OPTIMISATION OF THE SELECTIVE FLOTATION OF GALENA AND SPHALERITE AT ROSH PINAH MINE

By

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This thesis is dedicated to my lovely wife Blandine

and

to my dearest daughter Rachel

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Makunga Daudet Seke

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Summary

OPTIMISATION OF THE SELECTIVE FLOTATION OF GALENA AND SPHALERITE AT ROSH PINAH MINE

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Degree: Philosophiae Doctor (Metallurgical Engineering)

A study was carried out to improve the flotation selectivity between galena and sphalerite during the flotation of a Cu-Pb-Zn sulphide composite ore from the Rosh Pinah Mine (Namibia). Xanthate collectors were found to be unselective for the flotation of the Rosh Pinah composite sample. It was observed that the recovery of sphalerite increased with both the recovery of galena and the concentrate mass pull. In addition, the recovery of sphalerite increased after activation with Cu(II) ions while that of galena decreased when the composite was dry ground in a mild steel mill with mild steel grinding media. However, the recovery of galena was not affected after wet milling in a stainless steel mill. The recovery of Cu(II)-activated sphalerite was independent of the milling environment (wet or dry) and grinding media.

The activation of sphalerite by cuprous cyanide complexes, which are present in the recycled water, was clearly shown in this study. Both batch flotation tests and XPS analysis have confirmed that sphalerite was activated by copper(I) from the cuprous cyanide complexes. The recovery of copper(I)-activated sphalerite increased further when the composite was dry milled as compared to wet milling.

Batch flotation tests have shown that the use of cyanide alone is not efficient for the depression of sphalerite due to the mineralogical texture of the Rosh Pinah ore. A large quantity of galena locked and/or attached to sphalerite was observed in the lead concentrate. Their prevalence increased with increasing particle size. The use of both cyanide and zinc sulphate improved the depression of sphalerite much better than cyanide alone. A flowsheet has been proposed to improve selectivity between galena and sphalerite in the lead flotation circuit. It includes the regrinding of the lead rougher concentrate prior to the cleaning stage due to poor liberation between galena and sphalerite.

Keywords: Froth flotation, Sulphide ores, Flotation activators, Flotation depressants, Grinding, Mineralogy

Overview

This thesis focuses on the flotation selectivity between sphalerite and galena during the selective flotation of the Cu-Pb-Zn sulphide ore from the Rosh Pinah Mine (Namibia). The objectives of this study are outlined in Chapter 1. The main objective is to optimize the reagent suite in the lead flotation circuit, thus improving the flotation selectivity between galena and sphalerite. The optimization of the reagent suite is based on the mechanism of sphalerite activation by dissolved heavy metal ions.

Chapter 2 deals with an overview on the flotation of sulphide minerals with thiol collectors and the activation of sphalerite by heavy metal ions such as copper and lead. The different mechanisms of activation of sphalerite by copper and lead ions are discussed. The mineralogy of the Rosh Pinah ore is also presented in order to understand the parameters that may be involved during the selective flotation of the ore.

Since dissolved copper and lead ions are usually present in the process water used at the plant, the effect of water quality on the flotation response of the Rosh Pinah ore is discussed in Chapter 3. The effect of cuprous cyanide on the activation of sphalerite is also discussed. Based on the chemistry of cuprous cyanide complexes, it is assumed that these cyano complexes can promote the activation of sphalerite in the absence of free cyanide.

The experimental procedures are outlined in Chapter 4. The milling procedure and flotation conditions are presented in this chapter. Surface analysis equipment and methods used are also discussed.

The scoping results on the effect of collector dosage and Cu(II) and Pb(II) ions on the flotation recoveries of galena and sphalerite are discussed in Chapter 5. The flotation results indicate that high dosages of xanthate collector of long chain length such as PNBX are detrimental to the flotation selectivity between galena and sphalerite. As expected, Cu(II) is a much stronger activator for sphalerite than Pb(II) ions. It is also observed that the activation of sphalerite by Pb(II) is affected by the type of milling and thus by the pulp potential. However, the activation of sphalerite by Cu(II) and its subsequent flotation is not affected by the type of milling.

Chapter 6 focuses on the effect of dry and wet milling on the pulp chemistry and flotation response of the Rosh Pinah ore. In addition, the effect of cuprous ions on the flotation of sphalerite and galena is also studied. The measurements of the pulp chemistry show that higher dissolved oxygen and more positive pulp potential are observed when the ore is ground in a dry environment. More negative pulp potential and low dissolved oxygen are observed after wet milling of the ore. It is interesting to observe that both the recovery and grade of sphalerite are higher when the ore is ground in a dry environment compared to the flotation results achieved after wet milling. Since the recovery of galena is enhanced after wet milling while the recovery of sphalerite is lower, it is clear that the pulp chemistry achieved under wet milling conditions is suitable for better selectivity between galena and sphalerite in the lead circuit.

The grade and recovery of pyrite in the lead concentrate are higher after wet milling when compared to dry milling. Thus, it becomes clear that after wet milling the grade of zinc and lead are diluted by the presence of pyrite in the lead concentrate.

The effect of cuprous-cyanide complexes on the activation of sphalerite is also studied in Chapter 6. These cyanide complexes are usually found in the recycled water used at the plant, where cyanide is added to depress sphalerite in the lead flotation circuit. Batch Flotation and XPS results show that copper cyanide complexes present in the recycled water do activate sphalerite, especially when the pulp potential is more positive. This results in more sphalerite being recovered in the lead flotation circuit.

Surface analysis of natural sphalerite samples is investigated by X-ray photoelectron spectroscopy (XPS). XPS results show the presence of copper species on the surface of the activated sphalerite. In addition, the copper species can be removed from the surface of sphalerite by treatment with sodium cyanide.

In Chapter 7, the flotation selectivity between galena and sphalerite is studied in the presence of inorganic depressants such as sodium cyanide and zinc sulphate. The results show that sphalerite can be depressed efficiently with the use of both cyanide and zinc sulphate. However, better selectivity can be achieved with the use of 100g/t NaCN in the lead rougher circuit. Mineralogical analysis of the concentrate and tailings samples is carried out for the understanding of the deportment of sphalerite in the lead concentrate. It is shown that the presence of middlings contributes to the deportment of sphalerite in the galena concentrate due to the intergrowth and association of galena and sphalerite in the concentrate.

Chapter 8 presents the conclusions and recommendations based on the results presented in this study and those reported by investigators from Kumba Resources.

Contents

Chapter 1. Introduction

The Rosh Pinah zinc-lead sulphide deposit occurs in the Southwestern part of Namibia, close to the Orange River. Underground operations and housing projects started in 1967 and the mine came into production in 1969 (Van Vuuren, 1982). The Rosh Pinah Mine treats a composite of copper-lead-zinc sulphide ores from various sites. Pyrite is the main sulphide gangue mineral in the Rosh Pinah composite sample. Traces of chalcopyrite, gold and silver are found in the ore sample (Figure 1.1).

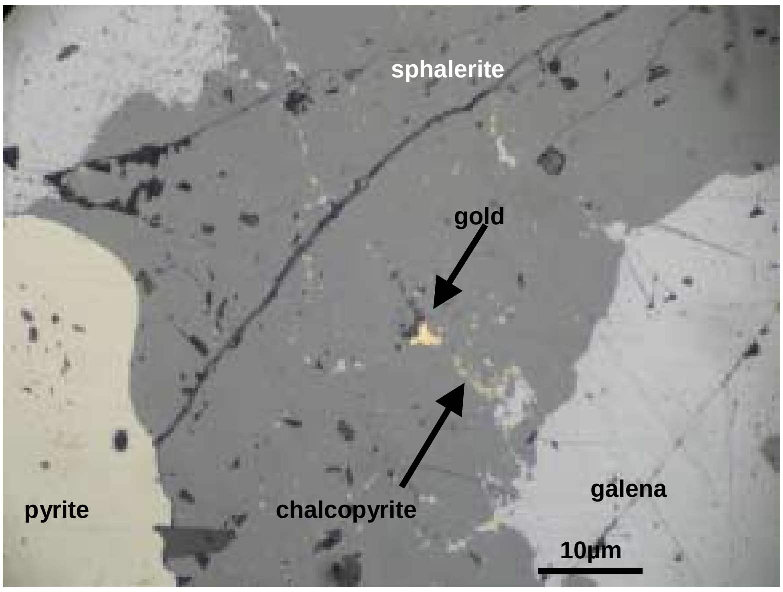


Figure 1.1. Photomicrograph showing sulphide minerals and gold in the Rosh Pinah ore sample.

The Rosh Pinah composite sample is processed by selective flotation, in which galena is floated first with sodium propyl xanthate (SNPX) as collector, while sphalerite and pyrite are depressed with cyanide. The sphalerite is floated further with xanthate in the zinc flotation circuit after activation with copper sulphate. Selectivity against sphalerite poses a difficult challenge in the lead flotation circuit at the Rosh Pinah Mine, where cyanide dosages as high as 150-180 g/t are being used to suppress the flotation of sphalerite and pyrite at the concentrator.

Although cyanide is an effective depressant in selective flotation of sulphide minerals, considerable amounts of zinc are still recovered together with lead, reflecting poor selectivity during the flotation of galena at Rosh Pinah. High dosages of cyanide are required to overcome this situation. Apart from the significant contribution to the loss of precious metals such as silver and gold by forming soluble metal complexes, the excessive use of cyanide is a cause for concern on environmental grounds. Furthermore, this necessitates the use of more copper sulphate to activate sphalerite for its subsequent flotation in the zinc circuit.

Analysis of the process water used at the Rosh Pinah Mine has shown that considerable amounts of copper, lead, iron, and calcium are regularly present in the recycled process water (Table 1.1). Thus, activation of pyrite and sphalerite can occur during the flotation of galena due to the presence of the dissolved copper and lead ions (Fuerstenau and Metzger, 1960; Trahar et al., 1997; and El-Shall et al., 2000). Houot and Raveneau (1992) have also shown that sphalerite can be activated by lead ions derived from galena and oxidised lead minerals.

Table 1.1. Survey of the process water used at the Rosh Pinah Mine (After Du Preez, 2000). Assays in mg/L

SLIMES (%)	28
pH	8.4
Eh (mV)	-90
Temperature (°C)	38-60
Oxygen in solution	0.1-0.3
Lead in solution	10-30
Copper in solution	10-80
Calcium in solution	600
Total dissolved solids	1000-3000

Rao and Finch (1989) have shown that an increase in the use of recycled water in flotation circuits often has a negative effect on flotation selectivity. This can be due to the combination of factors such as residual xanthate and dixanthogen, which adsorb unselectively on most sulphide minerals, metallic ions such as $Cu^{2+}$and Pb^{2+} that cause inadvertent activation, and alkaline earth metals which may activate the non-sulphide gangue.

It is usually difficult to quantify the exact amounts of dissolved heavy metal such as copper and lead present in the water system at alkaline pH value because these metals form hydroxides which do precipitate. Thus, it is also difficult to assess the activation of sphalerite from the complex Rosh Pinah ore by only assaying the dissolved lead and copper present in the process water. Since the plant uses recycled water from different flotation streams, it is believed that the quality of water might have an influence on the flotation response of the ore.

In flotation practice, the optimization of reagent at various stages can be very difficult to carry out when the processes involved are not well understood. Moreover, the Rosh Pinah Mine is located in an arid region necessitating the optimal use of the available water resources. Thus, the objectives of this study were to:

1. understand the mechanisms involved during the selective flotation of galena and sphalerite at Rosh Pinah Mine;
2. optimize the reagent suite for galena recovery based on the fundamentals which describe the activation of sphalerite by heavy metal ions;
3. study the influence of the recycled process water on the flotation selectivity of galena and sphalerite in the lead flotation circuit;
4. reduce the cyanide consumption for the depression of sphalerite during the flotation of galena by using cyanide in conjunction with another depressant such as zinc sulphate;
5. Study the deportment of sphalerite in the lead concentrate and the mineralogical texture of the flotation products.

The scope of this study was limited to optimizing the flotation selectivity between sphalerite and galena in the lead flotation circuit, because it is necessary to understand the phenomena that contribute to the presence of zinc in the galena concentrate at Rosh Pinah Mine. There was no attempt to produce generic data on the flotation of single sulphide minerals. However, flotation data from the literature were used during the interpretation of results.

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

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	

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:

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

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

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

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 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.

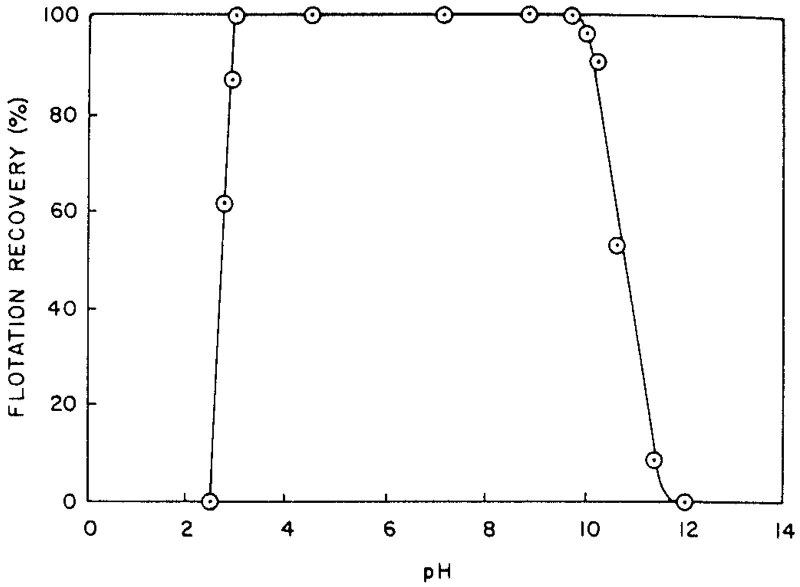


Figure 2.1. Flotation of galena as a function of pH in the presence of 10^{-4}M ethyl-xanthate (Fuerstenau, M.C., 1982).

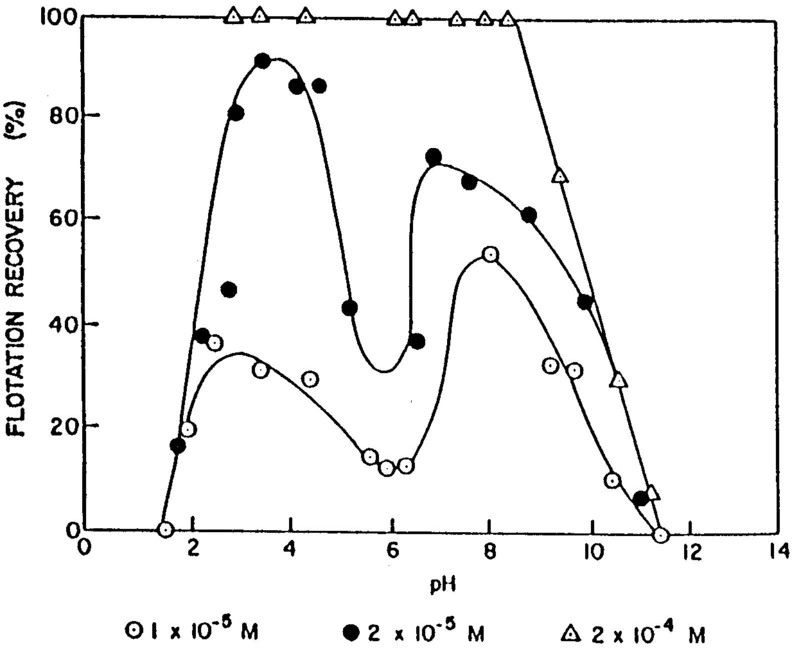


Figure 2.2. Flotation recovery of pyrite as a function of pH with various dosages of potassium ethyl xanthate (Fuerstenau et al., 1968).

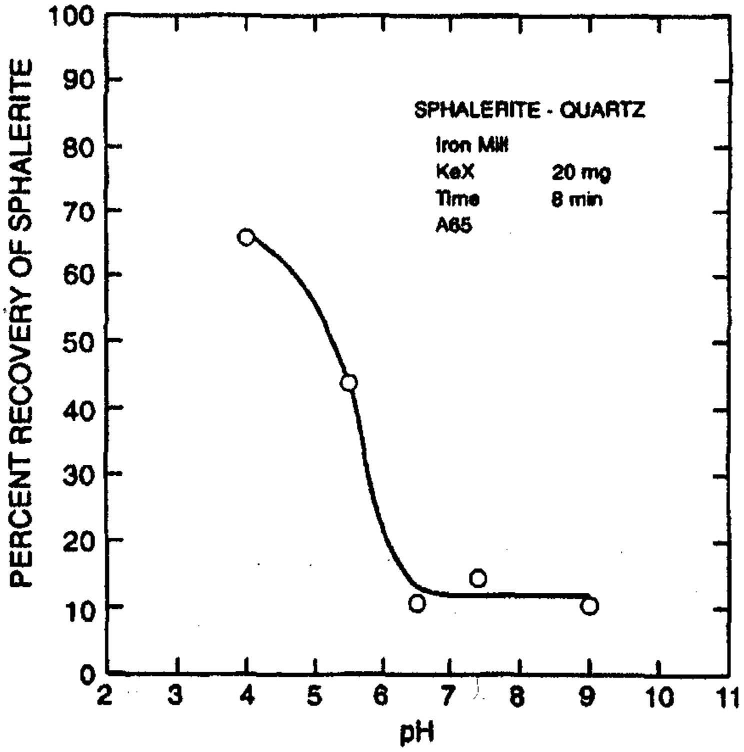


Figure 2.3. Flotation of sphalerite as a function of pH with 1.3x10^{-4}M ethyl-xanthate (Trahar et al.,1997).

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).

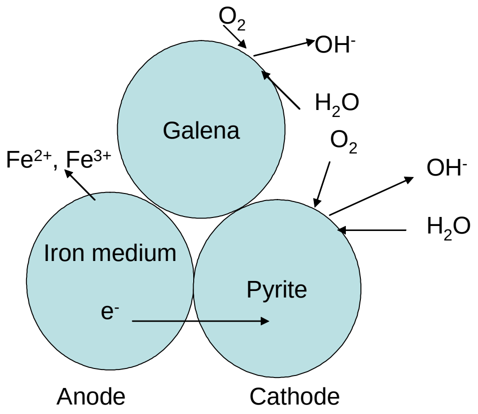


Figure 2.4. Schematic presentation of galvanic interactions occurring between minerals and grinding media during grinding (Peng et al., 2003a).

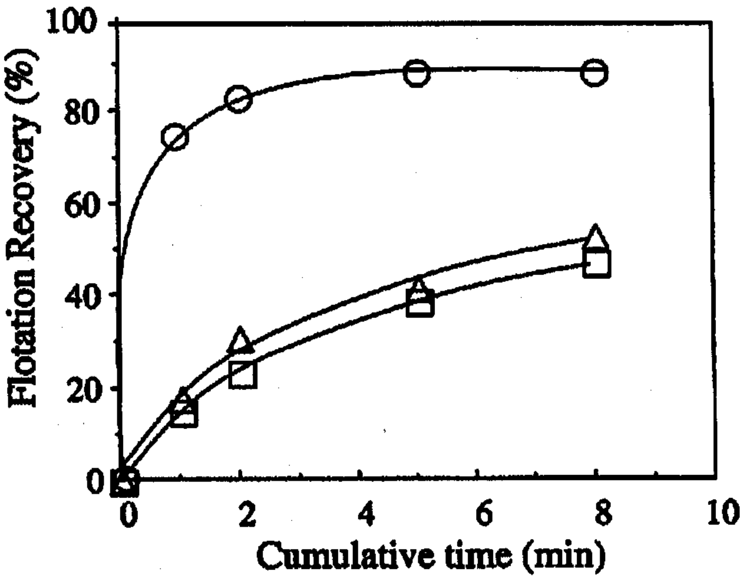


*Figure 2.5. Flotation recovery versus time for ethyl xanthate coated galena particles (25 to 38 μm) at pH 4: in the absence of iron oxide slimes (*O*), and with iron oxide slimes added before (*Δ *) and after ( ) ethyl xanthate. (Bandini et al., 2001).*

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.

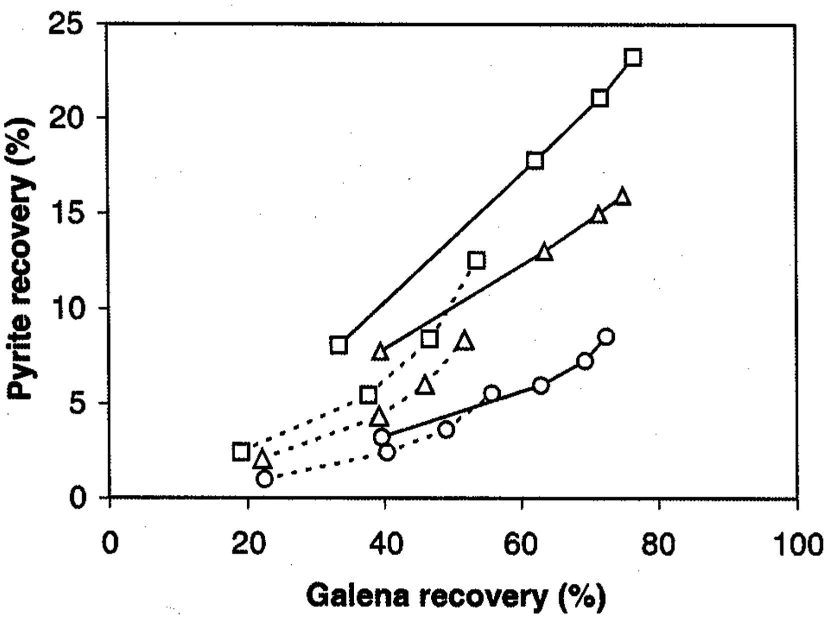


Figure 2.6. Effect of grinding media and gas purging on the separation of galena from pyrite: (dashed lines) mild steel; (solid lines) 30 wt.% chromium medium; ( ) nitrogen purging; (Δ) air purging; (O) oxygen purging. (Peng et al., 2003a).

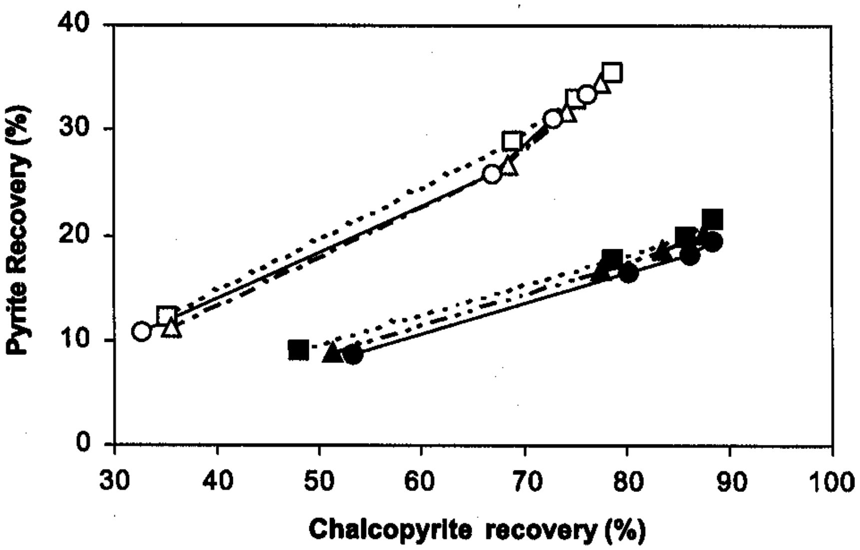


Figure 2.7. Effect of grinding media and gas purging on the separation of chalcopyrite from pyrite: (empty symbols) mild steel medium; (solid symbols) 30 wt.% chromium medium; ( ) nitrogen purging; (Δ) air purging; (O) oxygen purging (Peng et al., 2003b).

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 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 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.

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:

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

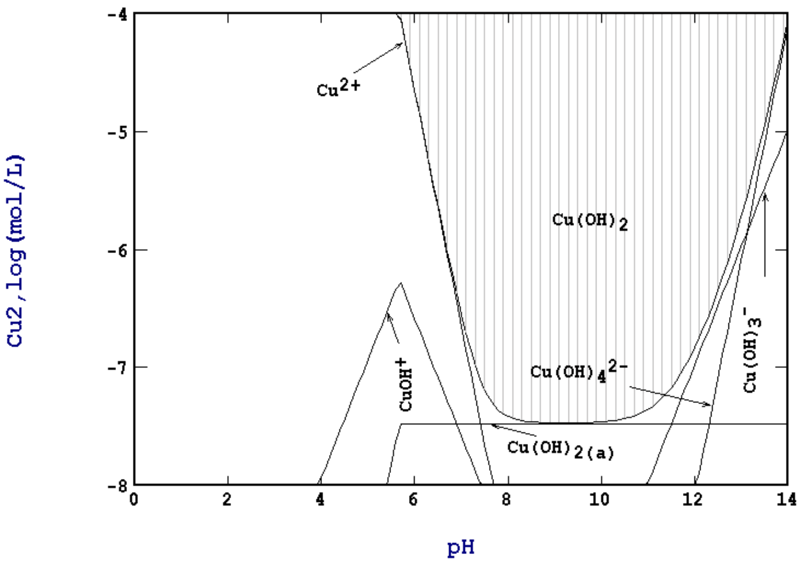


Figure 2.8. Species distribution diagrams for Cu(II) as function of pH at 25°C. Total copper concentration of 10^{-4}M. Stabcal software, NBS database (Huang, 2003). Shaded area shows the solid species.

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;

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

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 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.

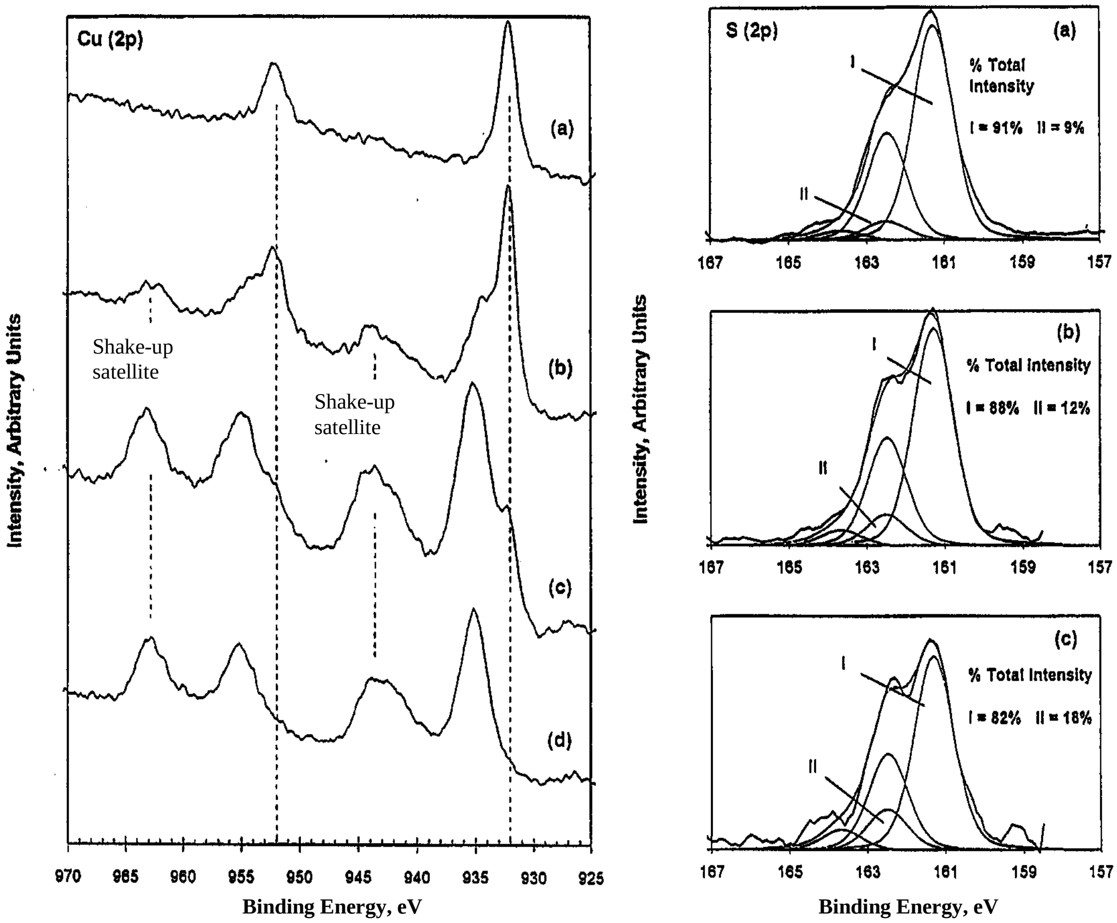


Figure 2.9. Cu 2p and S 2p X-ray photoelectron signals of zinc sulphide activated by copper(II) at pH 9 to a surface coverage of: (a) 1 equivalent monolayer (sample A), (b) 10 equivalent monolayers (sample B), (c) 100 equivalent monolayers (sample C) and (d) copper(II) hydroxide. (Prestige et al., 1997).

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.

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).

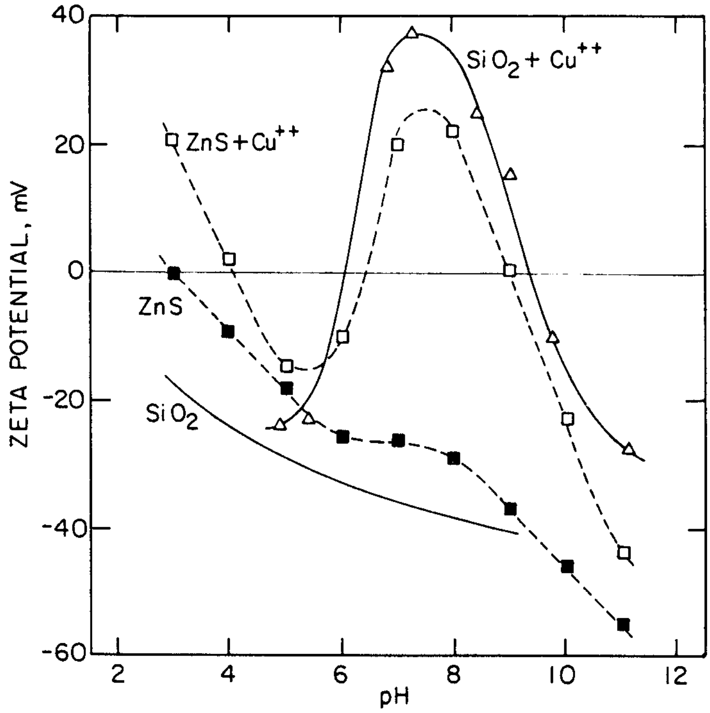


Figure 2.10. Electrokinetic behavior of SiO_2 *and sphalerite in the absence and presence of* 10^{-4} *M* Cu^{++}*(Jain and Fuerstenau, 1985).*

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).

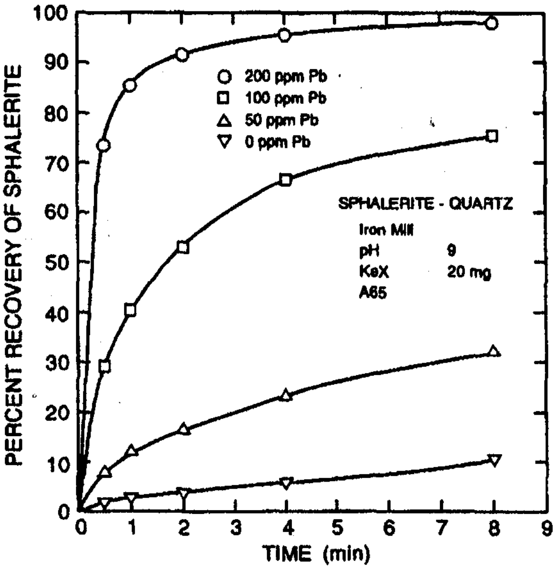


Figure 2.11. Influence of increasing additons of xanthate and lead on the floatability of sphalerite with xanthate at pH 9 (Trahar et al., 1997). A65: frother.

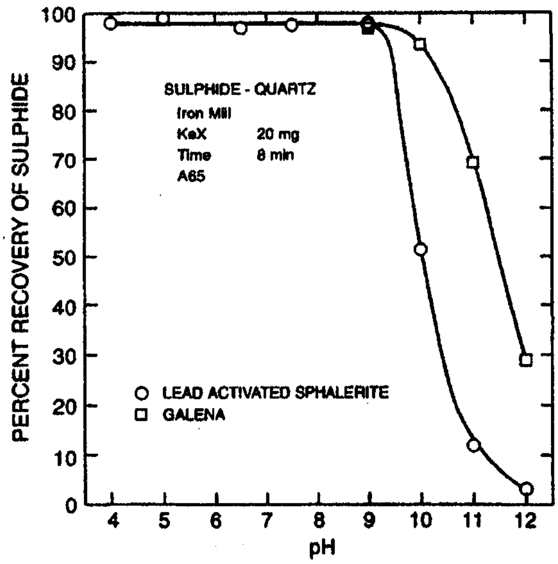


Figure 2.12. Comparison of the pH dependencies of the flotation responses of lead activated sphalerite and galena (Trahar et al., 1997). A65: frother.

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).

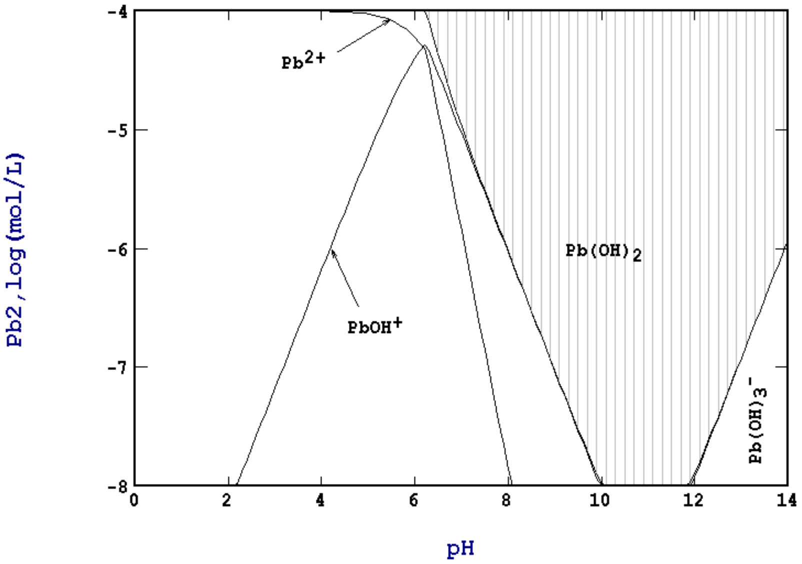


Figure 2.13. Solubility distribution diagram for Pb(II) as a function of pH at 25 °C. Total lead concentration of 10^{-4}M. Stabcal software, NBS database (Huang, 2003). Shaded area shows the solid species.

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).

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).

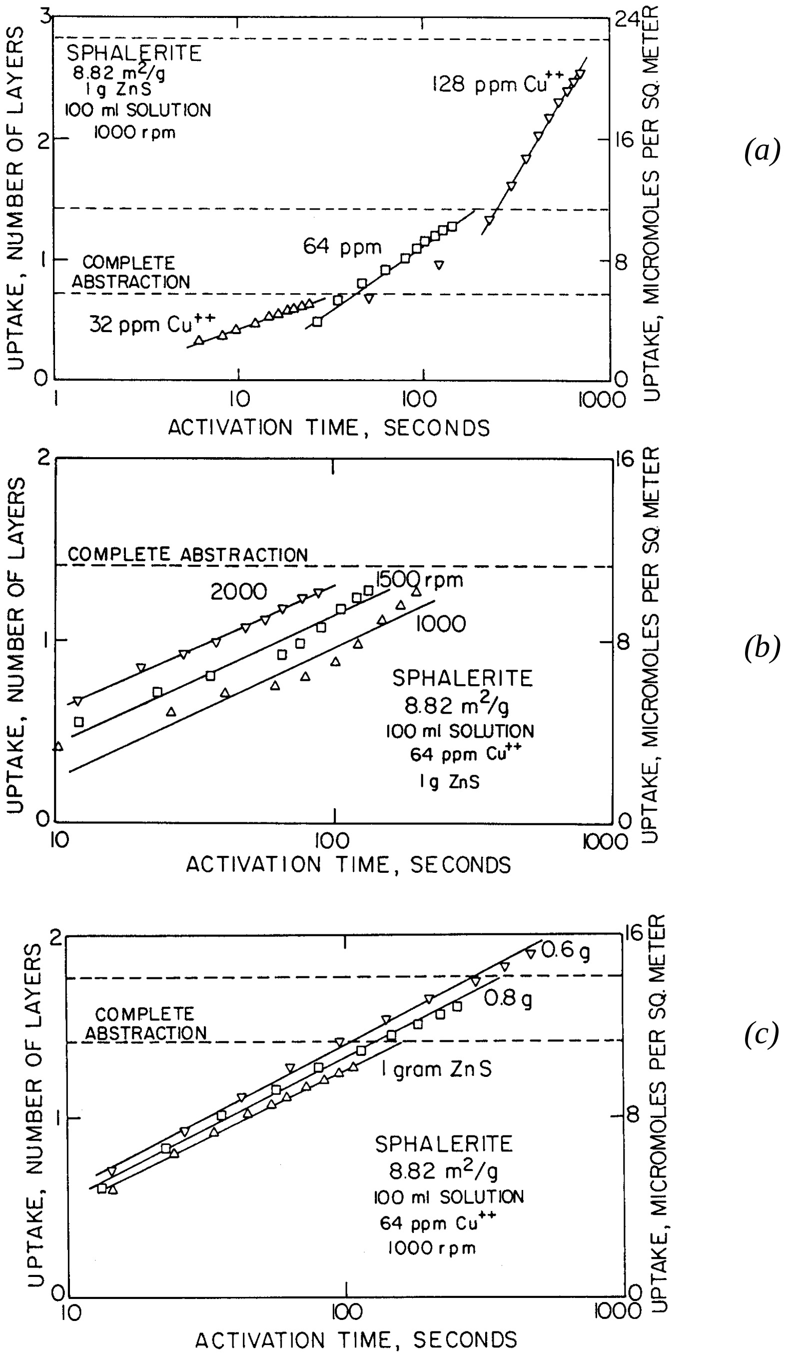


Figure 2.14. Effect of initial copper concentration (a), agitation (b), and solid-to-liquid ratio (c) on the amount of copper abstracted by sphalerite for short conditioning times at pH 3.2 (Jain and Fuerstenau, 1985).

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 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 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.

Chapter 3. Effect of free cyanide on the activation and deactivation of sphalerite

3.1. Introduction

As discussed in Chapter 2, flotation of individual minerals often occurs in different pH ranges. This effect can be used to achieve selectivity by controlling the pH during flotation. When more than one valuable mineral are present in the ore, it is often also necessary to add reagents such as depressants, which counteract the interaction between a given mineral surface and the collector. The action of depressants is complex, and in most cases poorly understood, making depression more difficult to control than the application of other types of reagents. Common depressants in lead-zinc sulphide flotation are sodium cyanide and zinc sulphate.

Sodium cyanide is used at the Rosh Pinah Mine to suppress the flotation of sphalerite in the lead flotation circuit and so improve the flotation selectivity. However, engineers at the Rosh Pinah concentrator believe that the current cyanide dosage of 150-180 g/t is higher than needed for the efficient performance of the plant. One effect of high cyanide dosage is the increased amount of copper sulphate required to activate the sphalerite in the zinc flotation circuit. Thus, an understanding of the mechanism by which cyanide controls the flotation of sphalerite is required before optimising the depressant dosage in the lead flotation circuit.

3.2. Deactivation of sphalerite with cyanide

In Cu-Pb-Zn flotation plant practice cyanide is usually added to depress the flotation of copper-activated sphalerite prior to copper and/or lead flotation. The removal by cyanide of copper species from the surface of the copper(II)-activated zinc sulphide is called deactivation and has been discussed in the literature (Prestidge et al., 1997; Buckley et al., 1989; Fuerstenau, 1982; Finkelstein and Allison, 1976). The deactivation of sphalerite usually depends on the concentration of free cyanide, the pH of the pulp, the deactivation time, and the concentration of activating copper species on the sphalerite surface.

In addition to removal of activating species, the selective depression of sulphide minerals by cyanide can be achieved through one of the following processes (Wang and Forssberg, 1996):

- Cyanide dissolves the metal xanthates to form metal-cyanide complexes or combines with surface metal ions to prevent the formation of metal-xanthates;
- Cyanide reduces the redox potential of the pulp and consumes oxygen in the flotation pulp to prevent the chemisorption and oxidation of xanthate;
- Cyanide is preferentially adsorbed on the sulphide mineral surfaces as cyano-metal complexes to inhibit the adsorption of xanthate and the oxidation of xanthate on the mineral surface; and
- Cyanide reacts with elemental sulphur and polysulphides to form thiocyanate, thereby removing the hydrophobic entity from the mineral surface.

Of all the sulphide minerals studied thus far, the depression of pyrite with cyanide is the best understood. As background, the Pourbaix diagram of the Fe-CN^--H_2O system at 25°C is shown in Figure 3.1.

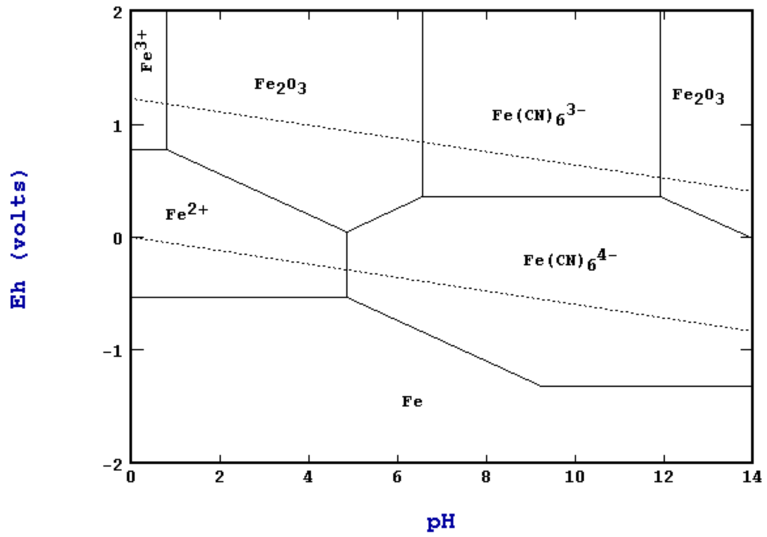


Figure 3.1. Pourbaix diagram of the Fe-CN^--H_2O system at 25 °C. [Fe] = $5x10^{-5}$M , [CN^-] = $6x10^{-4}$M. Stabcal software, NBS database (Huang, 2003).

It is clear that $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ are the stable species at the alkaline pH used in flotation. Most practical pulp potentials are in the range where the formation of $Fe(CN)_6^{4-}$ is thermodynamically favourable. Elgillani and Fuerstenau (1968) showed that the flotation recovery of pyrite can be depressed in the presence of cyanide ions by the formation of ferrocyanide ions (Equation 3.1) followed by the precipitation of ferric ferrocyanide ($Fe_4[Fe(CN)_6]_3$) onto the surface of pyrite:

$$Fe^{2+} + 6\ CN^- = Fe(CN)_6^{4-} \qquad [3.1]$$

The presence of ferric ferrocyanide on the surface of sphalerite will prevent the formation of dixanthogen and hence, suppressing the flotation of pyrite. The oxidation of pyrite is necessary for the production of Fe^{2+}, which will then react with CN^- ions. Wang and Forssberg (1996) have also shown that the oxidation of pyrite could be enhanced in the presence of cyanide ions at alkaline pH. It is also known that excessive oxidation of pyrite can reduce the floatability of pyrite in the absence of depressant due to the formation of $Fe(OH)_3$ at higher alkaline pH values.

Although there is a general agreement on the mechanism by which cyanide depresses pyrite, the mechanism by which it depresses the flotation of sphalerite is not well understood yet. In order to determine whether cyanide reacts with sphalerite itself, Buckley et al. (1989) investigated the deactivation of copper-activated sphalerite by cyanide at pH 9.5. They have observed that cyanide did not interact with zinc or sulphur on the sphalerite surface but that the copper present on the surface was dissolved. Thus, the thermodynamics of copper–cyanide solution will play an important role in the activation and deactivation of copper activated sphalerite.

For copper-bearing minerals, cyanide reacts with surface copper to form copper-cyanide complexes (Arbiter, 1985):

$$Cu^{2+} + CN^- = Cu^+ + \tfrac{1}{2}(CN)_2 \qquad [3.2]$$
$$Cu^+ + 2CN^- = Cu(CN)_2^- \qquad [3.3]$$

Arbiter (1985) postulated that the cupro-cyanide complex, $Cu(CN)_2^-$, was relatively stable and limited the concentration of free dissolved copper ions to such a low value that the activation of sphalerite would not occur. Figure 3.2 shows the solubility of Cu(I) as a function of free cyanide concentration at 25°C (Huang, 2003).

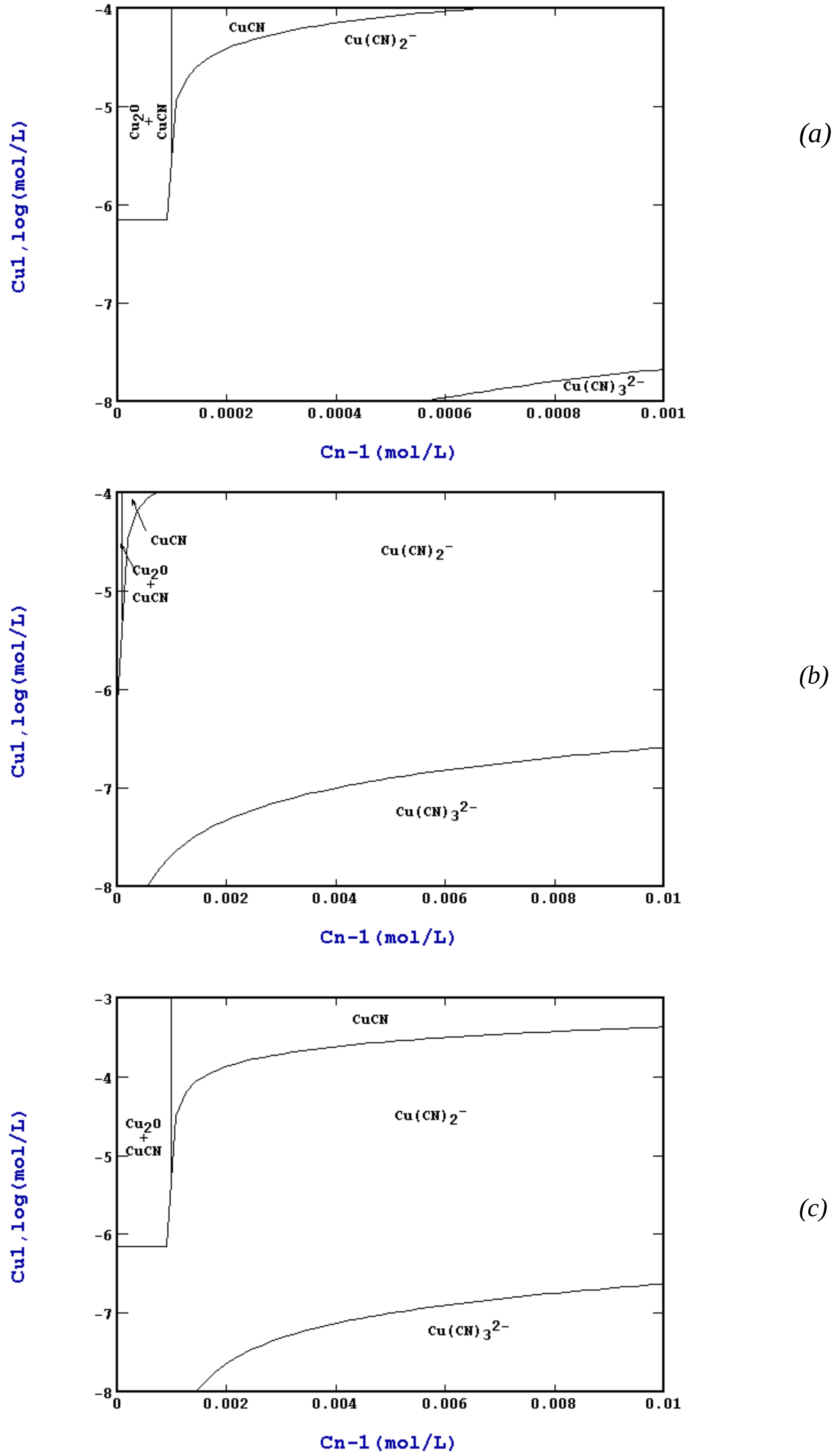


Figure 3.2. Solubility of Cu(I) as a function of cyanide concentration at pH 8 and 25 °C. Total Cu(I) of 10^{-4}M (a and b) and 10^{-3}M (c). Stabcal software, NBS database (Huang, 2003). Note different cyanide concentration range in (a), (b) and (c).

It can be observed that the solubility of Cu(I) cyanide complexes increases with the increasing concentration of free cyanide in solution, forming copper-cyano complexes such as $Cu(CN)_2^-$ and $Cu(CN)_3^{2-}$. For a total copper concentration of 10^{-4}M, the domain of stability of $Cu(CN)_2^-$ and $Cu(CN)_3^{2-}$ increased when the concentration of free cyanide increased from 10^{-3} to 10^{-2}M as shown in Figure 3.2 (*a, b*). In addition, Figure 3.2(*c*) predicts that CuCN species would be the most predominant species when the concentration of copper is increased to 10^{-3}M. The presence of copper oxide species (Cu_2O) can clearly be seen when the concentration ratio of total copper to free cyanide is larger than 1.0 as shown in Figures 3.2(*a, c*).

Since it has been shown in Chapter 2 that the reaction of copper hydroxide/oxide with the sphalerite does promote its activation (after formation of Cu(I) and oxidised S species) and subsequent flotation in the presence of xanthate, the concentration of dissolved copper ions should be minimised in the lead flotation circuit. Hence, for an effective depression of copper activated sphalerite, the concentration of free cyanide in solution has to be slightly higher than that required to form $Cu(CN)^-_2$ and $Cu(CN)_3^{2-}$ species. Analysis of the process water used at the concentrator indicated that copper concentration is in the range of 10^{-4}M. However, very high concentrations of free cyanide (approximately 10^{-2}M) are added in the mill at the Rosh Pinah concentrator. Thus, it is possible that copper cyanide would activate sphalerite in the absence of excess free cyanide due to the degradation of copper cyanide by reversing equations 3.2 and 3.3.

Use of recirculating water is expected to affect copper cyanide stability at Rosh Pinah. Figures 3.3 and 3.4. show the schematic diagram of the milling and lead flotation circuit at Rosh Pinah Mine, respectively. Reagent additions points are also illustrated. After the addition of sodium cyanide in the ball mill, soluble copper cyanide complexes such as $Cu(CN)_2^-$ and $Cu(CN)_3^{2-}$ are expected to form depending on the concentration of free cyanide. The tailings from the lead scavenger flotation circuit are sent to the zinc flotation feed thickener (P22) for dewatering after the flotation of galena.

The overflow of the thickener (P22), in which the galena rougher tailings are dewatered, is used to dilute the product from the primary ball mill and from the primary cyclone. As the P22 water is recirculated into the milling circuit for further milling operations and dilution, it is believed that dissolved compounds such as copper-cyanide complexes can release copper in solution when the concentration of free cyanide is depleted.

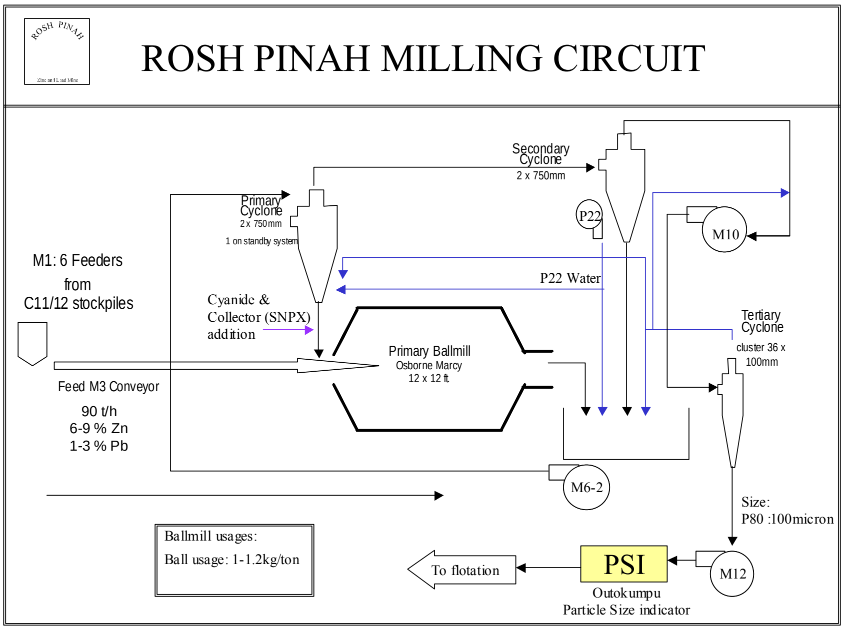


Figure 3.3. Schematic diagram of the milling circuit at Rosh Pinah Mine (Minsiomi, 2001).

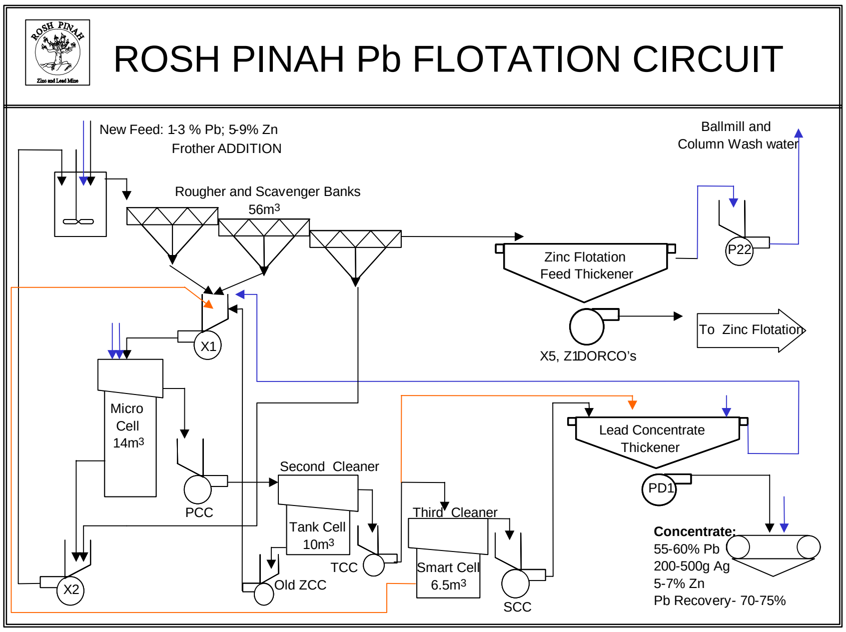


Figure 3.4. Schematic diagram of the lead flotation circuit at Rosh Pinah Mine (Minsiomi, 2001).

These chemical reactions are expected to occur in the thickener P22 due to the variation in both the concentration of dissolved oxygen and the pulp potential.

However, due to the high dosage of free cyanide added in the mill, it is possible to still find residual amount of free cyanide in the water stream from the thickener P22. Levay et al. (2001) and Williams and Phelan (1985) showed that variation in pH, Eh, and dissolved oxygen will usually affect the chemistry of the species present in the water stream. Thus, the chemical composition of recycle water used at the Rosh Pinah concentrator will depend upon the minerals being processed, the reagent suite and the electrochemical environment of the milling and flotation circuit. Possible effects of the recirculating water are considered next.

3.3. Effect of recirculating water on the activation of sphalerite

The flotation results of various studies have shown that the quality of the process water in general, and recirculating water in particular, can have an adverse effect on the flotation selectivity of complex sulphide minerals (Malysiak et al., 2003; Ng'andu, 2001; Levay et al., 2001; Rao and Finch, 1989). This is mainly due to one or more of the following factors:

- Residual xanthates and their oxidation products which adsorb unselectively on most sulphides;
- Metallic ions such as Cu^{2+}, Pb^{2+}, Fe^{2+} which cause inadvertent activation;
- Alkaline earth metal ions which may activate the non sulphide gangue; and
- Variation in the slurry pH and pulp potential in both the milling and the flotation circuit.

Williams and Phelan (1985) showed that the presence of zinc ions (in the region of 200ppm) in the recirculating water (pH 3), which was used in the mill, affected the recovery of sphalerite in the subsequent zinc circuit (pH 9.5) at the Woodlawn Mines (Australia) due to the presence of colloidal hydroxide on the surface of the mineral. The adverse effect of zinc ions on the flotation recovery of sphalerite was eliminated by treating the process water to remove zinc ions before the water entered the mill.

An example of the effect of process water on the flotation selectivity of a Cu-Zn ore (chalcopyrite and sphalerite) is given below. Water from the Tailings pond was used and its chemical composition is presented in Tables 3.1.

Table 3.1. Tailings pond water quality (ppm) (Broman, 1980)

PH	CU	FE	ZN	PB	AS	CD	HG (PPB)
8.0	0.03	0.23	0.32	0.013	0.011	0.008	0.66

The effect of the recycle water on the flotation selectivity of copper and zinc in the copper concentrate is presented in Table 3.2.

Table 3.2. Metallurgical data with and without recycle water (%) (Broman, 1980)

	ASSAYS (%)			CU CIRCUIT			ZN CIRCUIT	
	Mill feed			Conc.		Tails	Conc.	Tails
	Cu	Zn	S	Cu	Zn	Cu	Zn	Zn
Without recycle water	0.81	3.03	28.5	19.1	12.7	0.10	53.9	0.44
With recycle water	0.82	3.49	29.8	17.5	19.0	0.12	53.3	0.55

It was clear that the grade of zinc in the copper concentrate increased with the use of the recycle water, while the grade of copper decreased. Moreover, the grade of copper increased in the copper tailings, showing poorer flotation selectivity between copper and zinc in the copper concentrate. The presence of zinc in the copper concentrate might be due to the inadvertent activation of sphalerite by the dissolved copper ions from the recycle water.

At Rosh Pinah Mine, water from the Thickener P22 (Figure 3.3) is the main source of process water used in the milling and lead flotation circuit. In this way its quality can play a significant role on the flotation selectivity between galena and sphalerite in the lead flotation circuit. Du Preez (2000) conducted a survey on the composition of the water from different streams at the Rosh Pinah Mine and the results are summarised in Table 3.3. These results indicated that the concentration of the dissolved copper increased in the thickener overflow (17 mg/l) when compared to the mill discharge (14.1 mg/l). Unfortunately the residual concentration of free cyanide was not known at the time these data were made available.

Table 3.3.Plant survey on the quality of water and slurry at the Rosh Pinah Mine (Du Preez, 2000)

SAMPLING POINT	DISSOLVED OXYGEN	E_H	DISSOLVED ION (MG/L)	
	mg/l	mV	Pb	Cu
Mill discharge	0.18	-103	30.5	14.1
Primary cyclone underflow	0.18	-84	20.4	14.5
Dewatering cyclone overflow	0.07	-134	18.2	13.2
Thickener (P22) overflow	4.08	-30	32.4	17.0

As expected, the pulp potential increased with increasing dissolved oxygen (Figure 3.5); and higher values were recorded in the overflow of the Thickener P22. In addition, the amount of both the dissolved copper and lead also increased.

