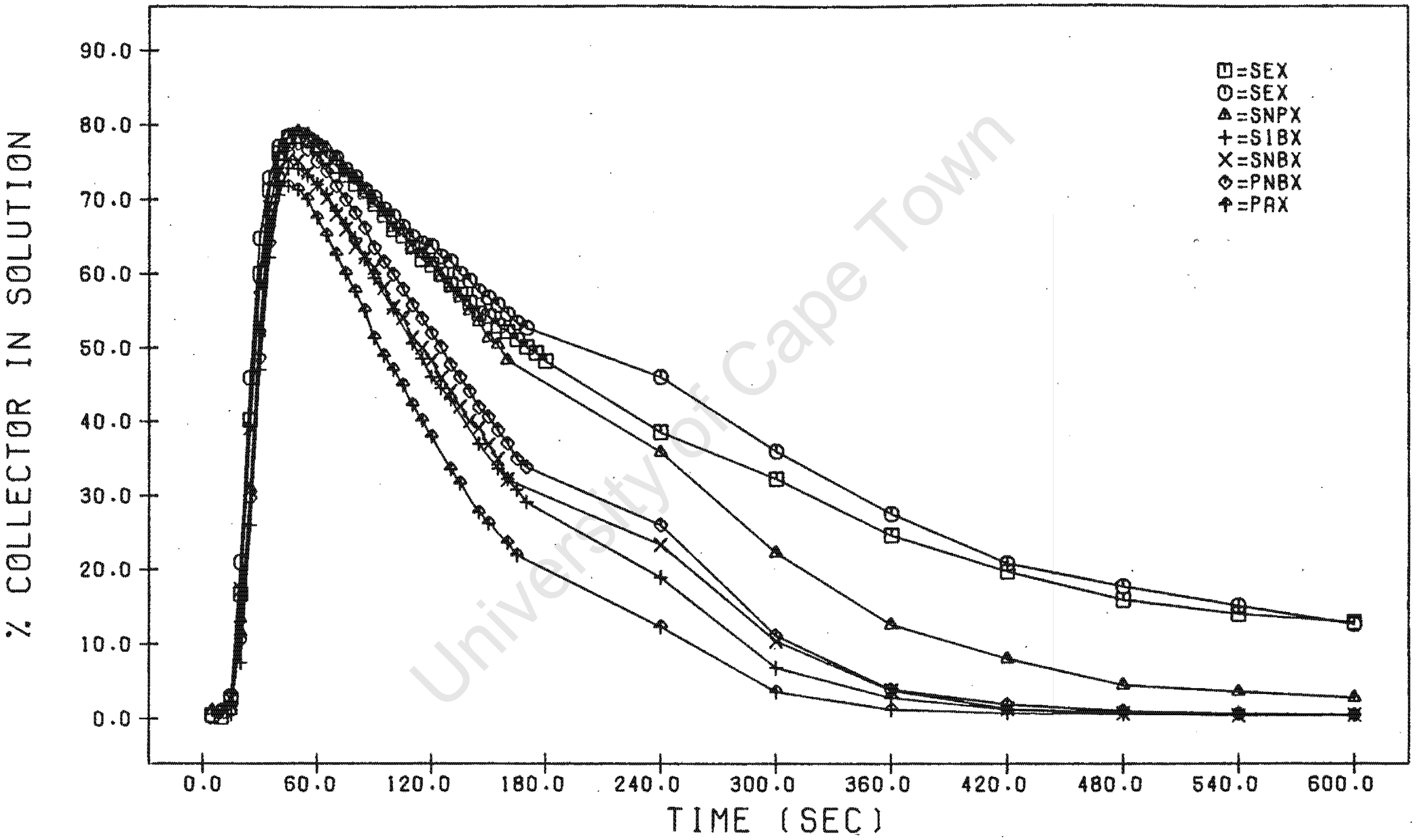


FIG 4.35 ADSORPTION EXPERIMENTS WITH OXIDIZED PYRITE AT PH=9 USING DIFFERENT TYPES OF XANTHATE COLLECTORS AT THE SAME MOLECULAR CONCENTRATION. PERCENTAGE OF THE COLLECTOR MOLECULES IN SOLUTION WITH INCREASING TIME.

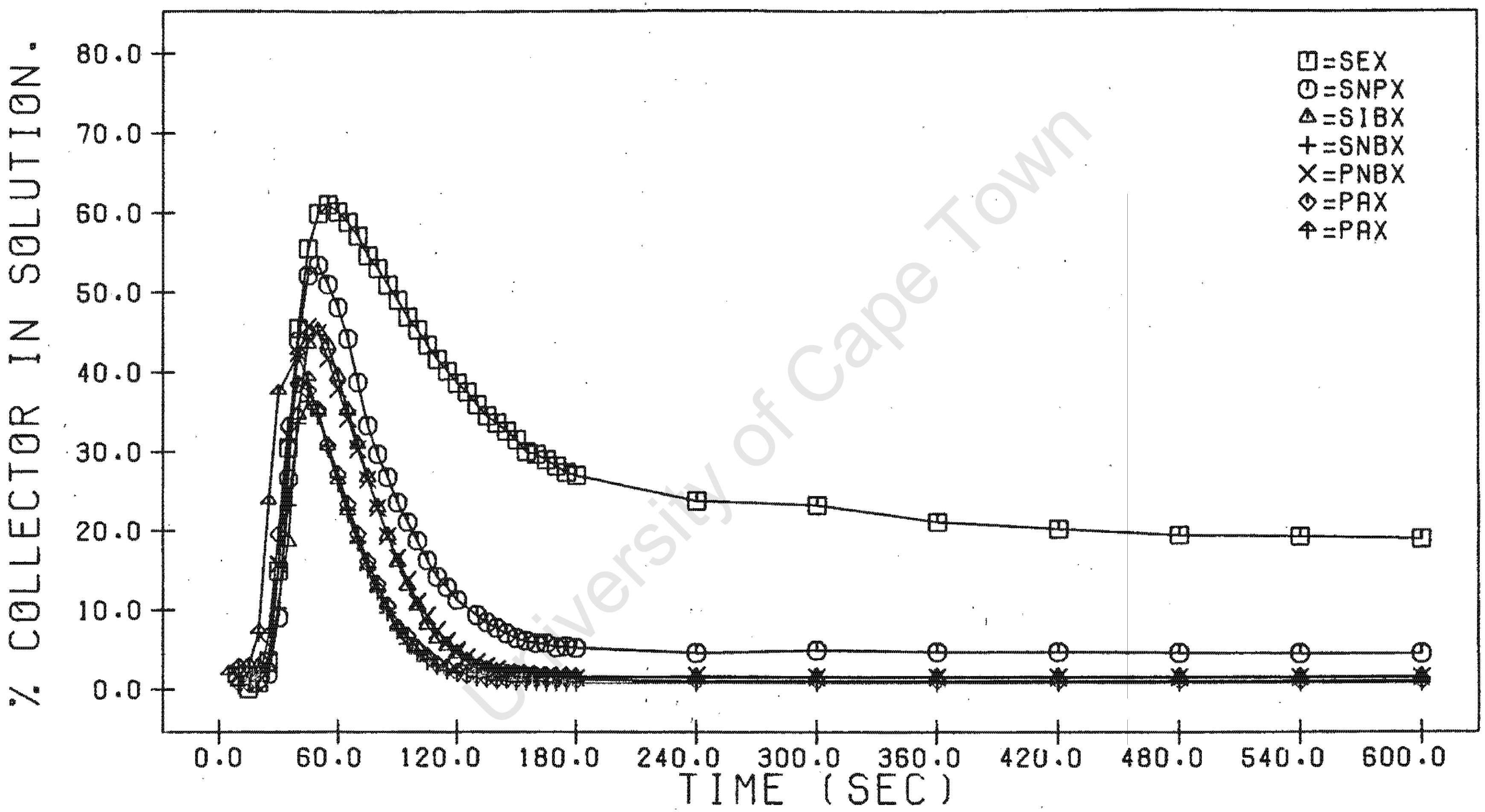


FIG 4.36 ADSORPTION EXPERIMENTS WITH ACID LEACHED PYRITE USING DIFFERENT XANTHATE COLLECTORS AT THE SAME MOLECULAR CONCENTREATION. PERCENTAGE OF COLLECTOR IN SOLUTION WITH INCREASING TIME.

4.2.2 Adsorption tests on quartz

The adsorption tests on quartz were carried out in order to investigate the possibility, (section 1.4.3), that anionic collector molecules can be adsorbed on activated quartz particles. Experiments were done at pH=9 and pH=12 where the highest quartz recovery was observed during the flotation tests. $Ca(OH)_2$ was used to modify the pH. The collector PAX was added at the dosage $2.1*10^{-5}$ moles/l. None of these runs showed any adsorption of collector in the limits of detection of the apparatus.

CHAPTER 5

DISCUSSION

The reproducibility experiments (Section 4.1.1) showed that the flotation technique used in this study gives adequately reproducible results. However, it was observed that variations in the pH influenced the degree of reproducibility of the system. It was thus decided to duplicate most of the flotation tests, especially when the pH was varied. Another important parameter which influenced the degree of reproducibility of the system was the state of oxidation of the pyrite. As a result of the slow oxidation of the pyrite over a period of months, it was found that although repeatable results could be obtained on a given sample at a particular time, the results were not reproducible over a period of six months or more. A marked decrease in the pyrite recovery especially in an alkaline medium was observed for the oxidized pyrite. These differences were, however, not noticed in the rates of flotation as expressed by the recovery at 30 sec, R_{30sec}. An increase in the final grade of the concentrates was observed in the case of the oxidized pyrite. The oxidation of pyrite was indicated by a variation in the natural pH of the pulp. The non-oxidized pyrite had a natural pH of approximately 5, while the oxidized pyrite pH was 2.8. In the case of acid leached pyrite the natural pH of the pulp was approximately 8.

The effect of oxidation on the pyrite flotation properties have already been described in the literature. Gaudin, (1957), reported that unoxidized pyrite is readily floated, but oxidized pyrite is comparatively less floatable. This was also confirmed by Glembostkii et al, (1972). No extensive work has been reported on the oxidation of pyrite in air, but it is mentioned that the effect is apparent after 30 min of exposure (Glembostkii, 1972). In water the oxidation effect is apparent after 20 min and it results in the formation of the stable $Fe(OH)_3$

species. Ferric hydroxide formation leads to an extremely high level of hydration and prevents the attachment of the collector onto the pyrite surface thus reducing the pyrite floatability (Glembostkii et al, 1972).

