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Chapter 2. Background

The flotation selectivity of galena and sphalerite at the Rosh Pinah Mine can be affected by the inadvertent activation of sphalerite in the lead flotation circuit. This chapter deals with the flotation of sulphide minerals with thiol collectors, mainly xanthate, and the activation of sphalerite by heavy metals such as copper and lead ions. An overview on the Rosh Pinah ore body is also given for better understanding of the composite sample used in this study.

2.1. The Rosh Pinah Zinc-Lead Mine

The Rosh Pinah ore bed consists of carbonaceous chert, carbonate-bearing rocks, argillite, quartzite and a massive sulphide (pyrite, sphalerite and galena). Barium-rich carbonate is an important constituent of the ore. The ore then mined was divided into different ore bodies namely the ore body A, which was composed of these ore-bearing rocks and had a central and upper zone of barium carbonates, followed downward by a main dolomite zone that terminated in a micro quartzite-rich zone (Watson and Botha, 1983). The ore body B on the other hand, was rich in argillite and microquartzite and poor in barium rock.

Galena and chalcopyrite have been traditionally floated first in the lead circuit after depression of sphalerite and pyrite with sodium cyanide (NaCN). This is followed by the activation of sphalerite with copper sulphate ($CuSO_4$) and its flotation in the zinc circuit, while pyrite is depressed at high pH with lime. The metallurgical performance and reagent suite of the plant during the earlier days of operation are given in Tables 2.1 and 2.2, respectively (Watson and Botha, 1983).

Currently, ore from the western and the eastern ore bodies are blended and ground in a ball mill at a feed rate of 90 tons per hour. As shown in Table 2.3, the mineralogy of the western and the eastern ore bodies is not very different from that of the ore bodies A and B. The feed composition includes 20-40 g/t of silver and the average iron content of the sphalerite (in solid solution) is in the range of 3-6% (Reyneke, 2000). The current metallurgical performance of the plant and the reagent suite are given in

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Tables 2.4 and 2.5. It is clear that the recovery of galena is low (70-75%) under the conditions used at the Rosh Pinah Mine.

Table 2.1. Plant results on ore from the A and B ore bodies (Watson and Botha, 1983)

	Ore from the ore body A				Ore from the ore body B			
	Analysis (%)		Distribution (%)		Analysis (%)		Distribution (%)	
Product	Zn	Pb	Zn	Pb	Zn	Pb	Zn	Pb
Feed	3.85 (1.35)†	1.08			6.80 (0.42)	1.89		
Pb Conc.	5.79	58.30	2.3	82.6	7.77	44.5	3.7	76.6
Zn Conc.	57.68	1.53	83.5	7.9	48.17	2.89	75.5	16.1
Tailings	0.59 (1.54)†	0.11	14.2	9.5	1.64	0.16	20.8	7.3

† Values in brackets are for non-sulphide Zn

Table 2.2. Plant reagent additions (Watson and Botha, 1983)

		Quantities of reagents in g/t (mill feed)					
Type of feed	Point of addition	NaCN	$ZnSO_4$	Collector	Frother	$CuSO_4$	Lime
Ore from the ore body A	Mill	128	315	12			
	Pb Conditioner				4		
	Zn Conditioner			24	4	292	104
Ore from the ore body B	Mill	118	400	30			
	Pb Conditioner				3		
	Pb Cleaners		245				
	Zn Conditioner			80	7	310	270
	Zn Scavengers			5			

Collector: Sodium isopropyl xanthate (SIPX)
Frother: Cyanamid Aerofroth 65 or 77

Table 2.3. Mineralogical composition of the western (WOF) and eastern (EOF) ore field samples (Reyneke, 2000)

Sample	Main	Minor	Accessory	Trace
WOF	Quartz, dolomite	Sphalerite	Pyrite, feldspar	Galena, chalcopyrite
EOF	Dolomite, sphalerite	-	Quartz, pyrite, galena	Chalcopyrite, feldspar

Dolomite: $CaMg(CO_3)_2$
Feldspar: $(K,Na,Ba)[(Al,Si)_4O_8]$

Table 2.4. Metallurgical performance of the Rosh Pinah plant from the WOF and EOF (Rosh Pinah, 2002)

	Analysis (%)		Distribution (%)	
Product	Zn	Pb	Zn	Pb
Feed	6-9	1-3		
Pb Conc.	5-7	55-60	2-3	70-75
Zn Conc.	52-55	1-2	80-85	

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Table 2.5. Rosh Pinah Mine reagent suite (November 2002)

		Quantities of reagents in g/t (mill feed)				
Type of feed	Point of addition	NaCN	SNPX	Frother	$CuSO_4$	$CaO.H_2O$
WOF & EOF	Mill	185	49			
	Pb Conditioner			6*		
	Zn Conditioner		73	9 #	215	473

* Senfroth 6005
\# Senfroth 1030

From the foregoing, it is important to understand the flotation of galena and sphalerite with xanthate if they have to be floated selectively from a complex sulphide ore.

2.2. Flotation of sulphide minerals with thiol collectors

The most widely used thiol collectors are the dithiocarbonates (technically known as xanthates) and the dithiophosphates, though the former are more extensively used than the latter for sulphide mineral flotation. Xanthates are usually available in solid form, totally soluble in water and are very good at recovering bulk sulphide minerals in an unselective manner. Increasing the carbon chain length of the non-polar group increases the recovery power of the xanthate while lowering the selectivity. Dithiophosphates are often used in combination with xanthates for the flotation of complex sulphide minerals.

It is generally accepted that the attachment of a xanthate collector to a sulphide mineral surface involves an electrochemical process and is controlled by the redox potential (Richardson and Walker, 1985; and Buckley and Woods, 1997). The anodic reaction may be in the form of chemisorption, formation of a metal xanthate, or the formation of dixanthogen depending on the specific collector and the mineral used:

$$X^- = X_{ads} + e \qquad [2.1]$$
$$MS + 2X^- = MX_2 + \text{“S”} + 2e \qquad [2.2]$$
$$2X^- = X_2 + 2e \qquad [2.3]$$

where MS, MX_2, X^-, X_{ads} and X_2 represent the sulphide mineral, the metal xanthate, the xanthate ion, the adsorbed xanthate and the dixanthogen, respectively. “S” represents elemental sulphur or polysulphide. The redox potential E for the oxidation of xanthate to dixanthogen is given by Nernst equation:

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$$E = E° - (0.059/2) \log ([X^-]^2 / [X_2]) \quad [2.4]$$

where $[X^-]$ and $[X_2]$ are the xanthate and dixanthogen concentration, respectively. Since dixanthogen is a pure liquid, its activity is unity (1) (Arbiter, 1985). E^o is the standard redox potential for the dixanthogen-xanthate couple. Some standard reduction potentials for dithiolates of varying chain lengths are given in Table 2.2.

Table 2.2. Standard reduction potentials for dithiolate/thiol couples of varying chain lengths (Crozier, 1991)

Xanthate	Potential (V SHE)
Methyl	-0.004
Ethyl	-0.060
Propyl	-0.091
Isopropyl	-0.096
Butyl	-0.127
Isobutyl	-0.127
Amyl	-0.159

The standard redox potential depends on the collector type or functional group and the number of carbon atoms in the hydrocarbon chain. Chander (1999) has reported that the higher the number of carbon atoms in the hydrocarbon chain, the lower the standard redox potential of the dithiolate/thiol couple.