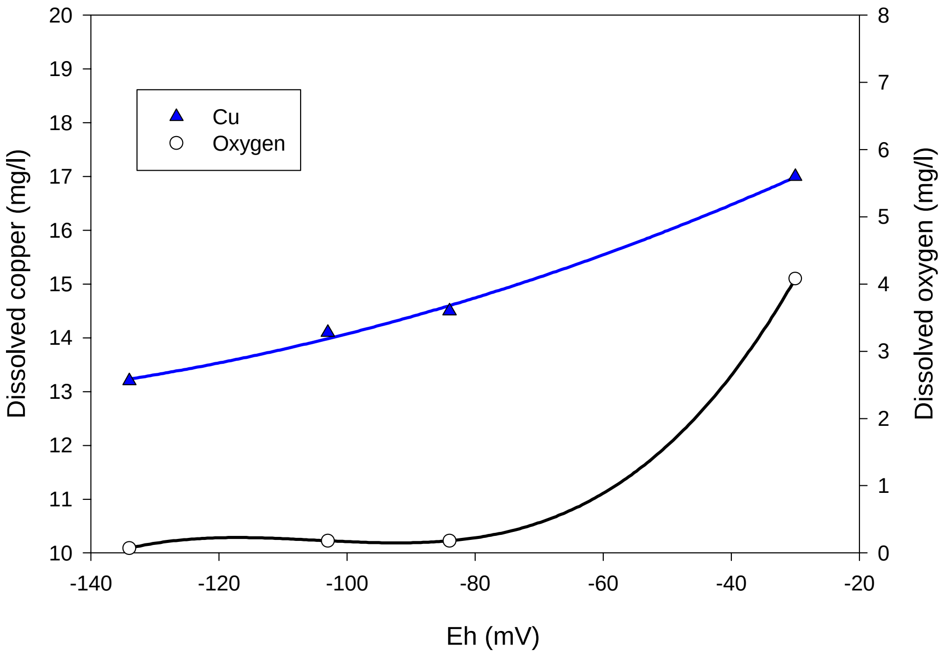


Figure 3.5. Variation of the dissolved copper and dissolved oxygen as functions of the pulp potential at the Rosh Pinah Mine milling circuit. Data of Table 3.3

It is likely that most of the copper in the mill discharge slurry will be present as cupro-cyano complexes due to the addition of sodium cyanide in the mill. Based on the mechanism of activation discussed in Chapter 2, the activation of sphalerite by copper-cyanide complexes can only occur if the copper-cyanide complexes undergo some decomposition/oxidation to make the copper available. It is believed that the electrochemical conditions in the thickener P22 might promote the degradation of copper-cyanide complexes. Although there is not a clear mechanism by which copper-cyanide complexes themselves activate sphalerite, the electrochemical oxidation of copper cyanide can be used to formulate such a mechanism, as discussed in the next section.

3.4. The electrochemical oxidation of copper-cyanide complexes

The need for treating large quantities of metal cyanide wastewater in the mining industry has resulted in the study of the electrochemical oxidation of alkaline copper cyanide solutions (Djokić, 2002; Cheng et al., 2002; Casella and Gatta, 2000; Dudek and Fedkiw, 1999). These authors have observed that copper from cyanide complexes such as $Cu(CN)_2^-$ and $Cu(CN)_3^{2-}$ can be deposited as $Cu(OH)_2$, CuO and Cu_2O on the surface of glassy carbon, gold and platinum electrodes following the oxidation of cyanide at high potential (Figures 3.6).

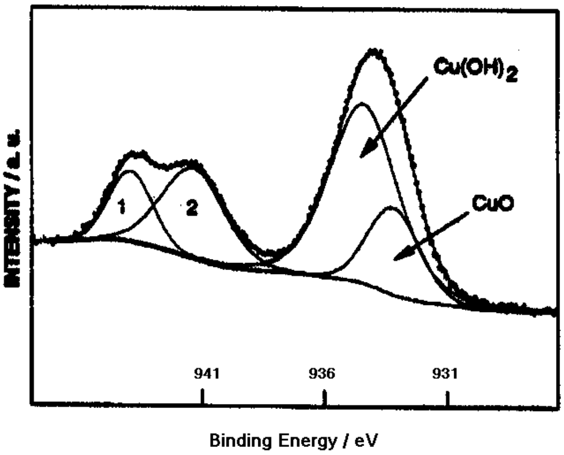


Figure 3.6. Curve fitting of $Cu2p_{3/2}$ spectrum of Cu/GC electrode just after X-ray irradiation. The copper-glassy carbon (Cu/GC) electrode was obtained by potential cycling between –0.1 and 0.65 V versus SCE in 0.2 M NaOH solution containing 0.5 g/l of $KCu(CN)_2$ + $K_3Cu(CN)_4$ (Casella and Gatta, 2000).

The mechanism by which copper(I) from cyano-complexes is oxidised to copper(II) hydroxide/oxide is not well understood. However, Figure 3.7 shows that the oxidation of copper(I) from copper cyanide complexes can occur at higher potential. Casella and Gatta (2000) also observed that the concentration of copper on both the glassy carbon and the platinum electrodes increased with increasing applied potential (Figure 3.8). Figure 3.8 also indicated that the loading of copper on both electrodes started at potentials where copper cyanide species are still thermodynamically stable (Figure 3.7). In addition, the copper loading decreased at potential higher than 550 mV SCE

(790 mV SHE) where the copper oxide is supposed to be thermodynamically stable. Although a potential of 500mV SCE is not likely to be achieved in flotation pulp, the possibilities of sphalerite activation by copper cyanide species alone cannot be ignored.

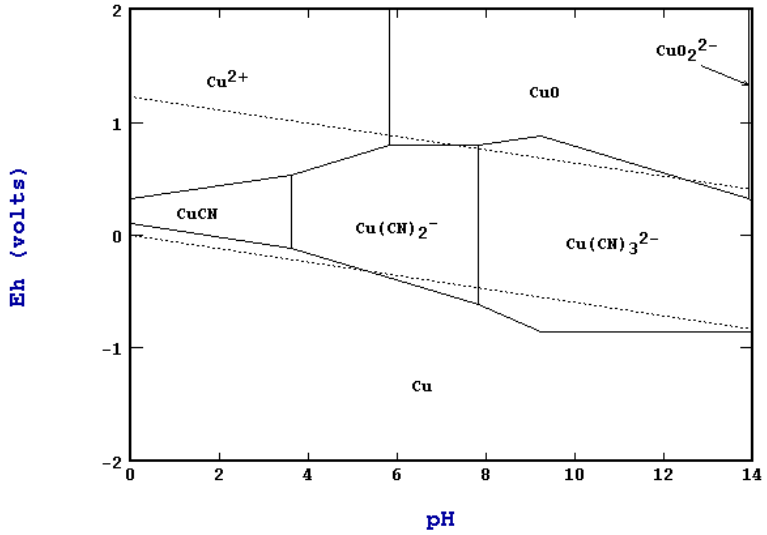


Figure 3.7. Pourbaix diagram of the Cu-CN^--H_2O system at 25 °C. [Cu] = $5x10^{-5}$M, [CN^-] = $6x10^{-4}$M. Stabcal software, NBS database (Huang, 2003).

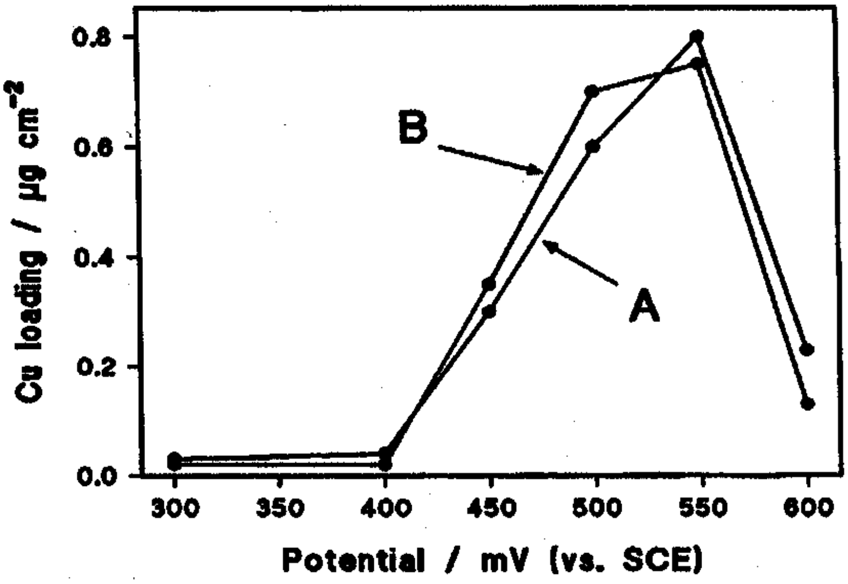


Figure 3.8. Film growth of Cu(II) oxide/hydroxide versus the applied potential at a glassy carbon (A) and platinum (B) electrodes, respectively. Potentiostatic deposition performed in 0.2 M NaOH solution containing 0.5 g/l $KCu(CN)_2$ + $K_3Cu(CN)_4$ (Casella and Gatta, 2000).

A mechanism which supports the simultaneous oxidation/dissociation of $Cu(CN)_x^{1-x}$ complex species followed by the deposition of copper oxide/hydroxide was proposed by Casella and Gatta (2000):

$$2Cu(CN)_n^{1-n} + 3H_2O = Cu(OH)_2 + CuO + 6H^+ + 2nCN^- + 4e \qquad [3.10]$$

After an initial incipient copper deposition, further deposition was obtained by simple immersion of the electrode in a cyanocuprate solution. Thus, the first monolayer of copper acted as a catalyst for further chemisorption of copper oxide/hydroxide (Casella and Gatta, 2000). It was observed that the amount of copper deposited on the surface of the electrode increased with increasing alkalinity and appeared to be independent of the electrode substrate (Cheng et al., 2002; Casella and Gatta, 2000).

Cheng et al. (2002) have shown that mining wastewater containing cyanide complexes can be treated electrochemically by controlling the solution potential and pH. They observed a rapid oxidation of cyanide and copper-cyanide complexes at high hydroxide concentrations. The oxidation of cyanide complexes was followed by the formation/deposition of copper hydroxide/oxide species. The relevance of the electrochemical oxidation of copper cyanide complexes on the flotation selectivity of the galena and sphalerite at the Rosh Pinah Mine is discussed in the next section.

3.5. Specific relevance to the flotation at the Rosh Pinah Mine

Understanding and then treating the recirculating water has been part of the challenging tasks for the efficient operations of concentrators worldwide, and the Rosh Pinah Mine should not be an exception to this. The critical issue would be whether the activity of dissolved ions is sufficiently reduced to levels where these would not interact strongly with sphalerite and promote its flotation in the lead circuit.

Since the scope of this study is limited to the flotation selectivity in the lead circuit, the inadvertent activation of sphalerite during the flotation of galena is of great importance. To date, most of the work done on the inadvertent activation of sphalerite has focused mainly on the effect of Cu(II) ions (Chen and Yoon, 2000; Pattrick et al., 1999; Laskowski et al., 1997; Prestidge et al., 1997; Finkelstein, 1997). Most of copper concentration used in previous studies is higher than that found in the recirculating water.

Since the identity of copper species in the recirculating water at the Rosh Pinah Mine is not known, it is possible that the copper-cyanide species could themselves affect the flotation selectivity between sphalerite and galena. Interactions between copper-cyanide species and sphalerite have not been studied extensively, and are of fundamental importance in selective flotation, especially when water from the lead rougher tailings is recycled to the milling circuit. It has been shown in section 3.4 that the electrochemical oxidation of the copper-cyanide species at alkaline pH values can promote the formation of copper activating species for sphalerite.

The present study will focus on a more integrated and practical approach to the inadvertent activation of sphalerite in the lead flotation circuit by taking into account the concentration of the dissolved ions in the recirculating water. A complex copper-lead-zinc ore instead of a single mineral will be used to study the effect of the dissolved ions on the activation of sphalerite in the lead flotation circuit.

3.6. Conclusion

The purpose of this chapter was to study the possibility of sphalerite activation in the presence of copper cyanide complexes. An understanding of this kind of activation is important for optimising the reagent suite and improving the flotation selectivity between galena and sphalerite in the lead flotation circuit at Rosh Pinah Mine.

It has been shown that the use of recycle water can have a detrimental effect on the flotation selectivity of galena and sphalerite in the lead flotation circuit. Based on the decomposition of copper cyanide species into copper oxide/hydroxide, the activation of sphalerite and its subsequent flotation with thiol collector such as xanthate can increase the amount of zinc in the lead concentrate. Flotation testwork of the Rosh Pinah ore in the presence of a solution containing copper cyanide complexes was conducted to study to effect of process water quality on the flotation selectivity between galena and sphalerite. The experimental approach is described in the next chapter.

Chapter 4. Experimental

4.1. Materials, reagents and solutions

The lead-zinc ore sample (-9 mm) used in this study was obtained from the crushing plant at the Rosh Pinah Mine in Namibia. The sample was removed from the actual feed to the milling circuit. The sample was screened at 1.7 mm and the oversize fraction crushed to -1.7 mm. A sub-sample was removed for head assays. The remainder of the sample was used for the flotation testwork. 1kg batch-sample was milled either dry or at 67% solids (w/w) in an unlined laboratory mild steel mill with mild steel rods for different periods of time to achieve the target grind. The mill was not vented during the grinding stage. The particle size distributions of the ground products were determined using a Malvern Mastersizer 2000 instrument. The chemical composition of the ore was determined using a sequential XRF spectrometer ARL 9400-241XP+ of which the results are shown in Table 4.1.

Table 4.1. The average chemical analysis of the lead-zinc ore sample used in this study, (weight %)

Pb	Zn	Cu	Fe	S	CaO	MgO	Al_2O_3	SiO_2
1.9	7.0	0.12	3.7	3.9	18.7	8.2	4.1	49.2

Natural sphalerite minerals from Elmwood Mine, Carthage (Tennessee, USA), were obtained from Ward's Natural Science and cut into a 10 x 10 mm sample, for surface analysis.

Sodium propyl xanthate (SNPX) and potassium butyl xanthate (PNBX) from Senmin (South Africa) were used as collectors. Senfroth 9325 (Polypropylene glycol) from Senmin (South Africa) and Dowfroth 200 from Betachem (South Africa) were used as frothers. The xanthate was purified by dissolution in acetone and reprecipitation with petroleum ether as proposed by Rao (1971). Xanthate solutions were prepared daily. Analytical grade copper sulphate ($CuSO_4.5H_2O$) from Bio-Zone Chemicals (South Africa) and lead nitrate ($Pb(NO_3)_2$) from NT Laboratory Supplies (South Africa) were used for the activation of sphalerite. Analytical grade copper cyanide (CuCN) from Saarchem (South Africa) was used for the preparation of solution containing copper cyanide complexes. Copper cyanide stock solutions (10^{-4} and 10^{-3}M Cu) were prepared by addition of CuCN powder to a sodium cyanide solution at a CN^-/Cu molar ratio of 3:1 and at pH of 10.5, which was maintained by additions of sodium hydroxide solutions. Sodium cyanide (NaCN) from Saarchem (South Africa) and zinc sulphate ($ZnSO_4.7H_2O$) from BDH Laboratory Supplies (England) were used for the depression of sphalerite. The cyanide solution was made up at pH 10.5 using NaOH to prevent the formation of HCN. Reagents were made up at 1% (w/w) with distilled water. However, the Dowfroth 200 and Senfroth 9325 were used neat.

4.2. Flotation

A Denver D12 flotation machine, a 3 dm^3 flotation cell and tap water (Rand Water Board, Pretoria) were used for the batch flotation tests. All flotation experiments were carried out at about 30% (w/w) solid. The impeller speed was set at 1250 rpm and the air flow rate was 6 dm^3min^{-1}. Although no attempt was made to control the pulp potential and dissolved oxygen, they were monitored throughout the experiments. The pulp potential was measured using a platinum electrode and a Ag/AgCl reference electrode. The platinum electrode (0.5mm Pt wire) was calibrated with a ferrous-ferric solution as described by Light (1972) (Tables 4.2-4.3).

Table 4.2. A standard Ferrous-Ferric solution for oxidation-reduction potential measurements (Light, 1972)

Composition	Concentration (M)
Ferrous ammonium sulphate 39.21 g/l $Fe(NH_4)_2(SO_4)_2.6H_2O$	0.1
Ferric ammonium sulphate 48.22 g/l $FeNH_4(SO_4)_2.12H_2O$	0.1
Sulphuric acid (56.2 ml/l concentrated H_2SO_4)	1

Table 4.3. Potentials of the platinum electrode vs. various reference electrodes at 25 °C in standard Ferrous-Ferric solution (Light, 1972)

Reference electrode	EMF, mV
Hg, Hg_2Cl_2, satd KCl (SCE)	+430
Ag, AgCl, 1M KCl	+439
Ag, AgCl, 4M KCl	+475
Pt, H_2 (p = 1), H^+ (a = 1) (SHE)	+675

The platinum electrode was cleaned with nitric acid and distilled water after every experiment to remove any coating on its surface. A Keithley Electrometer (model 614) was used for the potential measurements. Measured potential values were reported relative to the standard hydrogen electrode.

Flotation tests (in duplicate unless stated otherwise) were carried out at the natural pH (8.5 ± 0.2) of the pulp and room temperature (22 ± 2 °C), which were measured with an Orion pH meter model 420. The dissolved oxygen in the flotation cell was monitored with the WTW OX191 oxymeter. The volume of the pulp in the flotation cell was kept constant by additions of tap water using a pulp level control device. After transferring the ore into the flotation cell, the desired amount of Cu(II) and/or Pb(II) was added and the pulp was conditioned for 30 minutes (Chapter 5). For the activation with copper cyanide complexes, the pulp was conditioned for 10 minutes (Chapter 6). The xanthate was then added and the pulp was conditioned for 3 minutes after which the frother (Dow 200 or Senfroth 9325) was added and conditioned for a further 1 minute. For the depression of sphalerite with cyanide, zinc sulphate and sodium metabisulphite, the depressant was added simultaneously with the collector. After starting the air flow, the froth was removed by hand scraping every 15 seconds. Incremental rougher concentrates were collected after 1, 2, 4, 8 and 12 minutes, unless stated otherwise. Following the flotation tests, the concentrates and tailings were dried and analysed using XRF. Cumulative recoveries were calculated from the masses and chemical analyses of the concentrates and the tailings. The experimental data were fitted using the empirical flotation first order kinetics (Cullinan et al., 1999; Marin and Molina, 1988):

$$R = R_{max}[1-\exp(-kt)] \qquad [4.1]$$

where R is the recovery at a time t, k is the rate constant, and R_{max} is the recovery at infinite time. The SigmaPlot computer program was used for the fitting of the experimental data and calculations of the flotation rate constant and maximum recovery. Since the duplication of experimental data was within the acceptable statistical error, statistical analysis of the experimental results will not be discussed in this study.

4.3. X-ray photoelectron spectroscopy

4.3.1. Activation of sphalerite with Pb(II) ions

A sphalerite sample was either cleaved or wet ground using 600 grit silicon carbide paper, washed thoroughly with distilled water, and then introduced into the spectrometer. In some experiments, the sample was dried in air before being introduced into the XPS instrument. Another polished sample was immersed in a buffered borate solution (pH 9.2) containing $3\text{x}10^{-3}$M $Pb(NO_3)_2$ for 30 minutes. The activation of sphalerite was carried out in an air-saturated solution. After activation, the sample was washed with distilled water before being introduced into the instrument.

XPS spectra were obtained using a Perkin Elmer PHI Model 5400 spectrometer equipped with a Mg/Al dual anode source. An achromatic Mg K_α X-ray (1253.6 eV) source was operated at 300 W, 15 kV, and 20 mA. The vacuum pressure in the analyser chamber was at least 10^{-9} Torr during analysis. The instrument was calibrated against the C 1s peak at 284.6 eV. Spectra were obtained at a take off angle of 45° to the sphalerite surface with a pass energy of 17.9 eV. Data analysis was performed using PHI XPS software (version 2.0). Elemental atomic concentrations were calculated from the XPS peak areas and the respective sensitivity factor. Spectra presented in this study were corrected for background charging. Charge corrections were made using C 1s peak at 284.6 eV.

4.3.2. Copper activation and deactivation of sphalerite

A sphalerite sample was conditioned in an air-saturated solution for 30 minutes at pH 10.5 with 200 cm^3 of copper-cyanide complexes or copper nitrate solutions (10^{-2} and 10^{-3}M). After conditioning, the sphalerite sample was washed with water and dried before being introduced into the XPS for analysis. After XPS analysis, the sample was treated with 200 cm^3 of sodium cyanide solution (10^{-2}M), washed with distilled water, dried and then reintroduced in the instrument and analysed again. XPS spectra were obtained using a Perkin Elmer PHI Model 5400 spectrometer as described in section 4.3.1.

4.4. Fourier transform infrared spectroscopy

FT-IR spectra of copper-cyanide solutions were obtained using a Perkin Elmer GX spectrum 2000 Fourier Transform Infrared Spectrometer with a ZnSe horizontal ATR accessory. Fifteen scans were recorded over the frequency range of 4000-400 cm^{-1} and Fourier transformed to give a resolution of 8 cm^{-1}. The software Spectrum version 2 for Windows (Perkin Elmer) was used for the acquisition and processing of data.

4.5. Scanning electron microscopy (SEM)

A JEOL JSM-6300 scanning electron microscope with an attached Noran EDS was used for image analysis. Backscattered electron images were useful to distinguish the differences in mineral composition. The acceleration voltage was 30kV. The conditions of sample preparation for SEM are described in Chapter 7.

Chapter 5. Factors affecting the flotation selectivity of galena and sphalerite

5.1. Introduction

An analysis of the Rosh Pinah process water has shown that a considerable amount of dissolved copper and lead ions is present in the water used in the milling system (Table 1.1). It is believed that the presence of these dissolved ions can promote the inadvertent activation of sphalerite during the flotation of galena. Galena oxidation products such as hydroxide, carbonate, and sulphate are often detected in the pulp during the flotation of lead-zinc sulphide ores (Senior and Trahar, 1991). In addition, copper ions can originate from the oxidation/dissolution of copper-bearing minerals such as chalcopyrite. Thus, a better understanding of the factors that control the flotation response of sphalerite in the lead circuit should be invaluable to improve the flotation selectivity between galena and sphalerite at the Rosh Pinah Mine.

The objective of the work presented in this chapter was to study the flotation selectivity between galena and sphalerite from the Rosh Pinah ore sample. Although many factors can influence the flotation selectivity during the flotation of galena, the current chapter is limited to the following factors:

- Xanthate chain length and dosage.

  It is expected that high dosages and/or long chain xanthate will increase the recovery of sphalerite in the galena circuit.
- Concentration of dissolved Pb(II) and Cu(II) ions present in the process water as reported by Du Preez (2000).

  Activation of sphalerite by heavy metal was discussed in the previous chapters. Thus, the presence of these metal ions in the process water is detrimental to the selectivity between galena and sphalerite during the flotation of galena.

The experiments reported here tested whether the expected broad effects do occur with the Rosh Pinah ore, namely activation by copper and lead ions in the absence of cyanide. The experiments also served as a baseline for subsequent comparison.

The present chapter focuses on the effect of longer activation time and dry milling on the flotation response of the Rosh Pinah ore, because the Mine is considering shifting from the wet to the dry milling of the various ore bodies. Ralston and Healy (1980a,b) postulated that longer conditioning times are needed to ensure the conversion of hydroxide to their sulphide species when the activation and the flotation of sphalerite is carried out at alkaline pH. They also showed that the uptake of Pb(II) by the sphalerite was three times slower than that of Cu(II). In view of this, an activation time of 30 minutes was used in this study to account for the potential conversion of metal hydroxide to their sulphide species. The same activation time was used during the flotation of the Rosh Pinah composite and surface analysis of single sphalerite minerals. This particular activation time was chosen in order to compare the results obtained in this study with those reported by Prestidge et al. (1997). The flotation and XPS results are presented in the following sections.

5.2. Effect of xanthate chain length and dosages on the flotation recovery

Batch rougher flotation tests were carried out on the composite sample from the Rosh Pinah Mine to study the effects of collector type and dosage on the flotation selectivity between galena and sphalerite. The testwork was performed at a target grind of approximately 80% passing 75 micron size (Figure 5.1). The composite was dry milled in an unlined mild steel mill using steel grinding balls. Details of the flotation procedure were presented in Chapter 4.

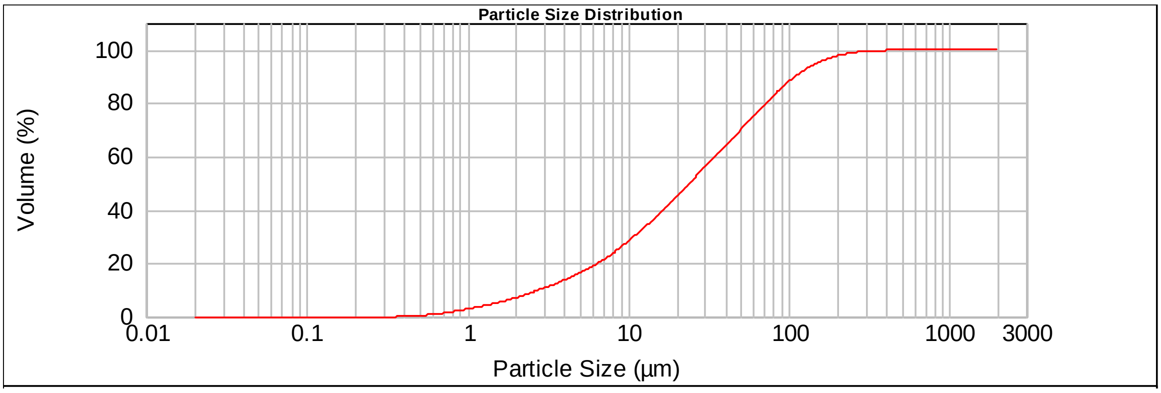


Figure 5.1.Typical particle size distribution of the Rosh Pinah composite used in this study.

The effects of potassium butyl xanthate (PNBX) dosages on the flotation recoveries of galena, sphalerite and non-sulphide gangue minerals are shown in Figures 5.2-5.6, and summarised in Table 5.1.

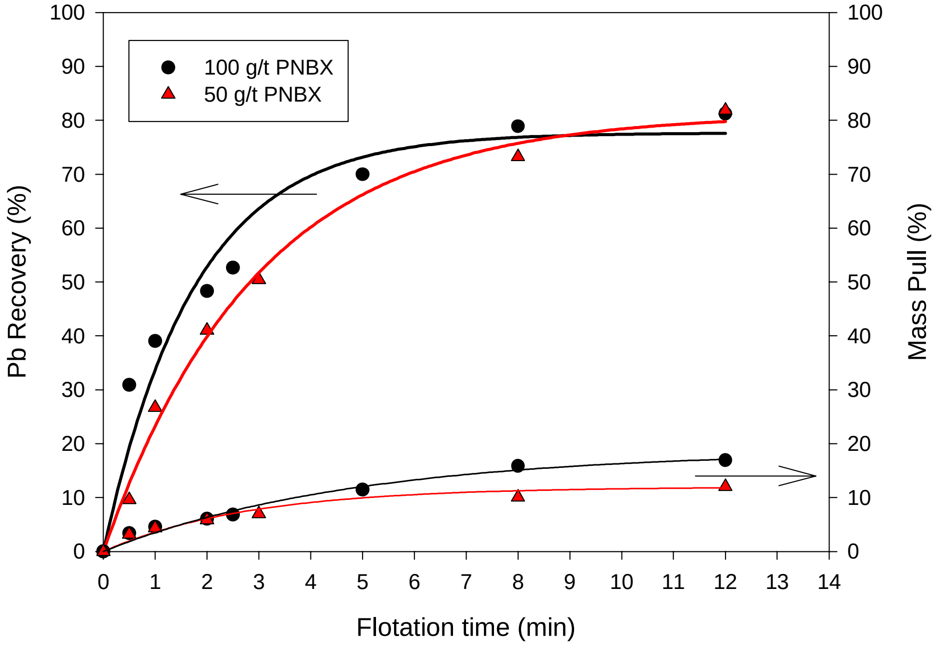


Figure 5.2. Flotation recovery of Pb and concentrate mass pull for two PNBX dosages at pH 8.5. Solid lines represent fitted curves.

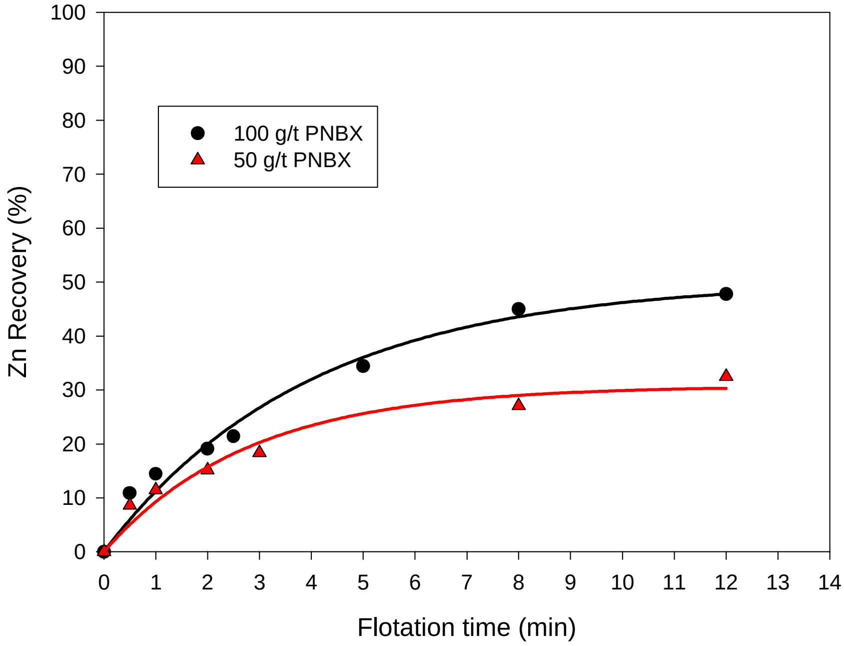


Figure 5.3. Flotation recovery of Zn in the lead rougher concentrate for two PNBX dosages at pH 8.5. Solid lines represent fitted curves.

The results presented in Table 5.1 showed that the concentrate mass pull in the rougher decreased from 16.9 to 12.0% when the xanthate concentration was dropped from 100g/t to 50 g/t. Assuming that all the assayed Pb and Zn were from galena and sphalerite, respectively, it can be seen from Figure 5.2 that approximately 81% of galena could be recovered at both xanthate concentrations of 50 and 100 g/t PNBX after 12 minutes of flotation time. However, the recovery of sphalerite increased from 33 to 48% when the dosage of xanthate was increased from 50 to 100g/t PNBX (Figure 5.3).

Table 5.1. Metallurgical results of the Rosh Pinah composite after 12 min flotation time in the presence of 50 and 100g/t PNBX at pH 8.5

PNBX dosage	Mass Pull	Recovery (%)		Grade (%)	
(g/t)	(%)	Pb	Zn	Pb	Zn
50	12.0	81.9	32.7	8.9	18.5
100	16.9	81.2	47.8	7.5	19.7

The slopes of flotation results presented in Figure 5.4 indicated that the flotation rate constant of galena is slightly higher than that of sphalerite at a collector dosage of 50g/t.

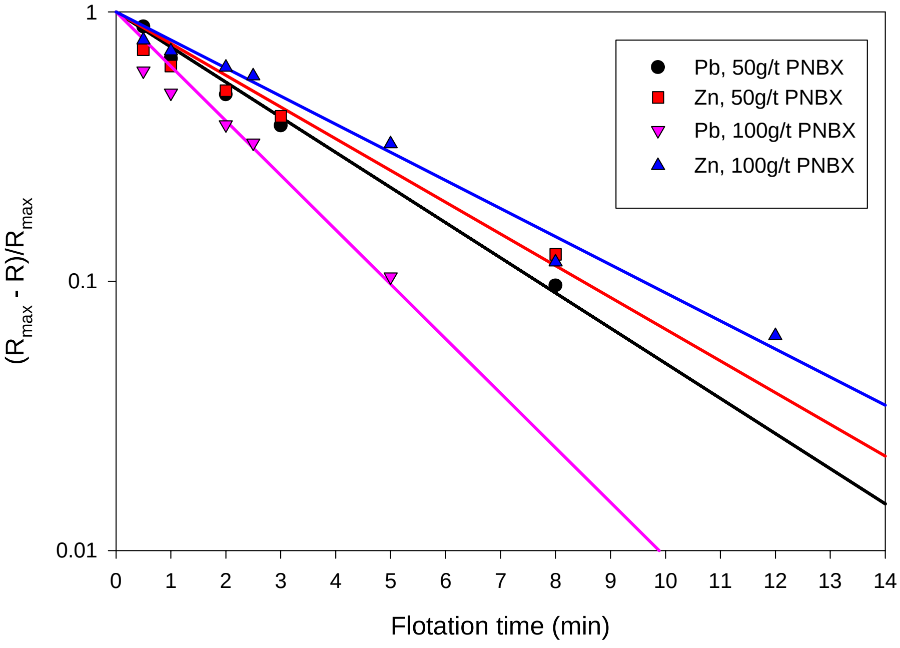


Figure 5.4. Rate of flotation of Pb and Zn in the lead rougher concentrate for two concentrations of PNBX at pH 8.5. Solid lines represent fitted curves.

The flotation rate constant of galena increased substantially at higher collector dosage of 100 g/t, while that of sphalerite is little changed. Thus, galena could be recovered faster at higher collector dosage. However, the amount of zinc in the lead rougher concentrate would also increase with the increasing dosage of PNBX.

Since the final recovery of galena was not improved at 100g/t PNBX, it was also believed that the observed increase in the concentrate mass pull at 100g/t PNBX was probably due to the presence of sphalerite and gangue minerals in the rougher concentrate. Table 2.3 showed that quartz and dolomite were the main component of the non-sulphide gangue in the Rosh Pinah ore used in this study. Thus, the presence of dolomite and quartz would decrease the grade of lead in the rougher concentrate

Figures 5.5-5.6 show the effect of PNBX dosages on the flotation recoveries of SiO_2 and MgO in the lead rougher concentrate, respectively.

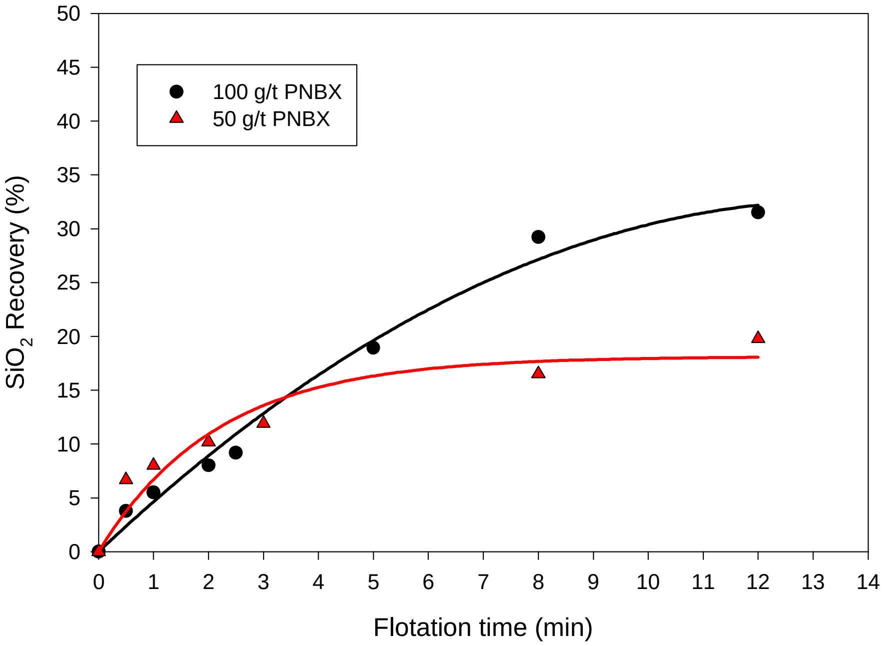


Figure 5.5. Flotation recovery of silica in the lead rougher concentrate for two PNBX dosages at pH 8.5. Solid lines represent fitted curves.

Approximately 35% of quartz was recovered in the rougher concentrate after 12 minutes of flotation time when 100 g/t PNBX was used. However, the recovery of quartz was reduced from 35 to 22% with the use of 50 g/t PNBX without affecting the recovery of galena. Likewise, Figure 5.6 showed that the recoveries of MgO decreased from 31 to 20% when the xanthate dosage decreased from 100 to 50 g/t PNBX.

Since the purpose of the reagent optimisation was to improve the flotation selectivity in the lead flotation circuit, it was clear that 50 g/t of PNBX would be suitable because of the reduced concentrate mass pull and lower recoveries of sphalerite and gangue minerals in the lead rougher concentrate.

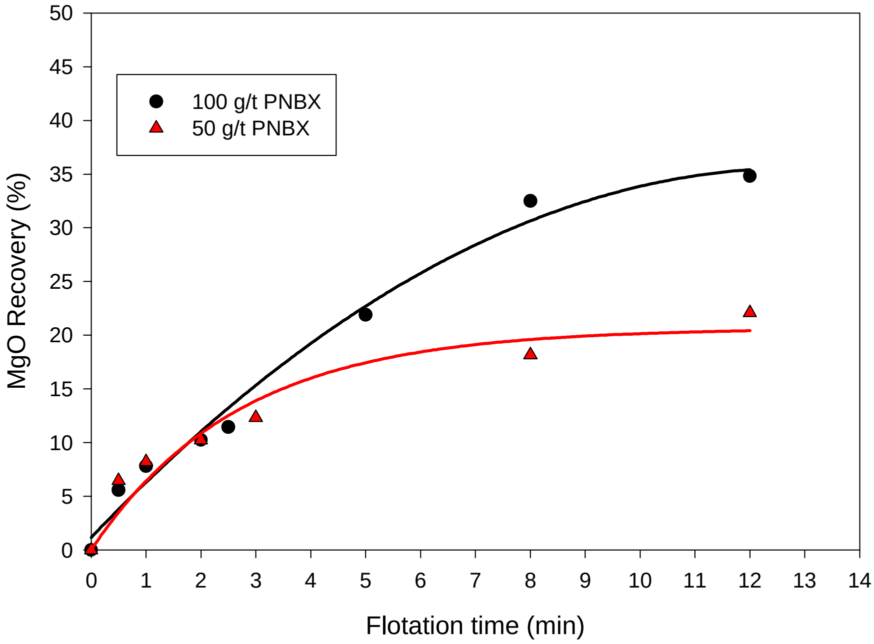


Figure 5.6. Flotation recovery of MgO in the lead rougher concentrate for two PNBX dosages at pH 8.5. Solid lines represent fitted curves.

When xanthate of shorter chain length such as sodium isopropyl xanthate (SNPX) was used, the concentrate mass pull was lower as compared to the results obtained in the presence of PNBX. Figure 5.7 showed that rougher concentrate mass pull of 7.9 and 12.1% were obtained at 50 and 100 g/t SNPX, respectively after 8 minute of flotation time. The recoveries of both galena and sphalerite as a function of SNPX dosages and flotation time are shown in Figures 5.7-5.8.

The recoveries of galena were 63 and 80% in the presence of 50 and 100 g/t SNPX, respectively, after 8 minutes of flotation time. In addition, the recovery of sphalerite increased from 26 to 44% when the dosage of SNPX was increased from 50 to 100 g/t.

The results presented thus far have shown that increasing the dosage of xanthate will increase the amount of zinc in the lead concentrate, hence decreasing the selectivity between galena and sphalerite. In addition, the results presented in Figure 5.9 indicated that xanthates are not selective collectors on the Rosh Pinah composite used in this study.

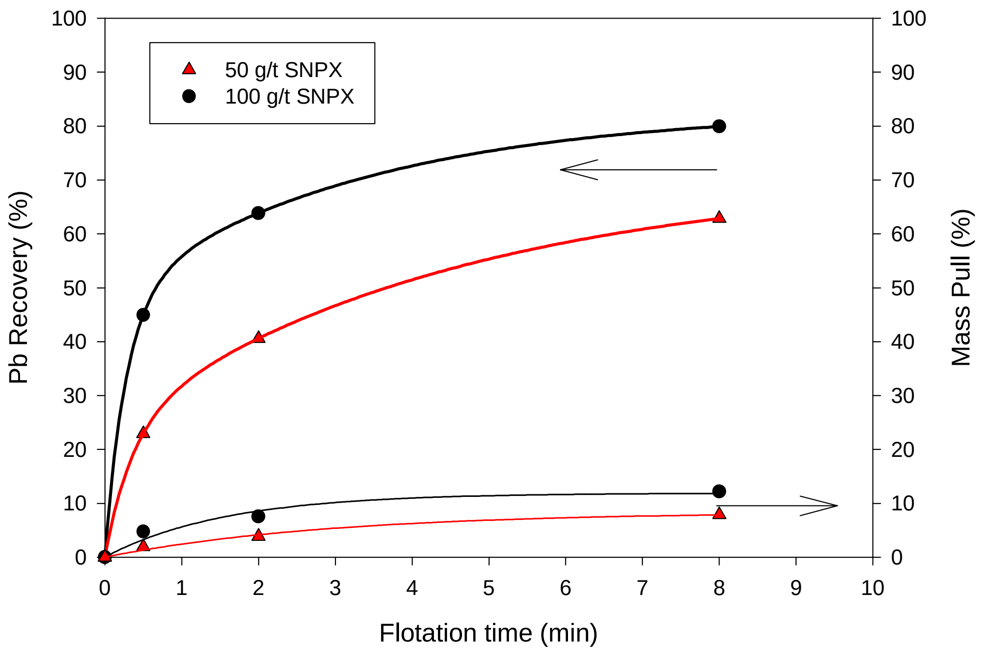


Figure 5.7. Flotation recovery of Pb and rougher concentrate mass pull at two SNPX dosages at pH 8.5. Solid lines represent fitted curves.

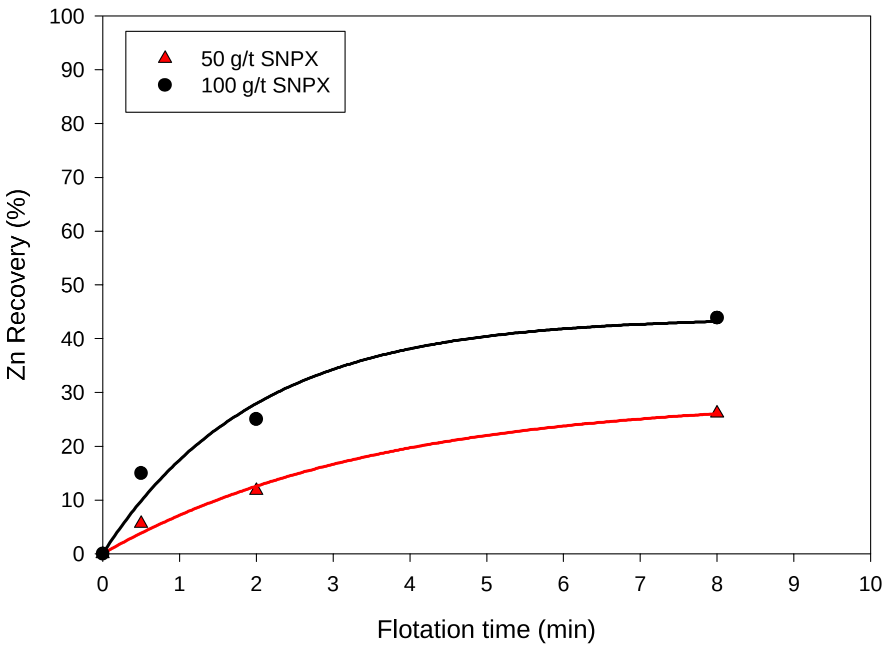


Figure 5.8. Flotation recovery of Zn in the lead rougher concentrate at two SNPX dosages at pH 8.5. Solid lines represent fitted curves.

These results showed that there is a direct correlation between the recoveries of galena and sphalerite, which is independent of the dosages and chain length of the xanthate collectors used.

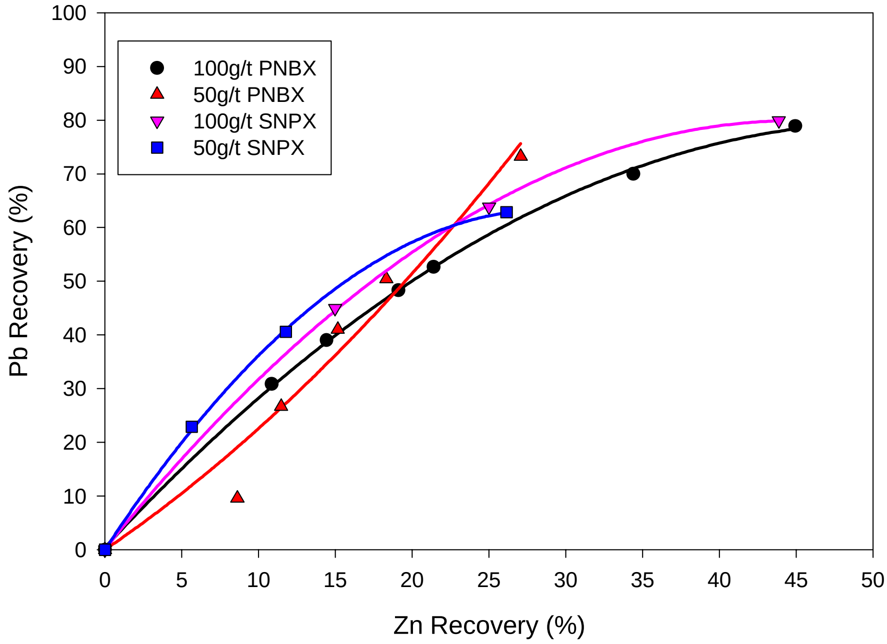


Figure 5.9. Flotation selectivity between galena and sphalerite from the Rosh Pinah ore at pH 8.5 after 8 minute of flotation time at various dosages of SNPX and PNBX

Figure 5.9 also showed that the recovery of sphalerite in the lead concentrate increased further with the recovery of galena when the dosage of xanthate increased from 50 to 100g/t, hence indicating that the selectivity was also affected by the flotation kinetics of both galena and sphalerite. In addition, it was observed that the recoveries of both galena and sphalerite increased with the increase of the concentrate mass pull (Table 5.2). It was also observed that the concentrate mass pull increased with increasing dosages and chain length of xanthate.

Table 5.2. Metallurgical results of the Rosh Pinah composite after 8 minutes of flotation time

REAGENTS		MASS PULL	RECOVERY (%)		GRADE (%)	
Name	Dosage	(%)	Pb	Zn	Pb	Zn
SNPX (MW = 158.2g)	50g/t (1.4x10^{-4}M)	7.9	62.3	26.2	13.8	24.0
	100g/t (2.8x10^{-4}M)	12.1	79.9	43.9	10.3	28.0
PNBX (MW = 188.4g)	50g/t (1.2x10^{-4}M)	10.1	73.2	27.1	9.5	18.4
	100g/t (2.4x10^{-4}M)	15.9	78.8	45.0	7.7	19.8

Note: The collector dosages are converted based on 2.2L of water in the flotation cell.

The lack of flotation selectivity observed with xanthate collectors in this study was in agreement with the reported results of additional flotation tests (Table 5.3) conducted at Kumba Resources by Bredenhann and Coetzer (2002).

Table 5.3. Metallurgical results of the Rosh Pinah composite after 10 minutes of flotation time in the presence of various dosages of sodium propyl xanthate (Bredenhann and Coetzer, 2002)

DOSAGE	MASS PULL	RECOVERY (%)		
(g/t)	(%)	Galena	Sphalerite	Pyrite
15	31.0	90.2	52.0	40.1
30	32.0	90.1	57.5	62.4
50	33.0	90.1	68.7	71.3

In their study, the flotation testwork was carried out after wet milling at 60%(w/w) solids. It was observed that the recovery of sphalerite in the rougher lead concentrate increased when the dosage of SNPX was increased from 15 to 50g/t. These results showed that the recovery of galena was not affected by the increase in the dosage of collector. The higher flotation recoveries of galena and sphalerite, even at lower xanthate dosage of 15g/t SNPX, can be related to the high concentrate mass pull of 31%. Since the recovery of the gangue has to be reduced in the concentrate, it is usually recommended to monitor both the concentration of collector and frother in such as way that less gangue is recovered with the valuable mineral (Seke et al., 2003a; Cho and Laskowski, 2002; Laskowski, 1993).

In practice, the concentration of collector can inadvertently increase when the recycled water, which contains residual flotation reagents, is used during the milling and flotation of the ore. Thus, improving the flotation selectivity in the presence of high concentrations of xanthate may require the use of excessive amounts of depressant. As an illustration, Figure 5.10 shows the flotation results of a preliminary test whereby the selectivity between galena and sphalerite could slightly be improved with lower dosage of cyanide (20g/t NaCN) in the presence of 50g/t PNBX.

The concentrate mass pull and the recovery of galena at various dosages of sodium cyanide concentration are shown in Figure 5.11, while the recovery of sphalerite is shown in Figure 5.12. The concentrate mass pull decreased slightly from 10.2 to 8.8 when 20g/t NaCN was used for the depression of sphalerite. However, the recovery of galena increased from 75 to approximately 80% with the addition of cyanide, while the recovery of sphalerite decreased from approximately 38 to 28%. In addition, both the recovery and grade of galena were improved when cyanide was used to depress the flotation of sphalerite (Figure 13). The effect of cyanide on the depression of sphalerite will be discussed in details in Chapter 7.

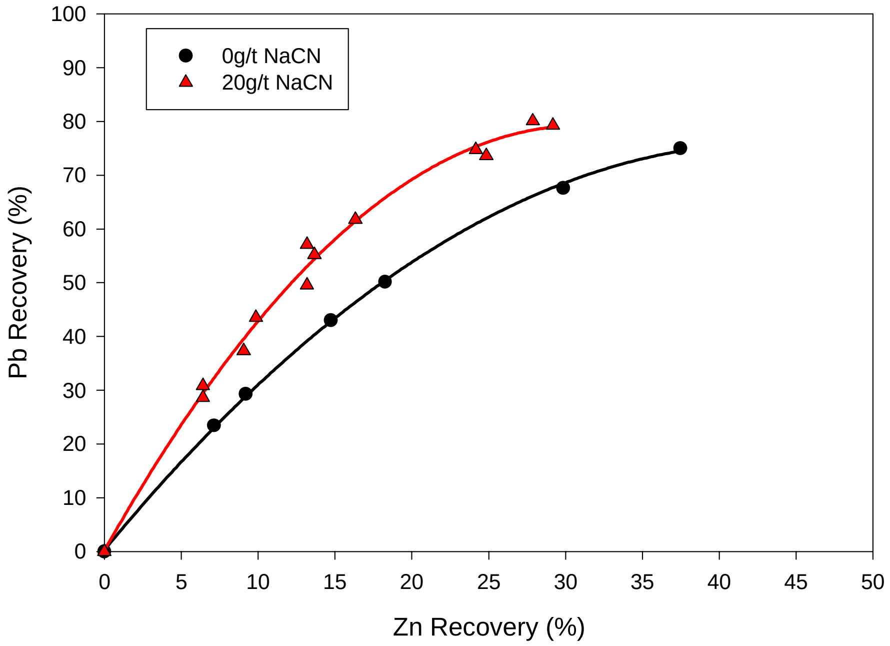


Figure 5.10. Flotation selectivity between galena and sphalerite from the Rosh Pinah composite at pH 8.5 after 12 minutes of flotation time at various dosages of NaCN and 50g/t PNBX.

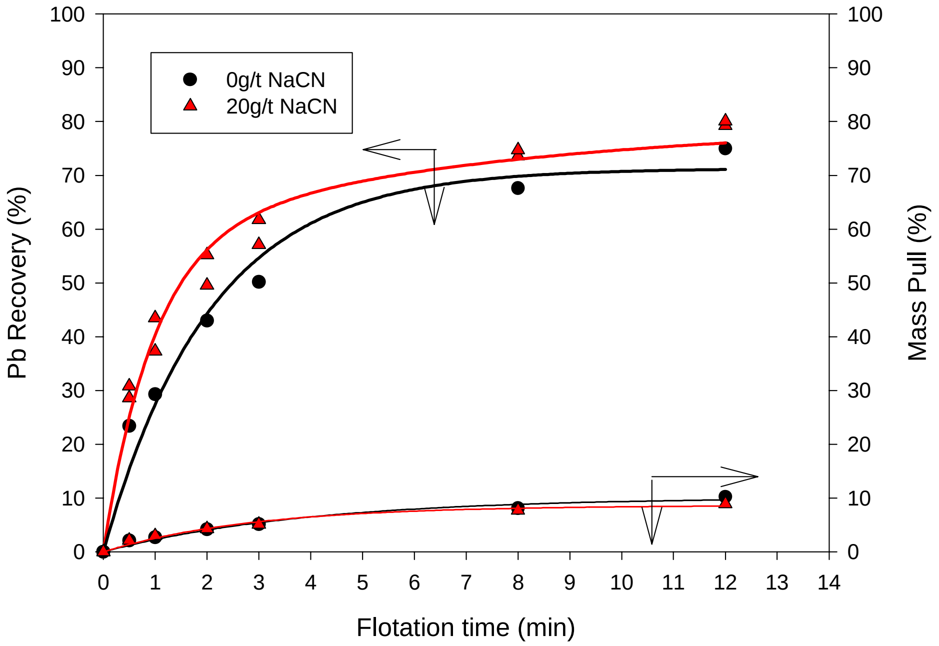


Figure 5.11. Flotation recovery of Pb in the lead rougher concentrate as a function of NaCN dosage in the presence of 50g/t PNBX. Solid lines represent fitted curves.

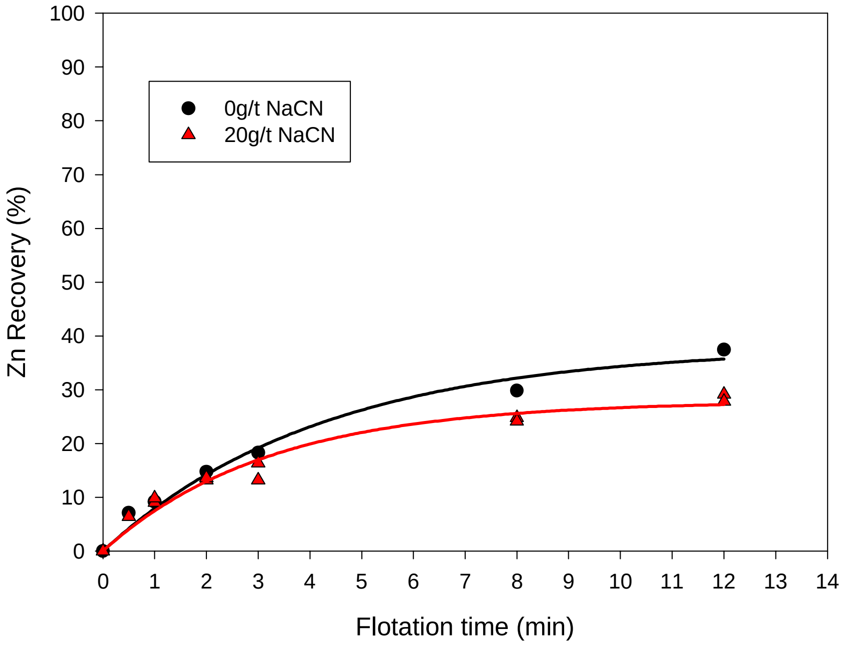


Figure 5.12. Flotation recovery of Zn in the lead rougher concentrate as a function of NaCN dosage in the presence of 50g/t PNBX. Solid lines represent fitted curves.

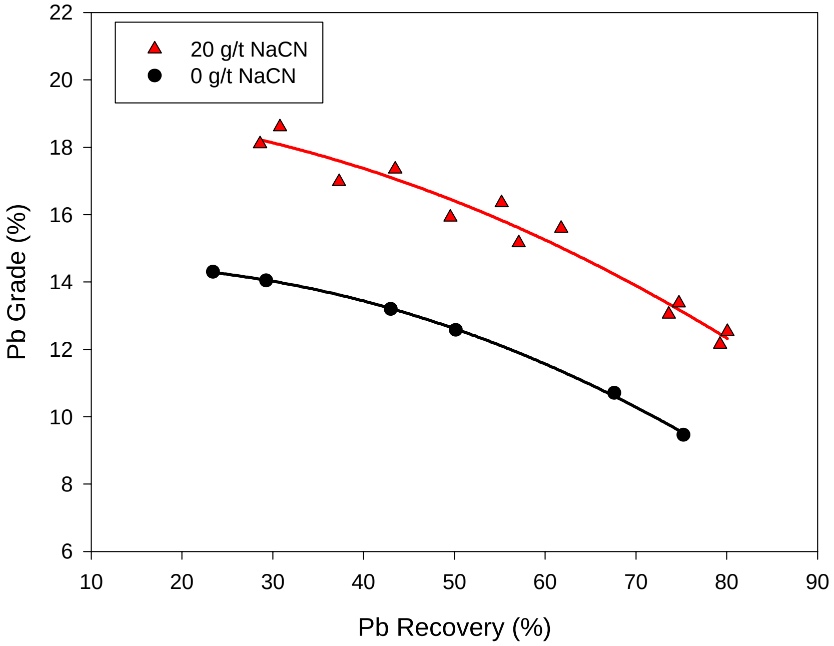


Figure 5.13. Lead recovery-grade relationship in the lead rougher concentrate at various concentration of NaCN in the presence of 50g/t PNBX. Solid lines represent fitted curves.

The effect of dissolved metal ions on the flotation response of the Rosh Pinah ore will be discussed in the next section.

5.3. Effect of Pb(II) and Cu(II) ions on the activation of sphalerite

It is well known that pure sphalerite does not float easily in the presence of xanthate collectors. Usually the recovery of sphalerite from single minerals in alkaline media (Rashchi et al., 2002; Trahar et al., 1997) is related to the impurities in the sphalerite lattice and to the entrainment of the sphalerite. In plant practice, the presence of sphalerite in the lead concentrate is usually related to the inadvertent activation of sphalerite by heavy metal ions such as copper or lead, which are often the products of the oxidation and/or dissolution of the complex sulphide ore. The effect of Pb(II) ions on the flotation response of the Rosh Pinah composite used in this study is discussed in the following section.

5.3.1. Activation of sphalerite with Pb(II) ions

The flotation test was carried out at the natural pH of 8.5 to study the selectivity between galena and sphalerite in the presence of various dosages of Pb(II) ions. The lead ions were added in the flotation cell and the pulp was conditioned for 30 minutes before the addition of 50 g/t PNBX. The concentrate mass pull and flotation recoveries of galena and sphalerite in the presence of 0, 50, 100 and 200ppm Pb(II) are presented in Figure 5.14 and summarised in Table 5.4.