This work showed that acid leaching prior to flotation can remove the oxidation products from the surface of the pyrite. Table 4.12 shows that the available time for oxidation also has an influence. The non-oxidized pyrite (pyrite vacuum sealed in plastic packets and used within two months of storage) actually showed a significant degree of oxidation. The same pyrite six months later showed even more pronounced oxidation effects. Adsorption tests which were also carried out with the oxidized and acid leached pyrite showed clearly that the rate and the extent of adsorption on acid leached pyrite surface is much higher than on the oxidized pyrite surface. The adsorption on the oxidized pyrite however is still significant. Thus these results are not in agreement with the conclusions made by Glembotskii as refered to above, and the poorer recovery of oxidized pyrite is not necessarily due to the prevention of attachment of the collector. It was also shown, and is discussed later, that the recovery of oxidized pyrite was not influenced by the concentration of the collector. The adsorption and flotation tests did, however, show that for the same extent of xanthate adsorption greater recoveries were obtained for acid leached pyrite. This indicates that the low recoveries of oxidized pyrite may be due to a froth phase phenomenon, possibly associated with the presence of products of air oxidation on the pyrite surface which are present in alkaline pHs. In this context it should be mentioned that during the flotation of oxidized pyrite a heavily mineralized layer was formed in the froth phase which might be an indication of pyrite flocculation.

Oxidation also affects the natural floatability of pyrite. The pyrite recoveries achieved with acid leached pyrite are double the recoveries obtained with non-oxidized pyrite. Acid leaching also benefitted the rate of the pyrite recovery as expressed by R_{30sec}, and the grade of the concentrates. The effects of oxidation are not pronounced if flotation occursin an acid medium. The recovery of oxidized pyrite at pH=5 did not decrease significantly. In acidic solutions in situ leaching occurs thus removing the oxidation products from the pyrite surface.

The flotation of pyrite as a function of pH was also investigated. Initially the natural floatability of pyrite was studied. Pyrite floated readily at pH≤6. As the pH was increased, a sharp decrease in the pyrite recovery was observed. This phenomenon was noticed both in non-oxidized pyrite and acid leached pyrite. It seems that the formation of the hydrophilic ferric hydroxide which is the stable iron species in an alkaline medium, is responsible for this phenomenon. In acidic solutions the hydrophilic $Fe(OH)_3$ is not formed. Majima (1971), reported that at very low pH values elemental sulphur is stable in the pyrite system. Glembotskii et al (1972), also reported that elemental sulphur is present on the surface of freshly crushed pyrite, and thus pyrite can be floated by the use of a frother alone. However, this is disputed by Finkelstein, Allison et al, (1975), who found that at up to several hypothetical monolayers of elemental sulphur, there is no correlation between the concentration of sulphur on the surface and the observed floatability. There is thus no clear explanation for the high natural recoveries of pyrite at acidic pHs.

The addition of a xanthate collector improved the flotation properties of pyrite at all pH values. In the acidic pH region, pH≤6, the main influence of the collector was on the rate of flotation as the natural floatability of pyrite in this region is very high. In the neutral and alkaline pH range the xanthate collector addition improved both recoveries and rates of flotation.

The pH has also been shown to have a significant effect on the grade of the concentrates, irrespective of the presence or absence of collector (Figures 4.8 and 4.9). The lower the pH value, the higher the grade obtained. The addition of a xanthate collector improved the grades significantly at all pH values. The variation of the final grade of the concentrate is caused by the continuous increase in the recovery of gangue with an increase in pH when collector is present in the system. When the collector is absent from the system the sharp reduction in the pyrite recovery is additionally responsible for the low grades.

The influence of the pH on the pure quartz system was investigated in order to obtain further information on the behaviour of the gangue. In the absence of collector the recovery of quartz increased significantly at $pH \geq 11$. The addition of a xanthate collector made the phenomenon more pronounced, and the increase in the recovery is observed from $pH=10$.

It is widely accepted in the literature that quartz is an extremely hydrophilic mineral. At $pH>3$ it is negatively charged and practically not floatable with anionic collectors. Glembotskii et al (1972), suggested that quartz can be floated with anionic collectors only if it is activated by heavy metal ions such as calcium, which in this case was added to modify the pH. These ions act as the connecting link between quartz particles and anionic collector ions, and use part of their charge to remain adsorbed on the quartz surface, and part to attract the collector anions. In order to investigate this theory adsorption experiments were carried out at $pH=9$ and $pH=12$. No indication of xanthate collector adsorption, however, could be detected. In addition, flotation experiments with pure quartz were also carried out, using NaOH to modify the pH, as sodium ions do not activate quartz. Although the phenomenon was not as pronounced as in the case of $Ca(OH)_2$, the quartz recovery was noticed to increase from $pH=12$. Barker, (1986), also found no activation of quartz by increasing the calcium ions concentration in the pyrite-quartz system. Trahar, (1981), and Warren, (1985), suggested that entrainment is the mechanism responsible for the quartz recovery, and that this affects mainly the fine particles. The finer the particle the more likely it is to remain suspended or even entrapped in the water films between the bubbles, and to be recovered by entrainment. These authors pointed out that there is a direct relation between the recovery of the particles by entrainment and the amount of the water removed from the cell.

A comparison between the quartz recovery vs pH and mass of water removal vs pH curves in Figures 4.10-4.11, 4.27-4.28, 4.29-4.30 and 4.31-4.32, show that there is a direct relation between the quartz recovery and the mass of water removal curves. Table 4.21 also shows that the percentage of fine quartz particles, (-38µm), in the concentrates is markedly higher than it is in the feed. These observations support the hypothesis that the quartz is entrained and not floated. The observed increase in the recovery of quartz at high pH values is probably due to $CaOH^+$ or Na^+ ions adsorption on to quartz particles. A comparison between Figures 1.19 and 1.20 shows that the pH of the observed calcium adsorption onto quartz is related to the increased $CaOH^+$ presence in solution. The reason that the quartz recovery increases in the presence of a xanthate collector could be attributed to the infuence of the collector ions on the froth stability. Dudenkov et al, (1959), showed that the presence of collectors decreases the bubble diameter which furthermore causes an increase in the air-water interface for a constant aeration rate. Thus, a more stable, viz. more water bearing froth, is produced, which subsequently can influence the degree of entrainment.

The investigation on the effects of different types of xanthate collectors was carried out by studing six different collectors with varying hydrocarbon chain lengths and degree of isomerization. This work showed that the variation of the type of xanthate collector does not have a significant influence on the floatability of pyrite, as the final recoveries do not vary markedly. There is a slight increase in the initial rate of pyrite recovery in the case of PAX collector. The type of collector does, however, significantly infuence the grade of the concentrates. Figure 4.16 clearly showed a trend of an increase in the final grade with an increase in the length of the alkyl group of the collector, except in the case of SIBX. The reason for this behaviour may be due to the gangue mineral behaviour, since the gangue recovery decreased with an increase in the length of the carbon chain, except in the case of SIBX.

Variations in the type of the xanthate collector has been shown to influence the equilibrium contact angle of pyrite (Glembotskii, 1968). Table 1.2 shows an increase in the value of the contact angle as the length of the hydrocarbon chain increases. It was also shown that the isomeric stucture resulted in higher contact angle values compared to the normal structure of the same number of carbons. Therefore it was expected that the use of collectors with longer hydrocarbon chain length should influence the hydrophobicity as measured by the value of the contact angle of the pyrite particles. This variation in the value of the contact angle however, does not appear to influence significantly the floatability of pyrite. Even the weak collector SEX provided sufficient attachment between the pyrite and the air bubble for 90 % recovery of pyrite. The slight increase in the rate, as expressed by R_{30sec}, in the case of PAX may be attributed to the fact that the pyrite surface was rendered more hydrophobic by the addition of the stronger collector, and that pyrite then attaches itself faster onto the bubble. The variation of the grade of the concentrates may be due, as stated above to the behaviour of the gangue mineral. The relation between the gangue recovery-pH curve and water removal-pH curve shows again that the gangue mineral seems to have been entrained by the water. According to Dippenaar, (1978), the variation in the hydrophobicity of the floatable particles strongly influences the stability of the froth phase. The floatable particles are situated in the liquid films between the bubbles and attempt to establish the corresponding equilibrium contact angle to their degree of hydrophobicity. An increase in the value of the contact angle of the solids present in the froth phase results in a thinning of the water films between the air bubbles which, in cases of particles of contact angle higher than 70°, can even cause bubble coalescence and subsequently froth instability (Dippenaar, 1978). Thus, the increased hydrophobicity of the floatable pyrite particles treated with a stronger xanthate collector cause a thinning of the inner bubble water films and thus a decrease in the water content of the froth. This on the other hand influences the extent of entrainment. This explanation is also supported by the results of the flotation experiments with zero froth height. The use of SEX and PAX collector did not influence markedly the final recovery of pyrite, but the gangue recovery, and therefore the grades were influenced. In the case of SEX, the gangue recovery at zero froth height was double that obtained at 3 cm froth height. In the case of PAX the gangue recovery was four times higher in the case of zero froth. This reveals as expected that the high grades obtained with PAX were a result largely of a high degree of elutriation in the froth phase. This work also showed that the structure of SNBX renders the pyrite particles more hydrophobic than its isomer, SIBX, as the grades obtained with SNBX were better than the grades obtained with SIBX. However, this is not in agreement with the values of the contact angles reported in the literature.

The adsorption experiments showed that the longer the hydrocarbon chain of the xanthate collector, the faster they adsorb onto the pyrite surface. In the case of oxidized pyrite, an increase in the extent of adsorption is noticed with an increase in the length of the hydrocarbon chain. In the case of acid leached pyrite most of the collector has been adsorbed in 4 min, with an exception of SEX where only 74% has been adsorbed. In this case, the reduced amount of collector being adsorbed additionally influences the hydrophobicity of the pyrite particles treated with SEX (Wark and Sutherland, 1955).

The effect of the various xanthate collectors on pure quartz system revealed the opposite trend on the recovery of quartz from that shown in the pyrite-quartz system. More quartz is recovered when collectors PAX and SIBX were used. This phenomenon is explained by the effect of the type of collector on the bubble diameter as suggested by Dudenkov (Figure 1.17). An increase in the length of the collector hydrocarbon chain causes a decrease in the bubble diameter, and thus, at constant aeration rate, the number of the bubbles increases. Therefore, an increase in the froth stability is expected and hence an increase in the water content of the froth. This explanation is in agreement with the increased mass of water observed in the case of SIBX and PAX.