The mechanisms for xanthate adsorption on sulphide minerals have been discussed in the literature (Woods et al., 1998; Buckley and Woods, 1995 and 1996; Stowe et al., 1995; Persson et al., 1991; Popov and Vucinic, 1990; Popov et al., 1989a,b; Vergara et al. 1988). It is accepted that an electrochemical process involving the formation of metal xanthate on the anode and the reduction of oxygen on the cathode occurs in almost all cases with the exception of pyrite. For pyrite, the anodic reaction is mainly the oxidation of xanthate to dixanthogen. However, Woods et al. (1997), Buckley and Woods (1997), and Kartio et al. (1999) are of the opinion that the first molecular layer of xanthate on galena is in the form of chemisorbed xanthate radicals, rather than lead xanthate molecules.

The cathodic reaction during the electrochemical adsorption of xanthate is mainly the reduction of oxygen, and it is known to consist of several partial processes. The first step is the reduction of oxygen to hydrogen peroxide and the second is the reduction

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of hydrogen peroxide to water. The formation of hydrogen peroxide depends on the catalytic properties of the mineral surface.

$$O_2 + 2H^+ + 2e = H_2O_2 \quad [2.5]$$
$$H_2O_2 + 2H^+ + 2e = 2H_2O \quad [2.6]$$

Ahlberg and Broo (1996b) have investigated the mechanism of oxygen reduction at galena and pyrite in the presence of xanthate. They found that the reduction of oxygen was inhibited in the presence of xanthate. On galena the reduction involved only two electrons and hydrogen peroxide could be detected at the ring-disc electrode in alkaline solution. However, the reduction of oxygen proceeded with four electrons on a pyrite surface. The authors concluded that the mineral (pyrite or galena) surface acted as an electrocatalyst for both the anodic and cathodic reactions. Since pyrite is more noble than galena, it was found to be a more effective catalyst for the reduction of oxygen (Ahlberg and Broo, 1996a,b,c). Equations (2.1-2.6) indicate that the following criteria should be met for the electrochemical interaction between collector and the sulphide mineral to be effective:

1. The mineral must be conducting or semi-conducting to permit the flow of electrons from the anodic site to the cathodic site;
2. Dissolved oxygen or another oxidiser must be present in solution to act as the electron accepting element.

Most xanthates form insoluble salts with heavy metal ions. The solubility product determines the conditions for precipitation of the xanthate salt. Precipitation is possible when the product of ionic activities in solution exceeds the solubility product. Table 2.6 gives the solubility products of some metal sulphides, xanthates, and hydroxides. Table 2.6 shows that zinc ethyl xanthate is more soluble than lead and copper ethyl xanthate. This implies that when copper, lead and zinc minerals are present in one system, the flotation of copper and lead minerals with xanthate will be more favourable than that of zinc mineral. Moreover, it is believed that the adsorption of xanthate on the surface of sulphide mineral is governed by the relative stabilities of metal xanthates and metal hydroxides complexes, i.e. there is competition between xanthate and hydroxyl complexes (Reddy and Reddy, 1988). Thus, the adsorption of

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xanthate on the surface of the sulphide mineral is due to the higher stability of the metal xanthate when compared to its respective metal hydroxide. It may be important to note that the complexation mechanism does not require the electrochemical mechanism and can operate in solution.

Table 2.6. Solubility products of some metal sulphides, xanthates, and hydroxides at 25°C (Kakovskii, 1957)

Metal sulphide	Salt	Solubility product (pKs)
FeS		18.60
ZnS		25.59
PbS		27.46
CuS		36.00
	Zinc ethyl xanthate	8.31
	Zinc amyl xanthate	11.80
	Lead ethyl xanthate	16.77
	Lead amyl xanthate	24.00
	Copper(II) ethyl xanthate	19.28
	Zinc hydroxide	16.79
	Lead hydroxide	16.09
	Copper(II) hydroxide	14.70

Most fundamental work on the flotation of sulphide minerals has been carried out using natural, synthetic or high grade single minerals. It is known that the flotation of sulphide minerals with xanthate depends strongly on the pH of the pulp as shown by Figures 2.1-2.3.

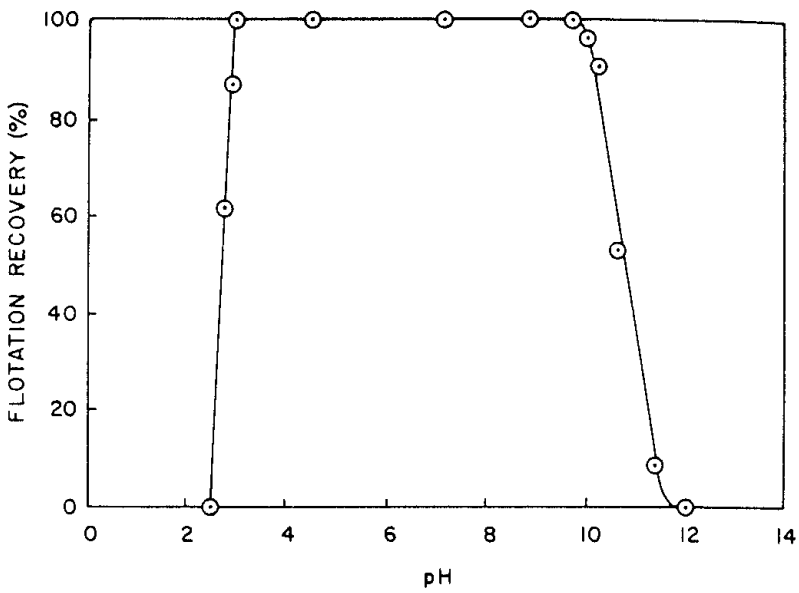

Figure 2.1. Flotation of galena as a function of pH in the presence of 10^{-4}M ethyl-xanthate (Fuerstenau, M.C., 1982).

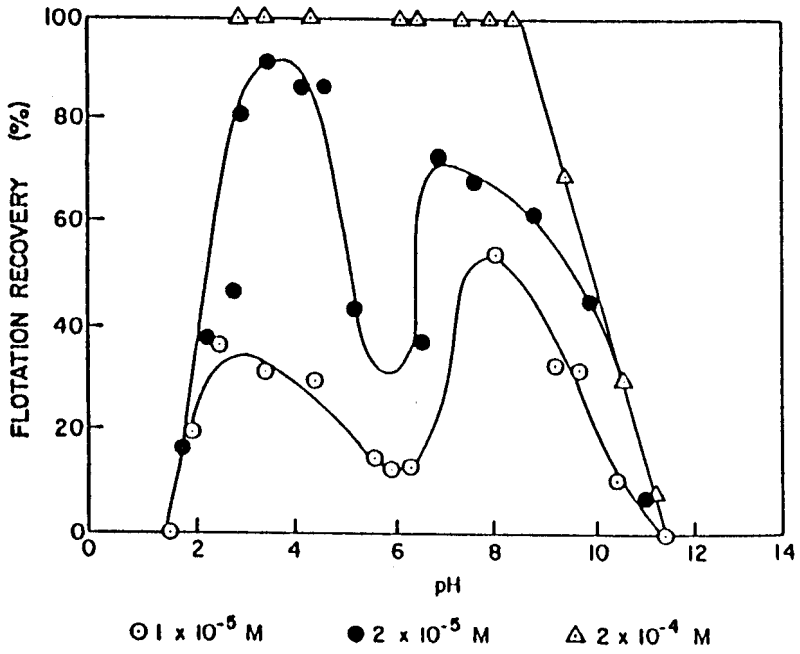

Figure 2.2. Flotation recovery of pyrite as a function of pH with various dosages of potassium ethyl xanthate (Fuerstenau et al., 1968).