Table 5.4. Metallurgical results of the Rosh Pinah composite after 12 min flotation time in the presence of 50 g/t PNBX and various concentrations of lead nitrate at pH 8.5

Activator	Mass Pull	Recovery (%)		Grade (%)	
$Pb(NO_3)_2$	(%)	Pb	Zn	Pb	Zn
0 M	12.1	81.9	32.5	8.9	18.5
50ppm Pb(II) (2.4×10^{-4}M)	11.1	67.7	32.9	8.1	20.1
100ppm Pb(II) (4.8×10^{-4}M)	9.6	54.2	32.3	8.4	20.2
200ppm Pb(II) (9.7×10^{-4}M)	10.7	55.6	36.1	8.6	20.9

The recovery of sphalerite increased slightly from approximately 33 to 36% after the addition of 9.7×10^{-4}M Pb(II), while the concentrate mass pull was approximately the same (Table 5.4). In addition, the recoveries of sphalerite were similar before and after the additions of 2.4×10^{-4} and 4.8×10^{-4}M Pb(II), whereas the recovery of galena decreased drastically in the presence of added lead ions.

Figure 5.15 shows the relationship between the recovery and the grade of zinc in the lead concentrate before and after the additions of Pb(II) ions. It can be seen that although the final recovery increased slightly when 9.7x10^{-4}M Pb(II) was used, the grade of zinc in the galena concentrate increased slightly from 18.5 to 20.9% with the additions of lead nitrate into the pulp.

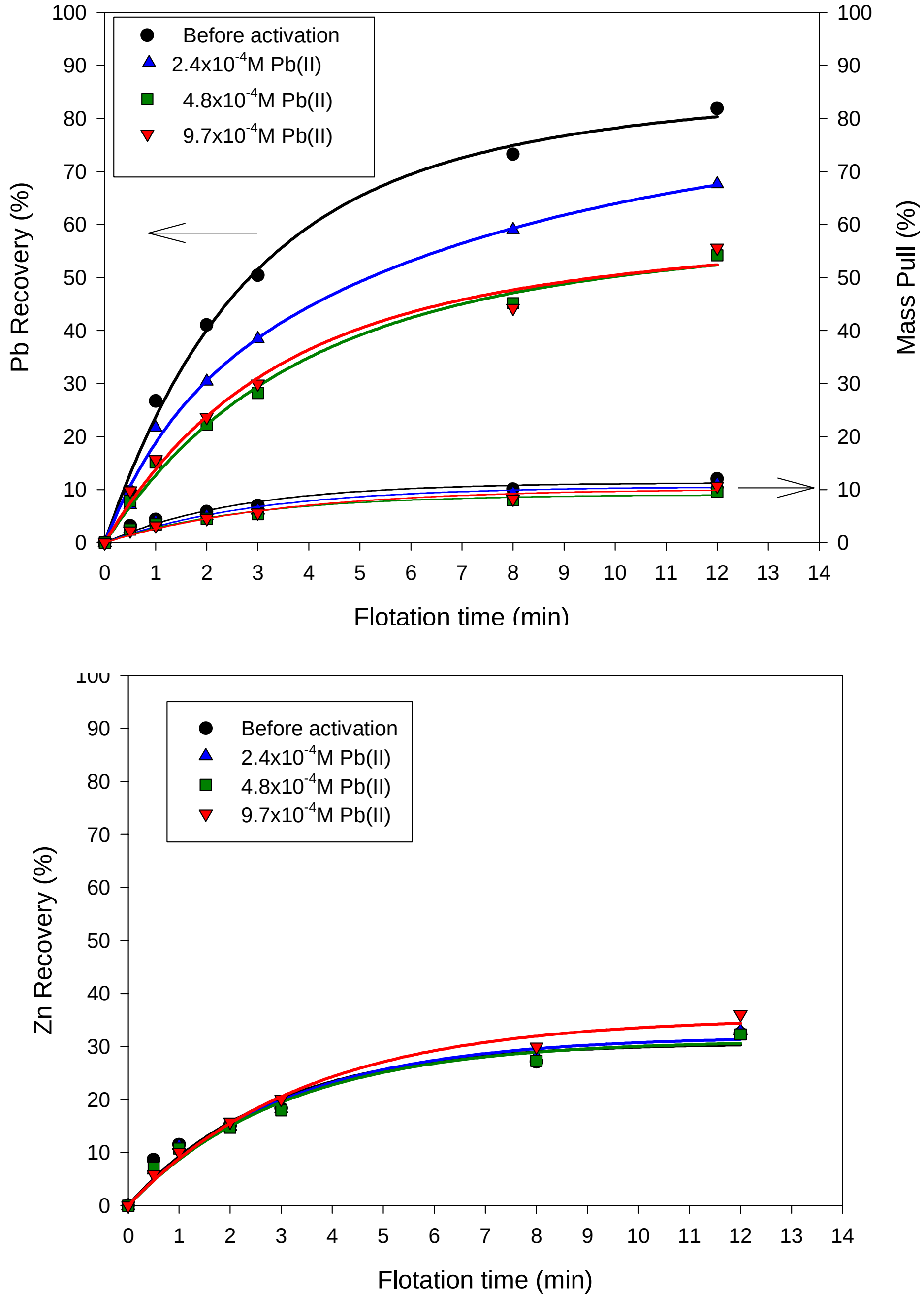


Figure 5.14. Recoveries of galena and sphalerite in the presence of various concentrations of Pb(II) and 50 g/t (1.2x10^{-4}M) PNBX at pH 8.5. Solid lines represent fitted curves.

However, the observed increase in grade of zinc was probably due to the decrease in the recovery of lead in the galena rougher concentrate as shown in Figure 5.14.

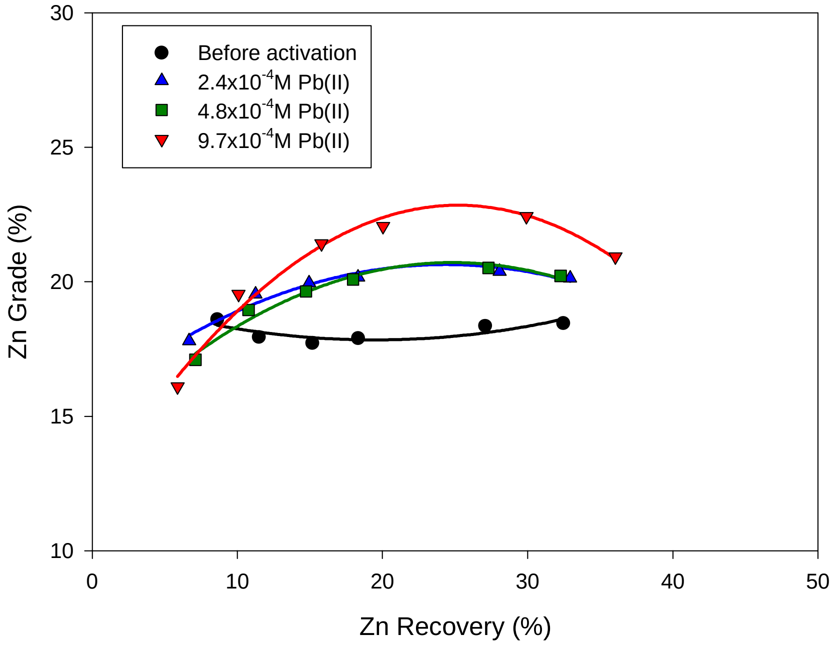


Figure 5.15. Zinc recovery-grade relationship in the absence and presence of various concentration of lead nitrate and 50 g/t ($1.2x10^{-4}$M) PNBX at pH 8.5

The flotation results of sphalerite from the Rosh Pinah composite used in this study are not in agreement with the reported results of Rashchi et al. (2002) and Trahar et al. (1997) where either single sphalerite minerals or a mixture of sphalerite and quartz were used.

Micro-flotation tests were carried out by Rashchi et al. (2002) in order to study the effect of pH on the activation of sphalerite (single mineral) by lead ions. They observed that for flotation conducted at pH 9, the recovery of sphalerite activated at acidic and neutral pH values (pH 5-7) increased with the concentration of added lead up to about $4.8x10^{-4}$M Pb(II). In addition, the recovery of sphalerite was lower when the activation occurred at alkaline pH values (pH 9-11). The flotation results of the Rosh Pinah composite indicated that the recovery of sphalerite was not highly improved for Pb(II) concentrations used in this study. However, batch flotation results from the study of Trahar et al. (1997) indicated that the recovery of sphalerite, from a sphalerite-quartz mixture, increased with the concentration of added Pb(II) when both the activation and the flotation were carried out at pH 9. The discrepancies found in various studies are probably due to the nature of the mineral surface prior to flotation and/or to the flotation conditions used. Thus, it is believed that the dry milling of the complex Rosh Pinah composite had an influence on the surface properties of the galena and sphalerite. It is also believed that the flotation of galena was drastically decreased in the presence of $Pb(OH)_2$ on its surface, and hence adversely affected the interaction between xanthate and galena. It is well known that the presence of oxidation products on the surface of galena will adversely affect the adsorption of the xanthate collector onto galena.

Since the flotation testwork was carried out at alkaline pH values, the thermodynamic calculations predicted $Pb(OH)_2$ to be the most predominant species at the flotation pH of 8.5±0.2 (Figure 5.16).

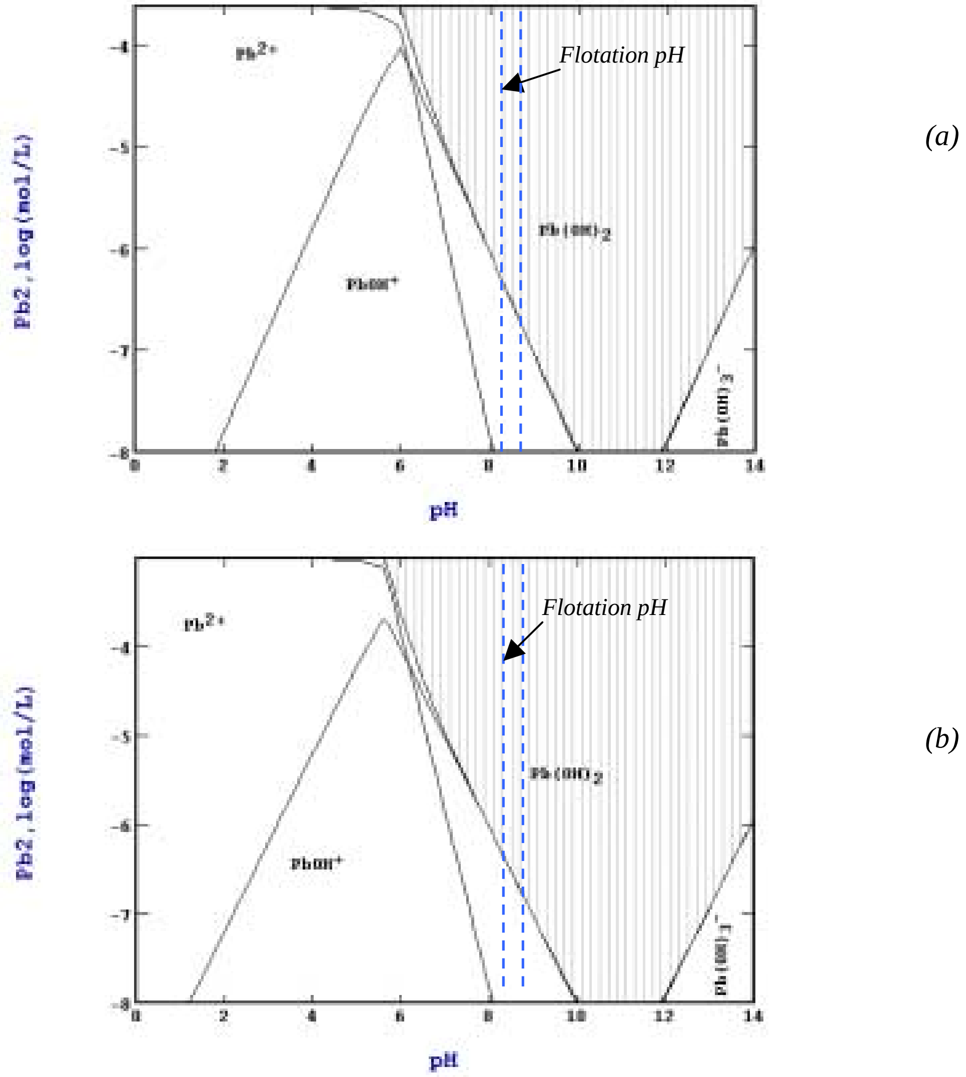


Figure 5.16. Solubility diagram for Pb(II) as a function of pH at 25°C. Total lead concentration: (a) $2.4x10^{-4}M$ and (b) $9.7x10^{-4}M$. Stabcal software, NBS database (Huang, 2003). Shaded area shows the solid species.

As seen in Figure 5.16, the onset of $Pb(OH)_2$ precipitation is at approximately pH 6 for the lead concentration used in this study. Figure 5.16 also showed that the concentration of Pb^{2+} species would be lower than 10^{-8}M at the natural pH (8.5) of the ore. Thus, the activation of sphalerite would mainly be affected by $Pb(OH)_2$ species when Pb(II) is added into the flotation pulp at alkaline pH values used in this study and in the work of Trahar et al. (1997).

When using single sphalerite minerals, Rashchi et al. (2002) supported the mechanism by which $PbOH^+$ was the activating species at mildly alkaline pH (7-10), while Trahar et al. (1997) showed that $Pb(OH)_2$ was the activating species. The activation mechanism of sphalerite by lead hydroxide, which is the most stable species at alkaline pH, was still unclear in the study of Trahar et al. (1997). They indicated that although $Pb(OH)_2$ was present on the sphalerite surface, it did not subsequently convert to the sulphide form to promote the flotation of sphalerite with the xanthate collector. Hence, the observed increase in the recovery of sphalerite could not necessarily be related to the amount of Pb(II) added into the flotation pulp.

The observed decrease in the flotation recovery of galena after the additions of Pb(II) (Figure 5.14) indicated that the hydrophilic $Pb(OH)_2$ species precipitated/adsorbed unselectively on both sphalerite and galena during the activation of the ore. In addition, the dry milling of the ore and the long activation time of 30 minutes prior to the flotation could also have contributed to the presence of more oxidation products on the surface of galena and to the subsequent poor flotation selectivity (O’Dea et al., 2001). O’Dea et al. (2001) showed that the adsorption of xanthate onto oxidised galena surfaces was not favourable as compared to unoxidised galena.

Parallel to the current study, more flotation testwork was carried out at Kumba Resources R&D by Bredenhann et al. (2001) after wet milling (60% solids). In their study, Bredenhann et al. (2001) added the Pb(II) ions in the mill, while the xanthate and frother were added in the flotation cell. As seen in Figure 5.17, the recovery of sphalerite increased from 43.1 to 65% when the dosage of Pb(II) in the mill increased from 0 to 800 ppm (3.86×10^{-3}M). The lower recovery of sphalerite obtained in the presence of 400ppm of Pb(II) (1.93×10^{-3}M) was due to poor reproducibility of the flotation test. The results of Bedenhann et al. (2001) showed that the concentrate mass pull obtained at 400ppm Pb(II) was lower as compared to that obtained at 0 and 800ppm Pb(II). Our earlier results have shown that the recovery of sphalerite in the lead concentrate was also related to the mass pull.

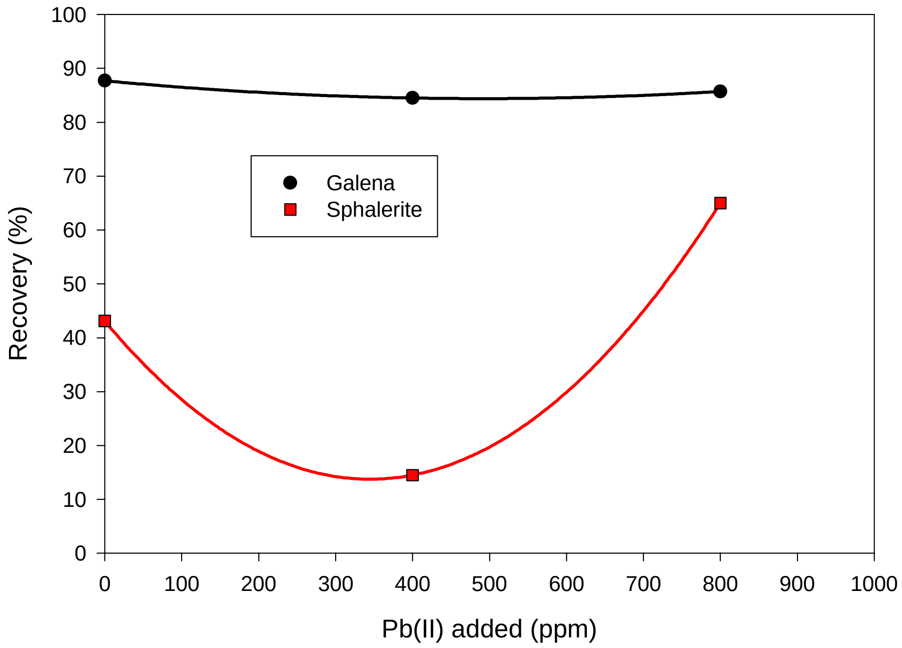


Figure 5.17. Effect of added Pb(II) on the recovery of galena and sphalerite with 50g/t SNPX and Senforth 6005 (Bredenhann et al., 2001). Solid lines represent fitted curves.

Unlike in the case of dry milling and long conditioning time, the recovery of galena only decreased slightly from approximately 88 to 86% after the addition of 800 ppm Pb(II). Therefore, it became clear that the effect of added Pb(II) on the flotation behaviour of the Rosh Pinah ore was strongly influenced by the milling environment, the conditioning time and the dosage of Pb(II) species.

The nature of the activating species was studied by XPS analysis of the surface of a natural sphalerite mineral after activation by Pb(II) at alkaline pH and the results are presented in the following section.

5.3.2. XPS analysis of Pb(II)- activated sphalerite samples

XPS analysis of the sphalerite sample was carried out after its activation by lead nitrate at pH 9.2 controlled by sodium tetraborate as discussed in Chapter 4. The XPS spectra of the sphalerite sample before and after activation by 3x10^{-3}M Pb(II) are presented in Figure 5.18.

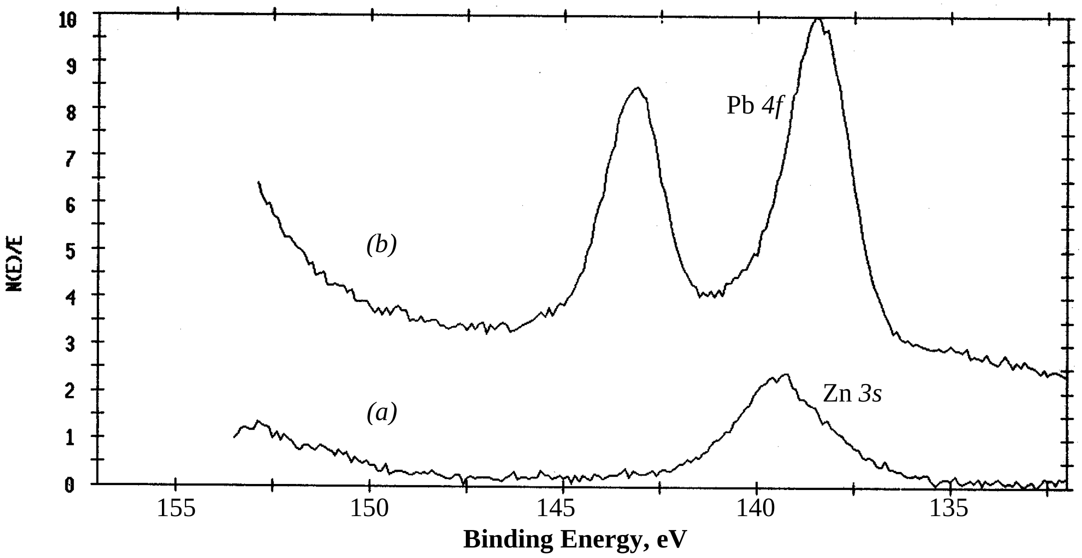


Figure 5.18. XPS photoelectron spectra obtained on a sphalerite surface at pH 9.2. (a) in the absence of Pb(II), (b) and in the presence of 3x10^{-3}M Pb(II).

The presence of lead species on the surface of sphalerite was clearly shown by the lead doublet peak (Pb *4f*) on the spectrum *(b)* when the sphalerite was activated by Pb(II) at pH 9.2. The single peak at about 140 eV on spectrum *(a)* was assigned to Zn *3s* from the unactivated sphalerite. The XPS results on the activation of sphalerite mineral by Pb(II) have shown that lead species were present on the surface of sphalerite. The relative intensities of the peaks have arbitrary units for comparison purposes.

The surface atomic concentrations of sphalerite samples treated in the absence and presence of Pb(II) are given in Table 5.5.

Table 5.5. Elemental surface concentrations of sphalerite samples determined by XPS

Conditioning	XPS atomic concentration (%)				
(time: 30 minutes)	Zn *2p*	C *1s*	S *2p*	O *1s*	Pb *4f*
0 M Pb(II), pH 9.2	6.9	65.5	18.1	9.5	0
3x10^{-3} M Pb(II), pH 9.2	3.3	65.9	14.6	14.3	1.9

Conditioning the sphalerite sample in a solution containing 3x10^{-3} M Pb(II) gave a Pb/Zn atomic concentration ratio 0.576, which indicated that approximately 42% of the sphalerite surface was covered by lead species. Basilio et al. (1996) obtained a

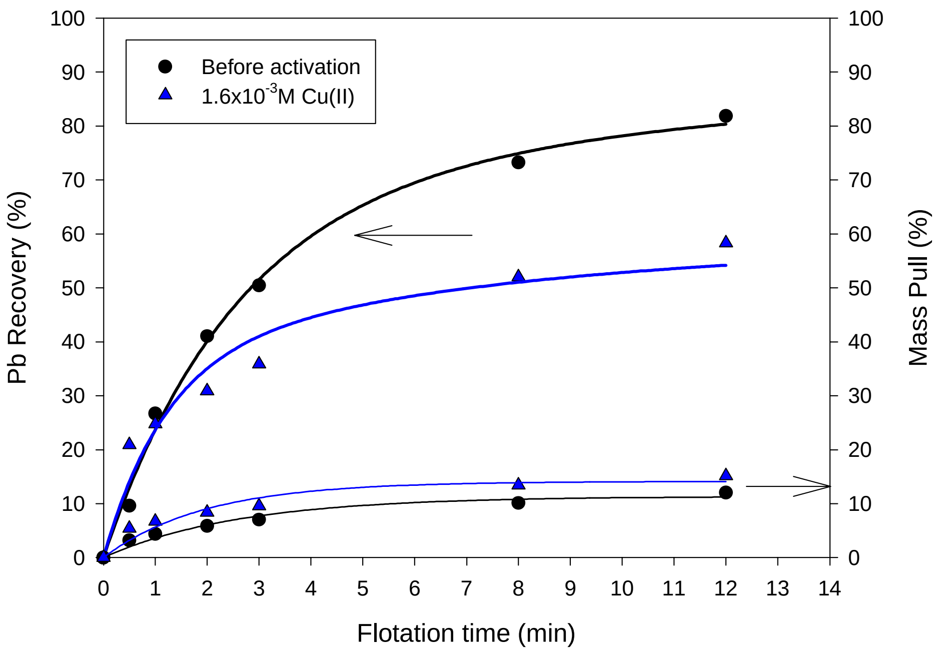
Pb/Zn atomic concentration ratio of 0.085 after the activation of a sphalerite probe in a 10^{-4}M Pb(II) solution for 1 minute. They also showed the presence of lead xanthate and dixanthogen when the activated sphalerite probe was conditioned in the presence of 10^{-4}M PAX.

The results presented in Table 5.5 indicated that the atomic concentration of oxygen increased after the activation of sphalerite by Pb(II) at pH 9.2, hence the presence of lead hydroxide on the surface of sphalerite could not be excluded although the atomic concentration of sulphide was still higher (14.6%) when compared to the decrease of about 50% in the atomic concentration of zinc.

The effects of grinding conditions and dissolved Cu(II) ions on the flotation behaviour of the Rosh Pinah composite are discussed in the following section. Since the results of the water survey presented in Table 1.1 indicated the presence of up to 80 ppm of copper in the Rosh Pinah process water, a total copper concentration of 100 ppm was used in this study.

5.3.3. Activation of sphalerite with Cu(II) ions

The activation of the Rosh Pinah composite by Cu(II) was conducted in the presence of copper sulphate. The composite was dry milled and the flotation pulp was conditioned for 30 minutes after the addition of copper sulphate prior to the addition of 50g/t PNBX and frother. The effect of 100 ppm Cu(II) ($1.6\text{x}10^{-3}$M) on the concentrate mass pull and the recoveries of galena and sphalerite is shown in Figure 5.19. As expected, the recovery of sphalerite increased from about 32 to approximately 80% after the addition of $1.6\text{x}10^{-3}$M Cu(II) in the pulp. The concentrate mass pull also increased from 12 to 15.2% after the addition of copper sulphate. In addition, the increase in the recovery of sphalerite in the lead rougher concentrate was accompanied by a decrease in the recovery of galena from 82 to 58% when copper sulphate was added in the flotation pulp (Figure 5.19).



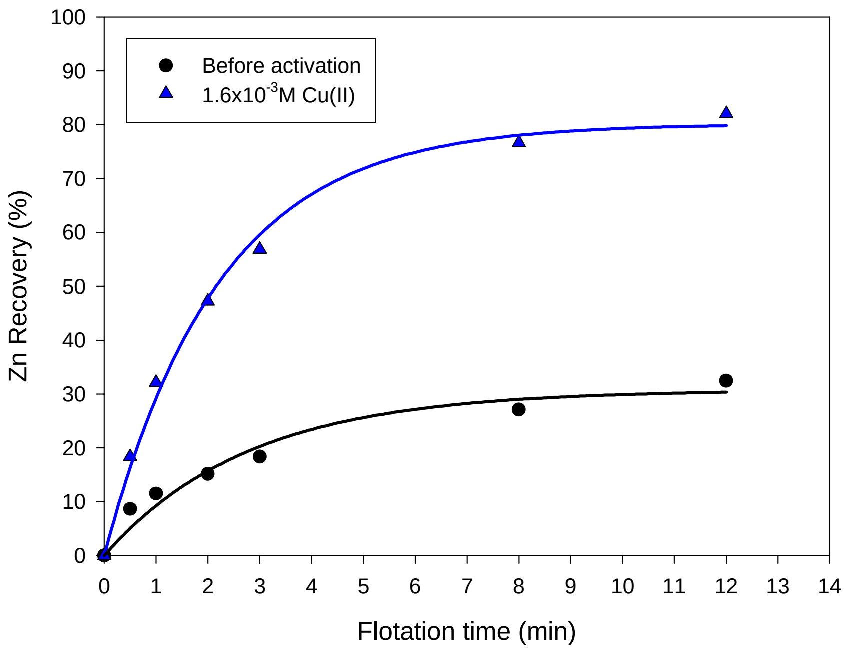


Figure 5.19. Effect of copper sulphate activation on the recovery of lead and zinc with 50 g/t (1.2x10^{-4}*M) PNBX at pH 8.5. Solid lines represent fitted curves.*

Figure 5.20 shows that $Cu(OH)_2$ is the predominant species in the range of alkaline pH used in this study, with the onset of $Cu(OH)_2$ precipitation being at pH 5.0. The mechanism of copper activation at alkaline pH is well understood and has been discussed in Chapter 2. It is generally accepted that the precipitation and adsorption of $Cu(OH)_2$ on the surface of sphalerite occurs at alkaline pH. This is usually followed by the reduction of Cu(II) to Cu(I) and the oxidation of S species. The presence of Cu(I) on the surface and in the lattice of sphalerite will then promote its flotation in the presence of xanthate. The decrease in the recovery of galena after activation of sphalerite by Cu(II) is mainly due to the presence of hydrophilic $Cu(OH)_2$ on the surface of galena.

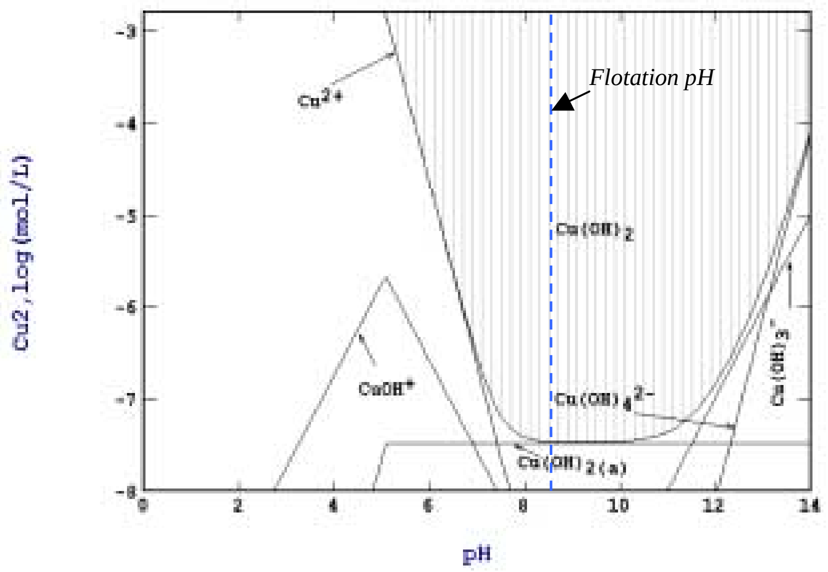


Figure 5.20. Speciation diagram for Cu(II) as a function of pH for [Cu] = $1.6x10^{-3}$M at 25°C. Stabcal software. NBS database (Huang, 2003). Shaded area shows the solid species.

Additional testwork was carried out after wet milling (60% solids) of the ore sample and shorter activation time by Bredenhann et al. (2001). The flotation recoveries of galena and sphalerite are presented in Figure 5.21. As seen in Figure 5.21, the recovery of sphalerite increased after the additions of Cu(II). However, the additions of a higher amounts of Cu(II) (800 ppm or 1.26x 10^{-2}M Cu(II)) decreased sphalerite recovery. It was also observed that the recovery of galena decreased when Cu(II) was added, as was the case after dry milling. It was interesting to observe that the activation of sphalerite by Cu(II) was not strongly affected by the milling conditions and conditioning time, unlike the activation by Pb(II) where only the wet ground sample showed better recovery of lead-activated sphalerite. The results presented in Figures 5.19 and 5.21 show that the activation of sphalerite by Cu(II) ions and its subsequent flotation are similar for wet and dry grinding. It is unfortunate that Bredenhann et al. (2001) did not generate additional data for Figure 5.21.

Since both dissolved copper and lead ions are generally found in the process water, their combined effect on the activation of sphalerite was also studied. The Rosh Pinah composite was dry milled as discussed in Chapter 4. Both copper sulphate and lead nitrate solutions were added simultaneously in the flotation cell and the pulp was conditioned for 30 minutes prior to the addition of collector. The recoveries of galena and sphalerite in the presence of 100ppm (1.6×10^{-3}M) Cu(II) and 100ppm (4.8×10^{-4}M) Pb(II) are shown in Figures 5.22-5.23, respectively.

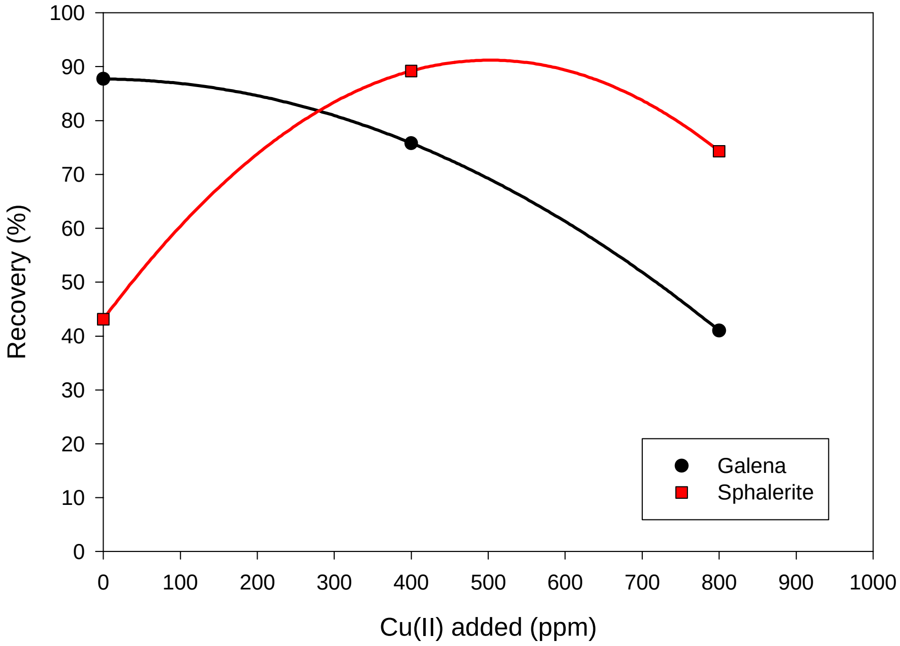


Figure 5.21. Effect of added Cu(II) on the recovery of galena and sphalerite with 50g/t SNPX and Senforth 6005 (Bredenhann et al., 2001). Solid lines represent fitted curves.

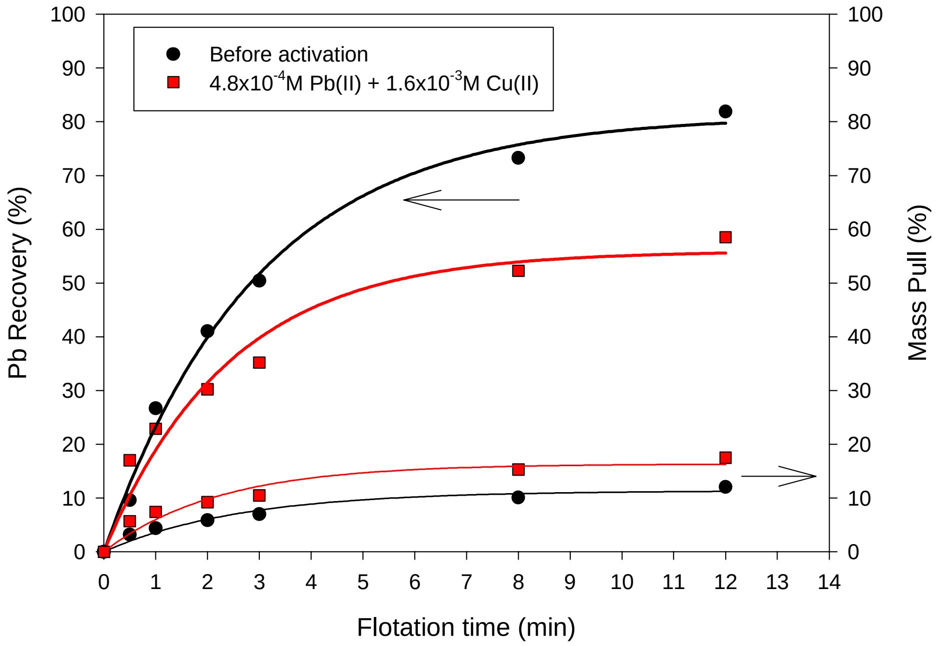


Figure 5.22. Flotation recovery of galena with and without added Cu(II) and Pb(II) in the presence of 50 g/t (1.2×10^{-4}M) PNBX at pH 8.5. Solid lines represent fitted curves.

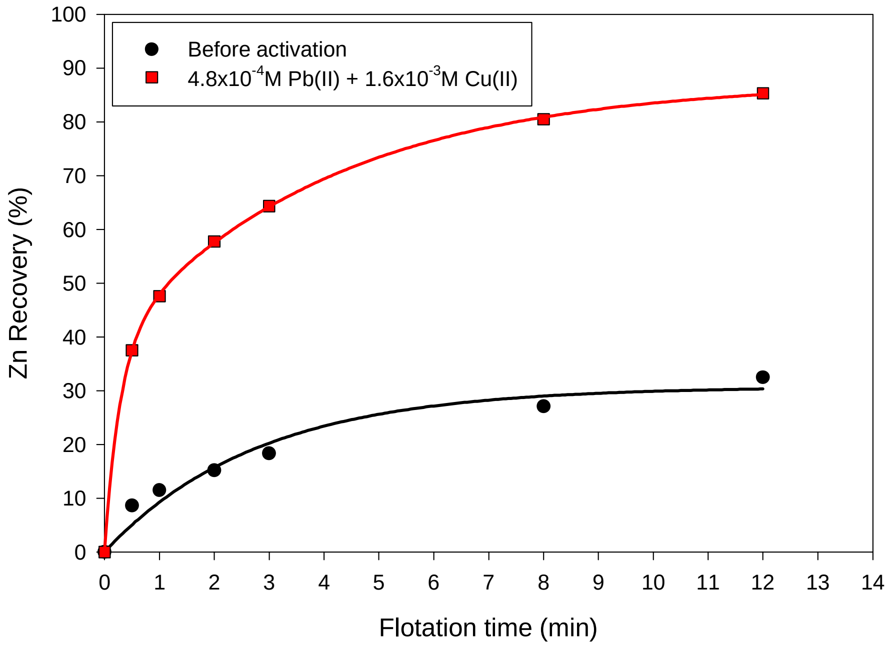


Figure 5.23. Flotation recovery of sphalerite with added Cu(II) and Pb(II) in the presence of 50 g/t (1.2x10^{-4}M) PNBX at pH 8.5. Solid lines represent fitted curves.

The concentrate mass pull increased from 12 to 17.5% in the presence of both 100ppm Cu(II) and 100ppm Pb(II), while the recovery of galena decreased from approximately 82 to 59%. However, the recovery of sphalerite increased from approximately 33 to 85% when both copper and lead ions were added. These results are very similar to those found with copper additions alone (see Figure 5.24 and Table 5.6 for a comparison of the sphalerite recoveries), hence indicating the strong effect of copper on the activation and flotation of sphalerite.

Table 5.6. Metallurgical results of the Rosh Pinah composite in the presence of 50 g/t PNBX and various concentrations of copper sulphate and lead nitrate at pH 8.5 (12 min flotation time)

Activator	Mass Pull	Recovery (%)		Grade (%)	
	(%)	Pb	Zn	Pb	Zn
0 M	12.1	81.9	32.5	8.9	18.5
4.8x10^{-4}M Pb(II)	9.6	54.2	32.3	8.4	20.2
1.6x10^{-3}M Cu(II)	15.2	58.4	82.1	5.7	26.6
1.6x10^{-3}M Cu(II) + 4.8x10^{-4}M Pb(II)	17.5	58.5	85.3	5.5	30.9

Figure 5.25 illustrates that the flotation selectivity between galena and sphalerite was adversely affected by the presence of either Cu(II) or Pb(II), although Cu(II) had the more detrimental effect under the experimental conditions used in this study.

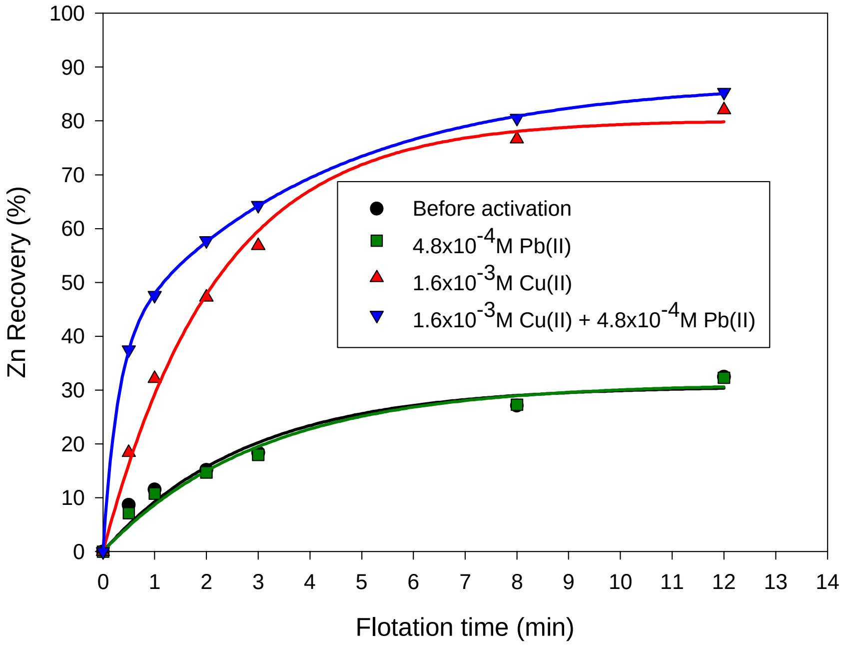


Figure 5.24. Zinc recovery-grade relationship with added Cu(II) and Pb(II) in the presence of 50 g/t (1.2x10^{-4}*M) PNBX at pH 8.5. Solid lines represent fitted curves.*

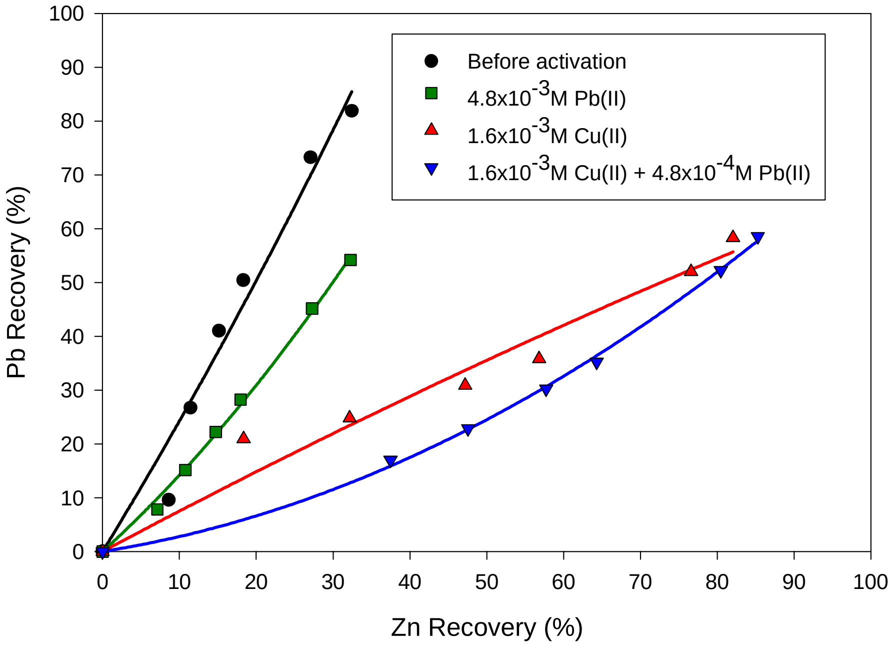


Figure 5.25. Flotation selectivity between galena and sphalerite as a function of added Cu(II) and Pb(II) in the presence of 50 g/t (1.2x10^{-4}*M) PNBX at pH 8.5. Solid lines represent fitted curves.*

5.4. Conclusion

Batch flotation testwork was carried out on a complex lead-zinc sulphide composite from the Rosh Pinah Mine with XPS analysis of lead-activated sphalerite. The effects of collector dosages and chain length, dissolved heavy metals such as Cu(II) and Pb(II), and grinding conditions (wet or dry) on the flotation selectivity between galena and sphalerite were studied. It has been shown that the recovery of galena was higher when xanthate of longer chain length such as PNBX was used under the flotation conditions described in this study. It was also shown that xanthate collectors are not selective for the composite used in this study.

The activation of sphalerite by Pb(II) was not efficient when the ore was milled in a dry environment using mild steel mill and grinding media. In addition, the flotation of galena was adversely affected under these conditions. When the ore was wet milled, activation of sphalerite and its subsequent flotation was improved at high dosage (3.9×10^{-3}M Pb(II)).

It was interesting to observe that the flotation of Cu(II)-activated sphalerite by Cu(II) was independent of the grinding conditions (wet or dry). The recovery of sphalerite was significantly increased in the presence of 100 ppm of Cu(II), while the recovery of galena in the lead circuit was decreased. When both Cu(II) and Pb(II) were added, the flotation of sphalerite was similar to that with only Cu(II) additions.

Since sodium cyanide is added in the mill to prevent the activation of sphalerite by copper activating species, it is believed that the copper present in the recycle process water might also be in the form of cuprous cyanide species instead of Cu(II) only. Thus, it is important to study the possibility of sphalerite activation in the presence of copper-cyanide complexes under both dry and wet milling conditions in order to understand the conditions that may affect the flotation selectivity in the lead flotation circuit at the Rosh Pinah Mine due to the recirculation of process water. This matter will be discussed in the next Chapter.

Chapter 6. Effect of cuprous cyanide, dry and wet milling on the selective flotation of galena and sphalerite

6.1. Introduction

The previous chapter has shown the detrimental effect of Cu(II) on the flotation selectivity between galena and sphalerite from the Rosh Pinah ore. It is usually assumed that the copper species that activate sphalerite in the lead flotation circuit originate from the bulk of the ore and from the process water used at the plant. This is supported by the results of a water survey conducted recently at the Rosh Pinah Mine by Coetzer et al. (2003) as reproduced in Table 6.1.

Table 6.1. Detailed analyses of water resources of Rosh Pinah Mine (After Coetzer et al., 2003). Assays in mg/l

	Western borehole	Eastern borehole	Lead tailings thickener (P22)	Lead concentrate thickener
Quantity (m^3/h)	15	8	4	120
pH	7.8	8	8.5	8.9
Total alkalinity	125	120	219	197
Cu	0.01-1.0	0.05	17.2	30
Zn	1.7	1.4	0.34	10
Pb	0.4	0.2	0.33	0.5
Fe	0.4	1.4	0.09	0.12
Ba	<0.01	0.07	0.22	0.12
Ag	<0.01	<0.01	0.03	2.75
Free cyanide	<0.01	0.15	53	60
Sulphate	800	750	309	185
Nitrate	40	17	15	2
Ca	275	150	45	18
Mg	190	100	72	19
TDS	2450	1400	949	825
TOC	3	5	43	71

TDS = Total dissolved solids
TOC = Total organic carbon

As seen in Table 6.1, the quantities of recycled water from the tailings (P22) and lead concentrate thickeners represent 2.7 and 81.6% of the total water resources. As shown in Figure 3.4, water from P22 is mainly used in the milling circuit, while water from the lead concentrate thickener is used in the lead flotation circuit. In addition, 17.2 and 30 mg/l of copper was present in the overflow of the lead tailings and lead concentrate thickeners, respectively. It was also observed that the amount of dissolved lead was lower than in the earlier survey (which is reproduced in Table 1.1). Although the decrease in dissolved lead was not explained by Coetzer et al. (2003), it was assumed that this was due to the fact that the plant was going through different phases of process optimisation that included the management of water resources. Seasonal change is also known to affect the chemical and biological composition of process water. Based on the copper content in the recirculating water, only the effect of dissolved copper on the flotation response of the Rosh Pinah composite ore will be studied in this Chapter. The effect of residual flotation reagents is out of the scope of this study, although it is known that residual reagents and surface active substances present in plants process water usually affect the flotation response of the ore.

Since sodium cyanide is added in the mill to depress the flotation of copper-activated sphalerite by complexation of free cyanide and copper, it is believed that the process water from the lead tailings thickener (P22), which is recycled to the milling circuit, will contain considerable amount of cuprous cyanide species. However, as seen in Table 6.1, the molar concentration ratio of free cyanide to copper in the P22 and lead concentrate thickener is approximately 7 and 5, respectively. This is much higher than the ratio of 2 in the $Cu(CN)_2^-$ complex. Thus, it was assumed that either the dosage of sodium cyanide in the mill was very high or the cuprous cyanide complexes formed during the deactivation of sphalerite decomposed to release free cyanide in the system.

Chapter 5 showed that the Rosh Pinah composite ore shows different activation and flotation responses after wet and dry milling. This is in line with the results of Yuan et al. (1996), where it was found that the grinding environment is the most predominant variable influencing the flotation of minerals. In addition, the oxidation of the minerals following mining and during milling can affect flotation selectivity significantly. The oxidation of sulphide minerals can be affected by the presence of oxidants such as air and the dissolved oxygen in the water, and also by the presence of other sulphide minerals in direct contact with the mineral under consideration (Arbiter, 1985). It is also known that oxidation reactions during milling can affect the concentration of cyanide.

In the case of lead-zinc ore, it has been reported that the flotation of sphalerite in the lead circuit can be enhanced by autogenous grinding and stainless steel grinding media (Martin et al., 1991). Woods (1996) has shown that the flotation of galena increased with increasing potential (from -100 mV SHE). Guy and Trahar (1984) reported that high pulp potentials in stainless, autogenous and ceramic mills are favourable for the flotation of galena. However, mild steel media showed excellent selectivity between galena and sphalerite. This was suggested to be due to galvanic interactions between minerals themselves and between minerals and grinding media.

O'Dea et al. (2001) have shown that the kinetics and mechanism of xanthate adsorption on the surface of galena was affected by the extent of its oxidation. Their conclusions can be summarised as follow:

- At low xanthate concentration (10^{-5}M) and high pulp potential, freshly cleaved galena surfaces showed very low xanthate adsorption due to dissolution, while adsorption of colloid PbX_2 was observed at high xanthate concentration (10^{-2}M);
- Oxidised galena surfaces had relatively low concentrations of adsorbed xanthate compared to freshly cleaved surfaces at both low and high xanthate concentrations and low and high Eh. In addition, colloidal PbX_2 was not found even at high xanthate concentrations due in part to surface oxidation products passivating against continuing dissolution.

For the flotation of galena to occur at lower xanthate dosages (approximately 10^{-4}M, see Chapter 5) used at the Rosh Pinah plant, it is believed that its oxidation is not so extensive as to cause the absence of PbX_2 that was observed by O'Dea et al. (2001). However, partial oxidation of galena will always occur under the conditions used at the plant, and the rate and extent of the oxidation can hinder the floatability of various minerals present in the composite ore.

Since corrosion processes are favoured by wet conditions, it might be expected that more corrosion products will be generated during wet grinding. However, studies on the oxidation of galena in both air and aqueous environments (Nowak et al., 2000; Ralston, 1994) have indicated that less oxidation product, mainly $Pb(OH)_2$, was found at the surface of galena in the aqueous environment, while lead carbonate was the main oxidation product in air. Therefore, the ion exchange mechanism between the xanthate and hydroxide and/or carbonate (galena oxidation products) and the subsequent flotation of galena can be affected by the grinding environment.

The experimental results on the effects of the grinding environment on the pulp chemistry and the flotation response of the Rosh Pinah composite are discussed in the following sections. As mentioned previously, the present study was limited to the rougher stage of the lead flotation circuit.

6.2. Effect of grinding environment on the pulp chemistry and flotation

The Rosh Pinah composite used in this study was milled in an unlined laboratory mill with mild steel rods as described in Chapter 4. The particle size distributions show that approximately 80% of the mill product was less than 75 micron after dry or wet milling (Figure 6.1a). A plant feed sample to the lead flotation circuit was also collected in November 2002, analysed and its particle size distribution was compared to that obtained in the laboratory. Figure 6.1b showed that the grind of the plant sample was approximately 80% passing 85 micron.

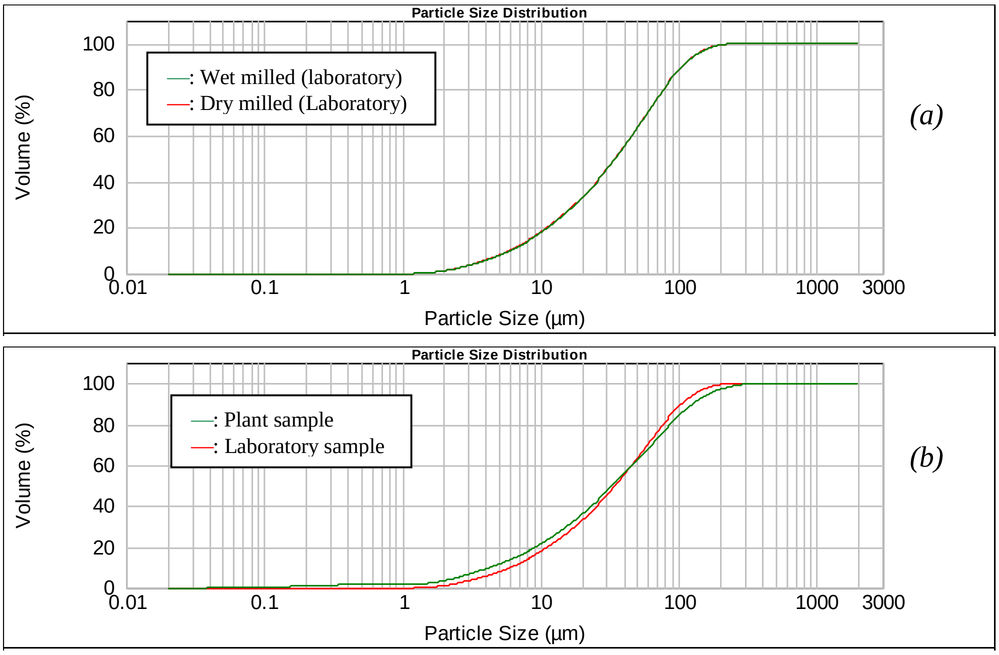


Figure 6.1 Particle size distributions of Roh Pinah ore samples. (a) Laboratory milled (wet and dry milling); (b) laboratory milled and sample from the feed of the lead flotation circuit at Rosh Pinah Mine (November 2002).

Figure 6.1 showed that the laboratory milled samples had a similar particle size distribution as the flotation feed sample from the Rosh Pinah plant. Therefore, it could be assumed that the degree of mineral liberation achieved at the plant was closely simulated in the laboratory.

The effects of the laboratory grinding environment on the pulp potential and dissolved oxygen during the beneficiation of the Rosh Pinah composite used in this study are shown in Figures 6.2 and 6.3.

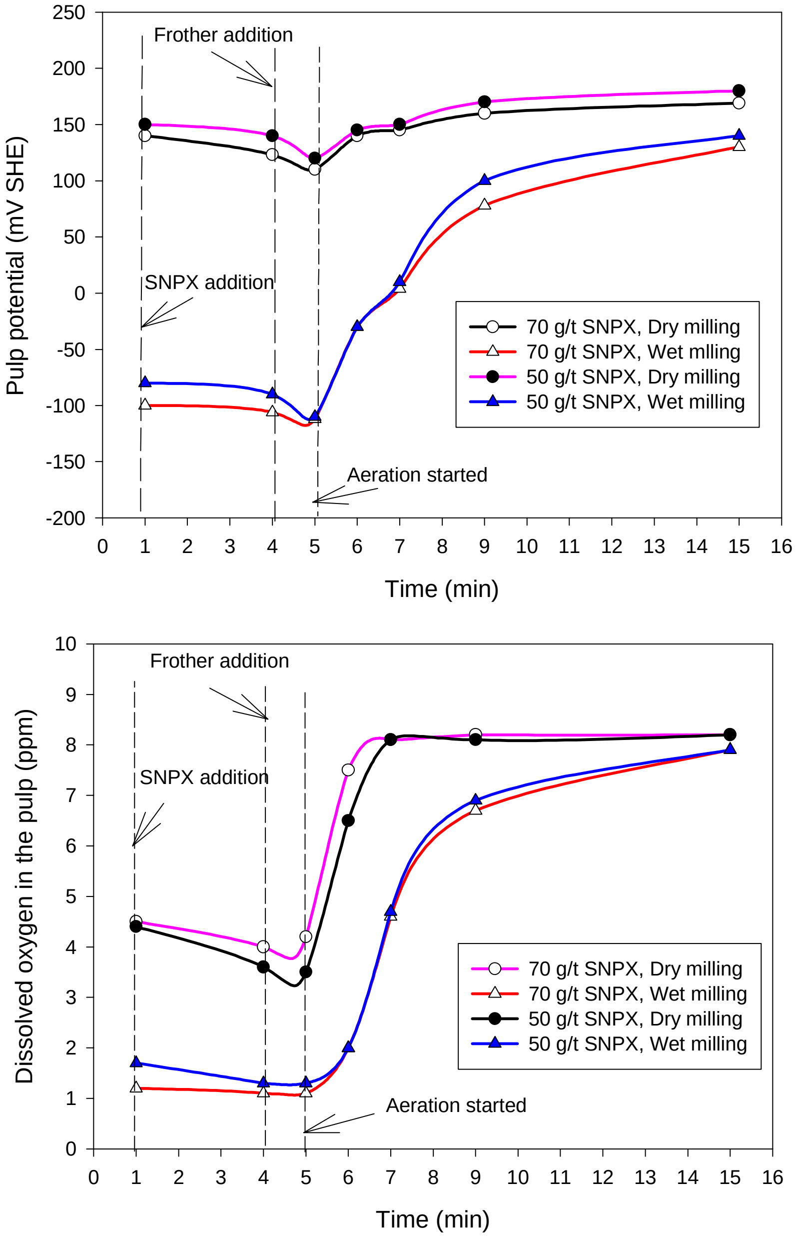


Figure 6.2. Evolution of the pulp potential and the dissolved oxygen concentration in the flotation cell during the flotation of a Rosh Pinah composite ground in either a dry or wet environment in a steel mill. Tests were carried out before the activation with cuprous cyanide species.

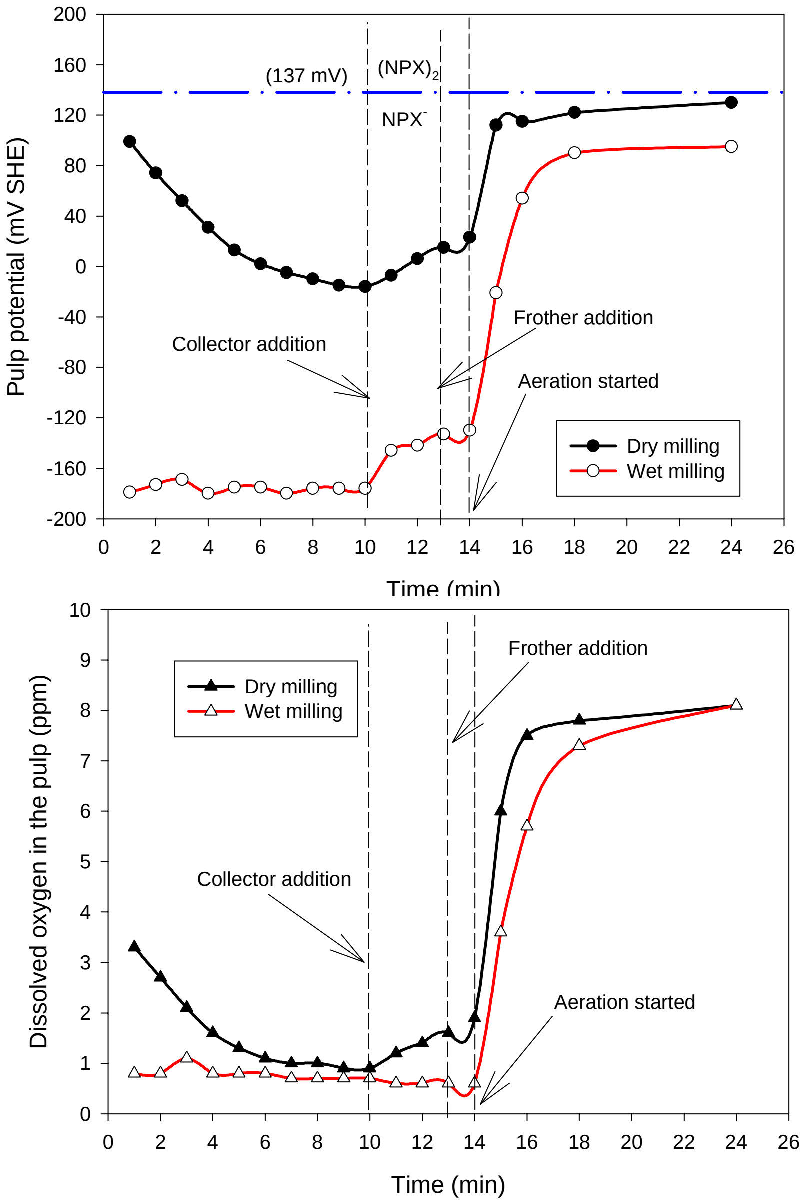


Figure 6.3. Evolution of the pulp potential and the dissolved oxygen concentration in the flotation cell during the flotation of a Rosh Pinah composite ground in either a dry or wet environment in a steel mill. Flotation tests were carried out in the presence of 10^{-4}M cuprous cyanide complexes. The activator was added at the beginning of the process (t = 0 min). The reversible half cell potential for the $NPX^-/(NPX)_2$ reaction is also shown for a SNPX concentration of $1.4x10^{-4}$M.