The variation of the collector concentration does not affect the pyrite recovery in the range of this investigation. This phenomenon has been observed both in the case of oxidized pyrite and acid leached pyrite. No effect was observed in the kinetic of the system as expressed by R_{30sec}. It does have an influence on the grade of the concentrates. There is a significant increase in the final grade with an increase in the collector concentration. The reason for this phenomenon is the increased hydrophobicity of the pyrite particles resulting from the increase in the collector concentration (Wark and Sutherland, 1955). The authors have reported that the contact angle for ethyl xanthate may lie anywhere between 0° and 60°, the last value only being obtained if sufficient collector is added. Therefore, according to Dippenaar, a less stable and thus less water bearing froth is expected with an increase in the collector concentration, as a result of the increased hydrophobicity of the floatable particles. The trend of the water removal and quartz recovery curves (Figures 4.23 and 4.24) at various collector concentrations, is in agreement with the above explanation. The peak which is observed in the gangue recovery vs collector concentration curve is related to the sharp increase in the recovery of pyrite with the addition of the collector. The observed variation in the slope of the lines in the quartz recovery versus water removal curves does not necessarily indicate floatability but rather an increasing degree of entrainment with a decrease in the collector concentration. The observed increase in the rate of water removal with a decrease in collector concentration shown in Table 4.17, shows that elutriation is taking place to a lesser extent in the froth phase when collector concentration decreases. The same conclusions are made on examining the behaviour of oxidized pyrite (Table 4.18).

CHAPTER 6

CONCLUSIONS

This work has shown that pyrite floated readily in acidic solutions with the mere use of a frother alone. The addition of a xanthate collector improved the rate of pyrite recovery and the grade of the concentrates significantly. In an alkaline surrounding a sharp decrease in the natural floatability of pyrite was observed. The addition of a xanthate collector improved both the recoveries and the rate of recovery of pyrite markedly as well as the grade of the concentrates. It was also shown that irrespective of the presence or absence of a xanthate collector the grades were improved with a decrease at the pH of the pulp. The variation of the pH showed no effect on the recovery of pyrite when it was treated with a xanthate collector.

Air oxidation has been shown to have a marked effect on the flotation properties of pyrite. This phenomenon was indicated by a marked decrease in pyrite recovery when flotation occurred in an alkaline media. In acidic solutions this phenomenon was not observed, as in situ leaching occurred, removing the oxidation products from the pyrite surface. Acid leaching prior to flotation removed the oxidation products, and enhanced the pyrite flotation properties.

The variation of the type of the xanthate collector had a significant effect on the grade of the concentrates. The longer the hydrocarbon chain of the collector, the higher the grade obtained. It was also shown that the normal structure of the hydrocarbon chain of the collector resulted in better grades than the isomeric structure of the same carbon number. No effect however was observed on the recovery of pyrite. A slight improvement was observed on the rate of pyrite recovery when PAX was used.

The adsorption studies showed that the longer the hydrocarbon chain length of the xanthates the faster they adsorb onto the pyrite surface. However in the time available for collector adsorption during flotation, most of the collector was adsorbed except in the case of SEX. The adsorption tests also showed that the xanthates adsorb faster and to a higher degree on the surface of acid leached pyrite rather than on oxidized pyrite.

The variation in the collector concentration affects markedly the final grade of the concentrates. The higher the collector concentration, the higher the grade obtained. No effect however was observed on the final recovery nor on the rate of the recovery of pyrite.

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APPENDIX A

Calculation of the sulphur content of the ore

Reactions in titrations are;

$KIO_3 + KI + 6HCl \quad 3I_2 + 6KCl + 3H_2O$

$SO_2 + I_2 + 2H_2O \quad H_2SO_4 + 2HI$

$$\text{Titre of } KIO_3 = V\text{ml} * \frac{1.1125}{1000\text{ml}} * \frac{1 \text{ mol}}{214 \text{ gr}}$$

1 mol KIO_3 reacts with 3 mol SO_2

mol SO_2 released $= V /(214 * 3 * 1.1125 * 10^{-3})$

mol S released $= V / 71.33 * 1.1125 * 10^{-3}$

mass S released $= V / 2.229 * 1.1125 * 10^{-3}$

$$\% \text{ S released} = \frac{\text{mass S released}}{\text{mass of sample} * 100}$$

$$= \frac{V}{\text{mass} * 20.037}$$

This has to be adjusted to take into consideration the efficiency of the Leco induction furnace.

APPENDIX B

A RAPID COMBUSTION METHOD FOR THE DETERMINATION OF SULPHUR IN ORES AND METALLURGICAL PRODUCTS.

In the proposed method for sulphur determination by combustion, the gaseous products including sulphur dioxide are absorbed in a dilute potassium iodide-hydrochloric acid solution containing sodium starch glycollate as indicator. As combustion proceeds, the solution is titrated with standard potassium iodate solution to a permanent faint blue colour. The method is applicable to a wide variety of samples with a sulphur content from a trace to 35%. A determination may be completed within 5 minutes with a precition of + 0.5%. The range of application has been extended to the determination of decomposition curves for sulphides and sulphates.

During the development of a hydrometallurgical process for the generation of sulphuric acid from the pyritic ore, a simple rapid routine method for pyrite determination was required, which could be available eventually to unskilled operators at the plant site. Two local combustion methods require the titrametric determination of absorbed sulphur dioxide after the completion of combustion, the absorption tube being emptied, washed, and refilled after each determination. The procedure described has been adapted from a method in common use for the determination of sulphur in petroleum products. The sample is burnt in a steam of air drawn by suction through the apparatus, the resulting sulphur dioxide being determined titrametrically as combustion proceeds, the cessation of evolution of the sulphur dioxide signalling the end of the determination. For low sulphur contents, up to 6 determination may be made with one charge of absorbing solution. The complete apparatus may be mounted on a basebord 29" * 16", and only service required is one electrical cutlet.

Pyrite and other sulphides were determined by oxidation at 2400°F. In a binary mixture of pyrite and calcium sulphate, the total sulphur was determined accurately at 2400°F, and the pyrite alone at 1600°F. In multi-component mixtures of pyrite with other metallic sulphates, mutual interference was too great for the estimation of any one component.

METHOD

REAGENTS

Standard Potassium iodate. Dissolve exactly 1.1125 gms. of good quality potassium iodate in de-ionised water and dilute to 1 litre in a grade A volumetric flask. 1ml. of this solution is empirically equal to 0.0005 gm. of sulphur, or 0.1% sulphur if an 0.5 gm. sample is taken. The exact factor for each class of sample must be determined by the described procedure.

Hydrochloric Acid. 2%v/v.

Starch-potassium iodide solution. Make a paste of 1.2 gms. of sodium starch glycollate and pour into about 500 mls. of boiling de-ionised water and stir. Cool, add 2 gms. of potassium iodide and dilute the solution to 1 litre.

APPARATUS

Air supply. A flow of 1000 mls. per minute is maintained using a flow-meter and a water pump or small rotary vacuum pump.

Combustion furnace. Dietert Varitemp 6.5 amp furnace No 3400, equipped with automatic electronic temperature control to 2800°F, and a needle valve for control of the air flow.

Combustion tube and boats. Zircotube 24" * 1 1/8" o.d. with tapered end. New boats should be ignited for a few minutes before use and stored in a closed container as they contain a trace of sulphur and will absorb sulphurous gases from the air.

Sample inserter. A 14 gauge stainless steel wire has a hook at one end and an appropriate obstruction along its length, so that the sample boat may be pushed into exactly the same position in the hot zone of the furnace at each insertion.

Absorption vessel and titration assemply. (Fig. 1). A cylindrical vessel of the approximate dimentions 7" long * 1 3/4" o.d. has a drain line and tape at the bottom and tapers to a B55 cone above. The B55 closure carries a coarse sintered-glass bubbler, a suitable jet for attachment to the titration assembly, a two way tap for introduction of the reagents, a suction tube and a perforated glass tube for washing out the vessel. The titration assembly is made from a long 10 ml. burette graduated to 0.05 ml. and having a 2-way tap.

The absorption vessel is calibrated at 50 mls. and 65 mls. allowence being made for displacement by the sintered-glass.

PROCEDURE

Set the furnace temperature to 2400°F. Spread evenly in the boat a 200 mesh sample of 50-500 mgms., depending on the sulphur content. Allow 50 mls. of 2% hydrochloric acid to run into the absorption vessel, followed by 15 mls. of starch potassium-iodide solution. Adjust the air flow-rate to 1000 mls. per minute, and add one drop of the potassium iodate to the solution to produce a faint blue colour. Note the burette reading and the intensity of the initial blue colour. Now add about 50% of the expected titre. Push the sample into the hot zone of the furnace from the open end of the combustion tube and add standard iodate solution sufficiently in advance of the evolution of the sulphur dioxide for the starch to remain a fairly deep blue until the end point is approached. Some samples give off sulphur dioxide very rapidly at first, and an excess of iodine must be maintained throughout the titration or low values will result. As evolution ceases, add iodate solution drop by drop permitting the blue colour to fade to the same intensity as before the titration and maintaining this faint coloration until the reaction ceases. The air-flow is sufficient to keep the solution stirred. Depending on their sulphur content, up to 6 samples may be assayed with the same absorbing solution. Samples should be classified into batches and the factor for the iodate solution determined daily or as required for each batch.