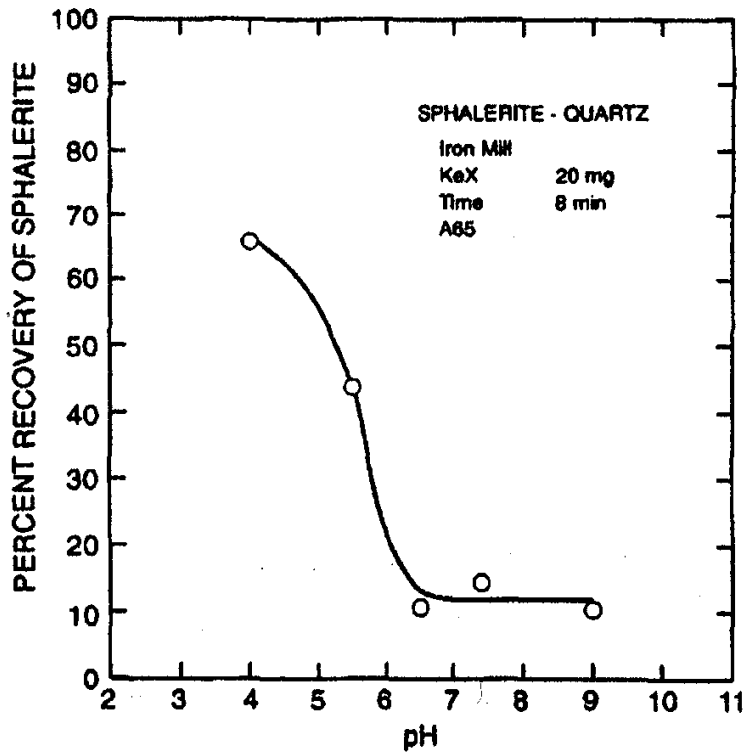

Figure 2.3. Flotation of sphalerite as a function of pH with $1.3x10^{-4}$M ethyl-xanthate (Trahar et al.,1997).

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Figure 2.1 shows that galena can float easily in the pH range of 3-10. However, sphalerite does not float above pH 5 (Figure 2.3), though there is some recovery which is due to the entrainment of the mineral in the froth phase. For these flotation tests, the single minerals are usually ground in a ceramic mortar where there is no presence of metallic iron from the grinding media. However, in plant practice, complex sulphide minerals from the ore are generally milled in a rubber-lined steel mill with mild steel balls or rods where interactions between minerals and grinding media occur. Therefore, their floatability is always affected by the interactions between different minerals and between minerals and grinding media.

2.2.1. Flotation of complex sulphide minerals

In the case of complex sulphide ore such as the Rosh Pinah ore, where galena and chalcopyrite are floated in the lead circuit, it is customary to decrease the presence of pyrite and sphalerite in the lead concentrate when flotation is carried out in mildly alkaline medium (pH 8-9). In practice, this is not always straightforward because complex ores usually behave differently from single minerals. This is due, amongst other things, to the interactions between different minerals from the same ore, between minerals and griding media, and the electrochemical conditions present in the system. A number of studies have reported that galvanic interactions between grinding media and different minerals, as well as between different minerals can affect the flotation selectivity of sulphide minerals depending on the electrochemical conditions in the mill (Mielczarski and Mielszarski, 2003; Peng et al., 2003a and b; Peng et al., 2002; Yuan et al., 1996; Natarajan, 1996; Cheng and Iwasaki, 1992; Guy and Trahar, 1985; Natarajan and Iwasaki, 1984).

Grinding in steel rod and ball mills is a common practice in minerals beneficiation. It is generally accepted that the electrochemical interactions between the grinding media and the minerals in a grinding mill influence the corrosive wear of balls/rods and the surface properties of the ground minerals (Natarajan and Iwasaki, 1984). Usually, the sulphide minerals behave like cathodes and the steel grinding media like anodes, which release iron ions into the pulp (Figure 2.4). The release of iron from the steel grinding media can have a detrimental effect on the recovery of a single mineral such as galena (Figure 2.5).

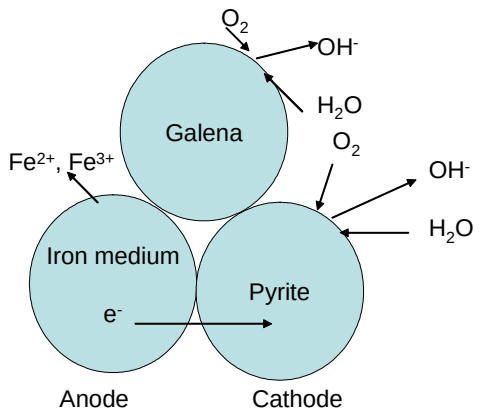

Figure 2.4. Schematic presentation of galvanic interactions occurring between minerals and grinding media during grinding (Peng et al., 2003a).

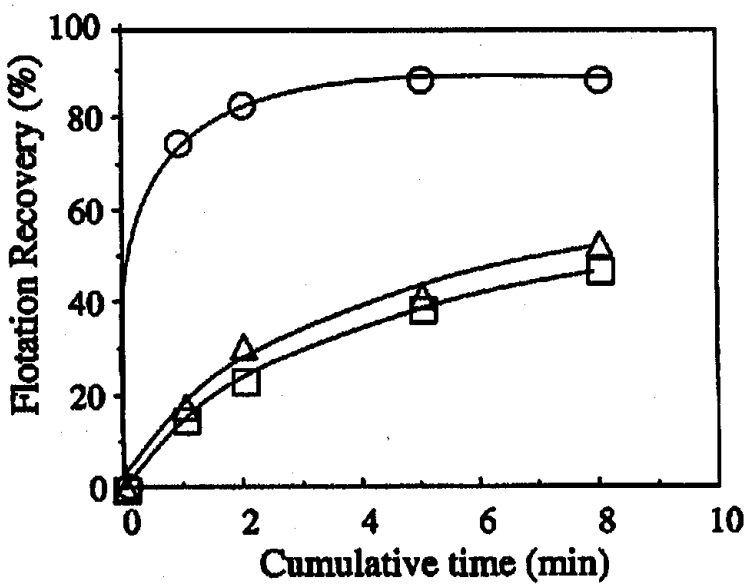

Figure 2.5. Flotation recovery versus time for ethyl xanthate coated galena particles (25 to 38 μm) at pH 4: in the absence of iron oxide slimes (O), and with iron oxide slimes added before (Δ) and after ( ) ethyl xanthate. (Bandini et al., 2001).

Peng et al. (2003a) have also shown that galena exhibited different flotation behaviour in single and mixed mineral experiments. Their results indicated that gas purging in the mill had a large influence on galena flotation in single mineral experiments, especially with mild steel grinding medium, but had little effect after galena was mixed with pyrite. In addition, pyrite also exhibited different flotation behaviour after being mixed with galena (Figure 2.6). The strong effect of gas purging and the type of grinding media on the flotation recovery of galena and pyrite can also be seen in Figure 2.6. In addition, the recovery of pyrite as a function of chalcopyrite is shown in Figure 2.7.