The low dissolved oxygen and low pulp potential after wet milling indicated the presence of oxygen consumers such as metallic iron and labile sulphides in the wet milled pulp. In addition, the dissolved oxygen was unchanged during the conditioning stage of the wet milled pulp.

The dissolved oxygen and pulp potential were higher after dry milling of the composite. Although the pulp potential dropped slightly before the addition of the collector for the composite sample which had been ground in a dry environment (Figure 6.2), the pulp potential of the dry milled pulp was still more positive than that of the wet milled pulp at the time of xanthate addition. However, the dissolved oxygen and pulp potential for the dry milled composite (Figure 6.3) decreased substantially when cuprous cyanide species was added in the flotation cell. This indicated that some oxidation/reduction reactions were occurring at different stages of the flotation test.

The sharp rise in the pulp potential with the starting of aeration is clearly due to the addition of oxygen to the pulp. The differences in the pulp potentials between the dry and wet milled sample were reduced at the end of the flotation stage. Thus, it was clear that the milling environment contributed to the variation in the pulp potential prior to the activation and conditioning stages of the composite. However, the dissolved oxygen and pulp potential observed during the flotation stage were mainly controlled by the aeration.

The reversible potential for the dithiolate-thiolate reaction was calculated from the standard half-cell potential and the concentration of the species using the Nernst equation (Equation 2.4). For the concentration of SNPX (1.4×10^{-4}M) used in this study, the oxidation of SNPX to its dithiolate species can occur at potentials above 137 mV, assuming $[X_2] = 1$. The standard redox potential for SNPX is $E^o = -0.091$ V SHE (Crozier, 1991). As seen in Figure 6.3, the formation of dixanthogen in the flotation pulp was not thermodynamically favourable when the collector was added in the slurry. This is in line with the proposal by Buckley and Woods (1997) that chemisorption of xanthate was the thermodynamically favourable process.

The measurements of the pulp chemistry have shown that higher dissolved oxygen and more positive pulp potential were observed when the composite had been ground in a dry environment. Thus, it is possible that further oxidation of minerals could occur in the flotation cell due to the presence of dissolved oxygen prior to aeration. In contrast, more negative pulp potentials and low dissolved oxygen were observed after wet milling of the ore; these would tend to diminish oxidation of minerals during the conditioning stage.

Since it is known that the flotation of sphalerite from the complex lead-zinc sulphide minerals is enhanced under more oxidizing conditions, the flotation recovery of sphalerite from the Rosh Pinah ore is expected to be higher after dry milling, with resulting poorer flotation selectivity between galena and sphalerite. This effect is visible in the results of flotation tests on the Rosh Pinah composite in the presence of 50 and 70g/t SNPX (Figure 6.4). The metallurgical data of the lead concentrate are summarised in Table 6.2.

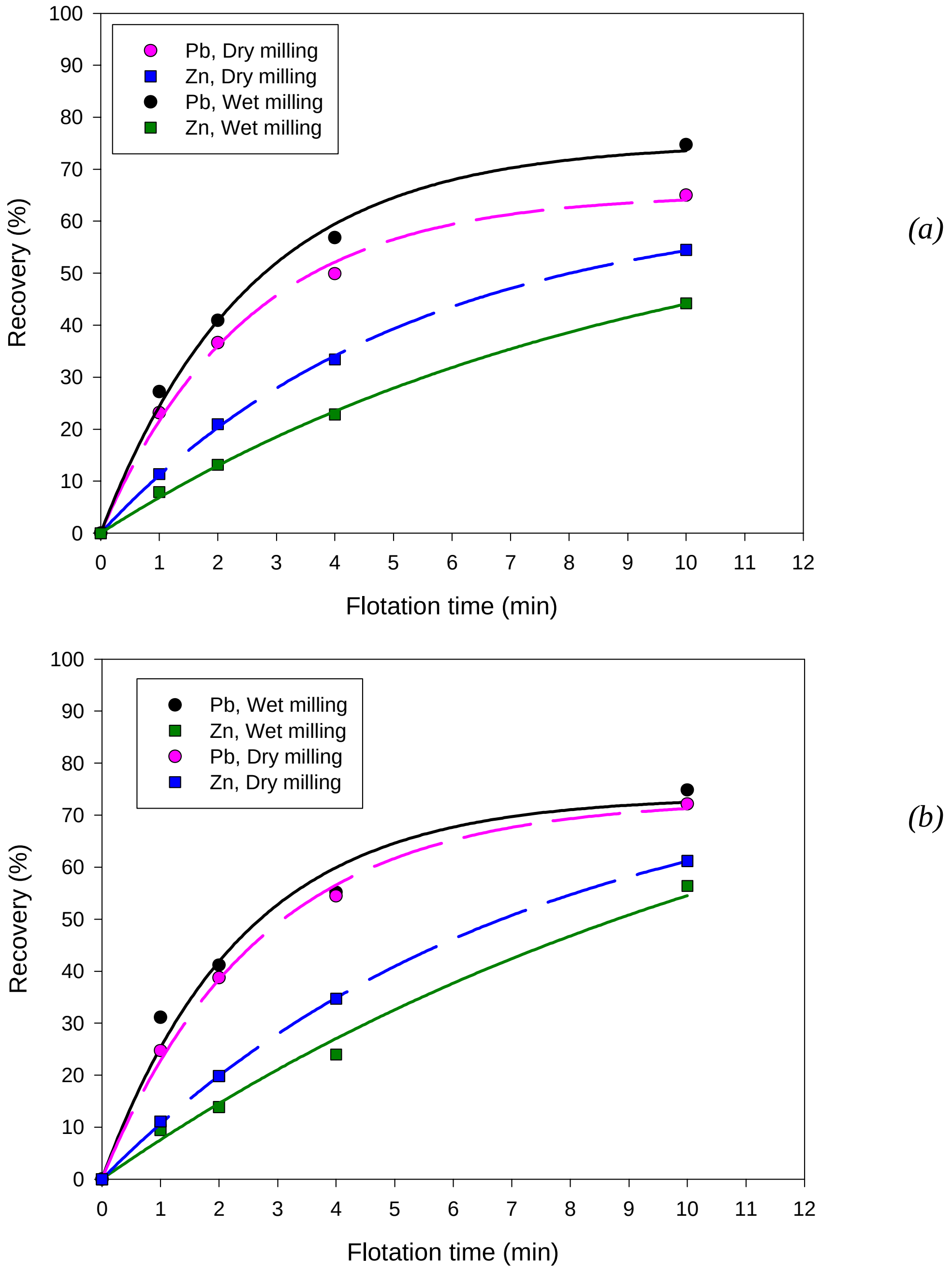


Figure 6.4. Flotation recovery of galena and sphalerite from a Rosh Pinah composite at pH 8.5 under various grinding conditions. (a) 50 g/t SNPX, (b) 70 g/t SNPX. Solid lines (after wet milling, 67% solids), dashed line (after dry milling).

Table 6.2. Flotation results of the Rosh Pinah composite after wet and dry milling.

SNPX	Milling Type	Eh[*]	Mass Pull	Recovery (%)		Grade (%)	
(g/t)		mV SHE	(%)	Pb	Zn	Pb	Zn
50	Wet	-80/+140	17.5	74.1	44.2	8.5	19.3
	Dry	+150/+180	16.5	65.0	54.7	8.8	27.5
70	Wet	-100/+130	21.1	74.8	56.4	7.8	21.9
	Dry	+140/+169	20.3	72.1	61.0	7.6	25.7

(*) Eh measured after 1 minute of conditioning time and at the end of flotation.

The flotation recoveries of sphalerite were approximately 44 and 55% when the composite was ground in a wet and dry environment, respectively. The corresponding numbers when the xanthate dosage was increased from 50 to 70 g/t SNPX were 56 and 61%. In contrast, the flotation of galena was higher after wet milling (74%) when compared to dry milling (65%), especially at lower xanthate dosage of 50 g/t SNPX.

Figure 6.5 confirms that the flotation selectivity between galena and sphalerite was adversely affected by dry milling and by higher collector dosages. The ratio of flotation recovery of galena and sphalerite at 50 g/t SNPX was 1.67 and 1.19 after wet and dry milling, respectively. When the collector dosage was increased to 70 g/t, the ratio was 1.33 for wet milling and 1.18 for dry milling.

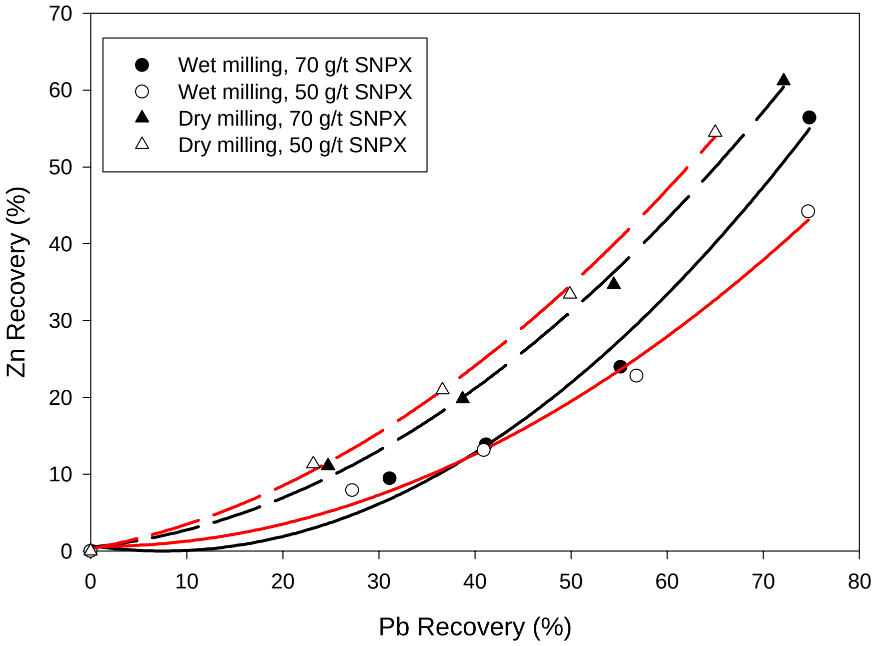


Figure 6.5. Effect of milling environment on the flotation recoveries of sphalerite and galena at various dosages of xanthate. Solid lines (after wet milling, 67% solids), dashed line (after dry milling).

The grade-recovery relationships of zinc and lead are shown in Figure 6.6. Both the recovery and grade of sphalerite were higher when the composite was ground in a dry environment. The grade of lead in the concentrate was higher at the earlier stage of flotation and decreased linearly when the composite was milled in a dry environment (Figure 6.6).

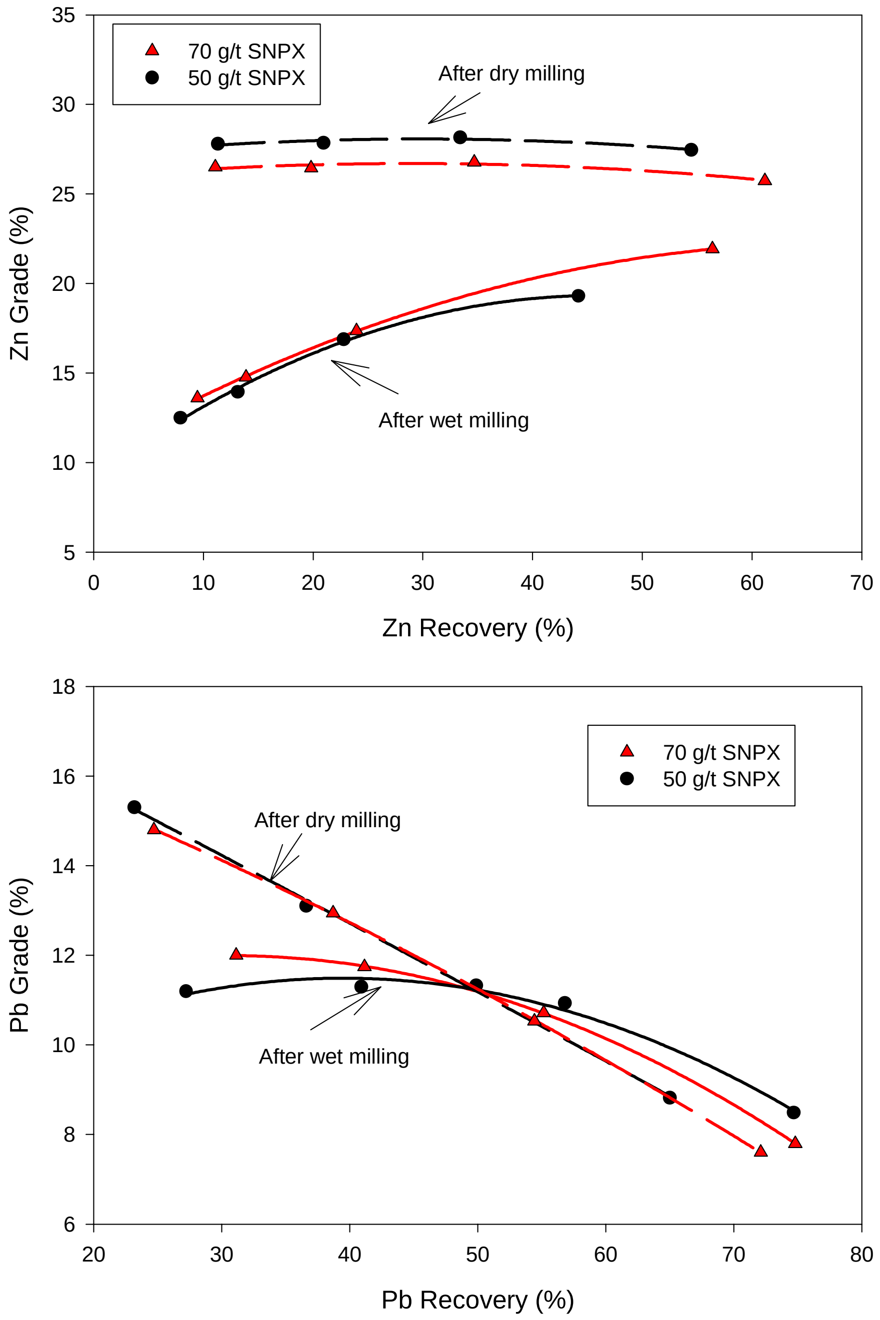


Figure 6.6. Effect of the milling environment on the recovery-grade of galena and sphalerite from a Rosh Pinah composite at pH 8.5 and in the presence of 50 and 70 g/t SNPX. Solid lines: after wet milling, 67% solids; dashed line: after dry milling.

Since the grade of zinc in the lead concentrate was higher after dry milling, it was suspected that there was a third fast floating mineral that was diluting the grade of zinc and lead when the composite was ground wet prior to flotation. Since pyrite is a major sulphide mineral in the Rosh Pinah ore, the grade-recovery relationship of Fe was studied.

As shown in Figure 6.7, the grade and recovery of pyrite in the lead concentrate were indeed higher after wet milling when compared to dry milling. After wet milling the zinc and lead in the concentrate were diluted by pyrite (see Table 2.3 which confirms that pyrite is present in the composite).

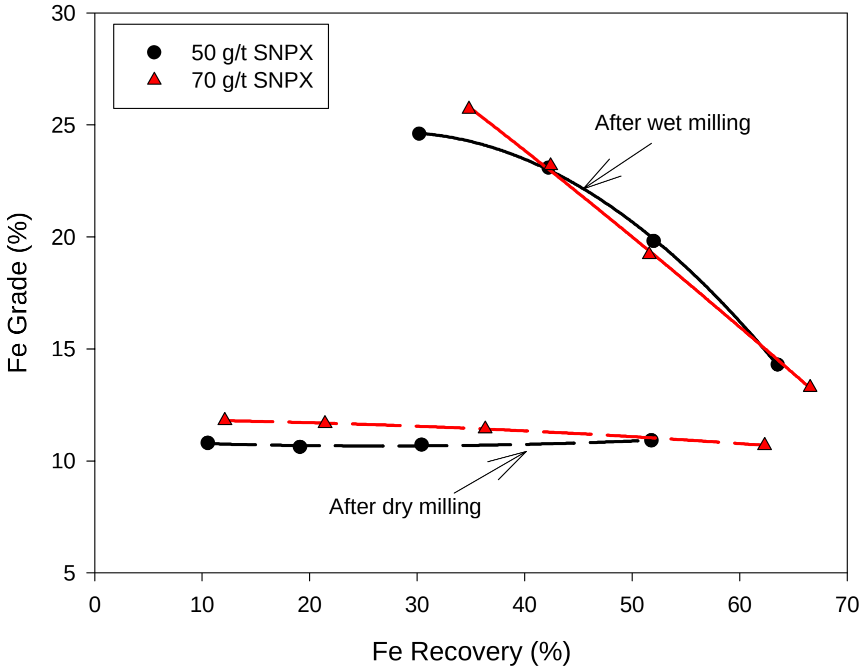


Figure 6.7. Effect of the milling environment on the recovery-grade of pyrite from a Rosh Pinah composite at pH 8.5 and in the presence of 50 and 70 g/t SNPX, respectively. Solid lines (after wet milling, 67% solids), dashed line (after dry milling).

The flotation recoveries of galena, pyrite and sphalerite are shown in Figure 6.8 as functions of time and milling environment. The figure confirms that the flotation kinetics of pyrite was faster after wet milling and the recovery of pyrite was approximately 52% in the case of dry milling compared with 64% in the case of wet milling. Oxidation of pyrite is a likely cause of the poorer recovery after dry milling.

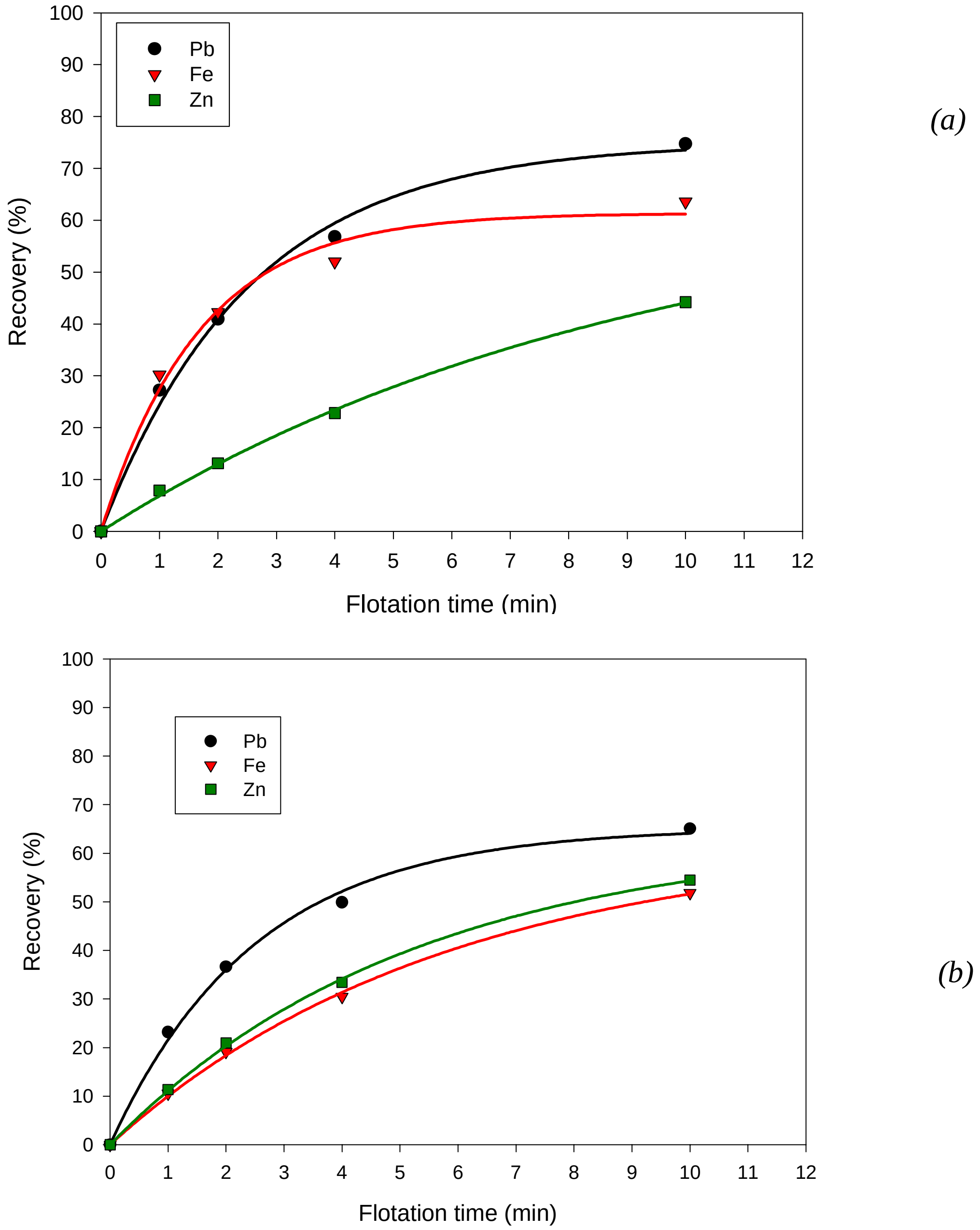


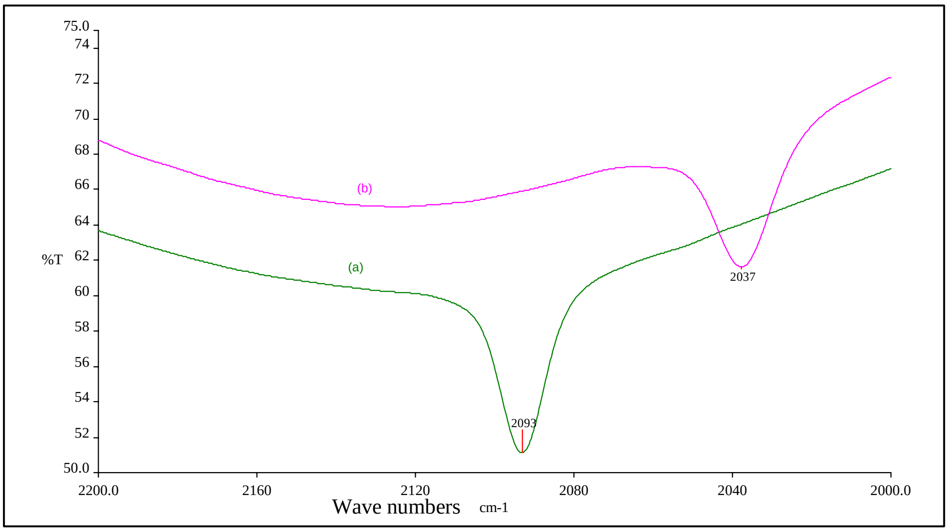
Figure 6.8. Flotation recovery of galena, pyrite and sphalerite in the presence of 50 g/t SNPX at pH 8.5. (a) Wet milling, (b) Dry milling. Solid lines represent fitted curves.

Since the recovery of galena was enhanced after wet milling while the recovery of sphalerite was lower, it was clear that the pulp chemistry achieved under wet milling conditions was suitable for better selectivity between galena and sphalerite in the lead circuit. These results are in agreement with the reported results where the pulp potential was controlled by changing the type of grinding media (mild and stainless steel grinding media) (Martin et al., 1991). However, it would have been interesting to compare the current results with those obtained after autogenous milling.

The effect of cuprous cyanide species on the flotation response of the Rosh Pinah composite sample is presented in the following section.

6.3. Influence of cuprous cyanide on the flotation recoveries

After the milling stage, the pulp was transferred into the flotation cell and diluted to 33% solids prior to flotation. The required amount of cuprous cyanide solutions was added to activate sphalerite and the pulp was conditioned for 10 minutes before the addition of xanthate. The cuprous cyanide solution was prepared and analysed using FTIR spectrometry as described in Chapter 4. Figure 6.9 shows that a peak assigned to $Cu(CN)_3^{2-}$ was observed at the wave number of 2093 cm^{-1} (Lukey et al., 1999). A ferrocyanide solution was also analysed for comparison purposes only. A peak assigned to the ferrocyanide species was observed at a wave number of 2037 cm^{-1}. The spectrum of copper-cyanide confirms that $Cu(CN)_3^{2-}$ species were in solution when the activation of sphalerite by Cu(I) was studied.



%T: Transmission (%)

Figure 6.9. FTIR spectra of aqueous cuprous cyanide and ferrocyanide species at pH 10.5. (a) [Cu(I)] = 10^{-3}M and CN/Cu molar ratio of 3, (b) 10^{-2}M Ferrocyanide

The effect of cuprous cyanide, xanthate dosages and type of milling on the recovery and grade of sphalerite in the lead concentrate is shown in Figures 6.10-6.13, while the recovery and grade of galena are presented in Figures 6.14-6.16. The metallurgical results of the lead rougher concentrate are summarised in Table 6.3.

Table 6.3. Flotation results of the Rosh Pinah composite at various dosages of cuprous cyanide and xanthate after wet and dry milling.

SNPX	Milling Type	Cu(I) concentration	Mass Pull	Recovery (%)		Grade (%)	
(g/t)		([CN$^-$]/[Cu] = 3)	(%)	Pb	Zn	Pb	Zn
50	Wet	0	17.5	74.1	44.2	8.5	19.3
		10^{-4}M	18.6	73.7	51.8	8.4	23.1
		10^{-3}M	17.5	69.1	58.6	8.2	27.3
	Dry	0	16.5	65.0	54.7	8.8	27.5
		10^{-4}M	19.5	66.2	70.1	7.4	30.9
70	Wet	0	21.1	74.8	56.4	7.8	21.9
		10^{-3}M	22.4	76.0	74.8	7.4	28.8
	Dry	0	20.3	72.1	61.0	7.6	25.7
		10^{-4}M	23.2	68.9	77.0	7.0	29.9

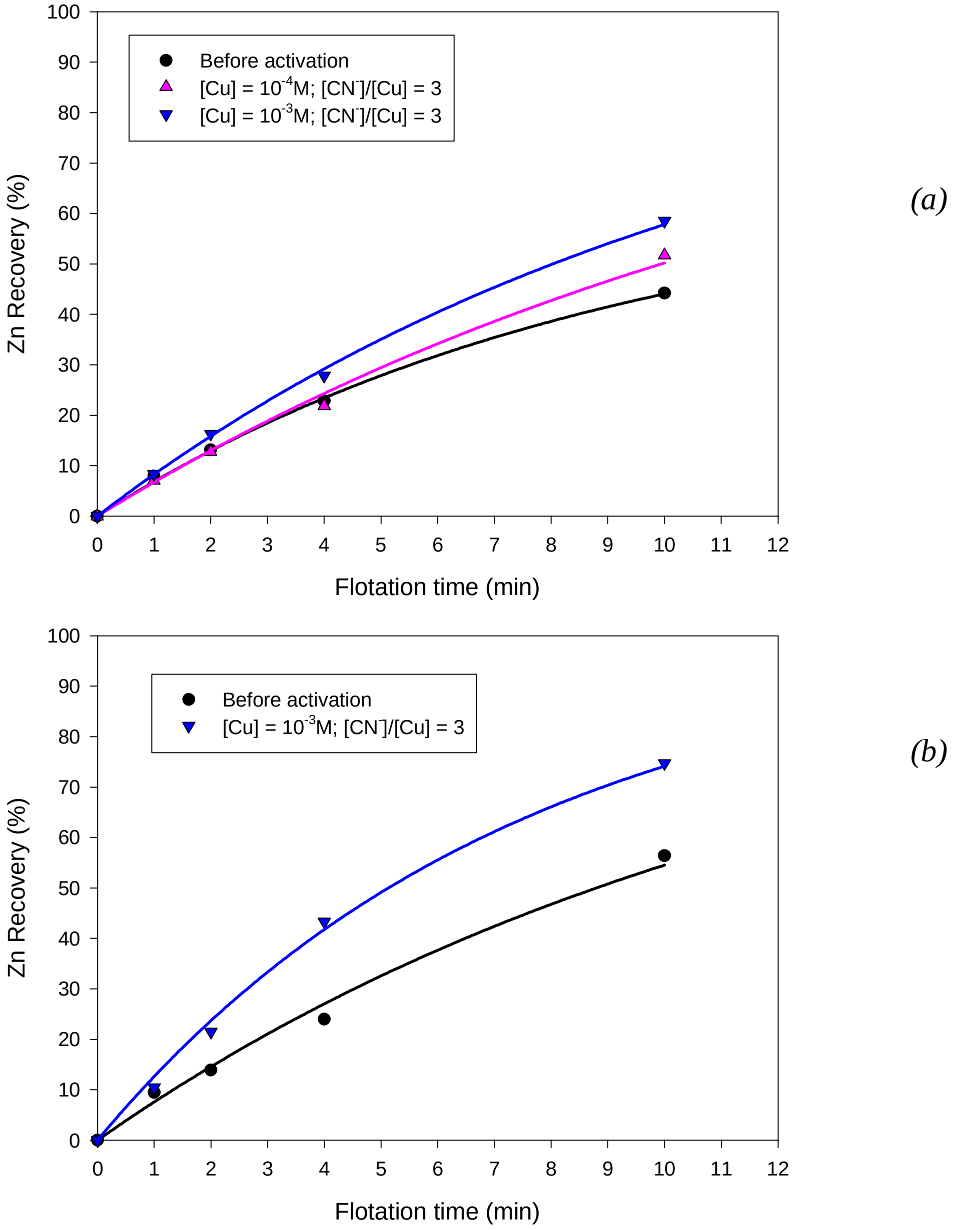
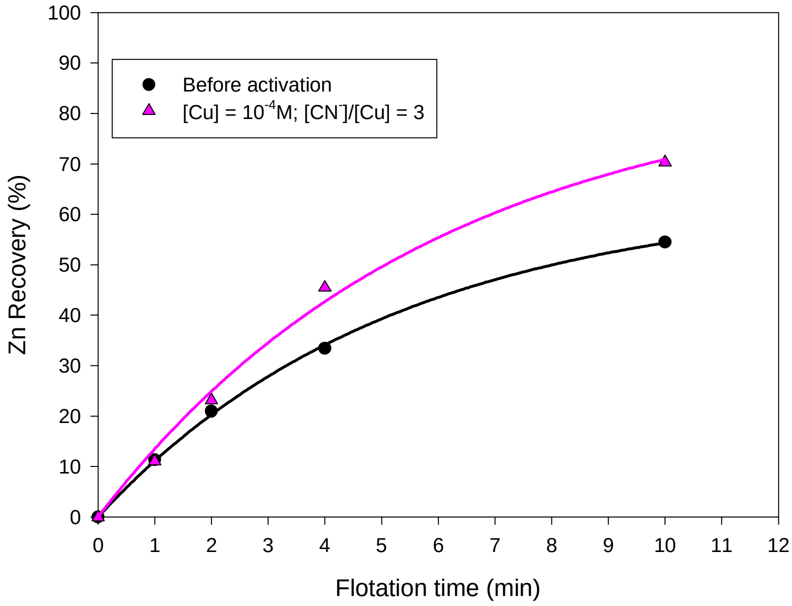
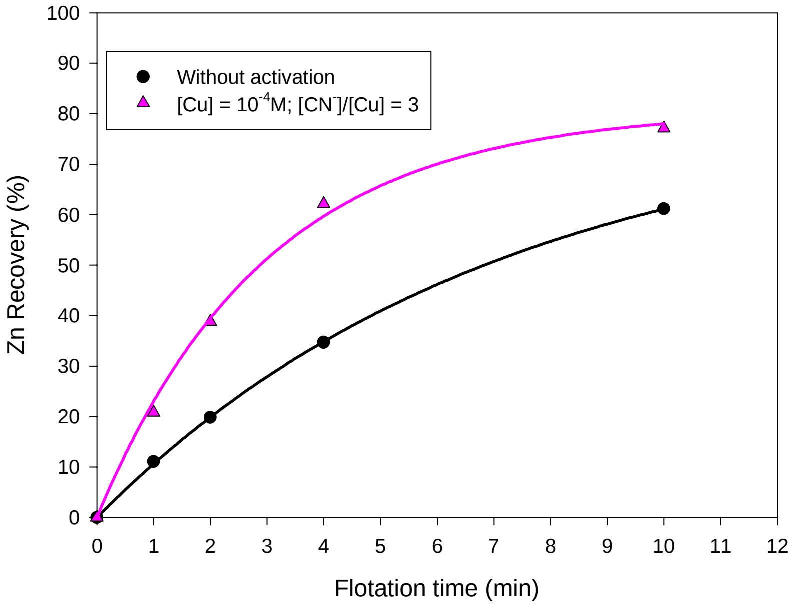


Figure 6.10. Flotation recovery of sphalerite from a wet milled Rosh Pinah composite before and after activation with cuprous cyanide at pH 8.5. (a) 50 g/t SNPX, (b) 70 g/t SNPX. Solid lines represent fitted curves.



(a)



(b)

Figure 6.11. Flotation recovery of sphalerite from a dry milled Rosh Pinah composite before and after activation with cuprous cyanide at pH 8.5. (a) 50 g/t SNPX, (b) 70 g/t SNPX. Solid lines represent fitted curves.

As shown earlier (Figure 6.4 and Table 6.2), the recovery of sphalerite in the lead concentrate increased, from 44 to 56%, when the dosage of xanthate was increased from 50 to 70 g/t SNPX when the composite was dry milled. However, when the composite was wet ground, 55 and 61% of sphalerite were recovered at 50 and 70 g/t SNPX, respectively. The new observation from these figures is that cuprous cyanide, at levels that could be typically present in the recycle water at Rosh Pinah Mine, does activate sphalerite and increases its recovery in the lead concentrate.

Figures 6.12 and 6.13 show the relationship between the grade and the recovery of zinc confirming the activating effect of cuprous cyanide on sphalerite.

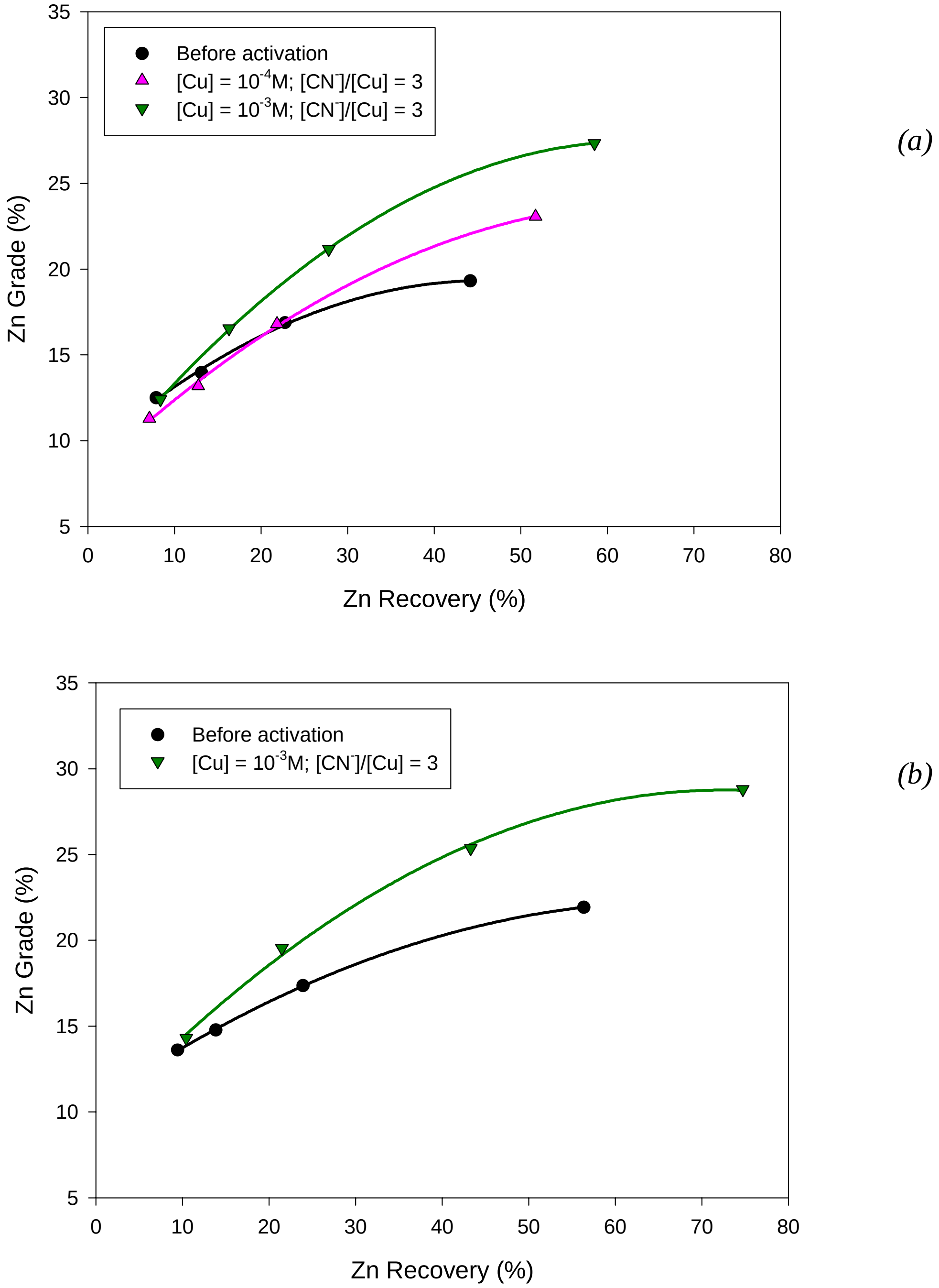


Figure 6.12. Recovery and grade of sphalerite from a Rosh Pinah composite after activation with cuprous cyanide at pH 8.5 and wet milling. (a) 50 g/t SNPX, (b) 70 g/t SNPX. Solid lines represent fitted curves.

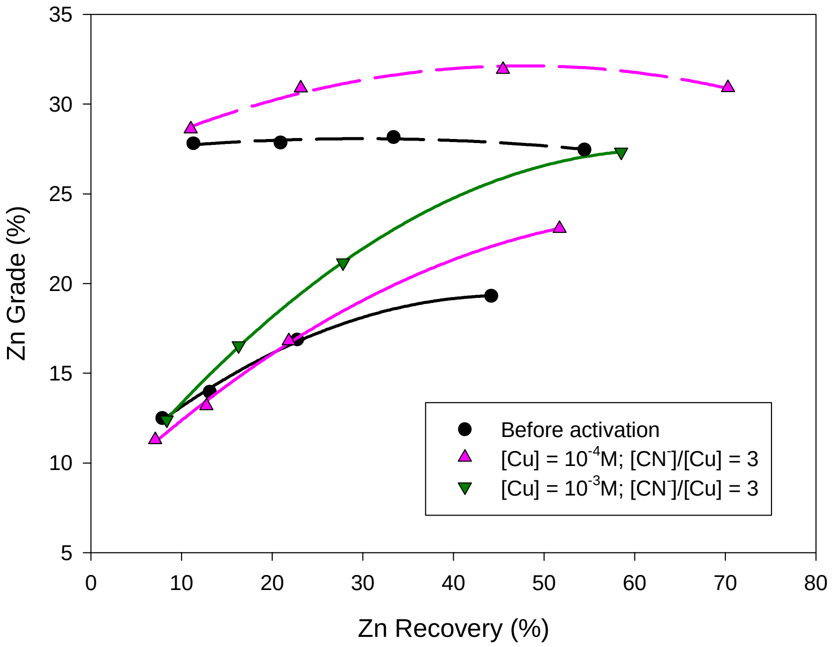


Figure 6.13. Effect of the milling environment on the recovery-grade of sphalerite from a Rosh Pinah composite at pH 8.5 and in the presence of 50 g/t SNPX and various concentration of cuprous cyanide. Solid lines: after wet milling, 67% solids; dashed line: after dry milling.

The improved recovery of sphalerite under more positive pulp potentials might be due to one or a combination of the following reasons:

- Oxidation of sphalerite followed by the formation of zinc-xanthate on its surface;
- Oxidation of sphalerite, galena and chalcopyrite followed by the activation of sphalerite by the oxidation products (Cu and Pb ions) of chalcopyrite and galena. The presence of pyrite in the Rosh Pinah ore would also be favourable for the anodic oxidation of sphalerite, chalcopyrite and galena since the rest potential of pyrite is more positive than those of the other sulphide minerals (this assumes that galvanic interactions may occur between the minerals);
- High pulp potentials would also be favourable for the oxidation/decomposition of cuprous cyanide species to $CuO/Cu(OH)_2$, which are known to activate sphalerite at alkaline pH values (Figures 3.7 and 3.8).

Since the zinc xanthate complex is very weak; it is believed that it might not form during the flotation of the composite. Therefore, the other two mechanism mentioned above are likely.

Since both the recovery and grade of sphalerite in the lead concentrate have to be at their minimum values for flotation selectivity, it is clear that the presence of cuprous cyanide species and more positive pulp potentials are detrimental to selectivity. The strongest effect of cuprous cyanide is on sphalerite rather than galena.

The concentrate mass pull and flotation recoveries of galena for different cuprous cyanide and xanthate dosages after wet milling are shown in Figure 6.14. See also Table 6.3 for a summary of the recoveries after 10 minutes of flotation.

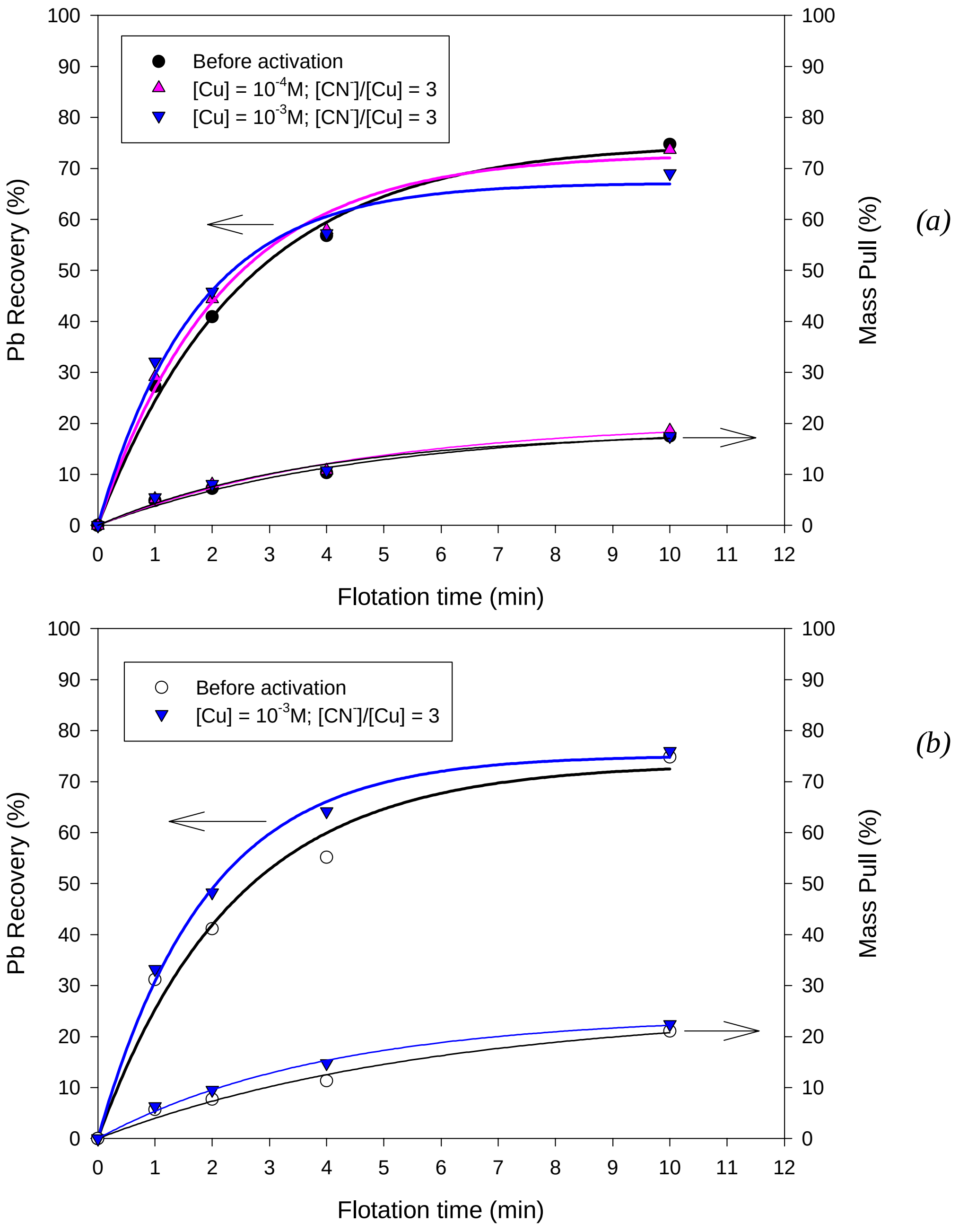


Figure 6.14. Flotation recovery of galena from a Rosh Pinah composite after activation with cuprous cyanide at pH 8.5 and wet milling. (a) 50 g/t SNPX, (b) 70 g/t SNPX. Solid lines represent fitted curves.

In the absence of cuprous cyanide species, the concentrate mass pull increased from 17.5 to 21.1% when the collector dosage was increased from 50 to 70g/t, while the recovery of galena was similar at 75% after 12 minutes of flotation time. The recovery of galena was not strongly affected by the presence of cuprous cyanide. Figure 6.15 confirms the weak effect of cuprous cyanide on galena. Similar observations hold for dry-milled ore (Figure 6.16).

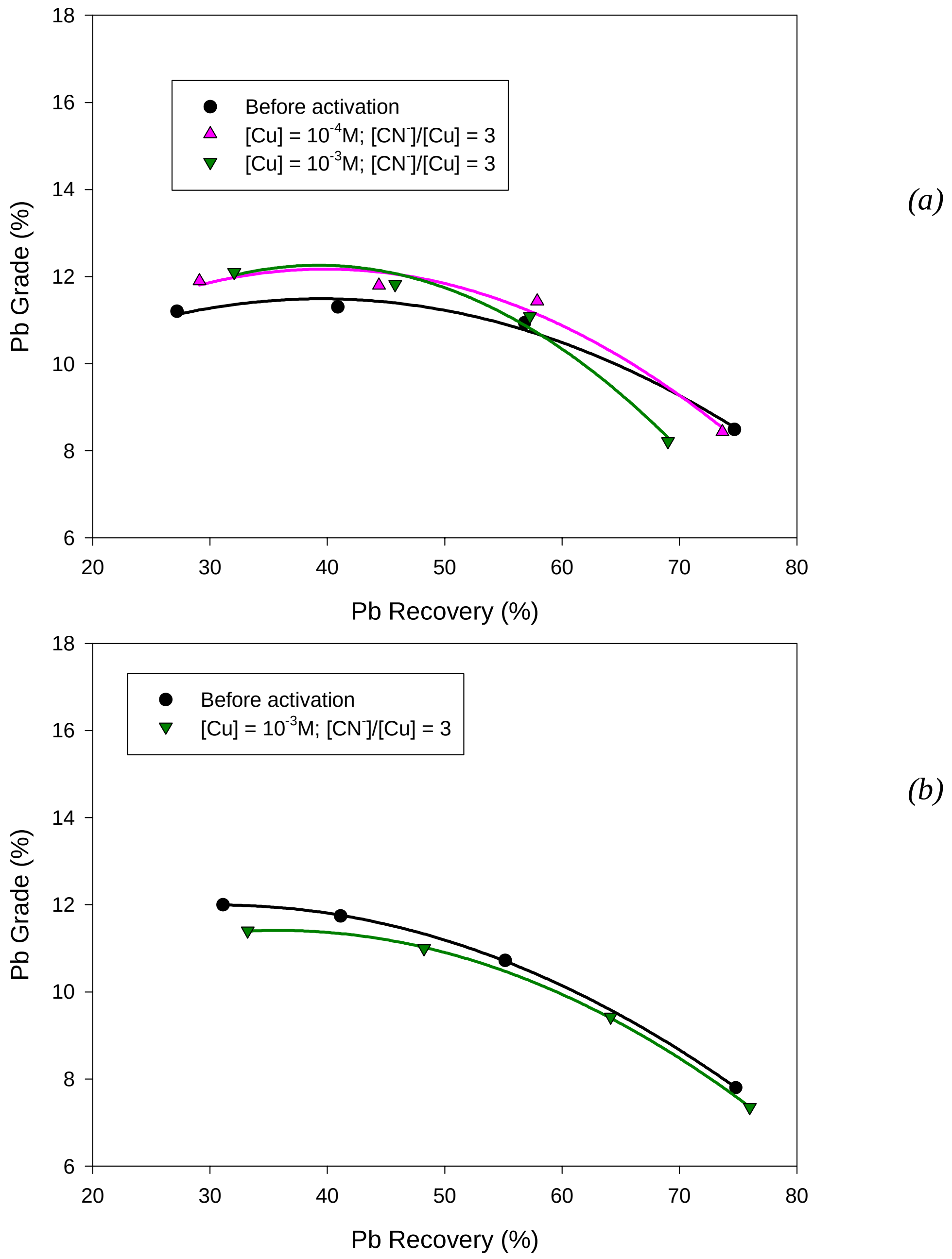


Figure 6.15. Recovery and grade of galena from a Rosh Pinah composite after activation with cuprous cyanide at pH 8.5 and wet milling. (a) 50 g/t SNPX, (b) 70 g/t SNPX. Solid lines represent fitted curves.

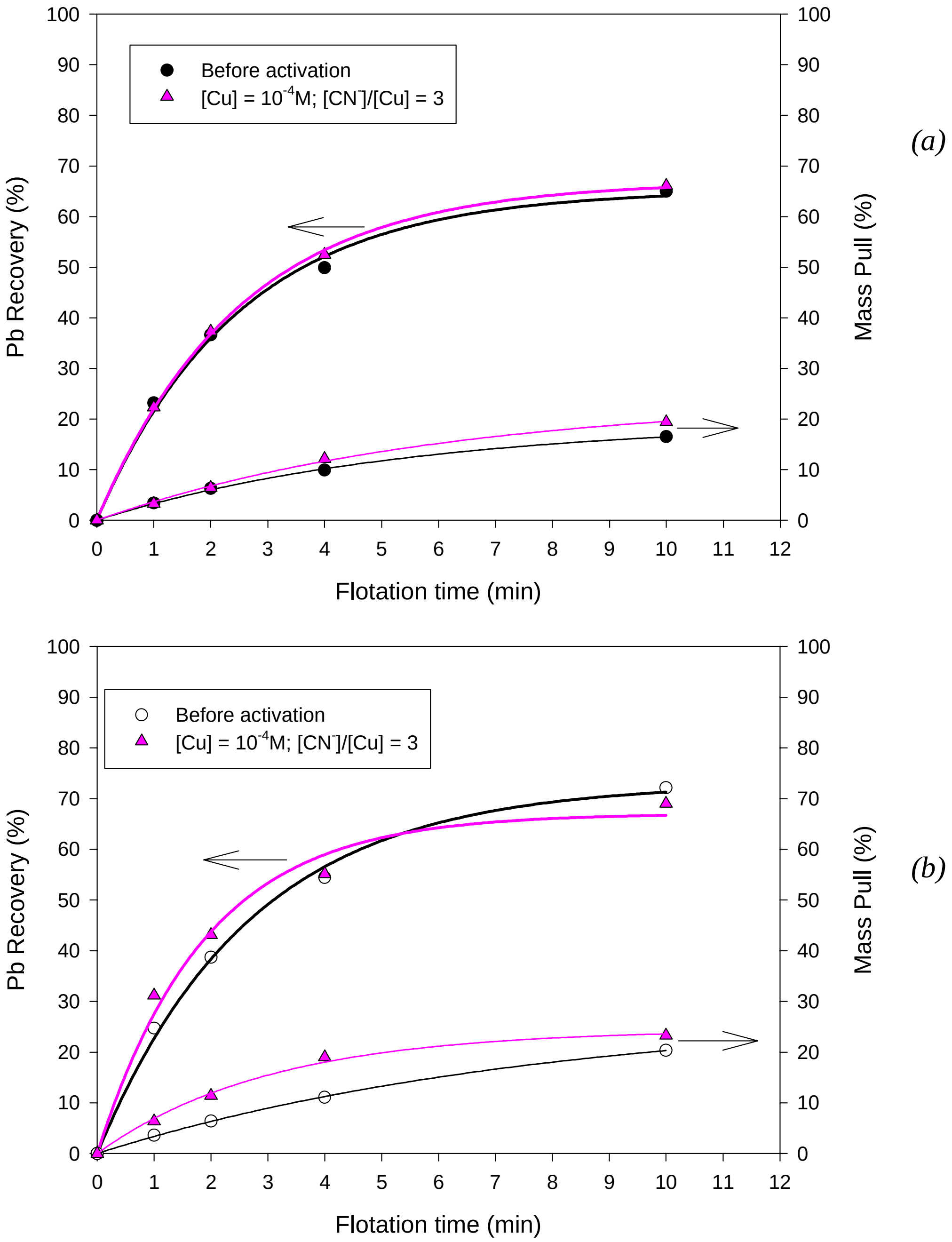


Figure 6.16. Flotation recovery of galena from a Rosh Pinah composite after activation with cuprous cyanide at pH 8.5 and dry milling. (a) 50 g/t SNPX, (b) 70 g/t SNPX. Solid lines represent fitted curves.

The lack of effect of copper cyanide on galena flotation (Figures 6.14-6.16) seems to be a very strong evidence for its decomposition and the normal exchange/redox mechanism on sphalerite.

The flotation selectivity of galena against zinc and iron as a function of various concentrations of cuprous cyanide and xanthate is summarised in Figures 6.17 and

6.18 for dry and wet milled composite samples, respectively. Clearly, cuprous cyanide adversely affected the selectivity between galena and sphalerite. For wet milling, the flotation selectivity between galena and pyrite was poorer than between galena and sphalerite. Figure 6.17 shows that better selectivity was obtained between galena and sphalerite for the wet milled ore at the beginning of the flotation stage but selectivity decreased with longer flotation times (that is, sphalerite flotation is slower than galena flotation).