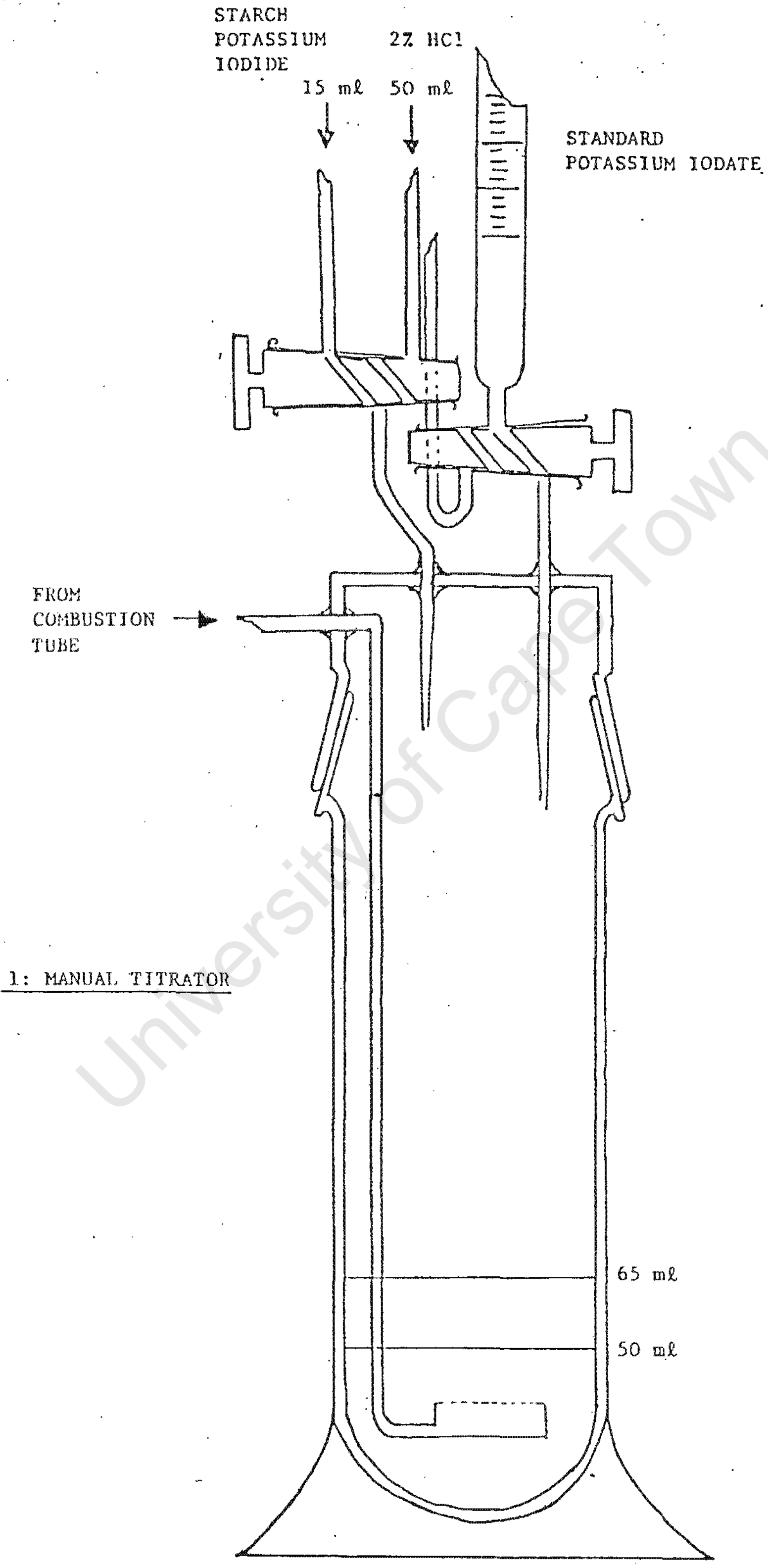

FIGURE 1: MANUAL TITRATOR

APPENDIX C

METHODS USED TO CALCULATE THE FLOTATION RESULTS.

Grade

The sulphur content was assayed for each concentrate and hence the grade (% sulphide S) of that fraction of the concentrate determined. In order to calculate the grade of the total concentrate (cumulative % S), the following calculations were carried out:

Let $C_1, \ldots\ldots, C_n$ be the masses of each fraction of the concentrate collected;

And let $c_1, \ldots\ldots, c_n$ be their corresponding percentage sulphur content.

Hence, the grade (cumulative % S) will be:

$$\text{cumul. grade } (\% \text{ S}) = \frac{C_1 c_1 + \ldots\ldots + C_n c_n}{C_1 + \ldots\ldots + C_n}$$

Recovery of pyrite.

In batch flotation tests only two products, a concentrate and a tailing, are obtained from a given feed. Concidering that:

f = (% S) in feed;
$c_1, \ldots\ldots, c_n$ = (% S) in the several fractions of the concentrate
t = (% S) in the tailing
F = Mass of feed
$C_1, \ldots\ldots, C_n$ = Masses of the several fractions of the concentrate
and T = Mass of tailing

Then the total mass balance is:

$$F = C_1 + \ldots\ldots + C_n + T$$

Concidering the assays, the sulphur material balance is:

$$Ff = C_1c_1 + \ldots\ldots + C_nc_n + Tt$$

where $C_1c_1 + \ldots\ldots + C_nc_n$ is the mass of pyrite recovered in the concentrate in terms of % S, and Tt is the mass of pyrite remained in the tailing in terms of % S.

The cumulative percentage of pyrite recovered in the concentrate in terms of % S is:

$$R\ (\%\ S) = \frac{C_1c_1 + \ldots\ldots + C_nc_n}{Ff} * 100$$

From the analysis of feed samples, the value for "f" was estimated through the determination of the sulphur content of pure pyrite of each pyrite parcel. Knowing the exact amount of pyrite and quartz mixed to prepare the synthetic mixture, the actual recovery "R" was calculated. The recoveries obtained in this way were later checked using the tailings assays done at MINTEK.

Recovery of gangue

In the pyrite flotation the feed sample can be divided into two materials: (i) pyrite (wanted); (ii) gangue (unwanted). To calculate the recovery of gangue in the concentrate the following calculations were made:

Let f_g = % gangue in the feed
$c_{g1}, \ldots c_{gn}$ = % gangue in the concentrate fractions
and t_g = % gangue in the tailing

The % S was converted to % pyrite by multiplying by the factor 1.865, which represents the ratio of the molecular weight of FeS_2 to the atomic weight of two sulphur atoms.

Hence,

$$f_g = 100 - 1.865 * f$$

$$t_g = 100 - 1.865 * t$$

$$c_{g1}, \ldots, c_{gn} = 100 - 1.865 * (c_1, \ldots, c_n)$$

and the cumulative percentage of gangue recovered in the concentrate is:

$$R_g\ (\%) = \frac{C_1 c_{g1} + \ldots\ldots\ldots + C_n c_{gn}}{F f_g} * 100$$

In all sulphur assays it is assumed that the only source of sulphide sulphur is FeS_2. Minerological examinations (Section 2.1.1) verified this assumption.

<u>The use of Klimpel model</u>

The recovery-time data obtained in all flotation tests was analysed using the Klimpel model (section 1.3). The program used for the calculations of ultimate time recovery, (y), and rate constant, (k), is the following:

```
1000 REM ****************************************************************
1010 REM *                                                              *
1020 REM * This program uses a Nelder - Mead optimisation method to     *
1030 REM * approximate the constants in the Klimpel model. The          *
1040 REM * constants are : " R " = ultimate recovery        and         *
1050 REM *                 " k " = rate constant                        *
1060 REM *                                                              *
1070 REM ****************************************************************
1080 CLS : PRINT "    KLIMPEL  MODEL   ":PRINT "      =============  "
1090 DIM T(20),R(20),RR(20),E1(20)
1100 REM
1110 REM
1120 REM * INPUT DATA *
1130 REM
1140  PRINT "READ YIELD TIME DATA":PRINT:PRINT
1150 INPUT "NO OF DATA POINTS ",N
1160 FOR I = 1 TO N
1170 INPUT "TIME";T(I):INPUT "RECOVERY";R(I)
1180 NEXT I
1190 CLS : LOCATE 2,1 : PRINT "TIME (s)" : LOCATE 2,20 : PRINT "RECOVERY (%)"
1200 P=4
1210 FOR I = 1 TO N
1220 LOCATE P,1 : PRINT T(I)
1230 LOCATE P,20 : PRINT USING "##.##";R(I)
1240 LOCATE P,45 : PRINT "OK Y/N"
1250 A$=INKEY$:IF A$="" THEN 1250
1260 IF A$="Y" OR A$="y" THEN 1300
1270 INPUT "INPUT NUMBER OF DATA POINT",I
1280 INPUT "TIME= ",T(I):INPUT "RECOVERY",R(I)
1290 LOCATE P,1 :PRINT T(I) :LOCATE P,20 : PRINT R(I)
1300 P=P+1
1310 NEXT I
1320 REM * NELDER -MEAD OPTIMISATION *
1330 N2 = 2 :AL = 1 :BT = .5 :GM = 2
1340 A = 1
1350 DIM F(N2 + 5),X(N2+5,N)
1360 X(1,1) = R(N)
1370 X(1,2) = .075
1380 FL = N2
1390 P = A/FL/SQR(2)*(FL-1+SQR(FL+1))
1400 Q1 = A/FL/SQR(2)*(SQR(FL+1)-1)
1410 LOCATE 10,45 : PRINT "I AM CALCULATING - BE PATIENT"
1420 FOR I =  2 TO N2+1
1430 FOR J = 1 TO N2
1440 IF J = I-1 GOTO 1460
1450 X(I,J) = X(I,J)+Q1 : GOTO 1470
1460 X(I,J) = X(I,J)+P
1470 NEXT J : NEXT I
1480 FOR I = 1 TO N2 + 1
1490 GOSUB 2410
1500 NEXT I
1510 IB = 1 :IW = 1
1520 FOR I = 1 TO N2 + 1
1530 IF F(I) < F(IB) THEN IB = I
1540 IF F(I) > F(IW) THEN IW = I
1550 NEXT I
1560 FOR J = 1 TO N2
1570 X(N2+2,J) = 0
1580 FOR I = 1 TO N2 +1
1590 X(N2+2,J) = X(N2+2,J) + X(I,J)
1600 NEXT I
1610 X(N2+2,J) = (X(N2+2,J) - X(IW,J)) / FL
1620 NEXT J : I = N2+2
1630 GOSUB 2410
1640 EP = 0
```

```
1650 FOR I = 1 TO N2 + 1
1660 EP = EP + (F(I)-F(N2+2))*(F(I)-F(N2+2))
1670 NEXT I
1680 EP = SQR((EP-(F(IW)-F(N2+2))*(F(IW)-F(N2+2)))/FL)
1690 IF EP < .00001 GOTO 2100
1700 FOR J = 1 TO N2
1710 X(N2+3,J) = X(N2+2,J) +AL * (X(N2+2,J) - X(IW,J))
1720 NEXT J : I = N2 +3
1730 GOSUB 2410
1740 IF F(N2+3) > F(IW) GOTO 1770
1750 IF F(N2+3) > F(IB) GOTO 1800
1760 GOTO 1940
1770 FOR J = 1 TO N2
1780 X(N2+4,J) = X(N2+2,J)-BT*(X(N2+2,J)-X(IW,J))
1790 NEXT J :I = N2 + 4 : GOTO 1830
1800 FOR J = 1 TO N2
1810 X(N2+4,J) = X(N2+2,J)- BT*(X(N2+2,J) - X(N2+3,J))
1820 NEXT J : I = N2 +4
1830 GOSUB 2410
1840 IF F(N2+4) > F(IW) GOTO 1890
1850 FOR J = 1 TO N2
1860 X(IW,J) = X(N2+4,J)
1870 NEXT J
1880 F(IW) = F(N2+4) : GOTO 1510
1890 FOR I = 1 TO N2+1
1900 FOR J = 1 TO N2
1910 X(I,J) =( X(I,J) + X(IB,J))/2
1920 NEXT J : NEXT I
1930 GOTO 1480
1940 FOR J = 1 TO N2
1950 X(N2+5,J) = X(N2+2,J) + GM * (X(N2+3,J)-X(N2+2,J))
1960 NEXT J :I = N2+5
1970 GOSUB 2410
1980 IF F(N2+5) < F(IB) GOTO 2040
1990 FOR J = 1 TO N2
2000 X(IW,J) = X(N2+3,J)
2010 NEXT J
2020 F(IW) = F(N2+3)
2030 GOTO 1510
2040 FOR J = 1 TO N
2050 X(IW,J) = X(N2+5,J)
2060 NEXT J
2070 F(IW) = F(N2+5)
2080 GOTO 1510
2090 REM * OUTPUT DATA *
2100 CLS : LOCATE 10,1:PRINT STRING$(80," ")
2110 LOCATE 2,1 : PRINT "TIME (s)" : LOCATE 2,20 : PRINT "RECOVERY (%)"
2120 FOR I = 1 TO N:P=3+I
2130 LOCATE P,1 :PRINT T(I) :PRINT B$ : LOCATE P,20 :PRINT R(I)
2140 NEXT I
2150 LOCATE 14,10 :PRINT " MIN = ";F(IB)
2160 LOCATE 16,10 :PRINT "    R = ";X(IB,1)
2170 LOCATE  18,10 :PRINT "    K = ";X(IB,2)
2180 LOCATE 2,40 :PRINT "PRED. RECOVERY "
2190 FOR J = 1 TO N
2200 LOCATE 3+J,45 :PRINT RR(J)
2210 NEXT J
2220 LOCATE 22,1
2230 INPUT "TO LINE PRINTER Y/N ",A$
2240 IF A$="N" OR A$="n" THEN 2390
```

```
2250 LPRINT TAB(1) "TIME (s)" ;
2260 LPRINT TAB(20) "RECOVERY (%)";
2270 LPRINT TAB(40) "PRED. RECOVERY"
2280 FOR I = 1 TO N:P=3+I
2290 LPRINT TAB(1) T(I) ;
2300 LPRINT TAB(20) ;
2310 LPRINT USING "##.##" ;R(I);
2320 LPRINT TAB(45);
2330 LPRINT USING "##.##" ;RR(I)
2340 NEXT I
2350 LPRINT " " : LPRINT " "
2360 LPRINT TAB(18) " MIN = ";F(IB)
2370 LPRINT TAB(18) "   R = ";X(IB,1)
2380 LPRINT TAB(18) "   K = ";X(IB,2)
2390 END
2400 REM * CALCULATE PREDICTED RECOVERIES *
2410 PH = X(I,1) : K = X(I,2) : ER =0
2420 IF K < 0 GOTO 2440
2430 GOTO 2450
2440 F(I) = 1E+08 : GOTO 2510
2450 FOR J = 1 TO N
2460 RR(J) = PH * (1- (1/(K*T(J)))*(1-EXP(-K*T(J))))
2470 E1(J) = (RR(J) - R(J))^2
2480 ER = ER + E1(J)
2490 NEXT J
2500 F(I) = ER
2510 RETURN
```