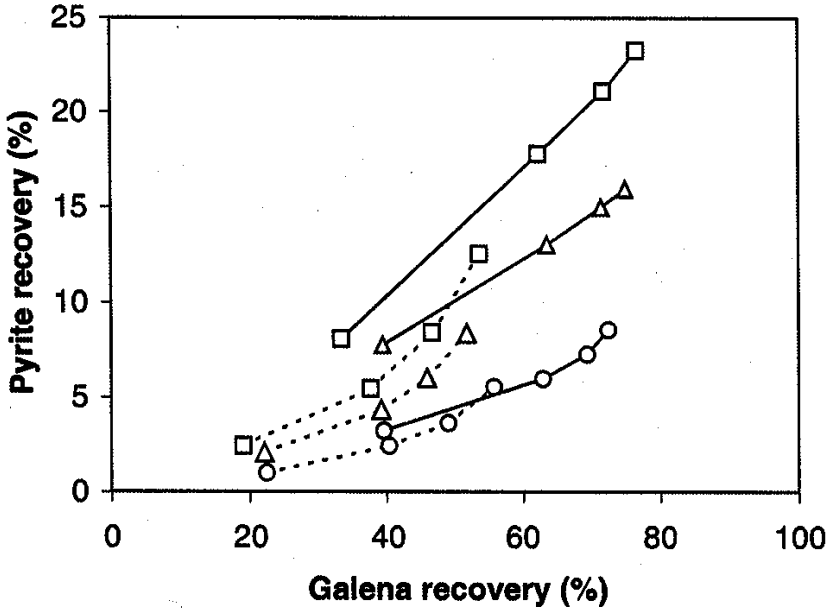

Figure 2.6. Effect of grinding media and gas purging on the separation of galena from pyrite: (dashed lines) mild steel; (solid lines) 30 wt.% chromium medium; ( ) nitrogen purging; (Δ) air purging; (O) oxygen purging. (Peng et al., 2003a).

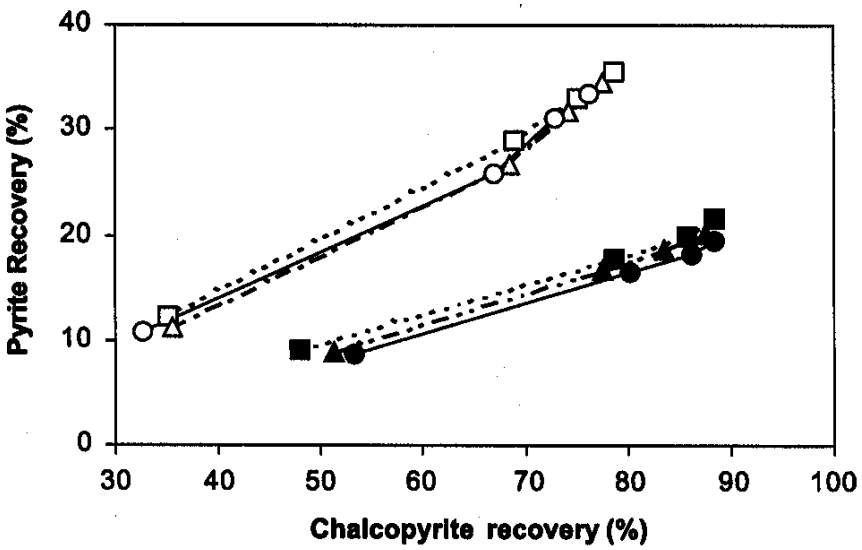

Figure 2.7. Effect of grinding media and gas purging on the separation of chalcopyrite from pyrite: (empty symbols) mild steel medium; (solid symbols) 30 wt.% chromium medium; ( ) nitrogen purging; (Δ) air purging; (O) oxygen purging (Peng et al., 2003b).

Figure 2.7 showed that 30% (w/w) chromium grinding medium produced higher chalcopyrite recovery than mild steel medium and gas purging had little effect on chalcopyrite flotation. Furthermore, mild steel grinding medium produced higher pyrite recovery than with the chromium grinding medium; gas purging during grinding had no or little influence on pyrite flotation. Thus, higher chalcopyrite

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selectivity against pyrite was produced by the chromium medium than by mild steel medium (Peng et al., 2003b).

The control of grinding conditions is a challenge in the mineral processing industry, and many attempts have been made to quantify the effect of the milling environment on pulp potential. The pulp potential has been used in many cases as an indication of the electrochemical environment and as a way of controlling the oxidation/reduction of the minerals present in the pulp. When pyrite is present in the complex ore, it is believed that it will increase the oxidation of other minerals because it is more noble than most of sulphide minerals. The value of pulp potential will usually change when there is an oxygen scavenger element such as metallic iron in the pulp.

The electrochemical conditions during minerals beneficiation have been related to the pulp potential using noble electrodes or pure sulphide electrodes (Buswell et al., 2002; Cullinan et al., 1999; Leppinen et al., 1998; Grano et al., 1990). Although there is still a debate on the relationship between the bulk solution potential and the mineral potential (Nicol and Lázaro, 2002), there seems to be agreement that in sulphide mineral flotation the potential of a platinum electrode in a flotation pulp is relatively close to the mixed potential experienced by the oxidising mineral (Ralston, 1991; Trahar, 1984; Rand and Woods, 1984). Measurements of pulp potential hence provide a useful tool for studying changes that occur at the mineral surface upon addition of electrochemically active reagents to the mineral suspensions and/or after galvanic interaction between different minerals of a complex ore, or between the grinding media and the mineral (Herrera-Urbina et al., 1999; Yuan et al., 1996; Hintikka and Leppinen, 1995; Wang and Xie, 1990; Grano et al., 1990). By controlling the pulp potential in the flotation system, it should in principle be possible to selectively float complex minerals, because of various electrochemical reactions that may occur at different potentials.

During the beneficiation of complex sulphide minerals containing sphalerite (such as the Rosh Pinah ore), the flotation of the sphalerite can be improved by the presence of surface modifier agents such as activators. The presence of metal hydroxide from the oxidation of minerals from a complex ore is one reason why flotation results on single minerals are not always consistent with that of the same mineral in ores. In the

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laboratory the effect of hydroxides is often eliminated or reduced by the use of ethylenediamine tetra acetic acid (EDTA) (Peng et al., 2003; Greet and Smart, 2002), which dissolves them from the surface of minerals to be recovered. A partial solution to the effect of hydroxide contamination is carefully controlling the grinding conditions during the beneficiation of complex ores at the plant.

The presence of metal hydroxide products from the oxidation of minerals remains a problem in many flotation plants because they usually activate some minerals at the wrong point in the flotation circuit. A classic example of this behaviour is the activation and subsequent flotation of sphalerite in a complex copper-zinc and/or copper-lead-zinc ore in the lead flotation circuit. Most of copper-lead-zinc plants suffer from the unwanted activation of sphalerite, by mainly $Cu(OH)_2$, in the copper-lead flotation circuit. An overview on the activation of sphalerite by copper and lead will hence be presented in the following sections.

2.3. Activation of zinc sulphide minerals

Activators are generally used in the flotation of zinc sulphide minerals because these minerals do not respond well to flotation with short chain thiol collectors. Activators alter the chemical nature of the mineral surfaces so that they become more floatable after their interactions with collector. The activators are generally soluble salts, which ionise in solution and then react with the mineral surface. Heavy metal ions such as Cu^{2+}, Pb^{2+}, Ag^{2+} and Cd^{2+} are known to activate zinc sulphide minerals and promote their flotation with xanthate (Popov et al., 1989a,b; Ralston and Healy, 1980 a,b).