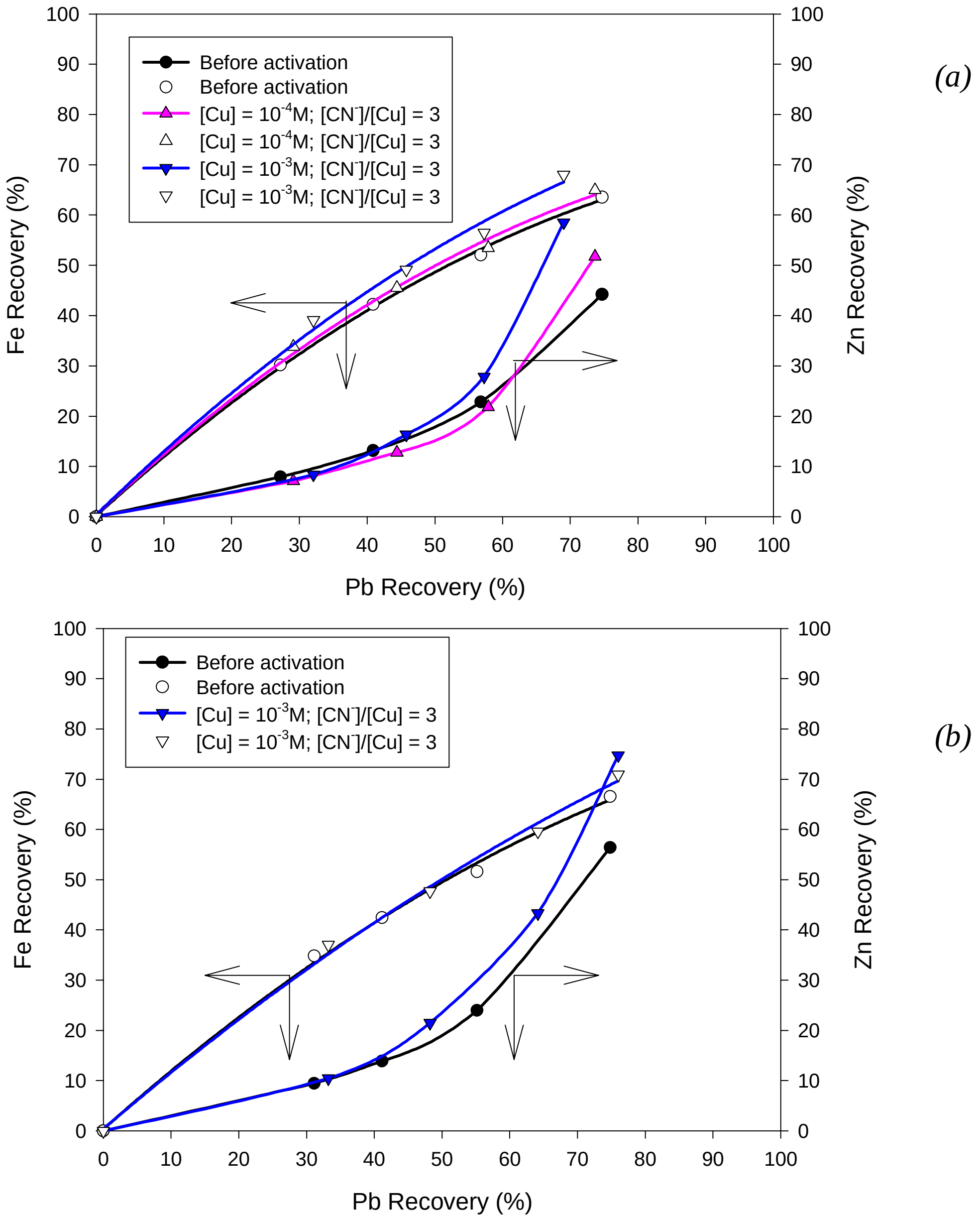


Figure 6.17. Flotation recoveries of Cu(I)- activated sphalerite, galena and iron sulphide for different copper (I) cyanide concentrations and flotation times of 1, 2, 4, and 10 minutes; after wet milling. (a) 50 g/t SNPX, (b) 70 g/t t SNPX

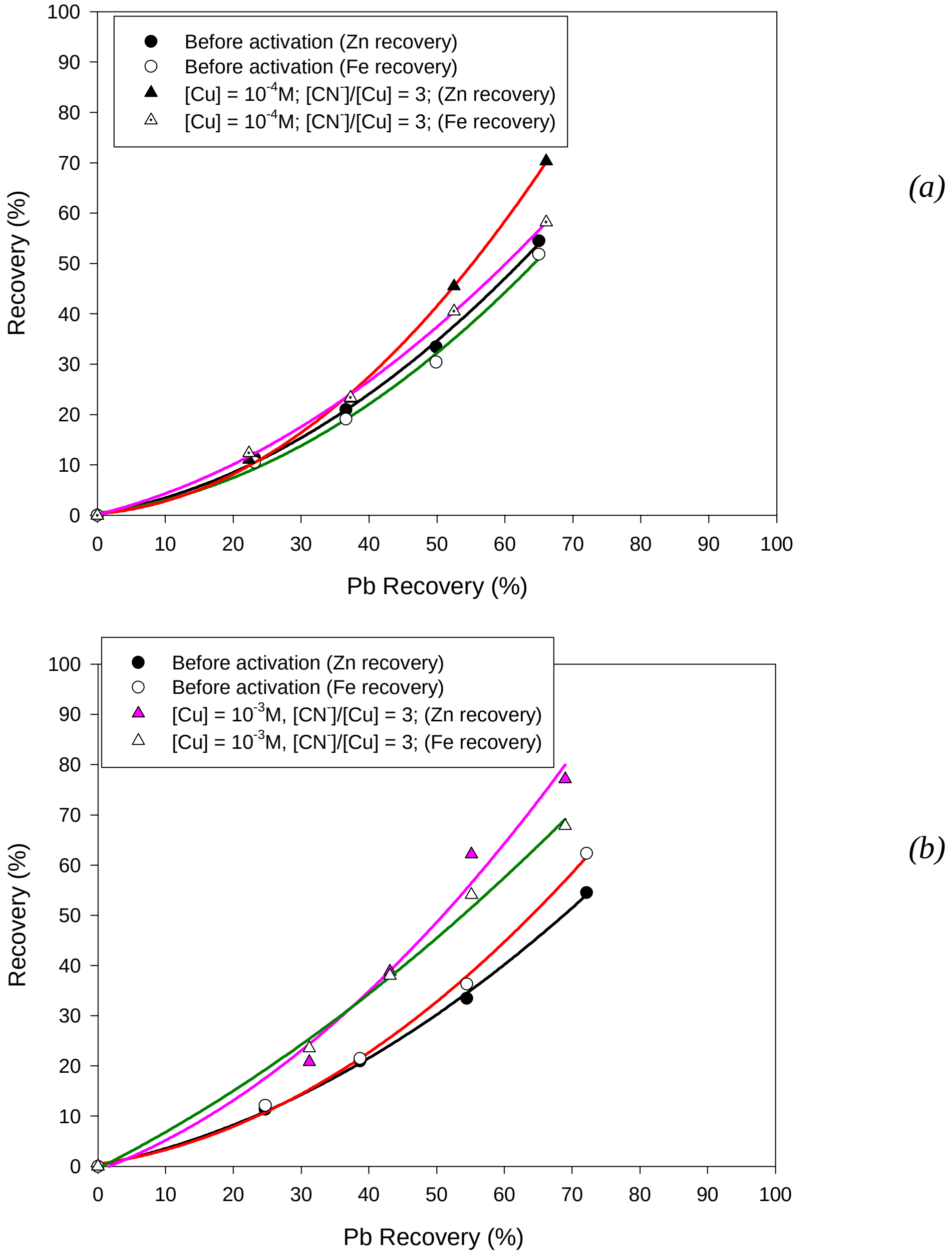


Figure 6.18. Flotation recoveries of Cu(I)- activated sphalerite, galena and iron sulphide for different copper (I) cyanide concentrations and flotation time of 1, 2, 4, and 10 minutes; after dry milling. (a) 50 g/t SNPX, (b) 70 g/t t SNPX. Solid lines represent fitted curves.

Since the decomposition of cuprous cyanide species can also lead to the formation of CuCN, flotation testwork was also carried out with CuCN as a potential activator for sphalerite. The Rosh Pinah composite used in this case was from a different batch though with similar chemical composition. Dry milling was selected based on the observed strong activation of sphalerite by cuprous cyanide. The recoveries of sphalerite for different CuCN dosages are shown in Figure 6.19. The results clearly showed that sphalerite was activated by CuCN. The recovery of sphalerite increased from 26 to 33 and 46% when the concentration of CuCN increased from 0 to 2x10^{-4}

and 2x10^{-3}M. Figure 6.20 shows the concentrate mass pull and the recovery of galena for different CuCN dosages. As with Cu(CN)$_3^{2-}$, galena is also unaffected by CuCN additions.

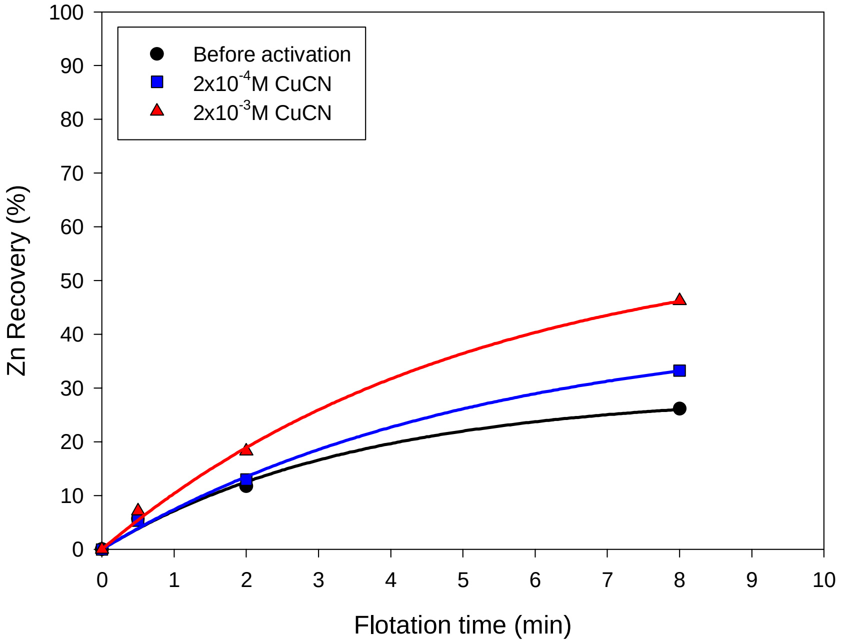


Figure 6.19. Flotation recovery of sphalerite from a dry-milled Rosh Pinah composite at pH 8.5 in the presence of various concentrations of CuCN and 50 g/t SNPX. Solid lines represent fitted curves.

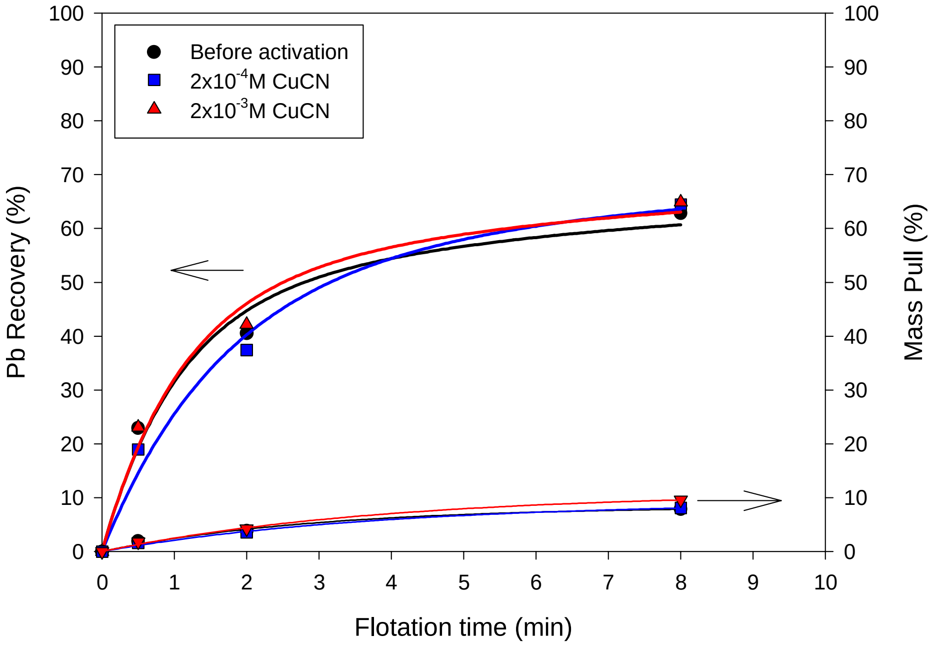


Figure 6.20. Flotation recovery of galena from a dry-milled Rosh Pinah composite in the presence of various concentrations of CuCN and 50 g/t SNPX. Solid lines represent fitted curves.

The net result is that flotation selectivity between galena and sphalerite is adversely affected by CuCN (Figure 6.21).

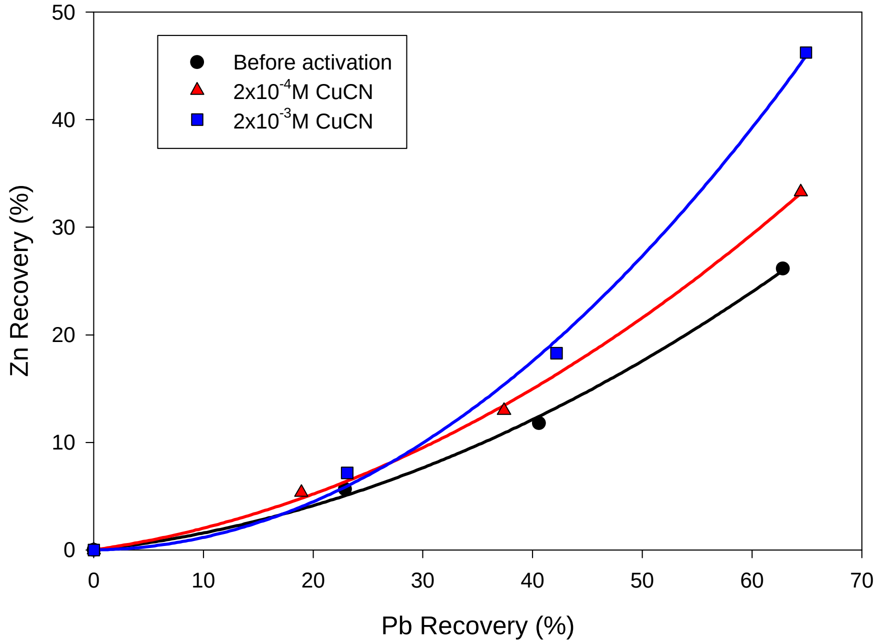


Figure 6.21. Flotation selectivity between galena and sphalerite at pH 8.5 as a function of various concentrations of CuCN and in the presence of 50g/t SNPX. Dry-milled composite.

In order to understand the mechanism of sphalerite activation by cuprous cyanide, surface analysis of natural sphalerite minerals was conducted. The results are discussed in the following section.

6.4. X-ray photoelectron spectroscopy on the activation of sphalerite

Four natural sphalerite samples were conditioned individually in water (pH 10.5 controlled by diluted solution of KOH), cuprous cyanide complexes and cupric nitrate solutions in contact with air as explained in Chapter 4. All elements present on the surface of sphalerite are initially identified in survey mode, then the various elemental regions are scanned for more details. Background charging is usually observed during the initial examination of the sample in survey mode. When the charging occurs, the binding energy of the C 1s peak is different from the calibrated value of 284.6 eV. Thus, all XPS spectra have to be charge-corrected accordingly prior to the interpretation of the results. The photoelectron peaks from the sphalerite samples were corrected for background charging by 4.5 and 4.1 eV before and after activation with cuprous cyanide complexes, respectively. The charging decreased from 4.5 to 1.1 eV when the sphalerite was activated with copper nitrate solution, thus indicating the presence of a conducting layer on the surface of sphalerite. The charge shift observed after the activation with cuprous cyanide complexes indicated that the insulating character of sphalerite was maintained and that any copper (as copper sulphide) was likely present in patches.

The charge corrected Cu *2p* and S *2p* XPS spectra are presented in Figures 6.22 and 6.23, respectively.

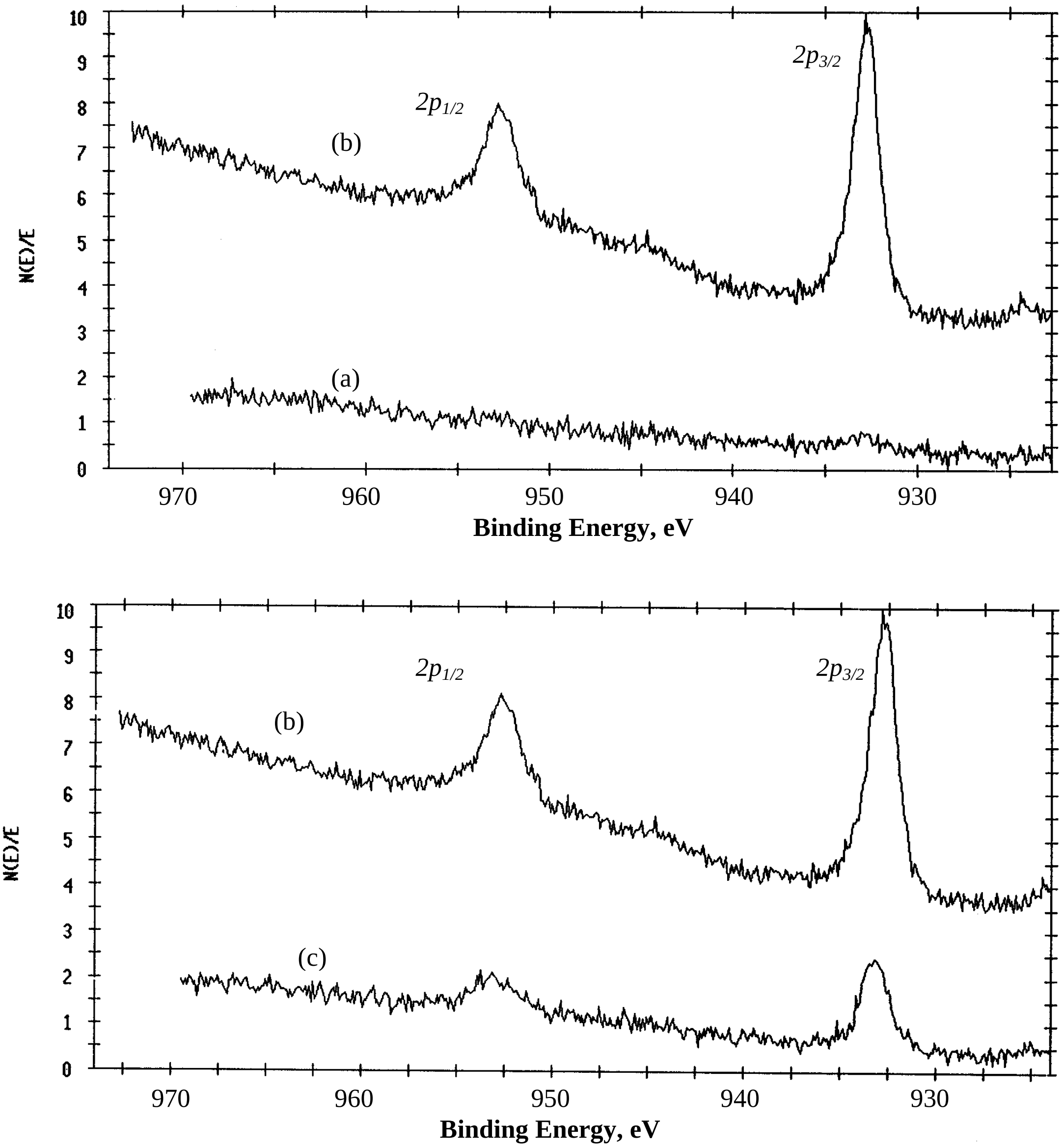


Figure 6.22. Normalised XPS spectra in the Cu 2p binding energy of the sphalerite samples treated with (a) water (pH 10.5), (b) 10^{-2} M Cu(II) from $Cu(NO_3)_2$, (c) 10^{-2} M Cu(I) from $Cu(CN)_x^{(x-1)-}$.

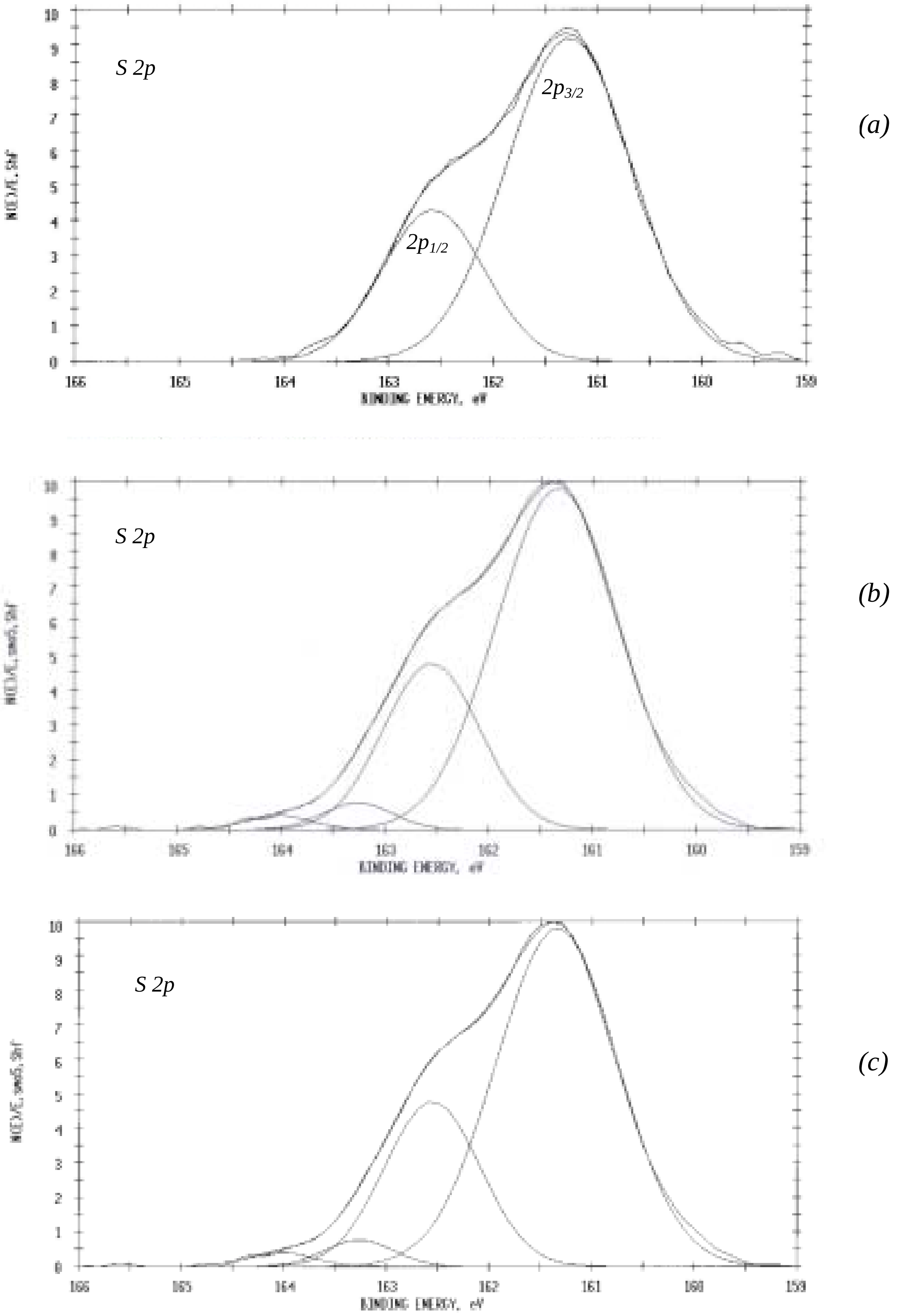


Figure 6.23. XPS spectra in the S 2p binding energy range of the sphalerite samples treated with (a) water (pH 10.5), (b) 10^{-2} M Cu(II) from $Cu(NO_3)_2$, (c) 10^{-2} M Cu(I) from $Cu(CN)_x^{(x-1)-}$.

As seen in Figure 6.22, there was no detectable copper on the surface of sphalerite treated with water. Since the covellite-like species, which is frequently mentioned in the literature as the main activation product on the surface of Cu(II) activated sphalerite, is known to have the copper in both Cu(I) and Cu(II) states, the binding energy of 932.5 eV is usually assigned to Cu_2S and CuS. The main Cu $2p_{3/2}$ peaks was found at the binding energy of 932.5 eV when the sphalerite was activated with copper nitrate and at the binding energy of 933.7 eV when the sphalerite was activated with cuprous cyanide complexes. The Cu $2p_{3/2}$ binding energies at 932.5 and 933.7 eV are assigned to Cu(I) species (Kartio et al., 1998). As seen in Figure 6.22 there was no shake-up satellite which would be typical of Cu(II) hydroxide as shown in Figure 2.8. It is interesting to observed that all the Cu *2p* spectra showed Cu(I) only. The absence of strong Cu(II) satellites near the 940 and 960 eV shows that Cu(II) was not on the sphalerite surface. The Cu in the surface from copper nitrate is also in the Cu(I) state which is the result of the exhange/redox reaction. This should be accompanied by the appearance of S *2p* peaks at 163.2 eV, which is usually assigned to polysulphide species.

The S *2p* spectra of the sphalerite sample before and after activation are shown in Figure 6.23a. The main S $2p_{3/2}$ XPS peak was found at the binding energy of 161.2 eV when the sphalerite sample was conditioned in water (at pH 10.5). This peak is usually assigned to the sulphide of the sphalerite mineral. When the sphalerite was activated with copper nitrate, the S $2p_{3/2}$ XPS peaks were found at 161.3 and 163.2 eV (Figure 6.23b). The peak at 163.2 eV can be attributed to the presence of polysulphides on the surface of Cu(II)-activated sphalerite (Prestidge et al., 1997). When the activation of sphalerite was carried out in the presence of cuprous cyanide complexes, S $2p_{3/2}$ XPS peaks were also found at 161.3 and 163.2 eV (Figure 6.23c). “There was no detectable elemental sulphur (which would give a peak at the binding energy of 164 eV) when the sphalerite was activated with copper.”

The elemental atomic concentrations of sphalerite samples determined by XPS are given in Table 6.4. Elemental concentrations were normalised by ignoring the atomic concentration of carbon for a more direct comparison of Zn, Cu, S and O.

Table 6.4. Elemental surface concentrations of copper activated sphalerite samples determined by XPS at pH 10.5

Sample	Conditioning	XPS atomic concentration (%)				
	30 min	Zn *2p*	S *2p*	O *1s*	N *1s*	Cu *2p*
A	Water (pH 10.5)	25.7	45.4	28.9	0	0
B	10^{-3} M Cu(I)*	19.0	40.0	32.1	8.6	0.3
C	10^{-2} M Cu(I)*	15.6	40.2	36.6	6.4	1.3
D	10^{-2} M Cu (II)**	3.8	36.6	46.8	9.0	4.2

(*) as $Cu(CN)_3^{2-}$
(**) as $Cu(NO_3)_2$

As expected, sphalerite A, which was conditioned in water (at pH 10.5), did not contain any copper on its surface. However, sphalerite B and C, which were treated with copper cyanide complexes, had some copper species on their surfaces. This shows that copper cyanide complexes could activate sphalerite. Sample D was conditioned with copper nitrate for 30 minutes. Copper nitrate is often used for the activation of sphalerite, and it is known that $Cu(OH)_2$ is the predominant species when zinc sulphide is activated by Cu(II) ions at alkaline pH (Wang *et al.*, 1989a,b; Reddy and Reddy, 1988). As expected, the amount of copper present on the surface of sphalerite was higher on the sample treated with copper nitrate as compared to the sample treated with copper cyanide complexes.

The increase in the concentration of copper was accompanied by a larger decrease in the concentration of zinc on the surface of sphalerite. In the case of cyanide complexes, the concentration of copper also increased with the initial concentration of Cu(I) present in solution. The concentration of oxygen in all activated sphalerite samples increased with the concentration of copper. The decrease in the atomic percentage of zinc can be explained by the adsorption of a copper species on the surface of sphalerite. From the results on B, C and D, it was clear that more copper species had adsorbed onto the surface when the sphalerite is exposed to copper nitrate than to copper cyanide complexes.

In order to investigate the effect of cyanide on the deactivation of copper activated sphalerite, samples previously activated with copper nitrate and copper cyanide complexes were treated with 10^{-2}M NaCN for 20 minutes and then analysed. Elemental surface concentrations of these samples are presented in Table 6.5.

Table 6.5. Elemental surface concentrations of cyanide treated sphalerite samples determined by XPS at pH 10.5

Sample	Conditioning 1	Condition. 2	XPS atomic concentration (%)				
	30 min	20 min	Zn *2p*	S *2p*	O *1s*	N *1s*	Cu *2p*
E	10^{-2} M Cu(I)*	10^{-2}M NaCN	13.7	45.8	37.2	3.3	0
F	10^{-2} M Cu(II)**	10^{-2}M NaCN	5.7	40.3	43.9	8.7	1.5

(*) as $Cu(CN)_3^{2-}$
(**) as $Cu(NO_3)_2$

These results showed that there was complete copper removal from the surface of sphalerite in the case of sample E, which had previously been treated with copper cyanide complexes. In the case of sample F, which had been activated by copper nitrate, only partial removal of copper species was achieved after 20 minutes.

The atomic concentration of oxygen was reduced when sphalerite which had been activated by Cu(II) was treated with cyanide. This is in agreement with the results of Prestidge et al. (1997) as presented in Table 6.6.

Table 6.6. Elemental surface concentrations of cyanide treated copper(II) activated zinc sulphide as determined by XPS (After Prestidge et al., 1997)

Conditioning 1	Conditioning 2	XPS atomic concentration (%)			
30 min	10 min	Zn *2p*	S *2p*	O *1s*	Cu *2p*
pH 9	-	49.9	40.8	9.3	0
1.2 x 10^{-4} M Cu(II) at pH 9		33.9	32.0	25.4	8.7
1.2 x 10^{-3} M Cu(II) at pH 9		15.9	19.7	46.5	17.9
1.2 x 10^{-2} M Cu(II) at pH 9		4.1	7.0	67.7	21.2
1.2 x 10^{-4} M Cu(II) at pH 9	10^{-3}M KCN	42.6	37.7	19.4	0.3
1.2 x 10^{-3} M Cu(II) at pH 9	10^{-3}M KCN	31.0	35.3	26.2	7.5
1.2 x 10^{-2} M Cu(II) at pH 9	10^{-3}M KCN	6.6	9.4	64.9	19.1

This could reflect the removal of $Cu(OH)_2$ from the surface of the sphalerite. Prestidge et al. (1997) also reported that the effectiveness of deactivation by cyanide is dependent on the form of copper at surface which, in turn, is controlled by the concentration of copper (II) during activation, pH, electrochemical potential, and times for activation and deactivation. Prestidge et al. (1997) used various dosages of Cu(II) to study the copper-surface coverage of sphalerite, and hence calculated the equivalent number of adsorbed copper monolayer.

It is concluded that copper abstraction from the surface of sphalerite can be achieved by adding excess cyanide to the pulp. The increase in free cyanide concentration during the depression of sphalerite by addition of sodium cyanide should leach out copper that had previously adsorbed onto the surface of sphalerite by complexation of cuprous cyanide species. Thus, it is believed that an excess of cyanide may be required to keep copper in solution as copper cyanide complexes rather than adsorbing onto the surface of sphalerite during the flotation of lead concentrate. However, the effect of free cyanide can be compromised at high pulp potential by cyanide oxidation.

6.5. Relevance to flotation in the galena circuit at Rosh Pinah Mine

The presence of zinc in the lead concentrate contributes to loss of income for the Rosh Pinah Mine. In order to minimise the presence of zinc in final lead concentrate, sodium cyanide is used to depress the flotation of copper activated sphalerite and of pyrite. However, the depression of sphalerite is achieved with high dosage of sodium cyanide during plant operation (see Table 2.5). An understanding of the factors affecting the selectivity between galena, sphalerite and pyrite is important for the optimisation of the cyanide dosage used at the plant. These factors include the pulp chemistry (Eh, pH and dissolved oxygen), the particle size distribution, the mineral distribution, the concentrate mass pull, the xanthate dosage and the froth stability. At Rosh Pinah Mine, milling is carried out using a steel ball mill with steel grinding media, which together with labile minerals in the ore, scavenges the oxygen in the pulp. From the findings of this study, it is believed that the milling environment of the ore and the presence of copper in the process water have a significant influence on the flotation selectivity between galena and sphalerite in the lead flotation circuit. Clearly, the electrochemical pulp potential would have to be monitored continuously at the Rosh Pinah plant to study its effect on the flotation behaviour of the ore in the lead flotation circuit. Various flotation plants have successfully applied the concept of controlled pulp potential in galena flotation of complex lead-zinc sulphide ores (Woods, 2003).

In addition, the quality of recycle water used in the milling system should be taken into account during the optimisation of the reagent suite for efficient flotation selectivity between galena and sphalerite. The concentration of dissolved copper in the process water (at the time of this study) was found to be relatively high (17-30 mg/L Cu). One possible solution is that the current volume of the recycled water (84% v/v), which is sent to the milling and lead flotation circuit, be decreased. However, since the Rosh Pinah Concentrator is located in an arid area, a more appropriate solution to the problem would be the removal of copper species from the recycle water. Various techniques are proposed in the literature (Rao and Finch, 1989). Organic matters and metal-cyanides can be removed by treating the process water with activated carbon. Moreover, seasonal survey of process water is required to study the effect of process water on the flotation selectivity in the lead circuit.

A previous water survey (Table 6.1) has also shown that the recycle water still contains excess of free cyanide (50-60mg/L). This indicates that the initial dosage of cyanide used in the milling circuit is much higher than the amount required for the depression of sphalerite. The activation of sphalerite by copper from the ore itself and copper from the recycle water can also explain the increase in the amount of cyanide that is currently used at the plant. However, an important aspect such the mode of occurrence of various minerals in the Rosh Pinah deposit has to be studied in order to optimise the reagent suite and the liberation of minerals.

6.6. Conclusion

The effects of the grinding environment, pulp potential and copper cyanide complexes on the flotation of the lead-zinc sulphide composite from the Rosh Pinah deposit were studied in this chapter. Measurements of the pulp potential have indicated that the grinding environment (wet and dry milling) can influence the pulp potential and subsequently the surface properties of the mineral to be floated. It was observed that:

- More positive pulp potentials were measured when the composite had been ground in a dry environment. The difference in pulp potentials between the dry and wet ground composite was approximately 260 mV after the grinding stage;

- The recovery of sphalerite from the complex lead-zinc sulphide composite was higher when the composite was milled in a dry environment compared with the wet environment. In addition, the recovery of galena decreased after milling in a dry environment, while wet milling improved its recovery. The net effect was that the flotation selectivity between galena and sphalerite was improved by wet milling ;

- Batch flotation and XPS results have demonstrated that copper cyanide complexes can activate sphalerite. The activation and subsequent flotation of sphalerite was greater after dry milling;

The results presented in this study have confirmed that the flotation selectivity of complex sulphide ore is still a function of the electrochemical potential of the pulp. Thus, controlling the pulp potential during the milling stage would have a significant impact on the conditioning and flotation response of the complex ores, because the excessive oxidation of minerals and grinding media generates oxidation products that are usually detrimental to flotation.

Chapter 7. Depression of sphalerite with cyanide and zinc sulphate

7.1. Introduction

Cyanide is the only depressant currently used at the Rosh Pinah Mine to depress sphalerite and pyrite in the lead flotation circuit. As explained in Chapter 2, cyanide dosages of 150-180 g/t NaCN are often used at the plant at the natural pH of about 8.5±0.3. Despite the high dosage of cyanide used in the lead flotation circuit, it is assumed that approximately 1250 tons of zinc is lost every year in the lead concentrate (Katabua and Molelekoe, 2003). For a zinc price of approximately US-$1100 (Metal prices LME, March 2004) per ton of zinc, the annual income loss due to zinc deportment in the lead concentrate can be estimated to a total net smelter value of $1 168 750. It is believed that this financial loss can be partly reduced if the reagent suite is optimised. In addition, decreasing the amount of cyanide in the lead circuit will also lead to a decrease in the dosage of copper sulphate that is needed to re-activate the sphalerite in the zinc flotation circuit.

Since chalcopyrite (0.3%) is also present in the Rosh Pinah Mine ore, it is believed that the dissolution and/or oxidation of chalcopyrite and galena can contribute to the presence of copper and lead ions in the flotation pulp during the beneficiation of the ore. The sphalerite can then be inadvertently activated by dissolved copper and lead ions during the flotation of galena. As discussed in Chapter 3, cyanide is known to depress the flotation of copper activated sphalerite by leaching out copper from the surface of sphalerite. However, the formation of stable lead cyanide complexes is thermodynamically unfavourable and hence cyanide cannot counteract activation by lead. In most plants, sodium cyanide is usually used in conjunction with zinc sulphate for the effective depression of sphalerite from Cu-Pb-Zn sulphide ore at alkaline pH values. Examples are presented in Table 7.1 (Tveter and McQuiton, 1962). The metallurgical results of the Rosh Pinah plant are also given for comparison purposes. The expected effect of zinc sulphate will be discussed in the next section.

As seen in Table 7.1, the dosage ratio of $ZnSO_4$ to NaCN varied from approximately 2.5 to 4. The high dosage of depressant used at Société Algerienne du Zinc was probably due to the high content of zinc (24.3%) in the feed material as compared to 6-9% Zn at the Rosh Pinah plant. In addition, the mineralogy of the ore treated at both the Bunker Hill and Société Algerienne du Zinc concentrators is similar to the Rosh Pinah ore (Table 2.3), despite the differences in their respective chemical compositions and metallurgical results (Tables 2.4 and 7.1).

Table 7.1. Selective flotation of complex lead-zinc sulphide minerals (Modified from Tveter and McQuiton, 1962).

MINE / MINERALOGY	DEPRESSANTS	PRODUCT	METALLURGICAL RESULTS			
	(g/t)		Assays (%)		Distribution (%)	
	Lead circuit		Pb	Zn	Pb	Zn
Bunker Hill Co., Kellogg, Idaho *(Galena, sphalerite, pyrite, quartz)*	NaCN: 46 $ZnSO_4$: 115	*Mill Feed*	*7.1*	*2.5*	*100*	*100*
		Pb Conc.	66.0	5.9	96.7	23.9
		Zn Conc.	1.8	54.1	0.8	65.2
		Tails	0.2	0.3	2.5	10.9
Société Algerienne du Zinc, Bou Beker, Morocco *(Galena, Sphalerite, pyrite, dolomite)*	NaCN: 130 $ZnSO_4$: 511	*Mill Feed*	*3.55*	*24.3*	*100*	*100*
		Pb Conc.	73.1	2.98	93	1
		Zn Conc.	0.39	62.4	4	98
		Tails	0.21	0.55	3	1
Rosh Pinah Mine *(Galena, sphalerite, pyrite, chalcopyrite, dolomite, quartz)*	NaCN: 150-180	*Mill Feed*	*1-3*	*6-9*	*100*	*100*
		Pb Conc.	55-60	5-7	70-75	2-3
		Zn Conc.	1-2	52-55		80-85

Based on the wide literature on sphalerite depression, it is necessary to study the flotation response of the Rosh Pinah ore in the presence of cyanide alone and in conjunction with zinc sulphate. The use of zinc sulphate alone has been ruled out since traces of chalcopyrite are present in the Rosh Pinah ore, and the deactivation of copper-activated sphalerite is not efficient at lower dosages of zinc sulphate alone. In addition, Trahar et al. (1997) have shown that the use of zinc salts at pH 9 decreased the recovery of galena due to the coating by hydrophilic zinc hydroxide. A study on the deportment of sphalerite in the lead flotation circuit was carried out in the work reported here for a better understanding of the high dosage of cyanide required for the depression of sphalerite at the Rosh Pinah plant.

Since an overview on cyanide depression was presented in Chapter 3, only the effect of zinc sulphate alone and in conjunction with sodium cyanide will be discussed in the following sections.

7.2. Deactivation with zinc sulphate

At Rosh Pinah Mine, the selective flotation of the lead-zinc sulphide composite is carried out at mildly alkaline pH values. However, depending on the flotation conditions, sphalerite can be activated by products from the dissolution and/or oxidation of galena and chalcopyrite.

Fuerstenau and Metzger (1960) and El-shall et al. (2000) proposed that the deactivation lead-activated sphalerite by zinc sulphate would occur by the replacement of the lead ions out of the surface of sphalerite by zinc ions according to the following equation:

$$PbS_{(s)} + Zn^{2+} = ZnS_{(s)} + Pb^{2+} \qquad [7.1]$$

They support the argument that zinc salts should be able to prevent Pb^{2+} activation of sphalerite only if the ratio of $[Zn^{2+}]/[Pb^{2+}]$ exceeds a value of 10^3 in solution. However, it is difficult to accept that lead ion, which has the ionic radius of approximately 1.2A would replace zinc ion which has a smaller ionic radius of 0.6A. It is likely that the adsorption of Zn^{2+} (at acidic pH values) onto the surface of lead-activated sphalerite will decrease its flotation because of the weakness of zinc-xanthate complexes. The solubility of zinc sulphate as a function of pH at 25°C is shown in Figure 7.1.

When flotation is conducted at alkaline pH values, Marsicano et al. (1975) assumed that the pH at which depression by zinc sulphate starts will coincide with the appearance of colloidal zinc compounds such as $Zn(OH)_2$. For a total concentration of 10^{-3}M $ZnSO_4$, which is usually used in plant practice, it can clearly be seen that the onset of $Zn(OH)_2$ precipitation is at pH 7.3. Thus, for mildly alkaline pH of about 8.5 used in the selective flotation of the lead-zinc sulphide composite at the Rosh Pinah Mine, it is clear that $Zn(OH)_2$ would be the depressing agent when zinc sulphate is used to depress the lead-activated sphalerite as shown in the following equation:

$$ZnS.PbS_{(s)} + Zn(OH)_2 = ZnS.PbS_{(s)}.Zn(OH)_2 \qquad [7.2]$$

Therefore, the presence of hydrophilic zinc hydroxide at the surface of sphalerite will prevent the interaction between the lead-activated sphalerite and xanthate, and subsequently decrease its floatability in the lead flotation circuit.

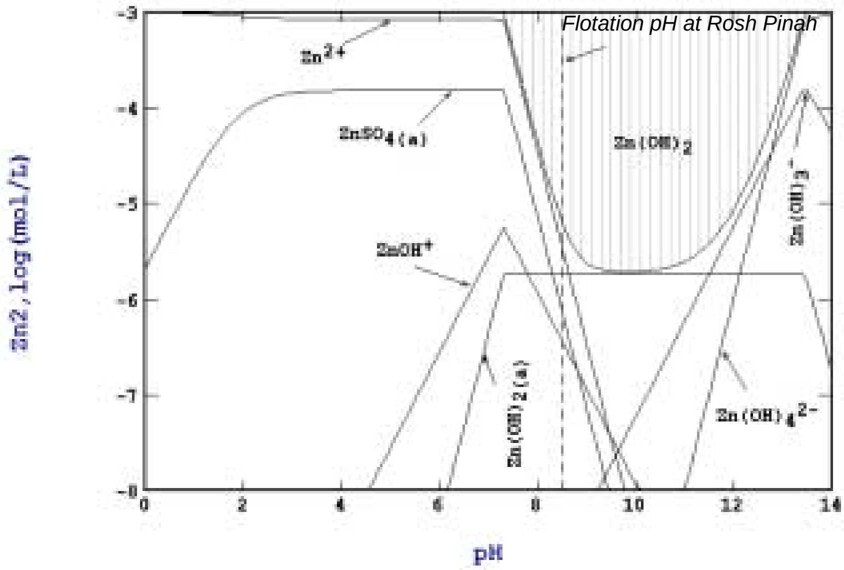


Figure 7.1. Speciation diagram for Zn(II) as a function of pH for [ZnSO$_4$] = 10^{-3}M at 25 °C. Stabcal software NBS database (Huang, 2003).

Overdosing of zinc sulphate will also decrease the recovery of galena due to the presence of zinc hydroxide on its surface. Since sphalerite from the Rosh Pinah composite is expected to be activated by copper ions, it is thus recommended that both sodium cyanide and zinc sulphate be used as depressants.

7.3. Deactivation with zinc sulphate and sodium cyanide

The solubility of zinc species as functions of pH in the presence of zinc sulphate and sodium cyanide is shown in Figure 7.2. As seen in Figure 7.2 the precipitation of colloidal zinc hydroxide can occur at the range of alkaline pH values used at the Rosh Pinah plant during the selective flotation of galena and sphalerite if both zinc sulphate and sodium cyanide are used.

However, it has been shown that sphalerite from the Rosh Pinah composite is primarily activated by copper ions present in the flotation pulp. Thus cyanide will react with the copper at the surface of sphalerite to form cuprous cyanide complexes. Thermodynamically, the cuprous cyanide complexes such as $Cu(CN)_3^{2-}$ and $Cu(CN)_2^-$

are predicted to be the most predominant cyanide species at alkaline pH values when sodium cyanide and zinc sulphate are used to depress sphalerite (Figure 7.3). In addition, a lower concentration of $Zn(CN)_4^{2-}$ is also expected to be present in the solution.

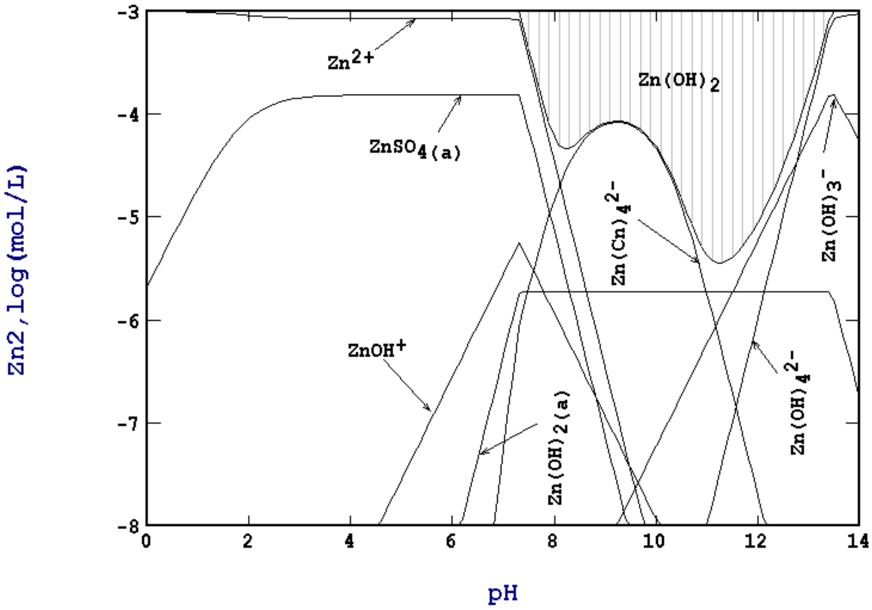


Figure 7.2. Speciation diagram for Zn(II) as a function of pH in the presence of 10^{-3}M NaCN and 10^{-3}M $ZnSO_4$ at 25 °C. Stabcal software. NBS database (Huang, 2003).

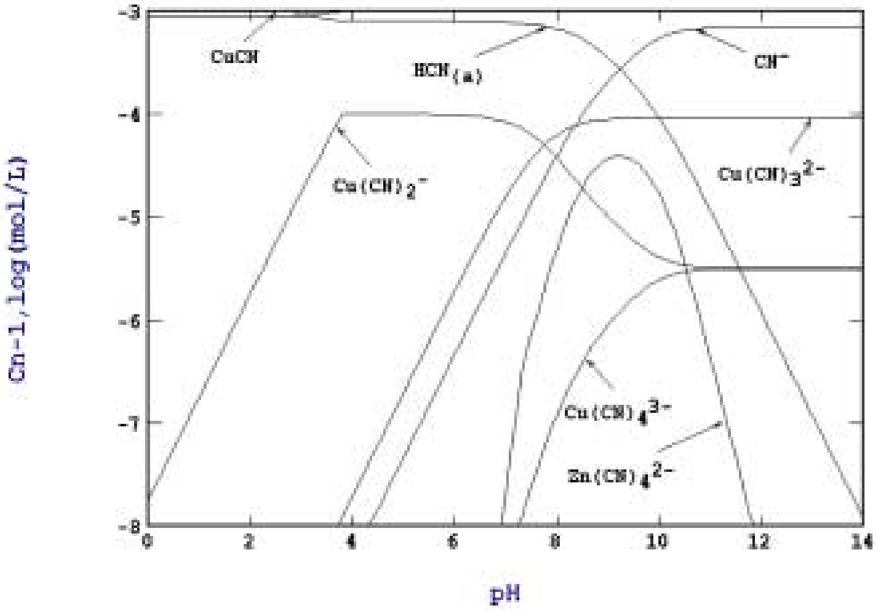


Figure 7.3. Speciation diagram for CN^- as a function of pH in the presence of 10^{-3}M NaCN, 10^{-3}M $ZnSO_4$, and 10^{-4}M Cu(I) at 25 °C. Stabcal software. NBS database (Huang, 2003).

As seen in Figure 7.3 the concentration of free cyanide in solution will decrease with decreasing pH. Thus, it is also important to monitor the pH of the flotation pulp for an efficient consumption of sodium cyanide during the depression of sphalerite to avoid the loss of free cyanide at pH values lower than 8.

Based on the thermodynamic information presented in Figures 7.2 and 7.3, it appears possible to depress sphalerite when it has been activated by both copper and lead ions by using sodium cyanide and zinc sulphate at alkaline pH values. The most plausible mechanisms of depression would be the complexation of surface copper with free cyanide and the precipitation of hydrophilic zinc hydroxide on the surface of sphalerite.

The experimentally determined effects of sodium cyanide and zinc sulphate dosages on the flotation of sphalerite from the Rosh Pinah composite ore are presented in the following sections.

7.4. Effect of sodium cyanide on the flotation response of the Rosh Pinah composite

The composite sample was milled at approximately 67% (w/w) solids in an unlined mild steel mill with mild steel rods. The target grind was 80% passing 100 micron as used previously in Chapter 6. After milling, the pulp was transferred into the flotation cell and then diluted to 33% (w/w) solids. The desired amounts of depressant and 50g/t SNPX were added simultaneously and the pulp was conditioned for 3 minutes. Senfroth 9325 was added and the pulp conditioned for a further 1 minute. Rougher rate tests were carried out at the natural pH of 8.5 without copper cyanide in order to study the effect of depressant in the presence of potential activating species from the composite itself. This testwork differs from that carried out in Chapter 5 (Figures 5.10-5.14) in the sense that in that case the composite sample was dry milled to 80% passing 75 micron (the effect of milling environment on flotation selectivity was discussed in detail in Chapter 6).

The effect of sodium cyanide dosage on the concentrate mass pull is presented in Figure 7.4. As seen in Figure 7.4, the concentrate mass pull decreased from 15.0 to

14.4% when 50 g/t NaCN was added into the flotation cell. The mass pull decreased from 15.0 to 12.8 and 12.9% when 100 and 150g/t NaCN were added, respectively.

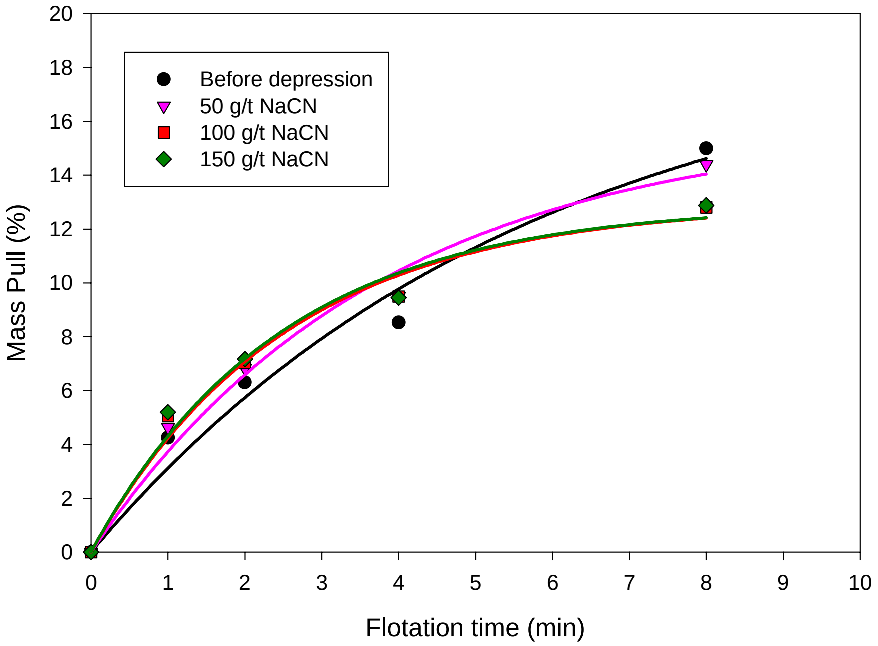


Figure 7.4. Effect of sodium cyanide dosages on the concentrate mass pull of the Rosh Pinah composite after flotation with 50g/t SNPX.

The recovery and grade of sphalerite at various dosages of sodium cyanide are presented in Figures 7.5 and 7.6, respectively.

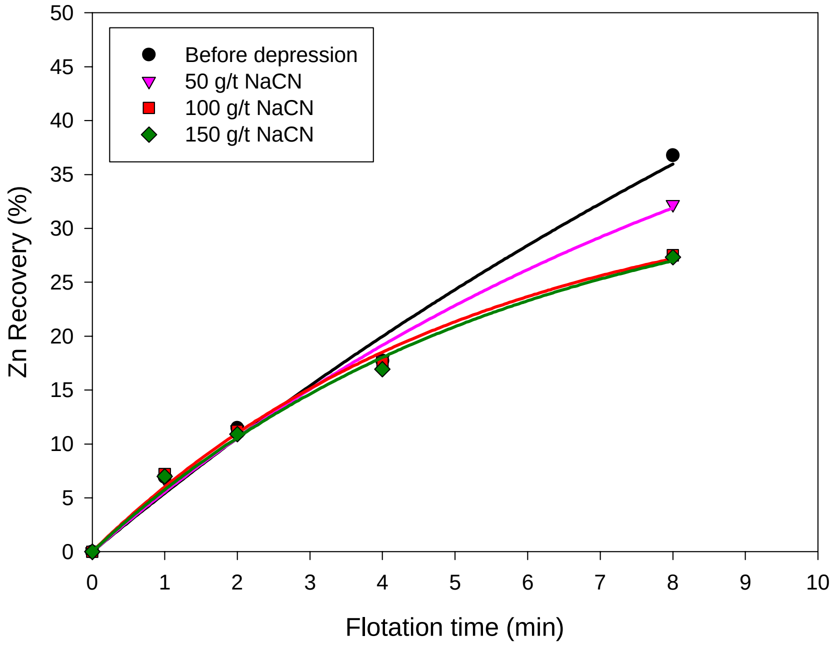


Figure 7.5. Flotation recovery of zinc from a galena-sphalerite composite from Rosh Pinah at various dosages of sodium cyanide, 50 g/t SNPX and pH 8.5.

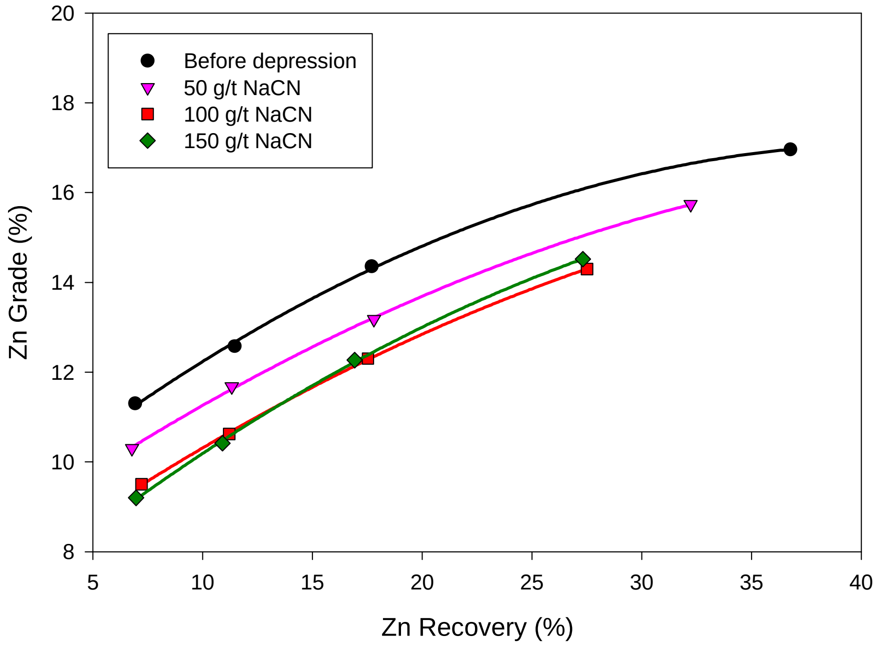


Figure 7.6. Recovery and grade of zinc from a galena-sphalerite composite from Rosh Pinah at various dosages of sodium cyanide, 50 g/t SNPX and pH 8.5.

The recovery of sphalerite decreased from 37 to 32 and 28% with the additions of 50 and 100 g/t NaCN, respectively. There was only a slight decrease of approximately 1%, which is within experimental error, in the recovery of sphalerite upon increasing the amount of cyanide from 100 to 150 g/t.

The flotation results presented in Figure 7.6 indicate that both the recovery and grade of sphalerite decreased with the addition of sodium cyanide. In addition, maximal depression of sphalerite was obtained after the addition of 100 g/t NaCN.

The decrease in the recovery of sphalerite is likely to be due to the deactivation of copper-activated sphalerite by cyanide ions, because of the presence of chalcopyrite in the Rosh Pinah composite. The activation and deactivation of copper-activated sphalerite is discussed in the literature (Prestidge et al., 1997).

The effects of sodium cyanide on the recovery and grade of galena are shown in Figures 7.7 and 7.8, respectively. As seen in Figure 7.7, the recovery of galena was not adversely affected by the presence of sodium cyanide. In addition, the grade of lead in the concentrate increased when cyanide was added in the flotation cell (Figure 7.8), as expected from the decreased sphalerite recovery.

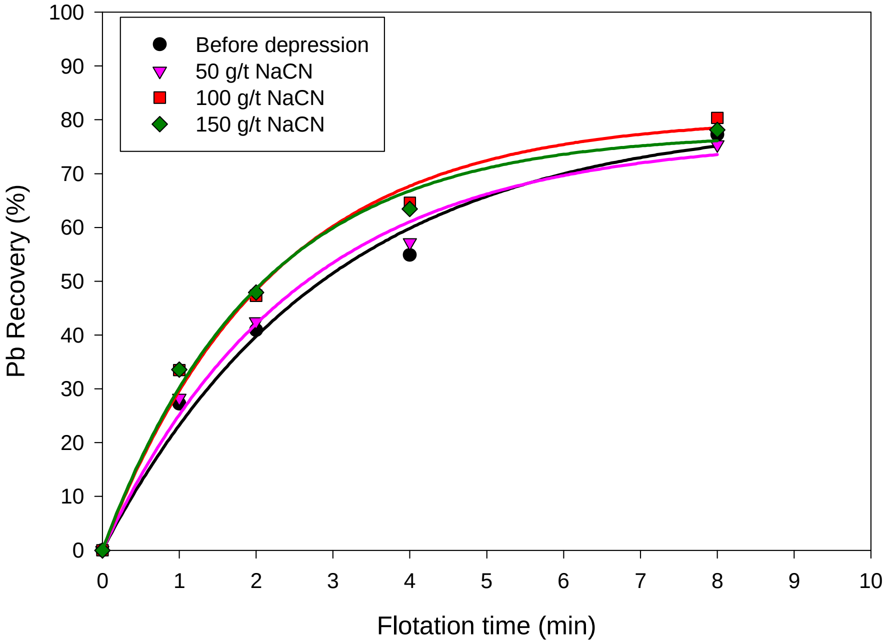


Figure 7.7. Flotation recovery of lead from a galena-sphalerite composite from Rosh Pinah at various dosages of sodium cyanide, 50 g/t SNPX and pH 8.5.

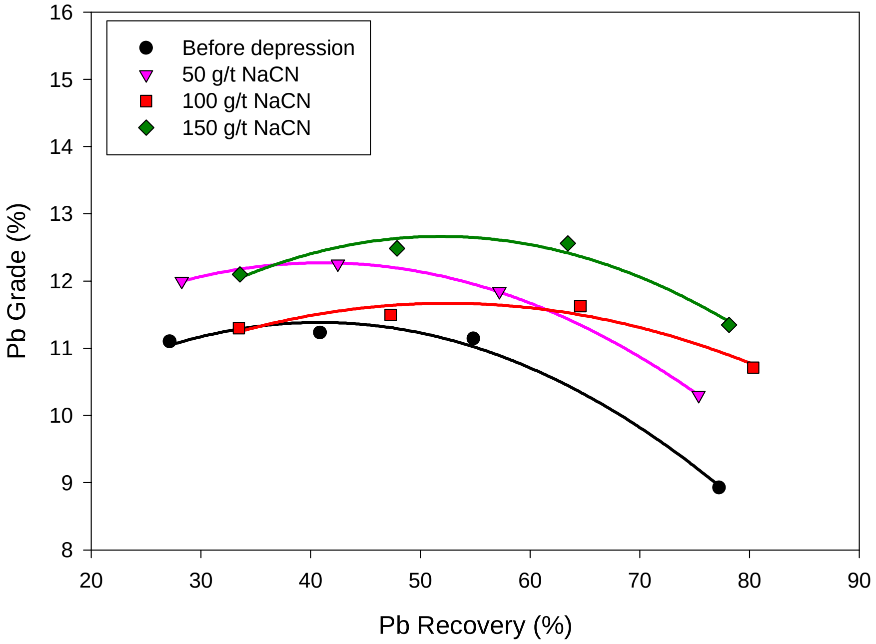


Figure 7.8. Recovery-grade of lead from a galena-sphalerite composite from Rosh Pinah at various dosages of sodium cyanide, 50 g/t SNPX and pH 8.5.

The influence of free cyanide on the flotation recovery of galena has been investigated in the literature (Prestidge et al. 1993; Grano et al., 1990). Prestidge et al. (1993) have studied the effect of cyanide on the adsorption of ethyl xanthate on galena at different pulp potentials. They have proposed an overall reaction, whereby cyanide ions enhance the dissolution of galena, as follows:

$$PbS + CN^- + 2X^- = PbX_2 + CNS^- + 2e \qquad [7.3]$$

Prestidge et al. (1993) and Ralston (1994) proposed that cyanide depleted the galena surface of sulphur, forming CNS^-, leaving a residual lead-rich surface, which is more receptive to ethyl xanthate interaction. Because lead hydroxide and lead xanthate species are less soluble and more stable than lead cyanide, it has been accepted that the depression of galena by cyanide is thermodynamically not favourable.