APPENDIX D

time(sec) \ pH	4	5	6	7	8	9	10	11	12
15	6.5	6.2	8.5	8.1	8.8	8.1	9.9	11.1	13.0
	6.1	6.7	8.4	8.0	7.6	9.2	9.1	11.3	11.6
30	11.2	10.5	15.1	14.9	16.1	14.8	17.3	20.4	24.2
	10.5	11.3	14.4	15.1	13.5	17.2	17.8	21.4	22.7
60	16.8	15.9	22.5	22.1	24.4	21.2	24.3	29.9	36.1
	15.8	17.0	21.9	21.9	19.7	24.8	25.8	32.0	34.1
120	21.4	20.2	27.3	25.5	27.0	23.4	26.7	33.6	44.6
	20.4	20.9	27.0	25.8	22.5	27.4	28.2	36.1	41.1
240	25.9	23.9	30.6	27.1	27.8	23.9	27.5	34.8	48.2
	24.3	24.4	30.6	27.4	23.4	28.3	28.8	37.5	43.6
420	28.5	25.8	32.3	28.0	28.2	24.5	27.8	35.3	49.3
	26.3	26.4	32.6	28.5	23.9	28.7	29.1	38.1	44.4
600	29.5	26.7	32.9	28.4	28.5	24.8	28.0	35.5	49.7
	27.2	27.1	33.5	29.0	24.2	29.0	29.3	38.4	44.8

Table D.1

Flotation of pyrite-quartz mixture in the absence of collector at different pH values. Cumulative mass of concentrate,(gr), with increasing flotation time.

pH time(sec)	4	5	6	7	8	9	10	11	12
15	29.9	29.6	20.2	10.2	5.1	5.1	3.2	3.2	2.4
	32.2	27.5	21.1	10.3	8.5	4.7	3.1	3.5	2.3
30	28.0	27.5	19.1	9.9	5.2	5.0	3.2	3.2	2.5
	29.8	25.6	19.7	10.2	8.2	4.7	3.1	3.5	2.3
60	26.1	25.8	18.3	10.5	5.8	5.5	3.5	3.5	2.6
	27.7	24.2	18.5	10.9	8.9	5.2	3.4	3.8	2.4
120	24.9	25.3	18.3	11.7	6.6	6.2	4.1	3.8	2.7
	26.3	24.2	18.3	12.2	10.1	5.9	3.8	4.3	2.6
240	23.5	24.3	18.3	12.3	6.8	6.4	4.3	4.1	2.8
	25.2	23.6	18.2	12.5	10.5	6.2	4.0	4.7	2.6
420	22.6	23.8	18.2	12.6	7.0	6.5	4.5	4.2	2.9
	24.5	23.1	18.0	12.8	10.9	6.4	4.1	4.9	2.7
600	22.3	23.6	18.2	12.7	7.1	6.6		4.2	2.9
	24.2	22.9	18.0	12.9	11.0			4.9	2.7

Table D.2

Flotation of pyrite-quartz mixture in the absence of collector at different pH values. Cumulative grade of concentrate, (%S), with increasing flotation time.

pH time(sec)	4	5	6	7	8	9	10	11	12
15	26.9	25.3	23.6	11.4	6.2	5.7	4.4	4.9	4.3
	27.2	25.5	24.6	11.4	8.9	6.0	3.9	5.5	3.7
30	43.4	39.8	39.7	20.4	11.7	10.2	7.8	9.0	8.3
	43.4	39.8	39.1	21.3	15.4	11.2	7.7	10.5	7.3
60	60.8	56.9	56.8	32.0	19.6	16.1	11.9	14.3	12.8
	60.6	56.8	56.0	32.9	24.2	17.7	12.2	16.8	11.4
120	73.9	70.7	69.2	41.4	24.5	19.9	15.0	17.9	16.7
	74.3	69.7	68.4	43.6	31.6	22.5	14.9	21.5	14.6
240	84.3	80.4	77.6	46.1	26.3	21.1	16.3	19.6	18.8
	84.6	79.7	76.9	47.3	34.0	24.4	15.9	24.7	15.9
420	89.3	85.2	81.2	48.7	27.2	22.1	17.2	20.3	19.5
	89.3	84.3	81.4	50.5	36.0	25.5	16.7	25.8	16.5
600	91.2	87.3	82.7	50.0	28.0	22.7		20.7	19.9
	91.2	86.1	83.3	51.9	37.0			26.3	16.7

Table D.3

Flotation of pyrite-quartz mixture in the absence of collector at different pH values. Cumulative recovery of pyrite, (%), with increasing flotation time.

pH time(sec)	4	5	6	7	8	9	10	11	12
15	0.29	0.28	0.54	0.67	0.81	0.74	0.95	1.06	1.26
	0.24	0.34	0.52	0.66	0.65	0.85	0.87	1.08	1.13
30	0.55	0.52	0.98	1.24	1.47	1.36	1.65	1.95	2.35
	0.48	0.60	0.92	1.24	1.16	1.59	1.71	2.03	2.20
60	0.87	0.83	1.51	1.81	2.21	1.93	2.30	2.84	3.49
	0.77	0.94	1.46	1.78	1.66	2.27	2.46	3.02	3.31
120	1.16	1.09	1.83	2.02	2.41	2.10	2.51	3.17	4.30
	1.06	1.17	1.81	2.02	1.85	2.48	2.66	3.37	3.97
240	1.47	1.33	2.05	2.12	2.47	2.14	2.57	3.27	4.64
	1.31	1.39	2.05	2.13	1.89	2.54	2.71	3.47	4.21
420	1.68	1.45	2.17	2.17	2.49	2.18	2.61	3.31	4.74
	1.45	1.52	2.19	2.20	1.93	2.57	2.73	3.51	4.28
600	1.75	1.51	2.21	2.20	2.51	2.20		3.32	4.77
	1.51	1.57	2.26	2.23	1.95			3.54	4.31

Table D.4

Flotation of pyrite-quartz mixture in the absence of collector at different pH values. Cumulative recovery of quartz,(%), with increasing flotation time.

time(sec) \ pH	4	5	6	7	8	9	10	11	12
15	47	47	70	83	93	91	113	112	104
	43	54	70	82	85	100	101	114	98
30	88	86	130	153	180	168	200	210	194
	82	97	125	158	151	191	200	219	191
60	148	144	213	241	290	260	302	333	301
	139	160	209	244	234	297	315	351	300
120	204	196	280	290	338	302	359	407	391
	195	207	281	302	279	351	371	433	377
240	267	249	336	316	352	313	380	441	444
	246	265	349	330	293	369	388	470	414
420	287	272	366	326	355	320	387	454	465
	265	290	392	347	298	375	395	486	431
	296	277	372	327	356	322	389	457	478
		293	412	352				490	440