When sphalerite is activated with Cu(II) ions, adsorbed Cu(II) ions are reduced to Cu(I) with oxidation of adjacent sulphide (S^{2-} from sphalerite) to polysulphides (Gerson et al., 1999; Pattrick et al., 1999). Popov and Vucinic (1990) have also shown that Cu(I)-ethyl xanthate was the dominant surface species when sphalerite is activated by Cu(II) under flotation-related conditions. When sphalerite is activated with Pb(II) ions, it is believed that lead species adsorb on the mineral surface. The presence of colloidal lead-xanthate has been observed on the surface of lead-activated sphalerite following the addition of xanthate in solution.

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The aqueous and surface chemistry of activation of sulphide minerals has been extensively discussed in the literature (Gerson et al., 1999; Pattrick et al., 1999; Prestidge et al., 1997; Laskowski et al., 1997; Kim et al., 1996; Wang et al., 1989a,b; M.C. Fuestenau, 1982; Finkelstein and Allison, 1976; and Gaudin, 1957). The electrochemistry of sphalerite activation has been investigated by Richardson et al. (1994) and Chen and Yoon (2000). Different instrumental techniques such as X-ray photoelectron spectroscopy (XPS), Auger scanning microscopy (ASM), Atomic force microscopy (AFM), Secondary ion mass spectrometry (SIMS) and X-ray absorption fine structure (XAFS) have been used for the identification of activation species. In the flotation system such as the one at Rosh Pinah concentrator, selective flotation of the lead-zinc ore can be affected by the activation and subsequent flotation of sphalerite in the lead circuit.

2.3.1. Activation of sphalerite by copper ions

Copper sulphate is the most common activator used for sphalerite flotation with xanthate. There is a general agreement that the mechanism of copper activation of sphalerite depends on the pH of the solution (Prestige et al., 1997; D.W. Fuerstenau, 1982; Girczys et al., 1972), due to the variation of the predominant copper species at acidic and alkaline pH values. Figure 2.8 shows the copper species that can be formed at different pH values (Huang, 2003). It can be seen that Cu^{2+} and $Cu(OH)_2$ are the most predominant species at acidic and alkaline pH values, respectively. In addition, Figure 2.8 shows that the onset of $Cu(OH)_2$ precipitation is at pH 5.6 for a total copper concentration of 10^{-4}M. The initial stage of sphalerite activation at acidic pH is known to be controlled by a chemical reaction in which Cu^{2+} ions replace Zn^{2+} ions in the sphalerite lattice as shown by the following reaction (Wang et al., 1989a; Pugh and Tjus, 1987; Finkelstein and Allison, 1976; Fuestenau and Metzger, 1960):

$$ZnS_{(s)} + Cu^{2+} = CuS_{(s)} + Zn^{2+} \qquad [2.7]$$

$$\text{with } K = [Zn^{2+}]/[Cu^{2+}] = 6 \times 10^{10} \qquad [2.8]$$

Under alkaline conditions, the initial stage of sphalerite activation will be the surface precipitation of copper hydroxide as shown by the reaction below:

$$ZnS_{(s)} + Cu(OH)_2 = ZnSCu(OH)_{2(s)} \qquad [2.9]$$

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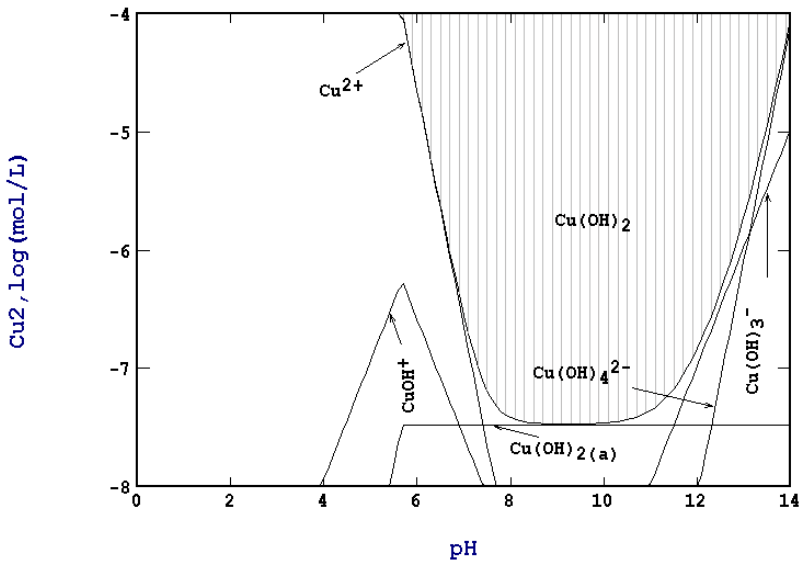

Figure 2.8. Species distribution diagrams for Cu(II) as function of pH at 25°C. Total copper concentration of 10^{-4}M. Stabcal software, NBS database (Huang, 2003). Shaded area shows the solid species.

Equation 2.8 shows that under equilibrium conditions very low concentrations of Cu(II) ions, i.e. ~ 10^{-10}M Cu(II) for 1M of Zn(II), will be able to activate sphalerite. However, such low copper concentrations are not usually enough to activate sphalerite efficiently at alkaline pH values. The most probable mechanism of activation of sphalerite by Cu(II) in alkaline medium is the three step model as described below (Prestidge et al., 1997; Wang et al., 1989b):

- Surface precipitation of the activator metal hydroxide onto the sulphide mineral surface (Equation 2.9);
- Cu-Zn replacement into the lattice of the sulphide mineral due to the thermodynamic instability of the $Cu(OH)_2$;

$$(ZnS)_n \cdot xCu(OH)_2 = Zn_{n-x}Cu_xS_n \cdot xZn(OH)_2 \qquad [2.10]$$

- The desorption of the $Zn(OH)_2$ from the surface of sphalerite to the solution (Equation 2.11) would then be important to expose the copper sulphide formed on the surface of sphalerite to the collector;

$$Zn_{n-x}Cu_xS_n \cdot xZn(OH)_2 = Zn_{n-x}Cu_xS_n + xZn(OH)_2 \qquad [2.11]$$

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Gerson et al. (1999) and Pattrick et al. (1999) have shown that the displacemtn of Zn by Cu in the sphalerite lattice is followed by the reduction of Cu(II) to Cu(I) with the oxidation of sulphide to higher oxidation states. In addition, they have observed that the replacement of Zn by Cu in the sphalerite occur differently on the surface and in the bulk.

It is clear from Equations 2.10 and 2.11 that the interaction between the activated sphalerite and the thiol collector and hence the flotation of sphalerite will be strongly controlled by the rates of these two reactions. However, it is practically difficult to differentiate which one of these two would be the rate determining step of sphalerite activation. More details on this problem are given in the section 2.4 where the kinetics of activation is presented.

There is a general agreement that the copper (II) species that substitutes zinc in the sphalerite lattice is generally reduced to Cu(I) species. Figure 2.9 shows photoelectron signals characteristic of copper and sulphide found on the sphalerite surface after activation with Cu(II) at pH 9 (Prestidge et al., 1997). It can be clearly seen that Cu(I) (Cu *2p* peaks at 932.5 and 952.0 eV) is the most predominant species at the surface of sphalerite after activation with Cu(II) ions. However, the concentration of Cu(II) on the surface of sphalerite seems to increase with the increasing amount of the initial copper (spectra b and c). Prestidge et al. (1997) showed that the Cu $2p_{3/2}$ signal position at approximately 935.0 eV compared with the characteristic energy for $Cu(OH)_2$ (934.4 eV). The presence of shake-up satellites on the Cu *2p* spectra in Figure 2.9 shows that the conversion of $Cu(OH)_2$ species into Cu(I) on the surface of activated sphalerite is usually not completed when the initial copper concentration is high. In practice, few monolayers are enough for the successful activation and subsequent flotation of sphalerite with thiol collectors. Overdosing of the copper sulphate can result into poor activation and flotation of sphalerite due to the presence of the hydrophilic copper hydroxide species on its surface.