Figure 7.9 shows the effect of sodium cyanide on the flotation selectivity between galena and sphalerite.

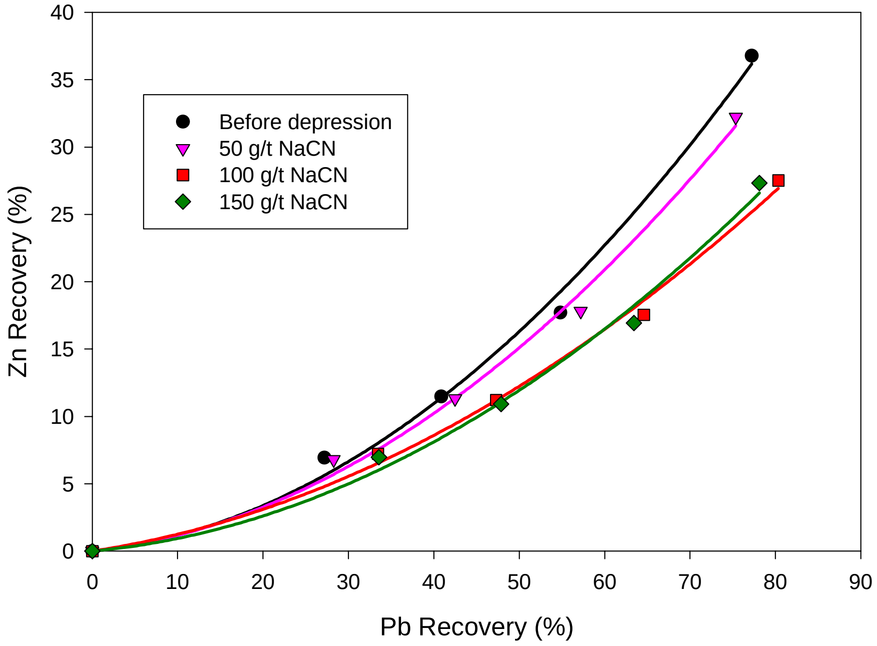


Figure 7.9. Recovery-grade of lead from a galena-sphalerite composite from Rosh Pinah at various dosages of sodium cyanide, 50 g/t SNPX and pH 8.5.

As expected, the flotation selectivity was improved by the addition of sodium cyanide. As stated above, increasing the cyanide dosage above 100 g/t NaCN gave no further improvement in flotation selectivity. These results are in agreement with those reported by Bredenhann and Coetzer (2002). They conducted flotation testwork on the same ore bodies and they failed to decrease substantially the recovery of sphalerite in the lead concentrate even at higher dosages such as 400 g/t NaCN (Figure 7.10). However, their sphalerite recoveries were much higher than that obtained in this study probably due to their higher concentrate mass pull (approximately 30%) as compared to lower values obtained in this study (Table 7.2).

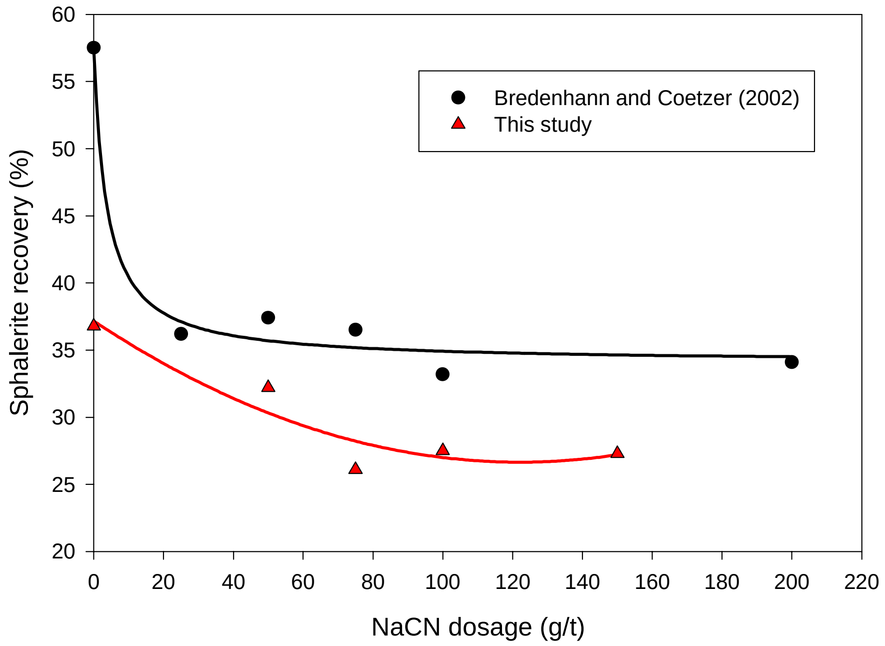


Figure 7.10. Effect of sodium cyanide on the recovery of sphalerite during the flotation of galena from a composite from Rosh Pinah.

Table 7.2. Metallurgical results of the Rosh Pinah composite after 8 minutes of flotation time in the presence of 50 g/t PNBX and various concentrations of sodium cyanide at pH 8.5

Depressant	Mass Pull	Recovery (%)		Grade (%)	
NaCN (g/t)	(%)	Pb	Zn	Pb	Zn
0	15.0	77.4	36.8	8.9	17.0
50	14.4	75.0	32.2	10.3	15.7
75	11.8	71.7	26.2	10.4	15.3
100	12.8	80.1	27.5	10.7	14.3
150	12.9	78.2	27.4	11.4	14.5

The results presented in this section have indicated that the depression of sphalerite from the Rosh Pinah ore can partly be achieved by using cyanide. However, the high dosage of cyanide used at the Rosh Pinah plant (up to 180g/t NaCN) could not be explained since there was no improvement in the flotation selectivity above 100 g/t NaCN as shown in Figure 7.9. The recovery of sphalerite can be decreased further by upgrading the rougher concentrate and hence decreasing the mass pull.

Based on the chemical and mineralogical composition of the Rosh Pinah ore, it is possible that the sphalerite is activated by both copper and lead ions. It is not possible to depress the lead-activated sphalerite with cyanide ions, which is the proposed role of the second depressant, zinc sulphate. The combined effect of sodium cyanide and zinc sulphate on the flotation of sphalerite in the lead circuit is presented in the next section.

7.5. Effect of sodium cyanide and zinc sulphate on the flotation response of the Rosh Pinah composite

Flotation testwork was conducted at the natural pH (8.5±0.1) of the ore in the presence of various concentrations of sodium cyanide and zinc sulphate as explained in the previous section. Both sodium cyanide and zinc sulphate were added simultaneously with xanthate in the flotation cell. The cyanide dosage of 75 g/t was used based on the flotation results presented in Figure 7.9. In addition, the zinc sulphate dosages of 200 and 400 g/t were used to give $ZnSO_4$ to NaCN dosage ratios of approximately 3 and 5. Figure 7.11 shows the effect of depressant dosages on the concentrate mass pull.

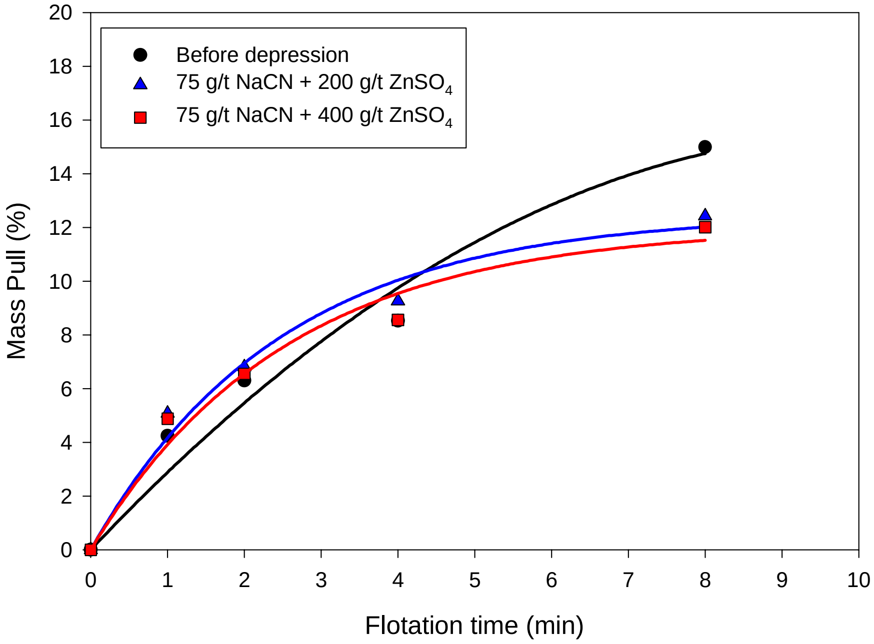


Figure 7.11. Effect of sodium cyanide and zinc sulphate dosages on the concentrate mass pull of a composite sample from Rosh Pinah in the presence of 50g/t SNPX.

As expected, the concentrate mass pull decreased from 15.0 to 12.4% after the addition of 75 g/t NaCN and 200 g/t $ZnSO_4$. However, the concentrate mass pull remained almost unchanged (12.0%) after increasing the dosage of zinc sulphate further to 400 g/t. These results indicated that the mass pull was decreased slightly further by the combination of 75 g/t NaCN and 200 g/t $ZnSO_4$ when compared to the use of 100 g/t NaCN alone (mass pull of 12.8% -see section 7.4).

The recovery of sphalerite at various dosages of depressants is shown in Figure 7.12 and summarised in Table 7.3. The grade-recovery relationship for different depressant dosages is shown in Figure 7.13.

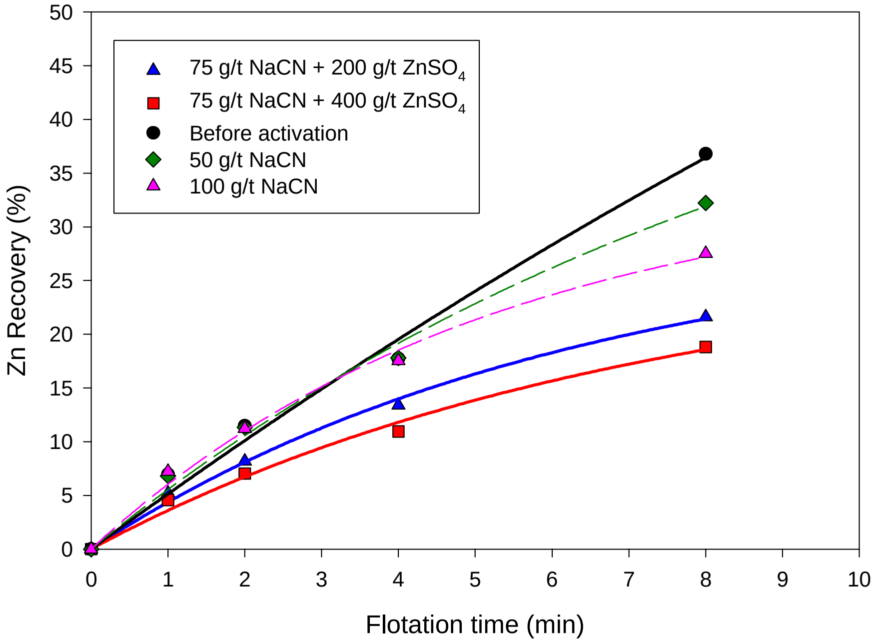


Figure 7.12. Flotation recovery of zinc from a Rosh Pinah composite sample at various dosages of sodium cyanide and zinc sulphate, 50 g/t SNPX and pH 8.5.

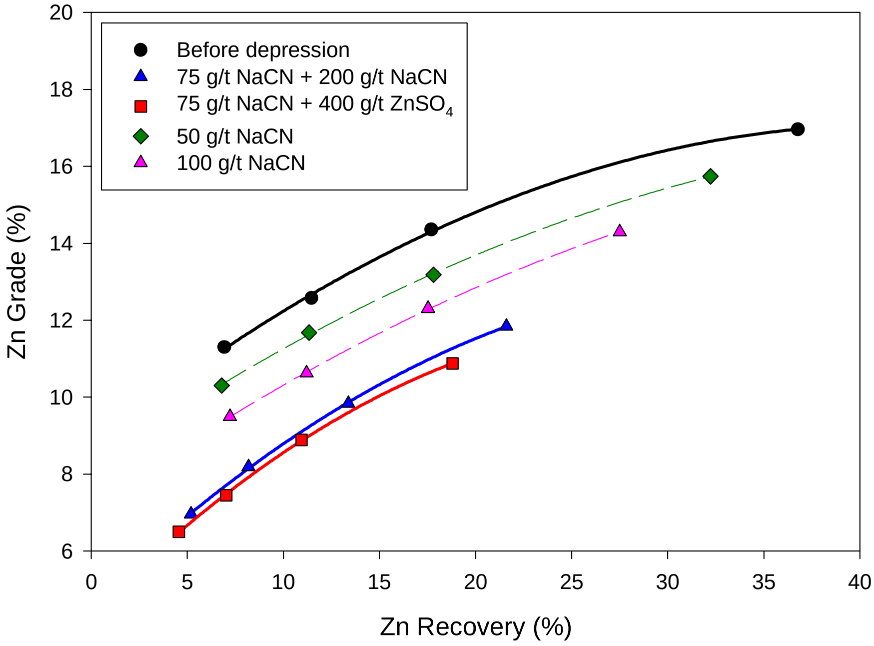


Figure 7.13. Recovery-grade relationship of zinc from a Rosh Pinah composite sample at various dosages of sodium cyanide and zinc sulphate, 50 g/t SNPX and pH 8.5.

Table 7.3. Metallurgical results of the Rosh Pinah composite after 8 minutes of flotation time in the presence of 50 g/t PNBX and various concentrations of sodium cyanide at pH 8.5

Depressants (g/t)		Mass Pull	Recovery (%)		Grade (%)	
NaCN	$ZnSO_4$	(%)	Pb	Zn	Pb	Zn
0	0	15.0	77.4	36.8	8.9	17.0
75	100	10.3	71.9	21.8	11.3	13.3
75	200	12.4	72.7	21.6	11.7	11.8
75	400	12.0	71.5	18.8	11.6	10.9
50	0	14.4	75.0	32.2	10.3	15.7
100	0	12.8	80.1	27.5	10.7	14.3

The recovery of sphalerite decreased from approximately 37 to 22 and 19% in the presence of 200 and 400 g/t $ZnSO_4$ together with 75 g/t NaCN, respectively. The combination of zinc sulphate and sodium cyanide resulted in better depression of sphalerite when compared to the recoveries of 27% achieved in the presence of 100 and 150 g/t NaCN (Figure 7.5). Furthermore, the final grade of zinc in the lead concentrate decreased from 17.0 to 11.8 and 10.9%, respectively when 200 and 400 g/t of zinc sulphate were used in conjunction with 75 g/t NaCN.

The recoveries of galena as a function of various dosages of cyanide and zinc sulphate are shown in Figure 7.14.

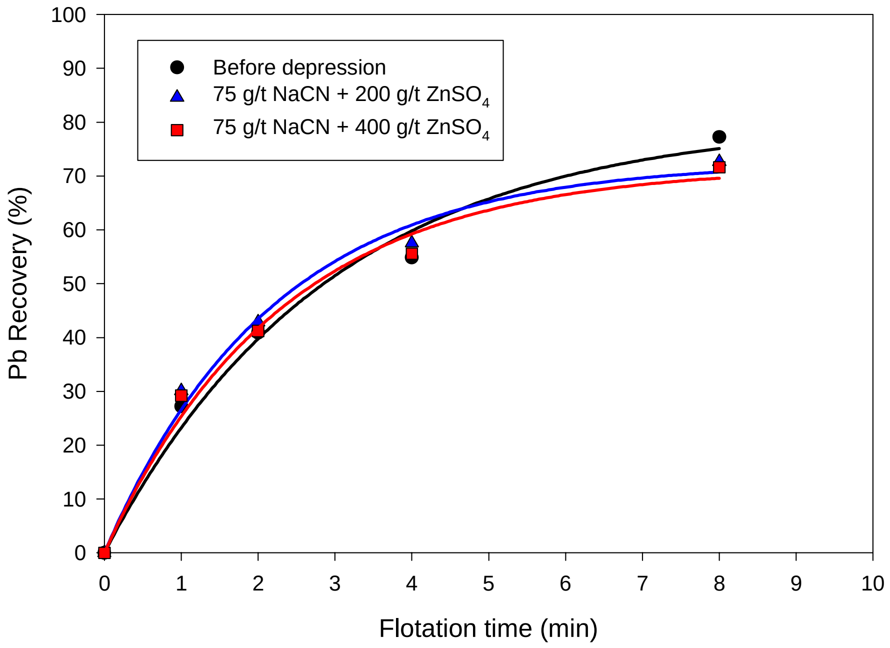


Figure 7.14. Flotation recovery of lead from a Rosh Pinah composite sample at various dosages of sodium cyanide and zinc sulphate,50 g/t SNPX and pH 8.5.

The recovery of galena decreased slightly from 77 to 73 and 72% after the additions of 200 and 400 g/t $ZnSO_4$, respectively in conjunction with 75 g/t NaCN. The observed decrease in the recovery of galena can be caused by the presence of hydrophilic zinc hydroxide on the surface of galena, since zinc hydroxide is not expected to adsorb/precipitate selectively on galena and sphalerite.

As shown in Figure 7.15, the grade of lead in the concentrate increased after the additions of depressant. This was due to the decrease in the recovery of sphalerite in the lead concentrate. The grade of lead increased from 8.9 to 11.7 and 11.6% in the presence of respectively 200 and 400 g/t $ZnSO_4$, when used in conjunction with 75 g/t NaCN.

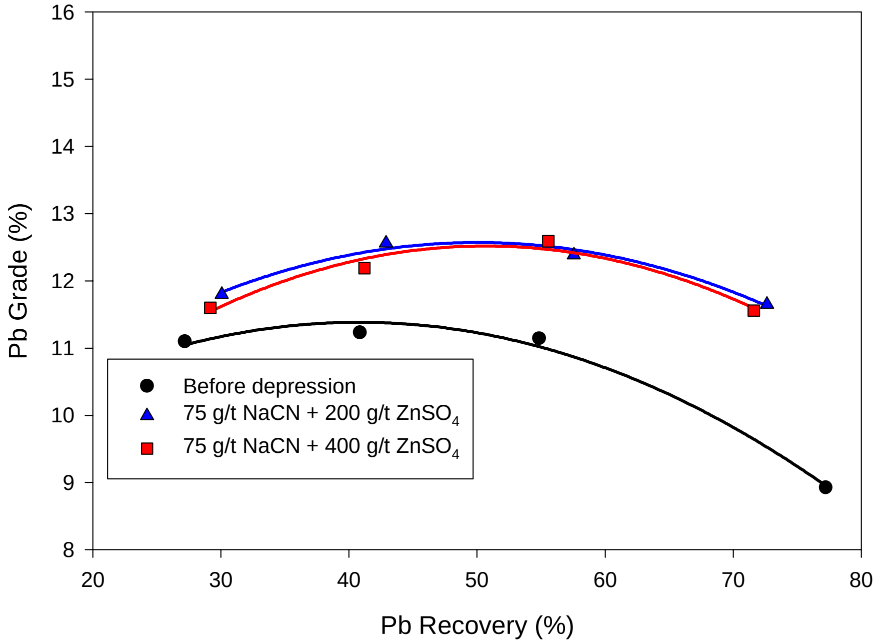


Figure 7.15. Recovery-grade of lead from a Rosh Pinah composite sample at various dosages of sodium cyanide and zinc sulphate,50 g/t SNPX and pH 8.5.

The flotation selectivity between galena and sphalerite for various dosages of depressants is shown in Figure 7.16. It can be seen that the selectivity improved with the addition of both cyanide and zinc sulphate. The additional effect of zinc sulphate on the flotation selectivity can be related to the depression of lead-activated sphalerite as discussed earlier (section 7.2). Although the amount of lead that can activate sphalerite was not quantified, Greet and Smart (2002) proposed a method for the diagnostic leaching of galena and its oxidation products using ethylene diaminetetraacetic acid (EDTA). They demonstrated that all oxygen containing galena oxidation products such as sulphate, hydroxide, oxide, and carbonate are rapidly solubilised in EDTA. They also showed that EDTA does not extract lead from un-reacted galena.

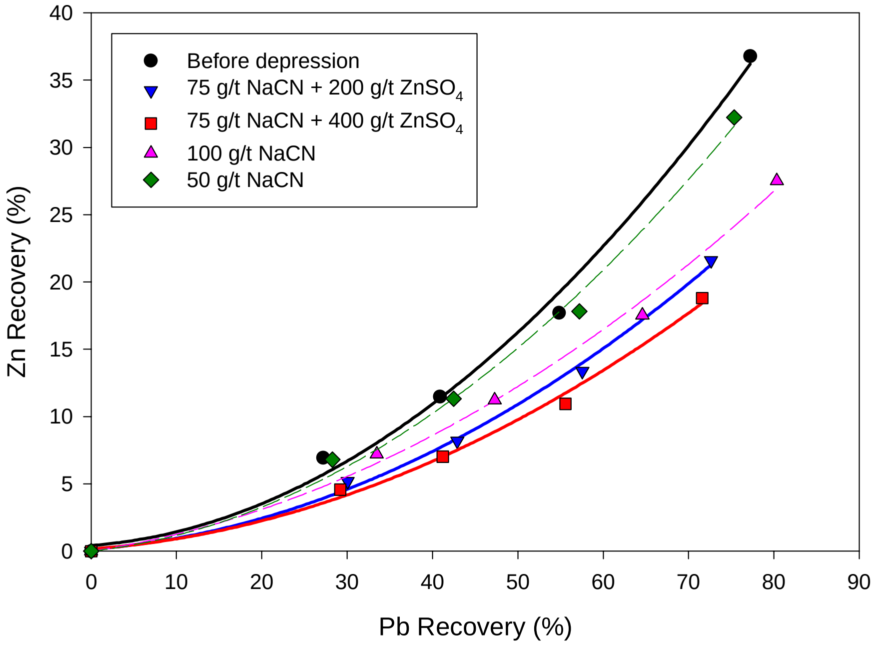


Figure 7.16. Lead and zinc recoveries from a Rosh Pinah composite sample at various dosages of sodium cyanide and zinc sulphate, 50 g/t SNPX and pH 8.5.

It was interesting to observe that the selectivity achieved with 100 g/t NaCN alone was similar to that achieved with the combination of 75g/t NaCN and 200 g/t $ZnSO_4$. However, the recoveries of galena and sphalerite were lower when zinc sulphate was used in conjunction with sodium cyanide in spite of the similarities in their respective concentrate mass pull (Figures 7.2 and 7.9). Since the recovery of galena in the lead rougher concentrate has to be maximised in plant practice, it would be convenient to use 100 g/t NaCN for the depression of sphalerite followed by the optimisation of the depressant in the cleaning stage.

Although the recoveries and grades of sphalerite were decreased with the use of both cyanide and zinc sulphate, separation between galena and sphalerite remains rather poor, and it is important to understand the inefficiency of cyanide on the depression of zinc in the galena concentrate. Mineralogical analysis was carried out to further understand the poor flotation selectivity between galena and sphalerite which persists even in the presence of sodium cyanide.

7.6. Deportment of sphalerite through the flotation products

Applied mineralogy has become a powerful tool to improve the understanding of the ore response to beneficiation practice in the mining industry. The main types of data required to provide an ore-dressing mineralogical assessment are generally as follows (Henley, 1983):

- Mineral identities;
- Mineral composition and proportion;
- Liberation and locking characteristics of the valuable and gangue minerals;
- Distribution of elements among various mineralogical sites throughout the particle size range being considered.

Of critical importance to assessing metallurgical performance during froth flotation are the liberation and locking characteristics of the minerals present in the ore. Optical and scanning electron microscopy usually supply detailed information on the textural properties of minerals and allow the comparison of these features between the various fractions (Seke et al., 2003b; Hope et al., 2001; Lätti et al., 2001). Thus, it is believed that the persistent poor flotation selectivity observed between galena and sphalerite in the presence of cyanide can be explained by the mineralogical texture of the Rosh Pinah flotation products.

7.6.1. Deportment of sphalerite in the lead concentrate from the Rosh Pinah Mine

Mineralogical examination of flotation products from the Rosh Pinah plant was conducted at Kumba Resources R&D (Pretoria) to study the presence of zinc in the galena concentrate in spite of the high dosage of cyanide used to decrease the recovery of sphalerite. The textural properties of the Rosh Pinah final lead concentrate were semi-quantitatively determined by optical particle counting and the results are presented in Table 7.4 with selected data being plotted in Figure 7.17.

As seen in Figure 7.17, most of liberated galena particles were recovered in the -75µm size fraction, while the amounts of liberated sphalerite and gangue particles increased in the +75µm size fraction. Since flotation in the lead circuit is carried out at a primary grind of 80% passing 100µm (Figure 3.3), the concentrate mass pull in the +106µm fraction size will be negligible.

Table 7.4. Particle-counting results (% of 500 particles counted)-Lead concentrate from Rosh Pinah Mine (Reyneke, 2000)

FRACTION	+106 µM	+75 µM	-75 µM
Liberated galena	0.6	4.4	68.8
Liberated sphalerite	2.2	14.8	5.2
Liberated pyrite	1.6	10.0	9.6
Gangue (quartz, dolomite)	92.0	47.4	2.0
Unliberated sphalerite & gangue	1.8	4.4	-
Galena + attached sphalerite (<10µm)	-	-	0.8
Galena + attached gangue (<10µm)	-	0.6	0.4
Galena + attached sphalerite (10-50µm)	0.4	10.6	8.4
Galena + attached gangue (10-50µm)	0.2	2.6	0.4
Galena + attached gangue (>50µm)	1.0	4.0	1.4
Galena + attached sphalerite (>50µm)	0.2	0.8	0.4
Galena + sphalerite inclusions (<10µm)	-	-	0.2
Galena + gangue inclusions (<10µm)	-	0.2	0.4
Galena + sphalerite inclusions (10-50µm)	-	0.2	1.6
Galena + gangue inclusions (10-50µm)	-	-	0.4

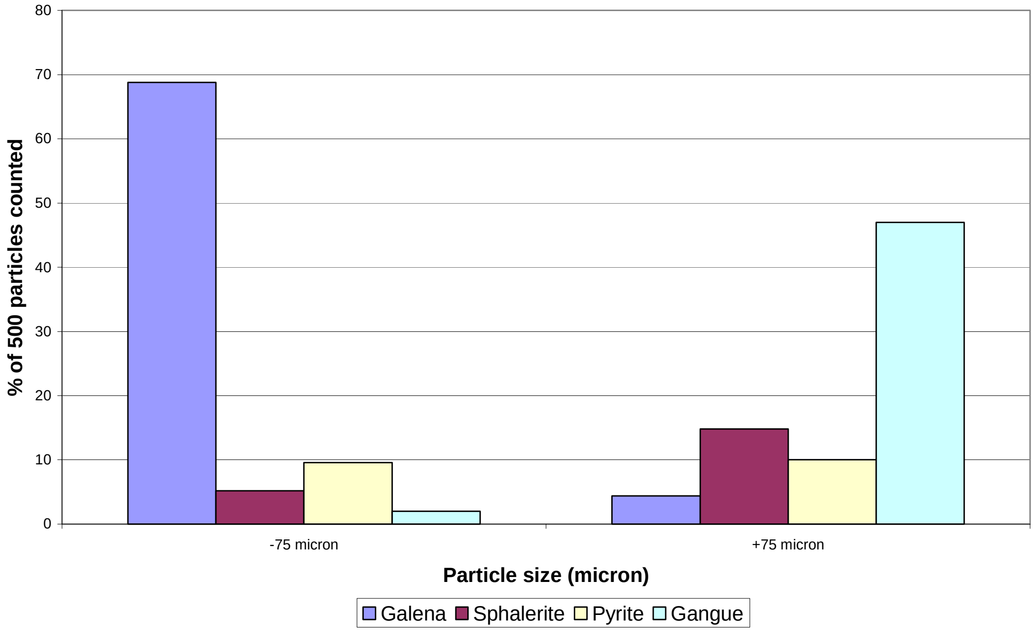


Figure 7.17. Minerals distribution in the lead concentrate from the Rosh Pinah Mine as a function of particle size (After Reyneke, 2000). (Fully liberated minerals only)

Thus, the results of particle counting of the +106µm size fraction were omitted in Figure 7.17. The distribution of liberated sphalerite and sphalerite attached to galena is shown in Figure 7.18.

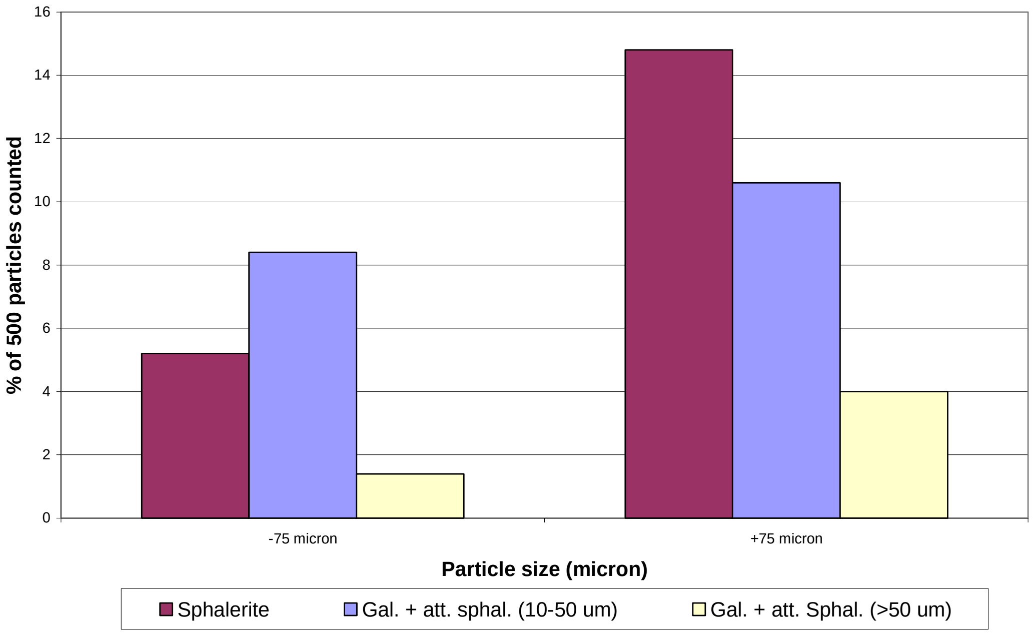


Figure 7.18. Sphalerite distribution in the lead concentrate from the Rosh Pinah Mine as a function of particle size (After Reyneke, 2000).

It was interesting to observe that the fraction of both liberated sphalerite and sphalerite particles attached to galena increased with increasing particle size. However, the fraction of binary locked particles of galena and sphalerite was higher than that of liberated sphalerite in the -75µm size. The fraction of sphalerite particles (size of sphalerite particle: 10-50µm) attached to galena increased in the +75µm size. Based on the primary grind of 80% passing 100µm used at the Rosh Pinah Mine, it was assumed that the concentrate mass pull would be higher in the -75 micron. Hence, it is believed that the fraction of sphalerite particles (10-50µm) attached to galena would adversely affect the flotation selectivity in the lead circuit. Therefore, it is clear that the liberation of sphalerite and galena particles has to be optimised instead of only increasing the depressant dosage during the flotation of galena.

Since the flotation response of ores is usually a function of the primary grind, the mode of occurrence of the Rosh Pinah feed sample was also semi-quantitatively determined by optical particle counting and the results are presented in Table 7.5 and Figure 7.19. As seen in Figure 7.19, it was clear that the fraction of liberated galena and liberated sphalerite increased with decreasing particle size. In addition, it was observed that the fraction of sphalerite and attached galena/gangue (10-50µm) particles decreased with decreasing particle size of the feed sample. However, a considerable amount of sphalerite particles with galena inclusions of less than 10µm in size was observed in all size fractions. These binary sphalerite-galena particles would be difficult to depress.

Table.7.5. Particle-counting results (% of 500 particles counted)-Feed sample from Rosh Pinah Mine (Reyneke, 2000)

FRACTION	+106 µM	+75 µM	-75 µM
Liberated galena	0.6	2.0	5.4
Liberated sphalerite	5.2	10.4	18.4
Liberated pyrite	2.8	12.0	21.0
Gangue (quartz, dolomite)	82.8	63.0	49.4
Unliberated sphalerite & gangue	0.6	0.2	-
Sphalerite + attached galena / gangue (<10µm)	0.2	0.4	-
Sphalerite + attached galena / gangue (10-50µm)	4.2	2.8	0.6
Sphalerite + attached galena / gangue (>50µm)	1.2	1.0	-
Galena + attached sphalerite / gangue (<10µm)	-	-	-
Galena + attached sphalerite / gangue (1-50µm)	0.4	0.6	-
Galena + attached sphalerite / gangue (>50µm)	-	0.2	-
Sphalerite + galena / gangue inclusions (<10µm)	1.6	6.2	5.0
Sphalerite + galena / gangue inclusions (10-50µm)	0.2	1.2	-
Sphalerite + galena / gangue inclusions (>50µm)	0.2	-	-
Galena + sphalerite / gangue inclusions (>50µm)	-	-	0.2

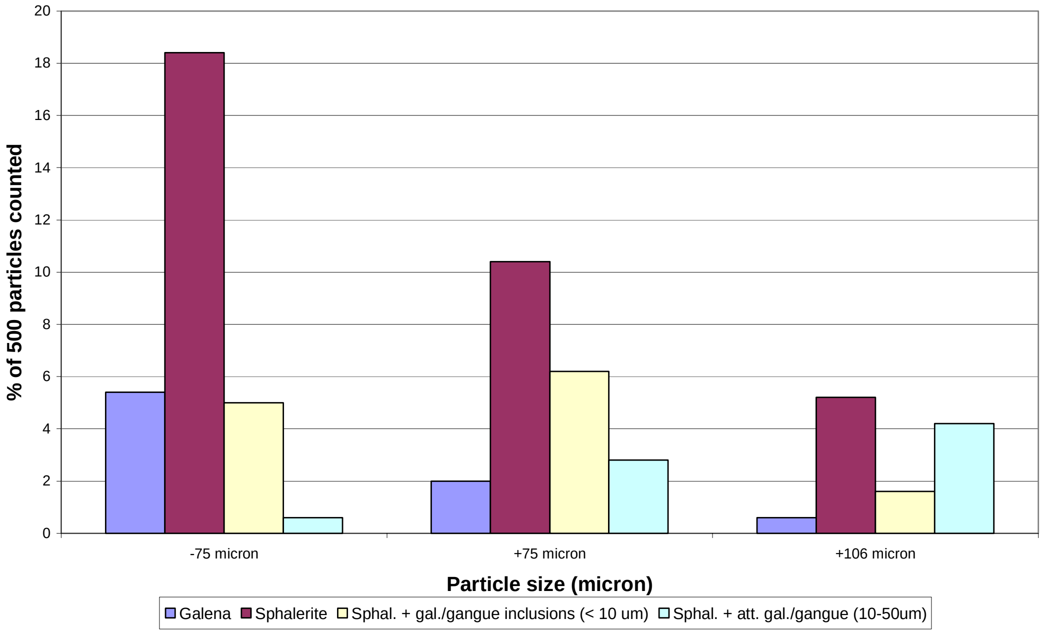


Figure 7.19. Galena and sphalerite distribution of the feed sample from the Rosh Pinah Mine as a function of particle size.

The rougher concentrates and tailings from the present laboratory study will be examined in the next section to ascertain the liberation characteristics of the sulphides and to establish whether other mineralogical factors could be responsible for the poor selectivity during flotation.

7.6.2. Deportment of sphalerite in the lead rougher concentrate

Qualitative mineralogy by image analysis on scanning electron microscopy (SEM) was performed on the flotation products after flotation of a composite ore from Rosh Pinah in the presence of 100 g/t NaCN and 50 g/t SNPX (Figure 7.20). These flotation results are similar to those presented in Figures 7.5 and 7.7.

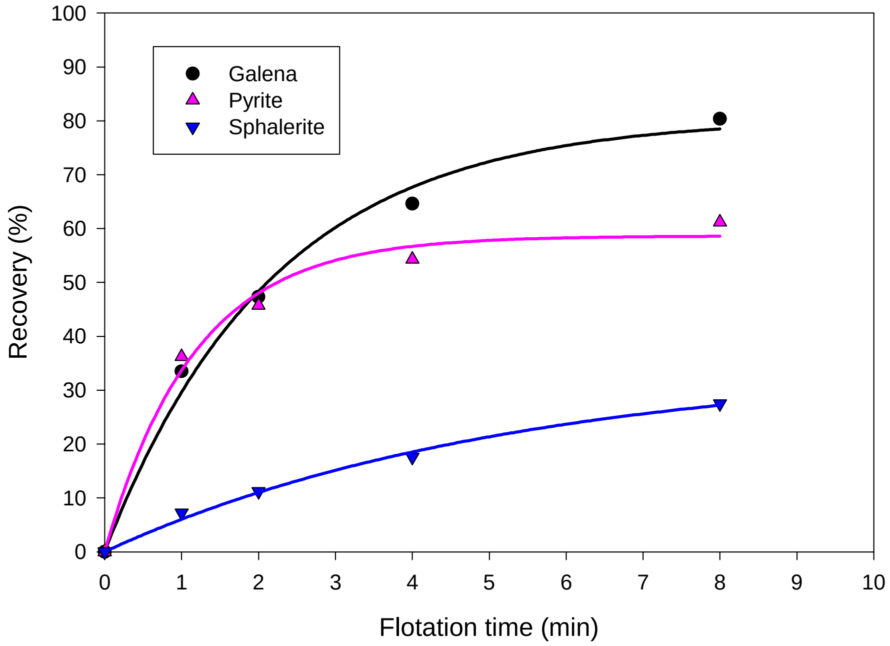


Figure 7.20. Recoveries of galena, pyrite and sphalerite after flotation of a composite from Rosh Pinah in the presence of 50 g/t SNPX and 100 g/t NaCN at pH 8.5.

The flotation results shown in Figure 7.20 indicate that galena and pyrite were the fast floating minerals, while sphalerite was the slow floating mineral. Figure 7.20 also indicates that approximately 36% of pyrite, 34% of galena and 7.2 % of sphalerite were recovered in the first minute of flotation. However, 16% of galena, 10% of sphalerite and 7% of pyrite were recovered in the last incremental concentrate (4-8 minutes).

The mineralogical textures of the concentrates obtained after one and 8 minutes of flotation are shown in Figures 7.21 and 7.22. As seen in Figures 7.21 and 7.22, the fractional amounts of galena and pyrite recovered in the concentrate decreased with the flotation time, while that of sphalerite and gangue increased. It was clear that the concentrate recovered in the first minute of flotation contained mainly liberated galena and pyrite.

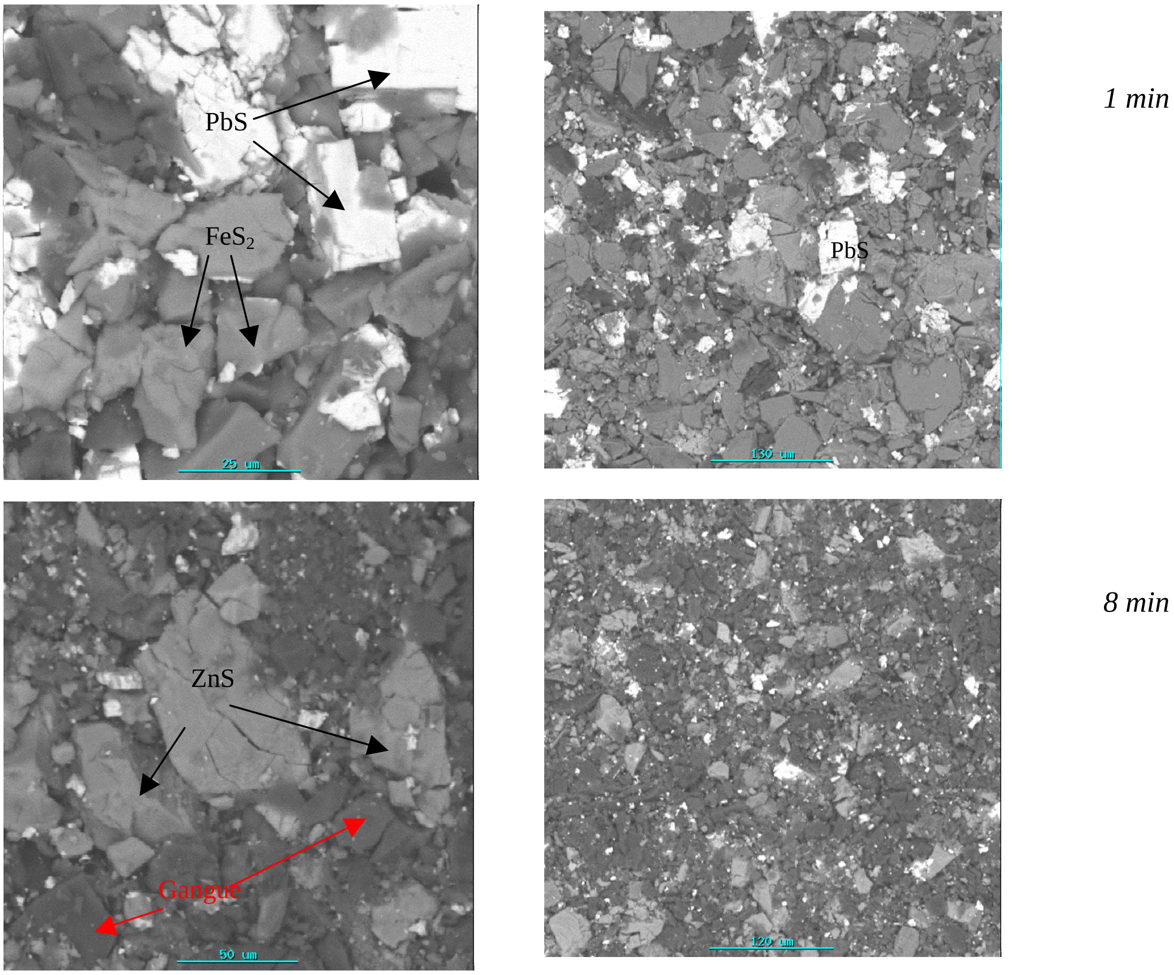


Figure 7.21. SEM- Backscattered images showing the general appearance of the rougher concentrates after 1 and 8 minutes. The flotation experiment was carried out in the presence of 100 g/t NaCN and 50 g/t SNPX.

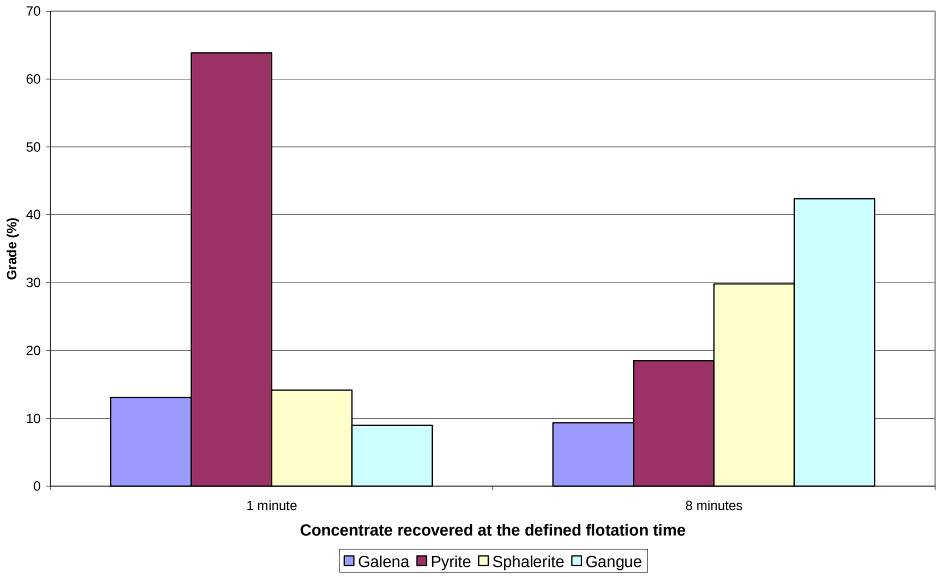


Figure 7.22. Mineralogical composition of the first and last concentrates after flotation in the presence of 50 g/t SNPX and 100 g/t NaCN at pH 8.5.(See appendices for details).

Figure 7.21 showed that liberated particles of galena were usually fine grained to about 25 micron, while pyrite particles seemed to be much coarser (more pictures are shown in the appendices). The mineralogical texture of the concentrate recovered after 8 minutes of flotation showed that the recovery and grade of gangue minerals (mainly silicate and dolomite) increased in the last concentrate when compared to the concentrate of the first minute. Figure 7.21 also showed that most of the slow floating materials were large sphalerite particles (+50µm). Their presence in the lead concentrate would be detrimental to flotation selectivity.

The striking feature of the texture of the concentrates was the large quantity of binary locked galena and sphalerite (Figure 7.23).

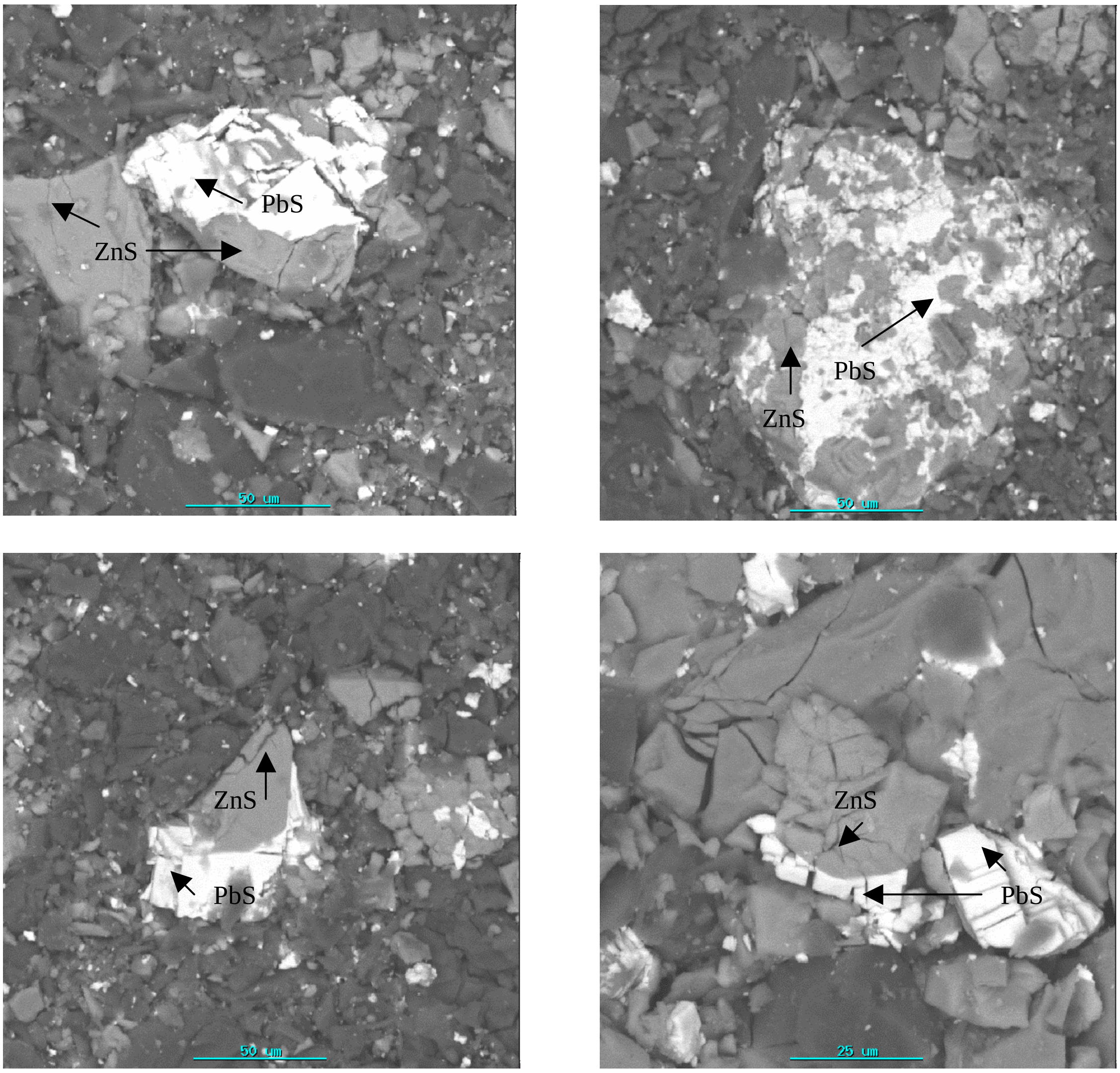


Figure 7.23. SEM- Backscattered images of concentrate showing the association between galena (white) and sphalerite (grey) in the galena concentrate.

It was observed that the occurrence of galena locked and/or attached to sphalerite increases with increasing particle size, especially above the 50 micron size. Thus, the poorly liberated sphalerite particles from the middlings would contribute to the problem of zinc deportment into the lead concentrate at the Rosh Pinah Mine. Hence, increasing the dosage of depressant would not solve the problem without affecting the recovery of galena. However, with severe depression of sphalerite, galena particles which are occluded in sphalerite may also be lost in the rougher tailings as shown in Figure 7.24. In addition, the loss of galena in the rougher tailings can be increased due to the presence of slow floating particles when the retention time is not long enough to account for their flotation.

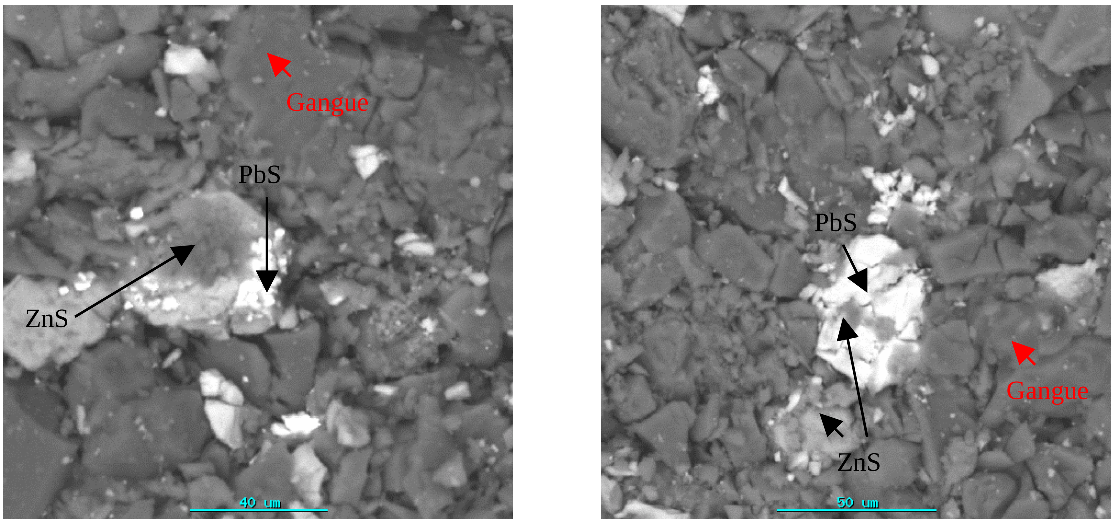


Figure 7.24. SEM- Backscattered images showing the association between galena and sphalerite in the lead rougher tailings.

As seen in Figure 7.25, the rougher tailings mostly contained liberated sphalerite and gangue, which are sent to the zinc flotation circuit. The sphalerite is then intentionally activated with copper sulphate followed by its flotation with xanthate at high pH values to depress the flotation of pyrite.

Selectivity can be improved by better liberation of galena from sphalerite in the milling circuit, or alternatively by regrinding the rougher concentrate before the cleaning stage. However, practical implementation of this would need to take into account the softness of galena. In practice, it would be recommended to install a classifying cyclone before the regrind mill in order to avoid the over-grinding of fine particles from the rougher concentrate.

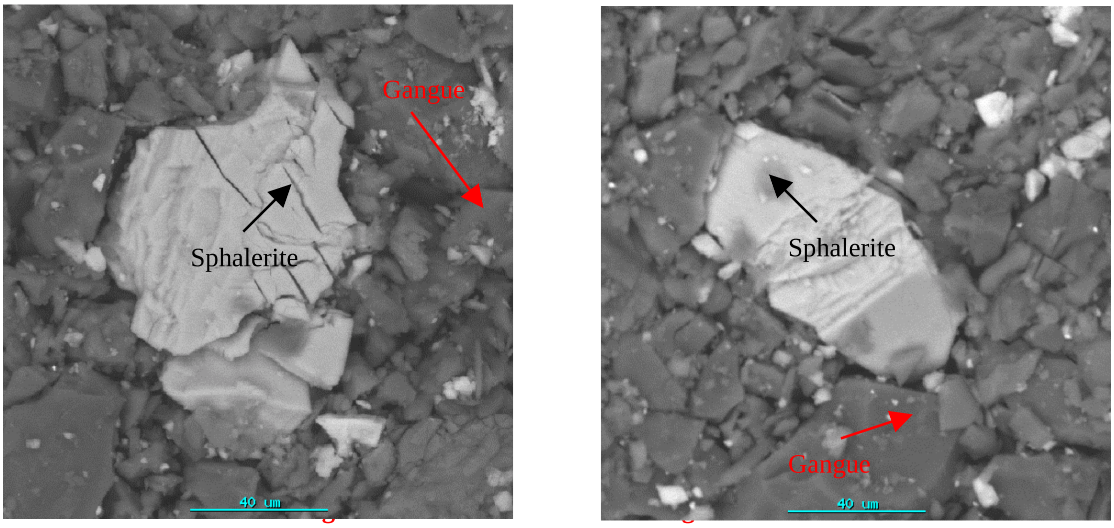


Figure 7.25. SEM- Backscattered images showing the general appearance of the rougher tailings. The flotation experiment was carried out in the presence of 100 g/t NaCN and 50 g/t SNPX.

Based on the flotation and mineralogical results presented in this chapter, it is believed that the flotation selectivity between galena and sphalerite can be improved by changing the current flowsheet, which is shown in Figure 7.26, by including a cyclone and re-grind mill after the rougher flotation stage as shown in Figure 7.27.

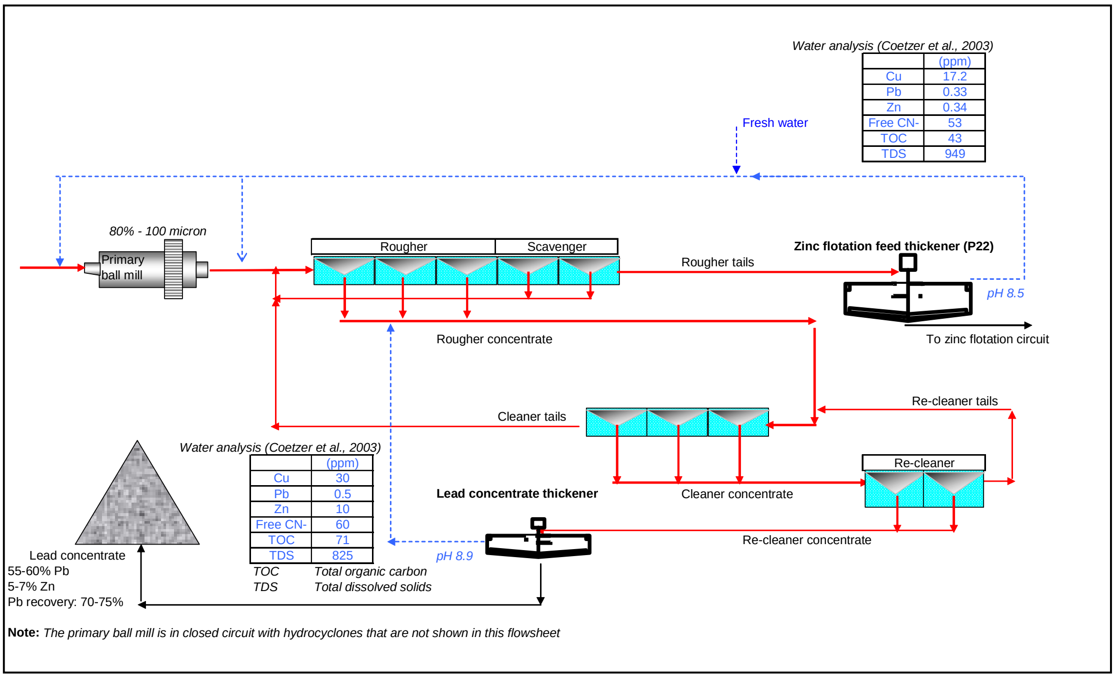
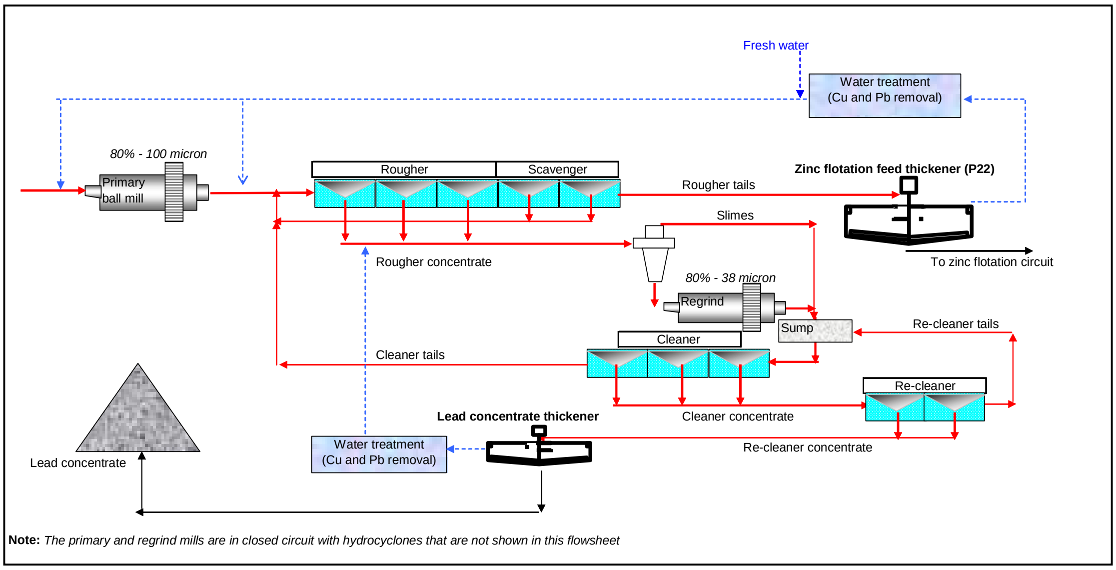


Figure 7.26. Current flowsheet diagram of the lead flotation circuit at the Rosh Pinah Mine



Note: *The primary and regrind mills are in closed circuit with hydrocyclones that are not shown in this flowsheet*

Figure 7.27. Proposed flowsheet diagram of the lead flotation circuit at the Rosh Pinah Mine.