Table D.5

Flotation of pyrite-quartz mixture in the absence of collector at different pH values. Cumulative mass of water, (gr), removed with increasing flotation time.

time(sec) \ pH	4	5	6	7	8	9	10	11	12
15	8.5	7.9	8.4	9.0	10.9	12.0	17.5	18.9	20.0
	8.5	8.1	8.7	10.1	11.1	14.3	14.6	19.7	19.3
30	11.7	11.9	13.3	14.9	20.1	24.2	31.5	36.9	36.9
	11.5	11.6	13.0	16.5	20.3	26.2	28.9	39.8	36.9
60	15.0	16.4	18.8	20.3	27.2	38.3	46.1	60.1	57.7
	15.0	15.7	17.5	22.3	29.4	38.5	43.9	63.8	56.2
120	16.9	19.7	22.1	22.7	29.4	44.4	51.3	67.5	69.6
	17.1	18.6	20.4	25.2	32.8	43.7	48.1	72.5	67.1
240	18.2	21.9	24.5	23.8	30.1	45.5	52.2	68.8	74.1
	18.3	20.8	22.3	26.7	33.8	44.4	48.9	74.7	70.8
420	19.2	23.1	25.9	24.9	30.8	46.2	52.6	69.4	75.5
	18.7	21.7	23.3	27.9	34.8	45.0	49.6	75.5	71.7
600		23.9	26.5	25.6	31.3	46.7	53.8	69.7	76.1
	18.9	22.2	23.9	28.6	35.4	45.0	50.0	76.0	72.1

Table D.6

Flotation of pyrite-quartz mixture using 71.7 g/t SIBX at different pH values. Cumulative mass of concentrate,(gr), with increasing flotation time.

pH time(sec)	4	5	6	7	8	9	10	11	12
15	43.7	35.2	27.8	28.2	20.8	16.5	13.0	11.6	8.4
	44.0	37.7	30.9	26.2	21.1	15.9	14.3	10.9	7.6
30	41.5	31.7	24.2	23.8	17.4	12.8	10.5	9.2	7.5
	41.3	34.8	27.3	22.3	16.9	12.6	11.3	8.7	6.8
60	38.9	29.0	22.9	22.1	16.3	11.3	9.5	7.7	7.2
	38.6	32.5	25.2	20.8	15.6	11.3	10.3	7.4	6.4
120	37.8	28.4	22.8	22.1	16.6	11.4	9.8	7.9	7.3
	37.4	31.7	24.9	20.8	16.0	11.5	10.6	7.5	6.6
240	37.1	28.0	22.9	22.3	16.8	11.7	9.9	8.0	7.5
	36.9	31.0	24.9	21.1	16.2	11.6	10.8	7.7	6.8
420	36.5	27.7	23.0	22.5	17.0	11.8	10.0	8.1	7.6
	36.6	30.7	24.9	21.3	16.5	11.8	10.9	7.8	6.8
600		27.4	23.1	22.6	17.2	11.9	10.0	8.1	7.7
	36.4	30.5	24.9	21.4	16.6	11.8	10.9	7.9	6.9

Table D.7

Flotation of pyrite-quartz mixture using 71.7 g/t SIBX at different pH values. Cumulative grade of concentrate,(%S), with increasing flotation time.

pH time(sec)	4	5	6	7	8	9	10	11	12
15	51.4	38.3	32.5	35.2	31.2	27.4	31.6	30.3	23.2
	51.6	42.3	37.2	36.6	32.4	31.5	28.9	29.7	20.3
30	67.0	52.3	44.7	49.0	48.5	42.8	45.7	46.7	38.5
	66.0	56.0	49.0	51.0	47.5	45.8	45.3	48.1	34.9
60	80.8	66.1	59.4	62.0	61.5	59.9	60.8	64.4	57.2
	80.2	70.7	60.8	64.2	63.4	60.3	62.6	65.7	49.9
120	88.5	77.5	69.7	69.6	67.6	70.4	69.6	73.6	70.3
	88.5	81.6	70.4	72.8	72.5	69.4	70.8	75.7	60.9
240	93.6	84.9	77.7	73.7	70.0	73.5	71.8	76.4	77.0
	93.2	89.1	76.8	77.8	75.9	71.4	72.9	80.1	66.2
420	97.1	88.6	82.5	77.4	72.5	75.6	72.9	77.7	79.5
	94.9	92.4	80.4	82.1	79.3	73.2	74.6	81.8	67.8
600		90.9	84.7	80.3	74.5	77.0	74.6	78.5	80.9
	95.5	94.0	82.5	84.6	81.4	73.0	75.6	82.7	68.6

Table D.8

Flotation of pyrite-quartz mixture using 71.7 g/t SIBX at different pH values. Cumulative recovery of pyrite, (%), with increasing flotation time.

pH time(sec)	4	5	6	7	8	9	10	11	12
15	0.16	0.27	0.41	0.43	0.68	0.84	1.34	1.50	1.72
	0.15	0.24	0.38	0.53	0.68	1.02	1.09	1.59	1.69
30	0.27	0.50	0.74	0.84	1.37	1.87	2.58	3.11	3.22
	0.26	0.42	0.65	0.97	1.41	2.03	2.31	3.38	3.27
60	0.42	0.76	1.10	1.21	1.92	3.07	3.84	5.21	5.08
	0.43	0.63	0.94	1.38	2.12	3.09	3.60	5.57	5.03
120	0.51	0.94	1.29	1.35	2.06	3.54	4.25	5.85	6.10
	0.53	0.77	1.11	1.57	2.34	3.49	3.92	6.32	5.98
240	0.57	1.07	1.42	1.41	2.10	3.61	4.31	5.94	6.47
	0.58	0.89	1.22	1.64	2.40	3.53	3.97	6.49	6.28
420	0.62	1.14	1.50	1.46	2.13	3.65	4.35	5.98	6.58
	0.60	0.94	1.27	1.72	2.45	3.56	4.02	6.55	6.36
600		1.19	1.53	1.50	2.16	3.69	4.45	6.00	6.62
	0.61	0.96	1.30	1.75	2.48	3.56	4.04	6.59	6.39

Table D.9

Flotation of pyrite-quartz mixture using 71.7 g/t SIBX at different pH values. Cumulative recovery of quartz,(%), with increasing flotation time.

pH time(sec)	4	5	6	7	8	9	10	11	12
15	28	45	55	59	72	71	105	113	120
	27	43	55	69	75	85	87	120	125
30	50	81	101	114	152	149	195	226	226
	48	74	97	130	152	164	178	248	243
60	78	128	160	175	233	264	311	404	377
	77	115	148	197	252	269	301	432	393
120	89	156	195	200	258	337	367	489	480
	88	137	177	228	294	333	346	533	495
240		169	213	201	259	344	368	495	528
		148	192	229	295	336	348	553	537
420									541
									546
600									544
									547

Table D.10

Flotation of pyrite-quartz mixture using 71.7 g/t SIBX at different pH values. Cumulative mass of water,(gr), removed with increasing flotation time.

pH time(sec)	5	7	9	11
15	9.0	6.9	11.3	29.6
		7.5	13.0	27.2
30	13.0	9.1	15.9	47.5
		10.1	19.5	46.4
60	17.1	11.0	19.2	64.9
		12.7	23.0	64.1
120	19.7	12.0	19.9	69.1
		13.6	23.8	69.0
240	21.4	12.8	20.8	70.4
		14.6	24.6	70.5
420	22.5	13.7	21.6	71.3
		15.6	25.3	71.5
600	23.1	14.3	22.2	72.0
		16.3	25.8	72.3

Table D.11

Flotation of oxidized pyrite-quartz mixtures using 71.7 g/t SIBX collector at different pH values. Cumulative mass of the concentrate, (gr), with increasing flotation time.

pH time(sec)	5	7	9	11
15	34.6	37.2	23.1	8.5
		37.2	19.6	8.4
30	31.2	35.0	20.5	7.0
		33.8	16.8	6.9
60	28.7	33.3	19.8	6.4
		31.6	16.4	6.2
120	28.3	32.6	19.8	6.6
		31.0	16.5	6.4
240	27.9	31.9	19.8	6.7
		30.4	16.6	6.6
420	27.5	30.9	19.8	6.8
		29.8	16.6	6.7
600	27.3	30.5	19.7	6.9
		29.4	16.7	6.7

Table D.12

Flotation of oxidized pyrite-quartz mixtures using 71.7 g/t SIBX collector at different pH values. Cumulative grade, (% S), of the concentrate with increasing flotation time.

pH time(sec)	5	7	9	11
15	43.2	35.3	35.7	34.5
		38.4	35.3	31.5
30	56.1	43.9	44.8	45.8
		47.2	45.0	44.6
60	67.9	50.4	52.1	56.8
		55.3	52.1	55.3
120	77.0	53.5	54.2	62.4
		58.2	54.2	61.2
240	82.6	55.9	56.6	64.8
		61.2	56.2	64.0
420	85.6	58.1	58.6	66.6
		64.1	58.1	65.8
600	86.9	59.6	59.9	67.7
		66.3	59.5	67.1

Table D.13

Flotation at oxidized pyrite-quartz mixture using 71.7 g/t SIBX collector at different pH values. Cumulative actual pyrite recovery,(%), with increasing flotation time.

pH time(sec)	5	7	9	11
15	58	40	80	182
		45	87	166
30	99	65	129	305
		74	147	299
60	150	90	170	466
		106	191	462
120	180	101	179	531
		117	199	538
240	203	113	190	554
		129	207	562
420	217	127	199	567
		141	215	574
600	223	135	205	574
		149	221	581

Table D.14

Flotation of oxidized pyrite and quartz mixture using 71.7 g/t SIBX collector at different pH values. Cumulative mass of water removed,(gr), with increasing flotation time.

time(sec) \ pH	5	7	9	11
15	0.32	0.22	0.65	2.53
		0.27	0.84	2.33
30	0.55	0.32	1.00	4.19
		0.38	1.36	4.10
60	0.81	0.42	1.23	5.80
		0.53	1.62	5.75
120	0.94	0.48	1.27	6.15
		0.58	1.67	6.17
240	1.04	0.53	1.33	6.25
		0.64	1.72	6.28
420	1.11	0.59	1.38	6.32
		0.70	1.77	6.35
600	1.15	0.63	1.42	6.37
		0.75	1.81	6.42