The debate on the identity of the activation product (chalcocite, covellite or both) has continued for more than two decades, because both Cu(I) and Cu(II) are frequently found on the mineral surface after activation by copper(II) ions (Prestidge et al., 1997; Kartio et al., 1998; Buckley et al., 1989). Reddy and Reddy (1988) have suggested

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that the formula of covellite be corrected as $Cu^{I}_{4}Cu^{II}_{2}(S_2)_2S_2$ though many authors represent it simply as CuS. However, no evidence of covellite has been shown based on either the structural or composition (e.g. Cu/S ratios) data despite several literature reports referring to the “covellite-like" species.

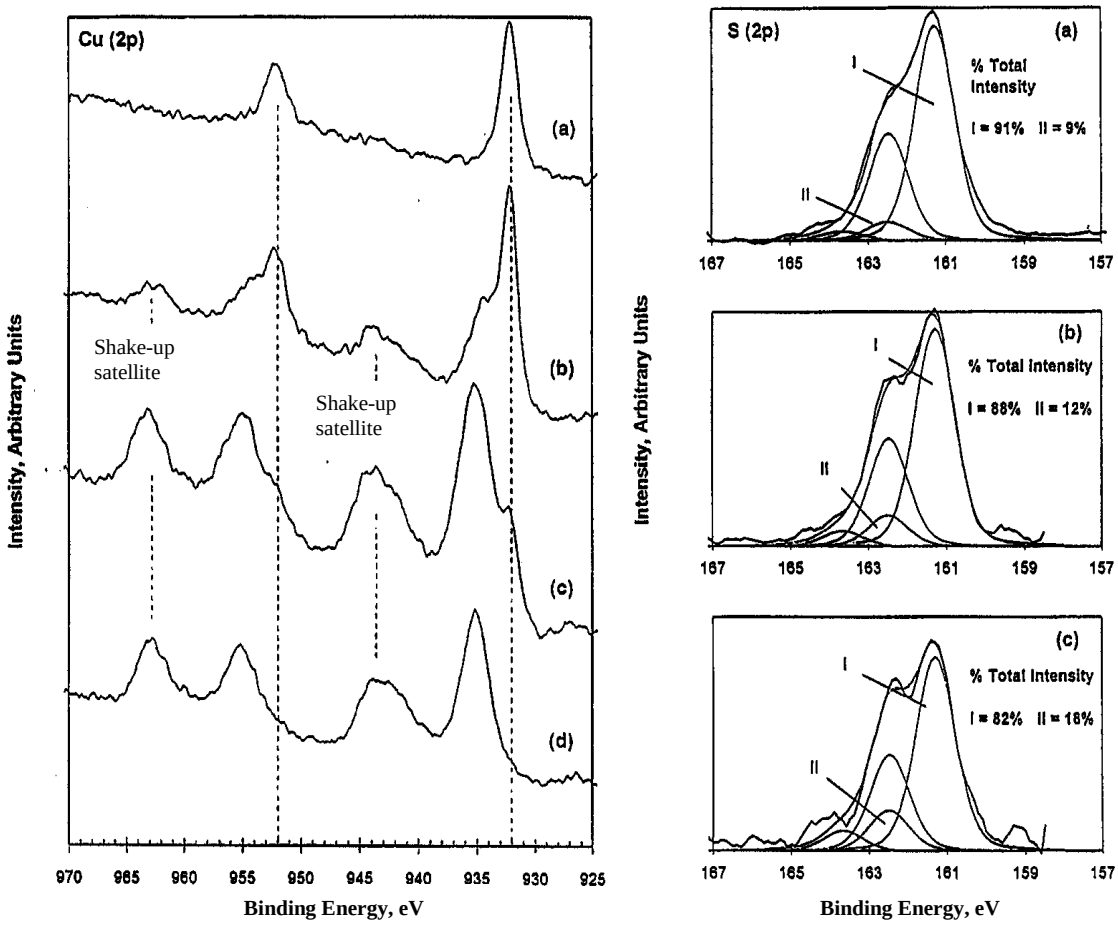

Figure 2.9. Cu 2p and S 2p X-ray photoelectron signals of zinc sulphide activated by copper(II) at pH 9 to a surface coverage of: (a) 1 equivalent monolayer (sample A), (b) 10 equivalent monolayers (sample B), (c) 100 equivalent monolayers (sample C) and (d) copper(II) hydroxide. (Prestige et al., 1997).

Since the intentional activation and subsequent flotation of sphalerite from complex sulphide minerals generally occurs at alkaline pH, Finkelstein (1997) agreed that the copper would initially attach to the surface of sphalerite in the form of cupric hydroxide. However the most crucial question is whether it is with these species that the xanthate collectors react. Numerous authors (Ralston and Healy, 1980b; Wang et al., 1989b) are of the opinion that the hydroxide products need to be converted to their sulphide form to promote the flotation of sphalerite with thiol collectors after activation by Cu(II) ions at alkaline pH values.

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In plant practice, sphalerite would be accompanied with gangue minerals such as quartz. Jain and Fuerstenau (1985) showed that the surface precipitation of $Cu(OH)_2$ occurs identically on both sphalerite and quartz (Figure 2.10).

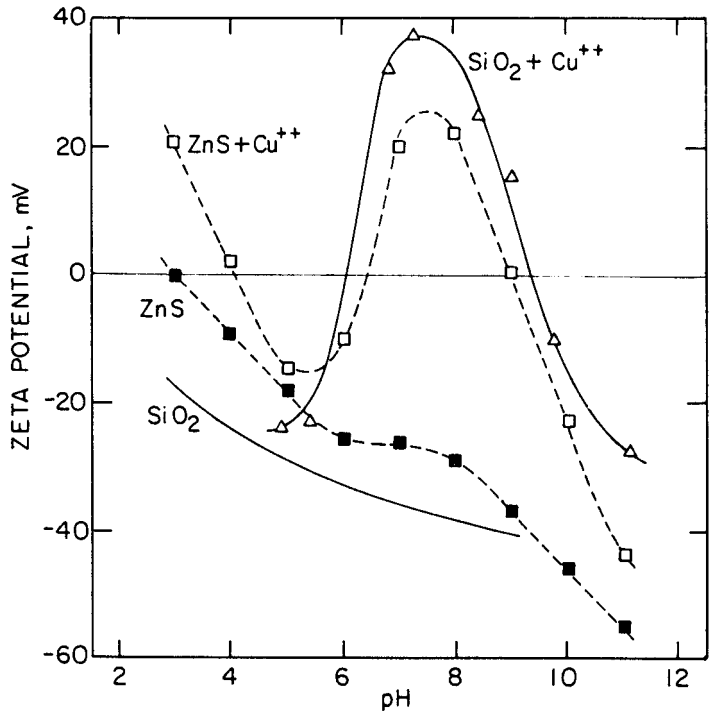

Figure 2.10. Electrokinetic behavior of SiO_2 and sphalerite in the absence and presence of 10^{-4} M Cu^{++} (Jain and Fuerstenau, 1985).