The modified flowsheet can be summarised as follow:

- Using a primary grind of 80% passing 100 micron to avoid the over-grinding of galena;
- Using up to 100 g/t NaCN to depress mainly copper-activated sphalerite in the lead rougher-scavenger flotation circuit and to maximise the recovery of galena;
- Using a cyclone to split the fine fraction (-38 micron) from the middlings to avoid the over-grinding of fine galena particles (Figure 7.27);
- Regrinding of the middlings from the rougher concentrate to improve the liberation of galena and sphalerite particles prior to the cleaning stages (Figure 7.27);
- Cleaning of the rougher concentrate to achieve the required smelter grade (Figure 7.27). Figure 7.22 shows that pyrite and sphalerite were the major impurity sulphides in the lead rougher concentrate. Thus, it is recommended to increase the pH during the cleaning stage for an effective depression of pyrite (pyrite can be depressed at pH values higher than 9).
- Using sodium cyanide and zinc sulphate in the cleaning stages to depress sphalerite and pyrite.

Since the dissolved heavy metals found in the process water are detrimental to the efficient performance of the flotation plant (Chapters 5-6), water quality surveys should be conducted regularly in order to correlate water quality with the flotation plant performance. The possible seasonal changes in the quality of process water can thus be identified and the water treated accordingly prior to the milling and flotation operations.

As stated in the section 7.4, this Chapter did not take into account the presence of substantial amount of $Cu(CN)_3^{2-}$ present in the recycle water, which is used in both the milling and the lead flotation circuits. This effect was discussed in details in Chapter 6. However, recent results of Katabua and Molelekoe (2004) have confirmed that the depression of sphalerite with high dosages of sodium cyanide is not effective when the concentrate mass pull increases in the range of 20-30% (Table 7.6).

Table 7.6. Metallurgical results of the Rosh Pinah composite after flotation with 15 g/t SNPX (Katabua and Molelekoe, 2003).

Reagents (g/t)		Mass Pull	Recovery (%)		Grade (%)	
$CuSO_4$	NaCN	(%)	Pb	Zn	Pb	Zn
0	0	32.8	85.8	49.3	10.0	16.5
10	0	34.6	91.1	59.0	8.9	14.5
0	120	23.2	88.6	52.0	13.4	19.4
10	120	26.6	91.3	51.3	11.3	16.4

They conducted their testwork at the Rosh Pinah plant and used 10g/t of copper sulphate to activate sphalerite prior to the flotation of galena. It was observed that the dosage of cyanide (120g/t) used was higher enough to suppress the effect of 10g/t $CuSO_4$ on the activation of sphalerite. As demonstrated in this study, the high recovery of sphalerite is believed to be due to the high mass pull and to the complex mineralogical occurrence of the Rosh Pinah ore body. The high concentrate mass pull is usually related to poor liberation of various minerals, entrainment and overdosing of the frother.

7.7. Conclusion

Batch flotation tests have shown that the use of cyanide alone is not efficient for the depression of sphalerite from the Rosh Pinah ore when milling is carried out according to the current plant particle size distribution. The use of both cyanide and zinc sulphate improved the depression of sphalerite much better than cyanide alone. In addition, an increase in the recovery and grade of galena was observed when cyanide or both cyanide and zinc sulphate were used.

Flotation selectivity is limited by the mineralogical texture of the Rosh Pinah ore sample. Microscopic analysis has shown that the presence of sphalerite in the galena concentrate is also due to poor liberation between galena and sphalerite, especially in the middlings. Hence selectivity could be improved by regrinding the rougher concentrate prior to the cleaning stage.

It is recommended that the flotation products such as rougher, scavenger and cleaner concentrates be analysed statistically using the QEM-SCAN to determine the correct fraction of locked and associated sphalerite particles in the lead concentrate.

It is also recommended that variability testwork be conducted on the Rosh Pinah Eastern and Western ore field samples using the proposed flowsheet. In addition, locked cycle test, which is a series of repetitive batch tests conducted in the laboratory, is required to simulate plant conditions before implementing the proposed reagent suite and flowsheet at the Rosh Pinah Mine.

Chapter 8. Conclusions and recommendations

This study has shown that the flotation of galena from the Rosh Pinah ore body can be affected by various factors such as the dosage of flotation reagents, the concentration of dissolved heavy metals (mainly copper), copper-cyanide complexes, the grinding environment, the quality of process water and the mineralogical occurrence of the ore. The flotation selectivity between galena and sphalerite in the lead rougher concentrate was studied and the following conclusions were made:

- Xanthate collectors such as SNPX and PNBX were found to be unselective for the flotation of the Rosh Pinah composite sample. It was observed that the recovery of sphalerite increased with both the recovery of galena and the concentrate mass pull. Reagent such Aerophine 3418A, which is a dialkyl dithiophosphinate collector developed by Cytec, has been found to be more selective during the flotation of galena from Cu-Pb-Zn sulphide ore, especially when the ore body contains silver. Thus, it is recommended that Aerophine 3418A be tested alone and in conjunction with xanthate on the Rosh Pinah ore body;

- The recovery of sphalerite was higher when the composite was milled in a dry environment as compared to wet milling. The recovery of galena decreased after milling in a dry environment, while wet milling improved its recovery. In addition, more positive pulp potentials were measured when the composite had been ground in a dry environment;

- The recovery of sphalerite increased after activation with Cu(II) ions while that of galena decreased when the composite was dry ground in a mild steel mill with mild steel grinding media. However, the recovery of galena was not affected after wet milling in a stainless steel mill. The recovery of Cu(II)-activated sphalerite was independent of the milling environment (wet or dry) and grinding media;

- The activation of sphalerite by cuprous cyanide complexes, which are present in the recycled water, was clearly shown in this study. Both batch flotation tests and XPS analysis have confirmed that sphalerite was activated by copper(I) from the cuprous cyanide complexes. The recovery of copper(I)-activated sphalerite increased further when the composite was dry milled as compared to wet milling. To the best of our knowledge, this is the first example of sphalerite activation by cuprous cyanide species from the process water. Although the activation mechanism is still unclear, it is believed that cuprous cyanide adsorb onto the sphalerite surface followed by the ion exchange reaction between the cyanide and xanthate ions. Another possibility is the decomposition/oxidation of cuprous cyanide followed by adsorption of cuprous/cupric oxide or hydroxide onto the surface of sphalerite. The presence of cuprous/cupric oxide or hydroxide will promote the activation of sphalerite as described during the activation of sphalerite by Cu(II) ions. It is recommended that more surface analysis be conducted to clarify this. Techniques such as XPS and secondary ion mass spectrometry (SIMS) can be used to examine the nature of the activating species when cuprous cyanide is used. Based on the results reported in this study, dry milling of the composite would not be recommended despite the arid location of the Rosh Pinah concentrator. In addition, more water survey is required to understand the seasonal effect of process (recycled) water on the metallurgical performance of the plant;

- Batch flotation tests have shown that the use of cyanide alone is not efficient for the depression of sphalerite due to the mineralogical texture of the Rosh Pinah ore. A large quantity of galena locked and/or attached to sphalerite was observed in the lead concentrate. Their prevalence increased with increasing particle size. The use of both cyanide and zinc sulphate improved the depression of sphalerite much better than cyanide alone. In addition, selectivity can be improved by regrinding the rougher concentrate prior to the cleaning stage due to poor liberation between galena and sphalerite. A flowsheet has been proposed to improve selectivity between galena and sphalerite in the lead flotation circuit.

References

Ahlberg, E. and Broo, A.E., 1996a. Oxygen reduction at sulphide minerals. 1. A rotating ring disc electrode (RRDE) study at galena and pyrite. *Int. J. Miner. Process.* 46: 73-89.

Ahlberg, E. and Broo, A.E., 1996b. Oxygen reduction at sulphide minerals. 2. A rotating ring disc electrode (RRDE) study at galena and pyrite in the presence of xanthate. *Int. J. Miner. Process.* 47: 33-47.

Ahlberg, E. and Broo, A.E., 1996c. Oxygen reduction at sulphide minerals. 3. The effect of surface pre-treatment on the oxygen reduction at pyrite. *Int. J. Miner. Process.* 47: 49-60.

Aldrich, C. and Feng, D., 2000. The effect of frothers on bubble size distributions in flotation pulp phases and surface froths. *Minerals Engineering.* 13(10-1): 1049-1057.

Allan, G.C. and Woodcock, J.T., 2001. A review of the flotation of native gold and electrum. *Minerals Engineering*, 14(9): 931-962.

Arbiter, N. (Ed.) Flotation, Chapter 5, in SME Mineral Processing Handbook, Edited by Weiss, N.L., Society of Mining Engineers, AIMMPE, New York (1985).

Ball, B. and Rickard, R.S., 1976. The chemistry of pyrite flotation and depression. In M.C. Fuestenau (Editor) *Flotation*, *(A.M. Gaudin memorial volume 1)*. AIMMPE, New York (USA), pp. 458-484.

Bandini, P., Prestidge, C.A., and Ralston, J., 2001. Colloidal iron oxide slime coatings and galena particle flotation. *Minerals Engineering.* 14(5): 487-497.

Basilio, C.I., Kartio, I.J. and Yoon, R.H., 1996. Lead activation of sphalerite during galena flotation. *Minerals Engineering*. 9(8): 869-879.

Beck, M.T., 1987. Critical survey of stability constants of cyano complexes. *Pure & Appl. Chem.* 59(12): 1703-1720.

Bredenhann, R. and Coetzer, G., 2002. Selective lead flotation from Rosh Pinah ROM material. *Report: Doc. No. MP-FT-R018*. Kumba Resources R&D (Pretoria, South Africa). p. 75.

Bredenhann, R. Du Preez, H.S., and Coetzer, G., 2001. Influence of different water resources and ions on flotation of Rosh Pinah milled material.. *Report: Doc. No. MP-FT-R012*. Kumba Resources R&D (Pretoria, South Africa). p. 51.

Broman, P.G., 1980. Water reuse at sulphide ore concentrates in Sweden: practice, experience and current developments. In: M.J. Jones (Editor) Complex Sulphide Ores. *Inst. of Min. and Met.,* London, pp. 28-39.

Buckley A.N. and Woods, R., 1997. Chemisorption-the thermodynamically favoured process in the interaction of thiol collectors with sulphide minerals. *Int. J. Min. Process.* 51:15-26.

Buckley A.N. and Woods, R., 1995. Identifying chemisorption in the interaction of thiol collectors with sulphide minerals by XPS: adsorption of xanthate on silver and silver sulphide. *Colloids an Surfaces A: Physicochemical and Engineering Aspects.* 104: 295-305.

Buckley, A.N., Woods, R., and Wouterlood, H.J., 1989. An XPS investigation of the surface of natural sphalerites under flotation-related conditions. *Int. J. Miner. Process.* 26: 29-49.

Buckley, A., and Woods, R., 1982. Investigation of the surface oxidation of sulfide minerals via ESCA and electrochemical techniques, In: Yarar, B., Spottiswood, D.J. (Eds.), *Interfacial Phenomena in Mineral processing Foundation Conference*, pp. 3-17.

Bulatovic, S.M. and Wyslouzil, D.M., 1999. Development and application of new technology for the treatment of complex massive sulphide ores. Case study-Faro lead/zinc concentrator-Yukon. *Minerals Engineering.* 12(2): 129-145.

Buswell, A.M., Bradshaw, D.J., Harris, P.J. and Ekmekci, Z., 2002. The use of electrochemical measurements in the flotation of a platinum group minerals (PGM) bearing ore. *Minerals Engineering,* 15: 395-404.

Casella, I.G. and Gatta, M., 2000. Anodic electrodeposition of copper oxide/hydroxide films by alkaline solutions containing cuprous cyanide ions. *J. Electroanal. Chem.*, 494: 12-20.

Chander, S., 1999. Fundamentals of sulfide mineral flotation. In: B.K. Parekh and J.D. Miller (Editors). *Advances in flotation technology.* SME. USA. Pp. 129-145.

Chander, S., 1988. Inorganic depressants for sulphide minerals. In: P. Somasundaran and B.M. Moudgil (Editors.), *Reagents in Mineral Technology.* Surfactant Science Series, 27. pp. 429-469.

Chander, S. and Khan, A., 2000. Effect of sulfur dioxide on flotation of chalcopyrite. *Int. J. Miner. Process.* 58: 45-55.

Chen, Z. and Yoon, R.H., 2000. Electrochemistry of copper activation of sphalerite at pH 9.2. *Int. J. Miner. Process.* 58: 57-66.

Cheng, S.C., Gattrell, M., Guena, T. and MacDougall, B., 2002. The electrochemical oxidation of alkaline copper cyanide solutions. *Electrochimia Acta.* 47: 3245-3256.

Cheng, X and Iwasaki, I., 1992. Pulp potential and its implications to sulphide flotation. *Miner. Process. Exctract. Metall. Review,* 11: 187-210.

Cho, Y.S. and Laskowski, J.S., 2002. Effect of flotation frothers on bubble size and foam stability. *Int. J. Miner. Process.* 64: 69-80.

Coetzer, G., Du Preez, H.S., Bredenhann, R., 2003. Influence of water resources and metal ions on galena flotation of Rosh Pinah ore. *J. S. Afr. Inst. Min. Metall.* 103(3):193-207.

Crawford, R. and Ralston, J., 1988. The influence of particle size and contact angle in mineral flotation. *Int.J. Min. Process.* 23: 1-24.

Crozier, R.D., 1991. Sulphide collector mineral bonding and the mechanism of flotation. *Minerals Engineering*. 4 (7-11): 839-858.

Cullinan, V.J., Grano, S.R., Greet, C.J., Johnson, N.W. and Ralston, J. 1999. Investigating fine galena recovery problems in the lead circuit of Mount Isa Mines lead/zinc concentrator. Part1: Grinding effects. *Minerals Engineering*, 12(2): 147-163.

Djokić, S.S., 2002. Electroless deposition of metals and alloys. *In:* B.E. Conway and R.E. White (Editors), *Modern Aspects of Electrochemistry. No. 35,* Kluwer Academic/Plenum Publishers, pp. 51-133.

Du Preez, H., 2000. Assesment of the physical and chemical conditions of the pulp in the Rosh Pinah milling system. Short Review. Presented at the Flotation short course. 1-2 August 2000. *University of Pretoria*, Pretoria (RSA).

Dudek, D.A. and Fedkiw, P.S., 1999a. Electrodeposition of copper from cuprous cyanide electrolyte. I. Current distribution on a stationary disk. *J. Electroanal. Chem.* 474: 16-30.

Dudek, D.A. and Fedkiw, P.S., 1999b. Electrodeposition of copper from cuprous cyanide electrolyte. II. Current distribution on a rotating disk. *J. Electroanal. Chem.* 474: 31-42.

El-Shall, H.E., Elgillani, D.A., and Abdel-Khalek, N.A., 2000. Role of zinc sulfate in depression of lead-activated sphalerite. *Int. J. Min. Process.* 58(1-4): 67-75.

Elgillani, D.A. and Fuerstenau, M.C., 1968. Mechanisms involved in cyanide depression of pyrite. *Trans. AIME*. 241: 437

Finkelstein, N.P., 1997. The activation of sulphide minerals for flotation: a review. *Int. J. Min. Process*. 52:81-120.

Finkelstein, N.P. and Allison, A.S., 1976. The chemistry of activation, deactivation and depression in the flotation of zinc sulphide: A review. In: M.C. Fuestenau (ed.) *Flotation (A.M. Gaudin Memorial Volume),* AIMMPE, New York (USA), 1: 414-457.

Forssberg, K.S.E., Subrahmanyam, T.V., and Nilsson, L.K., 1993. Influence of grinding method on complex sulphide ore flotation: a pilot plant study. *Int. J. Miner. Process, 38: 157-175.*

Fuerstenau. M.C., 1982. Sulphide mineral flotation. In: R.P.King (Editor). *Principles of Flotation.* South African Institute of Mining and Metallurgy, Johannesburg (South Africa), pp. 159-182.

Fuerstenau, D.W., 1982. Activation in the flotation of sulphide minerals. In: R.P.King (Editor). *Principles of Flotation.* South African Institute of Mining and Metallurgy, Johannesburg (South Africa), pp. 183-198.

Fuerstenau, D.W. and Metzger, P.H., 1960. Activation of sphalerite with lead ions in the presence of zinc salts. *AIME Trans.,* 217: 119-123.

Fuerstenau, M.C., Kuhn, M.C. and Elgillani, D.A., 1968. The role of dixanthogen in xanthate flotation of pyrite. *AIME Trans.,* 241: 148.

Gardner, J.R., and Woods, R., 1979. An electrochemical investigation of natural floatability of chalcopyrite. *Int. J. Miner. Process*. 6: 1-16.

Gaudin, A.M., 1957. *Flotation.* Second edition, McGraw-Hill, New York (USA), p.573.

Gerson, A.R., Lange, A.G., Prince, K.E., Smart, R.St.C., 1999. The mechanism of copper activation of sphalerite. *Applied Surface Science,* 137: 207-223.

Girczys, J., Laskowski, J., and Lekki, J., 1972. Copper activation studies of sphalerite. *Transactions Canadian Metallurgical Quarterly.* 11(4): 553-558.

Grano, S.R., Sollaart, M., Skinner, W., Prestidge, C.A., and Ralston, J., 1997(a). Surface modifications in the chalcopyrite-sulphite ion system. I. Collectorless flotation, XPS and dissolution study. *Int. J. Miner. Process*. 50: 1-26.

Grano, S., Johnson, N.W., and Ralston, J., 1997(b). Control of the solution interaction of metabisulphite and ethyl xanthate in the flotation of the Hilton ore of Mount Isa Mines Limited, Australia. *Minerals Engineering*. 10(1): 17-39.

Grano, S.R., Prestidge, C.A., and Ralston, J., 1997(c). Solution interaction of ethyl xanthate and sulphite and its effect on galena flotation and xanthate adsorption. *Int. J. Miner. Process*. 52: 161-186.

Grano, S.R., Ralston, J. and Smart, R.S.C., 1990. Influence of electrochemical environment on the flotation behaviour of Mt. Isa copper and lead-zinc ore. *Int. J. Miner. Process*. 30:69-97.

Greet, C. and Smart, R.St.C., 2002. Diagnostic leaching of galena and its oxidation products with EDTA. *Minerals Engineering*, 15:515-522

Guy P.J. and Trahar, W.J., 1985. The effects of oxidation and mineral interaction on sulphide flotation. In K.S. Forssberg (Ed.) *Flotation of sulphide minerals*. Development in minerals processing, 6. pp. 91-110.

Guy, P.J., and Trahar, W.J., 1984. The influence of grinding media and flotation environments on the laboratory batch flotation of galena. *Int. J. Miner. Process.* 12: 15-38.

Healy, T.W., 1973. Colloidal precipitates as activators and depressants in flotation. The *Austr.M.M. Conference,* Western Australia, May 1973.

Hefter, G.T. and May P.M., 1991. Chemical speciation in hydrometallurgical cyanide solutions. *In: Fith AusIMM Extractive Metallurgy Conference*, Perth (Australia), 2-4 October. pp. 139-146.

Henley, K.J., 1983. Ore-dressing mineralogy-A review of the techniques, Applications and recent developments. *Spec. Pub. Geo. Soc. S. Afr.,* 7: 175-200.

Herrera-Urbina, R., Sotillo, F.J. and Fuerstenau, D.W., 1999. Effect of sodium sulfide additions on the pulp potential and amyl xanthate flotation of cerussite and galena. *Int. J. Miner. Process*. 55: 157-170.

Hintikka, V.V. and Leppinen, J.O., 1995. Potential control in the flotation of sulphide minerals and precious metals. *Minerals Engineering,* 8(10): 1151-1158.

Högfeldt, E., 1924. Stability constants of metal-ion complexes. 1st Ed. IUPAC.

Hope, G.A., Woods, R. and Munce, C.G., 2001. Raman microprobe identification. *Minerals Engineering,* 14(12): 1565-1577.

Houot, R. and Duhamet, D., 1992. The use of sodium sulphite to improve the flotation selectivity between chalcopyrite and galena in a complex sulphide ore. *Minerals Engineering*, 5(3-5): 343-355.

Houot, R. and Ravenau, P., 1992. Activation of sphalerite flotation in the presence of lead ions. *Int. J. Miner. Process*., 35: 253

Hsu, L.T., Kim; M.J. and Tran, T., 1999. Electrochemical study on copper cementation from cyanide liquors using zinc. Electrochimia Acta, 44: 1917-1625.

Hsu, L.T., Tran, T. and Young, D., 1991. Modelling of the chemical speciation of cyanide species: Application to effluent treatment. *In: Fith AusIMM Extractive Metallurgy Conference*, Perth (Australia), 2-4 October. pp. 133-138.

Huang, H.H., 2003. *Stabcal Software: Stability Calculation for Aqueous Systems*. Metallurgical Engineering, Montana Tech. (USA).

Hukki, R.T., Palomaki, A. and Orivuori, E., 1952. An electrophoretic investigation of the activation of sphalerite by copper sulphate in flotation. *Soumen Kemistilehti,* 25B. 42.

Jain, S. and Fuestenau, D.W., 1985. Activation in the flotation of sphalerite. In K.S. Forssberg (Editor) *Flotation of sulphide minerals*. Development in minerals processing, 6. pp. 159-174.

Johnson, H.W., 1988. Application of the electrochemical concepts to four sulphide flotation separations. In: P.E. Richardson and R. Wood (Editors). *Proceedings of the International Symposium on Electrochemistry in Mineral and Metal Processing II.* The Electrochemical Society. Pp 131-149.

Kakovskii, I.A., 1957. Physicochemical properties of some flotation reagents and their salts with ions of heavy non-ferrous metals. *Proceedings of the second Int. Congress Surf. Act.,* pp. 225-241.

Kartio, I.J., Basilio, C.I., and Yoon, R.H., 1998. An XPS study of sphalerite activation by copper. *Langmuir*, 14: 5274-5278.

Kartio, I., Wittstock, G., Laajalehto, K., Hirsch, D., Simola, J., Laiho, T., Szargan, R., and Suoninen, E., 1997. Detection of elemental sulphur on the galena oxidized in acidic solution. *Int. J. Min. Process.* 51: 293-301.

Kartio, I., Laajaletho, K., and Suoninen, E., 1999. Characterization of the ethyl xanthate adsorption layer on galena (PbS) by synchrotron radiation excited photoelectron spectroscopy. *Colloids and Surfaces A: Physicochemical and Engineering Aspects.* 154: 97-101.

Katabua, J. and Molelekoe, R., 2003. Rosh Pinah Water Project. *Report: Doc. No. RD-AP-015*. Kumba Technology, R&D. Kumba Resources. Pretoria (South Africa). p. 12

Kelebek, S. and Tukel, C., 1999. The effect of sodium metabisulphite and triethylenetetramine system on the pentlandite-pyrrhotite separation. *Int. J. Miner. Process*. 57:135-152.

Kim, B.S., Hayes, R.A., Prestige, C.A., Ralston, J., and Smart, R.St.C., 1996. In-situ scanning tunnelling microscopy studies of galena surfaces under flotation-related conditons. *Colloids and Surfaces A: Physicochemical and Engineering Aspects.* 117:117-129.

Klassen, V.I. and Mokrousov, V.A., 1963. *An Introduction to the Theory of Flotation*. Butterworths & Co. (London). p. 493

Koryta, J., Dvorák, J., and Kavan, L., 1993. *Principles of Electrochemistry.* 2nd edition. John Wiley & Sons. P.486.

Laajalehto, K., Leppinen, J., Kartio, I. and Laiho, T., 1999. XPS and FTIR study of the influence of electrode potential on activation of pyrite by copper or lead. *Colloid and Surfaces. A: Physicochemical and Engineering Aspects*. 154: 193-199.

Laskowski, J.S., 1993. Frothers and flotation froth. *Mineral Processing and Extractive Metallurgy Review*. 12: 61-89.

Laskowski, J.S., Liu, Q., and Zhan, Y., 1997. Sphalerite activation: Flotation and electrokinetic studies. *Minerals Engineering,* 10(8): 787-802.

Lätti, D., Doyle, J. and Adair, B.J.I., 2001. A QEM*SEM study of a suite of pressure leach products from a gold circuit. *Minerals Engineering,* 14(12): 1671-1678.

Leja, J., 1982. *Surface chemistry of froth flotation.* Plenum Press, New York (USA), p.758.

Leppinen, J.O., Hintikka, V.V. and Kalapudas, R.P., 1998. Effect of electrochemical control on selective flotation of copper and zinc from complex ores. *Minerals Engineering*, 11(1): 39-51.

Levay, G., Smart, R.St.C. and Skinner, W.M., 2001. The impact of water quality on flotation performance. *J. S. Afr. Inst. Min. Metall.* 101(2): 69-75.

Light, T.S., 1972. Standard solution for redox potential measurements. *Analytical Chemistry*, 44(6): 1038-1039.

Linge, H.G., 1995. Anodic oxidation of pyrrhotite in simulated CIP liquors. *Minerals Engineering,* 8(7): 795-806.

Liu, G.Q. and Yen, W.T., 1995. Effects of sulphide minerals and dissolved oxygen on the gold and silver dissolution in cyanide solution. *Minerals Engineering*, 8(1/2): 111-123.

Lu, Y., Drelich, J., and Miller, J.D., 1997. Wetting of francolite and quartz and its significance in the flotation of phosphate rock. *Minerals Engineering,* 10(11):1219-1231.

Lu, J., Dresinger, D.B., Cooper, W.C., 2002. Copper electrowinning from dilute cyanide solution in a membrane cell using graphite felt. *Hydrometallurgy*, 64: 1-11.

Lukey, G.C., Van Deventer, J.S.J., Huntington, S.T., Chowdhury, R.L. and Shallcross, D.C., 1999. Raman study on the speciation of copper cyanide complexes in highly saline solutions. *Hydrometallurgy,* 53: 233–244.

Malysiak, V., Shackleton, N.J. and de Vaux, D., 2003. Effect of water quality on pentlandite-pyroxene floatability with emphasis on calcium ions. In: L. Lorenzen and D. Bradshaw (Editors) *Proceedings of the 22nd International Mineral Processing Congress*, 29 Sept-03 October 2003. Cape Town, South Africa. Pp. 734-742.

Marin, G. and Molina, E., 1988. Characterisation of collectors through flotation rate data. In: S.C. Flores and Moisan J.A. (Eds.), *Froth Flotation*, Developments in Minerals Processing, vol. 9. Elevier. pp. 329-340.

Marsicano, F., Harris, P.J., McDougall, G.J., and Finkelstein, N.P., 1975. Some thermodynamics aspects of systems relevant to the flotation of sphalerite. *National Institute for Metallurgy.* Johannesburg (South Africa), Report No. 1785.

Martin, C.J., McIvor, R.E., Finch, J.A. and Rao, S.R., 1991. Review of the effect of grinding media on flotation of sulphide minerals. *Minerals Engineering.* 4(2): 121-132.

Mielczarski, E. and Mielczarski, J.A., 2003. Influence of galvanic effect on adsorption of xanthate on pyrite, galena and chalcopyrite. In: L. Lorenzen and D. Bradshaw (Editors) *Proceedings of the 22nd International Mineral Processing Congress*, 29 Sept-03 October 2003. Cape Town, South Africa. Pp. 866-873.

Miller, J.D., Du Plessis, R., Kotlyar, D.G., Zhu, X. and Simmons, G.L., 2002. The low-potential hydrophobic state of pyrite in amyl xanthate flotation with nitrogen. *Int. J. Miner. Process*. 67: 1-15.

Minsiomi, J., 2001. *Restricted Report*. Kumba Resources (Pretoria, South Africa).

Misra, M., Miller, J.D., and Song, Q.Y., 1985. The effect of SO_2 in the flotation of sphalerite and chalcopyrite. In: Forssberg, K.S.E. (Ed.) *Flotation of Sulphide Minerals*- Development in Mineral Processing 6, Elsevier, Amsterdam. Pp. 175-196.

Morey, M.S., Grano, S.R., Ralston, J., Prestidge, C.A. and Verity, B., 2001. The electrochemistry of Pb(II) activated sphalerite in relation to flotation. *Minerals Engineering*. 14(9): 1009-1017.

Mycroft, J.R., Bancroft, G. M., McIntyre, N.S., Lorimer, J.W., and Hill, I.R., 1990. Detection of sulphur and polysulphides on electrochemically oxidized pyrite surfaces by X-ray photoelectron spectroscopy and Raman spectroscopy. *J. Electroanal. Chem.* 292: 139-152.

Natarajan, K.A., 1996. Laboratory studies on ball wear in the grinding of chalcopyrite ore. *Int. J. Miner. Process*. 46: 205-213.

Natarajan, K.A. and Iwasaki, I., 1984. Electrochemical aspects of grinding media-mineral interactions in magnetite ore grinding. *Int. J. Miner. Process*. 13: 53-71.

Ng'andu, D.E., 2001. The effect of underground mine water on the performance of the Mufulira flotation process. *J. S. Afr. Inst. Min. Metall.* 101(7): 367-380.

Nicol, M.J. and Lázaro, I., 2002. The role of E_h measurements in the interpretation of the kinetics and mechanisms of the oxidation and leaching of sulphide minerals. *Hydrometallurgy,* 63: 15-22.

Nowak, P. and Laajalehto, 2000. Oxidation of galena surface. An XPS study of the formation of sulfoxy species. *Applied Surface Sciemce*. 157: 101-111.

Nowak, P., Laajalehto, K., and Kartio, 2000. A flotation related X-ray photoelectron spectroscopy study of the oxidation of galena surface. *Colloids and Surfaces A: Physicochemical and Engineering Aspects.* 161: 447-460.

O'Dea, A.R., Prince, K.E., Smart, R.St.C. and Gerson, A.R., 2001. Secondary ion mass spectrometry investigation of the interaction of xanthate with galena. *Int. J. Miner. Process*. 61: 121-143.

Pattrick, R.A.D., England, K.E.R., Charnock, J.M., and Mosselmans, J.F.W., 1999. Copper activation of sphalerite in relation to flotation: an X-ray absorption spectroscopy (reflection extended X-ray absorption fine structure) investigation. *Int. J. Min. Process.,* 55: 247-265.

Pattrick, R.A.D., Charnock, J.M., England, K.E.R. and Wright, K., 1998. Lead sorption on the surface of ZnS with relevance to flotation: A fluorescence REFLEXAFS study. *Minerals Engineering*, 11(11): 1025-1033.

Peng, Y., Grano, S., Ralston, J. and Fornasiero, D., 2003(a). Control of grinding conditions in the flotation of galena and its separation from pyrite. *Int. J. Miner. Process.* 70: 67– 82

Peng, Y., Grano, S., Fornasiero, D., and Ralston, J., 2003(b). Control of grinding conditions in the flotation of chalcopyrite and its separation from pyrite. *Int. J. Miner. Process.* 69: 87-100.

Peng, Y., Grano, S., Ralston, J. and Fornasiero, D., 2002. Towards prediction of oxidation during grinding I. Galena flotation. *Minerals Engineering,* 15: 493-498.

Persson, I., Persson, P., Valli, M., Fozo, S., and Malmensten, B., 1991. Reactions on sulphide mineral surfaces in connection with xanthate flotation studies by diffuse reflectance FTIR spectroscopy, atomic absorption spectroscopy, and calometry. *Int. J. Miner. Process.* 33:67-81.

Pietrobon, M.C.; Grano, S.R. and Greet, C., 2000. The effect of process water quality on lead flotation in Pasminco Mining LTD's Elura ore. In: Flotation 2000 Conference, March 29-31, 2000. Adelaide (Australia). MEI, p.77

Popov, S.R., Vucinic, D.R., Strojek, J.W., and Denca, A., 1989a. Effect of dissolved lead ions on the ethyl xanthate adsorption on sphalerite in weakly acidic media. *Int. J. Min. Process.* 27: 51-62.

Popov, S.R., Vucinic, D.R., and Kacanik, J.V., 1989b. Floatability and adsorption of ethyl xanthate on sphalerite in an alkaline medium in the presence of dissolved lead ions. *Int. J. Min. Process.* 27: 205-219.

Popov, S.R., and Vucinic, D.R., 1990. Floatability and adsorption of ethyl xanthate on copper-activated sphalerite in weakly acidic medium. *Colloids and Surfaces.* 47:81-94.

Prestidge, C.A., Skinner, W.M., Ralston, J., and Smart, R.C., 1997. Copper (II) activation and cyanide deactivation of zinc sulphide under mildly alkaline conditions. *App. Surf. Sci.,* 108: 333-344.

Prestidge, C.A. and Ralston, J., 1996. Contact angle studies of ethyl xanthate coated galena particles. *J. Colloid Interf. Sci.,* 184: 512-518.

Prestidge, C.A. and Ralston, J., 1995. Contact angle studies of particulate sulphide minerals. *Minerals Engineering,* 9(1): 85-102.

Prestidge, C.A., Ralston, J., and Smart, R.C., 1993. Role of cyanide in the interaction of ethyl xanthate with galena. *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* 81: 103-119.

Pugh, R.J., and Tjus, K., 1987. Electrokinetics studies on Cu(II) coated zinc sulfide particles. *J. Colloid Interface Sci*. 117(1):231-241.

Raichur, A.M., Wang, X.H., and Parekh, B.K., 2000. Quantifying pyrite surface oxidation kinetics by contact angle measurements. *Colloids and Surfaces A: Physicochemical and Engineering Aspects.* 167: 245-251.

Ralston, J. 1994. The chemistry of galena flotation: Principles and practice. *Minerals Engineering,* 7(5/6): 715-735.

Ralston, J. 1991. E_h and its consequences in sulphide mineral flotation. *Minerals Engineering,* 4(7-11): 859-878.

Ralston, J. and Healy, T.W., 1980a. Activation of zinc sulphide with Cu^{II}, Cd^{II}, and Pb^{II}: I. Activation in weakly acidic media. *Int. J. Min. Process*. 7:175-201.

Ralston, J. and Healy, T.W., 1980b. Activation of zinc sulphide with Cu^{II}, Cd^{II}, and Pb^{II}: II. Activation in neutral and weakly alkaline media. *Int. J. Min. Process*. 7:203-217.

Rand, D.A.J. and Woods, R., 1984. Eh measurements in sulphide minerals slurries. *Int. J. Miner. Process*. 13: 29-42.

Rao, S.R., 1971. *Xanthates and related coumponds*. Marcel Dekker, New York (USA), p 504.

Rao, S.R. and Finch, J.A., 1989. A review of water re-use in flotation. *Minerals Engineering*, 2(1): 65-85.

Rashchi, F., Sui, C. and Finch, J.A., 2002. Sphalerite activation and surface Pb ion concentration. *Int. J. Min. Process.* 67: 43-58.

Reddy, G.S. and Reddy, K., 1988. The chemistry of activation of sphalerite. A review. *Mineral Processing and Extractive Metallurgy Review.* 4: 1-37.

Rees, K.I. and Van Deventer, J.S.J., 1999. The role of metal-cyanide species in leaching gold from a copper concentrate. *Minerals Engineering*. 12(8):877-892.

Reyneke, L., 2000. Mineralogical investigation into the occurrence of Ag in samples from the western and eastern ore fields in the Rosh Pinah area, Namibia. *Report No. M2000/090.* Kumba Resources R&D (Pretoria, South Africa). p. 25.

Reyneke, L., 2000. Mineralogical composition and particle-counting of zinc, lead, feed and waste samples from Rosh Pinah, Namibia. *Report No. M2000/33.* Kumba Resources R&D (Pretoria, South Africa). p. 9.

Richardson, P.E. and Walker, G.W., 1985. The flotation of Chalcosite, Bornite, Chalcopyrite, and Pyrite in an electrochemical-flotation cell. *XVth International Mineral Processing Congress,* Cannes, France, June 2-9. pp. 198-210.

Richardson, P.E., Finkelstein, N.P., and Yoon, R.H., 1994. An electrochemical method for the study of the flotation chemistry of sphalerite. *Int. J. Min. Process.* 41: 71-76.

Seke, M.D, Naik, S., and Lewis, G.O., 2003(a). Flotation appraisal on a Suzdal (Kazakhstan) composite sample. *SGS Lakefield Research Africa. Report No. MET 02/322*. 23 October 2003. p. 60.

Seke, M.D, Naik, S., and Lewis, G.O., 2003(b). Flotation of two gold bearing samples from Pueblo Viejo. *SGS Lakefield Research Africa. Report No. MET 03/070*. 31 October 2003. p. 36.

Senior, G.D. and Trahar, W.J., 1991. The influence of metal hydroxides and collector on the flotation of chalcopyrite. Int. J. Miner. Process. 33: 321-341.

Shen, W.Z., Fornasiero, D., and Ralston, J., 2001. Flotation of sphalerite in the presence of sodium sulphite. *Int. J. Miner. Process*. 63: 17-28.

Shen, W.Z., Fornasiero, D., and Ralston, J., 1998. Effect of collectors, conditioning pH and gases in the separation of sphalerite from pyrite. *Minerals Engineering*, 11(2): 145-158.

Shimiizaka, J., Usui, S., Matsuoka, I., and Sasaki, H., 1976. Depression of galena flotation by sulphite and chromate ion. In: M.C. Fuestenau (Editor) *Flotation (A.M. Gaudin Memorial Volume),* AIMMPE, New York (USA), 1: 393-413

Smart, R.St.C., 1991. Surface layers in base metal sulphide flotation. *Minerals Engineering*. 4(7-11): 891-909.

Smith, R.M. and Martell, A.E., 1976. *Critical stability constants. Volume 4.* Plenum Press, New York (USA).

Stowe, K.G., Chryssoulis, S.L., and Kim, J.Y., 1995. Mapping of composition of mineral surfaces by TOF-SIMS. *Minerals Engineering*. 8(4/5): 421-430.

Subrahmanyam, T.V., Prestige, C.A., and Ralston, J., 1996. Contact angle and surface analysis studies of sphalerite particles. *Minerals Engineering*. 9(7): 727-741.

Sui, C., Rashchi, F., Xu, Z., Kim, J., Nesset, J.E., and Finch, J.A., 1998. Interactions in the sphalerite-Ca-SO_4-CO_3 systems. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 137: 69-77.

Sutherland, K.L., and Wark, I.W., 1955. *Principles of Flotation*. Aus.IMM. Melbourne (Australia). p. 489.

Teague, A.J., Van Deventer, J.S.J. and Swaminathan, C., 1999. A conceptual model for gold flotation. *Minerals Engineering*, 12(9): 1001-1019.

Trahar, W.J., 1984. The influence of pulp potential in sulphide flotation. In M.H. Jones and J.T. Woodcock (Editors), *Principles of Minerals Flotation*. The Wark symposium. The AusIMM, Parkville, Australia, pp. 117-136.

Trahar, W.J., 1981. A rational interpretation of the role of particle size in flotation. *Int. J. Miner. Process*. 8: 289-327.

Trahar, W.J., Senior, G.D., Heyes, G.W., and Creed, M.D., 1997. The activation of sphalerite by lead: a flotation perspective. *Int. J. Miner. Process*. 49, 121-148.

Trahar, W.J., Senior, G.D. and Shannon, L.K., 1994. Interactions between sulphide minerals-the collectorless flotation of pyrite. *Int. J. Miner. Process*. 40: 287-321.

Tran, T., Nguyen, H.H., Hsu, Y.J., and Wong, P.M.L., 1997. Copper-gold interaction during the processing of copper-gold ores, presented at *World Gold '97 Conference,* Singapore, 1-3 September 1997. pp. 95-98.

Tveter, E.C. and McQuiston, F.W., 1962. Plant practice in sulphide mineral flotation. In D.W. Fuerstenau (Editor), *Froth Flotation. 50th Anniversary Volume*. AIME, New York, USA, pp. 382-426.

Van Vuuren, C.J.J., 1982. A contribution to the regional setting and structure of the Rosh Pinah zinc-lead deposit. Kumba Resources. Report Rosh R 186. p.30

Vera, M.A., Mathe, Z.T., Franzidis, J.P., Harris, M.C., Manlapig, E.V., O'Connor, C.T., 2002. The modeling of froth zone recovery in batch and continuously operated laboratory flotation cells. *Int. J. Miner. Process.* 64: 135-151.

Vergara, J.A., Castro, S.H., and Pagliero, J.A., 1988. A study of the covellite-ethyl xanthate system using cyclic voltammetry. In: S.H.C. Flores and J.A. Moisan. *Froth Flotation. Developments in mineral processing.* 9:341-354.

Vukcevic, S., 1997. The mechanism of gold extraction and copper precipitation from low grade ores in cyanide ammonia systems. *Minerals Engineering*, 10(3): 309-326.

Vukcevic, S., 1996. A comparison of alkali and acid methods for the extraction of gold from low grade ores, *Minerals Engineering*, 9(10): 1033-1047.

Wang, X., 1989. Ph.D. Thesis, Lulea University of Technology, Lulea, Sweden.

Wang, X. and Forssberg, E., 1996. The solution electrochemistry of the sulfide-xanthate-cyanide systems in sulfide mineral flotation. *Minerals Engineering. 9(5)*: 527-546.

Wang, X., Forssberg, E., and Bolin, N.J., 1989a. The aqueous and surface chemistry of activation in the flotation of sulphide minerals. A review. Part.1: An electrochemical model. *Miner. Process. Extra. Metall. Review*, 4:135-165.

Wang, X., Forssberg, E., and Bolin, N.J., 1989b. The aqueous and surface chemistry of activation in the flotation of sulphide minerals. A review. Part II: A surface precipitation model. *Miner. Process. Extra. Metall. Review,* 4:167-199.

Wang, X.H. and Xie, Y., 1990. The effect of grinding media and environment on the surface properties and flotation behaviour of sulfide minerals. *Miner. Process. Extra. Metall. Review,*7: 49-79.

Watson, M.D. and Botha, P.H., 1983. Mineralogical investigation of the ore and plant products as an aid for improved beneficiation of the Zn-Pb-Cu ore at Rosh Pinah, South West Africa. *Spec. Pub. Geo. Soc. S. Afr.,* 7: 217-223.

Weisener, C. and Gerson, A., 2000. An investigation of the Cu(II) adsorption mechanism on pyrite by ARXPS and SIMS. *Minerals Engineering,* 13(13): 1329-1340.

Williams, S.R. and Pheloan, J.M., 1985. Process development at Woodlawn Mines. In: A.D. Zunkel, R.S. Boorman, A.E. Morris and R.J. Wesely (Editors), *Complex Sulphides. Processing of ores, concentrates and by-products.* The AIME, Pennsylvania, USA. Pp 293-304.

Woods, R., 2003. Electrochemcal potential controlling flotation. *Int. J. Miner. Process.* 72: 151-162.

Woods, R., 1976. Electrochemistry of sulphide flotation. In: M.C. Fuestenau (Editor), *Flotation*, A.M. Gaudin Memorial Volume, Vol. 1. Am. Inst. Min. Metall. Eng., pp. 298-333.

Woods, R., Chen, Z., and Yoon, R.H., 1997. Isotherms for the chemisorption of ethyl xanthate on lead. *Int. J. Miner. Process.* 50: 47-52.

Woods, R., Hope, G.A., and Brown, G.M., 1998. Spectroelectrochemical investigations of the interaction of ethyl xanthae with copper, silver and gold: II SERS of xanthate adsorbed on silver and copper surfaces. *Colloids and Surfaces A: Physicochemical and Engineering Aspects.* 137: 329-337.

Yamamoto, T., 1990. Mechanism of depression of pyrite and sphalerite by sulphite. In Jones, M.J. (Ed.). *Complex Sulphide Ores.* Inst. Miner. Metall., London, pp. 71-78.

Yuan, X.M, Pålsson, B.I and Forssberg, K.S.E., 1996. Flotation of a complex sulphide ore. I. Cu/Zn selectivity control by adjusting pulp potential with different gases. *Int. J. Miner. Process.* 46: 155-179.

Zhang, Q., Xu, Z., Bozkurt, V., and Finch, J.A., 1997. Pyrite flotation in the presence of metal ions and sphalerite. *Int. J. Miner. Process.* 52: 187-201.

Appendix I. Details of flotation results presented in Chapter 5

Table I.1. Experimental data for the flotation of the Rosh Pinah composite at pH 8.5 in the presence of 50 g/t PNBX

Time	Product	Mass Pull (%)		Assay (%)				Pb Recovery		Zn Recovery		Fe Recovery		Cu Recovery		Cumulative Grade (%)			
(min)		Ind	Cumul	Pb	Zn	Fe	Cu	Ind	Cumul	Ind	Cumul	Ind	Cumul	Ind	Cumul	Pb	Zn	Fe	Cu
0.5	RC1	3.18	3.18	4.0	18.6	11.5	0.20	9.6	9.6	8.6	8.6	11.7	11.7	6.4	6.4	4.0	18.6	11.5	0.20
1	RC2	1.21	4.39	18.6	16.2	15.0	1.07	17.2	26.7	2.9	11.5	5.8	17.6	13.1	19.5	8.0	17.9	12.5	0.44
2	RC3	1.48	5.87	12.7	17.1	13.9	0.93	14.3	41.1	3.7	15.2	6.6	24.2	13.9	33.4	9.2	17.7	12.8	0.56
3	RC4	1.15	7.02	10.7	18.8	14.0	0.86	9.4	50.5	3.2	18.3	5.2	29.3	10.0	43.4	9.4	17.9	13.0	0.61
8	RC5	3.09	10.11	9.7	19.4	13.9	0.87	22.8	73.3	8.7	27.1	13.8	43.1	27.2	70.6	9.5	18.4	13.3	0.69
12	RC6	1.94	12.05	5.8	19.0	13.9	0.55	8.6	81.9	5.4	32.5	8.7	51.8	10.8	81.3	8.9	18.5	13.4	0.67
	RT	87.95		0.27	5.26	1.71	0.02	18.1		67.5		48.2		18.7					
	Head	**100.00**		**1.31**	**6.85**	**3.12**	**0.10**	**100.0**		**100.0**		**100.0**		**100.0**					

Experimental conditions:

Grind:	80% passing 75 micron (dry milling)
Collector dosage:	50 g/t PNBX
Conditioning time:	3 minutes
Frother:	100g/t Dowfroth 200

Table I.2. Experimental data for the flotation of the Rosh Pinah composite at pH 8.5 in the presence of 100 g/t PNBX

Time	Product	Mass Pull (%)		Assay (%)				Pb Recovery		Zn Recovery		Fe Recovery		Cu Recovery		Cumulative Grade (%)			
(min)		Ind	Cumul	Pb	Zn	Fe	Cu	Ind	Cumul	Ind	Cumul	Ind	Cumul	Ind	Cumul	Pb	Zn	Fe	Cu
0.5	RC1	3.37	3.37	14.2	22.5	14.4	0.85	30.8	30.8	10.9	10.9	14.4	14.4	32.1	32.1	14.2	22.5	14.4	0.85
1	RC2	1.17	4.54	10.8	21.3	13.2	0.69	8.1	39.0	3.6	14.4	4.6	19.0	9.0	41.1	13.3	22.2	14.1	0.81
2	RC3	1.51	6.05	9.6	21.7	13.3	0.67	9.3	48.3	4.7	19.1	6.0	24.9	11.3	52.5	12.4	22.1	13.9	0.77
2.5	RC4	0.75	6.80	9.0	21.5	13.8	0.63	4.3	52.7	2.3	21.4	3.1	28.0	5.3	57.8	12.0	22.0	13.9	0.76
5	RC5	4.68	11.48	5.7	19.4	12.6	0.38	17.2	69.8	13.0	34.4	17.5	45.5	19.9	77.7	9.4	20.9	13.4	0.60
8	RC6	4.39	15.87	3.2	16.8	10.9	0.16	9.1	78.9	10.6	45.0	14.2	59.7	7.9	85.6	7.7	19.8	12.7	0.48
12	RC7	1.05	16.92	3.5	18.7	11.4	0.16	2.4	81.3	2.8	47.8	3.6	63.3	1.9	87.4	7.5	19.7	12.6	0.46
	RT	83.08		0.35	4.39	1.49	0.01	18.7		52.2		36.7		12.6					
	Head	**100.00**		**1.55**	**6.99**	**3.37**	**0.09**	**100.0**		**100.0**		**100.0**		**100.0**					

Experimental conditions:

Grind:	80% passing 75 micron (dry milling)
Collector dosage:	100 g/t PNBX
Conditioning time:	3 minutes
Frother:	100g/t Dowfroth 200

Table I.3. Experimental data for the flotation of the Rosh Pinah composite at pH 8.5 in the presence of 50 g/t PNBX and 50 ppm (2.4x10^{-4}M) Pb(II)

Time	Product	Mass Pull (%)		Assay (%)			Pb Recovery		Zn Recovery		Fe Recovery		Cumulative Grade (%)		
(min)		Ind	Cumul	Pb	Zn	Fe	Ind	Cumul	Ind	Cumul	Ind	Cumul	Pb	Zn	Fe
0.5	RC1	2.54	2.54	3.7	17.8	13.5	7.1	7.1	6.7	6.7	10.9	10.9	3.7	17.8	13.5
1	RC2	1.36	3.90	14.1	22.8	15.8	14.5	21.6	4.6	11.3	6.8	17.7	7.3	19.5	14.3
2	RC3	1.18	5.08	9.9	21.3	14.5	8.8	30.5	3.7	15.0	5.4	23.2	7.9	20.0	14.3
3	RC4	1.08	6.16	9.8	21.2	14.5	8.0	38.5	3.4	18.3	5.0	28.2	8.3	20.2	14.4
8	RC5	3.17	9.33	8.6	20.8	14.2	20.6	59.1	9.7	28.1	14.3	42.5	8.4	20.4	14.3
12	RC6	1.75	11.08	6.5	18.8	14.5	8.6	67.7	4.9	32.9	8.1	50.5	8.1	20.1	14.3
	RT	88.92		0.48	5.11	1.75	32.3		67.1		49.5				
	Head	**100.00**		**1.32**	**6.77**	**3.15**	**100.0**		**100.0**		**100.0**				

Experimental conditions:

Grind:	80% passing 75 micron (dry milling)
Activator:	[Pb(II)] = 2.4x10^{-4}M
Activation time:	30 minutes
Collector dosage:	50 g/t PNBX
Conditioning time:	3 minutes
Frother:	100 g/t Dowfroth 200

Table I.4. Experimental data for the flotation of the Rosh Pinah composite at pH 8.5 in the presence of 50 g/t PNBX and 100 ppm (4.8x10^{-4}M) Pb(II)

Time	Product	Mass Pull (%)		Assay (%)			Pb Recovery		Zn Recovery		Fe Recovery		Cumulative Grade (%)		
(min)		Ind	Cumul	Pb	Zn	Fe	Ind	Cumul	Ind	Cumul	Ind	Cumul	Pb	Zn	Fe
0.5	RC1	2.51	2.51	4.6	17.1	14	7.8	7.8	7.1	7.1	11.4	11.4	4.6	17.1	14.0
1	RC2	0.92	3.43	11.8	24	14.3	7.3	15.1	3.7	10.8	4.3	15.7	6.5	19.0	14.1
2	RC3	1.09	4.52	9.6	21.8	12.9	7.1	22.2	3.9	14.7	4.6	20.2	7.3	19.6	13.8
3	RC4	0.87	5.39	10.2	22.4	13.2	6.0	28.2	3.2	18.0	3.7	24.0	7.7	20.1	13.7
8	RC5	2.62	8.01	9.6	21.4	13.1	17.0	45.2	9.3	27.3	11.1	35.1	8.4	20.5	13.5
12	RC6	1.6	9.61	8.4	18.7	13.2	9.1	54.2	5.0	32.3	6.9	41.9	8.4	20.2	13.5
	RT	90.39		0.75	4.51	1.98	45.8		67.7		58.1				
	Head	**100.00**		**1.48**	**6.02**	**3.08**	**100.0**		**100.0**		**100.0**				

Experimental conditions:

Grind:	80% passing 75 micron (dry milling)
Activator:	[Pb(II)] = 4.8x10^{-4}M
Activation time:	30 minutes
Collector dosage:	50 g/t PNBX
Conditioning time:	3 minutes
Frother:	100 g/t Dowfroth 200

Table I.5. Experimental data for the flotation of the Rosh Pinah composite at pH 8.5 in the presence of 50 g/t PNBX and 200 ppm (9.7x10^{-4}M) Pb(II)

Time	Product	Mass Pull (%)		Assay (%)			Pb Recovery		Zn Recovery		Fe Recovery		Cumulative Grade (%)		
(min)		Ind	Cumul	Pb	Zn	Fe	Ind	Cumul	Ind	Cumul	Ind	Cumul	Pb	Zn	Fe
0.5	RC1	2.27	2.27	7.13	16.1	13.4	9.8	9.8	5.9	5.9	10.4	10.4	7.1	16.1	13.4
1	RC2	0.94	3.21	10.4	27.9	13.5	5.9	15.7	4.2	10.1	4.3	14.8	8.1	19.6	13.4
2	RC3	1.38	4.59	9.51	25.8	12.3	8.0	23.7	5.7	15.8	5.8	20.6	8.5	21.4	13.1
3	RC4	1.06	5.65	9.8	24.8	13	6.3	30.0	4.2	20.1	4.7	25.3	8.8	22.1	13.1
8	RC5	2.64	8.29	8.89	23.2	13	14.2	44.2	9.9	29.9	11.7	37.0	8.8	22.4	13.0
12	RC6	2.41	10.70	7.8	15.8	10.4	11.4	55.6	6.1	36.0	8.6	45.6	8.6	20.9	12.5
	RT	89.3		0.82	4.45	1.78	44.4		64.0		54.4				
	Head	**100.00**		**1.65**	**6.21**	**2.92**	**100.0**		**100.0**		**100.0**				

Experimental conditions:

Grind:	80% passing 75 micron (dry milling)
Activator:	[Pb(II)] = 9.7x10^{-4}M
Activation time:	30 minutes
Collector dosage:	50 g/t PNBX
Conditioning time:	3 minutes
Frother:	100 g/t Dowfroth 200

Table I.6. Experimental data for the flotation of the Rosh Pinah composite at pH 8.5 in the presence of 50 g/t PNBX and 100 ppm (1.6x10^{-3}M) Cu(II)

Time	Product	Mass Pull (%)		Assay (%)			Pb Recovery		Zn Recovery		Fe Recovery		Cumulative Grade (%)		
(min)		Ind	Cumul	Pb	Zn	Fe	Ind	Cumul	Ind	Cumul	Ind	Cumul	Pb	Zn	Fe
0.5	RC1	5.41	5.41	5.8	16.7	13.8	21.1	21.1	18.4	18.4	23.0	23.0	5.8	16.7	13.8
1	RC2	1.31	6.72	4.4	51.8	5.4	3.9	24.9	13.8	32.2	2.2	25.2	5.5	23.5	12.2
2	RC3	1.65	8.37	5.5	44.9	6.9	6.1	31.0	15.1	47.2	3.5	28.7	5.5	27.8	11.1
3	RC4	1.18	9.55	6.3	40.2	7.6	5.0	36.0	9.6	56.9	2.8	31.4	5.6	29.3	10.7
8	RC5	3.92	13.47	6.1	24.8	10.4	16.1	52.1	19.8	76.6	12.6	44.0	5.8	28.0	10.6
12	RC6	1.71	15.18	5.5	15.7	9.7	6.3	58.4	5.5	82.1	5.1	49.1	5.7	26.6	10.5
	RT	84.82		0.73	1.04	1.95	41.6		17.9		50.9				
	Head	**100.00**		**1.49**	**4.92**	**3.25**	**100.0**		**100.0**		**100.0**				

Experimental conditions:

Grind:	80% passing 75 micron (dry milling)
Activator:	[Cu(II)] = 1.6x10^{-3}M
Activation time:	30 minutes
Collector dosage:	50 g/t PNBX
Conditioning time:	3 minutes
Frother:	100 g/t Dowfroth 200

Table I.7. Experimental data for the flotation of the Rosh Pinah composite at pH 8.5 in the presence of 50 g/t PNBX, 100 ppm ($1.6x10^{-3}M$*) Cu(II) and 100 ppm (*$4.8x10^{-4}M$*) Pb(II)*

Time	Product	Mass Pull (%)		Assay (%)			Pb Recovery		Zn Recovery		Fe Recovery		Cumulative Grade (%)		
(min)		Ind	Cumul	Pb	Zn	Fe	Ind	Cumul	Ind	Cumul	Ind	Cumul	Pb	Zn	Fe
0.5	RC1	5.7	5.70	4.9	41.7	5.1	17.1	17.1	37.5	37.5	10.1	10.1	4.9	41.7	5.1
1	RC2	1.7	7.40	5.6	37.7	6.9	5.8	23.0	10.1	47.6	4.1	14.2	5.1	40.8	5.5
2	RC3	1.82	9.22	6.6	35.3	7.7	7.4	30.3	10.1	57.8	4.9	19.1	5.4	39.7	5.9
3	RC4	1.26	10.48	6.4	33	8.2	4.9	35.3	6.6	64.3	3.6	22.6	5.5	38.9	6.2
8	RC5	4.79	15.27	5.8	21.4	10.8	17.0	52.3	16.2	80.5	18.0	40.6	5.6	33.4	7.7
12	RC6	2.22	17.49	4.6	13.7	11.5	6.3	58.5	4.8	85.3	8.9	49.5	5.5	30.9	8.1
	RT	82.51		0.82	1.13	1.76	41.5		14.7		50.5				
	Head	**100.00**		**1.63**	**6.34**	**2.88**	**100.0**		**100.0**		**100.0**				

Experimental conditions:

Grind: 80% passing 75 micron (dry milling)
Activator: [Cu(II)] = $1.6x10^{-3}$M and [Pb(II)] = $4.8x10^{-4}$M
Activation time: 30 minutes
Collector dosage: 50 g/t PNBX
Conditioning time: 3 minutes
Frother: 100 g/t Dowfroth 200

Table I.8. Experimental data for the flotation of the Rosh Pinah composite at pH 8.5 in the presence of 50 g/t SNPX

Time	Product	Mass Pull (%)		Assay (%)		Pb Recovery		Zn Recovery		Cumulative Grade (%)	
(min)		Ind	Cumul	Pb	Zn	Ind	Cumul	Ind	Cumul	Pb	Zn
0.5	RC1	1.94	1.94	20.5	21.1	22.9	22.9	5.7	5.7	20.5	21.1
2	RC2	1.93	3.87	15.9	23	17.7	40.6	6.1	11.8	18.2	22.0
8	RC3	4.03	7.90	9.6	25.8	22.3	62.9	14.4	26.2	13.8	24.0
	RT	92.1		0.7	5.8	37.1		73.8			
	Head	**100.00**		**1.74**	**7.23**	**100.0**		**100.0**			

Experimental conditions:

Grind:	80% passing 75 micron (dry milling)
Collector dosage:	50 g/t SNPX
Conditioning time:	3 minutes
Frother:	100 g/t Dowfroth 200

Table I.9. Experimental data for the flotation of the Rosh Pinah composite at pH 8.5 in the presence of 100 g/t SNPX

Time	Product	Mass Pull (%)		Assay (%)		Pb Recovery		Zn Recovery		Cumulative Grade (%)	
(min)		Ind	Cumul	Pb	Zn	Ind	Cumul	Ind	Cumul	Pb	Zn
0.5	RC1	4.7	4.70	14.9	24.4	44.7	44.7	14.9	14.9	14.9	24.4
2	RC2	2.8	7.50	10.6	27.6	18.9	63.6	10.1	25.0	13.3	25.6
8	RC3	4.6	12.10	5.5	31.8	16.2	79.8	19.0	44.0	10.3	28.0
	RT	87.9		0.36	4.9	20.2		56.0			
	Head	**100.00**		**1.57**	**7.69**	**100.0**		**100.0**			