Table D.15

Flotation of oxidized pyrite and quartz mixture using 71.7 g/t SIBX collector at different pH values. Cumulative actual recovery of gangue, (%), with increasing flotation time.

collector type time(sec)	SEX	SNPX	SIBX	SNBX	PNBX	PAX
15	29.5	18.6	20.6	17.2	17.4	15.3
	28.5		19.3			15.8
30	44.5	25.6	30.1	23.9	22.6	20.7
	44.4		27.1			21.8
60	57.3	30.4	36.5	28.6	26.4	24.8
	57.6		32.7			25.9
120	61.0	32.2	38.9	30.3	27.7	26.3
	61.2		34.8			27.5
240	62.5	33.0	39.6	31.0	28.0	26.7
	62.8		35.6			27.9
420	63.2	33.6	39.9	31.3	28.2	26.9
	63.6		35.9			28.2
600	63.5	33.9	–	31.6	–	–
	64.0		–			–

Table D.16

Flotation of acid leached pyrite-quartz mixtures at pH=9, using different types of xanthate collector. Cumulative mass of the concentrate,(gr), with increasing flotation time.

collector type / time(sec)	SEX	SNPX	SIBX	SNBX	PNBX	PAX
15	14.8	22.9	20.0	26.3	26.6	29.7
	14.9		21.9			29.3
30	12.2	21.0	18.3	23.8	25.0	27.7
	12.2		20.0			27.2
60	11.1	20.6	17.7	23.4	24.5	26.8
	11.2		19.5			26.2
120	11.4	20.8	17.9	23.5	24.5	26.6
	11.5		19.7			26.1
240	11.5	20.7	17.8	23.3	24.4	26.4
	11.6		19.5			25.8
420	11.4	20.5	17.7	23.2	24.3	26.3
	11.6		19.5			25.7
600	11.4	20.4	–	23.0	–	–
	11.5		–			–

Table D.17

Flotation of acid leached pyrite-quartz mixtures at pH=9 using different types of xanthate collectors. Cumulative grade,(%S), with increasing flotation time.

collector type time(sec)	SEX	SNPX	SIBX	SNBX	PNBX	PAX
15	55.4	54.1	54.1	57.4	58.6	59.1
	53.4		55.0			58.2
30	69.1	68.2	69.2	72.3	71.6	74.8
	68.3		70.7			74.3
60	80.8	79.4	80.9	85.1	82.1	86.8
	81.2		83.3			85.3
120	88.2	85.1	87.2	90.3	86.0	91.2
	88.5		89.4			89.9
240	90.8	86.8	88.4	91.6	86.7	92.0
	91.5		90.7			90.6
420	91.5	87.6	88.8	92.0	86.9	92.2
	92.3		91.2			90.8
600	91.8	87.9	–	92.3	–	–
	92.6		–			–

Table D.18

Flotation of acid-leached pyrite-quartz mixtures at pH=9 using different types of xanthate collectors. Cumulative pyrite recovery, (%), with increasing flotation time.

collector type / time(sec)	SEX	SNPX	SIBX	SNBX	PNBX	PAX
15	2.17 2.09	1.08	1.28 1.16	0.89	0.89	0.69 0.73
30	3.49 3.48	1.58	2.01 1.73	1.35	1.23	1.02 1.09
60	4.61 4.62	1.90	2.48 2.11	1.64	1.46	1.26 1.34
120	4.87 4.88	2.00	2.63 2.24	1.73	1.53	1.34 1.43
240	4.99 4.99	2.06	2.68 2.30	1.78	1.55	1.38 1.47
420	5.05 5.07	2.11	2.71 2.32	1.81	1.57	1.39 1.49
600	5.08 5.10	2.13	– –	1.83	–	– –

Table D.19

Flotation of acid leached pyrite-quartz mixtures at pH=9, using different types of xanthate collectors. Cumulative gangue recovery,(%), with increasing flotation time.

flotation parameter / time(sec)	mass of concentrate (gr)	grade (%S)	pyrite rec. %	gangue rec. %	mass of water (gr)
15	34.4	11.2	48.4	2.76	197
30	43.9	12.5	68.8	3.42	275
60	50.7	13.1	83.3	3.89	354
120	54.6	13.4	91.6	4.16	422
240	59.1	12.8	95.1	4.56	512
420	–	–	–	–	–
600	–	–	–	–	–

Table D.21

Flotation of acid-leached pyrite-quartz mixture at o.5 cm froth height and pH=9, using 84.2 g/t PAX collector. Cumulative values of flotation parameters with increasing flotation time.

flotation parameter / time(sec)	mass of concentrate (gr)	grade (%S)	pyrite rec. %	gangue rec. %	mass of water (gr)
15	43.4	7.6	41.5	3.78	229
30	64.2	7.7	61.8	5.59	378
60	88.6	6.8	76.2	7.85	621
120	99.6	6.8	84.8	8.83	818
240	104.2	6.8	89.1	9.24	945
420	106.3	6.8	90.4	9.43	1010
600	–	–	–	–	–

Table D.22

Flotation of acid-leached pyrite-quartz mixture at 0.5 cm froth height and pH= 9, using 60 g/t SEX collector. Cumulative values of flotation parameters with increasing flotation time.

concentration / time(sec)	zero	30g/t PAX	40 g/t PAX	60 g/t PAX	84.2 g/t PAX	
15	14.0	27.0	22.8	18.6	15.3	15.8
30	22.9	39.0	32.1	26.3	20.7	21.8
60	30.5	47.6	38.1	31.6	24.8	25.9
120	33.3	50.0	40.2	33.7	26.3	27.5
240	34.8	50.9	41.1	34.4	26.7	27.9
420	35.9	51.3	41.5	34.7	26.9	28.2
600	36.7	-	-	-	-	-

Table D.23

Flotation of acid leached pyrite-quartz mixtures at pH=9 varying the concentration of collector PAX. Cumulative mass of concentrate ,(gr),with increasing flotation time.

concentration / time(sec)	zero	30 g/t PAX	40 g/t PAX	60 g/t PAX	84.2 g/t PAX	
15	7.0	15.4	19.0	23.4	29.7	29.3
30	7.3	13.1	16.8	21.3	27.7	27.2
60	7.9	12.5	16.4	20.6	26.8	26.2
120	8.8	12.8	16.6	20.8	26.6	26.1
240	9.1	12.8	16.5	20.6	26.4	25.8
420	9.2	12.7	16.4	20.6	26.3	25.7
600	9.3	-	-	-	-	-

Table D.24

Flotation of acid-leached pyrite-quartz mixtures at pH=9, varying the concentration of collector PAX. Cumulative grade,(%S), with increasing flotation time.

concentration / time(sec)	zero	30 g/t PAX	40 g/t PAX	60 g/t PAX	84.2 g/t PAX	
15	12.9	55.7	58.2	54.7	59.1	58.2
30	21.9	68.6	72.3	70.4	74.8	74.3
60	31.6	79.6	83.8	81.8	86.8	85.3
120	38.4	85.7	89.5	87.8	91.2	89.9
240	41.5	87.2	90.8	89.0	92.0	90.6
420	43.6	87.7	91.2	89.5	92.2	90.8
600	44.8	-	-	-	-	-

Table D.25

Flotation of acid-leached pyrite-quartz mixtures at pH=9, varying the concentration of collector PAX. Cumulative pyrite recovery,(%), with increasing flotation time.

concentration / time(sec)	zero	30 g/t PAX	40 g/t PAX	60 g/t PAX	84.2 g/t PAX	
15	1.24	1.95	1.50	1.07	0.69	0.73
30	2.01	2.99	2.23	1.61	1.02	1.09
60	2.64	3.71	2.69	1.98	1.26	1.34
120	2.83	3.86	2.82	2.10	1.34	1.43
240	2.93	3.94	2.89	2.15	1.38	1.47
420	3.02	3.97	2.92	2.17	1.39	1.49
600	3.08	-	-	-	-	-

Table D.26

Flotation of acid leached pyrite-quartz mixtures at pH=9, varying the concentration of collector PAX. Cumulative gangue recovery,(%),with increasing flotation time.

concentration / time(sec)	zero	30 g/t PAX	40 g/t PAX	60 g/t PAX	84.2 g/t PAX	
15	127	153	134	108	81	90
30	216	243	209	170	123	140
60	311	333	275	224	162	182
120	355	360	298	241	173	194
240	379	370	309	248	176	197
420	401	374	313	250	177	198
600	415	–	–	–	–	–

Table D.27

Flotation of acid leached pyrite-quartz mixtures at pH=9, varying the concentration of collector PAX. Cumulative mass of water removed,(gr), with increasing flotation time.

concentration / time(sec)	zero	36 g/t SIBX	71.7g/t SIBX		108g/t SIBX	144 g/t SIBX
15	6.31	15.1	11.3	13.0	12.3	10.2
30	11.4	23.4	15.9	19.5	17.6	14.8
60	16.2	28.3	19.2	23.0	20.5	17.6
120	16.9	29.2	19.9	23.8	21.2	18.3
240	17.2	29.9	20.8	24.6	22.0	19.0
420	17.4	30.7	21.6	25.3	22.9	20.0
600	17.6	31.3	22.2	25.8	23.5	20.8

Table D.28

Flotation of oxidized pyrite-quartz mixtures at pH=9, varying the concentration of collector SIBX. Cumulative mass of concentrate,(gr),with increasing flotation time.

concentration time(sec)	zero	36 g/t SIBX	71.7g/t SIBX		108g/t SIBX	144g/t SIBX
15	3.5	16.1	23.1	19.6	21.4	24.7
30	3.8	13.5	20.5	16.8	18.8	21.8
60	4.3	13.2	19.8	16.4	18.5	21.5
120	4.6	13.4	19.8	16.5	18.6	21.6
240	4.7	13.4	19.8	16.6	18.6	21.6
420	4.8	13.5	19.8	16.6	18.6	21.6
600	4.9	13.5	19.7	16.7	18.6	21.6

Table D.29

Flotation of oxidized pyrite-quartz mixtures at pH=9, varying the concentration of collector SIBX. Cumulative grade,(%S), with increasing flotation time.

concentration time(sec)	zero	36g/t SIBX	71.7g/t SIBX		108g/t SIBX	144g/t SIBX
15	3.0	33.2	35.7	35.3	36.1	34.6
30	5.9	43.3	44.8	45.0	45.3	44.3
60	9.4	51.5	52.1	52.1	51.9	51.9
120	10.4	53.7	54.2	54.2	53.9	54.2
240	10.9	55.1	56.6	56.2	56.1	56.4
420	11.3	56.7	58.6	58.1	58.5	59.3
600	11.7	57.8	59.9	59.5	59.9	61.5