However, it is believed that the copper hydroxide coating on the gangue mineral will eventually be transferred to the sulphide surface because of the conversion that takes place on the surface of sphalerite. In practice, such transfer of the copper hydroxide species can be promoted by the hydrodynamic conditions.

At the Rosh Pinah Mine, the intentional activation process and subsequent flotation of sphalerite is carried out in an alkaline solution. It is also believed that the inadvertent activation of sphalerite in the lead circuit occurs at neutral and mildly alkaline pH values by a surface precipitation of the metal hydroxide $Cu(OH)_2$.

2.3.2 Activation by lead ions

The Pb(II) activation and subsequent flotation of sphalerite with xanthate have been studied by Rashchi et al. (2002), El-shall et al. (2000), Trahar et al. (1997), Houot and

Ravenau (1992), Popov et al. (1989a,b) and Ralston and Healy (1980a,b). The source of lead ions in the flotation of complex sulphide ores may be the dissolution of minerals present, added reagents, and the water used in the system (Popov et al., 1989a). Trahar et al. (1997) have shown that the recovery of sphalerite (from a mixture of sphalerite and quartz) increases with increasing lead concentration (Figure 2.11), and that the recovery of lead activated sphalerite is similar to that of galena (Figure 2.12).

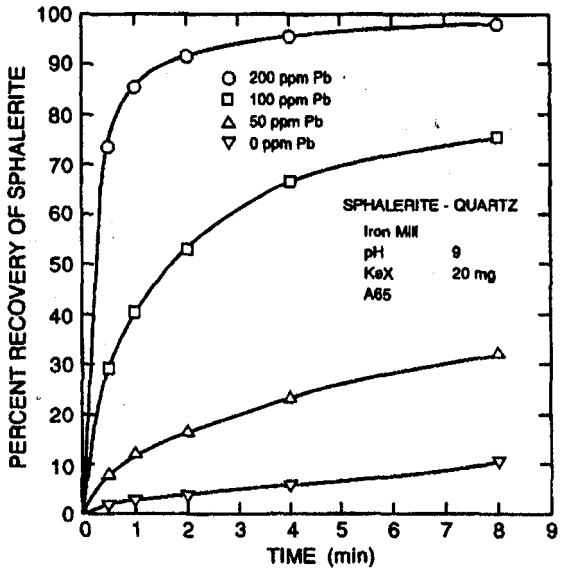

Figure 2.11. Influence of increasing additons of xanthate and lead on the floatability of sphalerite with xanthate at pH 9 (Trahar et al., 1997). A65: frother.

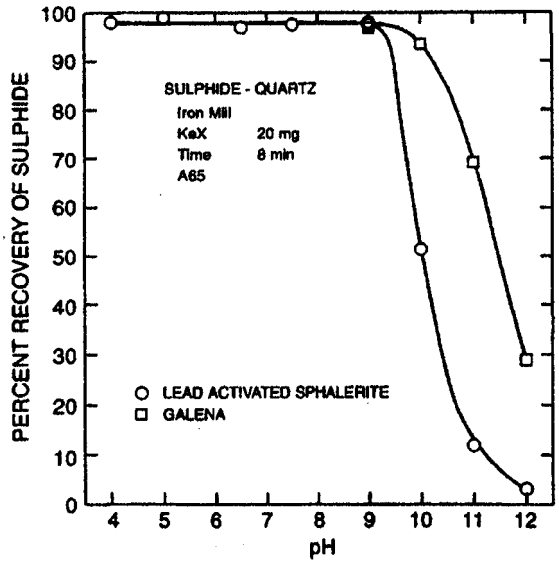

Figure 2.12. Comparison of the pH dependencies of the flotation responses of lead activated sphalerite and galena (Trahar et al., 1997). A65: frother.

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Generally, at least two mechanisms by which sphalerite can be activated by lead are proposed in the literature:

1. In moderately acidic solution, where the activating entity is the Pb(II) cation, sphalerite activation is due to the replacement of Zn^{2+} ions by Pb^{2+} ions according to Equation 2.12. The replacement of Zn^{2+} by Pb^{2+} is believed to occur until the activity of Zn^{2+} is 10^3 that of Pb^{2+} in solution

$$ZnS_{(s)} + Pb^{2+} = PbS_{(s)} + Zn^{2+} \quad [2.12]$$
$$\text{with } K = [Zn^{2+}]/[Pb^{2+}] = 10^3 \quad [2.13]$$

2. In mildly alkaline conditions, the activation is controlled by the precipitation of lead hydroxide as shown by Equation 14.

$$ZnS_{(s)} + Pb(OH)_2 = PbS_{(s)} + Zn(OH)_2 \quad [2.14]$$

Figure 2.13 shows the lead species distribution as a function of pH and lead concentration (Huang, 2003).

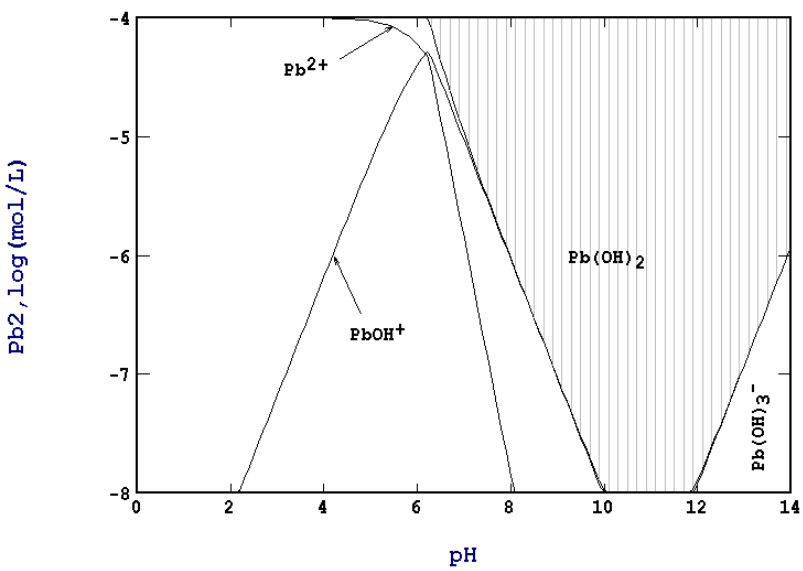

Figure 2.13. Solubility distribution diagram for Pb(II) as a function of pH at 25 °C. Total lead concentration of 10^{-4}M. Stabcal software, NBS database (Huang, 2003). Shaded area shows the solid species.

It can be seen that Pb(II) is the predominant species at acidic pH. The onset of lead hydroxide precipitation is at pH 6.2 for a total concentration of 10^{-4}M Pb(II).

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Although the displacement of Zn by Pb has been supported by many authors, this mechanism is still debatable based on the larger ionic radius of Pb as compared to that of Zn. Pattrick et al. (1998) have shown that the diffusion of Pb through the sphalerite lattice is difficult. They have proposed that $Pb(OH)^+$ would adsorb easily onto the surface of sphalerite despite the stability of Pb^{2+} at acidic pH values. Ralston and Healy (1980b) have shown that the activation of sphalerite by Pb(II) is enhanced at near neutral to alkaline pH values when compared to acid pH values. They have assumed a rapid bulk precipitation of $Pb(OH)_2$ and/or rapid surface nucleated $Pb(OH)_2$ precipitation, followed by a surface reaction between metal hydroxide and the zinc sulphide as shown by Equation 2.14. This mechanism is in agreement with the reported results of Popov et al. (1989a) on the electrokinetic behaviour of sphalerite in the presence of $5x10^{-4}$M $Pb(NO_3)_2$. However, Trahar et al. (1997) have shown that the adsorbed $Pb(OH)_2$ do not necessarily convert to PbS to promote the flotation of lead activated sphalerite in the presence of xanthate. They believe that the interaction between xanthate and adsorbed lead hydroxide occurs at the surface of sphalerite followed by the formation of lead-xanthate species.