Experimental conditions:

Grind:	80% passing 75 micron (dry milling)
Collector dosage:	100 g/t SNPX
Conditioning time:	3 minutes
Frother:	100 g/t Dowfroth 200

Table I.10. Experimental data for the flotation of the Rosh Pinah composite in the presence of 50 g/t PNBX and 20g/t NaCN

Time	Product	Mass Pull (%)		Assay (%)		Pb Recovery		Zn Recovery		Cumulative Grade (%)	
(min)		Ind	Cumul	Pb	Zn	Ind	Cumul	Ind	Cumul	Pb	Zn
0.5	RC1	2.16	2.16	18.1	19.2	28.6	28.6	6.4	6.4	18.1	19.2
1	RC2	0.84	3.00	14.1	20.3	8.7	37.3	2.6	9.0	17.0	19.5
2	RC3	1.25	4.25	13.4	21.3	12.3	49.5	4.1	13.1	15.9	20.0
3	RC4	0.9	5.15	11.5	18.5	7.6	57.1	2.6	15.7	15.2	19.8
8	RC5	2.57	7.72	8.8	22.9	16.6	73.7	9.1	24.8	13.0	20.8
12	RC6	1.21	8.93	6.4	23.3	5.7	79.3	4.4	29.2	12.1	21.1
	RT	91.07		0.31	5.04	20.7		70.8			
	Head	**100.00**		**1.37**	**6.48**	**100.0**		**100.0**			

Experimental conditions:

Grind:	80% passing 75 micron (dry milling)
Depressant dosage:	20 g/t NaCN
Collector dosage:	50 g/t PNBX
Conditioning time:	3 minutes
Frother:	100 g/t Dowfroth 200

Table I.11. Experimental data for the flotation of the Rosh Pinah composite in the presence of 50 g/t PNBX and 20g/t NaCN

Time	Product	Mass Pull (%)		Assay (%)		Pb Recovery		Zn Recovery		Cumulative Grade (%)	
(min)		Ind	Cumul	Pb	Zn	Ind	Cumul	Ind	Cumul	Pb	Zn
0.5	RC1	2.25	2.25	18.6	18.4	30.8	30.8	6.4	6.4	18.6	18.4
1	RC2	1.16	3.41	14.9	19.3	12.7	43.5	3.5	9.9	17.3	18.7
2	RC3	1.18	4.59	13.5	20.8	11.7	55.3	3.8	13.7	16.4	19.2
3	RC4	0.8	5.39	11.2	21.7	6.6	61.8	2.7	16.4	15.6	19.6
8	RC5	2.2	7.59	7.97	22.9	12.9	74.8	7.8	24.2	13.4	20.6
12	RC6	1.09	8.68	6.67	22	5.4	80.1	3.7	27.9	12.5	20.7
	RT	91.32		0.296	5.091	19.9		72.1			
	Head	**100.00**		**1.36**	**6.45**	**100.0**		**100.0**			

Experimental conditions:

Grind: 80% passing 75 micron (dry milling)
Depressant dosage: 20 g/t NaCN
Collector dosage: 50 g/t PNBX
Conditioning time: 3 minutes
Frother: 100 g/t Dowfroth 200

Appendix II. Details of experiments on the effect of copper cyanide and grinding environment on the flotation selectivity

Table II.1a. Pulp potential and dissolved oxygen during the flotation of the Rosh Pinah composite after dry and wet milling in a mild steel mill. Before activation

Time	Dry milling				Wet milling			
(Min)	Pulp potential (mV SHE)		Dissolved oxygen (ppm)		Pulp potential (mV SHE)		Dissolved oxygen (ppm)	
	50 g/t SNPX	70 g/t SNPX	50 g/t SNPX	70 g/t SNPX	50 g/t SNPX	70 g/t SNPX	50 g/t SNPX	70 g/t SNPX
1	150	140	4.4	4.5	-80	-100	1.7	1.2
4	140	123	3.6	4	-90	-106	1.3	1.1
5	120	110	3.5	4.2	-110	-112	1.3	1.1
6	145	140	6.5	7.5	-30	-30	2	2
7	150	145	8.1	8.1	10	4	4.7	4.6
9	170	160	8.1	8.2	100	78	6.9	6.7
15	180	169	8.2	8.2	140	130	7.9	7.9

Table II.1b. Pulp potential and dissolved oxygen during the flotation of the Rosh Pinah composite after dry and wet milling in a mild steel mill. Activation with 10^{-4}M Cu(I), 50 g/t SNPX

Time	Dry milling		Wet milling	
	Pulp potential	Dissolved oxygen	Pulp potential	Dissolved oxygen
(min)	(mV)	(ppm)	(mV)	(ppm)
1	99	3.3	-179	0.8
2	74	2.7	-173	0.8
3	52	2.1	-169	1.1
4	31	1.6	-180	0.8
5	13	1.3	-175	0.8
6	2	1.1	-175	0.8
7	-5	1	-180	0.7
8	-10	1	-176	0.7
9	-15	0.9	-176	0.7
10	-16	0.9	-176	0.7
11	-7	1.2	-146	0.6
12	6	1.4	-142	0.6
13	15	1.6	-133	0.6
14	23	1.9	-130	0.6
15	112	6.0	-21	3.6
16	115	7.5	54	5.7
18	122	7.8	90	7.3
24	130	8.1	95	8.1

Table II.2 . Experimental data for the flotation of the Rosh Pinah composite at pH 8.5 in the presence of 50 g/t SNPX

Time	Product	Mass Pull (%)		Assay (%)				Pb Recovery		Zn Recovery		Fe Recovery		Cu Recovery		Cumulative Grade (%)			
(min)		Ind	Cumul	Pb	Zn	Fe	Cu	Ind	Cumul	Ind	Cumul	Ind	Cumul	Ind	Cumul	Pb	Zn	Fe	Cu
1	RC1	3.39	3.39	15.3	27.8	10.8	0.53	23.1	23.1	11.4	11.4	10.5	10.5	16.0	16.0	15.3	27.8	10.8	0.53
2	RC2	2.87	6.26	10.5	27.9	10.4	0.5	13.4	36.6	9.6	21.0	8.6	19.1	12.8	28.8	13.1	27.8	10.6	0.52
4	RC3	3.64	9.90	8.2	28.7	10.9	0.46	13.3	49.9	12.6	33.6	11.4	30.5	14.9	43.7	11.3	28.2	10.7	0.50
10	RC4	6.65	16.55	5.1	26.4	11.2	0.45	15.1	65.0	21.2	54.7	21.4	52.0	26.6	70.3	8.8	27.5	10.9	0.48
	RT	83.45		0.94	4.5	2	0.04	35.0		45.3		48.0		29.7					
	Head	**100.00**		**2.24**	**8.30**	**3.48**	**0.11**	**100.0**		**100.0**		**100.0**		**100.0**					

Experimental conditions:

Weight of sample:	1000 g
Grind:	80% passing 100 micron
Grinding type:	dry
Collector dosage:	50 g/t SNPX
Conditioning time:	3 minutes
Frother:	100 g/t Senfroth 9325

Table II.3 . Experimental data for the flotation of the Rosh Pinah composite at pH 8.5 in the presence of 70 g/t SNPX

Time	Product	Mass Pull (%)		Assay (%)				Pb Recovery		Zn Recovery		Fe Recovery		Cu Recovery		Cumulative Grade (%)			
(min)		Ind	Cumul	Pb	Zn	Fe	Cu	Ind	Cumul	Ind	Cumul	Ind	Cumul	Ind	Cumul	Pb	Zn	Fe	Cu
1	RC1	3.6	3.60	14.8	26.5	11.8	0.51	24.9	24.9	11.1	11.1	12.1	12.1	15.3	15.3	14.8	26.5	11.8	0.51
2	RC2	2.8	6.40	10.6	26.4	11.5	0.51	13.9	38.7	8.6	19.8	9.1	21.2	11.9	27.2	13.0	26.5	11.7	0.51
4	RC3	4.7	11.10	7.2	27.2	11.1	0.44	15.8	54.5	14.9	34.7	14.8	36.0	17.2	44.4	10.5	26.8	11.4	0.48
10	RC4	9.2	20.30	4.1	24.5	9.8	0.38	17.6	72.1	26.3	61.0	25.6	61.6	29.1	73.5	7.6	25.7	10.7	0.43
	RT	79.7		0.75	4.2	1.7	0.04	27.9		39.0		38.4		26.5					
	Head	**100.00**		**2.14**	**8.57**	**3.53**	**0.12**	**100.0**		**100.0**		**100.0**		**100.0**					

Experimental conditions:

Weight of sample:	1000 g
Grind:	80% passing 100 micron
Grinding type:	dry
Collector dosage:	70 g/t SNPX
Conditioning time:	3 minutes
Frother:	100 g/t Senfroth 9325

Table II.4. Experimental data for the flotation of the Rosh Pinah composite at pH 8.5 in the presence of 50 g/t SNPX. [Cu] = 10^{-4}M, [CN$^-$]/[Cu] =3

Time	Product	Mass Pull (%)		Assay (%)				Pb Recovery		Zn Recovery		Fe Recovery		Cu Recovery		Cumulative Grade (%)			
(min)		Ind	Cumul	Pb	Zn	Fe	Cu	Ind	Cumul	Ind	Cumul	Ind	Cumul	Ind	Cumul	Pb	Zn	Fe	Cu
1	RC1	3.3	3.30	14.8	28.6	12.5	0.61	22.3	22.3	11.0	11.0	12.5	12.5	16.5	16.5	14.8	28.6	12.5	0.61
2	RC2	3.1	6.40	10.5	33.3	11.8	0.58	14.9	37.2	12.0	23.0	11.0	23.5	14.8	31.3	12.7	30.9	12.2	0.60
4	RC3	5.8	12.20	5.8	33.1	9.9	0.47	15.4	52.5	22.3	45.3	17.3	40.8	22.4	53.7	9.4	31.9	11.1	0.54
10	RC4	7.3	19.50	4.1	29.2	8.1	0.33	13.7	66.2	24.8	70.1	17.9	58.7	19.8	73.5	7.4	30.9	10.0	0.46
	RT	80.5		0.92	3.2	1.7	0.04	33.8		29.9		41.3		26.5					
	Head	**100.00**		**2.19**	**8.60**	**3.31**	**0.12**	**100.0**		**100.0**		**100.0**		**100.0**					

Experimental conditions:

Weight of sample: 1000 g
Grind: 80% passing 100 micron
Grinding type: dry
Activator: [Cu] = 10^{-4}M, [CN$^-$]/[Cu] =3
Activation time: 10 minutes
Collector dosage: 50 g/t SNPX
Conditioning time: 3 minutes
Frother: 100 g/t Senfroth 9325

Table II.5. Experimental data for the flotation of the Rosh Pinah composite at pH 8.5 in the presence of 70 g/t SNPX. [Cu] = 10^{-4}M, [CN$^-$]/[Cu] =3

Time	Product	Mass Pull (%)		Assay (%)				Pb Recovery		Zn Recovery		Fe Recovery		Cu Recovery		Cumulative Grade (%)			
(min)		Ind	Cumul	Pb	Zn	Fe	Cu	Ind	Cumul	Ind	Cumul	Ind	Cumul	Ind	Cumul	Pb	Zn	Fe	Cu
1	RC1	6.3	6.30	11.7	29.6	13	0.56	31.1	31.1	20.7	20.7	23.3	23.3	27.1	27.1	11.7	29.6	13.0	0.56
2	RC2	5.1	11.40	5.5	31.8	9.9	0.39	11.8	42.9	18.0	38.7	14.3	37.6	15.3	42.4	8.9	30.6	11.6	0.48
4	RC3	7.5	18.90	3.8	27.9	7.5	0.31	12.0	54.9	23.2	62.0	16.0	53.6	17.9	60.2	6.9	29.5	10.0	0.41
10	RC4	4.3	23.20	7.7	31.4	11.2	0.49	14.0	68.9	15.0	77.0	13.7	67.3	16.2	76.4	7.0	29.9	10.2	0.43
	RT	76.8		0.96	2.7	1.5	0.04	31.1		23.0		32.7		23.6					
	Head	**100.00**		**2.37**	**9.00**	**3.52**	**0.13**	**100.0**		**100.0**		**100.0**		**100.0**					

Experimental conditions:

Weight of sample:	1000 g
Grind:	80% passing 100 micron
Grinding type:	dry
Activator:	[Cu] = 10^{-4}M, [CN$^-$]/[Cu] =3
Activation time:	10 minutes
Collector dosage:	70 g/t SNPX
Conditioning time:	3 minutes
Frother:	100 g/t Senfroth 9325

Table II.6. Experimental data for the flotation of the Rosh Pinah composite at pH 8.5 in the presence of 50 g/t SNPX after wet milling

Time	Product	Mass Pull (%)		Assay (%)				Pb Recovery		Zn Recovery		Fe Recovery		Cu Recovery		Cumulative Grade (%)			
(min)		Ind	Cumul	Pb	Zn	Fe	Cu	Ind	Cumul	Ind	Cumul	Ind	Cumul	Ind	Cumul	Pb	Zn	Fe	Cu
1	RC1	4.8	4.80	11.2	12.5	24.6	0.98	27.0	27.0	7.8	7.8	30.3	30.3	40.7	40.7	11.2	12.5	24.6	0.98
2	RC2	2.4	7.20	11.5	16.9	20	0.86	13.9	40.9	5.3	13.1	12.3	42.6	17.9	58.5	11.3	14.0	23.1	0.94
4	RC3	3.1	10.30	10.1	23.6	12.3	0.49	15.7	56.6	9.5	22.7	9.8	52.4	13.1	71.7	10.9	16.9	19.8	0.80
10	RC4	7.2	17.50	5	22.8	6.3	0.18	18.1	74.7	21.4	44.1	11.6	64.0	11.2	82.9	8.5	19.3	14.3	0.55
	RT	82.5		0.61	5.2	1.7	0.024	25.3		55.9		36.0		17.1					
	Head	**100.00**		**1.99**	**7.67**	**3.90**	**0.12**	**100.0**		**100.0**		**100.0**		**100.0**					

Experimental conditions:

Weight of sample:	1000 g
Grind:	80% passing 100 micron
Grinding type:	wet (66% solids)
Collector dosage:	50 g/t SNPX
Conditioning time:	3 minutes
Frother:	100 g/t Senfroth 9325

Table II.7. Experimental data for the flotation of the Rosh Pinah composite at pH 8.5 in the presence of 70 g/t SNPX

Time	Product	Mass Pull (%)		Assay (%)				Pb Recovery		Zn Recovery		Fe Recovery		Cu Recovery		Cumulative Grade (%)			
(min)		Ind	Cumul	Pb	Zn	Fe	Cu	Ind	Cumul	Ind	Cumul	Ind	Cumul	Ind	Cumul	Pb	Zn	Fe	Cu
1	RC1	5.7	5.70	12	13.6	25.7	1.06	31.1	31.1	9.5	9.5	34.8	34.8	47.6	47.6	12.0	13.6	25.7	1.06
2	RC2	2	7.70	11	18.1	16	0.666	10.0	41.2	4.4	13.9	7.6	42.4	10.5	58.1	11.7	14.8	23.2	0.96
4	RC3	3.6	11.30	8.53	22.9	10.7	0.368	14.0	55.1	10.1	23.9	9.2	51.6	10.4	68.6	10.7	17.4	19.2	0.77
10	RC4	9.8	21.10	4.42	27.2	6.44	0.157	19.7	74.9	32.5	56.5	15.0	66.6	12.1	80.7	7.8	21.9	13.3	0.49
	RT	78.9		0.7	4.52	1.78	0.031	25.1		43.5		33.4		19.3					
	Head	**100.00**		**2.20**	**8.19**	**4.21**	**0.13**	**100.0**		**100.0**		**100.0**		**100.0**					

Experimental conditions:

Weight of sample:	1000 g
Grind:	80% passing 100 micron
Grinding type:	wet (66% solids)
Collector dosage:	70 g/t SNPX
Conditioning time:	3 minutes
Frother:	100 g/t Senfroth 9325

Table II.8. Experimental data for the flotation of the Rosh Pinah composite at pH 8.5 in the presence of 50 g/t SNPX. $[Cu] = 10^{-4}M$, $[CN^{-}]/[Cu] = 3$

Time	Product	Mass Pull (%)		Assay (%)				Pb Recovery		Zn Recovery		Fe Recovery		Cu Recovery		Cumulative Grade (%)			
(min)		Ind	Cumul	Pb	Zn	Fe	Cu	Ind	Cumul	Ind	Cumul	Ind	Cumul	Ind	Cumul	Pb	Zn	Fe	Cu
1	RC1	5.2	5.20	11.9	11.3	26.5	1.12	29.0	29.0	7.1	7.1	33.5	33.5	44.9	44.9	11.9	11.3	26.5	1.12
2	RC2	2.8	8.00	11.6	16.7	17.1	0.63	15.2	44.3	5.6	12.7	11.6	45.1	13.6	58.5	11.8	13.2	23.2	0.95
4	RC3	2.8	10.80	10.4	27.3	11.7	0.49	13.7	57.9	9.2	22.0	8.0	53.0	10.6	69.1	11.4	16.8	20.2	0.83
10	RC4	7.8	18.60	4.3	31.7	6.01	0.2	15.7	73.7	29.9	51.8	11.4	64.4	12.0	81.2	8.4	23.1	14.3	0.57
	RT	81.4		0.69	4.9	1.8	0.03	26.3		48.2		35.6		18.8					
	Head	**100.00**		**2.13**	**8.28**	**4.12**	**0.13**	**100.0**		**100.0**		**100.0**		**100.0**					

Experimental conditions:

Weight of sample:	1000 g
Grind:	80% passing 100 micron
Grinding type:	wet (66% solids)
Activator:	$[Cu] = 10^{-4}M$, $[CN^{-}]/[Cu] = 3$
Activation time:	10 minutes
Collector dosage:	50 g/t SNPX
Conditioning time:	3 minutes
Frother:	100 g/t Senfroth 9325

Table II.9. Experimental data for the flotation of the Rosh Pinah composite at pH 8.5 in the presence of 50 g/t SNPX. [Cu] = 10^{-3}*M, [CN*$^{-}$*]/[Cu] =3*

Time	Product	Mass Pull (%)		Assay (%)				Pb Recovery		Zn Recovery		Fe Recovery		Cu Recovery		Cumulative Grade (%)			
(min)		Ind	Cumul	Pb	Zn	Fe	Cu	Ind	Cumul	Ind	Cumul	Ind	Cumul	Ind	Cumul	Pb	Zn	Fe	Cu
1	RC1	5.5	5.50	12.1	12.4	28	1.06	32.0	32.0	8.4	8.4	39.2	39.2	49.3	49.3	12.1	12.4	28.0	1.06
2	RC2	2.6	8.10	11.2	25.5	15.6	0.58	14.0	46.0	8.1	16.5	10.3	49.5	12.8	62.1	11.8	16.6	24.0	0.91
4	RC3	2.7	10.80	8.9	35	10.8	0.4	11.5	57.5	11.6	28.0	7.4	56.9	9.1	71.2	11.1	21.2	20.7	0.78
10	RC4	6.7	17.50	3.6	37.2	6.8	0.2	11.6	69.1	30.5	58.6	11.6	68.5	11.3	82.6	8.2	27.3	15.4	0.56
	RT	82.5		0.78	4.1	1.5	0.025	30.9		41.4		31.5		17.4					
	Head	**100.00**		**2.08**	**8.16**	**3.93**	**0.12**	**100.0**		**100.0**		**100.0**		**100.0**					

Experimental conditions:

Weight of sample:	1000 g
Grind:	80% passing 100 micron
Grinding type:	wet (66% solids)
Activator:	[Cu] = 10^{-3}M, [CN^{-}]/[Cu] =3
Activation time:	10 minutes
Collector dosage:	50 g/t SNPX
Conditioning time:	3 minutes
Frother:	100 g/t Senfroth 9325

Table II.10. Experimental data for the flotation of the Rosh Pinah composite at pH 8.5 in the presence of 70 g/t SNPX. [Cu] = 10^{-3}M, [CN$^-$]/[Cu] =3

Time	Product	Mass Pull (%)		Assay (%)				Pb Recovery		Zn Recovery		Fe Recovery		Cu Recovery		Cumulative Grade (%)			
(min)		Ind	Cumul	Pb	Zn	Fe	Cu	Ind	Cumul	Ind	Cumul	Ind	Cumul	Ind	Cumul	Pb	Zn	Fe	Cu
1	RC1	6.3	6.30	11.4	14.3	24.7	1	33.1	33.1	10.4	10.4	36.8	36.8	46.7	46.7	11.4	14.3	24.7	1.00
2	RC2	3.2	9.50	10.2	29.9	14.1	0.51	15.0	48.1	11.1	21.5	10.7	47.5	12.1	58.8	11.0	19.6	21.1	0.83
4	RC3	5.2	14.70	6.6	35.9	9.6	0.31	15.8	64.0	21.6	43.2	11.8	59.3	11.9	70.7	9.4	25.3	17.1	0.65
10	RC4	7.7	22.40	3.4	35.4	6.2	0.19	12.1	76.0	31.6	74.8	11.3	70.6	10.8	81.6	7.4	28.8	13.3	0.49
	RT	77.6		0.67	2.8	1.6	0.032	24.0		25.2		29.4		18.4					
	Head	**100.00**		**2.17**	**8.62**	**4.23**	**0.13**	**100.0**		**100.0**		**100.0**		**100.0**					

Experimental conditions:

Weight of sample: 1000 g
Grind: 80% passing 100 micron
Grinding type: wet (66% solids)
Activator: [Cu] = 10^{-3}M, [CN$^-$]/[Cu] =3
Activation time: 10 minutes
Collector dosage: 70 g/t SNPX
Conditioning time: 3 minutes
Frother: 100 g/t Senfroth 9325

Appendix III. Detailed results on the effect of CuCN on the flotation selectivity

Table III.1. Experimental data for the flotation of the Rosh Pinah composite at pH 8.5 in the presence of 50 g/t SNPX.

Time	Product	Mass Pull (%)		Assay (%)		Pb Recovery		Zn Recovery		Cumulative Grade (%)	
(min)		Ind	Cumul	Pb	Zn	Ind	Cumul	Ind	Cumul	Pb	Zn
0.5	RC1	1.94	1.94	20.5	21.1	22.9	22.9	5.7	5.7	20.5	21.1
2	RC2	1.93	3.87	15.9	23	17.7	40.6	6.1	11.8	18.2	22.0
8	RC3	4.03	7.89	9.58	25.8	22.2	62.8	14.4	26.2	13.8	24.0
	RT	92.11		0.7	5.8	37.2		73.8			
	Head	**100.00**		**1.73**	**7.23**	**100.0**		**100.0**			

Experimental conditions:

Weight of sample:	1000 g
Grind:	80% passing 100 micron
Grinding type:	dry
Collector dosage:	50 g/t SNPX
Conditioning time:	3 minutes
Frother:	100 g/t Senfroth 9325

Table III.2. Experimental data for the flotation of the Rosh Pinah composite at pH 8.5 in the presence of 50 g/t SNPX.and 2x10^{-4}M CuCN

Time	Product	Mass Pull (%)		Assay (%)		Pb Recovery		Zn Recovery		Cumulative Grade (%)	
(min)		Ind	Cumul	Pb	Zn	Ind	Cumul	Ind	Cumul	Pb	Zn
0.5	RC1	1.57	1.57	19.3	22.4	18.9	18.9	5.3	5.3	19.3	22.4
2	RC2	1.97	3.55	15	25.4	18.5	37.4	7.6	13.0	16.9	24.1
8	RC3	4.54	8.09	9.54	29.4	27.0	64.4	20.3	33.3	12.8	27.1
	RT	91.91		0.62	4.78	35.6		66.7			
	Head	**100.00**		**1.60**	**6.58**	**100.0**		**100.0**			

Experimental conditions:

Weight of sample:	1000 g
Grind:	80% passing 100 micron
Grinding type:	dry
Activator:	2x10^{-4}M CuCN
Activation time:	10 minutes
Collector dosage:	50 g/t SNPX
Conditioning time:	3 minutes
Frother:	100 g/t Senfroth 9325

Table III.3. Experimental data for the flotation of the Rosh Pinah composite at pH 8.5 in the presence of 50 g/t SNPX.and 2x10^{-3}M CuCN

Time	Product	Mass Pull (%)		Assay (%)		Pb Recovery		Zn Recovery		Cumulative Grade (%)	
(min)		Ind	Cumul	Pb	Zn	Ind	Cumul	Ind	Cumul	Pb	Zn
0.5	RC1	1.82	1.82	18	26	23.1	23.1	7.2	7.2	18.0	26.0
2	RC2	2.39	4.21	11.3	30.7	19.1	42.2	11.1	18.3	14.2	28.7
8	RC3	5.39	9.60	5.98	34.3	22.7	64.9	28.0	46.2	9.6	31.8
	RT	90.40		0.55	3.93	35.1		53.8			
	Head	**100.00**		**1.42**	**6.61**	**100.0**		**100.0**			

Experimental conditions:

Weight of sample:	1000 g
Grind:	80% passing 100 micron
Grinding type:	dry
Activator:	2x10^{-3}M CuCN
Activation time:	10 minutes
Collector dosage:	50 g/t SNPX
Conditioning time:	3 minutes
Frother:	100 g/t Senfroth 9325

Appendix IV. Details of the experiments on the effect of sodium cyanide, zinc sulphate and ore mineralogy on the flotation selectivity

Table IV.1. Experimental data for the flotation of the Rosh Pinah composite at pH 8.5 in the presence of 50 g/t SNPX

Time	Product	Mass Pull (%)		Assay (%)				Pb Recovery		Zn Recovery		Fe Recovery		Cu Recovery		Cumulative Grade (%)			
(min)		Ind	Cumul	Pb	Zn	Fe	Cu	Ind	Cumul	Ind	Cumul	Ind	Cumul	Ind	Cumul	Pb	Zn	Fe	Cu
1	RC1	4.24	4.24	11.1	11.3	30.4	1.18	27.2	27.2	6.9	6.9	31.3	31.3	43.6	43.6	11.1	11.3	30.4	1.18
2	RC2	2.06	6.30	11.5	15.2	22.4	0.77	13.7	40.9	4.5	11.5	11.2	42.5	13.8	57.5	11.2	12.6	27.8	1.05
4	RC3	2.22	8.52	10.9	19.4	15.7	0.6	14.0	54.9	6.2	17.7	8.5	50.9	11.6	69.1	11.1	14.4	24.6	0.93
8	RC4	6.46	14.98	6	20.4	7.5	0.22	22.4	77.4	19.1	36.8	11.8	62.7	12.4	81.5	8.9	17.0	17.2	0.62
	RT	85.02		0.46	5.14	1.81	0.025	22.6		63.2		37.3		18.5					
	Head	**100.00**		**1.73**	**6.91**	**4.12**	**0.11**	**100.0**		**100.0**		**100.0**		**100.0**					

Experimental conditions:

Weight of sample:	1000 g
Grind:	80% passing 100 micron
Grinding type:	wet (67% solids)
Depressant dosage:	0 g/t NaCN
Collector dosage:	50 g/t SNPX
Conditioning time:	3 minutes
Frother:	100 g/t Senfroth 9325

Table IV.2. Experimental data for the flotation of the Rosh Pinah composite at pH 8.5 in the presence of 50 g/t SNPX and 50 g/t NaCN

Time	Product	Mass Pull (%)		Assay (%)				Pb Recovery		Zn Recovery		Fe Recovery		Cu Recovery		Cumulative Grade (%)			
(min)		Ind	Cumul	Pb	Zn	Fe	Cu	Ind	Cumul	Ind	Cumul	Ind	Cumul	Ind	Cumul	Pb	Zn	Fe	Cu
1	RC1	4.633	4.63	12	10.3	29.3	1.13	28.2	28.2	6.8	6.8	32.0	32.0	43.7	43.7	12.0	10.3	29.3	1.13
2	RC2	2.186	6.82	12.8	14.6	23.6	0.9	14.2	42.4	4.5	11.3	12.2	44.2	16.4	60.1	12.3	11.7	27.5	1.06
4	RC3	2.68	9.50	10.8	17	13.4	0.5	14.7	57.1	6.5	17.8	8.5	52.7	11.2	71.2	11.8	13.2	23.5	0.90
8	RC4	4.89	14.39	7.3	20.7	7.7	0.25	18.1	75.2	14.4	32.2	8.9	61.6	10.2	81.4	10.3	15.7	18.1	0.68
	RT	85.61		0.57	5.57	1.9	0.026	24.8		67.8		38.4		18.6					
	Head	**100.00**		**1.97**	**7.03**	**4.24**	**0.12**	**100.0**		**100.0**		**100.0**		**100.0**					

Experimental conditions:

Weight of sample: 1000 g
Grind: 80% passing 100 micron
Grinding type: wet (67% solids)
Depressant dosage: 50 g/t NaCN
Collector dosage: 50 g/t SNPX
Conditioning time: 3 minutes
Frother: 100 g/t Senfroth 9325

Table IV.3. Experimental data for the flotation of the Rosh Pinah composite at pH 8.5 in the presence of 50 g/t SNPX and 75 g/t NaCN

Time	Product	Mass Pull (%)		Assay (%)				Pb Recovery		Zn Recovery		Fe Recovery		Cu Recovery		Cumulative Grade (%)			
(min)		Ind	Cumul	Pb	Zn	Fe	Cu	Ind	Cumul	Ind	Cumul	Ind	Cumul	Ind	Cumul	Pb	Zn	Fe	Cu
1	RC1	4.66	4.66	11.3	10.6	29.4	1.1	30.7	30.7	7.1	7.1	33.7	33.7	44.9	44.9	11.3	10.6	29.4	1.10
2	RC2	1.83	6.49	11.3	15.1	21.1	0.81	12.1	42.8	4.0	11.1	9.5	43.2	13.0	57.9	11.3	11.9	27.1	1.02
4	RC3	2.28	8.77	10.9	17.9	14.4	0.53	14.5	57.3	5.9	17.0	8.1	51.3	10.6	68.5	11.2	13.4	23.8	0.89
8	RC4	3.05	11.82	8.1	20.7	8.8	0.31	14.4	71.7	9.1	26.2	6.6	57.9	8.3	76.8	10.4	15.3	19.9	0.74
	RT	88.18		0.55	5.79	1.94	0.03	28.3		73.8		42.1		23.2					
	Head	**100.00**		**1.71**	**6.92**	**4.06**	**0.11**	**100.0**		**100.0**		**100.0**		**100.0**					

Experimental conditions:

Weight of sample:	1000 g
Grind:	80% passing 100 micron
Grinding type:	wet (67% solids)
Depressant dosage:	75 g/t NaCN
Collector dosage:	50 g/t SNPX
Conditioning time:	3 minutes
Frother:	100 g/t Senfroth 9325

Table IV. 4. Experimental data for the flotation of the Rosh Pinah composite at pH 8.5 in the presence of 50 g/t SNPX and 100 g/t NaCN

Time	Product	Mass Pull (%)		Assay (%)				Pb Recovery		Zn Recovery		Fe Recovery		Cu Recovery		Cumulative Grade (%)			
(min)		Ind	Cumul	Pb	Zn	Fe	Cu	Ind	Cumul	Ind	Cumul	Ind	Cumul	Ind	Cumul	Pb	Zn	Fe	Cu
1	RC1	5.06	5.06	11.3	9.5	29.7	1.19	33.4	33.4	7.2	7.2	36.2	36.2	50.0	50.0	11.3	9.5	29.7	1.19
2	RC2	1.97	7.03	12	13.5	20.1	0.83	13.8	47.2	4.0	11.2	9.5	45.7	13.6	63.6	11.5	10.6	27.0	1.09
4	RC3	2.46	9.49	12	17.1	14.4	0.56	17.2	64.5	6.3	17.5	8.5	54.3	11.4	75.0	11.6	12.3	23.7	0.95
8	RC4	3.31	12.80	8.1	20	8.6	0.25	15.7	80.1	10.0	27.5	6.9	61.1	6.9	81.9	10.7	14.3	19.8	0.77
	RT	87.2		0.39	5.53	1.85	0.025	19.9		72.5		38.9		18.1					
	Head	**100.00**		**1.71**	**6.65**	**4.15**	**0.12**	**100.0**		**100.0**		**100.0**		**100.0**					

Experimental conditions:

Weight of sample: 1000 g
Grind: 80% passing 100 micron
Grinding type: wet (67% solids)
Depressant dosage: 100 g/t NaCN
Collector dosage: 50 g/t SNPX
Conditioning time: 3 minutes
Frother: 100 g/t Senfroth 9325

Table IV.5. Experimental data for the flotation of the Rosh Pinah composite at pH 8.5 in the presence of 50 g/t SNPX and 150 g/t NaCN

Time	Product	Mass Pull (%)		Assay (%)				Pb Recovery		Zn Recovery		Fe Recovery		Cu Recovery		Cumulative Grade (%)			
(min)		Ind	Cumul	Pb	Zn	Fe	Cu	Ind	Cumul	Ind	Cumul	Ind	Cumul	Ind	Cumul	Pb	Zn	Fe	Cu
1	RC1	5.19	5.19	12.1	9.2	29	1.15	33.5	33.5	7.0	7.0	36.8	36.8	53.1	53.1	12.1	9.2	29.0	1.15
2	RC2	2	7.19	13.5	13.6	20.9	0.82	14.4	47.9	4.0	10.9	10.2	47.0	14.6	67.7	12.5	10.4	26.7	1.06
4	RC3	2.28	9.47	12.8	18.1	13.7	0.6	15.6	63.5	6.0	17.0	7.6	54.7	12.2	79.8	12.6	12.3	23.6	0.95
8	RC4	3.43	12.90	8	20.7	8.3	0.23	14.6	78.2	10.4	27.3	7.0	61.6	7.0	86.8	11.4	14.5	19.5	0.76
	RT	87.1		0.47	5.71	1.8	0.017	21.8		72.7		38.4		13.2					
	Head	**100.00**		**1.87**	**6.85**	**4.09**	**0.11**	**100.0**		**100.0**		**100.0**		**100.0**					

Experimental conditions:

Weight of sample:	1000 g
Grind:	80% passing 100 micron
Grinding type:	wet (67% solids)
Depressant dosage:	150 g/t NaCN
Collector dosage:	50 g/t SNPX
Conditioning time:	3 minutes
Frother:	100 g/t Senfroth 9325

Table IV.6. Experimental data for the flotation of the Rosh Pinah composite at pH 8.5 in the presence of 50 g/t SNPX, 75 g/t NaCN and 100 g/t $ZnSO_4$

Time	Product	Mass Pull (%)		Assay (%)				Pb Recovery		Zn Recovery		Fe Recovery		Cu Recovery		Cumulative Grade (%)			
(min)		Ind	Cumul	Pb	Zn	Fe	Cu	Ind	Cumul	Ind	Cumul	Ind	Cumul	Ind	Cumul	Pb	Zn	Fe	Cu
1	RC1	4.28	4.28	11.5	7.9	31.3	1.25	30.3	30.3	5.4	5.4	33.6	33.6	46.1	46.1	11.5	7.9	31.3	1.25
2	RC2	1.67	5.95	13	11.9	21.6	1	13.3	43.6	3.2	8.5	9.1	42.7	14.4	60.5	11.9	9.0	28.6	1.18
4	RC3	1.5	7.45	14.9	17.1	18.1	0.81	13.7	57.3	4.1	12.6	6.8	49.5	10.5	71.0	12.5	10.6	26.5	1.11
8	RC4	2.89	10.34	8.2	20	9.4	0.36	14.6	71.9	9.2	21.8	6.8	56.3	9.0	79.9	11.3	13.3	21.7	0.90
	RT	89.66		0.51	5.5	1.94	0.026	28.1		78.2		43.7		20.1					
	Head	**100.00**		**1.63**	**6.30**	**3.98**	**0.12**	**100.0**		**100.0**		**100.0**		**100.0**					

Experimental conditions:

Weight of sample:	1000 g
Grind:	80% passing 100 micron
Grinding type:	wet (67% solids)
Depressant dosage:	75 g/t NaCN and 100 g/t $ZnSO_4$
Collector dosage:	50 g/t SNPX
Conditioning time:	3 minutes
Frother:	100 g/t Senfroth 9325

Table IV.7. Experimental data for the flotation of the Rosh Pinah composite at pH 8.5 in the presence of 50 g/t SNPX, 75 g/t NaCN and 200 g/t $ZnSO_4$

Time	Product	Mass Pull (%)		Assay (%)				Pb Recovery		Zn Recovery		Fe Recovery		Cu Recovery		Cumulative Grade (%)			
(min)		Ind	Cumul	Pb	Zn	Fe	Cu	Ind	Cumul	Ind	Cumul	Ind	Cumul	Ind	Cumul	Pb	Zn	Fe	Cu
1	RC1	5.08	5.08	11.8	6.96	31	1.27	30.1	30.1	5.2	5.2	36.7	36.7	48.1	48.1	11.8	7.0	31.0	1.27
2	RC2	1.73	6.81	14.8	11.8	24	1.1	12.9	43.0	3.0	8.2	9.7	46.4	14.2	62.2	12.6	8.2	29.2	1.23
4	RC3	2.45	9.26	11.9	14.4	14.1	0.58	14.6	57.6	5.2	13.4	8.1	54.4	10.6	72.8	12.4	9.8	25.2	1.06
8	RC4	3.16	12.42	9.5	17.7	9.2	0.35	15.1	72.7	8.2	21.6	6.8	61.2	8.2	81.1	11.7	11.8	21.1	0.88
	RT	87.58		0.62	6.09	1.9	0.029	27.3		78.4		38.8		18.9					
	Head	**100.00**		**1.99**	**6.80**	**4.29**	**0.13**	**100.0**		**100.0**		**100.0**		**100.0**					

Experimental conditions:

Weight of sample:	1000 g
Grind:	80% passing 100 micron
Grinding type:	wet (67% solids)
Depressant dosage:	75 g/t NaCN and 200 g/t $ZnSO_4$
Collector dosage:	50 g/t SNPX
Conditioning time:	3 minutes
Frother:	100 g/t Senfroth 9325

Table IV.8. Experimental data for the flotation of the Rosh Pinah composite at pH 8.5 in the presence of 50 g/t SNPX, 75 g/t NaCN and 400 g/t $ZnSO_4$

Time	Product	Mass Pull (%)		Assay (%)				Pb Recovery		Zn Recovery		Fe Recovery		Cu Recovery		Cumulative Grade (%)			
(min)		Ind	Cumul	Pb	Zn	Fe	Cu	Ind	Cumul	Ind	Cumul	Ind	Cumul	Ind	Cumul	Pb	Zn	Fe	Cu
1	RC1	4.88	4.88	11.6	6.5	31.6	1.13	12.0	12.0	4.6	4.6	37.2	37.2	44.0	44.0	11.6	6.5	31.6	1.13
2	RC2	1.68	6.56	13.9	10.2	23.4	1.04	4.9	16.9	2.5	7.0	9.5	46.7	13.9	57.9	12.2	7.4	29.5	1.11
4	RC3	2	8.56	13.9	13.6	16.1	0.66	5.9	22.7	3.9	10.9	7.8	54.5	10.5	68.5	12.6	8.9	26.4	1.00
8	RC4	3.45	12.01	90	15.8	8.7	0.38	65.5	88.3	7.8	18.8	7.2	61.8	10.5	78.9	34.8	10.9	21.3	0.82
	RT	87.99		0.63	6.41	1.8	0.03	11.7		81.2		38.2		21.1					
	Head	**100.00**		**4.74**	**6.95**	**4.14**	**0.13**	**100.0**		**100.0**		**100.0**		**100.0**					

Experimental conditions:

Weight of sample:	1000 g
Grind:	80% passing 100 micron
Grinding type:	wet (67% solids)
Depressant dosage:	75 g/t NaCN and 400 g/t $ZnSO_4$
Collector dosage:	50 g/t SNPX
Conditioning time:	3 minutes
Frother:	100 g/t Senfroth 9325

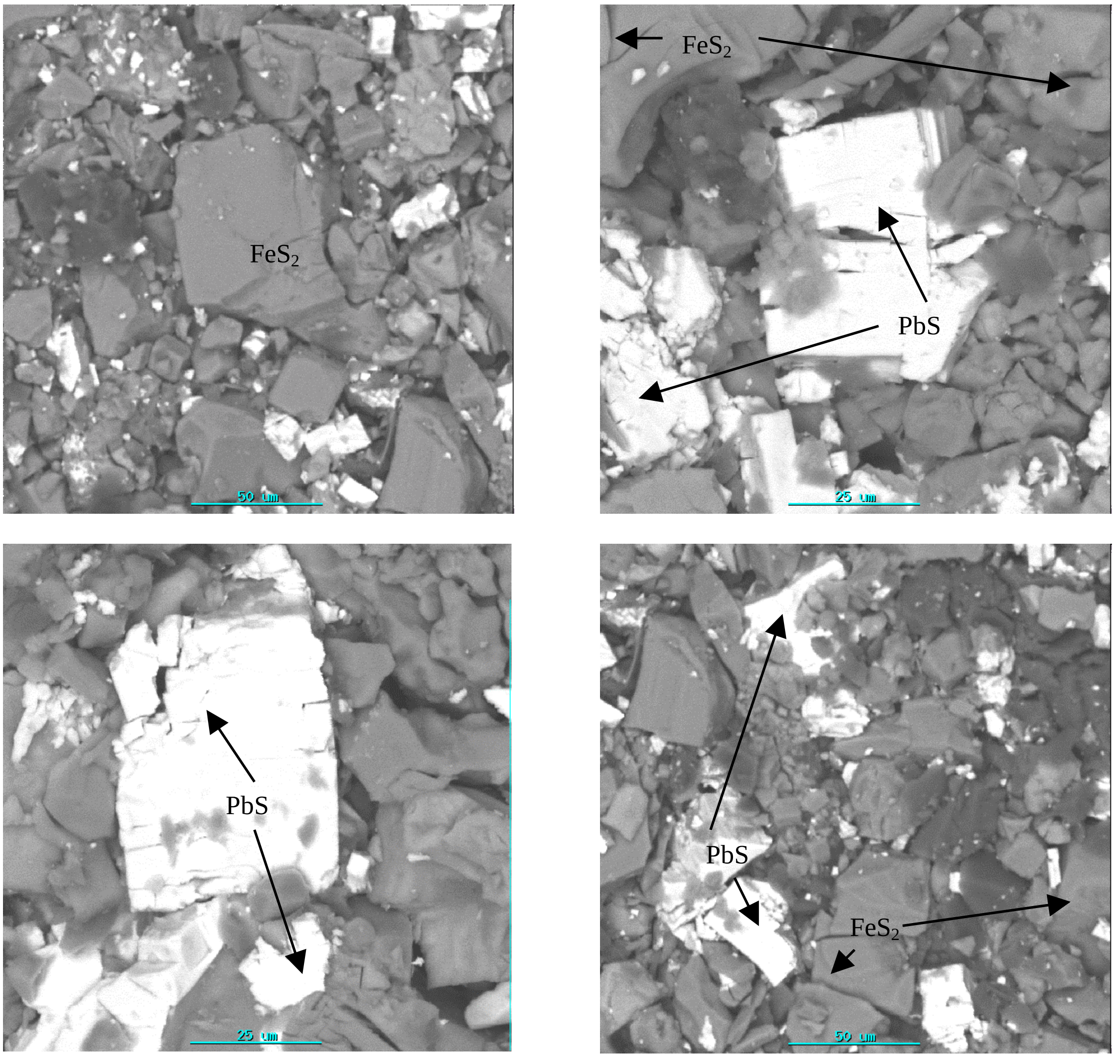


Figure IV.1. SEM- Backscattered images showing the presence of galena (white) and pyrite (grey) in the first concentrate. The flotation experiment was carried out in the presence of 100 g/t NaCN and 50 g/t SNPX.

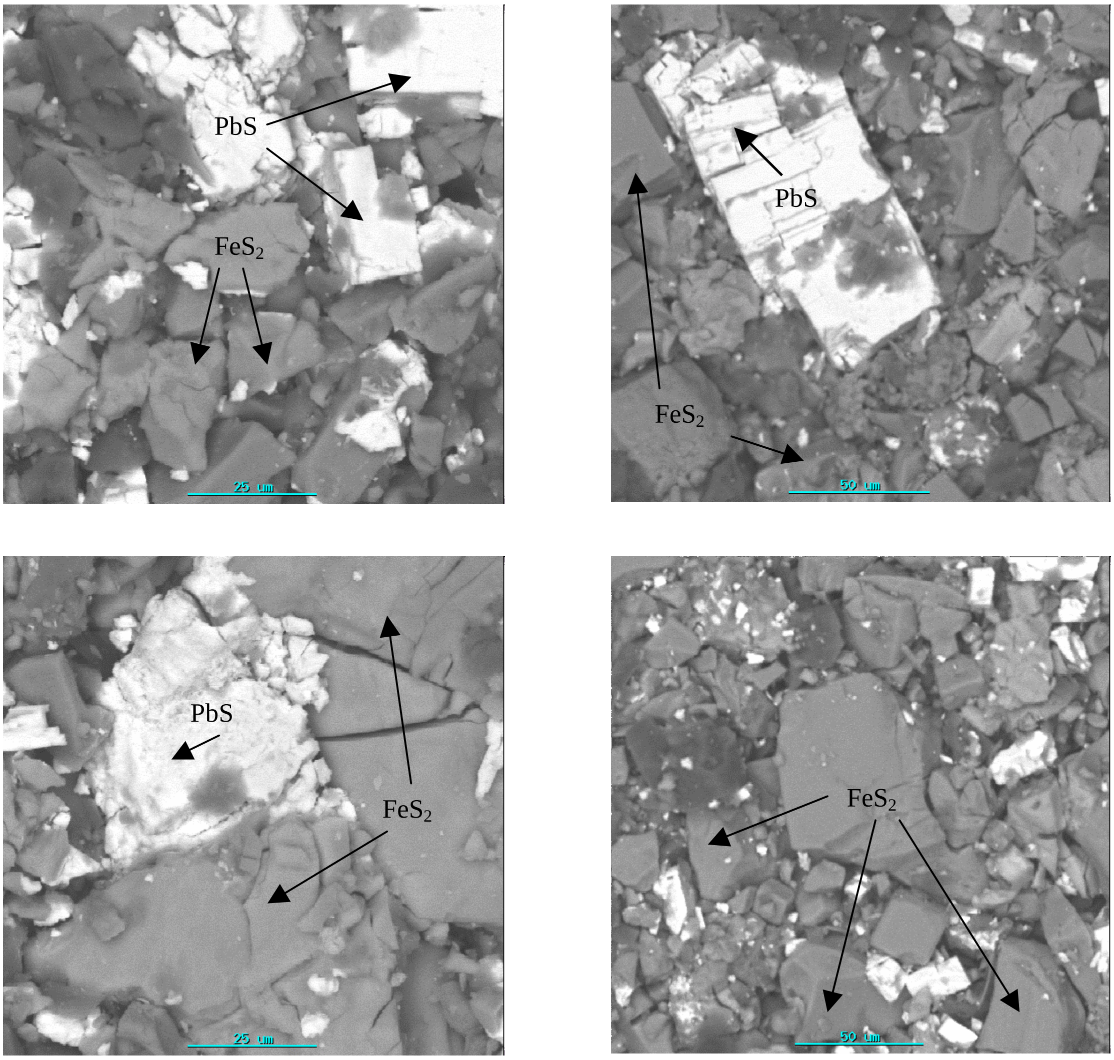


Figure IV.2. SEM- Backscattered images showing the presence of galena (white) and pyrite (grey) in the first concentrate. The flotation experiment was carried out in the presence of 100 g/t NaCN and 50 g/t SNPX.

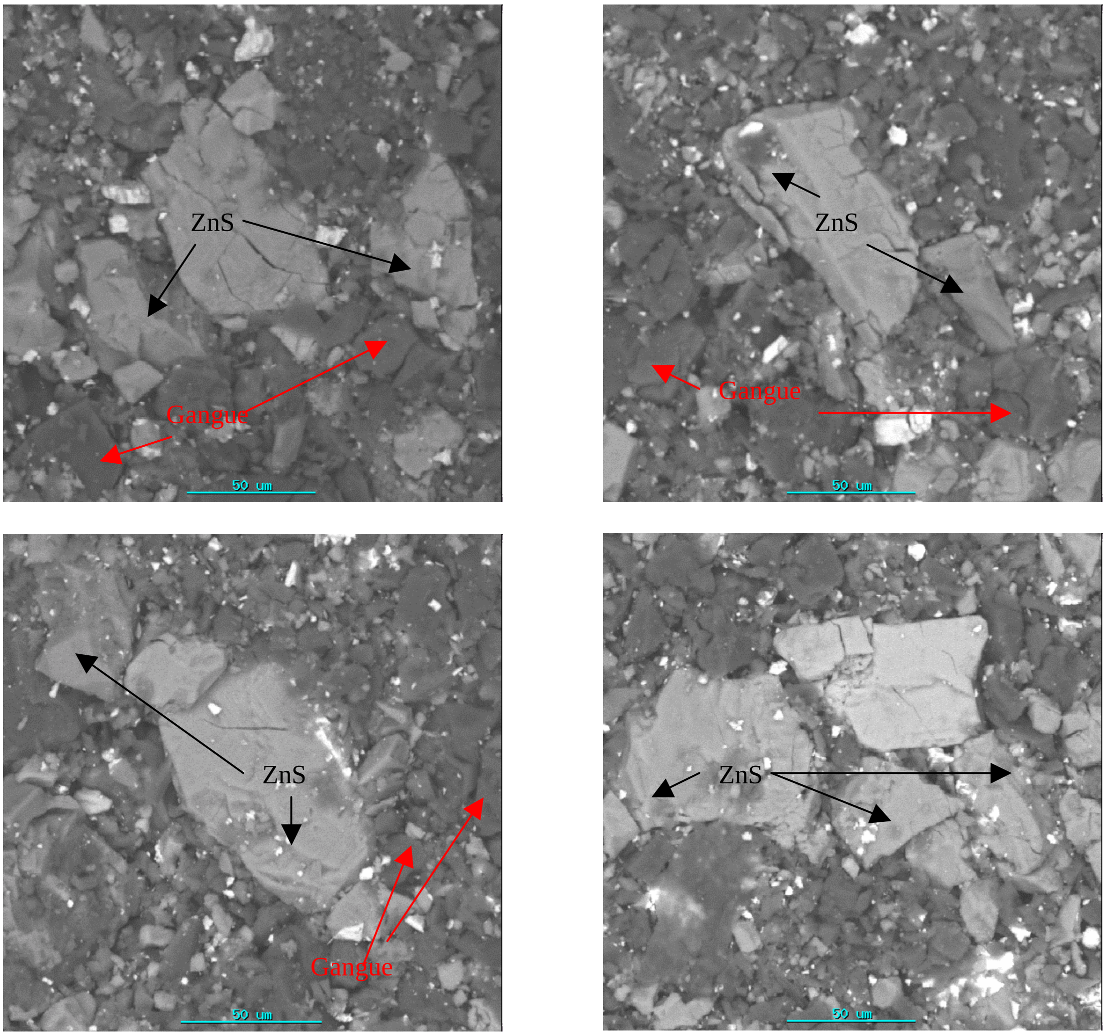


Figure IV.3. SEM- Backscattered images showing the presence sphalerite and gangue in the last concentrate. The flotation experiment was carried out in the presence of 100 g/t NaCN and 50 g/t SNPX.

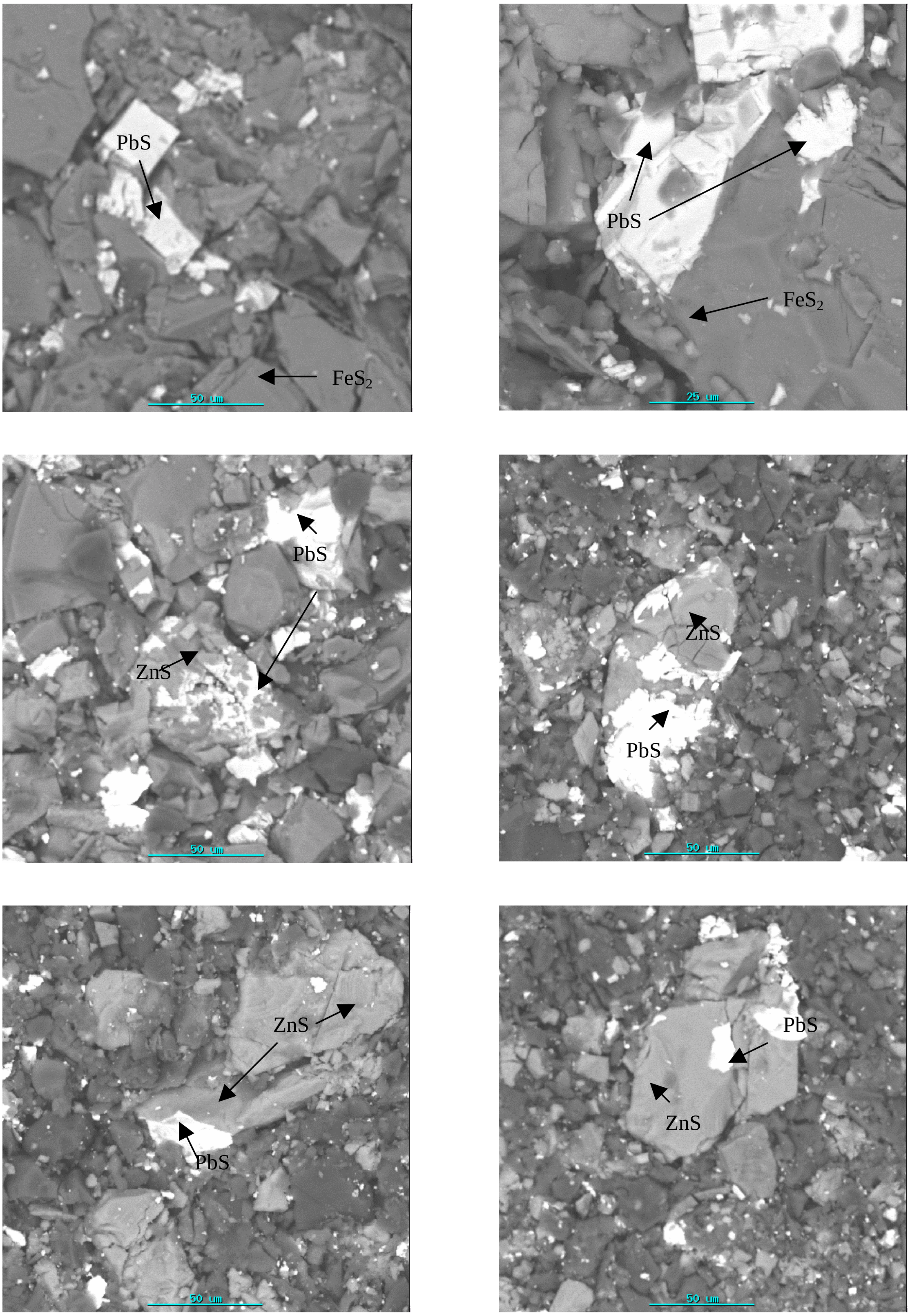


Figure IV.4. SEM- Backscattered images of concentrate showing the association between galena, sphalerite and pyrite in the galena concentrate.

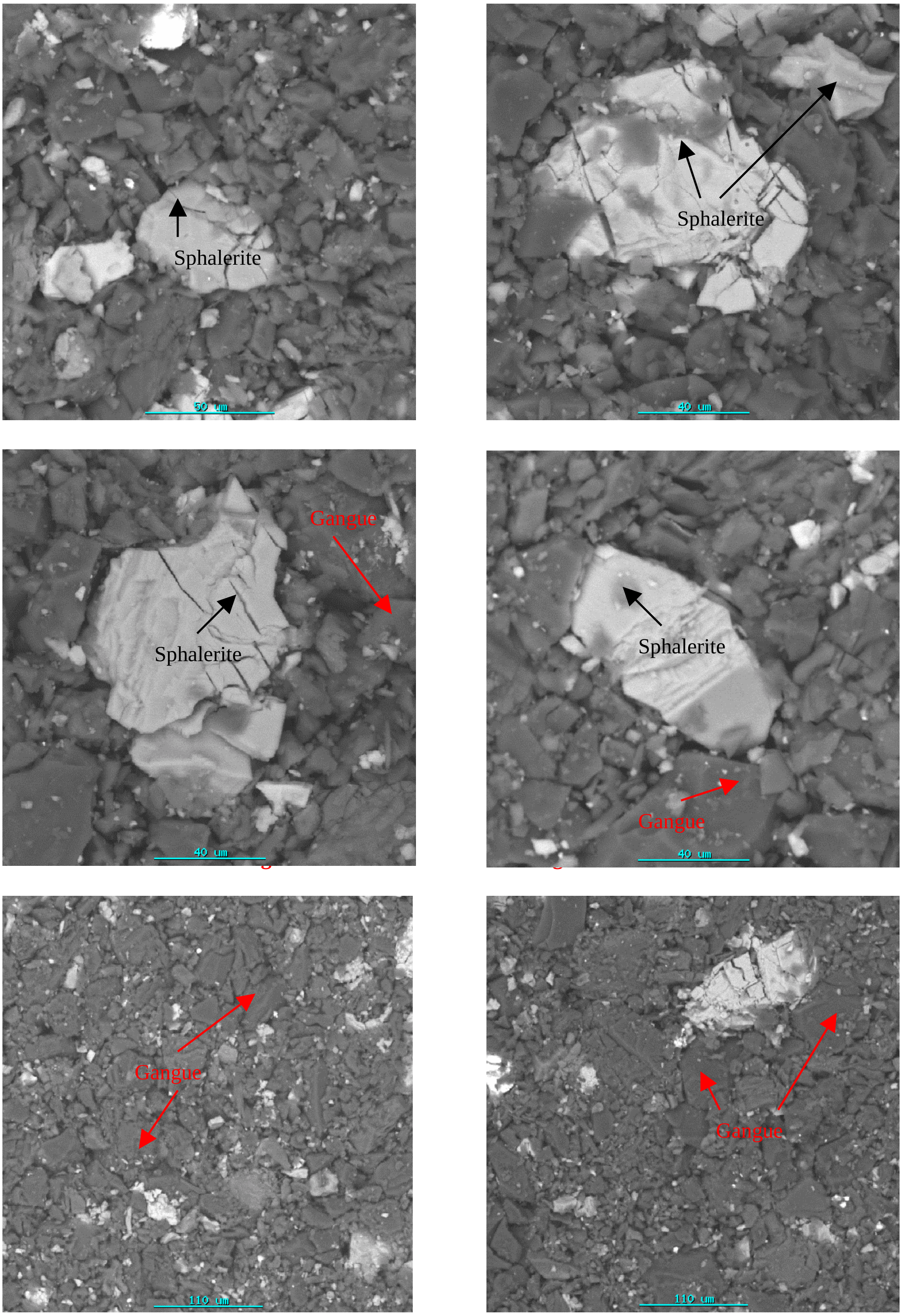


Figure IV.5. SEM- Backscattered images showing the general appearance of the rougher tailings. The flotation experiment was carried out in the presence of 100 g/t NaCN and 50 g/t SNPX.