Table D.30

Flotation of oxidized pyrite-quartz mixtures at pH=9, varying the concentration of collector SIBX. Cumulative pyrite recovery,(%), with increasing flotation time.

concentration / time(sec)	zero	36 g/t SIBX	71.7 g/t SIBX		108 g/t SIBX	144 g/t SIBX
15	0.60	1.07	0.65	0.84	0.75	0.56
30	1.08	1.78	1.00	1.36	1.16	0.89
60	1.51	2.17	1.23	1.62	1.36	1.07
120	1.57	2.22	1.27	1.67	1.41	1.11
240	1.60	2.27	1.33	1.72	1.46	1.15
420	1.61	2.33	1.38	1.77	1.52	1.21
600	1.62	2.37	1.42	1.81	1.56	1.26

Table D.31

Flotation of oxidized pyrite-quartz mixtures at pH=9, varying the concentration of collector SIBX. Cumulative gangue recovery, (%), with increasing flotation time.

concentration / time(sec)	zero	36 g/t SIBX	71.7 g/t SIBX		108 g/t SIBX	144 g/t SIBX
15	80	111	80	87	85	77
30	155	191	129	147	138	126
60	235	256	170	191	174	162
120	275	267	179	199	180	169
240	290	276	190	207	189	176
420	295	287	199	215	200	186
600	297	294	205	221	208	193

Table D.32

Flotation of oxidized pyrite-quartz mixtures at pH=9, varying the concentration of collector SIBX. Cumulative mass of water, (gr), removed with increasing flotation time.

APPENDIX E

pH / time(sec)	4	5	6	7	8	9	10	11	12
15	0.21	0.26	0.40	0.44	0.35	0.25	0.45	0.97	1.56
	0.20	0.20	0.33	0.43	0.29	0.28	0.52	0.94	1.46
30	0.34	0.41	0.73	0.70	0.59	0.38	0.72	1.73	2.91
	0.33	0.30	0.57	0.71	0.45	0.46	0.87	1.76	2.69
60	0.45	0.52	0.97	0.89	0.75	0.45	0.86	2.38	4.20
	0.45	0.33	0.74	0.91	0.56	0.56	1.09	2.49	3.94
120	0.49	0.54	1.02	0.92	0.77	0.46	0.87	3.55	4.76
	0.50	0.42	0.77	0.94	0.57	0.57	1.10	2.69	4.53
240	0.54	0.58	1.06	0.96	0.79	0.47	0.88	2.60	4.96
	0.54	0.45	0.80	0.97	0.58	0.58	1.12	2.74	4.74
420	0.58	0.62	1.11	0.99	0.80	0.47	0.89	2.63	5.05
	0.59	0.48	0.83	0.99	0.59	0.59	1.14	2.79	4.83
600	0.62	0.64	1.13	1.01	0.82	0.48	0.89	2.65	5.08
	0.62	0.50	0.86	1.01	0.60	0.61	1.15	2.81	4.87

Table E.1

Flotation of pure quartz in absence of collector at different pH values. Cumulative recovery,(%), with increasing flotation time.

pH / time(sec)	4	5	6	7	8	9	10	11	12
15	35	39	54	63	51	41	64	106	113
	34	31	47	55	44	44	69	102	113
30	57	64	100	102	87	66	107	192	214
	58	50	82	96	73	75	119	195	210
60	79	82	140	136	117	78	134	292	328
	82	67	109	128	93	93	160	302	329
120	86	85	144	140	118	79	136	328	390
	90	68	111	130		94	162	344	403
240	93	91	150	141	119		137	342	424
	98	71	112	132			164	357	443
420	100	96	153	142	120			349	441
	108	74	113	133			166	373	468
600	106	97		143				351	448
	112	75		134			167		479

<u>Table E.2</u>

Flotation of pure quartz in absence of collector at different pH values. Cumulative mass of water, (gr), removed with increasing flotation time.

time(sec) \ pH	4	5	6	7	8	9	10	11	12
15	0.14	0.24	0.31	0.44	0.43	0.59	1.39	1.60	2.17
	0.15	0.26	0.38	0.42	0.42	0.59	1.10	1.74	1.94
30	0.22	0.40	0.51	0.80	0.81	1.13	2.58	3.68	4.42
	0.25	0.32	0.68	0.71	0.78	1.11	2.36	3.67	3.96
60	0.30	0.49	0.65	1.02	1.01	1.40	3.44	5.92	6.93
	0.34	0.41	0.85	0.89	0.99	1.36	3.44	5.70	6.43
120	0.34	0.51	0.69	1.06	1.03	1.43	3.53	6.39	7.98
	0.38	0.44	0.87	0.93	1.02	1.38	3.55	6.11	7.39
240	0.38	0.53	0.73	1.10	1.04	1.46	3.56	6.49	8.37
	0.41	0.46	0.89	0.97	1.05	1.40	3.58	6.22	7.73
420	0.41	0.55	0.76	1.14	1.06	1.48	3.60	6.55	8.50
	0.43	0.48	0.92	1.01	1.08	1.42	3.61	6.29	7.86
600	0.42		0.78	1.16	1.07	1.49	3.63	6.58	8.56
	0.45	0.49	0.93	1.04	1.10	1.44	3.63	6.33	7.91

Table E.3

Flotation of pure quartz using 71.7 g/t SIBX at different pH values. Cumulative recovery,(%), with increasing flotation time.

pH time(sec)	4	5	6	7	8	9	10	11	12
15	22	41	43	52	53	57	93	112	134
	25	40	51	53	48	58	76	122	128
30	35	68	72	100	100	114	173	250	272
	44	67	95	93	93	112	156	255	258
60	48	84	93	134	131	151	253	432	461
	61	83	125	121	125	148	252	433	452
120	52	86	96	137	132	153	264	507	578
	67	85	127	125	127	149	266	501	564
240	57	88	100	140		154	268	526	643
	72	87	129	128			269	521	622
420	58		101	142			272	535	667
	75		130	130			272	532	645
600			102				274	538	674
							273	535	652

Table E.4

Flotation of pure quartz using 71.7 g/t SIBX at different pH values. Cumulative mass of water,(gr), removed with increasing flotation time.

pH time(sec)	8	9	10	11	12
15	54	70	68	75	138
	59	67	82	68	130
30	96	115	114	127	251
	98	105	137	114	242
60	123	140	142	157	370
	122	126	172	140	346
120	126	141		160	414
	124	127	173	141	386
240	128			162	417
	127	128	174	142	390
420	130			164	420
	130	129	175		393
600					242
					394

Table E.5

Flotation of pure quartz using 71.7 g/t SIBX collector and NaOH for pH adjustment at different pH values. Cumulative mass of water, (gr), removed with increasing flotation time.

pH time(sec)	8	9	10	11	12
15	0.43	0.66	0.88	1.02	2.24
	0.47	0.63	1.05	0.89	2.15
30	0.72	1.05	1.44	1.66	4.09
	0.75	0.94	1.69	1.45	4.00
60	0.89	1.22	1.69	1.93	5.54
	0.90	1.08	1.99	1.68	5.21
120	0.92	1.24	1.72	1.96	5.66
	0.93	1.11	2.02	1.71	5.30
240	0.95	1.26	1.73	1.99	5.69
	0.96	1.14	2.04	1.73	5.34
420	0.99	1.28	1.74	2.02	5.73
	0.99	1.17	2.07	1.76	5.39
600	1.02	1.29	1.75	2.05	5.77
	1.03	1.20	2.10	1.79	5.42

Table E.6

Flotation of pure quartz using 71.7 g/t SIBX collector and NaOH for pH adjustment at different pH values. Cumulative recovery,(%), with increasing flotation time.

pH time(sec)	8	9	10	11	12
15	64	72	57	80	133
	72	58	65	60	99
30	106	114	90	127	234
	119	94	102	95	178
60	138	138	108	156	325
	155	119	125	116	246
120	139	139		158	341
	158	120			253
240	140				345
	161	121			254
420	142				349
	163				256
600	143				351
	164				257

Table E.7

Flotation of pure quartz in absence of collector at different pH values, using NaOH for pH adjustment. Cumulative mass of water, (gr), removed with increasing flotation time.

pH time(sec)	8	9	10	11	12
15	0.45	0.51	0.36	0.63	1.25
	0.54	0.37	0.45	0.38	0.85
30	0.71	0.78	0.54	0.94	2.16
	0.88	0.57	0.68	0.59	1.50
60	0.88	0.90	0.62	1.09	2.73
	1.08	0.69	0.80	0.68	1.92
120	0.89	0.91	0.63	1.10	2.81
	1.11	0.70	0.82	0.70	1.97
240	0.91	0.92	0.64	1.11	2.83
	1.14	0.71	0.84	0.71	2.00
420	0.93	0.93	0.65	1.11	2.85
	1.18	0.73	0.86	0.73	2.03
600	0.95	0.94	0.65	1.12	2.86
	1.21	0.73	0.88	0.75	2.06

Table E.8

Flotation of pure quartz in absence of collector, using NaOH for pH adjustment at different pH values. Cumulative recovery,(%), with increasing flotation time.

collector type / time(sec)	SEX	SNPX	SIBX	SNBX	PNBX	PAX
15	1.18	1.29	1.84	1.25	1.08	2.46
30	1.83	1.99	2.94	1.92	1.74	4.23
60	2.21	2.37	3.63	2.28	2.06	5.67
120	2.27	2.43	3.72	2.33	2.11	5.86
240	2.33	2.48	3.77	2.37	2.15	5.94
420	2.38	2.53	3.83	2.41	2.19	5.97
600	2.41	2.55	3.87	2.44	2.21	6.06

Table E.9

Flotation of pure quartz at pH=9 using different types of xanthate collectors. Cumulative recovery ,(%), with increasing flotation time.

collector type / time(sec)	SEX	SNPX	SIBX	SNBX	PNBX	PAX
15	110	113	140	108	101	158
30	181	184	233	174	169	280
60	235	238	316	225	215	416
120	245	246	329	232	222	446
240	254	252	338	238	227	458
420	263	258	346	244	233	469
600	267	261	351	247	236	473

Table E.10

Flotation of pure quartz at pH=9, using different types of xanthate collectors. Cumulative mass of water removed,(gr),with increasing flotation time.