Laskowski et al (1997) have shown that long activation times are needed to reverse the zeta potential of sphalerite from the negative values typical at neutral pH values when activated with lead (longer than with copper). Therefore, the kinetics of activation is an important parameter during the flotation of activated sphalerite.

2.4. Kinetics of the activation of sphalerite

It is generally agreed that the activation of sphalerite by heavy metal ions is a two stage process, which includes a rapid uptake of the activating species followed by a slow diffusion stage (Wang et al., 1989a; Jain and Fuerstenau, 1985). To elucidate this mechanism, Pugh and Tjus (1987) and Laskowski et al. (1997), have studied the electrokinetics of sphalerite activation by copper. They have shown that the activation kinetics in acidic solution is fast and that longer conditioning times are not needed for efficient flotation. This is partly due to the presence of Cu(II) ions in solution at acidic pH values. Figure 2.14 shows the effect of the initial copper concentration, agitation and solid-liquid ratio on the amount of copper abstracted by sphalerite at pH 3.2 (Jain

and Fuerstenau, 1985). Their study was focused on the activation of sphalerite for short conditioning time (less than 1000 seconds).

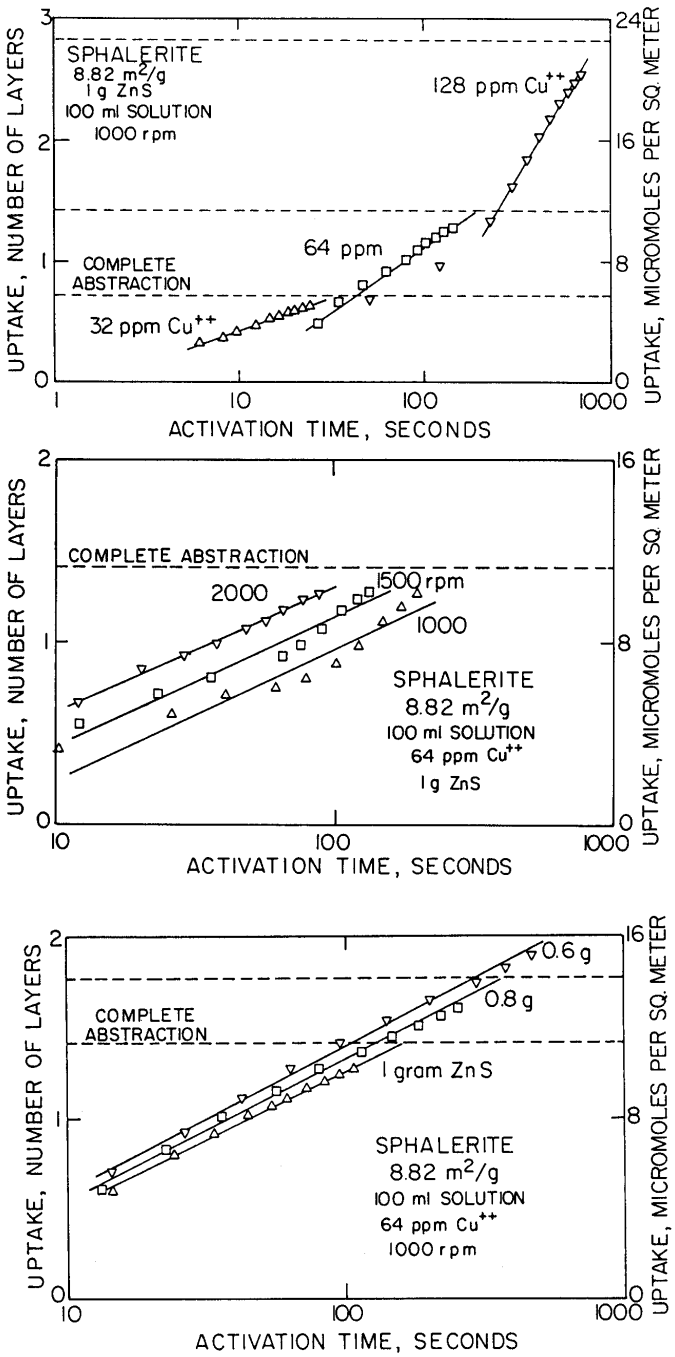

Figure 2.14. Effect of initial copper concentration (a), agitation (b), and solid-to-liquid ratio (c) on the amount of copper abstracted by sphalerite for short conditioning times at pH 3.2 (Jain and Fuerstenau, 1985).

It was observed that the time for the complete abstraction of copper ions by the sphalerite decreased with increasing agitation and amount of sphalerite present in the

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system. The time for complete abstraction of copper increased with increasing initial copper in the solution for constant amounts of sphalerite and agitation.

The kinetics of activation of sphalerite is slower in alkaline media because of the presence of $Cu(OH)_2$ that precipitates on the surface of the sphalerite. The slow diffusion of copper ions into the sphalerite lattice compared to the fast precipitation of $Cu(OH)_2$ on the surface of sphalerite is believed to be the main reason for the slow kinetics of activation at alkaline pH values.

When compared to the activation with copper ions, it has been shown that the uptake of Pb^{2+} is three times slower than that of copper although the abstraction of lead from solution also takes place in two stages as in the case of copper (Reddy and Reddy, 1988).

Laskowski et al. (1997) have also observed that the flotation rate of lead activated sphalerite was lower than that of copper activated sphalerite because of the high stability of the lead hydroxide coating. This agrees with the results of Popov et al. (1989b) who have shown that lead activated sphalerite requires a longer activation time in alkaline media.

2.5. Conclusion

The flotation of galena and sphalerite with xanthate collectors probably occurs via an electrochemical reaction. Metal xanthates such as lead xanthate and zinc xanthate are usually found on the surface of single minerals of galena and sphalerite, which have been in contact with xanthate collectors. However, dixanthogen is the collector species that is responsible for the flotation of pyrite and pyrrhotite with xanthate.

There is strong evidence that after addition of xanthate, the initial product on the surface of sulphide minerals is the chemisorbed xanthate, followed by the oxidation to dixanthogen and/or the formation of metal xanthate.

However, the flotation of complex sulphide minerals is different from that of single minerals. In most cases, flotation of valuable minerals from a complex ore does not

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necessarily follow the behaviour of the single mineral. Several interactions may be responsible for this. These include galvanic interactions and activation by dissolved ions.

It has been shown that sphalerite can be activated by heavy metals such as copper and lead, which originate from the oxidation of a complex sulphide ore and from dissolved species present in the process water. There is agreement that the activation of sphalerite at alkaline pH occurs through the precipitation of copper or lead hydroxide on the surface of sphalerite. Copper and lead activated sphalerite has a better affinity for xanthate than unactivated sphalerite. The activated sphalerite will then float together with galena and the selectivity against sphalerite will be reduced. Proper control of inadvertent activation of sphalerite is required to avoid the presence of significant amounts of zinc in the lead concentrate during the selective flotation of galena from a complex sulphide ore. One way to reverse inadvertent activation is with cyanide; this is discussed in the next chapter.